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RICARDO JUSTINO DA SILVA

ENVIRONMENTAL IMPACT ASSESSMENT OF THERMOCHEMICAL ROUTES FOR INTEGRAL USE OF BIOMASS AT A SUGARCANE BIOREFINERY

AVALIAÇÃO DE IMPACTOS AMBIENTAIS DE ROTAS TERMOQUÍMICAS PARA APROVEITAMENTO INTEGRAL DA BIOMASSA NA BIORREFINARIA DE CANA-DE-AÇÚCAR

CAMPINAS
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Dissertation presented to the School of Chemical Engineering of the State University of Campinas in partial fulfillment of the requirements for the degree of Master in Chemical Engineering.

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Orientador: Prof. Ph.D. Rubens Maciel Filho

Coorientador: D.Sc. Otávio Cavalett

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Preface

This research Master's degree is tied to the research project (FAPESP 2010/17139-3) entitled "*Environmental impact assessment of different sugarcane biorefinery configurations with integral use of biomass*." This research was developed in cooperation between the Laboratory of Optimization*,* Project and Advanced Control (LOPCA) - Department of Process and Product Development (DDPP) located in the School of Chemical Engineering (FEQ) of the State University of Campinas (UNICAMP), and the division of Integrated Evaluation of Biorefineries (AIB) located in the Brazilian Bioethanol Science and Technology Laboratory (CTBE) of the Brazilian National Center for Research in Energy and Materials (CNPEM).

This research Master's degree is focused on the environmental assessment by using standardized Life Cycle Assessment (LCA) methodology for different technological scenarios and biorefineries concepts under the scope of the Virtual Sugarcane Biorefinery (VSB) tool, which consider the specificities of the Brazilian sugar-energy sector.

This research Master's degree provides an assessment and analysis of the potential environmental impacts arising from the use of renewable resources (sugarcane bagasse and straw) on the co-production of bio-based heat, electricity, liquid biofuels, and chemicals through gasification-based thermochemical conversion routes of biomass integrated at a Brazilian first generation (1G) sugarcane biorefinery, in this case, with annexed ethanol distillery.

The concept of sugarcane biorefineries with the integral use of sugarcane was assessed taking into account the mass and energy integrations between the technologies involved in both biorefineries technologies (1G and thermochemical routes). Parameters and indicators presented for the thermochemical-biorefinery scenarios are based technical and operational parameter predicts in CanaSoft electronic spreadsheets models and Aspen Plus$^{®}$v8.4 (AspenTech, USA) process simulation platform. However, grounders by a comprehensive evaluation of the world scientific literatures, and of the research results obtained from UNICAMP and CNPEM about technologies involved in biomass conversion pathways.

LOPCA is coordinated by Prof. Ph.D. Rubens Maciel Filho, which makes developments and applications of Process System Engineering (PSE) concepts for the development of processes and products. They are therefore developed models, procedures and computer programs, and collected experimental data required for design, simulation, optimization, and process control (SCHOOL OF CHEMICAL ENGINEERING, 2015).

The AIB division is headed by Ph.D. Antonio Maria Jose Luiz Francisco Bonomi, works on developing a computational simulation tool called Virtual Sugarcane Biorefinery (VSB). It enables to technically assess the integration of new technologies in the production chain of sugarcane, along the three axes of sustainability: economic, environmental, and social (BRAZILIAN BIOETHANOL SCIENCE AND TECHNOLOGY LABORATORY, 2015).

“*Not everything that is faced can be changed. But nothing can be changed until it is faced.*”

James Baldwin

Abstract

Biorefineries have been considered an extremely important alternative to sustainable development and for developing of a ‘green economy’ based on local and renewable resources. Biomass is a renewable resource with the potential to reduce dependence on fossil resources and a viable alternative able to replace the main fossil fuels (coal, oil, and natural gas). In the case of Brazil, the sugarcane biorefineries take up a prominent position in this scenario, with the production of energy (thermal and electrical), sugar and fuel ethanol with potentials surplus biomass for bio-based products and/or bioenergy production. The biomass of sugarcane can be converted into various bio-based products by chemical, biochemical, and/or thermochemical routes. In this sense, this Master’s thesis contributes with the assessment of environmental impacts (cradle-to-gate system boundary) of the production of thermal energy, electricity, liquid biofuels, and chemicals by thermochemical conversion routes of biomass integrated at an optimized first generation (1G) sugarcane biorefinery with annexed ethanol distillery (two million tonnes of processed cane on-season), from the integral use of the available lignocellulosic biomass. The thermochemical conversion routes of biomass assessed are: Combined Heat and Power (CHP) generation based on Rankine-cycle by using Condensing-Extraction Steam Turbine (CEST) system or by using Extraction back-pressure steam turbine (EBPST) system; Biomass integrated directly-heated gasifier and Internal Combustion Engine in Combined-cycle (BIG-ICE/CC) system; Biomass integrated directly-heated gasifier and Gas Turbine in Combined-cycle (BIG-GT/CC) system; Biomass to Methanol production by Biomass integrated directly-heated gasifier and low-pressure Methanol catalytic-synthesis (Biomass-to-Methanol); Biomass to mixed alcohols production by Biomass integrated directly-heated gasifier and mixed alcohols catalyst-synthesis (Biomass-to-Mixed alcohols). The scenarios consider different possibilities of energy integration (thermal and electrical) between technologies (keeping or not keeping the traditional CHP/EBPST system), and the possibility/necessity of an upstream co-capture of CO_2/H_2S (presents in the synthesis gas). The environmental impacts assessment has been developed according to Life Cycle Assessment (LCA) methodology (ISO14040:2006 and ISO14044:2006) under the scope of the Virtual Sugarcane Biorefinery (VSB) tool (CTBE, Brazil) The Life Cycle Inventory (LCI) was obtained from CanaSoft (CTBE, Brazil) spreadsheet models (agricultural phase) and from mass and energy balances from Aspen Plus®v8.4 (AspenTech, USA) process simulation platform (industrial phase). The life cycle inventory was assessed according to World midpoint ReCiPe model in SimaPro®7.3.3 (PRé Consultants B.V., Netherlands) software. The potential environmental impacts for the main bio-based products, in general, showed advantages over corresponding products derived from fossil resources (Brazil case) in terms of: climate change; ozone depletion; ionizing radiation; marine ecotoxicity; natural land transformation; urban land occupation; mineral/metal depletion; fossil depletion. They also showed disadvantages in terms of: agricultural land occupation; particulate matter formation; terrestrial acidification; terrestrial ecotoxicity; photochemical oxidant formation; freshwater eutrophication; freshwater ecotoxicity; marine eutrophication; human toxicity; and water depletion.

Keywords: Anhydrous fuel ethanol from biomass (E2G). Bagasse. Bio-based products. Biomass integrated directly-heated gasifier and Gas Turbine in Combined-cycle (BIG-GT/CC). Biomass integrated directly-heated gasifier and Internal Combustion Engine in Combined-cycle (BIG-ICE/CC). Biomass-to-Methanol. Biomass-to-Mixed alcohols. Circulating Fluidized Bed (CFB). Combined Heat and Power Generation (CHP). Directly-heated gasification. **Environmental Life Cycle Assessment (LCA)**. Fuel grade AA methanol. High molecular weight alcohols. Lignocellulosic biomass. Liquid biofuels. Low-pressure methanol catalytic-synthesis. mixed alcohols catalyst-synthesis. Straw. Sugarcane biorefinery. **Thermochemical routes**. **Virtual Sugarcane Biorefinery (VSB)**.

Resumo

As biorrefinarias têm sido consideradas uma alternativa extremamente importante para o desenvolvimento sustentável e para o desenvolvimento de uma ‘economia verde’ baseada em recursos locais e renováveis. A biomassa é um recurso renovável com o potencial de reduzir a dependência em recursos fósseis e uma viável fonte alternativa capaz de substituir os principais combustíveis fósseis (carvão, petróleo e gás natural). No caso do Brasil, as biorrefinarias de cana-de-açúcar ocupam uma posição de destaque neste cenário, com a produção de energia (térmica e elétrica), açúcar e etanol combustível com potenciais excedentes de biomassa para produção de bioprodutos e/ou bioenergia. A biomassa de cana-de-açúcar pode ser convertida em diversos bioprodutos através de rotas químicas, bioquímicas e/ou termoquímicas. Neste sentido, esta dissertação de mestrado contribui com a avaliação dos impactos ambientais (berço-ao-portão) da produção de energia térmica, eletricidade, biocombustíveis líquidos e químicos através de rotas termoquímicas de conversão da biomassa integradas a uma biorrefinaria de cana-de-açúcar de primeira geração otimizada com destilaria de etanol anexa (dois milhões de toneladas de cana processada na safra), a partir da utilização integral da biomassa lignocelulósica disponível. As rotas termoquímicas de conversão da biomassa avaliadas são: produção combinada de calor e potência (CHP) baseada em ciclos Rankine usando turbina a vapor de condensação-extração (CEST) ou usando turbina a vapor de contra pressão-extração (EBPST); gaseificação direta da biomassa integrada a um motor de combustão interna operando em ciclo combinado (BIG-ICE/CC); gaseificação direta da biomassa integrada a uma turbina a gás operando em ciclo combinado (BIG-GT/CC); produção de metanol pela gaseificação direta da biomassa integrada a um processo de síntese catalítica de metanol a baixa pressão (*Biomass-to-Methanol*); produção de alcoóis pela gaseificação direta da biomassa integrada a um processo de síntese catalítica de alcoóis (*Biomass-to-Mixed alcohols*). Os cenários consideram as diferentes possibilidades de integração energética (térmica e elétrica) entre as tecnologias (preservando ou não o tradicional sistema de CHP/EBPST) e a possibilidade/necessidade de um sistema *upstream* de cocaptura de CO_2 e H_2S (presentes no gás de síntese). A avaliação de impactos ambientais foi desenvolvida de acordo com a metodologia de Avaliação de Ciclo de Vida (ACV) (ISO14040:2006 e ISO14044:2006) e com o escopo da Biorrefinaria Virtual de Cana-de-açúcar (BVC). O inventário do ciclo de vida foi obtido a partir de modelos do CanaSoft *spreadsheet* (fase agrícola) e de balanços de massa e energia da plataforma de simulação Aspen Plus®v8.4 (fase industrial). O inventário do ciclo de vida foi avaliado segundo o modelo *World midpoint* ReCiPe no *software* SimaPro®7.3.3. Os potenciais impactos ambientais obtidos para os principais bioprodutos, em geral, apresentaram vantagens sobre os correspondentes produtos derivados de recursos fosseis (caso Brasil) em termos de: mudanças climáticas; depleção da camada de ozônio; radiação ionizante; ecotoxicidade marinha;

transformação de área natural; ocupação de área urbana; depleção dos minerais/metal; depleção dos recursos fósseis. Também, apresentaram desvantagens em termos de: ocupação de área agrícola; formação de material particulado; acidificação terrestre; ecotoxicidade terrestre, formação de oxidante fotoquímico; eutrofização da água doce; ecotoxicidade da água doce; eutrofização marinha; toxicidade humana; e depleção da água.

Palavras-chave: Alcoóis superiores. **Avaliação Ambiental do Ciclo de Vida (ACV)**. Bagaço. Biocombustíveis líquidos. Biomassa lignocelulósica. Biorrefinaria de cana-de-açúcar. Bioprodutos. **Biorrefinaria Virtual de Cana-de-açúcar (BVC)**. Etanol anidro combustível (E2G). Gaseificação direta. Gaseificação direta da Biomassa Integrada a um Motor de Combustão Interna operando em Ciclo Combinado (BIG-ICE/CC). Gaseificação direta da Biomassa Integrada a uma Turbina a Gás operando em Ciclo Combinado (BIG-GT/CC). Geração Combinada de Calor e Potência (CHP). Metanol combustível grade AA. Palha. **Rotas termoquímicas**. Síntese catalítica de alcoóis. Síntese catalítica de metanol a baixa pressão.

List of publications

The following publications (under submission) are based on the results of this research Master's degree. The abstracts of the papers in submission process are appended (APPENDIX C) in the end of this Master's thesis.

- In submission process:

I. Process simulation and evaluation of different cogeneration system configurations to Combined Heat and power (CHP) generation at a Brazilian first generation sugarcane biorefinery

II. Process simulation and evaluation of Biomass integrated directly-heated gasifier and Internal Combustion Engine in Combined-cycle (BIG-ICE/CC) route integrated at a Brazilian first generation sugarcane biorefinery

III. Process simulation and evaluation of Biomass Integrated direct-heated Gasification and Gas Turbine in Combined-cycle (BIG-GT/CC) route integrated at a Brazilian first generation sugarcane biorefinery

IV. Process simulation and evaluation of Biomass integrated directly-heated gasifier and Low-pressure Methanol catalytic-synthesis (Biomass-to-Methanol) integrated at a Brazilian first generation sugarcane biorefinery

V. Process simulation and evaluation of Biomass integrated directly-heated gasifier and mixed alcohols catalyst-synthesis (Biomass-to-Mixed alcohols) integrated at a Brazilian first generation sugarcane biorefinery

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VI. Environmental Life Cycle Assessment (LCA) of electricity generation by advanced cogeneration systems integrated at a Brazilian first generation sugarcane biorefineries

VII. Environmental Life Cycle Assessment (LCA) of methanol and ethanol production by biomass-to-liquid biofuels thermochemical routes integrated at a Brazilian first generation sugarcane biorefineries

- Other related publications:

In addition, along with other authors, a comparative sustainability assessment of a different scenario was developed, which is not included in this Master’s thesis, but uses some of the date and results obtained during the development of this research master's degree.

a. Comparative technical, economic and environmental assessment of biomass-to-ethanol conversion technologies: biochemical and thermochemical routes integrated at a first generation sugarcane biorefinery.

The abstract was submitted and accepted as oral presentation at *37th Symposium on Biotechnology for Fuels and Chemicals* on April 27-30, 2015 in San Diego (CA). The complete full paper will be submitted for publication (with modifications and improvements) after the presentation at the symposium, in a scientific journal.

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List of abbreviations and definitions

1G	First Generation
2G	Second Generation
ABNT	Brazilian Association of Technical Standards
AF	Air-fuel ratio
AIB	division of Integrated Evaluation of Biorefineries
ALO	Agricultural Land Occupation
ALOP	Agricultural Land Occupation Potential
APED	Aspen Properties Enterprise Database
APV84	Aspen Properties Database version 8.4
ASTM	American Society of Testing and Materials
ASU	Air Separation Unit
ATR	Autothermal Reforming
BC	Bottoming Cycle
BIG-GT/CC	Biomass Integrated Directly-heated Gasifier and Gas Turbine in Combined-cycle
BIG-ICE/CC	Biomass Integrated Directly-heated Gasifier and Internal Combustion Engine in Combined-cycle
Biomass-to-Methanol	Biomass integrated directly-heated gasifier and Low-pressure Methanol catalytic-synthesis
Biomass-to-Mixed alcohols	Biomass integrated directly-heated gasifier and mixed alcohols catalyst-synthesis
BM	Boston-Mathias
BNDES	National Bank for Economic and Social Development
Brazilian electricity mix	Brazil’s total electricity final consumption
CAPES	Brazilian Coordination of Improvement of Higher Education Personnel
CAPEX	Capital Expenditure
CC	Climate Change
CC	Combined-cycle
CCS	Carbon Capture and Storage (or Sequestration)
CEST	Condensing-extraction Steam Turbine
CF	Candle Filter
CFB	Circulating Fluidized Bed
CGEE	Center for Strategic Studies and Management Science, Technology and Innovation

CHP	Combined Heat and Power
C.O.C	Cycles of Concentration
CSC	Convective synthesis gas cooler
CTBE	Brazilian Bioethanol Science and Technology Laboratory
daf	dry ash free
db	dry basis
DDPP	Department of Process and Product Development
deaf	dry, ash and extractives free
DIN	Deutsches Institut für Normung
E2G	Second generation ethanol
EBPST	Consider extraction Back-pressure Steam Turbine
ED	Damage to Ecosystem Diversity
EvGT	Evaporative-class Gas Turbine
EPE	Energy Research Office
ER	Equivalence ratio
FAPESP	State of São Paulo Research Foundation
E	Egalitarian
EV	EnVironmental
FC	Fixed Carbon
FD	Fossil Depletion
FDP	Fossil Depletion Potential
FE	Freshwater Eutrophication
FEP	Freshwater Eutrophication Potential
FEM	School of Mechanical Engineering
FEQ	School of Chemical Engineering
FET	Freshwater Ecotoxicity
FETP	Freshwater Ecotoxicity Potential
GCV	Gross Calorific Value
GDP	Gross Domestic Product
GE	General Electric Company
GHG	Greenhouse Gas
GWP	Global Warming Potential
H	Hierarchism
HCV	Higher Calorific Value
HGT	Humidified Gas Turbine
HH	Human Health
HHV	High Heating Value

HP	High-Pressure
HRSG	Heat Recovery Steam Generation
HT	Human toxicity
HTP	Human Toxicity Potential
I	Individualist
ICE	Internal Combustion Engine
IEA	International Energy Agency
IGT	Institute of Gas Technology
IP	Intermediate-pressure
IPCC	Intergovernmental Panel on Climate Change
IR	Ionizing Radiation
IRP	Ionizing Radiation Potential
ISO	International Organization for Standardization
LAR	Liquid Argon
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Inventory Assessment
LHHW	Langmuir-Hinshelwood-Hougen-Watson
LHV	Lower Heating Value
LNG	Liquid Nitrogen
LOPCA	Laboratory of Optimization, Project and Advanced Control
LP	Low-Pressure
M	Moisture
MD	Metal Depletion
MDEA	Methyl-diethanolamine
MDP	Mineral Depletion Potential
ME	Marine Eutrophication
MEA	Monoethanolamine
MEP	Marine Eutrophication Potential
MET	Marine Ecotoxicity
METP	Marine Ecotoxicity Potential
MP	Medium-Pressure
MRD	Mineral Resource Depletion
MSDU	Molecular Sieve Dehydration Unit
NBR	Brazilian Standard
NC	Non-conventional Component
NCV	Net Calorific Value

NLT	Natural Land Transformation
NLTP	Natural Land Transformation Potential
NREL	National Renewable Energy Laboratory
OD	Ozone Depletion
ODP	Ozone Depletion Potential
OECD	Organization for Economic Co-operation and Development
OPEX	Operational Expenditure
PM_{10}	Particulate Matter with 10 micrometers or less in diameter
PMF	Particulate Matter Formation
PMFP	Particulate Matter Formation Potential
POF	Photochemical Oxidant Formation
POFP	Photochemical Oxidant Formation Potential
PR	Pressure Ratio
PROXANAL	Proximate Analysis
PSD	Particle-size Distribution
PZ	Piperazine
RA	Damage to Resource Availability
REN21	Renewable Energy Policy Network for the 21st Century
RK	Redlich-Kwong
RKS	Redlich-Kwong-Soave
RPlug	Plug Flow type-reactor
RStoic	Stoichiometric type-reactor
SAGE	Strategic Advisory Group on the Environment
SC	Subcommittees
SC	Scenario
SETAC	Society of Environmental Toxicology and Chemistry
SEV	Sequential EnVironmental
SG	Single-gas fueled
SI	Spark-ignited
SMR	Steam Methane Reforming
SPEX	Single Pipes Exhaust
STBR or S/B	Steam-to-biomass ratio
STY	Space-Time Yeld
STRAW	Sugarcane leaves and tops
SULFANAL	Sulfur Analysis
TA	Terrestrial Acidification
TAP	Terrestrial Acidification Potential

tc	Tonnes of cane
TC	Topping Cycle
TET	Terrestrial Ecotoxicity
TETP	Terrestrial Ecotoxicity Potential
TFC	Total Final Consumption
Thermochemical-biorefinery	Specific biomass thermochemical conversion route integrated at an specific first generation sugarcane biorefinery
TIT	Turbine Inlet Temperature
TPES	Total Primary Energy Supply
TPSA	Temperature-pressure Swing Adsorption
TR	Technical Reports
TRS	Total Reducing Sugars
TS	Technical Specification
TSA	Temperature Swing Adsorption
ULO	Urban Land Occupation
ULOP	Urban Land Occupation Potential
ULTANAL	Ultimate Analysis
UNICAMP	State University of Campinas
UNEP	United Nations Environmental Programme
VLE	Vapor-Liquid Equilibrium
VM	Volatile Material
VOCs	volatile organic compounds
VSA	Vacuum Swing Adsorption (VSA)
VSB	Virtual Sugarcane Biorefinery
WCED	World Commission on Environment and Development
WD	Water Depletion
WDP	Water Depletion Potential
WESP	Wet Electrostatic Precipitator
WG	Working Groups
WGS	Water-gas-shift
RWGS	Reverse Water-gas-shift

Contents

1 Introduction

The sugar-energy sector is an important sector for the Brazilian economy, in 2008 generated US$ 28.15 billion in revenues and in 2013 US$ 43.8 billion in revenues, which is equivalent to almost 2% of national Gross Domestic Product (GDP) (BRAZILIAN SUGARCANE INDUSTRY ASSOCIATION, 2015; NEVES; TROMBIN, 2014). The area cultivated with sugarcane in Brazil in the 2013/2014 harvest year was 8,811.43 thousand of hectares with 658.8 million of tonnes of sugarcane milled for sugar and ethanol production (anhydrous and hydrated), an increase of 11.9% compared to the milled in 2012/2013 (NATIONAL SUPPLY COMPANY, 2014).

About 290.0 million of tonnes of residual biomass are generated as agricultural and industrial residues. Part of this biomass remains in the field (Straw) and other large part (bagasse) is currently used in low energy efficiency cogeneration systems aiming to achieve self-sufficiency in energy terms (thermal and electrical). Today (2015), only few biorefineries use the available biomass in high-pressure systems (high-efficiency) in order to generate surplus electricity to electric power grid.

“As the best renewable alternative to oil, the Brazilian sugarcane-derived ethanol has gained scope with the capacity to produce co-generate energy (electrical and thermal) in the same factory by processing sugarcane straw and bagasse (sugar and ethanol by products)” (SANTOS et al. 2015, p. 2). The available biomass (bagasse and straw) in a first generation (1G) sugarcane biorefinery can be converted competitively into bio-based products (e.g. heat, electricity, liquid biofuels and chemicals) by chemical, biochemical and/or thermochemical routes, with potential to be a significant contributor to expand and diversify the energetic bio-based products portfolio, providing a feedstock without increase the impact on Agricultural Land Occupation (ALO).

Production of bio-based heat, electricity, liquid biofuels and chemicals (multi-product plants) by thermochemical routes using biomass gasification process to produce synthesis gas (syngas) are very sustainable-attractive alternatives due high energy efficiency technologies and low pollutant emissions (negative-emissions of CO_2 by capture systems with storage/use), offer an alternative to chemical and biochemical processes. Therefore, the sugar-energy sector has become importance due to their surplus electricity and liquid biofuels production potential from renewable resources.

Indicators of environmental impacts for bio-based production using renewable resources in a thermochemical-biorefinery are largely unknown. Environmental assessment allows quantify advantages and disadvantages of thermochemical route and compare it with the performance obtained with others equivalents products obtained from different technologies.

1.1 Context and background

Today's (2015) society and its development are tied to excessive dependence on energy, especially the energy obtained from fossil resources. Energy is fundamental for human life, in a globalized modern society the human life has been affected by the energy market and scarcity. The supply and use of energy have powerful economic, social, and environmental impacts. Energy is used to meet the basic human needs (e.g. lighting, mobility, communication, food transportation, potable water) creating dependence between energy cost and the cost of living.

In 2011 fossil fuels supplied about 80.6~82.0% and the nuclear fuels about 2.7~5.0% (non-renewable) of the World final energy consumption (RENEWABLE ENERGY POLICY NETWORK FOR THE 21st CENTURY, 2012). Oil, mineral coal and natural gas are finite resources and the main fuels used to produce energetic products, oil mainly as transportation fuel and coal and natural gas as heat and power generation for the industry and non-industry sectors. In 2013, World final energy consumption growing 2.3% over 2012 (1.8%), the oil being the World’s leading fuel with about 32.9% of the global final energy consumption (BP, 2014).

The use of energy represents by far the largest source of Greenhouse Gas (GHG) emissions corresponding for 69% of global anthropogenic GHG Shares of 2010 (INTERNATIONAL ENERGY AGENCY, 2014b). Fossil fuels are the primary culprit behind Climate Changes (CC), 87% of all human CO_2 emissions come from the burning of fossil fuels, fossil fuel production and intensive livestock farming are responsible for 60% of all human CH_4 emissions.

In 2012, electricity and heat generation accounted for 42% of global CO_2 emissions, while transport accounted for 23%, industry accounted for 20%, residential accounted for 6%, and other accounted for 9% (INTERNATIONAL ENERGY AGENCY, 2014b). Globally, coal (the most carbon-intensive fuel) accounted for 44% and oil accounted for 35% of the of global CO_2 emissions in 2012, although oil still the largest primary energy supply, it accounted for 31.4% of the world primary energy supply (INTERNATIONAL ENERGY AGENCY, 2014b).

Global Warming is a reality and it will bring catastrophic consequences for biodiversity and human’s development and health. Average global temperatures are increasing and severe weather patterns are accelerating, the increase in global temperature unbalances the ultrasensitive Earth's climate system changing biomes.

Brazil's largest biome*s* (Amazon rainforest and Cerrado) are threatened by deforestation pressure from ALO and by the change in the Brazil’s rainfall systems. The most intense impacts on the energy supply due to insufficient rainfall are now being seen (2014/2015).

In Brazil, water and electricity go together, the increasing demand of water contribute for the Water Depletion (WD) and their scarcity also raises the risk of electricity rationing and energy blackouts in actual Brazil scenario (2015). In 2013, about 70.6% (89.0% of the share of all renewable resources for electricity production) of the total Brazil's electricity final consumption comes from hydropower plants (hydraulic source), and only 7.6% come from biomass (ENERGY RESEARCH OFFICE, 2014).

The water stress and scarcity have direct implications in the Brazilian energy security In 2014/2015, forcing the country to activate/run all fossil fuel-powered (oil products, coal and natural gas) thermoelectric plants on maximum generation capacity and import energy (fossil resource and electricity) from Paraguay and Argentina to complement the hydropower plants, making the Brazilian energy supply gradually become increasingly expensive and on a collision course with the Brazilian economic development and the costs of the basic human needs.

Energy sources must be diversified and we have to reduce dependency on hydropower plants and fossil fuels (main oil and natural gas). Although the sugar-energy sector also depends on the weather, the available biomass (bagasse and straw) are a potential resources for energy (thermal and electrical) production via advanced cogeneration cycles and replace a part of the expensive fossil fuel-powered thermoelectric plants.

The environmental degradation and Fossil Depletion (FD) are continually being aggravated by the rapid increase in the global energy consumption and by a growing human population and the consequent demand for primary resources.

At the end of 2013 stood the total world proved oil reserves reached 1687.9 billion barrels, sufficient to meet 53.3 years of global production, proved natural gas reserves reached 185.7 trillion cubic meters (tcm), sufficient to meet 55.1 years of global production and proved coal reserves were sufficient to meet 113 years of global production (BP, 2014).

According to International Energy Agency (IEA) (2014a) in 2011 oil resource supplied about 93.0% of the World transport energy consumption, drives global demand for oil and being responsible for a significant share of global GHG emissions. Therefore, the current cost of living is dependent mainly on the price of crude oil (actual main energy resource).

The current focus on solutions to the world's dependence on diminishing petroleum resources, as well as the environmental potential impacts associated with their production and utilization, has led to the exploration of many alternative energy sources to a compelling need for new, more sustainable energy sources. The implementation of a 'green economy' based on local and renewable resources has the potential to reduce the dependence on energy derived from fossil resource (oil, coal and natural gas scarcity).

The biomass-energy sector covers a very wide spectrum of feedstock options (e.g.: agriculture; forestry; municipal and industry waste; crops; sludge/liquor) to the end-use bio-based products (e.g.: heat; electricity; liquid bio-fuels; chemicals). The use of biomass and energetic-wastes has the potential to greatly reduce GHG emissions and dependence on out-of-state and foreign energy sources.

The liquid and gaseous fuels from renewable resources (biofuels) are seen as promising replacements for fossil fuels diversifying the energetic mix, "currently [2010] there are two liquid biofuels market, which partially replace the oil: (1) ethanol can replace gasoline, and (2) biodiesel can replace diesel "(DEMIRBAS; GUPTA 2010, p. 17).

Brazilian sugarcane ethanol program presents interesting results since the implementation in 1931 and with the creation of Pro-Alcohol program in 1975 to reduce dependence on oil imports, expanding the sugarcane culture for ethanol production. Ethanol replaced over 50% of the gasoline used in the country and the market is expanding at a rapid pace, mainly due to the "invasion" of flex-fuel technology (2003) (choice between gasoline, ethanol or a mixture of the two) in the country and its rapid dissemination (ABRAMOVAY, 2009). Brazil use only ethanol as a fuel or as a mixture containing alcohol in gasoline.

Looking forward, the upward trend in demand for ethanol, due the internal market, increase in flex fuel vehicles and by the increasing fraction of alcohol in gasoline, as well as the foreign market, with the incorporation of ethanol fuel a more viable alternative, especially from the environmental point of view.

Sugarcane bagasse represents 1/3 of the sugarcane, while another 1/3 is formed by leaves and pointer (straw), which in most cases after harvest remains in the field. Biomass is used for heat and power generation (low-efficiency systems) at Brazilian 1G sugarcane biorefinery and as wood chips replacement. Electricity production is only one of the alternatives to the use of sugarcane bagasse and straw, accounting for about 16.1% of the Brazil’s total energy consumption in 2013 (Figure 17), and about 49.2% of the share of modern renewable energy resources (ENERGY RESEARCH OFFICE, 2014). Many studies are being conducted for the efficient use of this raw material in the production of a wide range of bio-products through chemical, biochemical and/or thermochemical routes.

The sector of renewable bio-based products among multiple alternative technologies will assume strategic position in the post-petroleum era, providing a larger proportion of the world’s energy supply. Biomass is an increasingly competitive resource with the potential to reduce dependence on fossil resources and a viable alternative able to replace the main fossil fuels (coal, oil and natural gas). Thermochemical platform (routes) using biomass as raw material is a promising alternative with ability to turn biomass into a wide range of bio-based products efficiently by integrated thermochemical-biorefinery, reducing environmental impacts and diversifying the product portfolio of plants that process lignocellulosic materials.

1.2 General objective

The main objective of this research Master’s degree is to **propose** (select technologies and design scenarios), to **assess the environmental impacts** (environmental assessment) and to compare (scenarios, technologies, and products) scenarios of **integrated thermochemical-based biorefineries based on integral use of conventional sugarcane (on-season)** mainly targeting the co-production (Brazilian sugar-energy sector) of sugar, thermal energy, electricity, liquid fuels, and chemicals (multi-product plants).

Assess the environmental impacts by applying the methodology of Life Cycle Assessment (LCA) according to International Organization for Standardization (ISO) 14040:2006 (ABNT NBR ISO 14040:2009) and ISO 14044:2006 (ABNT NBR ISO 14044:2009) **under the scope of the Virtual Sugarcane Biorefinery (VSB) simulation and assessment platform (tool)**.

1.3 Specific objectives

This Master’s thesis consists specifically in implement process models (industrial phase) in the Aspen Plus$^{®}$v8.4 (AspenTech, USA) process simulation platform to predict the mass and energy balances, and consequently technical-operational parameters.

Propose scenarios considering mass and energy integration between the technologies required by the routes (sugarcane biorefinery and thermochemical biomass conversion routes) maximizing energy efficiency of the proposed thermochemical-biorefinery scenarios.

Integrate thermochemical biomass conversion routes in an optimized 1G sugarcane biorefinery with annexed ethanol distillery, aiming the integral use of the biomass available (sugarcane bagasse and straw).

Develop the Life Cycle Inventory (LCI) obtained for the proposed thermochemical-biorefinery scenarios and assess their environmental impact indicators (LCA) by using World midpoint ReCiPe Hierarchism (H) impact assessment methodology, available in SimaPro$^{®}$ (PRé Consultants B.V., Netherlands) software.

Compare the potential environmental impacts for the biomass-derived products obtained in the proposed thermochemical-biorefinery scenarios with the potential environmental impacts for equivalent products (e.g.: gasoline, methanol and electricity) derived from fossil resources (e.g.: oil and natural gas).

1.4 Contributions

This research Master's degree contributes to the construction of the VSB tool (under development) implementing the first industrial phase models (pioneer) for the biomass thermochemical conversion routes assessed in this research Master's degree.

The main contribution, indeed, is the thermochemical-biorefinery design taking into account the mass and energy (thermal and electrical) integration between the different technologies that existing in the proposed scenarios, as well as the detailed implementation of the different and numerous unitary processes and their representative models (e.g.: reaction; fluid dynamic, thermodynamic, empirical, estimated/approximate) needed to represent in detail a thermochemical-biorefinery in Aspen Plus®v8.4 process simulation platform.

A series of data providing technical-scientific information supplying, in part, the demand for more accuracy data and assessments of potential environmental impacts of the technological options (different routes), considering the integral use of available biomass in the Brazilian sugar-energy sector, besides enabling that these indicators forming part of the decisions-making process together with economic and social indicators.

The results obtained for the thermochemical-biorefinery scenarios running the processes models in Aspen Plus®v8.4 process simulation platform can contribute significantly to determining or estimate the Operational Expenditure (OPEX) and Capital Expenditure (CAPEX) for the thermochemical-biorefineries scenarios.

The detailed Aspen Plus®v8.4 flowsheet of the thermochemical-biorefinery scenarios can be used and/or altered in future studies/projects to perform and assess others process technologies, and obviously, to implement improvements (rigorous models) in the simulated thermochemical-biorefinery scenarios (accuracy).

The assessment of potential environmental impacts of the biomass-derived products obtained by thermochemical-based sugarcane biorefineries allow comparison with other developed or under development (research's) routes, enabling the identification of technological processes that need to be better studied in future studies/projects (bottleneck's) due their significance in only one specific environmental impact indicator or in several environmental impact indicators. Thermochemical conversion routes have several process technology options for the same purpose, thus allowing the selection of a technological option that presents an improvement in the environmental performance of the thermochemical-biorefinery (environmental optimization).

The potential environmental impacts obtained for the biomass-derived products will be part of the VSB database (SimaPro® in-house database) as new products and can be used in comparisons with equivalent products from other resources or technological routes.

1.5 Logical framework approach

The logical framework approach (Figure 1) developed for this research Master's degree shows the main logics interaction that is necessary for development of this research.

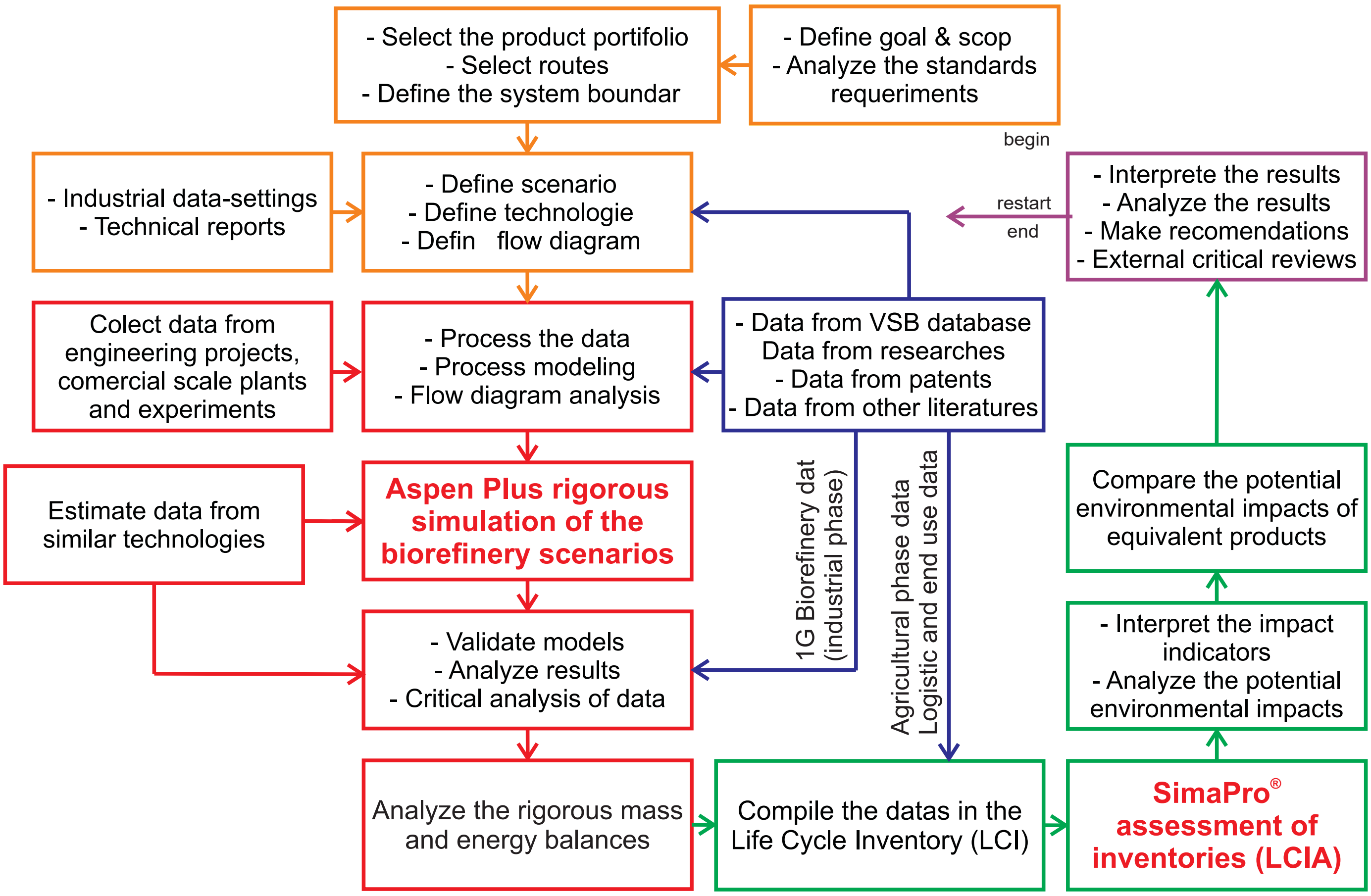

Figure 1 - Logical framework approach and interactive steps to assess the thermochemical routes

To develop the LCA and obtain the potentials environmental impacts of the biomass-derived products from the thermochemical-biorefinery scenarios is necessary two main steps:

a) **obtain mass and energy balances (input/output)** for the thermochemical routes (industrial phase) by using Aspen Plus®v8.4 process simulation platform (required for LCI development);
b) **obtain environmental impact indicators** for the thermochemical routes (this work) integrated at a 1G sugarcane biorefinery (agricultural and industrial phase obtained from VSB database) by using SimaPro® 7.3.3 software.

2 Fundaments

2.1 Energy

Energy is one of the key features responsible for the development of humanity, nearly all available energy (accumulated) and consumed by the humanity comes from solar energy, whether directly (light and heat) or indirectly (metabolized by living beings). Productive activities of goods and services needed to ensure adequate standards of quality of life (e.g.: passenger transport, cargo transport, food transport, mobility, communication, lighting, cooling, heating) use energy (BERMANN, 2002).

2.1.1 Primary energy sources

Fossil resources are considered a “non-renewable" resources (long life cycle) available only in dispersed and limited supply. Fossil resources available today are the result of decomposition of plant and animals (organic matter) trapped between layers of sediments that lived 300 million years ago in the primordial swamps. The fossil resources reserves occurs in different geological formations as: solid matter form (Mineral coal) occurs in mineral deposits in the sedimentary rock layers (strata) geologic formation as peat-forming, lignite, anthracite, bituminous coal, cannel coal and bog head coal; liquid form (Crude oil) occurs in profound porous and permeable geological formations in deep underground in the continental and oceanic earth’s lithosphere; and gaseous form (Natural gas and shale gas) occurs in a geological formations similar to crude oil reserves and associated with the liquid Crude oil, shale gas is a fossil gas resource (as natural gas) encountered in shale deposits (DEMIRBAS AND GUPTA, 2010; WORLD ENERGY COUNCIL, 2013).

Renewable resources is the natural sources (short life cycle) that can replenish itself naturally over time. Include the living portions of our natural World (plants and animals) as well as non-living resources (air and water). “Bioenergy is a broad category of energy fuels manufactured from a variety of feedstock’s of biological origin and by numerous conversion technologies to generate heat, power, liquid biofuels and gaseous biofuels” (WORLD ENERGY COUNCIL, 2013 p. 20).

Nuclear energy is the energy released from nuclear fission of the atom. Uranium, plutonium and thorium radioactive ores (non-renewable) present in the ground mineral deposits at relatively low concentrations are the main source of fission fuels (DEMIRBAS AND GUPTA, 2010).

2.1.2 World primary energy supply

World primary energy supply are dominated by fossil resources (coal, oil and natural gas), which accounted for about 81.7% of Total Primary Energy Supply (TPES) in 2012. Figure 2 shows a comparison between energy supply in 1973 and energy supply 2012 scenarios (INTERNATIONAL ENERGY AGENCY, 2014a).

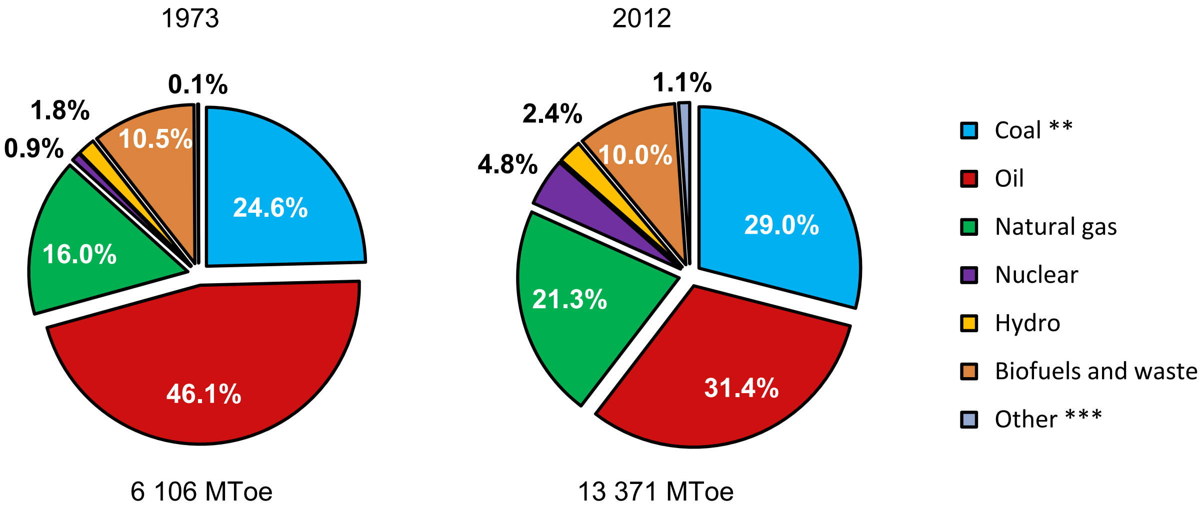

Figure 2 - World* TPES: 1973 and 2012 fuels shares - reported as million tonnes of oil equivalent

Source: IEA (2014a).
* World includes international aviation and international marine bunkers.
** In these graphs, peat and oil shale are aggregated with coal.
*** Includes geothermal, solar, wind, heat, etc.

According to Figure 2 between 1973 and 2012, the TPES was expanded by about 119.0%. Oil is the World's leading fuel since 1973 to 2012, but it lose market share (INTERNATIONAL ENERGY AGENCY, 2014a). The growth of the participation of natural gas and coal observed are the result of the increased demand for heat and power in the industry sector.

"Global oil reserves are almost 60% larger today than 20 years ago, and production of oil have gone up by 25%" (WORLD ENERGY COUNCIL, 2013 p. 12).

According to the National Bank for Economic and Social Development (BNDES) and the Center for Strategic Studies and Management Science, Technology and Innovation (CGEE) (2008) oil, natural gas and its derivatives (long-cycle renewable) are condemned to exhaust (economic infeasibility) in a few decades, due to the increasing energy demand.

2.1.3 World primary energy consumption

Figure 3 shows the share of the residential, industry and services sectors in the World Total Final Consumption (TFC) of energy in 2011 or the main primary energy supply. This is only a global average and there is a wide disparity of the share of the sector among countries due the characteristic aspects of each region (INTERNATIONAL ENERGY AGENCY, 2014b).

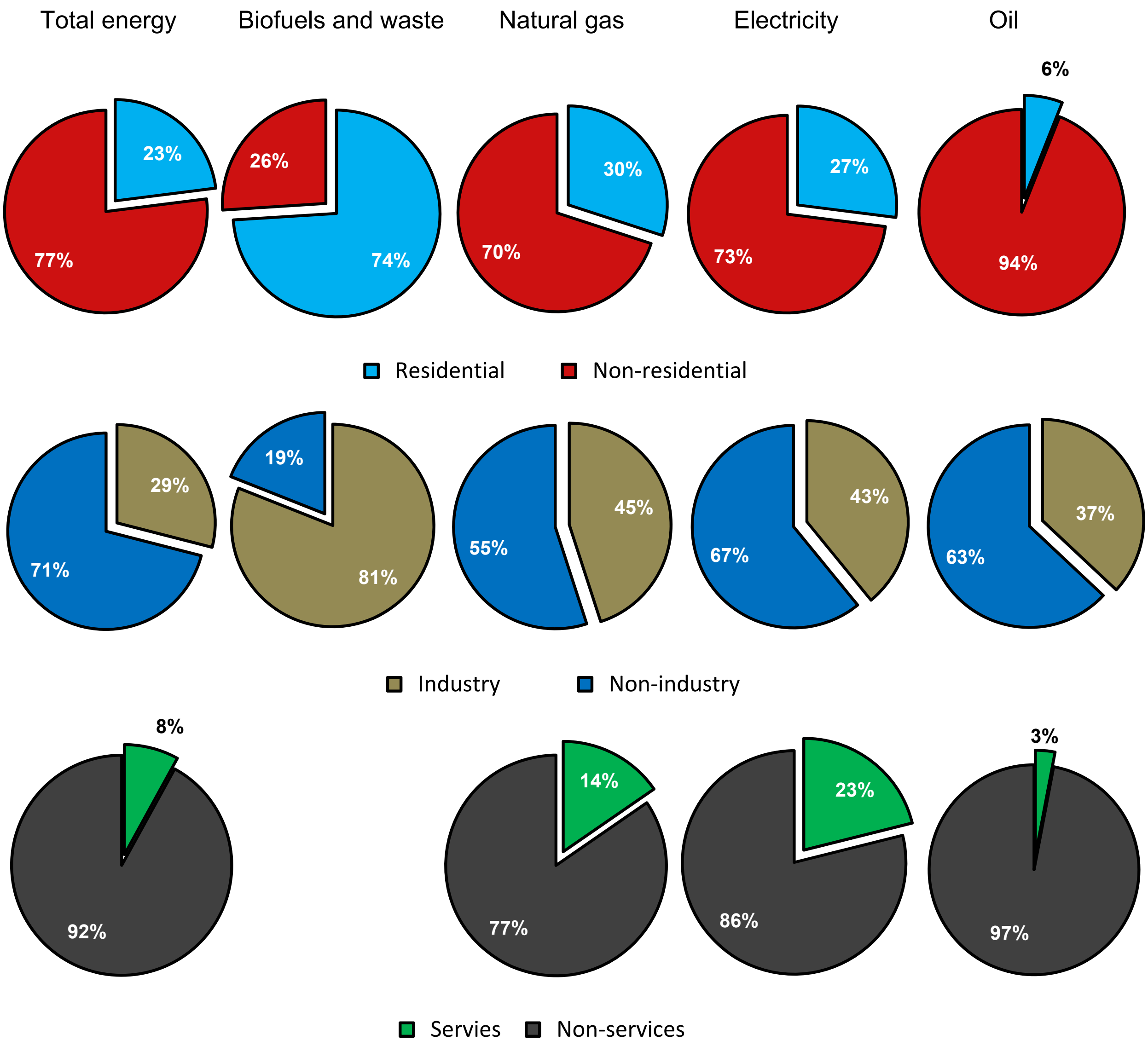

Figure 3 - Share of the residential, industry and services* sectors in the World TFC for selected energy sources (2011)

Source: adapted from IEA (2014b).
* Refers to the commerce and public services

As shown in Figure 3, the residential sector accounted for about 23.0% of World energy TFC and the industry sector accounted for about 29.0%. The residential sector uses more biofuels although the industry sector uses more fossil resources (INTERNATIONAL ENERGY AGENCY, 2014a).

The share of residential energy consumption could account for less than 10% or exceed 75% of World energy TFC depending on the development of the industrial and services sectors. Similarly, electricity consumption in the residential sector can often account for more than 90% of World energy TFC in countries with large electricity consumption (INTERNATIONAL ENERGY AGENCY, 2014a).

The service sector accounted for about 8.0% of World energy TFC, being electricity the most important energy source. Is currently often calculated as a residual difference between total energy consumption and the combined consumption of other sectors (residential, industry and transport), Figure 4 shows the share of the transport sector in the World energy TFC in 2011 (INTERNATIONAL ENERGY AGENCY, 2014b).

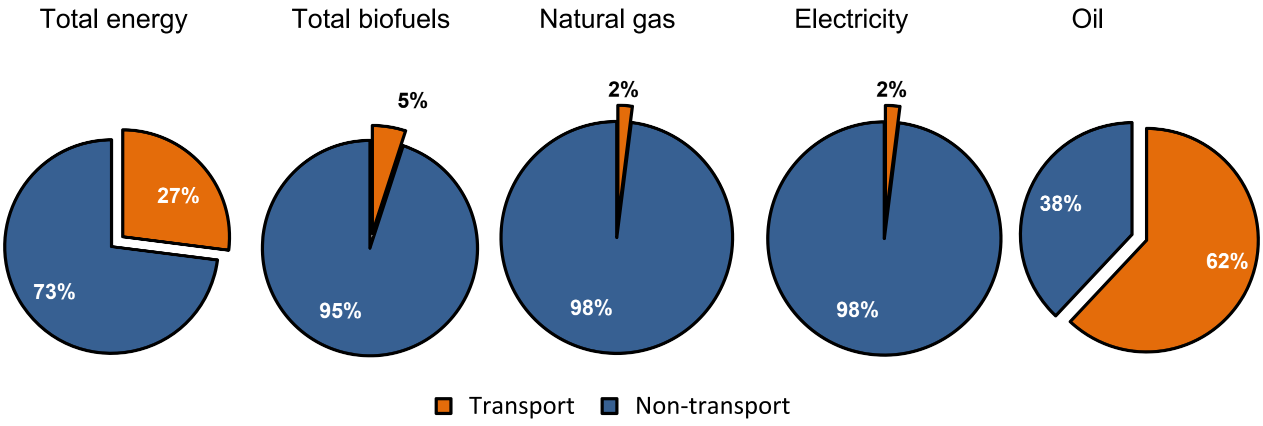

Figure 4 - Share of the transport sector in the World TFC for selected energy sources (2011)

Source: adapted from IEA (2014b).

As shown in Figure 4 the transport sector accounted for about 27.0% of World TFC. Oil has historically been the predominant energy source in the transport sector, accounted for 62% of the World oil consumed in 2011, transport sector drives the World demand for oil (INTERNATIONAL ENERGY AGENCY, 2014b).

“The share for total biofuels can also varying a lot from country to country; it is particularly high for Brazil at 23%, due to the policy in place to increase the use of Bioethanol” (INTERNATIONAL ENERGY AGENCY, 2014b p. 127).

Figure 5 shows the share of each energy source in the World transport energy consumption in 1973 and 2011.

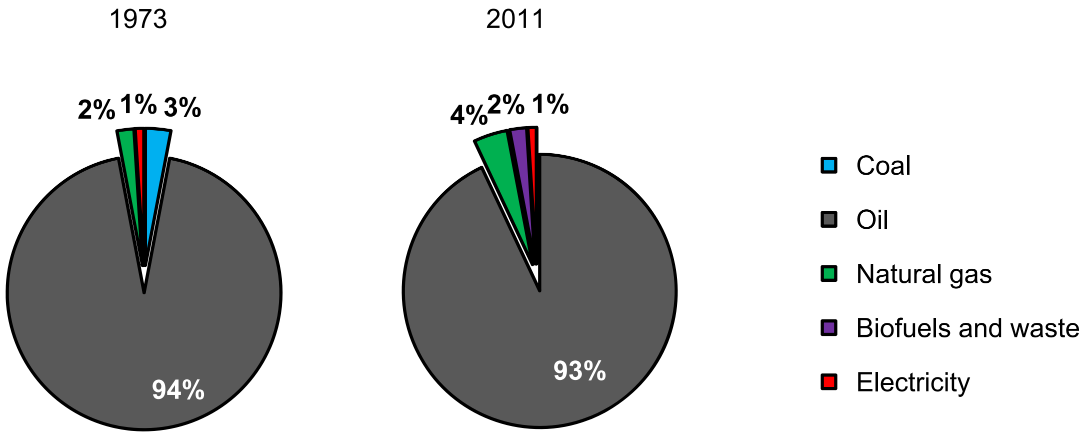

Figure 5 - Share of the various sources in the World transport energy consumption

Source: adapted from IEA (2014b).

As shown in Figure 5 the transport sector is more dependent on the World oil source than any other end-use sector, oil accounted for about 93.0% of the World transport energy consumption. In 2011, the non-renewable resources (fossil) accounted for about 97.0% of the World transport energy consumption (INTERNATIONAL ENERGY AGENCY, 2014b).

The consumption of oil as transport energy is in fact greater than 90% in most countries, except in Brazil which oil is responsible for about 80.0%, due the large consumption of biofuels for transport (INTERNATIONAL ENERGY AGENCY, 2014b).

Increasing industrialization in emerging countries (China and India) an the consequent high growth in freight transport activity increase the number of heavy-vehicles consuming fossil fuels (diesel), thus impacting in the FD an GHG emissions (THE INTERNATIONAL COUNCIL ON CLEAN TRANSPORTATION, 2012).

“On-road and rail emissions in Brazil are expected to grow at 1.7 percent annually through 2030 based on policies that have already been adopted” (THE INTERNATIONAL COUNCIL ON CLEAN TRANSPORTATION, 2012).

Figure 6 shows the breakdown of the World total transport consumption by sub-sector in 1973 and 2011.

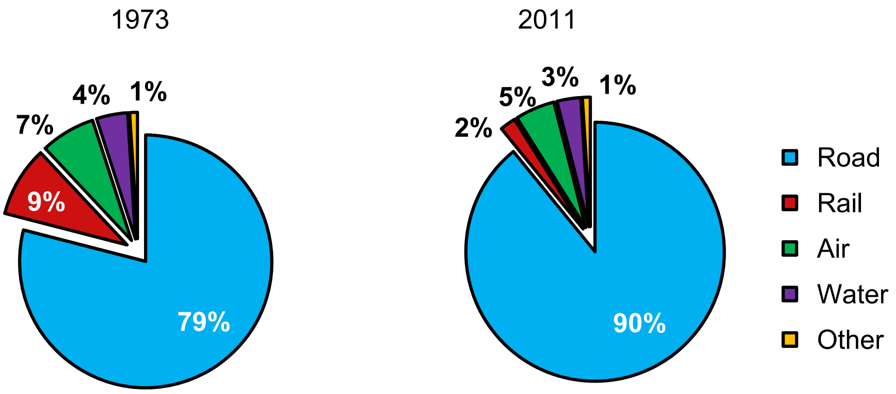

Figure 6 - Energy consumption by sub-sector for the World total transport consumption*

Source: IEA (2014b).
* Excluding international transport

As shown in Figure 6 the road dominates transport, with 90% of the World total transport consumption (INTERNATIONAL ENERGY AGENCY, 2014b).

Figure 7 shows the breakdown of the consumption by the passenger and freight transport sub-sectors in the countries of the Organization for Economic Co-operation and Development (OECD) in 2010.

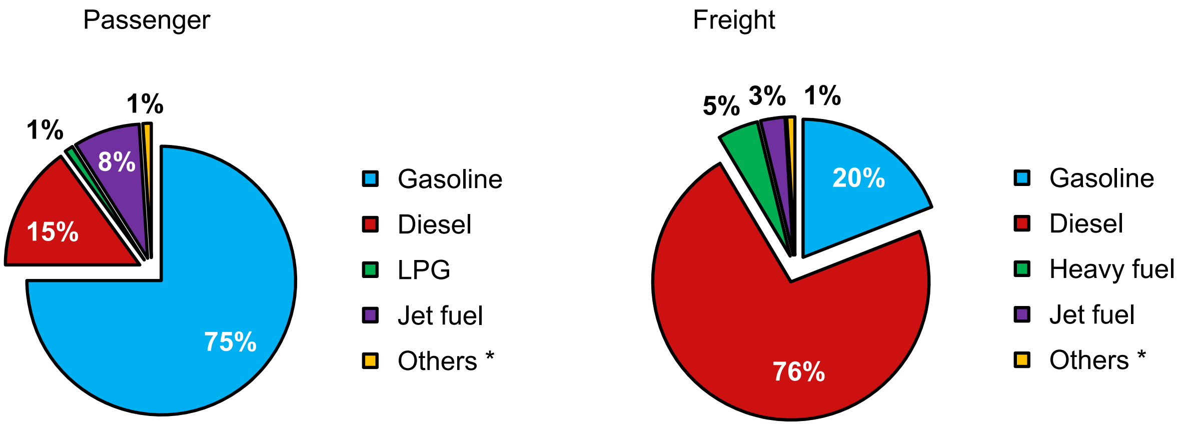

Figure 7 - Energy consumption by energy source for passenger transport and freight transport (for a total of 23 OECD countries, 2010)

Source: IEA (2014b).
* Others include heavy fuel, natural gas, electricity and coal (passenger); and liquefied petroleum gas, natural gas, electricity and coal (freight).

Energy sources for transport in the OECD countries (Figure 7) are based on the fuel oil for passenger transport (gasoline engines) and on fuel diesel for transporting loads (diesel engines). In 2013, countries outside the OECD accounted for about 51.0% of World total oil consumption (BP, 2014). For each of the fossil fuels, World energy TFC rose more rapidly than production (BP, 2014).

2.1.3.1 Renewable energy sources

According to Renewable Energy Policy Network for the 21st Century (REN21) (2014) renewable energy sources provide 19% of World final energy consumption in 2012, modern renewable accounted for approximately 10% in 2012. Figure 8 shows the share of the energy source of World total energy consumption in 2012.

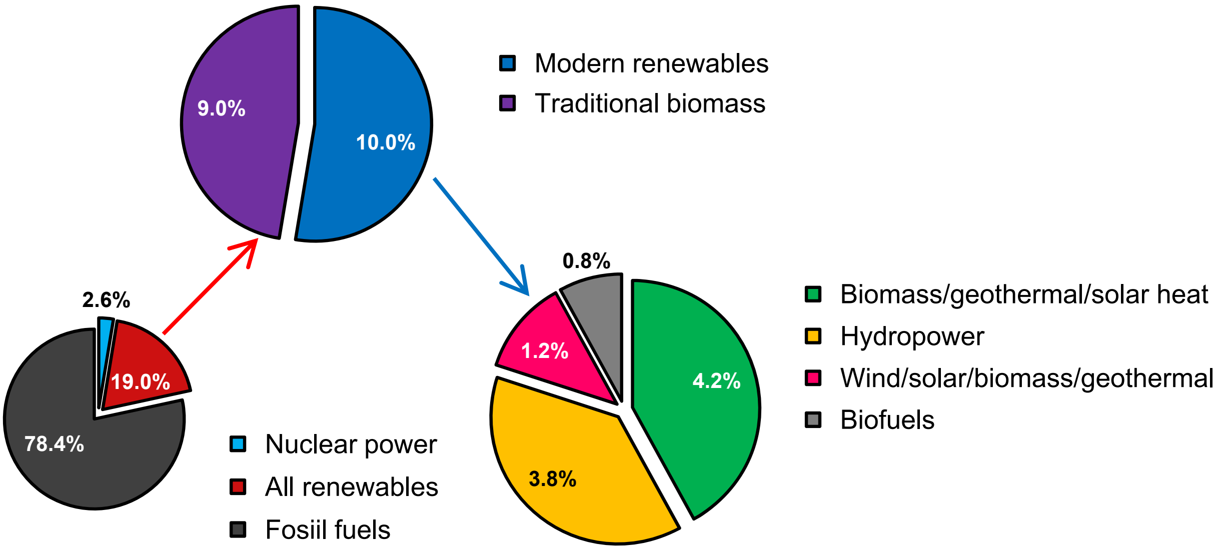

Figure 8 - Share of the renewable energy source in the World TFC (2012)

Source: REN21 (2014).

As shown in Figure 8 modern renewable energy sources accounted for 53% of the share of all renewable energy sources. According to REN21 (2014) hydropower generated is estimated on 3.8%; heat energy accounted for about 4.2%; and transport biofuels provided only about 0.8%.

2.1.3.2 Renewable electricity

Globally, electricity consumption is dominated by fossil resources (coal and natural gas), vehicles accounts for about 75.3% of the consumption in 2013. Figure 9 shows the share of the energy resource of World electricity consumption in 2013 (RENEWABLE ENERGY POLICY NETWORK FOR THE 21ST CENTURY, 2014).

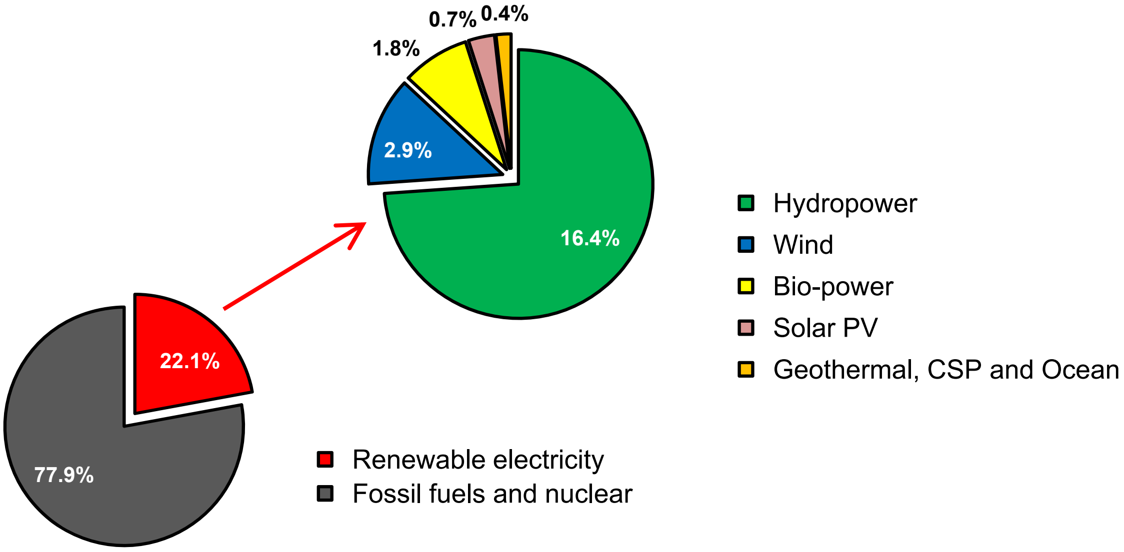

Figure 9 - Share of the renewable energy resources in the World electricity sector consumption (2013)

Source: REN21 (2014).

As shown in Figure 9 hydropower accounted for about 74% of the renewable electricity share, 16.4% of the renewable World electricity consumption. The bio-power provided only 1.8% of the renewable World electricity (RENEWABLE ENERGY POLICY NETWORK FOR THE 21ST CENTURY, 2014).

Wind-generated electricity accounted for about 2.9% of the renewable World electricity share, playing a major role in power supply in an increasing number of countries, Denmark (30%), Portugal (20%), and Spain (16.3%) in 2012 (RENEWABLE ENERGY POLICY NETWORK FOR THE 21ST CENTURY, 2014).

Coal account for a large share of the non-renewable energy resource in the World electricity sector. Coal-fired power plants it was responsible for about 41% of the World electricity consumption in 2012. In South Africa (93%), Poland (87%), China (79%) and Australia (78%) coal fuel correspond to a higher percentage of the electricity sector (INTERNATIONAL ENERGY AGENCY, 2014b).

2.1.4 Brazil’s primary energy supply

According to Energy Research Office (EPE) (2014) Brazil’s primary energy supply is predominant based on fossil resources (oil and natural gas), which accounted for about 40.6% of TPES in 2013, Figure 10 shows the comparative energetic scenarios of indicators recorded in 2004 and in 2013.

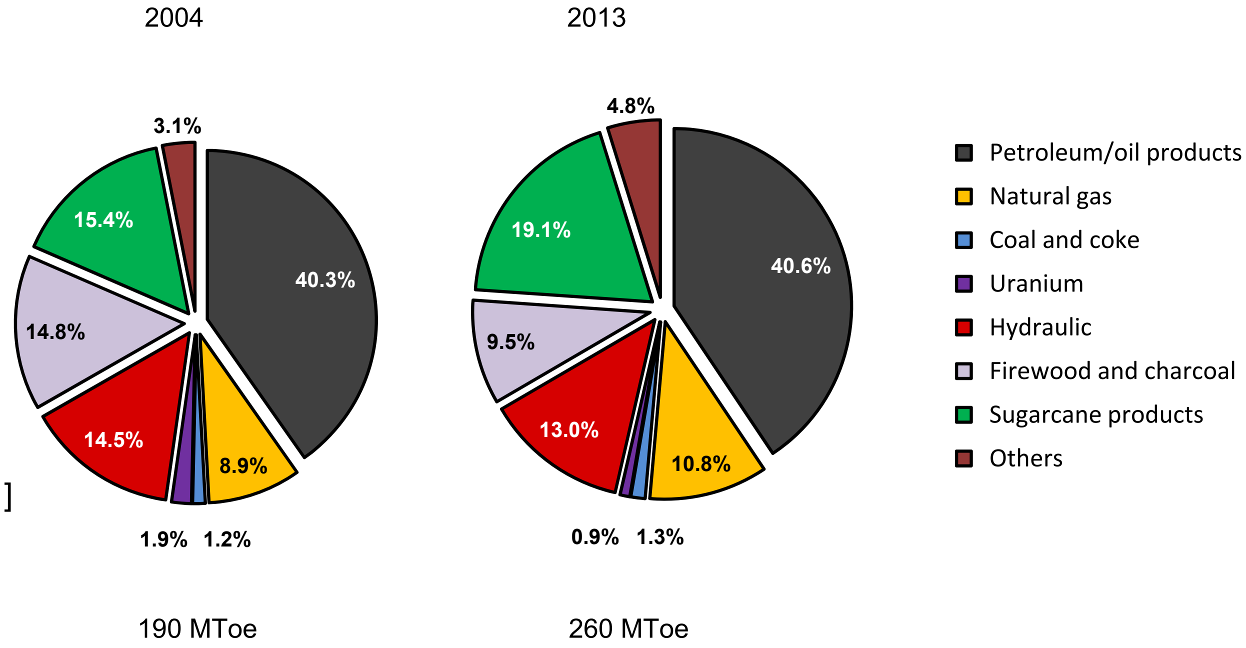

Figure 10 – Brazil’s TPES: 2004 and 2013 fuels shares

Source: EPE (2014).

According to Figure 10 between 2004 and 2013, Brazil’s TPES was expanded by about 37.0% (ENERGY RESEARCH OFFICE, 2014). The sugarcane sector provides about 19.1% of the Brazil’s TPES in 2013 extending the supply of modern sustainable and renewable supply. After the fossil resources, the sugar-energy sector is the most important economic sector in the country (ENERGY RESEARCH OFFICE, 2014).

Production of oil and shale oil in 2013 reached an average of 2.02 million barrels per day (bbl/d). Brazil export liquid biofuels (ethanol) and needs export heavy crude oil (import light oil and oil products) because Brazilian refineries are no able to refine the heavy oil to supply the internal demand of fossil fuels, resulting in large differences between energy supply and internal energy consumption (ENERGY RESEARCH OFFICE, 2014).

2.1.5 Brazil's final primary energy consumption

Figure 11 shows the comparative Brazil's final energy consumption by source by indicators recorded in 2004 and in 2013.

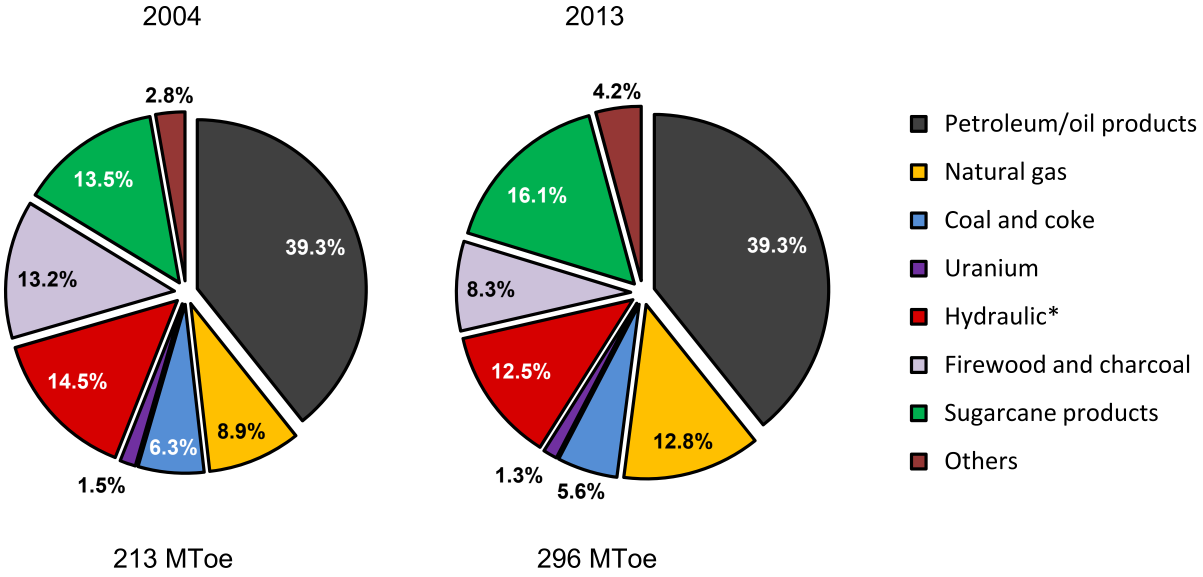

Figure 11 – Brazil's energy TFC: 2004 and 2013 fuels shares

Source: EPE (2014).
*Includes electricity imports originated from hydraulic sources.

According to EPE (2014) the industrial demand for natural gas decreased 1.1% in 2013 over 2012, but there a significant increase of 47.6% in thermal power generation, provided according to Figure 11 about 12.8% of the Brazil's TFC in 2013.

The share of oil products consumed in 2013 is practically the same as in 2004, as result of the increase in the share of the ethanol in the gasoline-ethanol blend and the Brazil's biofuels policy to reduce the dependence on imported fossil fuels (ENERGY RESEARCH OFFICE, 2014).

The demand for liquid fuels and biofuels (fossil and renewable) in 2013 reached 3.0 million bbl/d, while the national production remained in about 2.7 million bbl/d (ENERGY RESEARCH OFFICE, 2014).

Figure 12 shows the share of the residential, industry and services sectors in the Brazil's energy TFC in 2013 of the main primary energy supply.

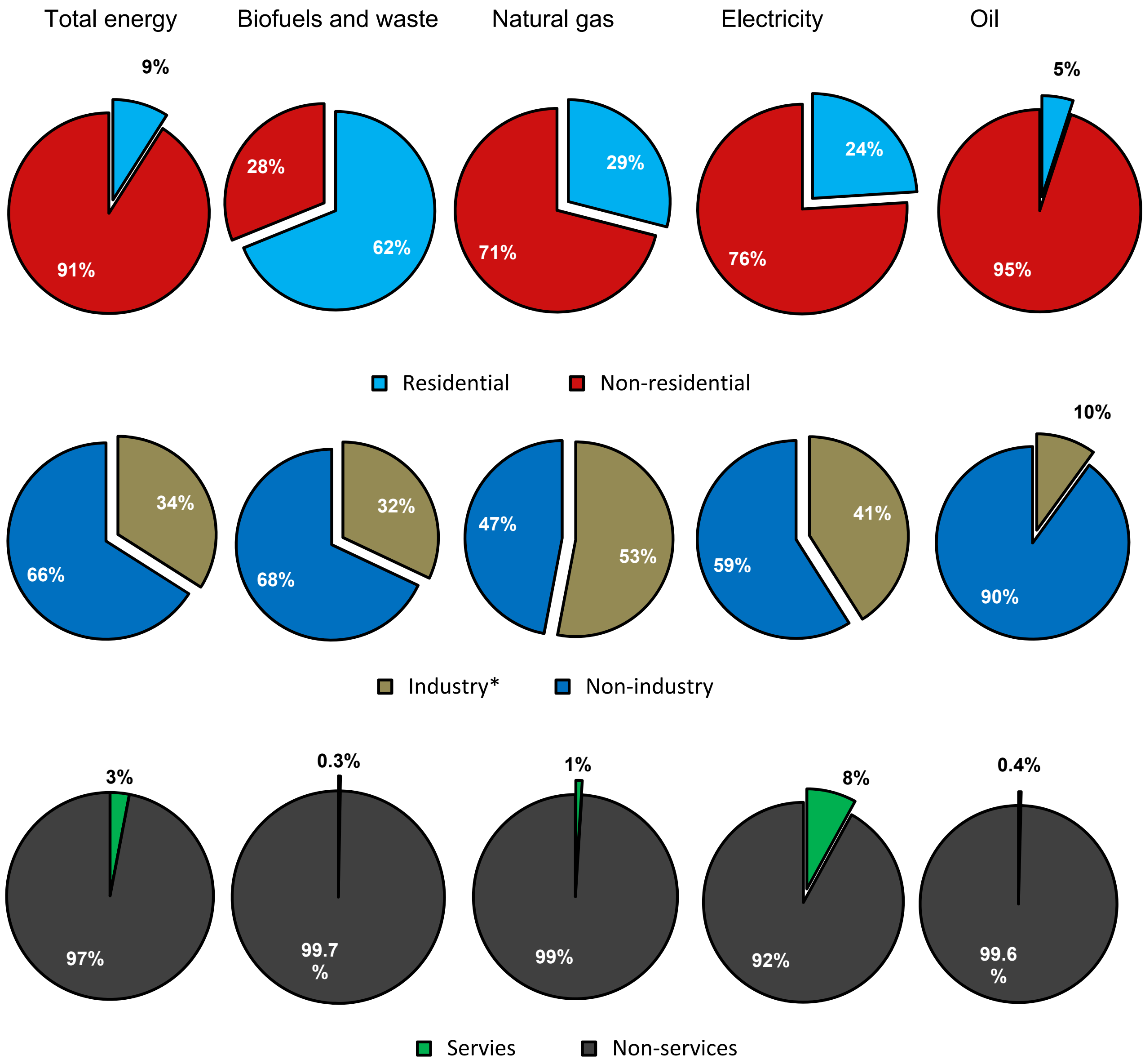

Figure 12 - Share of the residential, industry* and services sectors in the Brazil's energy TFC*** for selected energy sources (2013)**

Source: adapted from EPE (2014).
* Excluding the energy sector
** Refers to the public services
*** Includes natural gas liquids.

As shown in Figure 12, the residential sector accounts only for about 9.0% of Brazil's energy TFC and the industry sector accounts for about 34.0%. The residential sector uses more biofuels (especially biomass) and hydraulic energy (electricity) although the industry sector uses more fossil resources (Oil products and natural gas) (ENERGY RESEARCH OFFICE, 2014).

According to EPE (2014) industrial sector accounts for about 32.0% of biofuels/waste and for about 53.0% of natural gas in the Brazil's TFC, utilized for supply heat and power (local generation). The consumption of oil accounts only for 10.0% of Brazil's energy TFC excluding the electricity sector. The service sector accounts only for about 3.0% of Brazil's energy TFC, being electricity the most important energy source for the sector.

Figure 13 shows the share of the transport sector in the Brazil's energy TFC in 2013.

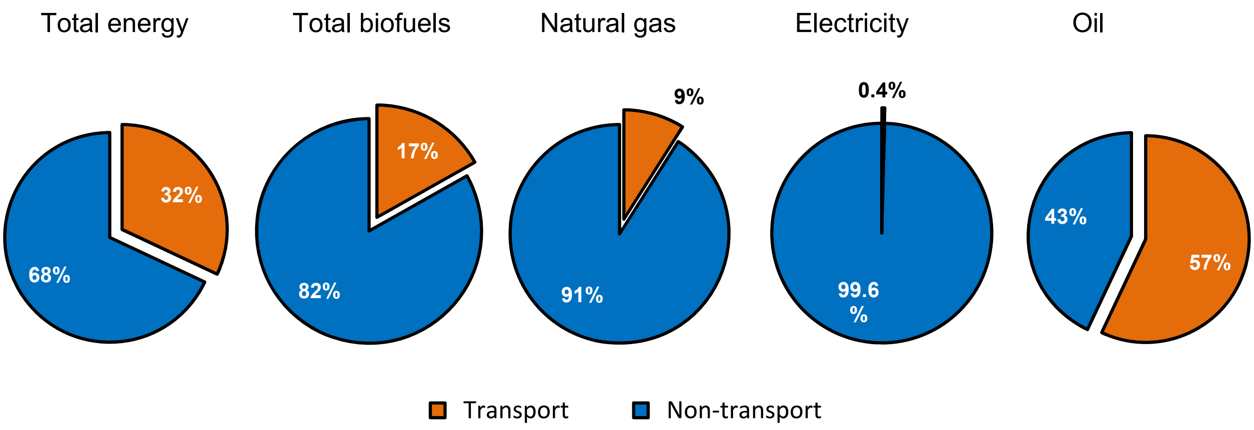

Figure 13 - Share of the transport sector in the Brazil's energy TFC for selected energy sources (2013)

Source: adapted from EPE (2014).
* Includes natural gas liquids.

As shown in Figure 13 the transport sector accounts for about 32.0% of the Brazil's energy TFC. The oil share consumed by the transport sector in 2013 accounts for about 57.0% of Brazil's energy TFC, the total biofuels for transport accounts for about 16.6% (ENERGY RESEARCH OFFICE, 2014)

In May 2013, the proportion of anhydrous ethanol in the ethanol-gasoline blend from 20% (E20) to 25% (E25), registering a fall of 0.2% in gasoline consumption (ENERGY RESEARCH OFFICE, 2014). The percentage of biodiesel (B100) in the biodiesel-diesel blend is 5.0% (2010), reaching a production of 2.917.488 m³ in 2013 (ENERGY RESEARCH OFFICE, 2014).

The transport sector has generated a most share of the total anthropogenic emissions which 215.3 Mt CO_2^{-eq} (ENERGY RESEARCH OFFICE, 2014).

Figure 14 shows the share of each energy source in the Brazil's transport energy consumption in 2013.

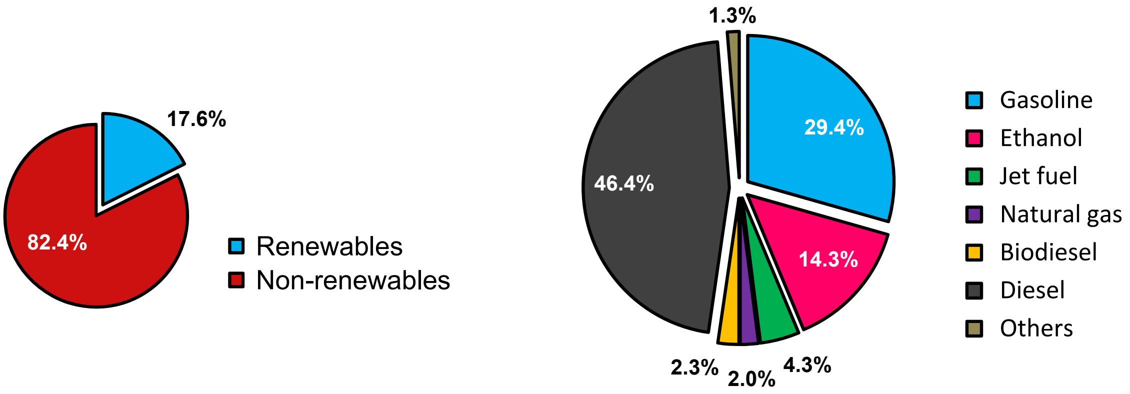

Figure 14 - Share of the various sources in the Brazil's transport energy consumption (2013)

Source: adapted from EPE (2014).

As shown in Figure 14 diesel oil (freight transport) is predominant energy source in the transport sector account for 46.4% of the transport energy consumption, gasoline (passenger transport) account for about 28.4%. The biodiesel (blended in mineral diesel) and ethanol (blended in gasoline or pure) accounted for about 17.6% of the Brazil's transport energy consumption (ENERGY RESEARCH OFFICE, 2014).

Figure 15 shows the breakdown of the Brazil's total transport energy consumption by sub-sector in 2004 and 2013.

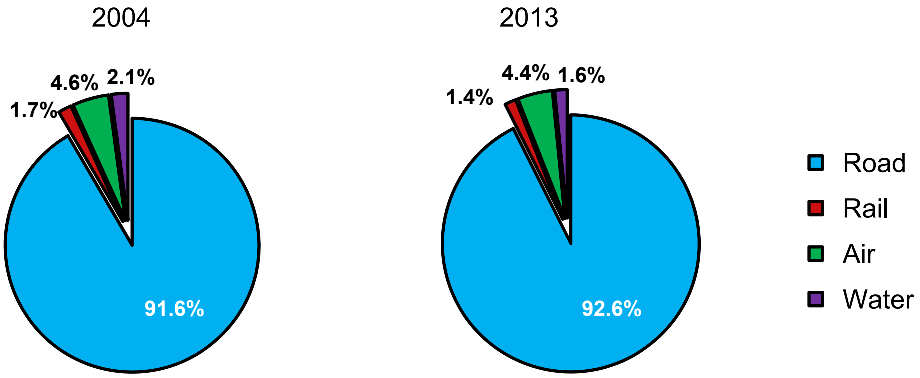

Figure 15 - Energy consumption by sub-sector for the Brazil's total transport consumption*

Source: adapted from EPE (2014).
* Excluding international transport

As shown in Figure 15 the road dominates transport, with 92.6% of the Brazil's total transport consumption (ENERGY RESEARCH OFFICE, 2014).

According to Figure 14 and Figure 15 can be estimate that the transport by heavy-duty vehicles (diesel engine) has the largest impact on the FD, due to the high percentage (more than 90%) of road transport in the Brazil's total transport consumption. The use of road for freight transportation is an unsustainable model an extremely dependent on the fossil fuels.

The transport energy sector has reached 26,139 Mtoe (ENERGY RESEARCH OFFICE, 2014). The sector consumption has increased by about 12.6% in 2013 over 2012.

Figure 16 shows the share of each energy source in the Brazil's energy sector consumption in 2013.

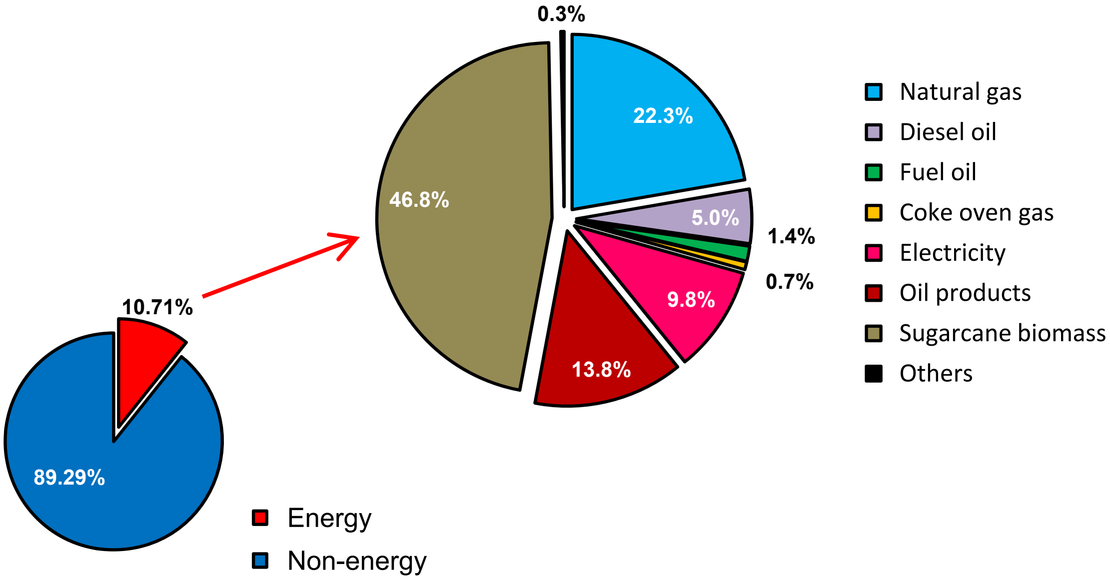

Figure 16 - Share of the various resources in the Brazil's energy sector consumption (2013)

Source: adapted from EPE (2014).

As shown in Figure 16 the sugarcane biomass is the most important resource of the energy sector corresponding for 46.8% of the total resources used in the Brazil's energy sector (ENERGY RESEARCH OFFICE, 2014).

2.1.5.1 Renewable energy resources

Traditional biomass resources (firewood and charcoal) were being replaced over time by the modern sources of energy (heat and power) generation and for fossil fuels (natural gas, coal and others). Figure 17 shows the share of the energy source of Brazil's total energy consumption in 2013 (ENERGY RESEARCH OFFICE, 2014).

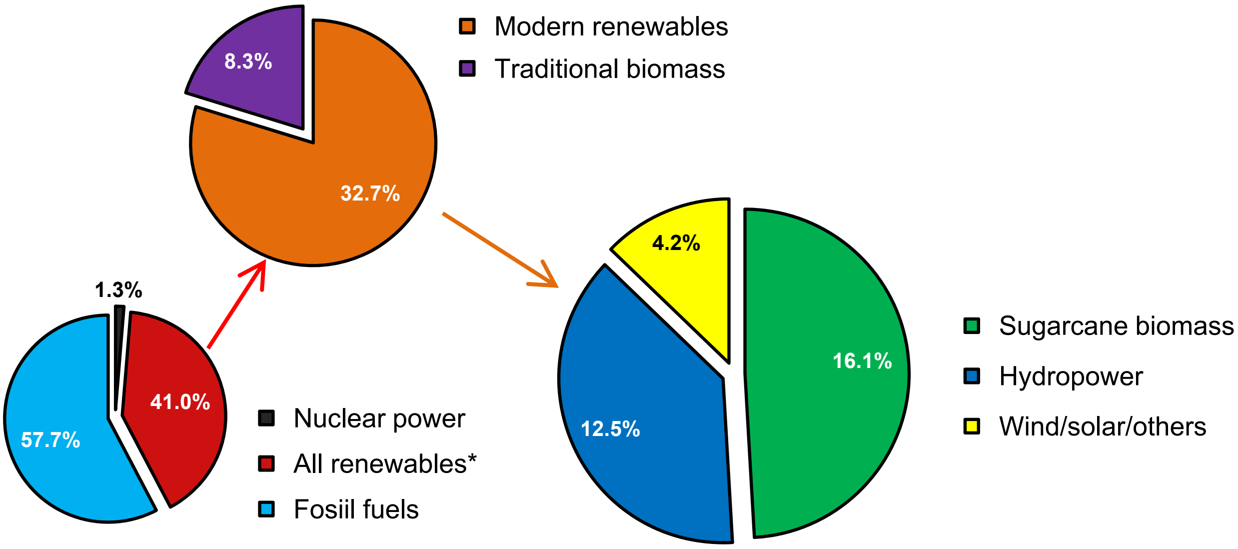

Figure 17 - Share of the renewable energy source in the Brazil's total energy consumption (2013)

Source: EPE (2014).
*Includes electricity imports originated from hydraulic sources.

As shown in Figure 17, modern renewable dominant the share of all renewable resources, in 2013 accounted for about 32.7% of Brazil's TFC (ENERGY RESEARCH OFFICE, 2014).

Sugarcane biomass is used for cogeneration to supply Brazilian 1G sugarcane biorefinery (self-sufficient in energetic terms) that can generate surplus electricity (exported to the electric power grid). Sugarcane biomass accounts for about 16.1% of the Brazil's total energy consumption and for about 49.2% in the share of modern renewable energy sources (ENERGY RESEARCH OFFICE, 2014).

As shown in Figure 18, in 2013 biomass accounted for 7.6% of the Brazil's total electricity final consumption and for about 10.4% in share of the renewable electricity (ENERGY RESEARCH OFFICE, 2014). The production of electricity from wind power reached 6,579 GWh in 2013, represent increased by 30.3% over 2012 (ENERGY RESEARCH OFFICE, 2014).

2.1.5.2 Renewable electricity

Brazil presents an electricity sector predominantly renewable, the electricity generation installed capacity reached 126,743 GW. Renewable resources share for about 79.3% of the domestic energy supply, Figure 18 shows the share of the energy sources of Brazil's total electricity consumption in 2013 (ENERGY RESEARCH OFFICE, 2014).

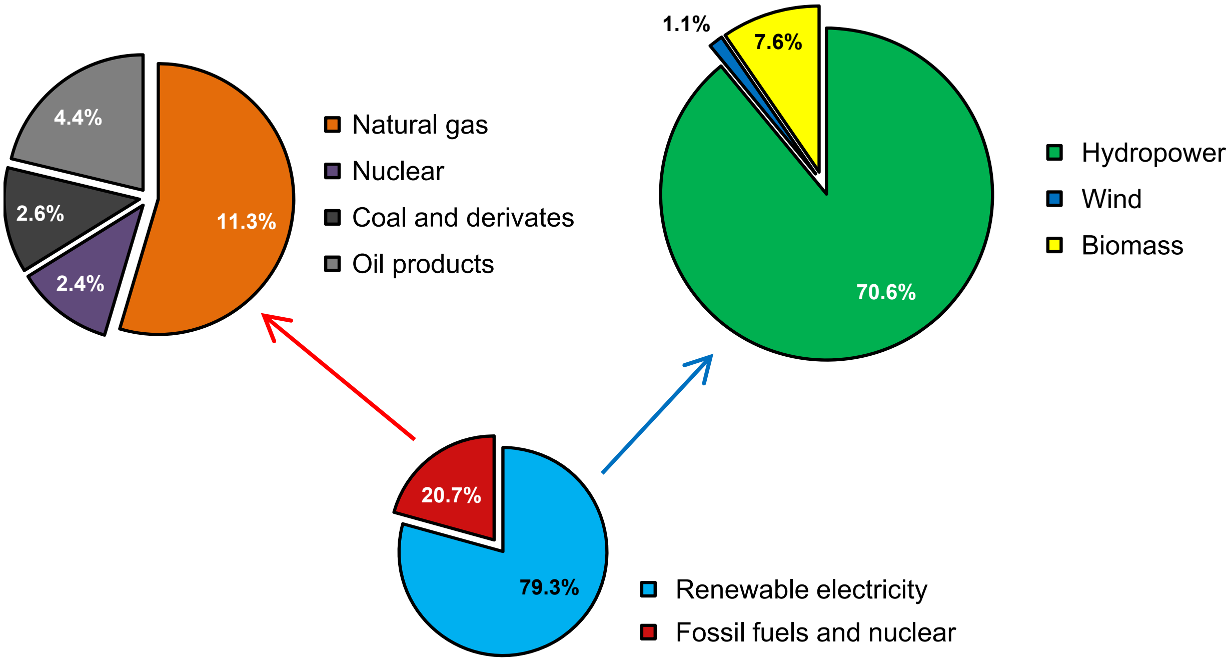

Figure 18 - Renewable energy sources share of Brazil's total electricity final consumption (2013)

Source: EPE (2014).

As shown in Figure 18, in 2013 hydropower (hydraulic source) is responsible for most of the electricity generated in Brazil, accounted for 70.6% of the total electricity final consumption and about 89.0% of the share of all renewable resources of the total electricity final consumption. There is an inversion of the values between renewable and non-renewable resources share when we comparing Brazil's electricity TFC with World electricity TFC (Figure 9).

The increase in hydropower plants accounted for 30% of the added capacity, while thermal power plants accounted for 65% of the added capacity (ENERGY RESEARCH OFFICE, 2014). The biomass is responsible only for 7.6% of the Brazil's total electricity final consumption, but according to Figure 17 was responsible for 16.1% of the Brazil's total energy consumption in 2013 (ethanol).

2.2 Sustainability

"Sustainable development is development that meets the needs of the present generation without compromising the ability of futures generations to meet their own needs" (WORLD COMMISSION ON ENVIRONMENT AND DEVELOPMENT, 1987, p. 43) is the definition published in *Our Common Future* report by Brundtland Commission of the World Commission on Environment and Development (WCED).

It is an approach to environmental and development issues that seeks to reconcile human needs with the capacity of the planet to cope with the consequences of human activities, Figure 19 shows the "three pillars" of sustainable development (environment, social and environmental concerns) (THE ROYAL ACADEMY OF ENGINEERING, 2005).

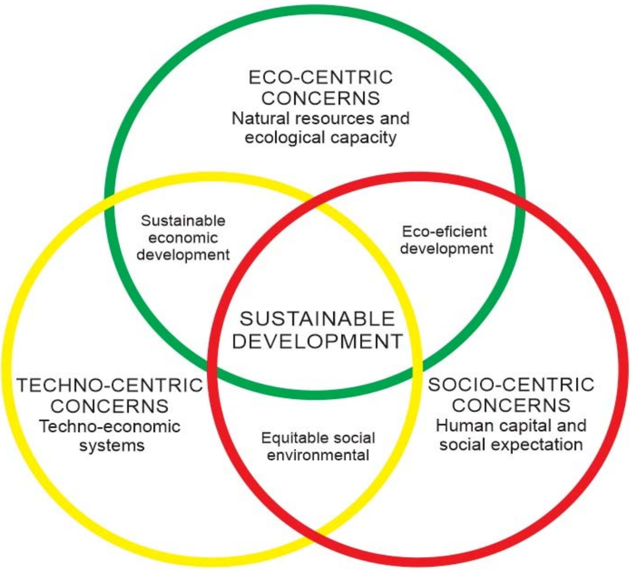

Figure 19 – Three dimensions of sustainability

Source: adapted from The Royal Academy of Engineering (2005).

> Economic sustainability requires that the different kinds of capital that make economic production possible must be maintained or augmented. These include manufactured capital, natural capital, human capital, and social capital. Some substitutability may be possible among these kinds of capital, but in broad terms they are complementary, so that the maintenance of all four is essential over the long term (HARRIS, 2003, p.2).
>
> The conservation of ecosystems and natural resources is essential for sustainable economic production and intergenerational equity. From an ecological perspective, both human population and total resource demand must be limited in scale and the integrity of ecosystems and diversity of species must be maintained. Market mechanisms often do not operate

> effectively to conserve this natural capital, but tend to deplete and degrade it (HARRIS, 2003, p.2).

> Social equity, the fulfillment of basic health and educational needs, and participatory democracy are crucial elements of development, and are interrelated with environmental sustainability (HARRIS, 2003, p.2).

A series of policy initiatives developed over more than 25 years, established principles aiming at sustainable development. Including the Brundtland report (World Commission on Environment and Development, 1987), the Montreal Protocol (United Nations Environment Programme, 1989), the Rio Summit ‘Rio+20’ (United Nations Environment Programme, 1992), Kyoto Protocol (United Nations Framework Convention on Climate Change, 1997), the Stockholm Convention (United Nations Industrial Development Organization, 2001), the World Summit on Sustainable Development (World Summit on Sustainable Development, 2002), and the Climate Change Fifth Assessment Report (Intergovernmental Panel on Climate Change, 2015).

According to Intergovernmental Panel on Climate Change (IPCC) (2015) to keep global warming below 2ºC over the 21st century relative to pre-industrial levels, the global emissions should be reduced in 40% to 70% at 2050 compared to 2010 levels, 201016, and emissions levels near zero or below in 2100.

As a consequence of the large inertia in the climate and carbon cycle, the long-term global temperature is largely controlled by total CO_2 emissions that have accumulated over time, irrespective of the time when they were emitted (INTERGOVERNMENTAL PANEL ON CLIMATE CHANGE, 2015). The report suggests renewables will have to grow from their current 30% to 80% share of the power sector by 2050 (INTERGOVERNMENTAL PANEL ON CLIMATE CHANGE, 2015).

Growing concerns about the impact of GHG emissions on CC and the energetic dependence on fossil fuels have led many countries to diversify its energy mix, based on higher proportion renewable resources and available locally. This international demand is ratified by the Kyoto Protocol, which sets targets for reducing GHG emissions caused mainly by the use of fossil fuels.

Today's society and its development are linked to the excessive dependency on energy, with increasing energy demand and use of "finite" resources for their generation, because of this dependence humanity faces significant problems that not only threaten the continued development, but human existence on the planet. The two major problems are the depletion of fossil fuels and environmental degradations, which are continuously aggravated by the accelerated energy consumption.

In this scenario we developed the ideality of sustainability and energy efficiency, challenging the development of society, especially in developing new technologies and balance or replacement the non-sustainable technologies existing, among them the main challenges is to obtain energy in a sustainable way, and clean allowing progress in overcoming the current paradigm, based on fossil fuels.

2.3 Life cycle

Life cycle is defined as "consecutive and interlinked stages of a product system, from raw material acquisition or generation of natural resources to the final disposal" (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2006a, p. 2).

With the oil crisis of the late 60's and early 70's the company began to wonder about the availability of natural resources and their use in the short and long term, worrying about the environmental impacts caused by the growth economic and industrialization (COLTRO, 2007).

The necessity to conservation of natural resources and the ideality of sustainability of a product (goods and services) promoted the develop methods to evaluate the product and quantify the impacts/implications of the decisions applied to stages of a product system over the product life cycle (BRAZILIAN ASSOCIATION OF TECHNICAL STANDARDS, 2014 a; INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2006a). In this context, one of the methods under development is the Life Cycle Assessment (LCA).

2.3.1 Environmental Life Cycle Assessment (LCA)

"An *environmental life cycle assessment* is a specific life cycle assessment in which environmental aspects are considered. *Environmental life cycle assessment of products* is often simply abbreviated to *life cycle assessment*" (GUINÉE et al., 1992, p. 4).

ISO (2006a) define LCA in the ISO 14040:2006 (Environmental management - Life cycle assessment - Principles and frameworks) as a technique for assessing the environmental aspects and potential impacts associated with a product throughout his life by compilation of inputs (inputs) and outputs (outputs) of a product system defined by evaluating a product (goods and services) throughout its life cycle (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2006a).

And according to European Commission (EC) (2010a) LCA is a structured, internationally standardized method for quantifying the emissions, resources consumed and environmental and health impacts that are associated with a product system.

2.3.1.1 Brief historic of life cycle assessment

The first studies with aspects of LCA (basic form) began in the late 60's and early 70's due to the oil crisis (energy crisis) to quantify the energy consumption of a product system (energy analysis), through flowcharts process with application of mass and energy balances to predict the supplies and consumption of raw materials and energy resources (focus on fuel consumption) (COLTRO, 2007; GUINÉE et al., 1992, 2002). The first study was performed and recognized in the United States of America (USA) as Resource and Environmental Profile Analysis (REPA) by the Midwest Research Institute (MRI) in 1969.

Studies carried out in the 80's and early 90's with different methodologies for the same product are generated distinct results putting into question the reliability of the LCA and its interpretation. With the expanding of applications and the lack of transparency of this LCA's efforts to standardize the LCA began, Society of Environmental Toxicology and Chemistry (SETAC) started the standardization process with criteria for the LCA development (COLTRO, 2007).

In 1991, was formed the Strategic Advisory Group on the Environment (SAGE) to assess the need of standardization in this area, in 1993 the SETAC was published its code of practice, goal and scope definition, inventory analysis, impact assessment, and improvement assessment (COLTRO, 2007).

In 1993, was formed the Technical Committee on Environmental Management (TC 207) by ISO divided into subcommittees (SC) and working groups (WG) in different thematic areas. Following the recommendations of SAGE, in order to regulate and develop environmental management standards at the international level (ISO 14000 series) the subcommittee five (SC 5) was responsible for development of LCA standards (GUINÉE et al., 1992, 2002).

The first international standard was ISO 14040:1997 (*Environmental management - Life cycle assessment - Principles and framework*) published in 1997. An additional standard ISO 14041:1998 (*Environmental management - Life cycle assessment - Goal and scope definition and inventory analysis*) was published in 1998 (required for the ABNT NBR ISO 14040:2001) (BRAZILIAN ASSOCIATION OF TECHNICAL STANDARDS, 2015; INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2015).

The additional standards ISO 14042:2000 (*Environmental management - Life cycle assessment - Life cycle impact assessment*) and ISO 14043:2000 (*Environmental* *management - Life cycle assessment - Life cycle interpretation*), and the technical report ISO/TR 14049:2000 (*Environmental management - Life cycle assessment - Examples of application of ISO 14041 to goal and definition and inventory analysis scope*) were published in 2000 (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2015).

The technical specification ISO/TS 14048: 2002 (*Environmental management - Life cycle assessment - Data documentation format*) was published in 2002 and the technical report ISO/TR 14047 2003 (*Environmental management - Life cycle impact assessment - Examples of application of ISO 14042*) was published in 2003 (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2015).

The ISO 14040:1997 and ISO 14041:1998 standards and the ISO 14042:2000 and ISO 14043:2000 additional standards were joined in only two standards ISO 14040:2006 (*Environmental management - Life cycle assessment - Principles and framework*) and ISO 14044:2006 (*Environmental management - Life cycle assessment - Requirements and guidelines*) (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2015).

The technical report ISO/TR 14047:2003 was replaced by the technical report ISO/TR 14047:2012 (*Environmental management - Life cycle assessment - Illustrative examples on how to apply ISO 14044 to impact assessment situations*) in 2012, in the same year the technical report ISO/TR 14049:2000 has been replaced by technical report ISO/TR 14049:2012 (*Environmental management - Life cycle assessment - Illustrative examples on how to apply ISO 14044 to goal and definition and inventory analysis scope*) (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2015).

The technical reports ISO/TS 14071:2014 (*Environmental management - Life cycle assessment - Critical review processes and reviewer competencies: Additional requirements and guidelines to ISO 14044:2006*) and the ISO/TS 14072:2014 (*Environmental management - Life cycle assessment - Requirements and guidelines for organizational life cycle assessment*) were published in 2014 (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2015).

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2.3.1.1.1 Life cycle assessment in Brazil

After creating the ISO/TC 207 in 1994 was created in Brazil the Environmental Standardization Support Group (GANA) to monitor and analyze the work of the ISO/TC 207 and evaluate the impact of the creation of international environmental standards in Brazil. GANA was concluded its activities in 1998; in place, the Brazilian Association of Technical Standards (ABNT) create the Brazilian Committee of

Environmental Management (ABNT/CB-38) in 1999, with a similar structure to the ISO/TC 207 (BRAZILIAN ASSOCIATION OF TECHNICAL STANDARDS, 2015)

The Brazilian subcommittee five (SC 5) was responsible for the elaboration of Brazilian standards (NBR) corresponding to the ISO 14000 series, which were developed by ISO/TC 207 (BRAZILIAN ASSOCIATION OF TECHNICAL STANDARDS, 2015.

ISO 14040:1997 was transcribed by ABNT/CB-38 and then published in 2001 under the name of ABNT NBR ISO 14040:2001 (first standard of ISO 14000 series related to LCA). In 2004, ABNT/CB-38 published the additional standards ABNT NBR ISO 14041:2004 (*Environmental management - Life cycle assessment - Goal and scope definition and inventory analysis*) and ABNT NBR ISO 14042:2004 (*Environmental management - Life cycle assessment - Impact assessment of life cycle*) and the additional standard ABNT NBR ISO 14043:2005 (*Environmental management - Life cycle assessment - life Cycle Interpretation*) in 2005 (BRAZILIAN ASSOCIATION OF TECHNICAL STANDARDS, 2015).

The standard ABNT NBR ISO 14040:2001 and the additional standards ABNT NBR ISO 14041:2004, ABNT NBR ISO 14042:2004 and ABNT NBR ISO 14043:2005 have been replaced in 2009 by ABNT NBR ISO 14040:2009 (*Environmental management - Life cycle assessment - Principles and framework*) and ABNT NBR ISO 14044:2009 (*Environmental management - Life cycle assessment - Requirements and guidelines*) (BRAZILIAN ASSOCIATION OF TECHNICAL STANDARDS, 2015). Corrections were made in the standards ABNT NBR ISO 14044:2009 and ABNT NBR ISO 14040:2009 and republished as released version in 2014 (BRAZILIAN ASSOCIATION OF TECHNICAL STANDARDS, 2015).

The technical report ABNT NBR ISO/TR 14049:2014 (*Environmental management - Life cycle assessment - Illustrative examples on how to apply ISO 14044 to goal and definition and inventory analysis scope*) was published in 2014 (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2015).

2.3.2 Life cycle assessment standardization

LCA methodology is internationally regulated by ISO and is internationally organized and coordinated by the International Life Cycle Partnerships for a Sustainable World (UNEP/SETAC) a partnership between the United Nations Environmental Programme (UNEP) and the Society of Environmental Toxicology and Chemistry (SETAC) (GUINÉE et al., 1992, 2002; INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2015).

2.3.2.1 ISO 14000 series of standards

The ISO 14000 series of standards of ISO/TC 207 aimed to standardize environmental issues in any type of organization have a link, through a linking group, with the ISO 9000 series of standards of ISO/TC 176, established in 1983 to develop quality management standards for organizations (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2015).

2.3.2.1.1 ISO/TC 207 SC5 standards in effect for 2014/2015 - Life Cycle Assessment

The standards relates with LCA was prepared by ISO/TC 207, *Environmental management*, Subcommittee SC5, *Life cycle assessment*. International standards related to LCA in effect for 2014/2015 are ISO 14040:2006 and ISO 14044:2006 (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2015). In addition to the standards, this series contain published the technical reports ISO/TR 14047:2012 and ISO/TR 14049:2012 (additional to ISO 14044:2006), and published the technical specifications ISO/TS 14048:2002, ISO/TS 14071:2014 and ISO/TS 14072:2014 (additional to ISO 14040:2006 and ISO 14044:2006) (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2015).

2.3.2.1.2 ABNT/CB-38 SC5 standards in effect for 2014/2015 - Life Cycle Assessment

The Brazilian standards related to LCA published by ABNT/CB-38 in effect for 2014/2015 are the ABNT NBR ISO 14040:2009 and ABNT NBR ISO 14044:2009 (released versions in 2014) organized and published by ABNT/CB-38 from the international standards ISO 14040:2006 and ISO 14044:2006. In addition to the standards, the series contain published the technical reports ABNT ISO/TR 14049:2014 as a means to satisfy certain provisions to ABNT NBR ISO 14044:2009) (BRAZILIAN ASSOCIATION OF TECHNICAL STANDARDS, 2015; INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2015). In Brazil, the transcripts of the ISO 14000 series by ABNT/CB-38 maintain the same corresponding number to the numbering of ISO/TC 207 (international standards).

2.3.2.1.2.1 ABNT NBR ISO 14040:2009 released version in 2014

ABNT NBR ISO 14040:2009 describes the principles and framework for life cycle assessment (LCA) including: definition of the goal and scope of the LCA, the life cycle inventory analysis (LCI) phase, the life cycle impact assessment (LCIA) phase, the life cycle interpretation phase, reporting and critical review of the LCA, limitations of the LCA, the relationship between the LCA phases, and conditions for use of value choices and optional elements (BRAZILIAN ASSOCIATION OF TECHNICAL STANDARDS, 2014a, 2015).

2.3.2.1.2.2 ABNT NBR ISO 14044:2009 released version in 2014

ABNT NBR ISO 14044:2009 specifies requirements and provides guidelines for life cycle assessment (LCA) including: definition of the goal and scope of the LCA, the life cycle inventory analysis (LCI) phase, the life cycle impact assessment (LCIA) phase, the life cycle interpretation phase, reporting and critical review of the LCA, limitations of the LCA, relationship between the LCA phases, and conditions for use of value choices and optional elements (BRAZILIAN ASSOCIATION OF TECHNICAL STANDARDS, 2014b, 2015)

2.3.2.1.2.3 ABNT NBR ISO/TR 14049:2014

ABNT NBR ISO/TR 14049:2014 provides examples about practices in carrying out a life cycle inventory analysis (LCI) as a means of satisfying certain provisions of ISO 14044:2006. These examples are only a sample of the possible cases satisfying the provisions of ISO 14044. They offer "*a way*" or "*ways*" rather than the "*unique way*" for the application of ISO 14044 (BRAZILIAN ASSOCIATION OF TECHNICAL STANDARDS, 2014c, 2015).

2.3.3 Phases of an life cycle assessment

ISO 14044:2006 and ABNT NBR ISO 14044:2009 describes the main four-bed process (phases) necessary for the development/conduct of an LCA, this standards include additional phases for reporting and certifying the results for LCA’s whose results will be compared with other LCA's. According to ISO (2006a) and EC (2010a) the LCA consist in four distinct phases:

a) goal and scope definition phase: Clearly define the goal and scope of the LCA describing the function and functional unit, system boundaries, and comparisons between systems;
b) inventory analysis phase: compile an inventory of relevant inputs and outputs (mass and energy) that are used in LCA;
c) impact assessment phase: Assess the potential environmental impacts using the inventory analysis to understand the magnitude and significance of the potential environmental impacts of a product system;
d) interpretation phase: compare impacts between two or more equivalent products or processes and interpret the results to identify the impacts that will aid in decision making processes.

2.3.4 Goal an scope definition

The intended application of LCA or LCI results is considered during the goal and scope definition phase, but the application itself is outside the scope of international standards EC (2010a). According to EC (2010a), ISO (2006a) and ABNT (2014a) the scope includes: the product system to be studied; the functions of the product system or, in the case of comparative studies, the systems; the functional unit; the system boundary; allocation procedures; select impact categories and impact assessment methodology, and subsequent interpretation to be used; data requirements; assumptions; limitations; initial data quality requirements; type of critical review, if any; type and format of the report required for the study.

2.3.5 Relative approach and functional unit

LCA is a relative approach, which is structured around a functional unit. All subsequent analyses are then relative to that functional unit, as all inputs and outputs in the life cycle inventory (LCI) and consequently the life cycle inventory assessment (LCIA) profile are related to the functional unit (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2006a).

Functional unit provide a reference to which the inputs and outputs are related in the product system, indicating how much of this function is to be considered in the intended LCA study and defining the scale for an environmental comparison between existing products and the development of new products. Comparisons between systems shall be done on the base of the same function, measured by the same functional unit in the form of equivalent reference flows (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2006a).

2.3.6 System boundary and level of detail

LCA is a systematic assessment process that quantifies the elemental material flows (mass balance) and the energy flows (energy balance) of a product in its life cycle within the boundary of a product system (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2006a). The product system boundaries (Figure 20) define the processes (e.g.: manufacturing, transport and waste management processes), and the inputs and outputs to be taken into account in the LCA (BAUER, 2003; INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2013).

Product systems are subdivided into a set of unit processes linked to one another by flows of intermediate products and/or waste for treatment, to other product systems by product flows, and to the environment by elementary flows include the use of resources and releases to air, water and land associated with the system (EUROPEAN COMMISSION, 2010a).

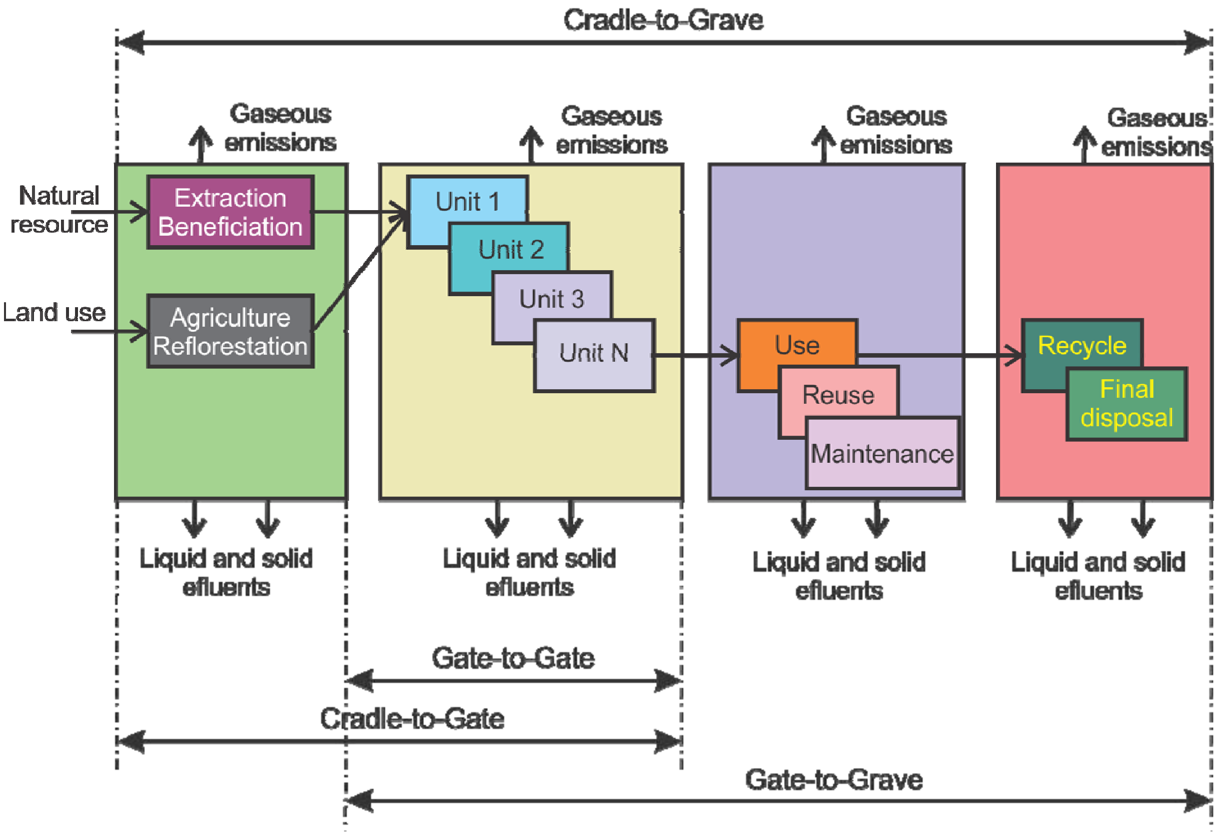

Figure 20 - Product system boundary

Source: adapted from Bauer (2003) according to ISO 14048:2002

Figure 20 shows the different types of process according to different product system boundary (processes) that are studied in life cycle assessment. According to ISO (2013, p. 12) these types can be:

1) Cradle-to-gate: a process starting with resource extraction, which may include some manufacturing or service operations but excluding all subsequent stages.
2) Cradle-to-grave: a process starting with resource extraction to the final disposal of the product.
3) Gate-to-gate: a process where all production stages occur within one site. The site may be geographically specified, or in the case of e.g. average data, the geographical specification may be more general. Processes outside the defined gates are not included.
4) Gate-to-grave: a process that includes the distribution, the use and the final disposal of the product.

The final system boundary of the analyzed system shall as far as possible include all relevant life cycle stages and processes (BAUER, 2003). To ensure a fair comparison of different scenarios, the chosen functional unit should reflect well-justified typical or average production, or operation, or unit scenarios (BAUER, 2003).

2.3.7 Life cycle inventory

According to ISO (2000a, p.1) LCI is “outcome of a life cycle inventory analysis that includes the flows crossing the system boundary and provides the starting point for life cycle impact assessment”.

LCI is a compilation of the elemental material flows (mass balance) and the energy flows (energy balance) quantified requirements, emissions, wastes (liquid gaseous and solids) and others releases for the entire life cycle of the boundary product system in the inventory analysis phases to forming a central repository with information about the product system to be assessed (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2006a; SEPPÄLÄ, 2003).

2.3.8 Life cycle inventory assessment

LCIA is a “phase of life cycle assessment aimed at understanding and evaluating the magnitude and significance of the potential environmental impacts for a product system throughout the life cycle of the product” (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2006a, p. 2).

For an LCIA, impacts are defined as the consequences that could be caused by the input and output streams of a system on human health, plants, and animals, or the future availability of natural resources (SEPPÄLÄ, 2003). This phase covers the activities related to the quantification of raw materials and energy needed, as well as the generated waste (solid, liquid, and gaseous) in all stages in the product system, inventories of emissions and resources consumed are assessed in terms of impacts. This is achieved using indicators for Human Health, Natural Environment, and Natural Resources (EUROPEAN COMMISSION, 2010a, SEPPÄLÄ, 2003).

According to EC (2010b) LCIA proceeds through four-bed:

a) selection of categories of impacts: environmental impacts are defined within the defined objectives and product system limitations;
b) characterization: impact of each emission or resource consumption is modeled quantitatively. The result is expressed as an impact score (factor) in a common drive for all contributions within the impact category in a unit common to all contributions within the impact category;
c) Normalization (optional phase): the characterized impact scores are associated with a common reference.
d) Weighting (optional phase): the different categories of environmental impact are classified according to their relative importance.

2.3.8.1 Selection of impact categories

The aspect on the basis of which different LCIA approaches can be distinguished is how a quantifiable representation of impact category is chosen in the cause-effect chain (environmental mechanism) in order to calculate indicator results (SEPPÄLÄ, 2003).

Problem-oriented approach (Midpoint) category (traditional) reflects the relative potential of the stressors at a common midpoint within the cause-effect chain (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2006a; Seppälä, 2003).

Damage approach (endpoint) category (alternative) reflect on the attributes or aspect of natural environmental human health, or resources, identifying an environmental issue giving cause for concern, describing observable environmental endpoints (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2006a; Seppälä, 2003).

2.3.9 Environmental impact indicators

Environmental impact indicators has the function of provide a quantitative easily measures that can illustrate and communicate complex phenomena in a simple way. An indicator provides a clue to a matter of greater importance or makes perceptible a trend or phenomenon that is not immediately detectable (EUROPEAN COMMISSION, 2010a, SEPPÄLÄ, 2003).

2.3.9.1 ReCiPe impact indicators

ReCiPe is a developing methodology for LCIA combining midpoint and endpoint methodologies in a consistent framework, is the successor of Eco-indicator 99 and CML 2002 methods (EUROPEAN COMMISSION, 2010b; PRÈ, 2014a).

ReCiPe 2008 comprises two sets of impact categories with associated sets of characterization factors. Eighteen impact indicators are addressed at the midpoint category: climate change (CC); ozone depletion (OD); terrestrial acidification (TA); freshwater eutrophication (FE); marine eutrophication (ME); human toxicity (HT); photochemical oxidant formation (POF); particulate matter formation (PMF); terrestrial ecotoxicity (TET); freshwater ecotoxicity (FET); marine ecotoxicity (MET); ionizing radiation (IR); agricultural land occupation (ALO); urban land occupation (ULO); natural land transformation (NLT); water depletion (WD); mineral resource depletion (MRD) or metal depletion (MD); and fossil fuel depletion (FD) (EUROPEAN COMMISSION, 2010b; GOEDKOOP et al., 2009). At the endpoint category, most of these midpoint impact categories are further converted and aggregated into the following three endpoint categories: damage to human health (HH); damage to ecosystem diversity (ED); and damage to resource availability (RA) (EUROPEAN COMMISSION, 2010b; GOEDKOOP et al., 2009).

All impact indicators of the same area of protection have the same indicator unit. Same environmental mechanism for midpoint and endpoint calculations is used. Each category (midpoint, endpoint) contains factors according to the three cultural perspectives (EUROPEAN COMMISSION, 2010b; GOEDKOOP et al., 2009). These perspectives represent a set of choices on issues like time perspective or expectations that proper management or future technology development can avoid future damages.

According to Goedkoop et al. (2009) and EC (2010b) for some of conversion and aggregation steps, uncertainties have been incorporated in the form of different perspectives:

a) Egalitarian (E): long term based on precautionary principle thinking;
b) Hierarchism (H): Consensus model, as often encountered in scientific models, this is often considered to be the default model;
c) Individualist (I): short term, optimism that technology can avoid many problems in future.

A midpoint indicator can be defined as a parameter in a cause-effect chain or network (environmental mechanism) for a particular impact category. The substances that contribute to an impact category are multiplied by a characterization factor that expresses the relative contribution of the substance (GOEDKOOP et al., 2009).

According to PRé (2014a, 2014b) and Goedkoop et al. (2009) the impact categories at a midpoint level are defined as:

a) ozone depletion: The characterization factor for ozone layer depletion accounts for the destruction of the stratospheric ozone layer by anthropogenic emissions of ozone depleting substances.
b) human toxicity and ecotoxicity: The characterization factor of human toxicity and ecotoxicity accounts for the environmental persistence (fate) and accumulation in the human food chain (exposure), and toxicity (effect) of a chemical.
c) ionizing radiation: The characterization factor of ionizing radiation accounts for the level of exposure.
d) photochemical oxidant formation: The characterization factor of photochemical oxidant formation is defined as the marginal change in the 24h-average European concentration of ozone (dCO_3 in $kg \cdot m^{-3}$) due to a marginal change in emission of substance x (dMx in $kg \cdot year^{-1}$).
e) particulate matter formation: The characterization factor of particulate matter formation is the intake fraction of PM_{10}.
f) climate change: The characterization factor of climate change is the global warming potential.
g) agricultural and urban land occupation: The amount of either agricultural land or urban land occupied for a certain time.
h) natural land transformation: The amount of natural land transformed and occupied for a certain time.
i) marine eutrophication: The characterization factor of marine eutrophication accounts for the environmental persistence (fate) of the emission of N containing nutrients.
j) freshwater eutrophication: The characterization factor of freshwater eutrophication accounts for the environmental persistence (fate) of the emission of P containing nutrients.
k) fossil fuel depletion: The characterization factor of fossil depletion is the amount of extracted fossil fuel extracted, based on the lower heating value.

l) Minerals/metal depletion: The characterization factor for minerals depletion is the decrease in grade.
m) freshwater depletion: The factor for the freshwater depletion is the amount of fresh-water consumption.

The model of interventions into midpoint indicators is performed by the use of characterization. Table 1 shows an overview of the midpoint categories and characterization factors.

Table 1 - Midpoint impact categories and characterization factors

Impact Category		**Characterization factor**	
Code	**Unit***	**Code**	**Name**
CC	kg (CO_2 to air)	GWP	global warming potential
OD	kg (CFC-11^5 to air)	ODP	ozone depletion potential
TA	kg (SO_2 to air)	TAP	terrestrial acidification potential
FE	kg (P to freshwater)	FEP	freshwater eutrophication potential
ME	kg (N to freshwater)	MEP	marine eutrophication potential
HT	kg (14DCB to urban air)	HTP	human toxicity potential
POF	kg ($NMVOC^6$ to air)	POFP	photochemical oxidant formation potential
PMF	kg (PM_{10} to air)	PMFP	particulate matter formation potential
TET	kg (14DCB to industrial soil)	TETP	terrestrial ecotoxicity potential
FET	kg (14DCB to freshwater)	FETP	freshwater ecotoxicity potential
MET	kg (14-DCB^7 to marine water)	METP	marine ecotoxicity potential
IR	kg (U^{235} to air)	IRP	ionizing radiation potential
ALO	m^2xyr (agricultural land)	ALOP	agricultural land occupation potential
ULO	m^2xyr (urban land)	ULOP	urban land occupation potential
NLT	m^2 (natural land)	NLTP	natural land transformation potential
WD	m^3 (water)	WDP	water depletion potential
MRD	kg (Fe)	MDP	mineral depletion potential
FD	kg (oil)	FDP	fossil depletion potential

Source: adapted from Goedkoop et al. (2009)
*The unit of the impact category is the unit of the indicator result, thus expressed relative to a reference intervention in a concrete LCA study.

2.3.10 Allocation

Allocation methods are used when product systems involving multiple products to divide the environmental load of a process between the various products generated (co-products), in a multifunctional product system, providing more functions than that in the functional unit. It is applied not only to situation of co-production, but also to situations of recycling and combined waste management (value creation) (GUINÉE et al., 1992, 2002).

ISO 14040:2006 and ISO 14044:2006 recommend avoiding allocation whenever possible by subdivision or expansion of the product system to include all inputs and outputs, but in a multifunctional system is difficult or not viable to do (complex system), and the allocation of the environmental impacts is necessary (CHERUBINI, STROMMAN and ULGIATI, 2011; INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2006a, 2016b).

The allocations methods should be based on the natural causality or an adequate approximation, on economic/social causality or on physical parameters (GUINÉE et al., 2002; PRÈ, 2014b). Energy and exergy-based and economic-based allocations is the most common methods applied for allocations in a multifunctional product system (CHERUBINI, STROMMAN and ULGIATI, 2011). Every method has advantages and disadvantages, and none of them is suitable for all the possible situations (CHERUBINI, STROMMAN and ULGIATI, 2011).

2.3.11 Normalization & Weights of the result impacts

Normalization of the impacts is an optional element within impact assessment. Involve relating all impact scores of a functional unit in the impact score profile to a reference situation scaling the data by a reference factor (SEPPÄLÄ, 2003; PRÈ, 2014a, 2014b). Results in a normalized impact scores helps to clarify the relative impact of a substance in a given context (SEPPÄLÄ, 2003).

The weighting step of an LCIA assigns weights or relative values to the different impact categories based on their perceived importance or relevance (GUINÉE et al., 1992, 2002; PRÈ, 2014a). The standard weighting set for each cultural or archetypical perspective (Hierarchic, Individualist, and Egalitarian) is based on a panel survey (GUINÉE et al., 1992, 2002; PRÈ, 2014a).

2.3.12 Life cycle interpretation

Life Cycle Interpretation is the phase in which the results of the analysis and all choices and assumptions made during the course of the analysis are evaluated. Interpretation intended to provide a readily understandable, complete and consistent presentation of the LCA results accordance with the goal and scope definition. ISO/TS 14040:2006 and ABNT NBR ISO 14040:2009 describes the life cycle interpretation phase (BRAZILIAN ASSOCIATION OF TECHNICAL STANDARDS, 2014a; INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2006a)

2.3.13 Critical review

Critical review by internal or external experts includes interested parties by the conclusions drained from the LCA testing of certain aspects of an LCA project during the process may facilitate understanding and enhance the credibility of LCA (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2006a). ISO/TS 14071:2014 provide requirements and guidelines for conducting a critical review of any type of LCA study and the competencies required for the review (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2014).

2.3.14 Limitation

The LCA according to Guinée et al. (2002), due the "holistic" nature, is the great strength and at the same time, its limitation. The full extent of the complete life cycle analysis of a product can only be achieved at the expense of simplifying other aspects not being a full assessment of all environmental issues of the product system. LCA cannot resolve localized impacts and cover all possible process units, the system or product does not include all the inputs and outputs of each process unit.

LCA is typically the steady-state and the model focuses on physical characteristics of the industrial activities and other economic processes; it does not include market mechanisms (GUINÉE et al., 2002; INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2006a; PRÈ, 2014a, 2014b).

Inadequate LCI data quality caused by uncertainties or differences in allocation and aggregation procedures (GUINÉE et al., 2002; PRÈ, 2014b).

LCA focuses only on the environmental aspects of products, and says nothing about economic, social and other aspects INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2006a.

Environmental impacts are not specified in time and are often described as "potential impacts" (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2006a).

3 Methodology and definitions

Thermochemical-biorefinery is defined as biomass-based thermochemical conversion route (different routes and scenarios) integrated at a Brazil's characteristic 1G sugarcane biorefinery with annexed ethanol distillery (sugar and ethanol production) mainly targeting integral use of available biomass (bagasse and straw) and co-production (Brazil's sugar-energy sector) of sugar, thermal energy, electricity, liquid fuels, and chemicals (multi-product plants).

Thermochemical-biorefinery scenarios were developed and assessed (environmental assessment) under the scope of the Virtual Sugarcane Biorefinery (VSB) simulation and assessment platform (tool).

3.1 Virtual Sugarcane Biorefinery (VSB) simulation and assessment platform (tool)

VSB simulation and assessment platform is a tool under development by the division of AIB of CTBE/CNPEM to perform assessments on the three pillars of sustainability (economical, environmental, and social) (BONOMI et al., 2016; BRAZILIAN BIOETHANOL SCIENCE AND TECHNOLOGY LABORATORY, 2015a).

The construction of VSB tool started in 2010, currently (2015) it is considered a worldwide unique tool for integrated biorefineries assessment (BRAZILIAN BIOETHANOL SCIENCE AND TECHNOLOGY LABORATORY, 2015a). VSB tool is not only single software, but a set of commercial software and in-house models (BRAZILIAN BIOETHANOL SCIENCE AND TECHNOLOGY LABORATORY, 2015b).

"The VSB tool is based on mathematical modeling and simulation of different processes and operations included in the sugarcane production chain (agricultural, industrial, and usage sectors)" (BONOMI et al., 2016 p. 7).

For a better understanding of VSB tool it is recommended read the publication named – *The Virtual Sugarcane Biorefinery (VSB)*: 2011 Report (BRAZILIAN BIOETHANOL SCIENCE AND TECHNOLOGY LABORATORY, 2012) – and the publication named – Virtual Biorefinery: An Optimization Strategy for Renewable Carbon Valorization (BONOMI et al., 2016).

3.1.1 Agricultural phase

CanaSoft spreadsheet models simulate and measure the most important agricultural parameters of biomass production system alternatives (BONOMI et al., 2016; BRAZILIAN BIOETHANOL SCIENCE AND TECHNOLOGY LABORATORY, 2012). The inventories are obtained through interconnected modules that represent different crop phases (i.e.: pre-planting, planting, cultivation, harvesting and transportation), from main agricultural production parameters that define a biomass production system (i.e.: yields, type of planting, type of harvesting, use of fertilizers, use of agrichemicals, transportation logistics) to specific parameters (i.e.: types of harvesters, tractors and implements, weights, costs, diesel consumption, annual use, life span, and depreciation) (BONOMI et al., 2016; BRAZILIAN BIOETHANOL SCIENCE AND TECHNOLOGY LABORATORY, 2012).

In this research Master’s degree, CanaSoft Model spreadsheet models are used to determine the LCI of the agricultural phase considering traditional sugarcane cultivation crops (Southeast region of Brazil) supplying cane stalks and straw (bales) for a optimized 1G sugarcane biorefinery with annexed ethanol distillery (2.0 Million of processed cane).

3.1.2 Industrial phase

To simulate and measure the industrial phase by VSB simulation and assessment platform is necessary mainly a complete mass and energy balances for the industrial system boundary, as well the Operational Expenditure (OPEX) and Capital Expenditure (CAPEX) for the proposed technological route-scenarios (BONOMI et al., 2016).

Currently (2015), most of the assessments performed under the scope of VSB tool obtain the mass and energy by simulating industrial technologies and processes (industrial phase) in the Aspen Plus processes simulation platform, which is part of AspenONE engineering software package developed by AspenTech Company (USA) (BONOMI et al., 2016).

In this research Master’s degree, Aspen Plus®v8.4 process simulation platform is used to simulate the industrial phase providing as result a rigorous mass and energy balances (not only, but also technical and operational parameters) for the proposed sugarcane biorefinery scenarios, the most important step in the VSB tool. Aspen Plus®v8.4 process simulation platform is used to solve the flowsheet by sequential modular (SM) approach, solving the process scheme module-by-module, calculating the outlet stream properties using the inlet stream properties for each block.

3.1.3 Logistic and end-use phases

Log&UsoSoft spreadsheet models are in the early development stages is structured to calculate and estimate (e.g.: social impacts, potential environmental impacts and economic impacts) operations (Brazil case) involved with: distribution logistics and commercialization (e.x.: distance, distribution agent, infrastructure, transportation mode); and product end-uses (e.x. product exerting a function) (BONOMI et al., 2016).

The assessment of the use of fuels in Brazil's vehicles (fuel consumption and emission databank) using Log&UsoSoft spreadsheet model allows identifying the different sources for airborne emissions, ranking the main pollutants (environmental assessment) (BONOMI et al., 2016). Specific fuel consumption and emission factors for other fuels (pure or blended) and for new automotive technologies can be included in Log&UsoSoft spreadsheet models (BONOMI et al., 2016).

In this research Master's degree, only the Log&UsoSoft spreadsheet models for product end-use are considered, employed in the comparison (consumed in Brazilian passenger average-vehicles) between the potential environmental impacts for: fuel ethanol obtained by biochemical-based biorefineries; fuel ethanol obtained by thermochemical-based biorefineries; and gasoline obtained from fossil resources (oil).

3.1.4 Environmental assessment

The evaluation of potential environmental impacts associated with a product and its function is conducted according to the standards ISO 14000 series and theirs equivalent Brazilian standards ABNT NBR ISO 14000 series related to LCA in effect (BONOMI et al., 2016).

Inventories obtained from the agricultural phase (from CanaSoft spreadsheet models), industrial phase (computer simulation platform), and logistic and end-use phases (Log&UsoSoft spreadsheet models) are compiled to form the biorefinery LCI, which is assessed (LCIA) considering the Brazilian context by using the SimaPro$^{®}$ software (PRé Consultants B.V., Netherlands) to obtain the environmental categorized impact indicators.

The evaluated results from LCIA provide information's to identify critical processes on the evaluated bio-based scenarios (thermochemical routes) and enable environmental comparisons between technologies and equivalent products derived from fossil resources and renewable resources.

In this research Master’s degree, LCA is developed under the scope of VSB tool according to standards ISO 14040:2006 and ISO 14044:2006 and equivalent Brazilian standards ABNT NBR ISO 14040:2009 and ABNT NBR ISO 14044:2009 (released versions in 2014).

3.1.4.1 Life cycle Inventory modeling and analysis

The LCA performed in this research Master’s degree is focused on identify and quantify the potential environmental impacts for thermochemical-biorefinery products: electricity generation (kWh) by CHP/EBPST, CHP/CEST, BIG-ICE/CC, BIG-GT/CC; Methanol (kg) by Biomass-to-Methanol; and Anhydrous ethanol (kg) by Biomass-to-Mixed alcohols.

The LCI combining the phase inventories of the thermochemical-biorefinery scenarios (biorefinery LCI) were developed on the comparative basis of 1.0 tonnes of cane stalks processed by the 1G sugarcane biorefinery (reference flow). The LCIA is performed by using SimaPro$^{®}$7.3.3 software using the World problem oriented (midpoint) ReCiPe hierarchism method on economic allocation approach to quantify and evaluate (in simplified form) the significance of the potential environmental impacts for the average conditions of Center-south of Brazil with focus on São Paulo state.

Results from LCIA provide information’s to identify critical processes and enable environmental comparisons between technologies (e.g.: 1G sugarcane biorefinery, 2G biochemical-based biorefinery, and thermochemical-based biorefinery) and equivalent products derived from fossil resources (e.g.: methanol derived from coal or natural gas, fossil gasoline, electricity) and renewable resources (1G and 2G anhydrous ethanol, biomass-derived methanol, electricity).

3.1.4.1.1 ReCiPe 2008

The results of LCIA of the different alternatives of biomass-derived products are express in terms of impact indicators (scores). The midpoint ReCiPe method include: climate change (CC); ozone depletion (OD); terrestrial acidification (TA); freshwater eutrophication (FE); marine eutrophication (ME); human toxicity (HT); photochemical oxidant formation (POF); particulate matter formation (PMF); terrestrial ecotoxicity (TET); freshwater ecotoxicity (FET); marine ecotoxicity (MECT); ionizing radiation (IR); agricultural land occupation (ALO); urban land occupation (ULO); natural land transformation (NLT); water depletion (WD); mineral resource depletion (MRD) or metal depletion (MD) and fossil fuel depletion (FD).

3.1.4.2 Economic allocation approach

The allocation method considered in this research Master's degree to divide the environmental impacts (load) of the thermochemical-biorefinery is based on the economic value approach (price) for products and co-product (multifunctional product system).

The prices/costs for products and co-products (Table 2) are based on average estimation from historical price series of bio-based products (sugar, electricity, and anhydrous ethanol) along the 10 last years (measured in the series), on estimation based in the average 2014 year prices (Liquid N_2 and Liquid Ar), and on estimation based on VSB analysis of costs (straw and bagasse) (BONOMI et al., 2016; BRAZILIAN BIOETHANOL SCIENCE AND TECHNOLOGY LABORATORY, 2012; CARDOZO, 2014).

Estimated prices were fixed to December of 2012 as base year, the same base year considered in the LCA of the optimized 1G sugarcane biorefinery (comparative base) assessed by the division of AIB of the CTBE/CNPEM.

Table 2 - Price data applied in economic allocation approach (2012 base year)

Products and co-products	Price (2012)	Unit
Anhydrous ethanol*	1.562	R$/kg
Sugar*	0.839	R$/kg
Electricity*	121.442	R$/MWh
Straw*	74.000	R$/tonnes
Bagasse*	37.834	R$/tonnes
Grade AA methanol	0.900	R$/kg
Mixed higher alcohol** (propanol, butanol, and pentanol)	1.800	R$/kg
Liquid argon (LAR) - high purity	2.800	R$/kg
Liquid nitrogen (LNG) - low purity	0.120	R$/kg

Note: US dollar converter in December 2012 (average) rate R$ 2.07
* values determined by CTBE
** value estimate by equivalent heat value - ethanol LHV basis

The amount of Liquid O_2 produced is equivalent to 5% in excess (reserve) and is intended to start-up as well as biomass reserve, therefore is not considered as product.

Environmental impacts have not been allocated for liquid CO_2 captured in scenarios that have system for co-capture of CO_2/H_2S and liquefaction (compression system) to use and/or storage (CCS).

3.2 Thermochemical conversion routes of biomass

Biomass can be converted into value-added products trough different pathways (platforms): chemical platform; biochemical platform; thermochemical platform; or hybrid platform (mix of platforms).

The biomass thermolytic processes can generally be categorized as: direct combustion (to produce thermal energy); torrefaction (thermal treatment to solid fuels); gasification (to produce synthesis gas); pyrolysis (to produce liquid and solid products); and liquefaction (to produce liquid products). There are different system configuration depending on type of gasifier (e.g.: fixed bed as up-flow, down-flow or cross-flow; bubbling fluidized bed; circulating fluidized bed; or entrained flow), on pressure level (e.g.: atmospheric or pressurized), on gasification agent (e.g.: air, oxygen, hydrogen, steam, and/or carbon dioxide), and on type of heating (e.g.: directly or indirectly).

In this research Master’s degree the thermochemical conversion routes of biomass consider the biomass thermolytic processes categorized as:

a) **direct combustion of biomass**: solid fuel fired boiler systems (thermal energy);
b) **gasification of biomass**: Low-Pressure (LP) Circulating Fluidized Bed (CFB) directly-heated gasifier (synthesis gas).

The gasifier simulated for the thermochemical-biorefineries scenarios and assessment is a low-pressure (atmospheric pressure) directly-heated CFB gasifier (autothermal) employing air/oxygen and steam gasification agents and olivine [$(Mg, Fe)_2SiO_4$] and magnesium oxide (MgO) as bed materials (DUTTA; PHILLIPS, 2009; WOOLEY; YALE, 2012). This gasifier type is capable of efficiently gasify a wide range of biomass materials, including sugarcane bagasse and straw.

Due innumerable possibilities of technologies combinations, choice one platform to convert biomass into value-added products depends on a rigorous evaluation of the advantages and disadvantages that each technology presents. Appropriate combinations of technologies depend on understanding the interactions between different platforms and processes, a systematic approach is essential that allow efficient integration between platforms and processes, leading to sustainable and economically attractive biorefinery scenarios.

In the case of this research Master’s degree, focused on thermochemical platform, that considers mass and energy integrations (in different levels) the choice of processes or technologies becomes even more challenging, since the design of a specific route can completely alter the energy efficiency of the 1G sugarcane biorefinery (base).

Sugar-energy sector has interest mainly in the production of energetic bio-based products (electricity and biofuels) derived from the available biomass (bagasse and straw), front of the current Brazil's 1G sugarcane biorefinery and sector scenarios the thermochemical conversion routes of biomass were selected (attractively), in a simplified way Figure 21 shows the selected routes.

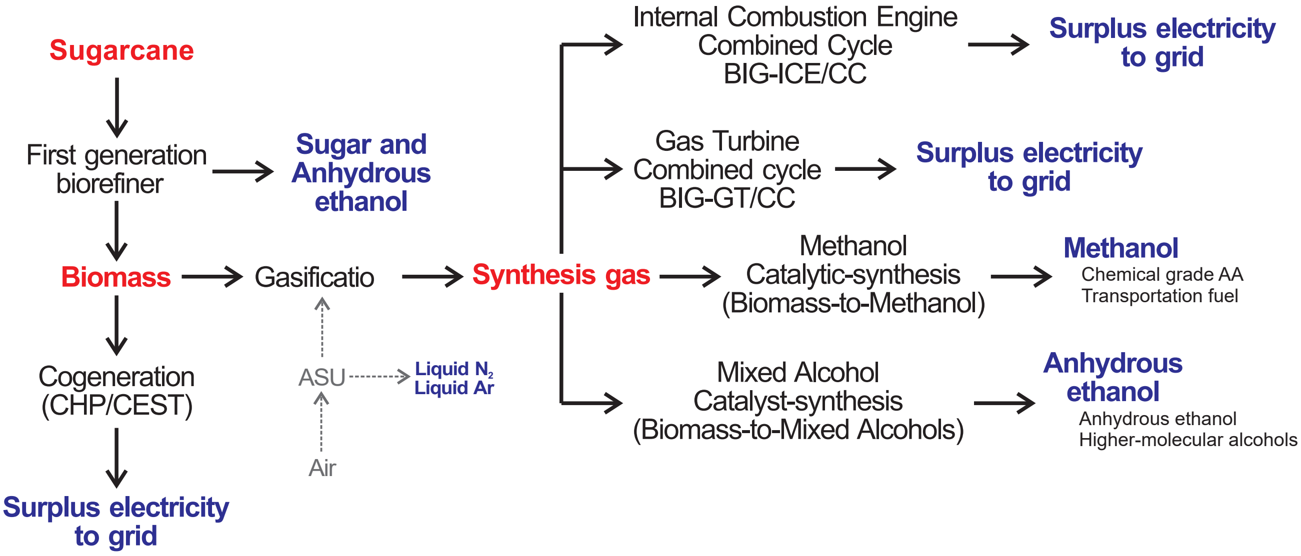

Figure 21 - Comprehensive diagram of the thermochemical routes selected and assessed in this research Master`s degree

The biomass thermochemical conversion routes (assessed in this research Master's degree) can be divided into two major categories according to their final-purpose.

a) **electricity generation**: combined heat and power generation (CHP) by condensing-extraction steam turbine (CEST) systems (for surplus electricity) or by extraction back-pressure steam turbine (EBPST) systems (for surplus biomass); biomass integrated directly-heated biomass gasification and internal combustion engine operating in combined-cycle (BIG-ICE/CC) systems; and biomass integrated directly-heated biomass gasification and gas turbine operating in combined-cycle (BIG-GT/CC) systems;
b) **biomass-based liquid-fuels and/or chemicals**: biomass-derived methanol production (chemical our transportations grades) by biomass integrated directly-heated biomass gasification and low-pressure methanol catalytic-synthesis (Biomass-to-Methanol); and biomass-derived mixed alcohols production (targeting ethanol) by biomass integrated directly-heated biomass gasification and mixed alcohols catalytic-synthesis (Biomass-to-Mixed alcohols).

3.3 Plant size and raw materials

In this research Master's degree is considered as a basis a Brazil's 1G sugarcane biorefinery sized to process about 2,000,000.0 (two million) tonnes of sugarcane stalks (nominal capacity) per year in the sugarcane harvest period (on-season). As the basis (reference) for this research Master's degree all scenarios under assessment consider a optimized 1G sugarcane biorefinery (2.0 Mtonnes) producing in the sugarcane harvest period (on-season) sugar, anhydrous ethanol (annexed ethanol distillery), with or without surplus electricity (surplus to grid). This 1G sugarcane biorefinery scenario (basis) was developed and assessed by the division AIB of the CTBE/CNPEM under the scope of the VSB simulation and assessment platform.

500.0 tonnes of cane stalks (clean) are processed per operational hour generating 133.150 tonnes/hr (50.0%$_{w/w}$ of moisture) of sugarcane bagasse. Also, is considered that 41.176 tonnes/hr (15.0%$_{w/w}$ of moisture) of sugarcane straw is recovered (bales) from the crops.

3.4 Scenario definitions

The thermochemical-biorefinery scenarios were defined taking into account mass and energy integration between the 1G sugarcane biorefinery and the different biomass thermochemical conversion routes. In this research Master's degree is considered the integral use of available biomass (sugarcane bagasse and straw) by the selected thermochemical routes, thus defining possible scenarios to be performed and assessed according to the peculiarities (steam and electricity capacities) of technological processes of each of the selected route.

Scenarios are defined according to mass and energy integration between the 1G sugarcane biorefinery (basis) and the biomass thermochemical conversion routes (excluding CHP):

a) **partial-integrated mode**: Thermochemical route supply part of the energy required by the 1G sugarcane biorefinery, other part needed to the 1G sugarcane biorefinery is supplied by their 1G-CHP system (EBPST SC1);
b) **fully-integrated mode**: Thermochemical route supplies all energy requirements (thermal and electrical energy) of the Thermochemical-biorefinery (without 1G-CHP system).
c) **standalone mode**: Thermochemical route (self-sufficient in energy terms) does not provide the energy requirements of the 1G sugarcane biorefinery.

3.4.1 Combined heat and power generation (CHP)

The amount of surplus biomass available for use depends on the energetic efficiency of the biorefinery. Actually (2015), CHP systems (Rankine-cycle) are used to supply heat (process steam) and electricity (self-sufficient in energy terms plant) to the sugarcane biorefinery by using sugarcane bagasse as the solid fuel in low-pressure solid fuel fired boiler (low efficiency system).

According to the optimized 1G sugarcane biorefinery with annexed ethanol distillery developed by the division of AIB of the CTBE/CNPEM, the biorefinery demand 14.175 tonnes/hr of saturated steam at a pressure of 6.0 bar and 184.975 tonnes/hr of saturated steam at a pressure of 2.5 bar.

The incentives for electricity generation from renewable resources have results in the restructuration of the Brazil's sugar-energy sector. Sugarcane biorefineries are investing in efficient CHP systems in order to generate surplus electricity to electric power grid, making efficiencies in steadily growing.

The surplus electricity generated by the biorefinery can be sold to the electric power grid, improving the revenues and diversifying the bio-product biorefinery portfolio. Competitively, surplus biomass (sugarcane bagasse and/or straw) can be sold as raw material, in the near future, for chemical, biochemical or thermochemical conversion routes of biomass to produce value-added bio-based products or can be exported to centralized advanced biorefineries (cluster formation).

Considering the different commercial (Brazil) plant configurations of cogeneration systems, the thermal and electrical generation by biomass fuel fired boilers are assessed considering integral use of the available biomass to generate the maximum possible of surplus electricity and assessed considering partial use of the available biomass to generate the maximum possible of surplus biomass while supply the self-sufficient in energy terms (thermal and electrical energy) biorefinery. These scenarios are intended to determine the best CHP system for electricity generation (comparative reference) and the best CHP system to generate surplus biomass (available biomass for use) for possible integrations with thermochemical routes (or others).

Generalizing, the scenarios can be divided into two major groups according to steam turbine (ST) type and their final-purpose as:

a) **surplus electricity scenarios**: consider condensing-extraction steam turbine (CEST) systems, evaluated at different parameter levels;
b) **surplus biomass scenarios**: consider extraction back-pressure steam turbine (EBPST) systems, evaluated at different parameter levels.

CHP/CEST scenarios and CHP/EBPST scenarios are defined according to parameters of the biomass fuel fired boiler (i.e.: steam pressure and temperature, exhaust-gas temperature, and oxygen mass flow rate) as:

a) **scenario 1 (SC1)**: CHP system operating at 22 bar and 320ºC with exhaust-gas temperature at 160ºC and 12% of combustion oxygen in excess;
b) **scenario 2 (SC2)**: CHP system operating at 45 bar and 450ºC with exhaust-gas temperature at 160ºC and 10% of combustion oxygen in excess;
c) **scenario 3 (SC3)**: CHP system operating at 65 bar and 480ºC with exhaust-gas temperature at 160ºC and 8% of combustion oxygen in excess;
d) **scenario 4 (SC4)**: CHP system operating at 85 bar and 520ºC with exhaust-gas temperature at 155ºC and 8% of combustion oxygen in excess;
e) **scenario 5 (SC5)**: CHP system operating at 90 bar and 530ºC with exhaust-gas temperature at 150ºC and 8% of combustion oxygen in excess;
f) **scenario 6 (SC6)**: CHP system operating at 96 bar and 530ºC with exhaust-gas temperature at 150ºC and 8% of combustion oxygen in excess;
g) **scenario 7 (SC7)**: CHP system operating at 120 bar and 530ºC with exhaust-gas temperature at 135ºC and 6% of combustion oxygen in excess;

3.4.2 Biomass integrated directly-heated gasifier and internal combustion engine in combined-cycle (BIG-ICE/CC)

Synthesis gas obtained from biomass gasification can be considered an alternative gas fuel to use in Internal Combustion Engine (ICE) with the potential to surplus electricity to electric power grid in large-scale biomass thermochemical-biorefineries.

The gasification of biomass by atmospheric directly-heated CFB gasifier using air and steam as gasification agents to low-medium lower heating value (LHV) synthesis gas production and its potential use for electricity generation was evaluating in a single-fueled ICE with turbo charging system. This engine works according to lean-burn four-stroke Otto-cycle spark-ignited gas engine operating in combined-cycle (CC) mode with ST system (Rankine-cycle).

BIG-ICE/CC routes are evaluated aiming generate surplus electricity to export to the electric power grid while supply the thermal and electrical energies needs of the thermochemical-biorefinery. The scenarios are defined according to the type of mass and energy integrations as:

a) **scenario 1 (SC1)**: considers partial-integrated mode of mass and energy integration (thermal and electrical) between the BIG-ICE/CC route and 1G sugarcane biorefinery. BIG-ICE/CC route supply part of the process steam (2.5 bar) and part of the electricity needed to the 1G sugarcane biorefinery, other part needed to the 1G sugarcane biorefinery as requirements is supplied by their 1G-CHP system (EBPST SC1);
b) **scenario 2 (SC2)**: considers standalone type of mass and energy integration (thermal and electrical) between the BIG-ICE/CC route and 1G sugarcane biorefinery. BIG-ICE/CC route use surplus biomass (bagasse and straw) and consider imported bagasse (cluster formation to maintain de comparative scale). 1G-CHP system (EBPST SC1) supplies all energy requirements (thermal and electrical energy) of the 1G sugarcane biorefinery.

The synthesis gas need be adjusted for engine specifications (e.g.: energy density), decreasing the cycle energy efficiency. BIG-ICE/CC routes (without supplementary-fired HRSG system, this work) cannot be integrated to 1G sugarcane biorefinery without CHP system (auxiliary thermal energy supplier) due its low capacity to generate steam and the large consumes of thermal energy in the form of steam by the entire thermochemical-biorefinery. The traditional Heat Recovery Steam Generation (HRSG) system is not able to meet the needs of the whole thermochemical-biorefinery.

3.4.3 Biomass integrated directly-heated gasifier and gas turbine in combined-cycle system (BIG-GT/CC)

The gasification of biomass by atmospheric directly-heated CFB gasifier using air and steam as gasification agents to low-medium LHV synthesis gas production and its potential use to power generation is evaluate in a high-performance full-flow advanced class evaporative (humidification tower) gas turbine (EvGT) considering air cooled blades. The gas turbine cycle apply the dual combustion chamber system (reheated), heat recovery intercooler/after-cooler, and exhaust-gas heat recovery system (recuperator), and operate in CC mode with ST system (cogeneration Rankine-cycle).

BIG-GT/CC routes are evaluated aiming generate surplus electricity to export to the electric power grid while supply the thermal and electrical energies needs of the thermochemical-biorefinery. The scenarios are defined according to the type of mass and energy integrations and according to presence of H_2S/CO_2 co-capture by using monoethanolamine (MEA) aqueous absorbing-solution process as:

a) **scenario 1 (SC1)**: considers partial-integrated mode of mass and energy integration (thermal and electrical) between the BIG-GT/CC route and 1G sugarcane biorefinery. BIG-GT/CC route supply part of the process steam (2.5 bar) and part of the electricity needed to the 1G sugarcane biorefinery, other part needed to the 1G sugarcane biorefinery as requirements is supplied by their 1G-CHP system (EBPST SC1). BIG-GT/CC route employ the process of H_2S/CO_2 co-capture by using MEA aqueous absorbing-solution;
b) **scenario 2 (SC2)**: considers fully-integrated mode of mass and energy integration (thermal and electrical) between the BIG-GT/CC route and 1G sugarcane biorefinery. BIG-GT/CC route supplies all energy requirements (thermal and electrical energy) of the Thermochemical-biorefinery (without 1G-CHP system). BIG-GT/CC route employ the process of H_2S/CO_2 co-capture by using MEA aqueous absorbing-solution;
c) **scenario 3 (SC3)**: considers fully-integrated mode of mass and energy integration (thermal and electrical) between the BIG-GT/CC route and 1G sugarcane biorefinery. BIG-GT/CC route supplies all energy requirements (thermal and electrical energy) of the Thermochemical-biorefinery (without 1G-CHP system). BIG-GT/CC route does not employ process to capture H_2S or CO_2;
d) **scenario 4 (SC4)**: considers standalone type of mass and energy integration (thermal and electrical) between the BIG-GT/CC route and 1G sugarcane biorefinery. BIG-GT/CC route use surplus biomass (bagasse and straw) and consider imported bagasse (cluster formation to maintain de comparative scale). 1G-CHP system (EBPST SC1) supplies all energy requirements (thermal and electrical energy) of the 1G sugarcane biorefinery. BIG-GT/CC route employ the process of H_2S/CO_2 co-capture by using MEA aqueous absorbing-solution.
e) **scenario 5 (SC5)**: considers standalone type of mass and energy integration (thermal and electrical) between the BIG-GT/CC route and 1G sugarcane biorefinery. BIG-GT/CC route use surplus biomass (bagasse and straw) and consider imported bagasse (cluster formation to maintain de comparative scale). 1G-CHP system (EBPST SC1) supplies all energy requirements (thermal and electrical energy) of the 1G sugarcane biorefinery. BIG-GT/CC route does not employ process to capture H_2S or CO_2.

BIG-GT/CC routes are a flexible and efficient option for integration at a 1G sugarcane biorefinery to generate surplus electricity. The synthesis gas does need extensive adjustments to specifications (only cleaned), which allows operate with or without capture of CO_2 and H_2S. However, depend on requirements of impurity concentration levels to operate without incurring damage to the turbine blades.

3.4.4 Biomass to methanol production by biomass integrated directly-heated gasifier and low-pressure methanol catalytic-synthesis (Biomass-to-Methanol)

The gasification of biomass by atmospheric directly-heated CFB gasifier using oxygen and steam as gasification agents to medium LHV synthesis gas production and its potential use for produce biomass-derived grade AA methanol (transportation fuel or chemical grades) is evaluate considering directly-heated gasification integrated 50 bar/250ºC methanol catalytic-synthesis ($CuO-ZnO/Al_2O_3$ catalyst) applying gas-cooled fixed bed synthesis reactor combined in series with isothermal water-cooled fixed bed synthesis reactor (two stages).

Biomass-to-Methanol route are evaluated aiming the methanol production (chemical grade AA) while supply the thermal and electrical energies needs for the thermochemical-biorefinery. The scenarios are defined according to the type of mass and energy integrations as:

a) **scenario 1 (SC1)**: considers partial-integrated mode of mass and energy integration (thermal and electrical) between the Biomass-to-Methanol route and 1G sugarcane biorefinery. Biomass-to-Methanol route supply part of the process steam (2.5 bar) and part of the electricity needed to the 1G sugarcane biorefinery, other part needed to the 1G sugarcane biorefinery as requirements is supplied by their 1G-CHP system (EBPST SC1);
b) **scenario 2 (SC2)**: considers fully-integrated mode of mass and energy integration (thermal and electrical) between the Biomass-to-Methanol route and 1G sugarcane biorefinery. Biomass-to-Methanol route supplies all energy requirements (thermal and electrical energy) of the Thermochemical-biorefinery (without 1G-CHP system);
c) **scenario 3 (SC3)**: considers standalone type of mass and energy integration (thermal and electrical) between the Biomass-to-Methanol route and 1G sugarcane biorefinery. Biomass-to-Methanol route use surplus biomass (bagasse and straw) and consider imported bagasse (cluster formation to maintain de comparative scale). 1G-CHP system (EBPST SC1) supplies all energy requirements (thermal and electrical energy) of the 1G sugarcane biorefinery.

High-pure gaseous oxygen ($98.3\%_{mol}$) gasification agent for the directly-heated gasifier is obtained from double-column cryogenic Air Separation Unit (ASU) with high-purity argon recovery. ASU consider nitrogen liquefaction cycle (electricity impact) to produce liquid nitrogen (2.0) and recovery column to produce pure liquid argon (5.0). Liquid nitrogen (LNG) and liquid argon (LAR) can be sold as bio-based product, improving the revenues and diversifying the bio-product portfolio of the thermochemical-biorefinery.

3.4.5 Biomass to mixed alcohols production by biomass integrated directly-heated gasifier and mixed alcohols catalyst-synthesis (Biomass-to-Mixed alcohols)

The gasification of biomass by atmospheric directly-heated CFB gasifier using oxygen and steam as gasification agents to medium LHV synthesis gas production and its potential use for produce fuel ethanol and higher molecular alcohols (fuel additives) is evaluate considering directly-heated gasification integrated 85 bar/350ºC mixed alcohols catalyst-synthesis (Sulfided K-Co-Mo/C catalyst) applying water-cooled fixed bed synthesis reactor (one stage).

Biomass-to-Mixed alcohols route are evaluated are evaluated aiming the maximum ethanol production (methanol recycle) while supply the thermal and electrical energies needs for the thermochemical-biorefinery. The scenarios are defined according to the type of mass and energy integrations as:

a) **scenario 1 (SC1)**: considers partial-integrated mode of mass and energy integration (thermal and electrical) between the Biomass-to-Mixed alcohols route and 1G sugarcane biorefinery. Biomass-to-Mixed alcohols route supply part of the process steam (2.5 bar) and part of the electricity needed to the 1G sugarcane biorefinery, other part needed to the 1G sugarcane biorefinery as requirements is supplied by their 1G-CHP system (EBPST SC1);
b) **scenario 2 (SC2)**: considers fully-integrated type of mass and energy integration (thermal and electrical) between the Biomass-to-Mixed alcohols route and 1G sugarcane biorefinery. Biomass-to-Mixed alcohols route supplies all energy requirements (thermal and electrical energy) of the Thermochemical-biorefinery (without 1G-CHP system);
c) **scenario 3 (SC3)**: considers standalone type of mass and energy integration (thermal and electrical) between the Biomass-to-Methanol route and 1G sugarcane biorefinery. Biomass-to-Mixed alcohols route use surplus biomass (bagasse and straw) and consider imported bagasse (cluster formation to maintain de comparative scale). 1G-CHP system (EBPST SC1) supplies all energy requirements (thermal and electrical energy) of the 1G sugarcane biorefinery.

High-pure gaseous oxygen (98.3$\%_{mol}$) gasification agent for the directly-heated gasifier is obtained from double-column cryogenic air separation unit (ASU) with high-purity argon recovery. ASU consider nitrogen liquefaction cycle (electricity impact) to produce liquid nitrogen (2.0) and recovery column to produce pure liquid argon (5.0). Liquid nitrogen (LNG) and liquid argon (LAR) can be sold as bio-based product, improving the revenues and diversifying the bio-product portfolio of the thermochemical-biorefinery.

3.5 Biomass representation

Sugarcane plant (Figure 22) is comprised mainly by stalks, tops and leaves, for a more detailed representation is recommend read the publication named – *The Virtual Sugarcane Biorefinery (VSB)*: 2011 Report (BRAZILIAN BIOETHANOL SCIENCE AND TECHNOLOGY LABORATORY, 2012) – and in the publication named – Virtual Biorefinery: An Optimization Strategy for Renewable Carbon Valorization (BONOMI et al., 2016).

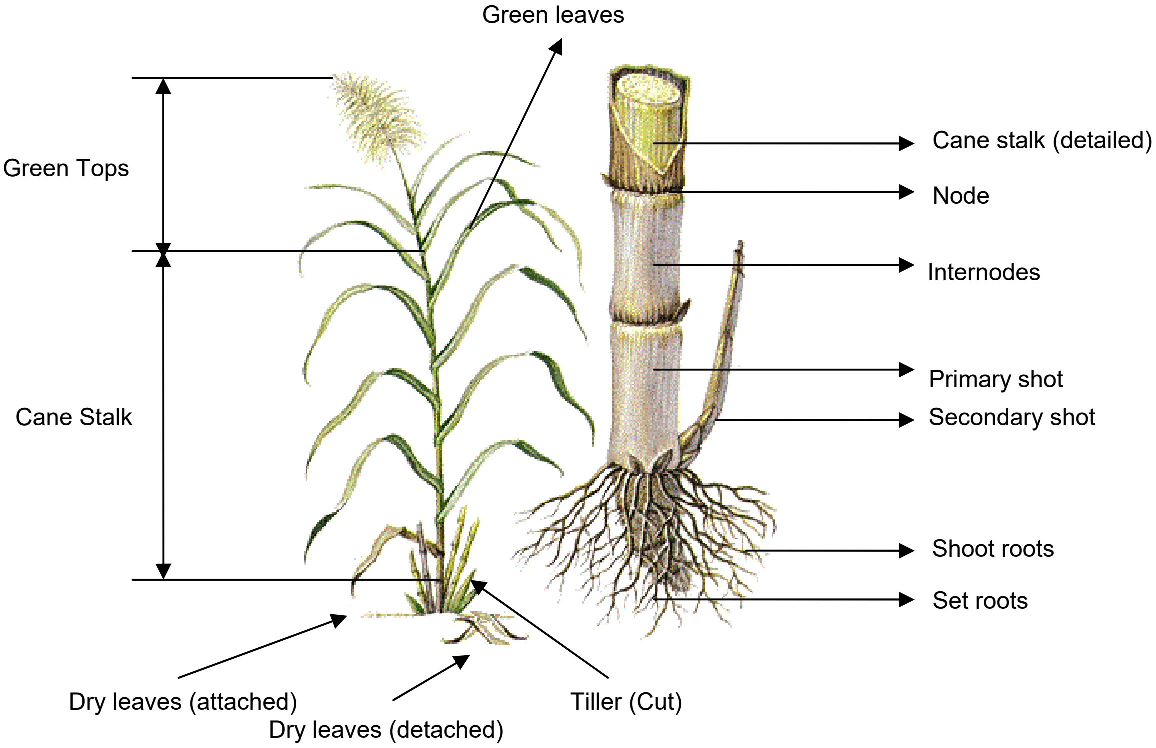

Figure 22 - Main constituent parts of sugarcane plant

Source: adapted from HowStuffWorks (2013), and Hassuani, Leal and Macedo (2005).

According to Figure 22, the main constituent parts of sugarcane plant can be generally grouped as:

a) **cane stalks**: solid material made up of nodes and internodes rich in sugars, are milled to obtain a cane juice;
b) **sugarcane bagasse**: solid material generated after the milling the cane stalks;
c) **sugarcane straw/trash**: all solid residual materials generated at harvest time mainly after the sugarcane harvesting process (including tops and leaves - green and dry -attached and detached).

Aspen Plus$^{®}$v8.4 process simulation platform does not have in their standard database (APV80) components that simulate lignocellulosic materials (complex materials), and important components related to biofuels.

Aspen Plus$^{®}$v8.4 process simulation platform allows user set (input) of materials (chemical composition, physical properties and parameters for models) in a different ways, in biorefineries simulation the two approaches most used (classic) are:

a) **conventional**: user create compounds (solid, liquid or gaseous) and specifies its properties and parameters, required to solve the models;
b) **non-conventional (solid)**: software uses generic and empirical correlations (published by various authors) to determine the necessary properties of the components (solid) using its constituents specified by: proximate analysis; elemental analysis; analysis of sulfur forms; and general analysis of the constituents.

In 1996, the National Renewable Energy Laboratory (NREL) developed for the Aspen Plus$^{®}$ process simulation platform a specific database for the biofuels sector, known as '*Aspen Plus Database for Biofuels*' (in-house), which is available for researchers and others interested in the viability and development in biofuels. The database includes compositions, properties (chemical, physical) and parameters for over 150 samples of analyzed materials (related to biofuels) (NATIONAL RENEWABLE ENERGY LABORATORY, 2012; WOOLEY; PUTSCHE, 1996).

The division of AIB of the CTBE/CNPEM developed an adapted database on the basis of 'Aspen Plus$^{®}$ Database for Biofuels', specific for the Brazil’s cases containing compositions and suitable properties for the major materials founding in the Brazil’s sugar-energy sector.

The representation of sugarcane cane stalks and straw can be found in more detail in the publication named – *The Virtual Sugarcane Biorefinery (VSB)*: 2011 Report (BRAZILIAN BIOETHANOL SCIENCE AND TECHNOLOGY LABORATORY, 2012) – and the publication named – Virtual Biorefinery: An Optimization Strategy for Renewable Carbon Valorization (BONOMI et al., 2016).

3.5.1 Conventional: generalized representation of biomass

Biomass representation (bagasse and straw cane sugar) by conventional components (liquids and solids) can be understood by the fractions that comprise the biomass according to Chemical equation c.1.

$$Biomass \rightarrow [Biomass]_{daef} + Extractive + Ashes + Moisture + Soil \qquad (c.1)$$

Biomass consists of a fraction of fibers without ash, extractives and moisture (deaf - dry, ash and extractives free material) ($[Biomass]_{daef}$), a fraction of extractives, an ash fraction composed of minerals, salts and inert, a moisture fraction (water), and a soil fraction from external media (field and storage area).

Fiber fraction as represented according to Chemical equation c.2 is composed of structural components as nitrogen (N), sulfur (S) chlorine (Cl), cellulose (represented by 'glucose' ($C_6H_{10}O_5$)), hemicelluloses (represented by 'xylose' ($C_5H_8O_4$)), and lignin ($C_9H_{8,6}O_{2,9}(OCH_3)$).

$$\begin{aligned}[Biomass]_{daef} \rightarrow\ & x_1C_2H_4O_2 + x_2C_6H_{10}O_5 + x_3C_9H_{8,6}O_{2,9}(OCH_3) + \ x_4C_5H_8O_4 \\ & + x_5N + x_6S + x_7Cl \qquad (c.2)\end{aligned}$$

O-acetyl groups are represented by acetate ($C_2H_4O_2$). Biomass (daef) can also be represented according to Chemical equation c.3. Cellulose, hemicelluloses, lignin, acetate, nitrogen, sulfur and chlorine in represented equivalently by only one component (molar amount of each element).

$$[Biomass]_{daef} \rightarrow \left[CH_{a_1}O_{a_2}N_{a_3}S_{a_4}Cl_{a_5}\right]_{daef} \qquad (c.3)$$

The fraction of extractives contained in lignocellulosic biomass is represented according to Chemical equation c.4. Glucose ($C_6H_{12}O_6$) and sucrose ($C_{12}H_{22}O_{11}$) as representative of the total reducing sugars (TRS), aconitic acid ($C_6H_6O_6$) as soluble fraction of organic acids, and phosphoric acid (H_3PO_4) as fraction of soluble phosphate present in the biomass.

$$Extractive \rightarrow x_8C_6H_{12}O_6 + x_9C_6H_6O_6 + x_{10}C_{12}H_{22}O_{11} + \ x_{11}H_3PO_4 \qquad (c.4)$$

Ashes fraction contained in the lignocellulosic biomass is represented according to Chemical equation c.5. Is considered an fraction of oxides represented by calcium oxide (CaO), magnesium oxide (MgO), phosphorus pentoxide (P_2O_5), potassium oxide (K_2O), an mineral fraction (salts) represented by potassium chloride (KCl) (majority), and an fraction of inert and other (minerals and the minor proportion of oxides) by silicon dioxide (SiO_2).

$$Ashes \rightarrow x_{12}SiO_2 + x_{13}CaO + x_{14}MgO + x_{15}P_2O_5 + x_{16}K_2O + x_{17}KCl \qquad (c.5)$$

The representative water content retained in the biomass (Moisture) is represented by water (H_2O) according to Chemical equation c.6.

$$.Moisture \rightarrow x_{18}H_2O \qquad (c.6)$$

The soil fraction loaded with the biomass is represented by the silicon dioxide (SiO_2) according to Chemical equation c.7.

$$Soil \rightarrow x_{19}SiO_2 \qquad (c.7)$$

Various components (minority) such as proteins, starches, soluble polysaccharides, waxes, phospholipids, some minerals and other compounds, are not considered in this approach and the presence do not provide significant relevance on the major models (for specific cases can be considered).

3.5.2 Non-conventional: generalized representation of biomass

Biomass as non-conventional solid is represented by the component attributes, described in terms of empirical factors.

Proximate analysis quantify the moisture content (M), expressed as amount of water contained in the solid by weight (dry or wet basis), the volatile material content (VM), expressed as a fraction of biomass that volatilizes (in inert atmosphere) during heating up to temperatures of 850.0°C (dry basis), fixed carbon content (FC), expressed as the mass fraction remaining after volatile matter assay (dry base), and the ash content (ASH), expressed as the fraction of residues resulted after combustion and oxidation processes.

Through ultimate analysis the elemental composition of biomass (dry basis) are quantified and expressed by its main chemical elements, carbon (C), hydrogen (H), nitrogen (N), chlorine (Cl), total sulfur (S), oxygen (O), and other elements. Ultimate analysis quantify also the total ash content (dry basis) in the biomass, by analysis of ash (specific) are quantified the main components present in the ash.

The ash analysis quantifies composition (dry basis) of the main constituent of the biomass ash fraction, which is formed by components in the form of salts, oxides and inert components, containing (main quantified) silicon (Si), potassium (K), sodium (Na), sulfur (S), calcium (Ca), magnesium (Mg), iron (Fe), and phosphorus (P).

In sulfur analysis are quantified different forms of sulfur content in the material as organic sulfur, normally associated with aromatic structures, the pyritic sulfur content related to the presence of pyrite (FeS_2) and sulfur content related to the presence of sulfate salts, usually calcium, magnesium and iron.

In the general constituents analysis of Aspen Plus®v8.4 process simulation platform is possible specify (weight or volume percentage) other component contents that characterize the material.

3.5.3 Sugarcane bagasse and straw

The lignocellulosic biomass can be represented on different forms, it depends on the purpose. In simulation of biochemical routes the biomass is represented through the biomass constituents (e.g.: cellulose, hemicelluloses, and lignin contents), is the most common form. However, in simulation of thermochemical routes the biomass elemental representation (e.g.: proximate, ultimate, ashes and sulfur analysis) is the most common form.

The composition of sugarcane bagasse adopted in the simulations performed in this research Master’s degree is based on its constituents (biochemical processes), as shown in Table 3. In the composition is considered a moisture content of $50\%_{w/w}$ (water), cellulose content of $21.69\%_{w/w}$, hemicelluloses content of $12.82\%_{w/w}$ (xylose and acetate), lignin content of $11.62\%_{w/w}$, extractive content of $2.41\%_{w/w}$ (glucose, phosphoric acid, organic acids and sucrose), and ash content of $1.47\%_{w/w}$ (salts, minerals and soil) (BRAZILIAN BIOETHANOL SCIENCE AND TECHNOLOGY LABORATORY, 2012).

The composition of sugarcane straw (green leaves, tops and straw) adopted in the simulations performed in this research Master’s degree is based on the composition of constituents applied in simulations of the biorefineries by the division of AIB of the CTBE/CNPEM, as shown in Table 3. In the composition is considered a moisture content of $50\%_{w/w}$ (water), cellulose content of $39.14\%_{w/w}$, hemicelluloses content of

$23.12\%_{w/w}$ (xylose and acetate), lignin content of $20.97\%_{w/w}$, and salts content of $1.77\%_{w/w}$ (considered as ash) (BRAZILIAN BIOETHANOL SCIENCE AND TECHNOLOGY LABORATORY, 2012).

Table 3 - Composition of sugarcane bagasse and straw adopted in 1G sugarcane biorefineries assesseds using VSB tool by the division of AIB of the CTBE/CNPEM

Component Substream: MIXED	**Bagasse**		**Straw**	
	Mass fraction	**0.4622**	**Mass fraction**	**0.1677**
Glucose	0.001659		0.000000	
Water	0.929627		0.894540	
Phosphoric acids	0.000226		0.000000	
Minerals	0.002872		0.000000	
Organic acids	0.004218		0.000000	
Salts	0.022685		0.105460	
Sucrose	0.038713		0.000000	
	Mass flow rate (kg/h)	71,609.710	Mass flow rate (kg/h)	6,904.63
Component Substream: CISOLID	**Mass fraction**	**0.5378**	**Mass fraction**	**0.8323**
Acetate	0.025788		0.025838	
Cellulose	0.469200		0.470244	
Lignin	0.251441		0.251924	
Xylose	0.251502		0.251994	
Soil	0.002069		0.000000	
	Mass flow rate (kg/h)	61,540.300	Mass flow rate (kg/h)	34,271.840
	Total (kg/h)	133,150.01	Total (kg/h)	41,176.47

Source: CTBE (2012)

Based on the composition presented in the Table 3 changes were made in the composition of sugarcane bagasse and sugarcane straw in order to represent it in the elemental composition form, some important elements in gasification reactions and to determine operational conditions of equipment (processes) on the thermochemical routes, and being also important for improving accuracy of LCA.

According to Hassuani, Leal and Macedo (2005) data were added the elements nitrogen (N), sulfur (S) and chlorine (Cl) in the sugarcane bagasse composition ($[Bagasse]_{daef}$), and in the ash fraction were added calcium oxide (CaO), magnesium oxide (MgO) and phosphorus pentoxide (P_2O_5), the addition was carried out based on ultimate analysis and ash analysis data.

Sugarcane bagasse can be represented and understood by the fractional form according to Chemical equations from c.1 to c.7, as:

$$Bagasse \rightarrow [Bagasse]_{daef} + Extractive + Ashes + Moisture + Soil$$

$$\left[CH_{1,49687}O_{0,68798}N_{0,01114}S_{0,00081}Cl_{0,00015}\right]_{daef} \rightarrow 0.01055C_2H_4O_2 + 0.07112C_6H_{10}O_5 + 0.03182C_{10}H_{11,6}O_{3,9} + 0.04679C_5H_8O_4 + 0.01114N + 0.00081S + 0.00015Cl$$

$$Extractive \rightarrow 0.00026C_6H_{12}O_6 + 0.00069C_6H_6O_6 + 0.00323C_{12}H_{22}O_{11} + 0.00007H_3PO_4$$

$$Ashes \rightarrow 0.00067SiO_2 + 0.00008CaO + 0.00008MgO + 0.00001P_2O_5 + 0.00087K_2O + 0.00870KCl$$

$$Moisture \rightarrow 1.48670H_2O \qquad (50\%_{w/w}\ de\ umidade)$$

$$Soil \rightarrow 0.00045SiO_2$$

Carbon content extractives content as representative form by glucose, sucrose and aconitic acid is not accounted in the $[Bagasse]_{daef}$ fraction.

The soil fraction represented by the silicon dioxide (silica) represent only the soil loaded with the sugarcane bagasse, the silicon dioxide (SiO_2) content in Ashes fraction represent the constitutional silicon dioxide (SiO_2) of the sugarcane bagasse.

According to Hassuani, Leal and Macedo (2005) data were added the elements nitrogen (N), sulfur (S) and chlorine (Cl) in the sugarcane straw composition ($[Straw]_{daef}$), the addition was carried out based on ultimate analysis and ash analysis data.

Straw can be represented (simplified due to lack of data) and understood by the fractional form according to Chemical equations from c.1 to c.7, as:

$$Straw \rightarrow [Straw]_{daf} + Ashes + Moisture + Soil$$

$$\left[CH_{1,49690}O_{0,68799}N_{0,00882}S_{0,00077}Cl_{0,00070}\right]_{daf} \rightarrow 0,01055C_2H_4O_2 + 0,07113C_6H_{10}O_5 + 0,03182C_{10}H_{11,6}O_{3,9} + 0,04678C_5H_8O_4 + 0,00882N + 0,00077S + 0,00070Cl$$

$$Ashes \rightarrow 0,00699KCl$$

$$Moisture \rightarrow 0,25610H_2O \qquad (15\%_{w/w}\ de\ umidade)$$

$$Soil \rightarrow 0,01298SiO_2$$

Was added 3.0%$_{w/w}$ (db) of soil in the sugarcane straw (without mixing with the constitutional ashes), as seen from the sugarcane field.

From the Table 3 and according to Hassuani, Leal and Macedo (2005) data the equivalents proximate analysis (PROXANAL), ultimate analysis (ULTANAL), and sulfur analysis (SULFANAL) was obtained to represent sugarcane bagasse and straw by unconventional solids was obtained, that is required by Aspen Plus®v8.4 process simulation platform to define the biomass (elemental form) and parameters for enthalpy and density models.

3.5.3.1 Proximate analysis (PROXANAL)

Proximate analysis of sugarcane bagasse and straw (Table 4) considers moisture content (M) and ash content (Ash) data according to biorefineries performed under the scope of VSB by the division of AIB of the CTBE. Volatile material content (VM) and fixed carbon content (FC) were implemented according to Hassuani, Leal and Macedo (2005) data.

Table 4 - Proximate analysis* of sugarcane bagasse and straw

Component	**Mass fraction**	
	Bagasse	**Straw**
Moisture (M)	50.00	15.00
Fixed carbon (FC)	18.00	15.00
Volatile material (VM)	79.06	80.00
Ashes (Ash)	2.94	5.00

Source: adapted from CTBE (2012) and Hassuani, Leal and Macedo (2005)
* Proximate analysis without fractionate (total mass)

3.5.3.2 Ultimate analysis (ULTANAL)

Ultimate analysis of sugarcane bagasse (Table 5) considers the composition of constituents (macromolecules) applied in the simulations of biorefineries by the division of AIB of the CTBE/CNPEM, as shown in Table 3. Conventional compounds are represented in our elemental composition form, to obtain the carbon content (C), the hydrogen content (H) and the oxygen content (O). Nitrogen (N) content, chlorine content (Cl), and total sulfur content (S) were implemented according to Hassuani, Leal and Macedo (2005) data.

Table 5 - Ultimate analysis of sugarcane bagasse

Component	Mass (%)	
	Dry ash free (daf)	**Dry extractive and ash free (daef)**
Carbon (C)	48.262	48.600
Hydrogen (H)	6.108	6.105
Nitrogen (N)	0.600	0.631
Chlorine (Cl)	0.020	0.021
Sulfur (S)	0.100	0.105
Oxygen (O)	44.885	44.538

Source: adapted from CTBE (2012) and Hassuani, Leal and Macedo (2005)

Ultimate analysis of sugarcane straw (Table 6) considers the composition of constituents (macromolecules) applied in the simulations of biorefineries by the division of AIB of the CTBE/CNPEM, as shown in Table 3. Conventional compounds are represented in our elemental composition form, to obtain the carbon content (C), the hydrogen content (H) and the oxygen content (O). Nitrogen (N) content, chlorine content (Cl), and total sulfur content (S) were implemented according to Hassuani, Leal and Macedo (2005) data.

Table 6 - Ultimate analysis of sugarcane straw

Component	Mass (%)
	Dry ash free (daf)
Carbon (C)	48.627
Hydrogen (H)	6.109
Nitrogen (N)	0.500
Chlorine (Cl)	0.100
Sulfur (S)	0.100
Oxygen (O)	44.564

Source: adapted from CTBE (2012) and Hassuani, Leal and Macedo (2005)

3.5.3.3 Ash analysis

There is no input for the ash analysis in Aspen Plus$^{®}$v8.4 process simulation platform, because the ash fraction analyzes is considered as an inert fraction by the models of physical properties. Ash fraction is simulated as conventional solid (Table

7), considering only the main components with reactive potential (thermochemical routes) and representing a significant fraction in the sugarcane bagasse and straw.

Table 7 - Ashes analysis of sugarcane bagasse and straw

Component	Mass fraction (%)	
	Bagasse	Straw
Calcium oxide	0.0097	0
Magnesium oxide	0.0070	0
Phosphorus pentoxide	0.0070	0
Minerals (K_2O)	0.3066	0
Salts (KCl)	2.4224	2.004
Silicon dioxide*	0.0877	0
Total**	2.8404	2.004

Source: adapted from CTBE (2012) and Hassuani, Leal and Macedo (2005)* Compositional SiO_2 is calculate to close the mass balance
** Only compositional ashes, without soil

3.5.3.4 Sulfur analysis (SULFANAL)

Sulfur analysis of sugarcane bagasse and straw (Table 8) is not widely used due the little influence on the enthalpy and density, but you must provide some data to Aspen Plus® v8.4 process simulation platform rum, in this research Master's degree is considered for sugarcane bagasse and straw only the sulfur content in organic and sulfated form, the composition of sulfur is the same for both (0.1%$_{w/w}$ daf).

Table 8 - Sulfur analysis of sugarcane bagasse and straw

Compositional form	Mass (%) (daf)
Pyritic	0.00
Sulfate	0.080
Organic	0.020
Sulfur (S)	0.100

3.4.2.5 General constituents analysis

General analysis is not necessary in the Aspen Plus®v8.4 process simulation platform to characterize and define sugarcane bagasse and straw.

3.5.3.5 Complete composition of bagasse and straw

The representative composition of sugarcane bagasse considered in the Thermochemical-biorefinery scenarios is estimated based on the data obtained from biorefineries assessed by the division of AIB of the CTBE/CNPEM and on modifications based on bagasse constituent analysis according to Hassuani, Leal and Macedo (2005) data.

The representative composition of sugarcane straw contents green leaves, dry leaves, green tops and trash consider the average composition taking into account each of these sugarcane parts according to Hassuani, Leal and Macedo (2005) data.

Table 9 shows the mass and molar fractions in dry basis of the sugarcane bagasse and straw representative chemical compositions.

Table 9 - Composition of sugarcane bagasse and straw

Component	Bagasse		Straw	
	Molar fraction (%)	Mass fraction (%)	Molar fraction (%)	Mass fraction (%)
Carbon (C)	31.13	44.81	31.10	46.19
Hydrogen (H)	46.60	5.63	46.56	5.80
Nitrogen (N)	21.42	41.06	21.40	42.33
Oxygen (O)	0.35	0.58	0.27	0.47
Chlorine (Cl)	0.03	0.10	0.02	0.09
Sulfur total (S)	0.00	0.02	0.02	0.09
Sucrose ($C_{12}H_{22}O_{11}$)	0.01	0.18	0.00	0.00
Glucose ($C_6H_{12}O_6$)	0.02	0.45	0.00	0.00
Organic acids ($C_6H_6O_6$)	0.10	4.13	0.00	0.00
Phosphoric acids (H_3PO_4)	0.00	0.02	0.00	0.00
Salts (KCl)	0.27	2.42	0.22	2.00
Minerals (K_2O)	0.03	0.31	0.00	0.00
Phosphorus pentoxide (P_2O_5)	0.00	0.01	0.00	0.00
Calcium oxide (CaO)	0.00	0.02	0.00	0.00
Magnesium oxide (MgO)	0.00	0.01	0.00	0.00
Silicon dioxide (SiO_2)	0.02	0.15	0.00	0.00
Soil (SiO_2)	0.01	0.10	0.40	3.00
Water (H_2O) - (dry basis)	0.00	0.00	0.00	0.00

Non-conventional parameters can be setted in the Aspen Plus$^{®}$v8.4 process simulation platform according to elemental composition form presented in the Table 9, representing the fractions of C, H, N, O, C (reactive) and S in the BAGASSE (NC) and STRAW (NC). By choice, the carbonaceous component (glucose, sucrose and aconitic acid) in the fraction of extractives are not included as elemental constituents (extractives are not included in Ultimate analysis), Table 5 and Table 6 presents the complete elemental analysis.

The choice of type depends on the process characteristics and in the reactions form/models implemented in according to the requirements of process simulation platform. For thermochemical routes makes more sense work with the biomass represented in the elemental composition form (on which models are based).

3.5.4 Biomass properties

Mott and Spooner correlation use PROXANAL (proximate analysis), ULTANAL (ultimate analysis) and SULFANAL (sulfur analysis) analysis to estimate the heat of combustion and heat of formation. For density, estimate by DCOALIGT standard property method using Institute of Gas Technology (IGT) equations based on ULTANAL and SULFANAL analysis.

3.6 Conventional physical property methods

Different methods are used according to the characteristics and parameters of the streams and processes involved in certain areas of the thermochemical route scenarios.

Basically are used six methods for determining physical properties, bellow is a brief description of the methods used according to Aspen Technology (2013) physical property models:

a) **ELECNRTL** property method: is designed for electrolyte solutions can handle mixed solvent systems at any concentration. The Redlich-Kwong (RK) equation of state is used for all vapor phase properties, the method is based on correlations can handle specific components under well-described conditions; rigorous models are generally applicable. It can handle aqueous and mixed solvent systems;

b) **IAPWS-95** steam tables: are designed for water proprieties (steam tables) in the Aspen Physical Property System and implemented like any other equation-of state. These steam tables are the most accurate steam tables in the Aspen Physical Property System and can calculate any thermodynamic property of water;

c) **IDEAL** property method: accommodates both Raoult’s law and Henry’s Law is recommended for systems in which ideal behavior can be assumed. Can be used for systems with and without condensable components. Sometimes is used for solids processing where vapor-liquid equilibrium (VLE) is unimportant (for example, in coal/biomass processing). Appropriate only at low-pressure and low liquid mole fractions of the non condensable components;

d) **NRTL-RK** property method: (liquid activity coefficient property methods) is designed for non-ideal and strongly non-ideal mixtures at low-pressures, can model permanent gases in liquid solution using Henry's law;

e) **RKS-BM** property method: is designed for mixtures of hydrocarbons and light-gas using the Redlich-Kwong-Soave (RKS) cubic equation of state with Boston-Mathias (BM) alpha function for all thermodynamic properties. Used for non-polar or mildly polar mixtures;

f) **VANL-RK** property method: use Van Laar model for calculates liquid activity coefficients for the property methods and the Redlich-Kwong equation-of-state calculates vapor phase thermodynamic properties. Van Laar models can handle any combination of polar and non-polar compounds with positive deviations from Raoult's law.

3.6.1 Physical property methods selected

The property methods selected for properties and parameters calculations or estimation as based on Aspen Technology (2013) premises and on the characteristics of each unit process in the thermochemical biorefinery.

Selected methods for each thermochemical-biorefinery parent scenario are:

a) **CHP scenarios**: IDEAL; IAPWS-95; RKS-BM;
b) **BIG-ICE/CC scenarios**: IDEAL; IAPWS-95; RKS-BM; ELECNRTL;
c) **BIG-GT/CC scenarios**: ELECNRTL; IDEAL; IAPWS-95; RKS-BM;;
d) **Biomass-to-Methanol scenarios**: ELECNRTL; IAPWS-95; IDEAL; NRTL-RK; RKS-BM; VANL-RK;
e) **Biomass-to-Mixed alcohols scenarios**: ELECNRTL; IAPWS-95; IDEAL; NRTL-RK; RKS-BM; VANL-RK.

In some specific scenarios are not used some of the specified methods, depending on the presence of ASU and capture of CO_2 and H_2S.

3.7 Non-conventional solids physical property methods

In the Aspen Plus®v8.4 process simulation platform non-conventional solid components do not participate in phase and chemical equilibrium methods, but are included in the enthalpy balance. Density and enthalpy are the unique physical properties calculated by the platform for the unconventional solid components. Calculation approaches for general coal models in Aspen Plus process simulation platform use the elemental composition referred to a dry and mineral matter (Ash) free mass basis (daf).

Heating values calculations in Aspen Plus®v8.4 process simulation platform for non-conventional solids really on the empirical correlations developed for coal (e.g.: Boie correlation, Dulong correlation, Grundel and Davis correlation, Moot and Spooner correlation, Institute of gas Technology (IGT) correlation and Kirov correlation).

“The higher heating value is underestimated by most correlations. The best results are achieved applying the Mott and Spooner correlation, whereas the Dulong formula leads to the highest deviation compared to the statistical value” (RÖNSCH and VAGNER, 2012).

3.8 Components selected

Aspen Plus®v8.4 process simulation platform does not have in their standard database lignocellulosic materials as bagasse and straw, it is necessary the inclusion of this material type by user defined parameters.

User defined components are: BAGASSE (NC); and STRAW (NC). Sugarcane bagasse (BAGASSE) and straw (STRAW) are defined and detailed in the section - 3.5.3 Sugarcane bagasse and straw - by conventional, solids, and non-conventional components.

Common components available in Aspen Plus®v8.4 databases (alias nomenclature) and employed in the simulation scenarios performed in this research Master’s degree are: C5H13NO2; C4H10N2; H2O; CO2; H3O+; OH-; HCO3-; CO3-2; CO3-2; C4H11N2+; C5H14NO2+; C4H12N2+2; C5H10N2O2; C5H9N2O2-; C6H8N2O4-2; N2; O2; CO; H2; H2S; NE; HE-4; AR; KR; XE; CH4; O2S; O3S; NO; NO2; N2O; H3N; CL2; HCL; HCLO; C2H2; C2H4; C2H6; CHN; C6H6; C10H8; COS; FE3C; C3H8; C7H8; SIO2; SIO2; MGO; CAO; C; H3PO4; KCL; K2O; K3PO4; CAS; MGS; S; P2O5; HS-; S-2; NH4+; NH2COONH4; (NH4)2HPO4; (NH4)2SO3; NH4HS; NH4HSO3; NH4CL; NH6PO4; NH4HCO3; NH2COO-; H2PO4-; HSO3-; CN-; CL-; CLO-; HPO4-2; SO3-2; PO4-3; (NH4)3PO4; H3PO4*W; CH4O; C2H6O-1; (NH4)2SO3*W; NH4CN; H3PO4*0.5W; C2H6O-2; C3H8O-1; C4H10O-1; CA3(PO4)2; MGSO4; MG3(PO4)2; MGCO3; CACO3; CASO4; C5H12O-1; C4H10-1; C4H10-2; and C5H12-1.

Some scenarios do not use all of these components, depending on the route and process unit selected only some of these components are inserted.

3.9 Process parameters

The main energetic parameters (thermal and electrical efficiencies) and operational parameters (conversions and compound ratios) of the processes can be directly obtained from the simulation or calculated to obtain specifications about one process or product, allowing evaluations and comparisons front other configurations. Only the calculation of few parameters is presented in this section, other parameters (calculation form) are defined and presented along the text or simply reported

3.9.1 Lower heating values (LHV) and higher heating values (HHV)

The calorific value measurement method is based on the energy balance in complete combustion of the sample, usually with pure oxygen, at constant volume. Heating value of a fuel is measured experimentally in terms of the high heating value (HHV) by use of a device called calorimeter according to specifics American Society of Testing and Materials (ASTM) or Deutsches Institut für Normung (DIN) standards (e.g.: ASTM Standards, Vol. 05.05, D3588-91).

HHV also called Gross energy or upper heating value or gross calorific value (GCV) or higher calorific value (HCV) is determined by bringing all the products of combustion back to the original pre-combustion temperature.

Lower heating value (LHV) also called net calorific value (NCV) or lower calorific value (LCV) is determined by subtracting the heat of vaporization of the water from the HHV. The HHV and the LHV are related according to Equation 1.

$$LHV = HHV - h_{lv}\left(\frac{m_{H_2O,out}}{m_{fuel,in}}\right) \tag{1}$$

Where, LHV is the lower heating value (MJ/kg), HHV is the higher heating value (MJ/kg), h_{lv} is the heat of vaporization of water per unit mass at reference temperature (MJ/kg), $m_{H_2O,out}$ is the mass of water formed and vaporized in the combustion of H_2 present in the sample (fuel) (kg), and $m_{fuel,in}$ is the mass of fuel combusted (kg).

HHV refers to a condition in which the water is condensed out of the combustion products including sensible heat and latent heat of condensation. LHV on the other hand, refers to the condition in which water in the final combustion products remains as steam. HHV can be expressed on dry basis (db) of the fuel sample (dry mass content) according to Equation 2.

$$HHV_{db} = \frac{HHV_{AR}}{1 - M} \qquad (2)$$

Where, HHV_{db} is the higher heating value referenced by mass of fuel on dry basis (db) (MJ/kg), HHV_{AR} is the higher heating value as received (AR) (MJ/kg), and M is the moisture content of fuel in decimal mass fraction (dimensionless).

The reference conditions (standard) usually used for quantify the HHV and LHV is temperature at 25ºC (for MJ/kg measurement) and pressure at 1 atm (gaseous substances on ideal state) or ambient conditions of temperature and pressure (inlet oxidizing).

3.9.1.1 Aspen Plus®v8.4 heating value measurement

The heat values for non-conventional solids (Bagasse and Straw) are achieved applying the Mott and Spooner correlation (empirical correlations developed for coal estimative), that best represents sugarcane bagasse and straw (3.7 Non-conventional solids physical property methods). After the breakdown phase (non-conventional to elemental conventional components), Aspen Plus®v8.4 process simulation platform shall use the heat values of APED (specific data in Enterprise Database) for each elemental conventional component present in the stream.

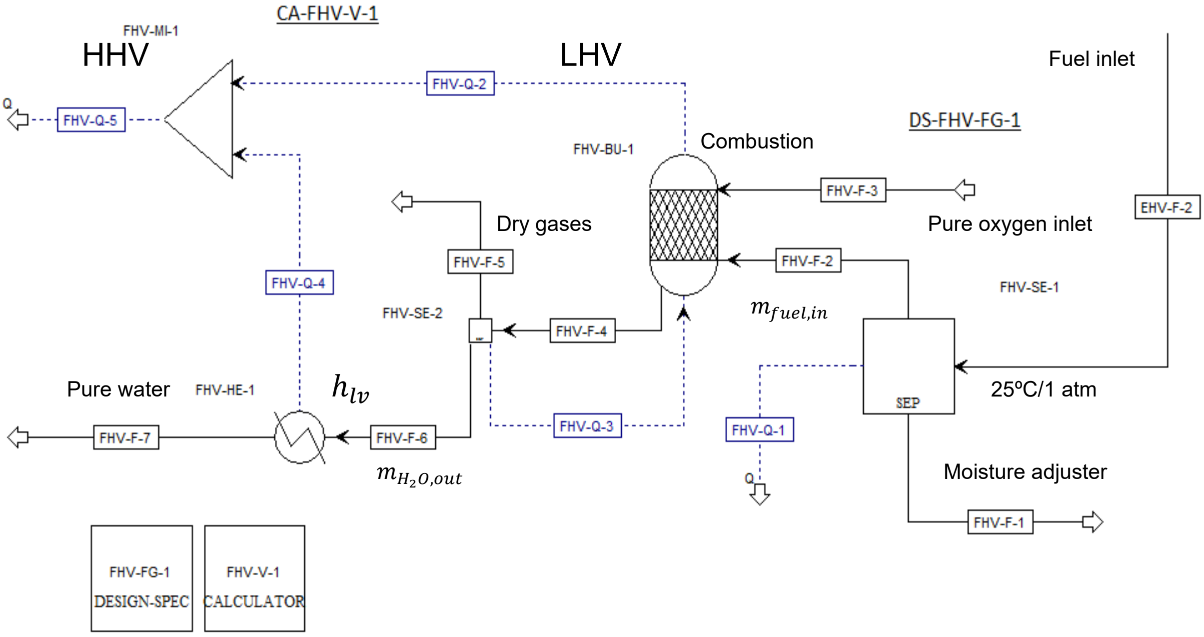

Figure 23 - Aspen Plus®v8.4 flowsheet of heating value measurement (calorimeter)

Figure 23 shows HHV and LHV calculation method from stoichiometric combustion in RStoic reactor highlighting the stream-parameters. LHV is calculated from the HHV by subtracting the heat of water vaporization formed from combustion of hydrogen present in the fuel applying the FORTRAN calculator FHV-V-1. The design specification FHV-FG-1 adjusts the exact stoichiometric oxygen necessary for complete fuel combustion (without oxygen in excess).

The model (Figure 23) for heating value measurement of conventional components (solids, liquids and gaseous) and non-conventional components (Bagasse and straw) is capable of directly and automatically estimate the HHV and LHV (biomass as received or on dry basis) in the Aspen Plus$^{®}$v8.4 process simulation platform without external calculations to determine the parameters of Equation 1 and Equation 2.

3.9.2 Total system energy efficiency

Total system energy efficiency ($\eta_{S,E+Th}$) or thermal efficiency provides measure of the energy system efficiency for evaluate the energetic use of the system, in this research Master's degree the system is thermochemical routes and optimized 1G sugarcane biorefinery (electricity and thermal energy). The $\eta_{S,E+Th}$ is calculated as the total useful net electrical and thermal energy output divided by the potential energy (chemical and sensible heat), LHV basis, content in the consumed raw materials, according to Equation 3.

$$\eta_{S,E+Th} = \frac{W_{E,net} + \sum \dot{Q}_{Th,net}}{LHV_{AR,fuel} + h_{fuel}} \tag{3}$$

$$h_{fuel} = m_{fuel}.C_{p,fuel}(T)\left(T_{fuel} - T_{ref}\right)$$

Where, $\eta_{S,E+Th}$ is the total system energy output efficiency (dimensionless), $W_{E,net}$ is the electric potential power output of the system (MW), $\sum \dot{Q}_{Th,net}$ is the sum of the all useful thermal potential energy output (MW), $LHV_{AR,fuel}$ is the lower heating value of fuel as received (MW), m_{fuel} is the mass flow rate of fuel (kg/s), h_{fuel} is the sensible heat of fuel (MW), T_{fuel} is the temperature of fuel (K), $T_{ref}$is the reference temperature (25ºC/298K standard) and $C_{p,fuel}(T)$ is the specific heat of the fuel, (MJ/kg.K).

3.9.3 Net-electric energy efficiency

Net-electric energy efficiency ($\eta_{S,E}$) or effective electric efficiency provides a partial measure of the system efficiency and a valid metric for evaluate the electrical production. In this research Master's degree the efficiency is measured for the thermochemical route (advanced cogeneration systems) and therefore for the entire thermochemical-biorefinery. The $\eta_{S,E}$ is calculated essentially as the net-electric energy output divided by the potential energy, LHV basis, content in the consumed raw materials, according to Equation 4.

$$\eta_{S,E} = \frac{W_{E,net}}{LHV_{AR,fuel} + h_{fuel}} \tag{4}$$

$$h_{fuel} = m_{fuel}.C_{p,fuel}(T)\left(T_{fuel} - T_{ref}\right)$$

Where, $\eta_{S,E}$ is the net electric energy output efficiency (dimensionless), $W_{E,net}$ is the electric potential power output of the system (MW), $LHV_{AR,fuel}$ is the lower heating value of fuel as received (MW), m_{fuel} is the mass flow rate of fuel (kg/s), h_{fuel} is the sensible heat of fuel (MW), T_{fuel} is the temperature of fuel (K), $T_{ref}$is the reference temperature (25ºC/298K standard) and $C_{p,fuel}(T)$ is the specific heat of the fuel, (MJ/kg.K).

3.9.4 Boiler thermal efficiency

Boiler efficiency (η_h) is defined as the ratio of the useful heat output (exported) by steam or hot water to the heat supplied by the fuel chemical potential energy (type 1) or supplied by the fuel and air (chemical potential and sensible energies) (type 2). The η_{cg} is expressed according to Equation 5 (type 1) or Equation 6 (type 2).

$$\eta_{bo,ef1} = \frac{Q_{exp,steam}\cdot}{HV_{db,fuel} + h_{fuel}}.100 \quad = \quad \frac{Heat\ exported\ by\ the\ fluid\ in\ the\ boiler}{Heart\ suplied\ by\ the\ fuel} \tag{5}$$

or

$$\eta_{bo,ef2} = \frac{Q_{exp,steam}\cdot}{HV_{db,fuel} + h_{fuel} + h_{air}}.100 \tag{6}$$

$$h_i = m_i.C_{p,i}(T)\left(T_i - T_{ref}\right)$$

Assumption: $HV_{db,fuel} = LHV_{db,fuel}$

Where, $\eta_{bo,ef}$ is the boiler thermal efficiency (%), $LHV_{db,fuel}$ is the lower heating value of fuel on dry basis (MJ), m_i is the mass flow rate of fuel (kg), h_i is the sensible heat of fuel and air (MJ), T_i is the temperature of fuel and air agents (K), $T_{ref}$is the reference temperature (25ºC/298K standard) and $C_{p,i}(T)$ is the specific heat of the fuel and air (MJ/kg.K).

The energy supplied by the fuel ($HV_{db,fuel}$) may be expressed in two ways gross calorific value or net calorific value. In this research Master’s degree is used only de efficiency expressed by net calorific value. The latent heat necessary for evaporate the water content in the fuel is considered as loss thermal energy.

3.9.5 Steam-to-biomass ratio

Steam-to-biomass (S/B) ratio for the atmospheric directly-heated gasification (CFB) is calculated from the mass flow rate of steam to mass flow rate of the biomass (dry basis). The steam-to-biomass ratio (STBR) is expressed according to Equation 7.

$$STBR\ or\ S/B\ ratio = \frac{m_S}{m_{B_{db}}} = \frac{Steam\ flow\ rate}{Dry\ biomass\ flow\ rate} \tag{7}$$

Where, $STBR$ is the steam-to-biomass ratio (dimensionless),m_S is the mass flow rate of steam (kg/h), $m_{B_{db}}$ is the mass flow rate of the dry biomass (kg/h).

3.9.6 Equivalence ratio

The amount of air used in combustion or gasification processes is also expressed in terms of the equivalence ratio (ER) and can be expressed in two ways depending on the basis. The ER is defined in the literature as the actual air-fuel flow ratio to stoichiometric air-fuel flow ratio and can be obtained according to Equation 8.

$$ER_{Air} = \frac{\left(\frac{m_{Air}}{m_{fuel}}\right)_O\ actual/operational}{\left(\frac{m_{Air}}{m_{fuel}}\right)_S\ stoichiometric}\quad or\ ER_{O_2} = \frac{\left(\frac{m_{O_2}}{m_{fuel}}\right)_O\ actual/operational}{\left(\frac{m_{O_2}}{m_{fuel}}\right)_S\ stoichiometric} \tag{8}$$

Where, ER_{Air} is the equivalence ratio (air basis) (dimensionless), ER_{O_2} is the equivalence ratio (oxygen basis), m_{Air} is the mass flow rate of air (kg/h), m_{O_2} is the mass flow rate of oxygen (kg/h), m_{fuel} is the mass flow rate of fuel (kg/h), O is the operational condition indicator and S is the stoichiometric condition indicator.

In this research Master's degree, we used two different combinations of gasification agents, as follows: Air (atmospheric composition) and steam; and High pure oxygen (about 98.3$\%_{mol}$ of purity) and steam.

3.9.7 Air-fuel ratio

Air-fuel ratio (AF) is defined as the mass of air to mass of fuel and expressed according to Equation 9, in mass basis.

$$AF = \frac{m_{ar}}{m_{fuel}} = \frac{air\ mass\ flow\ rate}{fuel\ mass\ flow\ rate} \tag{9}$$

Where, Air_{stoich} *is the percentage of theoretical air (%),* Air_{excess} *is the percent excess air (%)* ER_{Air} *is the equivalence ratio of air (dimensionless).*

3.9.8 Excess air

The amount of excess air (Air_{excess}) (amount of air in excess of the stoichiometric amount) is usually expressed in terms of the stoichiometric air as percent excess air or percent theoretical air. The amount of air used is expressed in terms of the ER (Equation 8) according to Equation 10 and Equation 11.

$$Air_{stoich} = ER_{Air}.100\% \qquad refered\ to\ stoichometric\ theorical\ air \tag{10}$$

$$Air_{excess} = (ER_{Air} - 1).100\% \qquad refered\ to\ excess\ air \tag{11}$$

Where, Air_{stoich} *is the percent theoretical air (%),* Air_{excess} *is the percent excess air (%)* ER_{Air} *is the equivalence ratio of air (dimensionless).*

Amounts of air less than the stoichiometric amount are called deficiency of air and often expressed as percent deficiency of air.

3.9.9 Oxygen excess and percent in flue-gas

The percentage of excess oxygen $\%_{O_2}$ can be defined in mass basis (most common) or in molar basis. The $\%_{O_2}$ can be expressed according to Equation 12.

$$\%_{O_2} = \frac{m_{O_{2,oper}} - m_{O_{2,stoich}}}{m_{O_{2,stoich}}}.100\% \tag{12}$$

Where, $\%_{O_2}$ *is the mass percentage of excess oxygen (%$_M$),* $m_{O_{2,oper}}$ *is the mass flow rate of oxygen (kg/h),* $m_{O_{2,stoich}}$ *is the mass flow rate of oxygen for stoichiometric combustion (kg/h).*

When operating with 5.0%$_{w/w}$~20.0%$_{w/w}$ of excess air, it corresponds to a 1.0%$_{M/M}$~3.0%$_{M/M}$ of oxygen measurement (dry basis) in the stack. The value of oxygen content in flue-gas is obtained from a flue-gas analysis.

3.9.10 Net gasification efficiency

In this research Master's degree the net gasification efficiency (η_{net}) accounts the synthesis gas (hot) potential chemical and sensible energy output over the energy inputs from fuel and gasification agents (chemical and sensible energy). The η_{net} is obtained according to Equation 13.

$$\eta_{net} = \frac{LHV_{db,syngas}. + h_{syngas}}{LHV_{db,fuel} + h_{fuel} + h_{oxyd\ agent} + h_{steam\ agent}} \tag{13}$$

$$h_i = m_i.C_{p,i}(T)(T_i - T_{ref})$$

Where, η_{net} *is the net gasification efficiency (dimensionless),* $LHV_{db,syngas}$ *is the lower heating value of synthesis gas on dry basis (MJ),* $LHV_{db,fuel}$ *is the lower heating value of fuel on dry basis (MJ),* m_i *is the mass flow rate of fuel, synthesis gas, and gasification agents (kg),* h_i *is the sensible heat of fuel, synthesis gas and gasification agents (MJ),* T_i *is the temperature of fuel, synthesis gas and gasification agents (K),* T_{ref}*is the reference temperature (25ºC/298K standard) and* $C_{p,i}(T)$ *is the specific heat of the fuel, synthesis gas and gasification agents (MJ/kg.K).*

3.9.11 Gasifier cold-gas efficiency

Cold gas efficiency (η_{cg}) is most commonly used definition for gasifier efficiency, the synthesis gas (cooled) potential chemical energy output over the energy inputs from fuel and gasification agents (chemical and sensible energy). The η_{cg} is obtained for tar-free gas at standard conditions (25ºC and 1 atm) according to Equation 14.

$$\eta_{hg} = \frac{LHV_{db,syngas}.}{LHV_{db,fuel} + h_{fuel} + h_{oxyd\ agent} + h_{steam\ agent}} \tag{14}$$

$$h_i = m_i . C_{p,i}(T)\left(T_i - T_{ref}\right)$$

Where, η_{cg} is the cold-gas efficiency (dimensionless), $LHV_{db,syngas}$ is the lower heating value of synthesis gas on dry basis (MJ), $LHV_{db,fuel}$ is the lower heating value of fuel on dry basis (MJ), m_i is the mass flow rate of fuel and gasification agents (kg), h_i is the sensible heat of fuel, synthesis gas and gasification agents (MJ), T_i is the temperature of fuel and gasification agents (K), $T_{ref}$is the reference temperature (25ºC/298K standard) and $C_{p,i}(T)$ is the specific heat of the fuel and gasification agents (MJ/kg.K).

3.9.12 Gasifier hot-gas efficiency

Hot-gas efficiency (η_{hg}) accounts the synthesis gas with tar and soot potential chemical and sensible energy output over the energy inputs from fuel and gasification agents (chemical and sensible energy), is obtained according to Equation 15.

$$\eta_{hg} = \frac{LHV_{db,syngas}. + h_{syngas} + LHV_{db,tar} + h_{tar} + LHV_{db,soot} + h_{soot}}{LHV_{db,fuel} + h_{fuel} + h_{oxyd\ agent} + h_{steam\ agent}} \tag{15}$$

$$h_i = m_i . C_{p,i}(T)\left(T_i - T_{ref}\right)$$

Where, η_{hg} is the hot-gas efficiency (dimensionless), $LHV_{db,syngas}$ is the lower heating value of synthesis gas on dry basis (MJ), $LHV_{db,fuel}$ is the lower heating value of fuel on dry basis (MJ), $LHV_{db,tar}$ is the lower heating value of tar on dry basis (MJ), $LHV_{db,soot}$ is the lower heating value of soot on dry basis (MJ), m_i is the mass flow rate of fuel, synthesis gas, tar, soot and gasification agents (kg), h_i is the sensible heat of fuel, synthesis gas, tar, soot and gasification agents (MJ), T_i is the temperature of fuel, synthesis gas, tar, soot and gasification agents (K), $T_{ref}$is the reference temperature (25ºC/298K standard) and $C_{p,i}(T)$ is the specific heat of the fuel, synthesis gas, steam, tar, soot and gasification agents (MJ/kg.K).

3.9.13 Heat losses to surrounding ambient

Hot surfaces lose heat to the surrounding ambient by radiative and convective thermal fluxes, for boiler systems (steam generation) a simple representation of these phenomena is based on the LHV_{db} of the fuel, obtained according to Equation 16.

$$Q_{loss} = LHV_{AR,fuel}\left[0.007 + \left(\frac{m_{water}}{4.0e^{9}}\right)\right] \tag{16}$$

Where, $\eta_{S,E}$ is the net electric energy output efficiency (MWh), $LHV_{AR,fuel}$ is the lower heating value of fuel as received (MW), m_{water} is the mass flow rate of water inlet in the boiler (kg/hr).

3.9.14 Biomass conversion

Biomass conversion efficiency (η_B) is defined as the ratio of the biomass converted to products to the total of biomass supplied, is obtained according to Equation 17.

$$\eta_B = \frac{m_{B,converted}}{m_{B,suplied}} = \frac{Biomass\ converted\ to\ produducts}{Biomass\ suplied\ (inlet)} \tag{17}$$

Where,η_B is the biomass conversion efficiency (dimensionless),$m_{B,converted}$ is the mass flow rate of biomass converted to products (kg/h), $m_{B,suplied}$ is the mass flow rate of biomass inlet(kg/h).

3.9.15 Carbon conversion

The carbon conversion efficiency (η_c) is defined as the ratio of the carbon (solid) converted to gaseous products to the total carbon supplied by the fuel (carbon content). The conversion is measured by the carbon content in the gas, liquid and solids fractions of products (not converted) and related to the carbon-fuel supplied. The η_c is obtained according to Equation 18.

$$\eta_c = 1 - \frac{\dot{m}_{C,products}}{\dot{m}_{C,fuel}} = 1 - \frac{Carbon\ content\ in\ the\ gas\ and\ solid\ produducts}{Carbon\ content\ in\ the\ fuel\ suplied} \tag{18}$$

Where, η_c is the carbon conversion efficiency (dimensionless), $\dot{m}_C$ is the mass flow rate of carbon non converted present in the gas, liquid and solids fractions of products (kg/h), $\dot{m}_{C_{fuel}}$ is the mass flow rate of the carbon content in the fuel supplied (kg/h).

3.9.16 Hydrogen to carbon ratios

The composition of synthesis gas (i.e.: H_2, CO, CO_2, CH_4, and other minority compounds) is given in terms of stoichiometric number (S), which can be expressed as a ratio of the diference between the moles of H_2 and CO_2 and the summation of the moles of CO_2 and CO, according to Equation 19, or can be expressed simply as a ratio between the moles of H_2 and the moles of CO, according to Equation 20.

$$S_1 = \frac{moles\ H_2 - moles\ CO_2}{moles\ CO_2 + moles\ CO} \tag{19}$$

$$S_2 = \frac{moles\ H_2}{moles\ CO} \tag{20}$$

Where, S is the stoichiometric number (dimensionless), $moles\ of\ H2,\ CO, and\ CO_2$ are thiers specific compound moles present in the synthesis gas stream (moles).

3.9.17 Water-cooling tower

There are several different methods in the literature to calculate water cycle and water uses in a water-cooling tower, some definitions and forms to estimate the water cycle in this research Master's degree are defined in this section.

The water evaporation rate can be obtained by the Equation 21.

$$Evaporation_{\%} = \frac{C_p(T)(T_{top} - T_{base})}{h_{lv}} \qquad basis{:}\ \frac{1.0kg}{h}\ of\ water \tag{21}$$

Where, $Evaporation_{\%}$ is the percentage of water evaporated (dimensionless), $C_p(T)$ is specific heat of water in function of temperature (T) (kJ/kg°C), T_{top} is the temperature of water inlet on the top of tower (°C), T_{base} is the temperature of water outlet on the base of tower (°C), h_{lv} is the latent heat of vaporization of water (kJ/kg).

Drift loss varies between 0.1% and 0.2% of the mass flow rate of water that are circulating in the tower system. In this research Master's degree is considered 0.2% of $Drift_{frac}$ (maximum factor). The drift mass flow rate can be obtained by the Equation 22.

$$Drift = Drift_{frac}\ m_{water} \tag{22}$$

Where, $Drift$*is the mass flow rate of entrained water in the tower discharge vapors (kg/h),* $Drift_{frac}$ *is the fraction of the entrained water in the tower discharge vapors (dimensionless),* m_{water} *is the mass flow rate of circulating water (kg/h).*

Make-up water for multi-cells water-cooling tower is determined based on the water losses by evaporation, drift, and tower basin blowdown, according to Equation 23. And the make-up raw water is determined considering the losses according to Equation 24.

$$Water_{makeup} = Evaporation + Drift + Blowndown \tag{23}$$

$$Fresh\ water_{makeup} = Evaporation + Drift + X.Blowndown \tag{24}$$

In this research Master's degree is considered 13% of losses

$$X = 0.13 \quad 87.0\%\ of\ the\ water\ blowndown\ is\ recovered\ and\ recycled\ to\ tower\ basin$$

Where, $Water_{makeup}$ *is the mass flow rate of make-up water to the tower basin (kg/h),* $Fresh\ water_{makeup}$ *is the mass flow rate of make-up raw water to the tower basin considering the water recycle (kg/h),* $Evaporation$ *is the mass flow rate of water evaporated (kg/hr),* $Drift$ *is the mass flow rate of water drifted with the flow of air/vapor (kg/hr),* $Blowndown$ *is the mass flow rate of water purged from the tower basin to treatment (kg/hr), and* X *is the discharged fraction of the water blowdown (not recovered water) (dimensionless).*

The tower basin blowdown can be obtained by the Equation 25, relating the evaporation rate and the number of cycles of concentration, which is defined as comparison of dissolved solids level of the blowdown with the makeup water.

$$Blowndown_{\%} = \frac{Evaporation_{rate}}{C.O.C - 1} \tag{25}$$

In this research Master's degree is considered 10 cycles of concentration ($C.O.C$)

Where, $Blowndown_{\%}$ *is the percentage of the tower basin blowdown based on the evaporation rate,* $Evaporation_{rate}$ *is the percentage of the water evaporated (%),* $C.O.C$ *is the number of cycles of concentration in the treatment system (dimensionless).*

The electricity consumed by the large mechanically driven axial fans to induce air upward through the fill in the cell-tower is estimated of 63.0 kWh per driver fan ($elect_{driver}$). To obtain the total electricity consumption is necessary the number of cells that compose the multi-cell water-cooling tower system. The electricity consumed by mechanical drivers in the axial fans is estimated based on the Equation 26.

$$W_{elect} = n_{cells}.\,elect_{driver} \tag{26}$$

Where,W_{elect} *is the electricity consumed per fan driver (KWh),* n_{cells} *is the number of cells necessary in the water-cooling tower system (fan),* $elect_{driver}$ *is the specific electricity consumption per fan drivers (kWh)*

4 Thermochemical route thecnologies: survey and considerations

A simplified overview based on the main concepts for design thermochemical routes according to assumptions and technologies issues to be considered in the Aspen Plus®v8.4 process simulation platform for integrated processes are presented, some of the main important aspects considered in the conceptualized biorefinery scenarios are commented.

4.1.1 Atmospheric air composition

The surrounding atmospheric air (ATMOSPHERIC AIR) is considered at ambient conditions composed on the molar basis by: 76.170% of nitrogen (N_2); 20.420% of oxygen (O_2); $9.250e^{-1}$% of Argon (Ar); $1.811e^{-3}$% of Neon (Ne); $5.200e^{-4}$% of Helium (He); $8.500e^{-6}$% of Xenon (Xe); $1.150e^{-4}$% of Krypton (Kr); $3.230e^{-2}$ of carbon dioxide (CO_2); $2.000e^{-4}$ of methane (CH_4); 2.450% of water vapor (H_2O) as conventional mixed fraction; and fine particulate matter as conventional solids fraction.

4.1.2 Ambient conditions

Surrounding ambient conditions is considered at 25.0ºC and 1.01325 bar (atmospheric pressure) with relative humidity around 75.0% and web bulb temperature at about 21.3ºC. Fine particulate matter in the air is simulated in the Aspen Plus®v.4 considering the density of 450.0 µg of particles per m³ of air (average for industrial open-area) and as inert dust (SiO_2) with particles diameters of about 30.0% smaller than 10.0 µm and 70% smaller than 5.0 µm.

4.1.3 Biomass handling and sizing

Depending on the feedstock characteristics and as-delivered characteristics, the feedstock preparation system could potentially require equipment to screen-out over sized or hardest biomass and heavier particles (e.g.: hard wood, metals, rocks) delivered with the straw bales, remove soil content accumulated due to contact with the agricultural soil (gathering after rainy weather), remove metals collected from the field (HASSUANI; LEAL; MACEDO, 2005). Biomass can be received in pellets form or just in nature form as gathering in the field (straw) or as it comes out of the cane mills (BRAZILIAN BIOETHANOL SCIENCE AND TECHNOLOGY LABORATORY, 2012; HASSUANI; LEAL; MACEDO, 2005). In this research Master's degree was just proposed the simple system without in site biomass pelletizing (future works).

Biomass handling and sizing systems are customized to supply the requirements of the subsequent gasification process (in this research Master's degree, is for directly-heated gasifiers). Part of the raw bagasse feedstock reserved in the pile for brief stops and start-up and other part of raw bagasse from sugarcane mills or bagasse pile (temporary storage) can be belt-conveyed directly to pre-cutting/milling machine to gross size reduction and conveyed (belt or screw) to dryer system (rotary or flash dryers) to reduce the moisture content before the second size reduction stage (grinding/milling/crushing system) to final size requirement (DUTTA; PHILLIPS, 2009; PHILLIPS et al., 2007; WOOLEY; YALE, 2012). Before the second size stage the biomass is classified in a screen-deck solid-solid classifier, fines are directly conveyed to dryers and the oversized particles (2.0 cm) are sent through a grinding/milling/crushing system for the second size stage of reduction.

For integrated scenarios with 1G-CHP/EBPST system with surplus biomass a part of available bagasse is belt-conveyed directly to the traditional CHP/EBPST system or to bagasse pile for burning purpose, generating thermal and electrical energy to supply a part of the energy demand of the 1G sugarcane biorefinery while thermochemical route supply the other part. For the standalone scenarios a part of available bagasse is burned to generate the thermal and electrical energy to supply the entire energy demand of the 1G sugarcane biorefinery with surplus bagasse available to use by the thermochemical routes.

The straw bales are delivered to the biomass handling and sizing area for storage and/or size reduction, if the baler machinery do not perform a pre-chopping the straw bale can be chopped directly as received for pre-size reduction and unpacking the bales, if the baler machinery perform a pre-chopping in own field is just necessary unpacking the straw bales. Unpacked and pre-sized straw is conveyed (drag or belt) to magnetic head pulley (magnetic separator) to removes ferromagnetic tramp metals (avoiding damage to the cutting/milling machine) before the fine-size reduction process, after the straw is conveyed to cutting/milling/crushing machine to fine-size reduction stage to final size requirement (DUTTA; PHILLIPS, 2009; HASSUANI; LEAL; MACEDO, 2005; PHILLIPS et al., 2007). Classifier solid-solid separators (screen on deck or multiple decks) are used to separate the oversized fibers, which are returned to the cutting/milling/crushing/grinding machine for the fine-size stage of reduction adjusts to size requirement. Sized straw are conveyed to dryer and mixed together with the sized bagasse.

4.1.4 Biomass multi-step drying process and particulate emission control

The moist bagasse and straw are conveyed to specific dryer feeder drum and stages, entering by screw-conveyor into parallel dryer trains and multi-steps drying process to low-moisture content (normally less than 15.0%$_{w/w}$ of moisture content), “the moisture content of the biomass fed to the gasifier should be in the range 10-20%” (Lau et al., 2003 apud LARSON et al., 2006a p. 18). The biomass can be dried by hot-air, steam or high-purity nitrogen (ASU vent) agent in co-current rotary drum dryer type or in flash dryer type (HASSUANI; LEAL; MACEDO, 2005; PHILLIPS et al., 2007). The drying agent is forced trough the dryer by blowers to heat the biomass and remove the moisture content by direct contact evaporative and mass transfer effect.

The flue-gas or exhaust-gas from the HRSG system and/or from the CHP/EBPST system (when employed) are used to indirect heat the fresh or pre-heat the air agent (safeguard to fire risk disadvantage) or steam agent (water cycle system disadvantage) or high-purity nitrogen agent (ASU without nitrogen as product disadvantage) used to dry sugarcane bagasse and straw in multiple-step dryer system coupled with the size reduction system (HASSUANI; LEAL; MACEDO, 2005). A high drying agent inlet temperature must be avoided to minimize release of volatile organic compounds (VOCs) (steam and air agents), and risk of ignition (air agent) (LARSON et al., 2006a, 2006b).

The flue-gas temperature in the stack can be controlled by the drying agent (air/steam) cooling the hot flue-gas to low-temperature and reducing the atmospheric pollutants emission (advanced wet pollutants control system), are not necessary remove particles system in the HRSG flue-gas in the scenarios without the traditional 1G-CHP/EBPST due the flue-gas not come into contact with the biomass, but is necessary remove particles content in the drying agent, in the scenarios with the traditional 1G-CHP/EBPST the flue-gas from the solid-fuel fired boiler have particulate matter and a particles removal system can be optional.

The flue-gas cleaning can be done by wet methods efficiently by wet scrubbers to control particulate emissions and reduce the atmospheric pollutants emission, in addition to cool the flue-gas and condense the water-vapor content in the flue-gas.

The direct contact of the drying agent with biomass can drag fine particles (e.g.: fine biomass fibers, soil and others) due the high mass flow rate and the turbulent movement of the drying agent, extractive and VOCs present in the biomass can be evaporate and emitted to atmosphere together the drying agent and the vaporized water content in the dryer exhaust humidified gas. This gases enters in the after-dryer cyclone system (single cyclone or multi-cyclone) to remove the gross particulate content in the dryer humidified exhaust-gas, and then in an electrostatic precipitator or in a baghouse filter to reduce the persistent fine particulate matters and theirs emissions to atmosphere (DUTTA; PHILLIPS, 2009; PHILLIPS et al., 2007). The gross and fine particulate matters are sent to directly-heated gasifier together the sized-dry biomass (mixed in the feed gasifier conveyors) (DUTTA; PHILLIPS, 2009; PHILLIPS et al., 2007) Part of the drying agent after leaving the dryer is recycled whereas the other part is used in the heat recovery unit for preheating the incoming fresh drying agent.

4.1.5 Gasification of biomass in an atmospheric circulating fluidized bed directly-heated gasifier

The gasifier system in this research Master`s degree selected for the thermochemical-biorefinery simulation and assessment scenarios is a low-pressure (atmospheric pressure) biomass directly-heated gasifier (autothermal) employing air/oxygen and steam agents in an CFB gasifier, which is directly-heated from the combustion reactions occurring in the bed. CFB directly-heated gasifiers are both capable of efficiently gasifying a wide range of biomass materials, including sugarcane bagasse and straw with char conversion slightly higher than for bubbling fluidized bed (BFB) gasifiers (atmospheric types comparison), due to the recycling of the char (DUTTA; PHILLIPS, 2009; WOOLEY; YALE, 2012).

The target size for lignocellulosic biomass as feedstock for atmospheric CFB directly-heated gasifiers is approximately 1.0 to 13.0 cm minus with a thickness of 0.1 to 1.5 cm (DUTTA; PHILLIPS, 2009; HASSUANI; LEAL; MACEDO, 2005; PHILLIPS et al., 2007; WOOLEY; YALE, 2012). A properly designed gasifier in-feed system and sugarcane bagasse and straw handling, sizing and drying processes are required, larger sizes are acceptable if the thickness remains near 0.1 cm to 0.5 cm (HASSUANI; LEAL; MACEDO, 2005; PHILLIPS et al., 2007). The biomass size directly influences the energetic (thermal and electrical) consumption of upstream processes (e.g.: sizing; and drying) and the own process of gasification.

The moisture content of the fuel entering the directly-heated gasifier strongly affects the heating value of the produced gas, as energy is required for the vaporization of the moisture (increasing the oxidizing agents demand) (DUTTA; PHILLIPS, 2009; LARSON et al. 2006b). According to Hassuani, Leal and Macedo (2005) drying to $10.0\%_{w/w}$ is recommended, in this research Master’s degree is considered $50.0\%_{w/w}$ of moisture content in the bagasse and $15.0\%_{w/w}$ of moisture content in the straw, it’s a conservative estimate (moisture can vary).

From the biomass handling and sizing for gasification process and biomass multi-step dryer (areas) the sugarcane bagasse and straw with low-moisture content ($10.0\%_{w/w}$) and sized (less than about 2.0 mm of tickles) are feed by conveyors and screw-hoppers into the low-pressure gasifier near the bottom of the gasifier bed

(DUTTA; PHILLIPS, 2009; HASSUANI; LEAL; MACEDO, 2005; PHILLIPS et al., 2007).

The directly-heated gasification process can be split into four basic linked zones, during directly-heated gasification are: a) drying zone; b) devolatilization (thermal decomposition) or pyrolysis zone; c) gasification or reduction zone; and d) combustion or oxidation zone.

The biomass are converts to a mixture of components content gaseous (inerter elements present in the surrounding air, H_2O, CO, H2, CO2, CH4, H_2S, HCl, Cl_2, COS, NH_3, NO_x, SO_x and light hydrocarbons) solid matters (e.g.: bed material, specifics catalytic active materials, unconverted biomass/carbon, coke, ashes content, soil, salts and minerals) and tar (heavy carbon-content compounds in suspension) (DUTTA; PHILLIPS, 2009; LARSON et al., 2006a, 2006b; WOOLEY; YALE, 2012).

Sugarcane bagasse and straw gasification by atmospheric CFB directly-heated gasifiers using air and steam as gasification agents can produce low or medium heating value (LHV) crude synthesis gas (less than 10.0 MJ/kg), because the large amounts of N_2 and CO_2 content in the crude synthesis gas. Directly-heated gasifiers using air/steam gasification agents operate with 97.0%~99.0% carbon conversion efficiency where 3.0%~1.0% of the unconverted carbon is generated (char). The temperature distribution in the fluidized bed is relatively constant and typically ranges between 700.0°C and 900.0°C. Equivalence ratio (ERAIR) (Equation 8) for air/steam agents gasification process can vary from 0.20 to 0.45 and the steam-to-biomass (S/B) ratio (Equation 7) can vary from 0.5 to 2.5 kg of steam per kg of biomass inlet (DUTTA; PHILLIPS, 2009; HASSUANI; LEAL; MACEDO, 2005; PHILLIPS et al., 2007; WOOLEY; YALE, 2012). The ERAIR are directly dependent on the biomass moisture content and in the inlet temperature of the gasification agents with influence on the CO yield and the S/B ratio is dependent on the bed fluidization requirements with influence on the H2 yield (DUTTA; PHILLIPS, 2009; WOOLEY; YALE, 2012).

Fresh air oxidant agent is feed by advanced blower system (with air filter to protect the blower and gasifier air distributor from debris) to an heat exchanger for preheating before inlet in directly into the gasifier bed injected at the bottom of the bed at one or several secondary air injection points (close to biomass feed point) as a carrier gas for the fluidized bed plus the oxidant for burning char, coke and part of biomass within the gasifier, supplying the thermal energy required for endothermic gasification reactions (HASSUANI; LEAL; MACEDO, 2005; PHILLIPS et al., 2007; WOOLEY; YALE, 2012). Steam agent can be generated in the synthesis gas heat recovery cooling system or in the HRSG system and injected at the bottom of the bed in the directly-heated gasifier and in the loop-seal (fluidization agent) in order to fluidize the bed and promote the gasification reactions.

The product gas resulting from the gasification process after the gasifier freeboard is fed to a gasifier cyclone (gas–solid separator) to separate solid particles content in the crude synthesis product gas. The majority of the bed material, specifics catalytic active materials and gross-biomass derived particles are separated in the primary gasifier cyclone and sent back (recycled) into the riser and to the gasifier bed using loop-seal steam fluidized system (DUTTA; PHILLIPS, 2009; PHILLIPS et al., 2007; WOOLEY; YALE, 2012). A secondary multi-cyclone system removes a large part of the residual fines-particulate matters (Ashes, biomass/carbon unconverted, bed and additives materials) leaved on the top of the gasifier cyclone, this particles are mixed with the bottom particulate material to disposal (waste disposal or agricultural land application) (PHILLIPS et al., 2007).

The bottom particulate material (e.g.: sand; ash; slag; specifics catalytic active materials; and unconverted materials) mixture (bed) is discharged from the bottom of the gasifier, cooled using directly contact water by water-cooled screw conveyor (heat loss) and stored together the fines-particulate matters from multi-cyclone system in the ashes temporary storage bins to humidified ashes/slag until offloaded for disposal (field disposal) (DUTTA; PHILLIPS, 2009; PHILLIPS et al., 2007).

The gasifier loop bed media and specifics catalytic active materials for makeup system are delivered by truck in the supplies offloading area equipped with a pneumatic line to feed the top of the gasifier loop bed media feed bin, .which transfers the supplies to the atmospheric CFB directly-heated gasifier (DUTTA; PHILLIPS, 2009).

The gasifier bed material is typically an inert mineral solid (resistant to the high-hot ambient condition) with addition of specifics catalytic active materials to promote char gasification, facilitate the chemical reactions inside the gasifier increasing the yield of a particular compound in the synthesis gas (product gas), reduce tar and poisoning (control of alkalis, chlorine and sulfur) formation, reduce or avoid ash agglomeration and subsequent choking of the bed, minimize particulates formation and as effective heat transfer material (PHILLIPS et al., 2007; WOOLEY; YALE, 2012)

The presence of additives influences the gas composition and the heating value of the product gas. Silica sand is the cheapest media with low catalytic active. Dolomite is an effective bed additive in terms of tar reduction and prevention of bed agglomeration (GRIMM et al., 2012). Zeolite can be used as high-surface-area binders to support catalysts. Olivine is a mineral very resistant to attrition (greater than dolomite), and its activity is comparable to dolomite. Limestone is very effective as a sorbent to reduce or prevent agglomeration of the bed. It is, however, the softest sorbent material with the least resistance to attrition and can result in large particulate and dust carryover. Magnesium oxide is also widely used as a sorbent to minimize agglomeration. Engineering materials such as crushed fired clay with high alumina content is a very effective heat transfer material and is very resistant to attrition (GRIMM et. al 2012; WOOLEY; YALE, 2012).

4.1.6 Syngas cooling and heat recovery

The synthesis gas for effective use in atmospheric-based gasifier thermochemical-biorefineries requires the compression of the synthesis gas (normally on the mains thermochemical routes) to higher-pressure requirements of the downstream processes. To compression process is necessary reduce the gas temperature in order to reduce the consumption of electrical energy consume (main demand of electrical energy) and fit the maximum temperature allowed by the compressor. Hot synthesis gas have a great potential to thermal energy generation (sensible heat) and recovery this heat is extremely important in the thermochemical routes integrated at 1G sugarcane biorefinery due the largest thermal energy requirements (DUTTA; PHILLIPS, 2009; LARSON et al., 2006a, 2006b; WOOLEY; YALE, 2012).

The hot-synthesis gas is cooled and the thermal energy content as sensible heat in the synthesis gas is recovered in a first water cooler section in the high-temperature convective synthesis gas cooler (CSC) vertical designed to minimize deposition of condensed alkali species, particulates and melting salts, generating high-pressure steam (first-section of) to thermal use or electrical energy generation in the steam turbines (power train) and cooled in a second water cooler section in the low-temperature convective synthesis gas cooler (CSC) vertical designed to additional heat recovery generating low or intermediate-pressure steam (second section) to thermal use or to gasifier steam agent generation, between the cooling stages can be a ceramic filter or catalyst candle filter (CF) to remove particulates and/or reduce the hydrocarbons content in the cooled synthesis gas (LARSON et al., 2006a, 2006b). After the heat recovery section the cooled synthesis gas is send to low-temperature synthesis gas wet cleaning system to direct water-cooling (scrubbers system) and remove impurities and pollutants.

4.1.7 Tar and hydrocarbons control

Between the high-temperature vertical CSC and the low-temperature vertical CSC a catalytic high-performance candle filter (CF) can be used to reforming the reminiscent tar and other heavy hydrocarbons (non-condensable) with particle removal efficiency higher than 99.9%$_{w/w}$ of particulate present in the hot-synthesis gas (COMMUNITY RESEARCH AND DEVELOPMENT INFORMATION SERVICE, 2010).

A reduction of up to 80.0%$_{w/w}$ of tar content in the synthesis gas produced can be obtained, the tar abatement increased up to 92.0%$_{w/w}$ when iron-olivine catalyst in-bed and catalytic CF were combined together (COMMUNITY RESEARCH AND

DEVELOPMENT INFORMATION SERVICE, 2010; GALLUCCI; van Sint ANNALAND, 2015).

4.1.8 Low-temperature synthesis gas wet cleaning system

The synthesis gas cleaning system (wet scrubbing unit) depends on the synthesis gas composition and the requirements of the downstream processes and systems, there are various technologies used for synthesis gas cleaning (dry or wet systems and cold or hot gas systems), in this research Master's degree a low-temperature and wet cleaning system are implemented.

After the initial particulate removal accomplished by the multi-cyclones system and the syngas cooling and heat recovery the cooled synthesis gas is fed in very-low-temperature (sub-cooled) direct water contact quench/scrubber unit to additional cooling to reduce/adjust the temperature to lower temperatures required by efficient synthesis gas wet cleaning system and co-capture of CO_2 and H_2S by using amine-based aqueous absorbing-solution (LARSON et al., 2006b; NEXANT INC, 2006). The scrubbing system consists of a direct contact water quench, water venturi scrubber and spray condenser quench chamber and demister to remove any remaining ammonia, particulates, metals, halides, or alkali in the system. (NEXANT INC, 2006; WOOLEY; YALE, 2012).

Low-temperature synthesis gas is first cooled to saturation in an evaporative vertical quencher (spray tower), condensed tar, fine particles (e.g.: bed materials, char, and ashes) and salts formed in the quench are collected by venturi scrubber (vertical or horizontal design) according to the aerodynamic size (LARSON et al., 2006a, 2006b; WOOLEY; YALE, 2012). The gas passes through a packed bed condenser/absorber to direct contact with pure water or alkaline water (caustic solution) sub-cooling in order to remove contaminants such as entrained fine particulates (e.g.: inorganic mineral material, unconverted biomass or char, and ash), tar and soluble contaminants such as NH_3, HCl, Cl_2 and small amounts of CO_2 and H_2S (BARTOCCI; PATTERSON 2010; WOOLEY; YALE, 2012). The sub-cooled synthesis gas exits the condenser/absorber and enters the demister, in which additional tar and fine particles are removed. The persistent fine particles after the demister can be removed from the synthesis gas by wet electrostatic precipitator (WESP) operate with water vapor satured air (100% relative humidity), fine particles are stored in the ashes bins and sent to disposal or application in the sugarcane field together the gasifier bottom particulate materials (BARTOCCI; PATTERSON 2010; LARSON et al., 2006a, 2006b; NEXANT INC, 2006; WOOLEY; YALE, 2012).

The low-temperature synthesis gas wet cleaning system can contain a water loop tar removal, if tar remains on the line after the directly-heated gasifier, in systems with tar cracker this system is not essentially necessary for virtually all the tar is converted into the tar cracker to gaseous or light hydrocarbons. In the presence of tar and liquid heavy hydrocarbons the venturi scrubber recirculation water passes through a water-recycle unit to separate the heavy hydrocarbons from the water, heavy hydrocarbons is send back to the directly-heated gasifier to reprocess (BARTOCCI; PATTERSON 2010;).

A blower (fan) after the WESP can be used to equalize/adjust the synthesis gas pressure to further process, due the drop pressure resulting from various stages in the cleaning system (main in the scrubber). After compression the synthesis gas is air-cooled and flashed to remove the condensate water content, water removed is send back to the clarifier to recycle.

The water resulting from the entire cleaning process is collected in a end-drum tank (liquid residue) to separate the tar from the water (loop tar removal) and sends to a clarification system to removing dispersed solids and other impurities using a primary clarifier (liquid organic extractant) and a secondary clarifier to remove soot from carbon-water dispersions and floating solids (BARTOCCI; PATTERSON 2010; WOOLEY; YALE, 2012). Cooled (natural air cooling) and cleaned scrubber water is recirculated to the quench sprayers and into the venturi scrubber in closed-looping. The sludge and scum from the clarifier bottom are sent to sludge thickening equipment to concentrate and send disposal or application in the sugarcane field (together vinasse/ashes).

Vapor content in the synthesis gas after gasification process and heat recovery and cooling process is condensate in the low-temperature synthesis gas wet cleaning system, this large amount of water obtained is enough to keep the wet cleaning process self-sufficient in terms of water, without need make-up raw water. The water circulation rate to the scrubber is adjusted such that the exiting synthesis gas is quenched to the appropriate inlet temperature in the CO_2 and H_2S amine-based co-capture system, the excess of water is sent off-site to a wastewater treatment facility to reuse as make-up in other processes in the thermochemical route (NEXANT INC, 2006; PHILLIPS et al., 2007; WOOLEY; YALE, 2012).

4.1.9 Co-capture of CO_2 and H_2S by using amine-based absorbing-solution

Amine-based for acid gas removal carbon dioxide (CO_2), hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbonyl disulfide (CS_2) (if formation) and mercaptans co-capture systems in order to increase the energy density of the synthesis gas (remove the CO_2 as inert gas) and to control the atmosphere emissions, causing minimal adverse impact on the environment when implemented for the GHG reduction purposes (AUSTRALIAN NATIONAL LOW EMISSIONS COAL RESEARCH & DEVELOPMENT, 2012; DAVE et al. 2010)

The most common amine-based aqueous absorbing-solutions (family) used to acid gas removal are monoethanolamine (MEA), diethanolamine (DEA), trietanolamine (TEA), methyl-diethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP), di-isopropylamine (DIPA) and diglycolamine (DGA). Amine-based aqueous absorbing-solutions can be used in conjunction with the piperazine (PZ) reaction rate promoters (forming blend solutions) (AUSTRALIAN NATIONAL LOW EMISSIONS COAL RESEARCH & DEVELOPMENT, 2012; DAVE et al. 2010; NEVEUX et al., 2013).

Heat integrations play a significant role in the amine-based system, each type of amine and system configurations have different thermal requisites with strong influence over the steam generation system lead to large penalties on the electric production (NEVEUX et al., 2013).

Amine-based solution are used, depending on the downstream process requirements, to remove from $70.0\%_{w/w}$ to $98.0\%_{w/w}$ of CO_2 content in the synthesis gas with co-capture from $20.0\%_{w/w}$ to $80.0\%_{w/w}$ (circulating solution dependency) of the H_2S content. The amine concentration in the aqueous solution depends on the inlet CO_2 concentration and on the synthesis gas mass flow rate updraft in the absorption column, amounts of circulating amine solution depends on the CO_2 remove requirement and thermal limits necessary to avoid degradation in the system (Amine-CO_2 is a exothermic interaction increasing the solution temperature). Amine concentration can vary from $15.0\%_{w/w}$ to $40.0\%_{w/w}$ in the simple solutions, in blended solutions with PZ amine concentration can vary from $5.0\%_{w/w}$ to $30.0\%_{w/w}$ and PZ concentration from $1.0\%_{w/w}$ to $15\%_{w/w}$. Typical amine-based gas treatment by absorption-striping system to CO_2 and H_2S co-capture use $30.0\%_{w/w}$ of MEA in aqueous solution (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION, 2012; DAVE et al. 2010)

MDEA is a tertiary amine slow reactant and needs a catalytic rate promoter such as piperazine, PZ, or a fast reacting amine such as, monoethanolamine, MEA, in solution to accelerate CO2 absorption AUSTRALIAN NATIONAL LOW EMISSIONS COAL RESEARCH & DEVELOPMENT, 2012).

PZ is being used as rate promoter for the slow reacting MDEA systems, can react and create PZ-based species include protonated PZ (H^+PZ), diprotonated PZ ($H_2^{+2}PZ$).PZ, carbamate ($PZCOO^-$), PZ dicarbamate [$PZ(COO^-)_2$] and protonated PZ carbamate $(H^+PZCOO^-)_4$ (AUSTRALIAN NATIONAL LOW EMISSIONS COAL RESEARCH & DEVELOPMENT, 2012)

Amine-based co-capture of CO_2 and H_2S process consist mainly of absorption column, desorption column (stripping), cross-solution heat exchanger and auxiliary equipments operating in loop-cycle (NEVEUX et al., 2013). Process involves exposing a synthesis gas stream to aqueous amine solution (pre-combustion system) to separate the CO_2 content form the synthesis gas by chemical absorption in the solvent (NEVEUX et al., 2013). In the desorber, the CO_2 and H_2S are stripped from the aqueous solution into the gas (acid gas) and the amine-based solution are thermally regenerated, the lean amine (regenerated) in the bottom of the desorber are cooled changing heat with the rich amine (from the absorption column) and returned to the absorption column in closed-loop cycle, a fraction of the lean amine is reclaimed and filtered (carbon filters) to remove sulphur and nitrogen compounds, amine salts, particles and degradation products formed over time in the amine cycle (AUSTRALIAN NATIONAL LOW EMISSIONS COAL RESEARCH & DEVELOPMENT, 2012; DAVE et al. 2010; NEVEUX et al., 2013).

Part of the amine reclaimed is recovered in the presence of a strong alkali (e.g.: NaOH) solution and with the application of heat, and other part is send to wastewater treatment plant together impurities removed from the amine cycle and to disposal (e.g.: landfill) with carbon filter active medium (AUSTRALIAN NATIONAL LOW EMISSIONS COAL RESEARCH & DEVELOPMENT, 2012; DAVE et al. 2010, KOTHANDARAMAN; 2010). The acid gas flows is send to carbon dioxide compression to storage or further use.

Amine undergoes three types of degradation, according to AUSTRALIAN NATIONAL LOW EMISSIONS COAL RESEARCH & DEVELOPMENT, 2012; DAVE et al. 2010).

a) thermal degradation: thermolytic reactions forming simple degradation products under higher temperature conditions;
b) carbamate polymerization: polymerization reactions occurs at higher temperature conditions in the presence of CO2;
c) oxidative degradation: degradation of amine with oxygen dissolved in the amine solution occurs due the oxygen content the gas stream or due to the air-ingress

The amine solvents considered in the Australian National Low Emissions Coal Research & Development (ANLEC R&D 2012) revision are ranked in order of their likely maximum adverse impact to minimal adverse impact as: PZ > AMP > MEA > MDEA. According to ANLEC R&D (2012 pp. 7-8):

> i. Secondary amines have highest risk of nitrosamine formation, followed by tertiary amines, while primary amines have the lowest risk of nitrosamine formation.
>
> ii. All other things being equal, solvents with low vapor pressure are safer than solvents with high vapor pressure.
>
> iii. All other things being equal, a more stable solvent that will resist degradation is safer than a less stable one since the more stable solvent will have lower emissions of degradation products

During the process, chemical compounds are produced as a result of complex chemical reactions occurring in the absorber. Some of these products continue to recycle in the plant while others such as amines, ammonia, aldehydes, carboxylic acid etc are released to the atmosphere (AUSTRALIAN NATIONAL LOW EMISSIONS COAL RESEARCH & DEVELOPMENT, 2012; DAVE et al. 2010).

Absorber operating temperature and the wash tower operating parameters will decide the level of atmospheric emissions of MEA and its degradation products (AUSTRALIAN NATIONAL LOW EMISSIONS COAL RESEARCH & DEVELOPMENT, 2012; DAVE et al. 2010).

The advantage of these solvents is related to the fact that they have excellent effectiveness and efficiency to absorb CO2 in the flue-gas from plants operating with low partial pressures. Amine-based co-capture of CO_2 and H_2S technology has already used for pos-combustion CO_2 capture on amine absorption-stripping system at coal-fired power plants and natural-gas fired plants and is already a mature and well developed technology (DAVE et al. 2010).

4.1.10 Carbon dioxide compression and storage/use

Captured CO2 can be safely stored in underground geological formations (aquifers), in depleted oil and gas fields, or in deep unmineable coal beds. The depth of such geologic formations varies with geographic locations but usually the final pressure of 136 bar to 204 bar is required to inject the CO2 into the formation (WITKOWSKI; MAJKUT, 2012). Carbon capture and sequestration (permanent geological storage) (CCS) is foreseen to be one of the temporary solutions to reduce the atmospheric emissions until the development of a technology that allows sustainable large-use of CO_2 as a feedstock, if there is no option to disposal the CO_2 captured this can be vented to the atmosphere as last option.

The captured CO_2 can be used for biofuels production by micro-algae. Algae-based plant can fast-convert the CO_2 removed from the synthesis gas into algae biomass. It is also possible by means of catalytic synthesis produce methanol from CO_2, being necessary to have hydrogen available to use, which can be obtained by electrolysis of water (electricity consumption).

The “Selection and design of an efficient CO_2 compression technology is dependent on the applied carbon separation method” (LUDTKE, 2004 apud WITKOWSKI; MAJKUT, 2012 p. 2), which determines the thermodynamic state of the inlet CO_2. Reciprocate inline compressor train (single shaft) with intercooler stages, single-shaft radial centrifugal compressors or integrally-geared centrifugal compressor (multiple shafts) with or without intercooler system (large energy consumption than inlet train) and advanced supersonic compressor (shockwave) are used to compress CO_2, depending on inlet and outlet conditions (subcritical or supercritical conditions) and volumetric flows (USHER, 2011; WITKOWSKI; MAJKUT, 2012). The acid gas from amine-based co-capture of CO_2 and H_2S system has a significant moisture content making the intercooler/knock out stages a important step to drying the gas avoiding the formation of an condensed phase and corrosions in the compressor and pipeline AUSTRALIAN NATIONAL LOW EMISSIONS COAL RESEARCH & DEVELOPMENT, 2012; DAVE et al. 2010; KOTHANDARAMAN; 2010)

4.1.11 Synthesis gas compression (conditioning)

Low-pressure synthesis gas can be compressed by multi-stage reciprocate inline compressor train with intercooler stages or by integrally-geared high-efficiency multi-stage centrifugal compressor (multiple shafts) with intercooler system, the type and the number of stages depending on inlet/outlet conditions (pressure and temperature), gas temperature limits and mass flow rate requirements.

Synthesis gas leave the amine-based co-capture of CO_2 and H_2S system at low-temperature and pressure (atmospheric gasification process type) must be compressed to the pressure required by the downstream process. The compress-conditioning process of the synthesis gas from amine-based co-capture system with significant moisture content (saturation condition) make necessary the knock out stages to remove the condensed phase for acceptable performance of gas compressors.

4.1.12 Internal combustion engine

BIG-ICE/CC route are based on the well-known reciprocating engine technology (SANTOIANNI, 2015). In the thermochemical-biorefinery scenarios for large electricity generation (large-power thermochemical-biorefinery) applying the gasification of biomass with air and steam agents in an atmospheric CFB directly-heated gasifier is necessary diverse engines operate in parallel mode, the world's largest engine can produce a maximum electrical energy outputs of about 18.76 MWh (60 Hz and 514 rpm), at which has an efficiency of 48.6% at the generator terminals (WIDESKOG, 2011)

The conditioned low-medium LHV synthesis gas and its potential use for electricity generation in a SG-ICE with turbo charging system depend on the synthesis gas conditions and engine operational parameters.

Wärtsilä world's largest dual-fuel (or "tri-fuel") engine 18V50 are selected to run on conditioned synthesis gas working according to lean-burn process in four-stroke Otto-cycle SI gas engine principles in CC mode employing a HRSG system to recovery and utilize the heat energy in the exhaust-gas to provide district industrial process steam and steam to the ST system (Rankine-cycle cogeneration system) for more electricity generation (NEIL, 2003; SANTOIANNI, 2015; WIDESKOG, 2011). "In a modern gas engine, lean-burn technology is a necessity in achieving low emission levels without external exhaust-gas after-treatment" (WIDESKOG, 2011 p. 16)

The ICEs in the market are developed for use natural gas or an equivalent gas with high heating value (about 28.0 MJ/Nm^3), the gas quality requirement by the ICEs are one of the major obstacles to the use of synthesis gas for large-scale electricity generation by ICEs large-power plants. The synthesis gas produced by gasification of biomass with air and steam agents in an atmospheric CFB have a low heating value and in some scenarios after cleaning and conditioned a medium heating value, not being suitable for efficient use in ICEs. The cleaning and condition process in the BIG-ICE/CC scenarios are the most important processes to increase the energetic density and make feasible the use of synthesis gas in adapted SG-ICEs.

"The required fuel-gas feed pressure depends on the expected minimum lower heating value (LHV) of the fuel-gas, as well as the pressure losses in the feed system to the engine. The LHV of the fuel-gas has to be above 28.0 MJ/m^3 at 0°C and 101.3 kPa" (WÄRTSILÄ, 2012 p. 54).

Raw synthesis gas produced (after the directly-heated gasifier) in the biomass gasification with air and steam agents in an atmospheric CFB directly-heated gasifier has a LHV around of 5.0 MJ/m^3 up to 10.0 MJ/m^3 (without conditioning steps), being required raise your energy density for efficient use in SG-ICEs or porpoises and make changes in the operation parameters and maybe in structure of the engine.

As an option to achieve the energy density requirements a compress-conditioning process can be implemented to achieve the energy density in the piston-cylinder, this process consume electrical energy (net-electricity potential is reduced) reducing the power plant net-electrical efficiency.

A large consumption of energy in the gas conditioning step may make the thermochemical-biorefinery scenario unfeasible forward the traditional high-pressure CHP/CEST technologies, it is still (2013) not possible evaluate the synthesis gas use (requirements) in detail due to the lack of data for this (under development technologies). A way to reduce the electrical energy consumption and achieve the energy density requirements is remove the CO_2 (non-combustible gas) from the raw synthesis gas (reducing the mass flow rate), taking advantage of the potential environmental benefits of this process.

In the compress-conditioning process according to section 6.1.10 (Synthesis gas compression (conditioning)), raw synthesis gas is compressed until reaching the energetic density requirement (in the injection system) after remove part of the on-combustible gas by using amine-based co-capture of CO_2 and H_2S. Intake combustion air is compressed by high-efficiency turbocharger increasing the energy density per cylinder-unit volume (Petchers, 2003; Petrov, 2006)

The combustion air is taken by air fans from the engine room an intake through a air filter into the turbocharger (charged aspiration), air filter is used to remove/reduce contamination and particulate matter avoiding damages by debris in the turbocharger and piston chamber (NEIL, 2003; WÄRTSILÄ, 2012). The air-fuel ratio is adjusted to lean-burn process using a large mass of air more than are needed for complete stoichiometric combustion condition (air in excess), for the Wärtsilä 18V50SG the operation air-fuel ratio window is from 2.0 at 2.3 for natural gas fueled-engine (WÄRTSILÄ, 2012).

The conditioned synthesis gas and the air (oxidant) are mixed in a pre-chamber and injected into the top of a cylinder and compressed by the piston, during the compression stroke in the SG engines the combustible mixture cannot reach the auto ignition state (pressure and temperature dependence), the ignition of the lean air-syngas mixture is initiated with a spark plug located in the pre-chamber after the compression stroke, “the expansion of hot gases pushes a piston within a cylinder, converting the linear movement of the piston into the rotating movement of a crankshaft to generate power” (WIDESKOG, 2011 p. 7).

The compression stroke is dependent on the constructive dimensions of the combustion chamber (volumetric space) and the volumetric compression ratio for a given engine is almost always constant in SG-ICEs, for spark-ignited engines volumetric compression ratio is fixed by antiknock quality of the synthesis gas and can vary from 6.0 bar to 12.0 bar (PETROV, 2006; WÄRTSILÄ, 2012, 2013)

The optimum energy density synthesis gas conditioned and the injection strategy results in a high-peak in-cylinder pressure before the ignition and high-peak in-cylinder temperature, this parameter are extremely important therefore, it cannot be achieved the auto-ignition condition of the air-syngas mixture. In-cylinder the peak pressure and peak temperature in the combustion process cannot be overcomes the ICE limits remaining within into the predetermined operational and structural limits.

The gas admission valves control feed the correct amount of gas to each cylinder and the pressure sensor determine the rate of heat release, the magnitude and location of peak pressures and the knock severity used to control the cylinder specific ignition timing and gas admission (WIDESKOG, 2011).

The multiples single-fueled ICEs uses high-efficiency single pipes exhaust (SPEX) turbo charging system (turbine and compressor) designed streamlined with engine exhaust-gas side (expansion) and air-side (compression) to intensify the power output per unit cylinder volume and unit engine mass, in-line engines have one turbocharger and V-engines have one turbocharger per cylinder bank (NEIL, 2003;

PETROV, 2006; SANTOIANNI, 2015; WÄRTSILÄ, 2013). Fresh-water is injected into the turbocharger during operation to cleaning of the turbine and the compressor. Part of the charge air is conducted directly into the exhaust-gas manifold (without passing through the engine), which increases the speed of the turbocharger (SANTOIANNI, 2015).

SG-ICEs exhaust-gas at lower-temperature was ducted to the low-pressure HRSG designed to heat recovery and low-pressure steam generation to supply the thermal demand of the thermochemical-biorefinery and the subcritical ST system to ranging up the electricity generation (NEIL, 2003; WIDESKOG, 2011).

The engine has four separate advanced cooling water circuits integrated lubricating oil and cooling water channels, heat is absorbed with high-temperature (HT) cooling water circulates through cylinder jackets, cylinder heads, while low-temperature (LT) cooling water circulates through the charge air cooler and the lubricating oil cooler, which is built on the engine (SANTOIANNI, 2015; WIDESKOG, 2011). The hot water can be cooled in a single circuit radiator unit without heat recovery system or each circuit can be individually connected to an external cooling system to heat recovery (NEIL, 2003; PETROV, 2006; WIDESKOG, 2011).

Hot water from the cooling water circuit can be individually connected to an external cooling system to heat recovery by preheat the cooled-water and maybe the make-up raw water before the deaerator unit in the specific HRSG systems with CEST, increasing the CC thermal efficiency (NEIL, 2003; PETROV, 2006; WÄRTSILÄ, 2012).

The compressed-air after the turbo charging system (air-side) normally is cooled in the charge air cooler by the standard 2-stage cooling system, consisting of HT and LT water stage (WIDESKOG, 2011). An external cooling system to cooling this charged air at high-temperature and high-heat content can be used to heat recovery and to significant steam generation (process steam), helping to supply the steam demand of the thermochemical-biorefinery (NEIL, 2003; WÄRTSILÄ, 2012, 2013).

Some equipment can be built on the engine, and the rest can be delivered separately or grouped in modules as engine auxiliary systems. Depending on the engine type and application, lubricating oil pump, HT and LT cooling water pumps, fuel pump, oil filters and coolers, pre-lubricating oil pump and thermostatic valves can be built on the engine (SANTOIANNI, 2015; WÄRTSILÄ, 2012, 2013).

The lubricating oil system has an internal complex system composed by pumps, filters, valves and others, and external system composed by separator system with pumps, heat exchangers and separators, and by oil tank system with sludge tank, renovating and renovated tanks, and new oil tank. The make-up of new and renovated lubricant oil and the losses can be determined by technical data in function of the power output (SANTOIANNI, 2015; WÄRTSILÄ, 2012, 2013).

4.1.13 Advanced gas turbines

In this research Master's degree, thermochemical-biorefinery scenarios for electricity generation (as large-power biomass-based plant) by applying biomass gasification considerers the Brayton-cycle according to a modified and estimated (developing technologies) ALSTOM advanced-class GT24 gas turbine and a GE H-class 7HA gas turbines, the world's largest and most efficiently gas turbines (GT), as a operational parameters basis for the Aspen Plus®v8.4 process model simulation of the GT.

Modified to run using conditioned synthesis gas, works according to sequential combustion principles in CC mode employing a HRSG system to recovery and reuse the heat energy contained in the exhaust-gas (subcritical Rankine-cycle cogeneration system) increasing the generation of electricity (ALSTOM, 2014; GENERAL ELECTRIC COMPANY, 2015; GÜTH; HELLAT; FLOHR; 2007).

Humidified Gas Turbine (HGT) cycles are a group of advanced GT cycles that have been studied as an alternative to the traditional CC and reciprocating engines for electrical energy generation, based on the injection of water or steam increases the mass flow rate through the GT reducing the work required in the compression stages (BARTLETT; WESTERMARK, 2005; BOYCE, 20012; JONSSON; YAN, 2005). "An additional advantage of humidifying the GT working fluid is a reduced formation of NO_x in the combustion process" (JONSSON; YAN, 2005 p. 1015).

HGT cycles can be classified as GT cycles that utilize water-air mixtures as the working fluid through the expander and evaporative-class gas turbine (EvGT) cycles can be defined as cycles which evaporate water directly into the working fluid (BARTLETT; WESTERMARK, 2005; JONSSON; YAN, 2005). The main advantages identified with HGT cycles are electrical efficiencies (BARTLETT; WESTERMARK, 2005).

The evaporative-class of GT be divided in two concepts: part-flow EvGT cycle (PEvGT) whereby only a fraction of the compressed air is used in the high-pressure counter-current double-stage humidification packaged-tower (non-intercooled turbine); and full-flow EvGT cycle (FEvGT) whereby all of the compressed air is used in the counter-current multistage humidification column (BARTLETT; WESTERMARK, 2005; BOYCE, 20012; JONSSON; YAN, 2005).

ALSTOM advanced-class GT24 gas turbine is originally designed for operation on natural gas at frequency of 60.0 Hz with net electrical efficiency of about 40.0% in simple cycle, gross heat rate of 9000 kJ/kWh and exhaust-gas temperature of 608.0ºC (ALSTOM, 2014). An efficient 22-stage compressor can feed combustion air into the first annular EV combustor at a pressure ratio (PR) of 30:1.

GE H-class 7HA gas turbines is designed for operation on natural gas at frequency of 60.0 Hz with net electrical efficiency of about 41.4% in simple cycle, gross heat rate of 8694 kJ/kWh and exhaust-gas temperature of 619.0ºC (GENERAL ELECTRIC COMPANY, 2015). An efficient 22-stage compressor can feed combustion air into the first can-annular combustor at a PR of 23:1.

Combustion system on a well-proven ALSTOM combustion concept with 40.0% less NO_x emissions over a wide load range using the EV (EnVironmental) burner in the first combustion stage into the annular combustion chamber arrangement followed by the SEV (Sequential EnVironmental) burner in the second combustion stage (reheat principle for GTs) into the annular combustion chamber arrangement (ALSTOM, 2014; GÜTH; HELLAT; FLOHR; 2007).

The main reasons to choose an sequential combustion (dual-chamber) EvGT was due to thermochemical-biorefinery scenario thermal energy (process steam) requirements, the sequential combustion process offers high GT exhaust conditions allowing achieve the necessary steam generation optimally adjusting the recuperator heat exchanger temperature output conditions (GÜTH; HELLAT; FLOHR; 2007).

In the advanced-class GT24 gas turbine first combustor is an annular combustion chamber with 30 EV burners and the second combustor consists of 24 SEV diffuser-burner assemblies arranged around the circumference, 24 air-cooled fuel nozzles inject the fuel and distribute it in such a way that a perfect fuel/air mixture is formed prior to combustion (ALSTOM, 2014).

Biomass gasification by CFB directly-heated gasifiers using air and steam as gasification agents produce low or medium heating value (LHV) crude synthesis gas (less than 10.0 MJ/kg), because the large amounts of N_2 and CO_2 content in the crude synthesis gas. The increased mass-flow of exhaust-gas can cause mismatch between the flows through the compressor and turbine sections, counteract this increased mass-flow there are various forms of adjustment (e.g.: compressed air bleed, integration between EvGT and ASU, water injection, part of the humid air is expanded in a expander or separate turbine) and various technologies in developments to circumvent this unbalance decrease the need for extensive GT design changes (BOYCE, 20012; JONSSON; YAN, 2005).

4.1.14 Heat recovery steam generator (HRSG)

The primary purpose of a HRSG is to extract heat energy that would be wasted by the SG-ICEs exhaust-gas, or some other process of industrial application of combustion to produce steam. Due to the lower exhaust-gas temperatures from SG-ICEs, HRSG systems designed (bottom cycle) for BIG-ICE/CC scenarios are much simpler in design, creating steam at one or two pressure levels only with lower mass flow rate than HRSG systems for BIG-GT/CC scenarios. The SG-ICEs exhaust-gas temperature is around 320.0ºC to 480.0ºC (PETROV, 2006; SANTOIANNI, 2015; WÄRTSILÄ, 2012).

Horizontal-gas-flow HRSGs or vertical-gas-flow HRSGs (heavy fuel oil) drum type can be customized as single, dual or triple pressure with or without reheat, different HRSG configurations are possible depending on heat characteristics to be recovered with advantages and disadvantages (ALSTOM, 2014; BARTLETT; WESTERMARK, 2005; BOYCE, 20012).

The HRSG is an integrated cluster of economizers, evaporators, and super-heaters and reheaters bundle at a given pressure level, when the exhaust-gas pass over HRSG heating elements, water inside tubes absorb (recover) energy from hot gases, and change the phase into steam, which is used for driving STs and supply the process thermal energy (ALSTOM, 2014; MANSOURI et al., 2012) A HRSG system may contain up to three pressure circuit-levels (multi-pressure HRSG system), named low-pressure (LP), intermediate-pressure (IP) and high-pressure (HP) (ALSTOM, 2014; BARTLETT; WESTERMARK, 2005; BOYCE, 20012; MANSOURI et al., 2012)

Deaerated and preheated water from deaerator unit is pumped at pressure level required by the specific steam-circuit to economizer sections to be heated at bellow saturation conditions and send to evaporator section where the evaporation of saturated liquid-water until the saturated vapor-water condition occur (phase change). After separating the liquid water and steam in drum, water goes through evaporator down comers while steam enters superheater sections for heating the saturated vapor-water to a temperature much higher than that of the water saturation (BOYCE, 20012; MANSOURI et al., 2012). In some cases once-through HRSG can be employed eliminates the need for steam drums, and superheats sections, serpentine circuits encompassing the economizer, evaporator and superheater sections with advantages and disadvantages (BARTLETT; WESTERMARK, 2005; NEIL, 2003).

Steam reheat section can be considered in the BIG-ICE/CC integrated scenarios when the steam availability is greater than the amount demanded by the thermochemical-biorefinery and in the BIG-ICE/CC standalone scenario to improve the net-electricity generation without hindrance or limits by the thermal energy demand (BIG-ICE/CC produce more thermal energy than consume), apply reheat section decrease the steam generation and increase the net-electricity generation and the thermal efficiency (BOYCE, 20012).

A efficient approach would attempt to utilize the most hot water generated in the ICEs cooling water circuit can be individually connected to an external cooling system to heat recovery and reduce the low-pressure steam consumption in the deaerator by preheat the low-temperature condensed water flow after the condenser pump in the CEST systems (NEIL, 2003; PETROV, 2006). This is a simple heat-exchange solution and can avoid the traditional use/reduce of the energy content (heat potential) in the flue-gas, leaving more energy to the biomass drying process (high energy consumption) or improving the steam generation in the HRSG system and the electrical energy potential of the ST.

Supplementary fired exhaust-gas steam generator (duct burner), using external fuel source or part of the synthesis gas produced, can be applied when the exhaust-gas was high oxygen content (excess) after the combustion process in the SG-ICEs (lean-burn SG-ICE was a large amount of oxygen in the exhaust-gas) sufficiently to provide a efficiently supplementary combustion to track the energetic demand producing more steam by raising the inlet HRSG temperature (BOYCE, 20012; LARSON et al., 2006a, 2006b; NEIL, 2003). The exhaust-gas temperature can be elevated to 980ºC without radiant section increasing the steam cycle efficiency, adding a radiant heat section the exhaust-gas temperature ranging up to nearly 1600ºC (depending on the fuel) (BOYCE, 20012; NEIL, 2003).

Steam can be generated at 540ºC (limit by material quality cost) to ST use increasing the electrical energy potential of the system and generate process steam to supply the thermochemical-biorefinery in substitution of the traditional CHP/EBPST system (NEIL, 2003).

Flue-gas wet cleaning system can be employed to reduce the pollutant emissions and condensing the water vapor content in the flue-gas, send to wastewater treatment plant with possibility to water recovery and reuse. To improve the carbon sequester and a net zero carbon emissions polices a post-combustion CCS can be employed coupled with the wet cleaning system to remove the CO_2 and pollutants produced in the SG-ICE synthesis gas combustion reactions (AUSTRALIAN NATIONAL LOW EMISSIONS COAL RESEARCH & DEVELOPMENT, 2012; DAVE et al. 2010).

4.1.15 Steam turbine applied in combined-cycles

Thermochemical-biorefinery scenarios can apply diverse arrangements of steam turbine trains depending on the scenario and energy integration form, multiple STs and different subcritical or supercritical types can compound the train (HASSUANI; LEAL; MACEDO, 2005, PETROV, 2006). The main objectives of the HRSG system in this study is recovery heat for process steam generation and supply the thermal energy requirements by the thermochemical-biorefinery scenario.

Condensing-extraction ST expands the high-pressure and intermediate-pressure steam generated at exhaust steam pressure below the atmospheric pressure (vacuum pressure), achieving maximum possible pressure drop across the blades providing the maximum electrical energy output. One or more portions of the steam may be extracted from the ST for processes use (thermal energy) at pressures between the inlet and outlet pressures.

Extraction back-pressure ST expands the high-pressure and intermediate-pressure steam generated at exhaust steam pressure above the atmospheric pressure. One or more portions of the steam may be extracted from the ST processes use (thermal energy) at pressures between the inlet and outlet pressures. The output steam is exhausted at a relatively low-pressure suitable for onsite heat requirements.

Last stages of the steam turbines are able to operate with wet steam, where the fraction of condensed steam has been kept at maximum 10% (minimum 0.9 dryness factor) (PETROV, 2006).

4.1.16 Water-gas-shift (WGS) and reverse Water-gas-shift (RWGS) reaction

Water-gas-shift (WGS) reaction is a reversible exothermic chemical reaction type, CO is converted be steam to H_2 and CO_2 or CO_2 is converted by H_2 to CO and H_2O, according to Chemical equation c.8 (SMIRNIOTIS; GUNUGUNURI, 2015).

$$CO + H_2O \leftrightarrows \mathrm{CO_2} + \mathrm{H_2} \qquad \Delta H^0_{298K} = -\frac{41.1kJ}{mol} \qquad (c.8)$$

The WGS reaction is carried out as direct direction reaction mode to increase the H_2 concentration (content) reducing the CO concentration in the synthesis gas based on the thermochemical plant concepts, being largely used to control e adjust the H_2/CO ratio of the gas (SMIRNIOTIS; GUNUGUNURI, 2015). Depending on the reaction conditions, the equilibrium can be displaced in the reverse direction reaction mode (RWGS) to increase the CO concentration reducing the H_2 concentration in the synthesis gas based on the thermochemical plant concepts (SMIRNIOTIS; GUNUGUNURI, 2015).

WGS reaction is a moderately exothermic reversible reaction that is thermodynamically favored at low temperatures and kinetically favored at high temperatures (thermodynamically unfavorable at elevated temperatures). According to Smirniotis and Gunugunuri (2015) there are three diferrrent ways to conduct WGS reaction with the respect of the reactors.

a) WGS reaction in traditional catalytic reactor: Homogeneous catalytic WGS reaction; Heterogeneous catalytic WGS reaction ;
b) WGS reaction in membrane catalytic reactor;
c) Photo-catalytic WGS reaction using visible or ultra violet (UV) light to irradiate the catalyst.

WGS catalyst can be classified in three categories: HT WGS catalysts; LT WGS catalyst; and Co-Mo sulphided catalysts (SMIRNIOTIS; GUNUGUNURI, 2015.

In order to overcome this thermodynamic limitation the reaction is industrially performed in several stages (adiabatic stages) with different catalysts to optimize the greater CO equilibrium conversion, while maintaining high reaction rates. Normally conducted in multiple adiabatic stages with inter-stage cooling to obtain higher conversions overall, classified according Smirniotis and Gunugunuri (2015) the operating conditions as:

a) High-temperature shift (HTS): operation temperatures range of 310°C to 500°C, and exiting at between 400°C and 500°C, applying iron oxide-based catalysts (with an effluent CO concentration of approximately 5%);
b) Low-temperature shift (LTS): operation temperature range of 150°C to 300°C exiting the reactor at up to 280°C, applying copper-zinc oxide-based catalysts.

WGS reactors utilizes normally two commercial catalysts, a Fe_3O_4/Cr_2O_3 catalyst for the High-temperature (HT) catalyst WGS reactor stage, and a $CuO/ZnO/Al_2O_3$ catalyst for the low-temperature (LT) catalyst WGS reactor stage. Modern water-gas shift reaction occurs over two adiabatic stages, with intercooling stages is used in sequential combined arrangement to increase the overall (SMIRNIOTIS; GUNUGUNURI, 2015).

HT WGS catalysts (Fe-Cr based) are stable to sulfur poisoning at an tolerance limit (large amount of sulphur deactivate), several inorganic salts, boron, oils, phosphorus content compounds, sulfur compounds with concentrations more than 50 ppm are poison. LT-WGS catalysts (Cu based) cannot tolerate low levels of sulfur (RASE, 1977 apud SMIRNIOTIS; GUNUGUNURI, 2015). Although, Co-Mo sulphided catalysts need an minimum of sulphur concentration in the gas since they are only active in sulphided form (SMIRNIOTIS; GUNUGUNURI, 2015).

Before the HT-WGS reactor, if the stream are in low-temperature levels, can be employed an guarde bed adsorber with ZnO catalyst adsorb sulfur poisoning compounds (e.g.: H_2S, COS, and SO_x) and chlorine poisoning compounds (e.g.: HCl and Cl_2), an additional layer of CuO catalyst guaranteeing lower sulphur and chlorines poisoning in the HT-WGS catalyst layer-bed (working as a non-regenerative guard bed adsorber).

The pressure varies greatly between 10 and 60 bar an typical steam-to-carbon ratio between 2.5 and 5 is used depending on temperature e catalyst activity to both enhance equilibrium conversion.

4.1.17 Regenerative guard bed adsorbers

TSA adsorbers are used as dual (most common) or three bed system, when the concentration of the adsorber effluent reaches nearly that of the feed stream, the adsorber vessel in the adsorption time-cycle pass to the regeneration time-cycle and the regenerated vessel pass to the adsorption time-cycle (RAMASWAMY; HUANG; RAMARAO, 2013).

The adsorption takes place at low-temperatures and high-pressures and the regeneration takes place either by higher temperature (TSA) or lower pressure (PSA) (HOFBAUER; RAUCH; RIPFEL-NITSCHE, 2007). Temperature or thermal swing adsorption (TSA) is a simple adsorption/desorption cycle, when "the adsorbent is regenerated by heating the bed, usually by a hot-gas stream, to a temperature at which the adsorbate is desorbed and removed from the bed with the gas stream" (RAMASWAMY; HUANG; RAMARAO, 2013,).

Long life Metallic oxides-based sorbents are used to remove a wide range of poison-contaminants by selective chemical reactions (flexible system) (HOFBAUER; RAUCH; RIPFEL-NITSCHE, 2007). Sulfur compounds (e.g.: H_2S, COS, and SO_x) and chlorine compounds (e.g.: HCl and Cl_2) are not complete removed by the low-temperature synthesis gas wet cleaning system and by co-capture of CO_2 and H_2S amine-based aqueous absorbing-solution.

ZnO catalyst layer and CuO catalyst layer removal of H_2S, light mercaptans, sulfides, disulfides, thiophenes and other organic sulfur compounds, and carbonyl sulfide (COS), and mercury, an advantageous use of the adsorbent front the absorbent systems (HOFBAUER; RAUCH; RIPFEL-NITSCHE, 2007). According to Hofbauer, Rauch And Ripfel-Nitsche (2007) the main reactions considered in the interaction between the synthesis gas and the ZnO catalyst layer and CuO catalyst layer are represent by the Chemical equations c.9, c.10, c.11 and c.12.

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O \quad (c.9)$$

$$ZnO + H_2S \rightarrow ZnS + H_2O \quad (c.10)$$

$$CuO + 2HCl \rightarrow CuCl_2 + H_2O \quad (c.11)$$

$$CuO + H_2S \rightarrow CuS + H_2O \quad (c.12)$$

Sulphidation reaction should be thermodynamically favorable while the reduction reaction of the metal oxide should not be favored or at least very slow (HOFBAUER; RAUCH; RIPFEL-NITSCHE, 2007). Side-reaction as competitive reaction with low activity occurs according to Chemical equation c.13.

$$ZnO + CO_2 \rightarrow ZnCO_3 \qquad (c.13)$$

The side reaction (Chemical equation c.13) is dependent on the concentration of CO_2 in the synthesis gas competing for the active sites on the ZnO catalyst layer (HOFBAUER; RAUCH; RIPFEL-NITSCHE, 2007).

Metal sulfides formed in the ZnO catalyst layer and CuO catalyst layer are regenerated to oxides and byproducts contain gaseous sulfur and chlorine, rebuilding the metal oxide by using oxygen (HOFBAUER; RAUCH; RIPFEL-NITSCHE, 2007; RAMASWAMY; HUANG; RAMARAO, 2013). According to Hofbauer, Rauch And Ripfel-Nitsche (2007) Chemical equations c.15, c.16 and c.17 by partial oxidation, to Chemical equations c.18 and c.19 by total oxidation (in presence of oxygen), and by catalytic reaction in presence of water according to chemical equations c.20 and c.21.

$$H_2S + 3O_2 \leftrightarrows 2SO_2 + H_2O \qquad \text{equilibrium} \qquad (c.14)$$

$$CuCl_2 + 0.5O_2 \rightarrow CuO + Cl_2 \qquad (c.15)$$
$$ZnS + 0.5O_2 \rightarrow ZnO + S_2 \qquad (c.16)$$
$$CuS + 0.5O_2 \rightarrow CuO + S_2 \qquad (c.17)$$
$$ZnS + 1.5O_2 \rightarrow ZnO + SO_2 \qquad (c.18)$$
$$CuS + 1.5O_2 \rightarrow CuO + SO_2 \qquad (c.19)$$

$$ZnS + H_2O \rightarrow ZnO + H_2S \qquad (c.20)$$
$$CuS + H_2O \rightarrow CuO + H_2S \qquad (c.21)$$

According to Hofbauer, Rauch And Ripfel-Nitsche (2007) side-reactions forming sulfates occurs in lower extension according to Chemical equations c.22 and c.23.

$$ZnS + 2O_2 \rightarrow ZnSO_4 \qquad (c.22)$$
$$CuS + 2O_2 \rightarrow CuSO_4 \qquad (c.23)$$

Sulfates form is not reactive composts with respect to the desulphurization reactions in the conditions during the regenerative-cycle and thus there is a loss of active material. SO_2 is formed and can be used as regeneration gas (unfeasible), as guard bed the emission can be acceptable (low-concentration) (HOFBAUER; RAUCH; RIPFEL-NITSCHE, 2007). According to Hofbauer, Rauch And Ripfel-Nitsche (2007)

ZnO catalyst layer and CuO catalyst layer can be regenerated in presence of SO_2 by reaction between metal sulfide and SO_2 to form oxides and/or elemental sulfur according to Chemical equations c.24, c.25 and c.26.

$$ZnS_{(s)} + 0.5SO_{2\,(g)} \rightarrow ZnO_{(s)} + 0.75S_{2\,(g)} \qquad (c.24)$$

$$CuS_{(s)} + 0.5SO_{2\,(g)} \rightarrow CuO_{(s)} + 0.75S_{2\,(g)} \qquad (c.25)$$

$$2H_2S + SO_2 \rightarrow 1.5S_2 + 2H_2O \qquad (c.26)$$

4.1.18 Pressure Swing Adsorption (PSA)

Pressure Swing Adsorption (PSA) is based on a physical binding of gas molecules to adsorbent materials (LINDE, 2012?). Highly VOCs with low-polarity and molecular low-weight (e.g.: H_2), are practically non-adsorbable as opposed to molecules with polarity (e.g.: N_2, CO, CO_2, H_2O, hydrocarbons) can be selectively adsorbed on the surface of the adsorbent (the strength of adsorption increase with increasing molecular weight) from a hydrogen-containing gas-stream and high-purity hydrogen is recovered (LINDE, 2012?; LIU; SONG; SUBRAMANI, 2010).

H2 can be separated (recovered) using basically three forms: cryogenic to recovery multi-products (e.g.: H_2, CO, CO_2, N_2) by low-temperature liquefaction (phase changes); adsorption to recovery selectively one or two products (e.g.: H_2, CO) by solid molecular sieves (physical binding); and membrane to recovery selectively two products (e.g.: H_2, CO) by membrane materials (diffusivity) (LIU; SONG; SUBRAMANI, 2010).

The PSA process works at basically constant temperature and uses the effect of alternating pressure and partial pressure to perform adsorption and desorption (LINDE, 2012?). Adsorption is carried out at high-pressure (and hence respective high partial pressure) being determined by the pressure of the feed gas, typically in the range of 10 bar to 40 bar (partial-pressure), at low-temperatures, typically in the range of 5 ºC to 60ºC (isothermal) (LINDE, 2012?; LIU; SONG; SUBRAMANI, 2010).

The pressure swing adsorption process has four basic process steps: adsorption; depressurization; regeneration; and repressurization. The regeneration phase consists of basically five consecutive steps: pressure equalization; provide purge; dump; purging; and repressurization (LINDE, 2012?; LIU; SONG; SUBRAMANI, 2010). The steps are combined to maximize the recovery rate of the PSA system ensuring a desired purity.

PSA process recovery a primary gaseous component from a feed gas at purity from $99.5\%_v$ to $99.999\%_v$ exits the adsorber vessel (LINDE, 2012?; LIU; SONG;

SUBRAMANI, 2010). After a defined time, the adsorption phase of this vessel stops and regeneration starts. Different solid adsorbents (e.g.: carbon molecular sieves, Zeolites, activated carbon, alumina, silica gel) can be used as bed materials in the vessels according to characteristics of the feed-gad, arranged in specific-layers to absorb an certain quantity of determined gaseous compounds during the adsorption time-cycle, adsorbents can adsorb grater quantity of certain gaseous component than others (LIU; SONG; SUBRAMANI, 2010).

To provide continuous hydrogen supply, minimum 4 adsorber vessels are required. Short cycles within the range of minutes are achieved, since heating or cooling is not required (LINDE, 2012?). Many configurations are possible (e.g.: 6, 8 10, 12 parallel adsorber vessels, or more), Poly-bed systems, and their application basically dependent on the characteristics of the feed gas, pressure and the desired purity for the hydrogen stream.

PSA processes can be integrated with adsorbent membrane separators to increase the recovery of hydrogen and/or reduce the size of the PSA systems.

4.1.19 Low-pressure methanol catalytic-synthesis

Methanol is currently mainly produced from fossil resources (e.g.: petroleum, natural gas, and coal) using synthesis gas (i.e.: H_2, CO, CO_2, and CH_4) as feed stock (LEE; SPEIGHT; LOYALKA, 2014).

CO and CO_2 reacts whit H_2 in many different ways. According to Beratu, et al. (2014) the reactions that are involved in the production of methanol from various synthesis gases are as Chemical equation c.27 (CO hydrogenation) as Chemical equation c.28 (CO_2 hydrogenation):

$$CO + 2H_2 \leftrightarrows \mathrm{CH_3OH} \qquad \Delta H^0_{(298K,50bar)} = -90.7\,\frac{kJ}{mol} \qquad (c.27)$$

$$CO_2 + 3H_2 \leftrightarrows \mathrm{CH_3OH} + \mathrm{H_2O} \qquad \Delta H^0_{(298K,50bar)} = -40.9\,\frac{kJ}{mol} \qquad (c.28)$$

These reactions are highly exothermic and the heat of reaction must instantaneously be removed from the catalyst bed (BERTAU, et al. 2014). The synthesis of methanol from carbon monoxide and carbon dioxide are tied through the WGS reaction:

$$CO + H_2O \leftrightarrows \mathrm{CO_2} + \mathrm{H_2} \qquad \Delta H^0_{(298K,50bar)} = -42\,\frac{kJ}{mol}$$

The production of methanol is strongly influenced by thermodynamics. Methanol formation is therefore favored by increasing pressure and decreasing temperature, with the maximum conversion being determined by the equilibrium composition (BERTAU, et al. 2014; LEE; SPEIGHT; LOYALKA, 2014). However, the kinetic rate at low-temperature is very slow over most catalysts and relatively high-temperature operation becomes almost mandatory (BERTAU, et al. 2014). Higher-pressure operation, on the other hand, may represent higher capital investment, grater energy demands, and more severe operational conditions (BERTAU, et al. 2014; LEE; SPEIGHT; LOYALKA, 2014).

Owing to the unfavorable equilibrium nature, the once-thought conversion (per-pass conversions) of the synthesis reactions from synthesis gas is significantly low (BERTAU, et al. 2014). Conversions range from only of 15% to 25% to as high as 40% or 50 % (with advanced catalysts). Thus, making the recycle duty of the reactor higher, all commercial processes recycle the unconverted synthesis gas back to the methanol synthesis for enhancement of overall conversion (BERTAU, et al. 2014; LEE; SPEIGHT; LOYALKA, 2014).

Typical operating conditions for the methanol synthesis reaction in high-pressure processed are typically at 350ºC and 200 bar, and for low-pressure process are typically at 220ºC to 270ºC and 50 bar to 100 bar (BERTAU, et al. 2014; LEE; SPEIGHT; LOYALKA, 2014). If the pressure of the reaction is increased, the conversion of CO also increases. However, the increase is not very substantial above a pressure of 80 bar (BERTAU, et al. 2014).

Low-pressure methanol catalytic-synthesis conditions are close to critical point of pure methanol, that is, about 240ºC and 80 bar (BERTAU, et al. 2014; LEE; SPEIGHT; LOYALKA, 2014). These conditions can theoretically result in per-pass methanol yields in the range of 55% to 75% (LEE; SPEIGHT; LOYALKA, 2014).

Under ideal conditions, methanol requires the stoichiometric number (S_1) of the synthesis gas equal to 2.0 (Equation 19), which is different from the H_2/CO molar ratio (Equation 20), as described in the section 3.9.16 (Hydrogen to carbon ratios) (BERTAU, et al. 2014). However, a small increment in hydrogen that increases the S_1 to 2.05 and even to 2.08 has been found to improve catalytic performance, leading to more efficient production of methanol (BERTAU, et al. 2014).

The methanol synthesis may be performed in two-phase or three-phase reactors. Two-phase reactors can be categorized (based on the mechanism of the cooling) in: multiple catalyst bed reactors (several sections and the cooling is performed between the sections); single bed reactors (heat is continuously removed through a media such as water). Three-phase processes, methanol is removed from the reactor with the liquid phase through which the heat is also regulated (BERTAU, et al. 2014; LEE; SPEIGHT; LOYALKA, 2014).

Commercial catalyst for is based on the $CuO/ZnO/Al_2O_3$ (BERTAU, et al. 2014). Other types of catalysis are Pd-based catalysts, alkali metal-promoted, MoS_2, Cu-based with Zirconium as support material, an others (BERTAU, et al. 2014; LEE; SPEIGHT; LOYALKA, 2014). For all commercial catalyst available $CuO/ZnO/Al_2O_3$ catalysts for low-temperature methanol catalyst-synthesis, methanol is produced with selectivity (referred to the COx in the feed), typically above 99 % (BERTAU, et al. 2014). The overall catalyst lifetime of an industrial catalyst for the methanol synthesis is found in practice to be at least 4 years (BERTAU, et al. 2014)

Deactivation of methanol synthesis catalyst may be attributed to: chemical poisoning by chlorine compounds (e.g.: HCl), sulfur compounds (e.g.: H_2S, COS, CS_2, thiophenes, and CH_3SCN); sintering, thermal deactivation, or annealing; copper crystallite size growth; carbon and high hydrocarbons deposition (BERTAU, et al. 2014; LEE; SPEIGHT; LOYALKA, 2014).

> The sulphur content in the synthesis gas (or nitrogen circulation) should be less than 0.05 ppmv as H_2S. Sulphur that exceeds $0.8\%_w$ on the catalyst deactivates the catalyst completely. Chlorine in any form, such as Cl_2, HCl, or R-Cl, is a strong poison to the methanol synthesis catalyst. Copper chloride sinters quickly, which reduces active copper surface area of the catalyst. Chlorine should be excluded completely from the system. The chlorine content in the synthesis gas should be at a nondetectable level. Chlorides that are more than 500 ppmw on the catalyst deactivate the catalyst completely (BERTAU, et al. 2014).
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Graaf, Stamhuis and Beenackers (1988) developed a kinetic model considering the three reactions, Chemical equation c.27 (CO hydrogenation), Chemical equation c.28 (CO_2 hydrogenation), and the Chemical equation c.8 (WGS reaction). This model is based on the Langmuir–Hinshelwood-mechanism and the final set of kinetic equations of the elementary steps is:

$$r_{CH_3OH,A3} = \frac{K'_{PS,A3}K_{CO}\left[f_{CO}f_{H_2}^{3/2} - f_{CH_3OH}/(f_{H_2}^{3/2}K_{P_1}^{\circ}\right]}{(1 + K_{CO}f_{CO} + K_{CO_2}f_{CO_2})\left[f_{H_2}^{1/2} + \left(K_{H_2O}/K_{H_2}^{1/2}\right)f_{H_2O}\right]}$$

$$r_{H_2O,B2} = \frac{K'_{PS,B2}K_{CO_2}\left[f_{CO_2}f_{H_2} - f_{H_2O}f_{CO}/(K_{P_2}^{\circ}\right]}{(1 + K_{CO}f_{CO} + K_{CO_2}f_{CO_2})\left[f_{H_2}^{1/2} + \left(K_{H_2O}/K_{H_2}^{1/2}\right)f_{H_2O}\right]}$$

$$r_{CH_3OH,C3} = \frac{K'_{PS,C3}K_{CO_2}\left[f_{CO_2}f_{H_2}^{3/2} - f_{CH_3OH}f_{H_2O}/(f_{H_2}^{3/2}K_{P_3}^{*}\right]}{(1 + K_{CO}f_{CO} + K_{CO_2}f_{CO_2})\left[f_{H_2}^{1/2} + \left(K_{H_2O}/K_{H_2}^{1/2}\right)f_{H_2O}\right]}$$

By this model, a wide range of experimental conditions can predict the methanol process performance with sufficient accuracy (BERTAU, et al. 2014). Parameter estimation can be found in the original publications:

GRAAF, G. H. et al. The chemical equilibria of the methanol reaction and the water-gas shift reaction. *Chemical Engineering Science*, Oxford, New York, v. 41, n. 11, 1986. p. 2883-2890.

GRAAF, G. H.; STAMHUIS, E. J.; BEENACKERS, A. A. C. M. Kinetics of Low-Pressure Methanol Synthesis. *Chemical Engineering Science*, Oxford, New York, v. 43, n. 12, 1998. p. 3185-3195.

4.1.20 Mixed alcohols catalytic-synthesis: Ethanol

Mixed alcohols containing linear-chain alcohols can be produced from synthesis gas, the catalytic conversion of synthesis gas to form an alcohol mixture currently (2015) is developed to occur across a fixed bed catalyst reactor (not commercial technologies) (STUART; EL-HALWAGI, 2012).

The main primary products are methanol, methane, and water, depending on the operational conditions and catalysts. Ethanol, propanol, butanol, and more higher-molecular alcohols are gradually formed by successive methanol homologation reactions (STUART; EL-HALWAGI, 2012). Methanol homologation can improve the ethanol yield and subsequently the higher-molecular alcohols yields, methanol homologation reactions play a key role when it is desired to produce ethanol.

The stoichiometric reaction for mixed alcohols synthesis can be summarized according to Chemical equation c.29 for alcohol formation and Chemical equation c.30 for hydrocarbon formation (DUTTA; PHILLIPS, 2009; STUART; EL-HALWAGI, 2012).

$$n\,CO + 2nH_2 \rightarrow \mathrm{C_nH_{2n+1}OH} + (\mathrm{n}+1)H_2O \qquad (\mathrm{c.29})$$

$$n\,CO + (2n+1)H_2 \rightarrow \mathrm{C_nH_{2n+2}} + \mathrm{n}H_2O \qquad \text{side reactions} \qquad (\mathrm{c.30})$$

$$CO + H_2O \leftrightarrows \mathrm{CO_2} + \mathrm{H_2}$$

From the Chemical equation c.29 linear-chain alcohols (e.g.: methanol, ethanol, propanol, butanol, and other higher-molecular alcohols) are formed, but several side reactions are also possible including oxygenates (methyl acetate, ethyl acetate, acetic acid and acetaldehyde), non-linear alcohols (i.e.: branched-chain alcohols), and from the Chemical equation c.30 higher hydrocarbon gases (e.g.: ethane/ethene, propane/propene, butane/butene and methane) (GERBER; WHITE; STEVENS, 2007).

Chemical equation c.29 for alcohol formation suggests an optimum H_2/CO ratio of 2.0. However, the mixed-alcohols synthesis catalysts are also active as WGS catalysts that generate H_2 from CO and H_2O. As result, the optimal H_2/CO ratio delivered to the reactor is close to 1.0.

The space-time yield of both alcohols and hydrocarbons are increased with an increase in reaction temperature, causing an overall decrease in total alcohol selectivity as temperature increases (GERBER; WHITE; STEVENS, 2007). Alcohol yield decreases with increasing partial pressure of H_2 and increases with greater partial pressures of CO.

From the Chemical equation c.29 e Chemical equation c.30, Dutta and Phillips (2009) proposed a set of stoichiometric reactions to represent the mixed alcohols catalyst-synthesis as being:

WGS	$CO + H_2O \leftrightarrows CO_2 + H_2$
Methanol	$CO + 2H_2 \rightarrow CH_3OH$
Methane	$CH_3OH + 2H_2 \rightarrow CH_4 + H_2O$
Ethanol	$CO + 2H_2 + CH_3OH \rightarrow C_2H_5OH + H_2O$
Ethane	$C_2H_5OH + H_2 \rightarrow C_2H_6 + H_2O$
Propanol	$CO + 2H_2 + C_2H_5OH \rightarrow C_3H_7OH + H_2O$
Propane	$C_3H_7OH + H_2 \rightarrow C_3H_8 + H_2O$
n-Butanol	$CO + 2H_2 + C_3H_7OH \rightarrow C_4H_9OH + H_2O$
Butane	$C_4H_9OH + H_2 \rightarrow C_4H_{10} + H_2O$
Pentanol+	$CO + 2H_2 + C_4H_9OH \rightarrow C_5H_{11}OH + H_2O$
Pentane+	$C_5H_{11}OH + H_2 \rightarrow C_5H_{12} + H_2O$

According to Dutta and Phillips (2009) experiments have been typically conducted using H2/CO molar ratio (Equation 20), Stoichiometric number S2, in the range of 1.0 to 1.2, as described in the section 3.9.16 (Hydrogen to carbon ratios) (DUTTA; PHILLIPS, 2009; STUART; EL-HALWAGI, 2012). Lower H_2/CO molar ratios that would reduce or eliminate the need to adjust the H_2 and CO composition of the product gas from a biomass gasifier (DUTTA; PHILLIPS, 2009; STUART; EL-HALWAGI, 2012).

Dutta and Phillips (2009) consider in their studies the synthesis reactor operating (targets) at temperature of 300 ºC, pressure of 1,000 psia, H_2/CO ratio of 1.2, concentration of sulfur compounds at limit of 50 ppmv, and concentration of CO_2 at 5%$_M$.

The representative catalyst systems that have prospects for industrial applications are the following six general classes: modified methanol catalysts (Cu/Zn and Cu/Mn based); modified molybdenum sulfide catalysts; modified molybdenum oxide catalysts; rhodium-based catalysts; and modified Fischer-Tropsch catalysts (GERBER; WHITE; STEVENS, 2007; STUART; EL-HALWAGI, 2012).

Normally, the alkali-doped oxides (zinc and chromium oxides) and alkali-doped sulfides (molybdenum sulfides) are used as catalysts for the mixed alcohols synthesis STUART; EL-HALWAGI, 2012. Alkali-doped sulfides catalyst type is resistant against sulfur poisoning, so the gas treatment is much simpler reducing the operational and investment costs (STUART; EL-HALWAGI, 2012).

Table 10 shows according to Gerber, White and Stevens (2007 p. 12) the general characteristics and typical operational conditions of different classes of mixed alcohols synthesis catalysts

Table 10 – Miixed alcohols synthesis typical operational conditions

Catalyst class	Promoters	Pressure (bar)	Temperature (ºC)
Modified Methanol (Cu/ZnO)	Alkali	50-150	275-400
Modified Methanol (Cu/ZnO/Mn)	Alkali, Co, Cr_2O_3	100-170	400
Modified Methanol (Cu/Mn)	Ni, Fe, Co	60-120	280-340
Molybdenum Sulfide	Alkali, Co	70-200	250-330
Molybdenum Oxide	Alkali, Co	60-120	230-300
Rhodium	NA	70	300-320
Fischer-Tropsch (Fe-based)	Cu/Zn, Pd, Ga	80	330-350

Source: Gerber, White and Stevens (2007)

Gerber, White and Stevens (2007) performed several catalytic tests for different catalysts that represent the general classes. The results can be found in their publication:

GERBER, M. A.; WHITE, J. F.; STEVENS, D. J. Mixed Alcohol Synthesis Catalyst Screening. Richland, Washington, Pacific Northwest National Laboratory, Sep. 2007. 54 p. il. color. Report, PNNL-16763.

Dutta and Phillips (2009) was modeled a simple conversion-specified reactor using a series stoichiometric reactions (above presented) to represent the mixed alcohols catalyst-synthesis considering specific conversion of each reactions set in order to reach catalyst performance targets, according to Table 11.

Table 11 – Mixed alcohols reaction performance results

Result	Stats of technology*	Target results used in Process designs & Aspen Plus models
Total CO Conversion (per-pass)	10%-40%	60%
Total Alcohol Selectivity (CO_2 free basis)	70%-80%	90%
Gas Hourly Space Velocity (hr^{-1})	1,600-12,000	4,000
Catalyst Alcohol Productivity ($g/kg_{catalyst}/hr$)	150-350	600

Source: Dutta and Phillips (2009)
* Herman (1991) and Forzatti, Tronconi, and Pasquon (1991) apud Dutta and Phillips (2009)

Table 12 shows the mixed alcohols product distributions reported by Dutta and Phillips (2009).

Table 12 – Miixed alcohols synthesis product distributions

Alcohol	Dow* (wt %)	SRI$^+$ (wt %)	NREL Model (wt %)
Methanol	30-70	30.77	4.83
Ethanol	34.5	46.12	67.13
Propanol	7.7	13.3	9.48
Butanol	1.4	4.14	1.17
Pentanol +	1.5	2.04	0.15
Acetates (C_1 & C_2)	2.5	3.63	-
Others (CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_5+)	-	-	14.58
Water	2.4		2.66

Source: Dutta and Phillips (2009)
* Quarderer (1986) apud Dutta and Phillips (2009)
$^+$ Nirula (1986) apud Dutta and Phillips (2009

“The most significant differences between the NREL model product distribution and those shown in literature are with regard to the methanol and ethanol distributions. This is primarily due to the almost complete recycle of methanol within this process” (DUTTA; PHILLIPS, 2009 p. 24).

Nexant Inc. (2006) report CO conversions (per-pass), selectivity for C_2+OH, and alcohol Space-Time Yelds (STY) in their report:

NEXANT INC. *Equipment Design and Cost Estimation for Small Modular Biomass Systems, Synthesis Gas Cleanup, and Oxygen Separation Equipment*: Task 9: Mixed Alcohols from Syngas: State of Technology. Golden, CO, USA: National Renewable Energy Laboratory, May 2006. Subcontract Report, NREL/SR-510-39947.

Stuart and El-Halwagi (2012 p. 542) present performance and single-pass products for catalysts to mixed-alcohols synthesis: by alkali-promoted modified fischer-tropsch catalyst, and by rhodium-based catalysts.

4.1.21 Solid-fuel fired boiler

The sugarcane bagasse from mills and the prepared/conditioned sugarcane straw as fuels material is fed by drum and hydraulic/pneumatic fuel feeders in the biomass-fired steam boiler BC system for thermal energy (heat) generation to steam generation required to supply and drivers a ST which produces electricity and extractive and exhaust steam to supply the biorefinery energy demand.

The steam quality required for the ST defines the boiler system according to turbine steam inlet temperature, the turbine steam inlet pressure and steam mass flow rate. The water quality must be adapted to the boiler type and the water pre-treatment and treatment plant must be adapted to the raw water (nature font).

The bottom and fly-ashes can be periodic cleaned (grate water cleaning and conveyor system) or continue removed from the unit automatically into self-contained ash bins and sent to disposal in the sugarcane crops (agricultural land), reuse of nutrients in the ashes.

The flue-gas cleaning can be done by dry or wet methods efficiently with advantages and disadvantages, dry scrubbers require an excess of chemicals for high removal efficiency while wet scrubbers normally require special treatment of the wastewater.

Mechanical collectors and wet scrubbers are commonly used to control particulate emissions from biomass-fired steam boilers. Mechanical collectors may be installed in single or multiple cyclone arrangements coupled with fabric filters or electrostatic precipitators. Venturi wet scrubbers can remove significant gaseous emissions, and the water system can be coupled with the grills cleaning and sent to the water treatment plant.

Air excess parameter have directly influence in the thermal efficiency of boilers and pollutants emissions, the particle emission and gaseous emissions (main NO_x emission) can increasing with the increase of air excess parameter, on the other hand, the reduction of excess air can reduce the conversion of carbon and biomass (incomplete combustion).

STs are available in a multiple configurations and capacities, the major classifications of ST based on application are referent at quality and conditions of the exhaust steam generation, condensing or non-condensing steam turbines.

5 First generation sugarcane biorefinery

Brazil is not only the largest sugarcane producer, is followed by India and China, as well as the largest sugar producer (over 50.0% of sugar sold worldwide). (NATIONAL SUPPLY COMPANY, 2014).

Actually (2015), sales of flex-fuel vehicles account for approximately 90.0% of light vehicles sealed in Brazil, despite the large potential market emerged hydrated ethanol market prices were not competitive compared to gasoline in most Brazilian states (NATIONAL SUPPLY COMPANY, 2014).

Sugarcane cultivated area destined for sugar activity in the 2014/15 (on-season) was approximately 9,004,500 hectares, distributed in all producing states (NATIONAL SUPPLY COMPANY, 2014). The Brazil’s total production of milled sugarcane in 2014/15 was 658.8 million tonnes (NATIONAL SUPPLY COMPANY, 2014). The average total reducing sugars (TRS) obtained in the 2014/15 season was 136.5 kg/tc (NATIONAL SUPPLY COMPANY, 2014).

In the 2014/15 season, ethanol production was 28.66 billion liters, of which 11.73 billion liters of anhydrous ethanol and 16.93 billion liters of hydrated ethanol (NATIONAL SUPPLY COMPANY, 2014). In the 2014/15 season, sugar production was 35.56 million tonnes (NATIONAL SUPPLY COMPANY, 2014).

According to Demirbas and Gupta (2011) for each tonnes of sugarcane are produced 130.0 kg of dry bagasse, the World’s sugarcane bagasse production is estimated at 200.0 million tonnes per year. In the harvest of 2014/2015 is estimated that Brazil has produced about 173.0 million tonnes of wet bagasse wet bagasse.

Each tonnes of processed cane generates about 140.0 kg of dry straw (BRAZILIAN BIOETHANOL SCIENCE AND TECHNOLOGY LABORATORY, 2012). Thus, for the 2014/2015 season Brazil has produced about 173.0 million tonnes of dry straw.

In Brazil at the end of 2014, the electricity capacity Installed reached 133.9 GW. A highlight was the 89.2 GW of hydroelectric power (67% of the total), followed by 12.6 GW of natural gas (9.4%) and 12.3 GW of biomass (9.2%) (BRAZIL, 2015). Only sugarcane biomass reached 9.9 GW (80% of the total of biomass), an average of 26.0 MW per mill (BRAZIL, 2015).

5.1 First generation sugarcane biorefinery with annexed ethanol distillery

In Brazil (until 2013), sugarcane biorefineries is based on the fermentation of the juice and/or molasses to produce ethanol in autonomous distilleries type (ethanol) or in annexed distilleries type that include a facility co-located with sugar mills to produce sugar (ethanol and sugar).

In this research Master's degree, as a basis (reference) for all scenarios (1G CHP systems and thermochemical routes) under study is considered an optimized Brazilian first generation (1G) sugarcane biorefinery with annexed ethanol distillery for co-production of value-added bio-based sugar (sugar mill), anhydrous ethanol (annexed distillery), and electricity (CHP/CEST) and/or surplus biomass (CHP/EBPST).

The optimized 1G sugarcane biorefinery (simplified named) was developed by the division of AIB of the CTBE/CNPEM under the scope of the VSB tool which is called – optimized annexed distillery – it is recommended read the publication named – *The Virtual Sugarcane Biorefinery (VSB)*: 2011 Report (BRAZILIAN BIOETHANOL SCIENCE AND TECHNOLOGY LABORATORY, 2012) – and the publication named – Virtual Biorefinery: An Optimization Strategy for Renewable Carbon Valorization (BONOMI et al., 2016).

5.1.1.1 Optimized sugarcane biorefinery with annexed ethanol distillery

The capacity adopted is 500 tonnes of cane processed (clean) per operational hour. Soil content is 0.6%$_{w/w}$, and therefore, 3.0181 tonnes/hr of soil that results in a total of 503.0181 tonnes/hr of material processed by the optimized annexed distillery.

After the sugarcane mills, are generated 136.16 tonnes/hr of 'residues' (bagasse, and residual soil and straw), which correspond at 13.616%$_{w/w}$ of the total cleaned sugarcane (processed). From this residue, are removed 1.31 kg/hr of fine particles and sent to the filter system of sugarcane juice (50.0%$_{w/w}$ for sugar and 50.0%$_{w/w}$ for ethanol production).

The amount of residues (bagasse) sent to be burned in the boiler system (cogeneration system) are 133.150 tonnes/hr (50.0%$_{w/w}$ of moisture content). Remaining soil content in bagasse is determined by the efficiency of the cane washing process, for about 97.0% wash efficiency is removed 75.0%$_{w/w}$ of soil, resulting in 66.574 kg/hr of soil remaining as residue.

VSB tool in the optimized annexed distillery also considers the generation and availability of biomass in the crops (straw), is considered an equivalent generation of 14.0%$_{w/w}$ (dry basis) of the amount of clean sugarcane (wet basis) processed by the optimized annexed distillery, resulting in 70.0 tonnes/hr of clean straw (dry basis). Also consider, that 50.0%$_{w/w}$ (dry basis) of the straw (ungrounded) that is left in the field are available and recovered to be subsequent submitted (bales) to the boiler system, Consider the moisture content as 15.0%$_{w/w}$ (on plant), resulting in 41.176 tonnes/hr of straw (wet basis) burned to thermal energy generation.

The optimized annexed distillery consumes a total of 30.0 kWh per tonnes of processed cane (wet basis) when consider electric drives in the mills, then the cogeneration system needs to have at least 15.0 MW (minimum electricity generation) of power energy capacity (process demand). Also, the plant employs 14.175 tonnes/hr of saturated steam at a pressure level of 6 bar (molecular sieves) and 184.975 tonnes/hr of saturated steam at a pressure level of 2.5 bar.

The optimized annexed distillery produces 542.316 tonnes/hr of sugar cane juice, 50.0%$_{w/w}$ for the production of sugar and 50.0%$_{w/w}$ for the production of anhydrous ethanol. What results in a productivity of 25.5591 tonnes/hr of sugar (102,440.873 tonnes/year of sugar), and 21.013 tonnes/hr of anhydrous ethanol (106,260.096 m^3 /year).

5.2 Scenarios assessed

In order to allow the evaluation and assessment of other boiler systems and to allow the integration with the biomass thermochemical conversion routes, different boiler systems are evaluated at different levels of technological development.

Seven optimized 1G sugarcane biorefinery scenarios applying CHP/CEST system and seven optimized 1G sugarcane biorefinery scenarios applying CHP/EBPST system evaluated at different parameter levels were simulated in Aspen Plus$^{®}$v8.4 process simulation platform and assessed under the scope of VSB tool.

Optimized 1G sugarcane biorefinery scenarios applying different CHP/CEST system or CHP/EPBST system are defined in the section 3.4.1 (Combined heat and power generation (CHP)). A scheme of the sugar, ethanol and electricity production from optimized 1G sugarcane biorefinery applying CHP/CEST system (integral use of available biomass) is detailed in the Figure 24, and a scheme of the sugar, ethanol and electricity production with surplus biomass from optimized 1G sugarcane biorefinery applying CHP/EBPST system (partial use of available biomass) is detailed in the Figure 25.

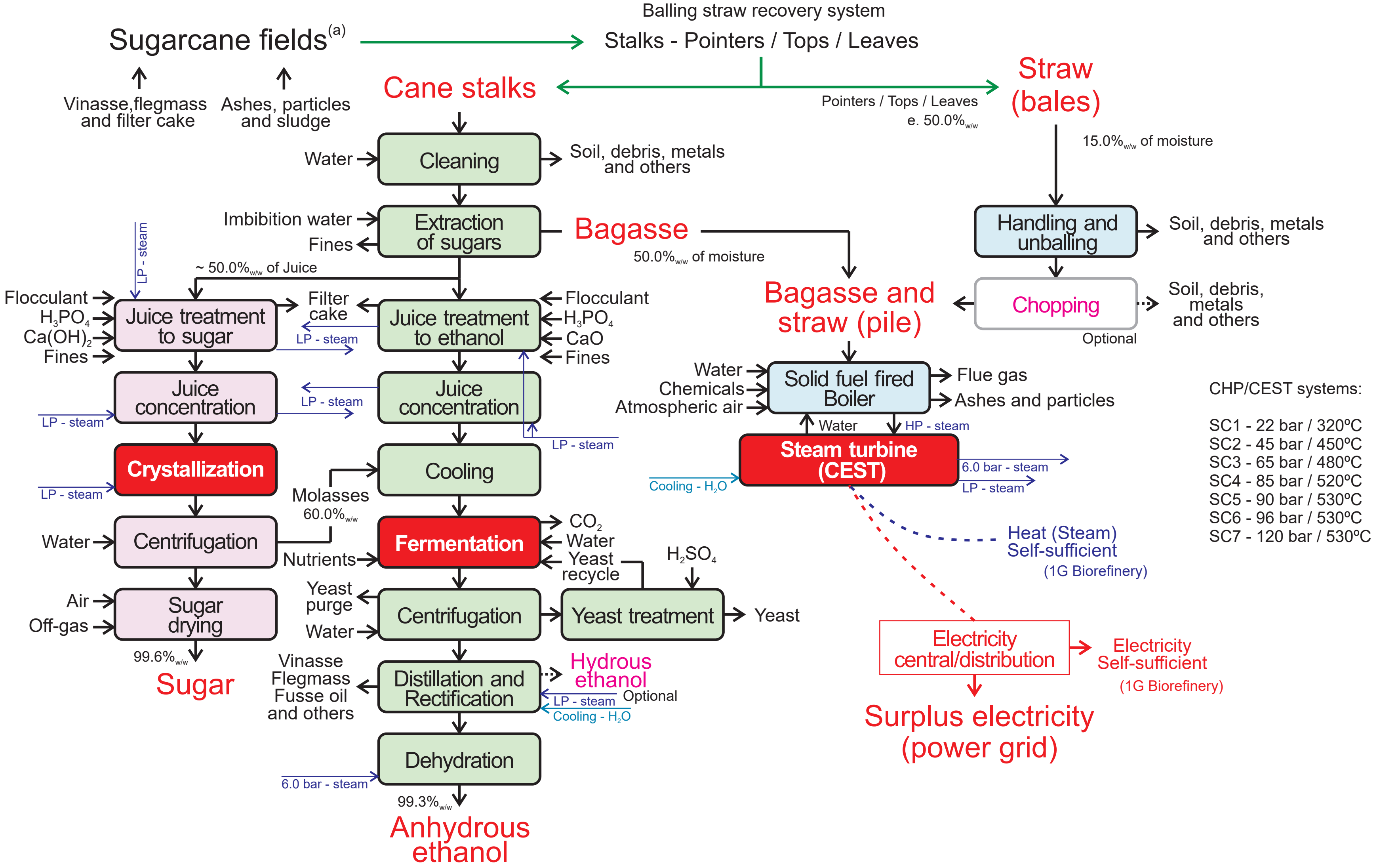


Figure 24 - Flow block diagram of the optimized 1G sugarcane biorefinery with annexed ethanol distillery and CHP/CEST - surplus electricity from integral use of available biomass

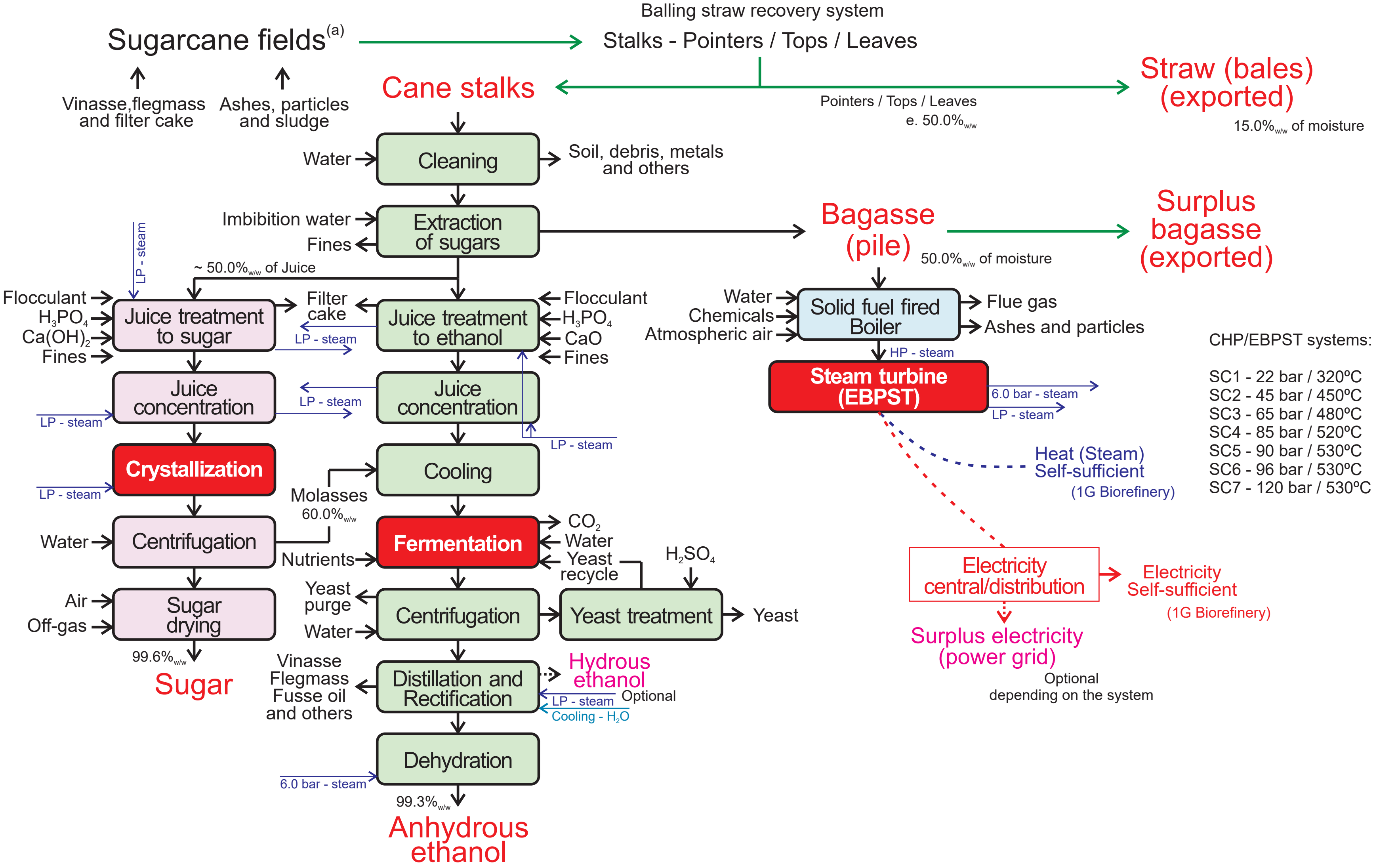


Figure 25 - Flow block diagram of the optimized 1G sugarcane biorefinery with annexed ethanol distillery and CHP/EBPST - surplus biomass while supply the biorefinery energy demands

Aspen Plus$^{®}$v8.4 complete flowsheet`s of 1G-CHP/EBPST detailed scenarios are presented in the APPENDIX A. Figure A2 - 22 bar and 320ºC: Scenario 1 (SC1); Figure A4 - 45 bar and 450ºC: Scenario 2 (SC2); Figure A6 - 65 bar and 480ºC: Scenario 3 (SC3); Figure A8 - 85 bar and 520ºC: Scenario 4 (SC4); Figure A10 - 90 bar and 530ºC: Scenario 5 (SC5); Figure A11 - 96 bar and 530ºC: Scenario 6 (SC6); Figure A14 - 120 bar and 530ºC: Scenario 7 (SC7).

Aspen Plus$^{®}$v8.4 complete flowsheet`s of 1G CHP/CEST detailed scenarios are presented in the APPENDIX A. Figure A1 - 22 bar and 320ºC: Scenario 1 (SC1); Figure A3 - 45 bar and 450ºC: Scenario 2 (SC2); Figure A5 - 65 bar and 480ºC: Scenario 3 (SC3); Figure A7 - 85 bar and 520ºC: Scenario 4 (SC4); Figure A9 - 90 bar and 530ºC: Scenario 5 (SC5); Figure A11 - 96 bar and 530ºC: Scenario 6 (SC6); Figure A13 - 120 bar and 530ºC: Scenario 7 (SC7).

Table 13 shows the energetic demand targets (thermal and electrical) for the 1G CHP systems according to results of the optimized annexed distillery (efficient optimization practice to save energy), section 5.1.1.1 (Optimized sugarcane biorefinery with annexed ethanol distillery).

Table 13 - Target enerergetic (thermal and electrical) demand of the optimized 1G sugarcane biorefinery with annexed ethanol distillery

Demand characterization	Target
Electricity*	30.0 kWh/tc 15 MWh installed potential
Saturated steam at 6.0 bar (molecular sieves)	28.35 tonnes/tc 14.175 tonnes/hr
Saturated steam at 2.5 bar (process steam)	369.99 tonnes/tc 184.975 tonnes/hr

Note: values per tonnes of processed cane (tc) in wet basis

* include consumption of electricity by the CHP systems

5.2.1 Physical properties

The GLOBAL property method used is RKS-BM.

The local properties method used is: IDEAL for biomass handling and sizing; IAPWS-95 for all pure water-side streams and for all pure steam-side streams; and RKS-BM for gaseous streams side.

Non-conventional solids physical property method used for BAGASSE and STRAW component properties is the HCOALGEN model (general coal models) applying the Mott and Spooner correlation (4 option code) according to section 3.7 (Non-conventional solids physical property methods) for estimate the enthalpy, and COALIGT model for estimate the density.

5.2.2 Biomass handling and sizing

Raw bagasse feedstock content 50.0%$_{w/w}$ of moisture from cane mills (driver by electrical motors) is conveyed (screw, drag, or belt) directly to boilers area to burning, 5.0%$_{w/w}$ of the wet bagasse is reserved for brief stops and start-up. In CHP/CEST systems is considered the integral use of available bagasse and in CHP/BPEST a surplus bagasse is conveyed to bagasse pile as available biomass for use (exported biomass).

In CHP/CEST systems it was considered that the straw bales content 15.0%$_{w/w}$ of moisture are delivered by trucks to the feed handling area and preparation for integral use by 1G-bioreifnery. The straw bales are broken and conveyed to magnetic head pulleys to removes tramp metals before the chopping process, after size reduction (gross sized) the straw is conveyed to boilers area to burning together with bagasse. Whereas, in CHP/BPEST scenarios it was not considered the straw processing at the 1G-biorefinery, the straw can be collected from the field and directly intended for export (sale). The use of straw in the 1G-biorefinery implies the need for biomass handling and preparation system.

CHP/BPEST scenarios are evaluated as steam closed-balance without leftovers with the minimum possible use of bagasse, may be possible surplus electricity to the electric power grid depending on the CHP/BPEST configuration applied.

Assuming biomass delivery by road train with a capacity of 70.0 tonnes/vehicle of straw (in bales) at 15.0%$_{w/w}$ of moisture content, approximately 14 truck deliveries per day would be required to operate the CHP/CEST for an 1G-bioreifnery at design capacity of 500.000 tonnes/hr of cleaned-cane processed per operational hour. Biomass is one of the more difficult materials to handle, a simplified handling and chopping models was implemented due to the lack of accuracy of data and large variations regarding the distances and energetic consumption for the biomass handling system and uncertainty about the size of the particle/fibers of raw sugarcane bagasse and straw.

Figure 26 shows the Aspen Plus$^{®}$v8.4 flowsheet of the biomass handling and sizing for: a) CHP/CEST systems whit preparation of straw bales to be burned in solid-fuel fired boiler; and b) CHP/EBPST systems using only sugarcane bagasse for steam generation, without use of straw and chopping system

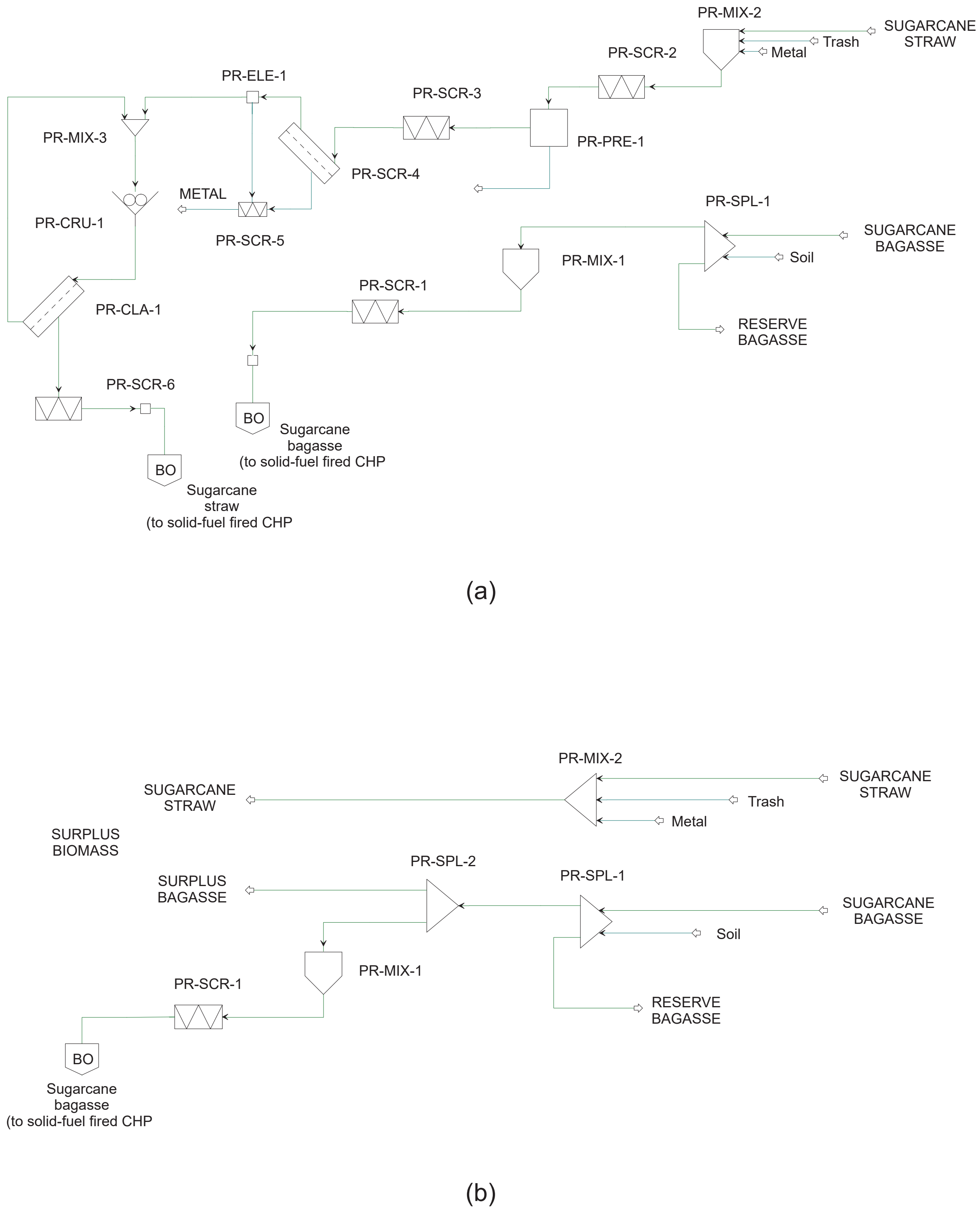


Figure 26 - Aspen Plus$^{®}$v8.4 flowsheet of the biomass handling and sizing area for: a) CHP/CEST systems whit preparation of straw bales to be burned in solid-fuel fired boiler; and b) CHP/EBPST systems using only sugarcane bagasse for steam generation, without use of straw and chopping system

The actual model implemented only account the electricity demand for chopping and/or cut milling the sugarcane straw and the mass balance of: bagasse reserve; tramp metals removed, and straw soil content reduction by the handling, storage and unpack processes.

Figure 26 (a) shown the model for raw straw (SUGARCANE STRAW) preparation to burning into biomass-fired steam boiler system for CHP/CEST system, the straw bales delivered (STRAW+TRASH+METAL) by trucks or road train are dumped (PR-MIX-2) and transported (PR-SCR-2) to storage area for further reduction size process, consider a pre-chopping process in the field by baling machine. From the storage area (PR-PRE-1) or directly from the truck the straw bales are just unpacked (PR-PRE-1) or directly chopped and conveyed to the bagasse pile (mixture) resulting in a reductions of 50.0%$_{w/w}$ of the soil content (TO SOIL), after unpacked the straw is conveyed (PR-SCR-3) to the magnetic separation (prevent damages) by magnetic head pulleys (PR-SCR-4) to remove the tramp metals (METALS) form the unpacked straw with a reduction of 5.0%$_{w/w}$ of the soil content. The straw without tramp metals is feed by drag conveyor to reduction size machine (PR-CRU-1) for gross cutting-milling or chopping consuming 3.0 kWh/tonnes of raw unpacked straw inlet in the machine (DS-PR-PC-1), solids-solids screens separation (PR-CLA-1) classifies the straw. Oversized straw is recycled to secondary particle size reduction cycle (increase the biomass conversion), the prepared/conditioned sugarcane straw as fuels material is conveyed (PR-SCR-6) and mixed with sugarcane bagasse from mills or directly fed by drum and hydraulic/pneumatic fuel feeders in the biomass-fired steam boiler bottoming-cycle system.

Figure 26 (b) shown the model for bagasse handling and conveying system for CHP/EBPST system, the bagasse (SUGARCANE BAGASSE) from mills (BAGASSE+SOIL) is directly conveyed (belt) (PR-SCR-1) to boiler fuel feeders or can be storage in pile for further process, from the pile an tractor (actual system) carries the bagasse to the conveyor feed tray (PR-MIX-1), 5.0%$_{w/w}$ of the wet bagasse is stored (PR-SPL-1) as reserve. Figure 26 (b) shown the model for bagasse handling and conveying system for CHP/BPEST system, the bagasse (SUGARCANE BAGASSE) from mills (BAGASSE+SOIL) are conveyed to storage in the bagasse pile (PR-SPL-1), 5.0%$_{w/w}$ of the wet bagasse is stored (PR-SPL-1) as reserve (RESERVE BAGASSE). From the pile a tractor (actual system) carries only a part of the bagasse available (necessary for surplus the energetic demand of the 1G-biorefinery) to the conveyor feed tray (PR-MIX-1) to burning in biomass-fired steam boiler. Surplus bagasse and the integral raw straw are available (SURPLUS BIOMASS from CHP/BPEST system) for sale and export (use in other units) as raw feedstock.

In the CHP/BPEST systems the amount of bagasse used (influence in the entire water cycle) to supply the thermal and electrical energy demand of the 1G-biorefinery is controlled and adjusted by exactly steam production needed to supply the thermal energy, the control is made in the block ST-SPL-2.

5.2.3 Solid-fuel fired boiler

A typical solid-fuel fired boiler bottoming-cycle system (grate type) for steam generation was simulated (BO area) operating in combined Rankine-cycle mode for thermal energy generation (steam). Boilers available in the Brazilian market can generate steam at from 22.0 bar up to 120.0 bar and from 300.0ºC up to 530.0ºC.

Biomass is fed by drum and hydraulic/pneumatic fuel feeders in the combustion chamber (BO-COMBU), fresh combustion air is feed by advanced blower system (BO-ASP-1) (with air filter (BO-FIL-1) to protect the blower and burner from debris) to an heat exchanger (BO-PRE-1), preheating the air before inlet in the burner chamber (BO-COMBU), to complete combustion an excess of oxygen is required (based on theoretical amount of stoichiometric combustion condition). Air or oxygen (combustion agent) excess depends on the chamber design with influence on temperature in the burner chamber (BO-COMBU), conversion of sugarcane bagasse and straw and other carbon content materials, thermal efficiency and on pollutants formations and emissions (e.g.: NO_x, SO_x and particle matter) to atmosphere.

Water flows through the pipes and the flue-gas pass around the pipes banks changing thermal energy into usable steam for further process. The feed-water enters the solid-fuel fired boiler in the low-temperature economizers (BO-ECO-1) (installed after the combustion zone) and is heated to below the saturation condition by convective heat (BO-HEA-3) and to saturation condition in the high-temperature economizers (BO-HEA-3) by radiant and convective heat. Saturated liquid water continues to an evaporator (BO-VAP-1) where is converted to saturated steam and then in the superheater exchanger (BO-SUP-1) the saturated steam is dried by overheating beyond its saturation point. The superheated steam out the solid-fuel fired boiler and then enter in the ST system (ST area).

The flue-gas temperature is further reduced down to approximate 180.0°C (actual) or down to 120.0ºC (advanced) before entering the condensing unit (in advanced boilers) with reduce the temperature to below 55.0ºC (not simulated), or can be emitted directly to atmosphere without pollutants control system, the energy contained in the flue-gas is lost. The bottom ashes are removed from the boiler by wet system (BO-SEP-2) and fly-ashes are removed by a multi-cyclone battery (BO-CYC-1) and electrostatic precipitator or baghouse filter (BO-ESP-1). Water blowdown remove impurities from boiler water and can be made by continuously or periodically manual (accumulated sludge) bleeds (BO-SPL-3).

Figure 27 shows the Aspen Plus®v8.4 flowsheet of the solid-fuel fired boiler to steam generation model implemented in CHP/CEST scenarios for integral use of available biomass. Figure 28 shown the Aspen Plus®v8.4 flowsheet of the solid-fuel fired boiler to steam generation model implemented in CHP/BPEST scenarios with partial use of available biomass

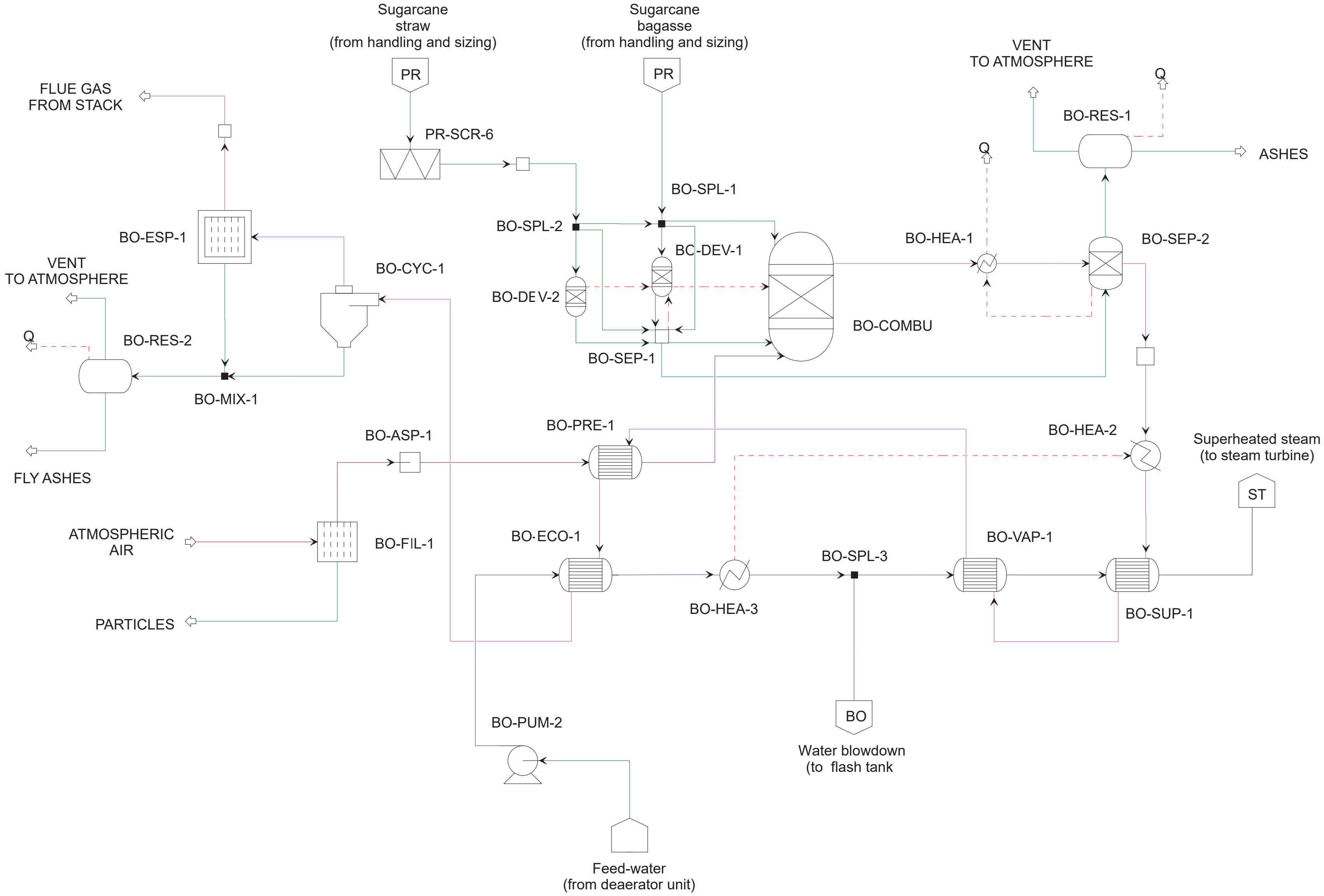


Figure 27 - Aspen Plus® v8.4 flowsheet of the Solid-fuel fired boiler (grate type) system to steam generation model implemented in the CHP/CEST scenarios for integral use of available biomass

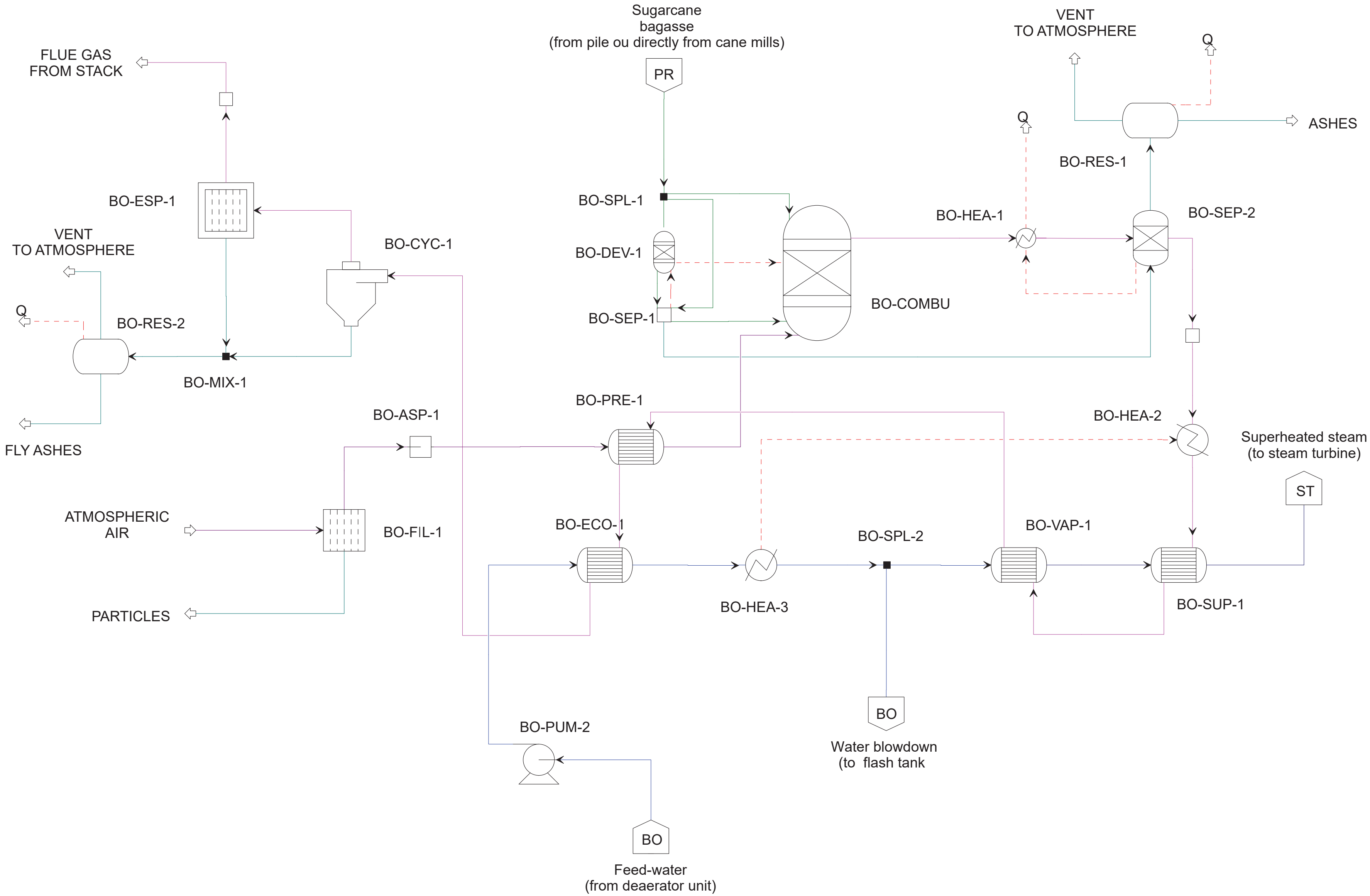


Figure 28 - Aspen Plus® v8.4 flowsheet of the Solid-fuel fired boiler (grate type) system to steam generation model implemented in the CHP/EBPST scenarios with partial use of available biomass

As shown in Figure 27 the breakdown RYield reactors type used as a theoretical artifice to simulate the decomposition of the non-conventional solids BAGASSE (BO-DEV-1) and STRAW non-conventional solids (BO-BEV-2) into its 'constituting' conventional components ('ELEMENTS') including carbon (C), hydrogen (H_2), oxygen (O_2), chlorine (Cl_2), nitrogen oxide (NO), sulfur dioxide (SO_2), and hydrogen sulfide (H_2S) using about 16.67%$_{w/w}$ of the sulfur (S) content, by specifying the yield distribution according to the biomass ultimate analysis (Table 9 or Table 5 for bagasse and Table 6 for straw) controlled by FORTRAN calculator block (CA-BO-CS-1 for BAGASSE and CA-BO-CS-2 for STRAW). The blocks BO-SPL-1 and BO-SPL-2 split the volatile material from the biomass.

The block BO-SEP-1 is used to adjust the biomass conversion, the carbon conversion (CA-BO-XS-1) and the ashes content (solids formation) as bottom ashes or fly-ashes. The amount of bottom ashes (ASHES) and fly-ashes (FLY-ASHES) and hers composition are controlled by BO-SEP-2 block which simulate the grate system and the automatically wet ashes removal system (BO-SEP-2), without considering the water use (due to a lack of data) in the simulation (cleaning grate system). The ashes temporary storage bins (BO-RES-1) consider the heat loss (heat transported with ashes) by natural heat changes with the ambient conditions. The solid-fuel fired boiler models consider a heat loss (BO-HEA-1) due the surface radiation and convection with to surrounding ambient (CA-BO-QL-1).

The burner chamber (BO-COMBU) is modeled with RGibbs reactor type which uses the Gibbs free energy minimization method, considering all the possible solids emissions (soil and atmosphere) and gaseous emissions (atmosphere). This model determines the equilibrium composition of the products resulting from the many reactions that can occur, can determine in the gaseous phase the formation of NO_2, N_2O, NO, SO_2, SO_3, NH_3, H_2S, HCL, Cl_2, COS, CHN, VOCs, and particulate matter formation (salt and solid compounds), and in the solid phase (ashes and fly-ashes) the formation of unconverted biomass (BAGASSE and STRAW) and carbon (C), SiO_2 (biomass constitutional ash content), soil, MgO, CaO, KCl, K_2O, K_3PO_4, salts and mineral (biomass constitutional content). Combustion Gibbs free energy minimization method cannot estimate the formation of CaS, MgS and S, this sulfur are emitted as sulfur content gaseous form in Gibbs combustion models (oxidized metals are more stable form).

Combustion air (ATMOSPHERIC AIR) is preheated (BO-PRE-1) and forced-injected in the chamber (BO-COMBU) by advanced blower system (BO-ASP-1) with pre-filter unit (BO-FIL-1) to protect the blower and burner from debris (PARTICLES). Excess air employed for the combustion reaction in the chamber is a parameter obtained from the industrial boiler producer (based on DEDINI data) for specific indicated configuration and operational conditions, the excess air is controlled by a simplified design specification (DS-BO-FG-1) which relates the mass amount of outlet oxygen to the amount of input oxygen in the combustor. The DS-BO-FG-1 does not make the estimative of stoichiometric combustion condition as a comparative basis (simplified control). The stoichiometric excess air can be calculated externally to the model according to Equations 9, 10, 11 or 12 with the aid of parameter calculation blocks (BHV blocks group) implemented.

Non-saturated feed-water from deaerator water unit (BO-DEA-1) is pumped (BO-PUM-2) at operational pressure and fed into the pipes banks in solid-fuel fired boiler, changing thermal energy from the hot combustion gases to generate steam in the low-temperature and high-temperature economizers (BO-ECO-1) to saturation condition by radiant (BO-HEA-2 and BO-HEA-3) and convective heat (BO-ECO-1). Saturated liquid water is evaporated to saturated steam conditions in the evaporator (BO-EVA-1) and is superheated in the superheater (BO-SUP-1), leaving the boiler area with the temperature and pressure required to inlet in the ST system.

Continue water blowdown system is considered in the boiler models, $4.0\%_{w/w}$ of the saturated water is purged (BO-SPL-3) from the boiler at high-pressure and flashed to atmospheric pressure in the flash vessel (BD-FLASH-1). Water blowdown remove impurities from the water-side boiler streams as dissolved impurities. In the implemented model is not considered the presence of impurities in the water-side streams (considered in waste water treatment unit to estimate chemicals and costs), they depends on the fresh-water quality, on make-up water treatment process and maintenance treatment of process water cycle.

The temperature of the flue-gas after the air pre-heater exchanger is set according to design and parameters of the solid-fuel fired boiler industrial producer (based on DEDINI data). Flue-gas temperature control is made by amount of feed-water flowing (DS-BO-FL-1) in the water-side pipes (useful-heat generation) with influence of the excess air (DS-BO-FG-1).

Particulate material content in the flue-gas (FLY-ASHES) are reduced by control particulate emissions system applying a multi-cyclone unit (BO-CYC-1) designed for 80.0% of separation efficiency and by electrostatic precipitator unit (BO-ESP-1) designed for 92.0% of separation efficiency, the fly-ashes are stored in the ashes temporary storage bins (BO-RES-2). The fly-ashes (FLY AHSES) collected are mixed with the bottom ashes (ASHES) and sent to application/destination in the sugarcane crops.

After the particulate control system, the flue-gas are sent to the stack and then emitted to atmosphere (FLUE-GAS FROM STACK) content steam (H_2O), NO_2, N_2O, NO, SO_2, SO_3, NH_3, H_2S, HCL, Cl_2, COS, CHN, volatile organic compounds, and particulate matter (MgO, CaO, KCl, K_2O, K_3PO_4, BIOMASS, C, salts and mineral).

5.2.4 Condensing-extraction steam turbine

Condensing steam turbines (condensing type) are used when electricity generation is the main purpose. High-pressure steam from solid-fuel fired boiler (BO blocks) is expanded within the turbine to produce mechanical energy to be used to drive an electricity generator (EE-MIX-1). Steam extractions at intermediate-pressure levels (ST-SPL-1) before the condensing section is useful for supply the specific industrial process heat requirements. Condensing turbine stage (ST-LPT-1) are directly connected to a condenser (ST-CON-1), where the low-pressure steam (vacuum pressure) is condensed to lower pressures and after pumped (ST-PUM-1) back to deaerator unit (BO-DEA-1), returning to cycle.

Temperature and pressure parameters admitted (design parameters) in the turbine inlets and outlets are directly influence on the characteristic thermal and mechanical energy (electrical potential) efficiencies. The pressure and temperature of the exhaust steam depend on the operational quality of inlet steam (temperature and pressure) in the turbine stages (ST blocks), as well the fraction of liquid-vapor obtained in the exhaust steam (ST-LPT-1). The condensing stage (ST-LPT-1) is able to operate with wet steam at minimum 0.9 dryness factor (a fraction of condensed steam has been kept at maximum of 10.0%$_{w/w}$).

Figure 29 (a) shows the Aspen Plus$^{®}$v8.4 flowsheet of the CEST system to surplus electricity to electric power grid while ensure the self-sufficiency of the 1G sugarcane biorefinery (integral use of biomass available).

5.2.5 Extraction back-pressure steam turbine

Back-pressure steam turbines (non-condensing type) are used in the industrial plants that use the entire exhaust steam flow to supply the industrial process heat requirements. High-pressure steam from solid-fuel fired boiler (BO blocks) is expanded within the turbine to produce mechanical energy to be used to drive an electricity generator (EE-MIX-1). Steam extractions at intermediate pressure (ST-SPL-1) are useful for supply the specific industrial process heat requirements, as well the exhaust steam.

Figure 29 (b) shows the Aspen Plus$^{®}$v8.4 flowsheet of the EBPST system to supply the thermal and electrical energy demand of the 1G sugarcane biorefinery while generate surplus biomass and some surplus electricity to electric power grid (surplus bagasse and straw).

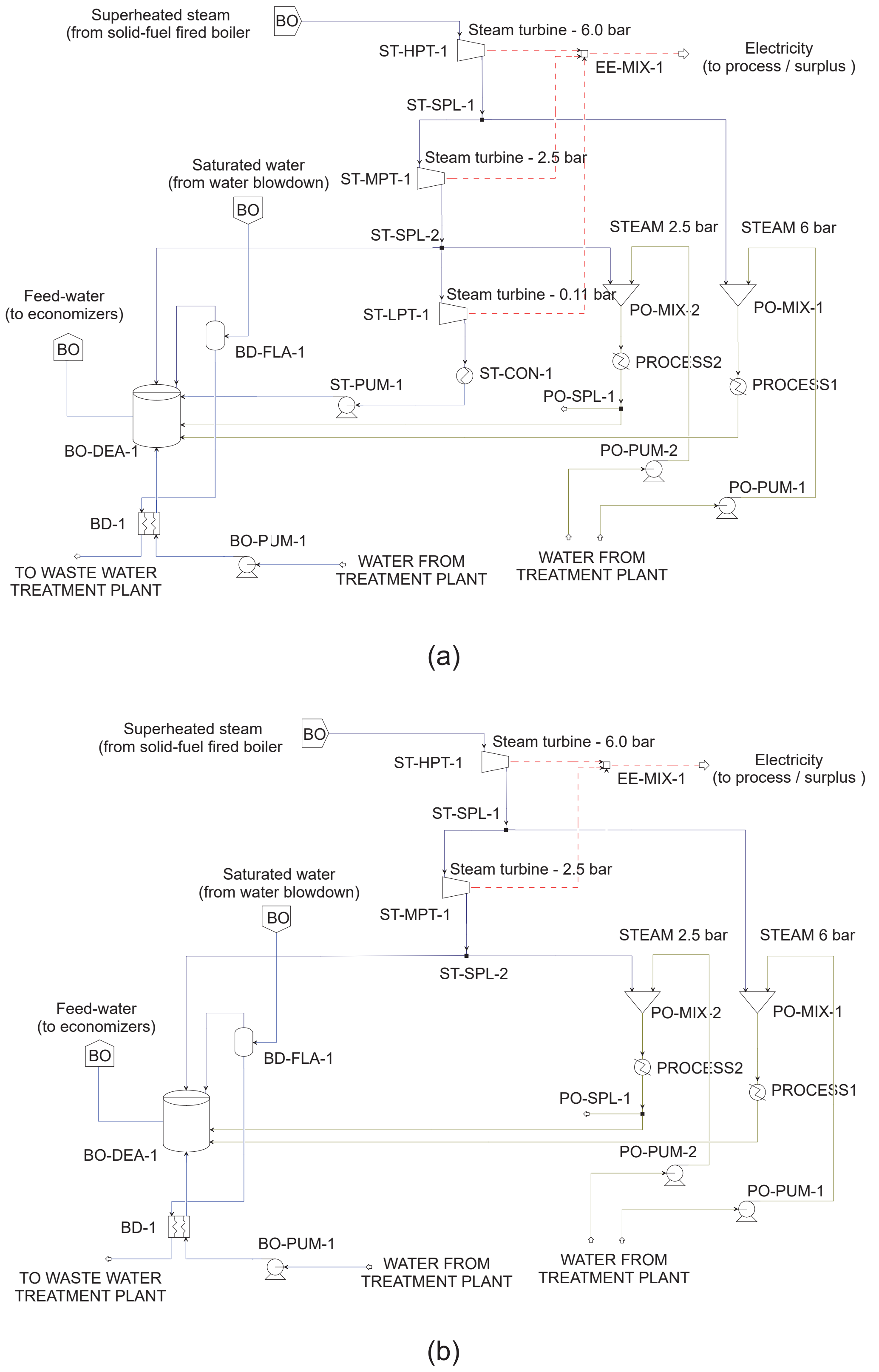


Figure 29 - Aspen Plus®v8.4 flowsheet of the steam turbine system models for the optimized 1G sugarcane biorefinery with annexed ethanol distillery: a) CEST system to surplus electricity to electric power grid while supply the thermal and electrical energy demand of the 1G sugarcane biorefinery; b) EBPST system to supply the thermal and electrical energy demand of the 1G sugarcane biorefinery while generate surplus biomass and some surplus electricity to electric power grid

Figure 29 (a) and Figure 29 (b) shows the same models for the first (ST-HPS-1) and for the second (ST-MPS-1) expansion stages. The first-section of the ST (ST-HPS-1) represents the expansion of high-pressure steam to 6 bar and power generation stage before the first extraction of steam (ST-SPL-1), the first extraction (ST-SPL-1) supply the thermal energy demand of the dehydration ethanol process. In CEST systems (Figure 29 (a)), the second-section of the steam turbine (ST-MPS-1) before the second steam extraction (ST-SPL-2) or in EBPST systems before the steam exhaust (ST-SPL-2) represents the expansion of the steam from 6 bar to 2.5 bar and power generation stage. The condensing stage (third section) of the CEST (ST-LPS-1) represents the expansion of the steam from 2.5 bar to 0.11 bar (vacuum) and power generation stage.

Steam at 2.5 bar and 130.0ºC generated in the second extraction (CEST) or as exhaust steam (EBPST) is used to supply the process thermal demands. Desuperheater units for 6.0 bar steam (PO-MIX-1) and for 2.5 bar steam (PO-MIX-2) can reduce the steam temperature to saturation conditions if necessary (PO-MIX-1 and PO-MIX-2). The heater blocks PROCESS1 represent the heat consumed in the dehydration ethanol process and PROCESS2 represent the total heat consumed in the 1G sugarcane biorefinery according to Table 13.

Estimated isentropic efficiencies of the steam turbines are made from operational parameters obtained from the inlet admitted parameters (manufacturer) and the steam conditions (temperature) available at 2.5 bar for use as main heat carrier, the steam conditions are fixed at 2.5 bar and 130.0ºC (process steam).

Steam at 2.5 bar for deaerator unit (BO-DEA-1) required to heat the water to 105.0ºC at 1.4 bar is determined by a design specification (DS-AE-FG-1) adjusting the amount of steam are sent (ST-SPL-2) to the deaerator unit.

In a turbine-mechanical generator (EE-MIX-1) operating in synchronous or asynchronous mode the mechanical energy of a turbine is converted to electricity, in Aspen Plus®v8.4 process simulation platform is simulated as a mechanical efficiency (turbine block). The electrical potential losses by attrite in the mechanical move parts was considered as 1.0% of the mechanical energy generated by the turbine stage (99.0% mechanical efficiency).

5.2.6 Multi-cells water-cooling tower

The low-pressure steam exhaust (vacuum pressure) from CEST system is condensed in a water-cooled surface condenser (ST-CON-1) by indirect heat exchange, heating the cooled water side and generating hot water. Water-cooling tower system (CT-TOW-1) for CHP/CEST systems (multi-cells towers) is used to withdraw heat from the hot water by cold-air through direct contact in counter-flow. Portion of heat is removed from the hot water by evaporative effect (CT-SPL-1) using induced draft counter-flow and mechanical axial propeller fans to induce the air vertically upward through the fill in the tower.

Was assumed that the necessary heat sink is available in the form of fresh-water (ambient conditions) for make-up and available in the cold-water basin at 27.0ºC, temperature of water inlet the condenser. The condition of low-pressure steam exhaust considered is 0.11 bar and about 48.0ºC (minimum of 0.9 dryness factor).

The Aspen Plus®v8.4 process model simulation consider modules of draft-packaged water-cooling induced-tower 43.0ºC/30.0ºC/27.0ºC type with capacity for 700.0 m³/hr of water mass flow rate. The model was developed using IAPWS-95 physical property methods for the water-side streams, and RKS cubic equation of state with BM alpha function property method to simulate the air-side streams and the heat transfer between the atmospheric air-side and the water-side in the water tower module (CT-TOW blocks). The heat transfer in the gas-side or liquid-side streams in the cooling water equipment users depends on the physical property methods employed in the area in which they are allocated.

The ambient condition of the atmospheric surrounding air (ATMOSPHERIC AIR) considered in the Aspen Plus®v8.4 process model simulation is 25.0ºC at atmospheric pressure with relative humidity of 80.0% and web bulb temperature at about 21.3ºC.

The Aspen Plus®v8.4 process model simulation of water-cooling tower system operating in water recirculation mode determine the requirements of cooling water heat exchanger, make-up of recycled and fresh water, water blowdown, and electric motor drives (fan drivers and pumps). In the model are used the standards design equations as defined in the section 3.9.17 (Water-cooling tower) for the modular single fan-cells arrangement operates as staged mode by sections each with variable-frequency drivers.

Multi-cells water-cooling tower (CT-TOW blocks) is determined based on the cooling capacity of 700 tonnes/hr of hot water per modular cells (CT-TOW blocks) considering mechanical axial propeller single fan-cells counter-flow draft designed (CT-TOW blocks). The numbers of cells and fans are estimated based on the mass flow rate of cooling water circulating in each of the specific sections (first and second sections).

The induced surrounding air exchange convective heat with the hot water in the water-cooling tower (CT-TOW blocks), represented as a simple HeateX exchange block (CT-TOW blocks). The surrounding air is induced upward through the fill (CT-TOW blocks) being heated from 25.0ºC to 40.0ºC. The hot cooling water flow downward through the fill (CT-TOW blocks) been cooled down from 43.0ºC to

30.0ºC. This simple model results in the overestimated amount of air in relation to reality or a more complex model (direct contact model).

Figure 30 shows the Aspen Plus®v8.4 flowsheet of the water-cooling tower system model for the CHP/CEST scenarios for condensing the exhaust low-pressure steam from the condensing steam turbine stage.

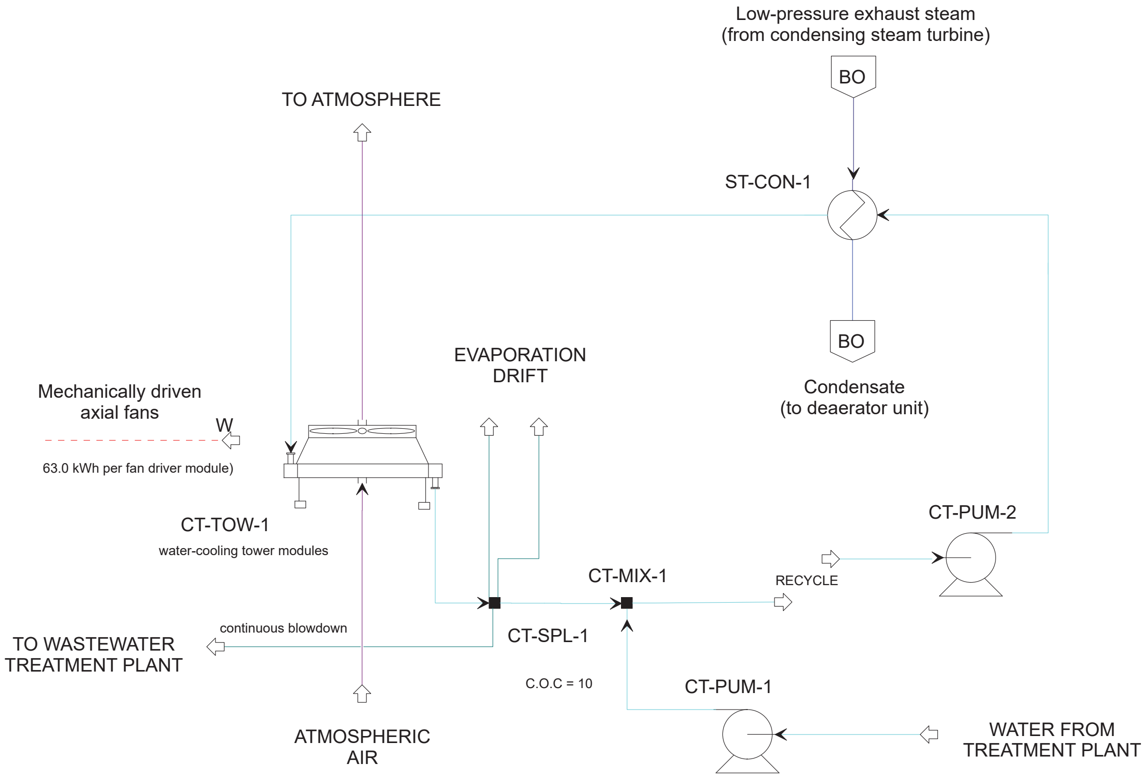


Figure 30 - Aspen Plus®v8.4 flowsheet of the water-cooling tower system model for CHP/CEST scenarios

As shown in Figure 30 the Aspen Plus®v8.4 flowsheet of the simplified water-cooling tower system in the 1G CHP/CEST scenarios are composts by: pumps (CT-PUM blocks); fans (CT-EFT work streams); water-cooling tower modules (CT-TOW blocks); water-cooling tower basin (CT-MIX blocks); adjust losses (evaporation and drift) and blowdown system (CT-SPL blocks); and spreadsheet calculation of blowdown cycles of concentration (C.O.C).

The multi-cells water-cooling tower (CT-blocks) provides cooling water to remove heat and adjust the process temperature to appropriate levels. The cooling water is distributed to the cooling water equipment users in the 1G CHP/CEST scenarios to:

a) condense the low-pressure exhaust steam from the condensing turbine stage employed in the CEST scenarios;

The amount of surrounding air flowing through the fill (CT-TOW blocks) of the multi-cells water-cooling tower is determined and controlled by design specification DS-CT-FG-1, varying the mass flow rate (CT-AIR streams) of surrounding air passing through the fill (CT-TOW blocks), required to cooling down the hot water.

Treated fresh and recycled water as make-up water (WATER FROM TREATMENT PLANT) at atmospheric pressure and 25.0ºC is pumped (simplified by one pump) by make-up pump (CT-PUM-1) to the multi-cells water-cooling tower and mixed with the down flow cooled-water at 30.0ºC in the water-cooling tower basin (CT-MIX-1).

Cooling water available at 27.0ºC (heat sink) in the multi-cells water-cooling tower is pumped (CT-PUM-1) to CEST condenser (ST-CON-1).

All pumps (CT-PUM) and fans (CT-EFT) utilizing electric motor drivers are modeled and quoted according to commercial data for water-cooling tower-cell (capacity to cooling 700 tonnes/hr of hot water), in the calculus is considered only the pressure drop in the equipments the head loss in water/steam pipes were not considered due to lack of design information (pipe distance, height and diameter).

Fresh-water sources contain dissolved or suspended impurities, when water evaporates from the cooling tower the solids remain and become more concentrated. Eventually the solubility of the dissolved solids is exceeded resulting in the formation of mineral scale and sludge deposits in the condenser, tower fill and basin. A tower basin blowdown is necessary to reduce the concentration of impurities, is considered a continuous blowdown system (CT-SPL-1) and a treatment process to remove the solids formed (not simulated).

The cooling water at 27.0ºC is heated by passing through the user equipments to 43.0ºC (tower design limit), the hot water is duct-sent back to the multi-cells water-cooling tower (CT blocks) and discharged inlet into the cooling tower cells (CT-TOW blocks) at 43.0ºC to be cooled in a water closed-loop cycle system. The amount of water necessary for cooling down the equipments at required levels is determined and controlled by design specification DS-CT-FL-1, varying the mass flow rate of cooling water flows through the equipment users. The cooling water is heated at the limit of 43.0ºC (water-cooling tower design) and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

Hot water at 43.0ºC is fed in the multi-cells water-cooling tower (CT-TOW blocks) to be cooled down to 30.0ºC by direct contact in counter-flow with vertically upward induced (mechanical axial propeller fans) surrounding air through the fill (CT-TOW blocks) at atmospheric pressure and 25.0ºC. The model consider relative humidity of 80.0% and web bulb temperature at about 21.3ºC, which results in a range of 13.0ºC and an approach of 8.7ºC.

The Aspen Plus®v8.4 process model simulation of water-cooling tower system considers the water evaporation rate obtained by the Equation 21, and the drift loss rate obtained by the Equation 22, and employed in the CT-SPL-11 for the multi-cells water-cooling tower to determine the CT-EVA-1 and CT-DRI-1 streams by using FORTRAN calculator block CA-CT-LL-1.

A tower basin blowdown (CT-BLO streams) to remove or reduce the concentration of the impurities is developed in the Aspen Plus®v8.4 process model simulation according to Equation 25 as continuous blowdown system considering the tower basin blowdown (CT-BLO-1) and blowdown cycles of concentration (C.O.C) determined by using FORTRAN calculator block CA-CT-LL-1 to remove the solids formed (not included in the Aspen Plus®v8.4 process model simulation).

Make-up water (WATER FROM TREATMENT PLANT) is pumped by make-up pump (CT-PUM-1) to multi-cells water-cooling tower basin (CT-MIX-1), determined based on the water losses by evaporation (CT-EVA streams), drift (CT-DRI streams), and tower basin blowdown (CT-BLO streams), according to Equation 23.

In this research Master's degree, is considered a recovery of 87.0%$_{w/w}$ of the water blowdown after the treatment as available cooling water to reuse/recycle at 27.0ºC. The amount of water recovered is determined by spreadsheet calculation model of the cooling water treatment process according to Equation 24. The discarded water fraction contains a high concentration of impurities (e.g.: minerals and salts), not included in the Aspen Plus®v8.4 process model simulation.

The electricity required by the large mechanically driven axial fans (CT-EFT work streams) to induce the surrounding air upward through the fill in the cell-tower module (CT-TOW blocks) are estimated of 63.0 kWh per fan driver (module). The total of electricity required by the fan drivers is based on the number of cells (CT-TOW blocks) that compose the multi-cells water-cooling tower. The electricity consumed by the mechanical drivers in the axial fans (CT-EFT work streams) is determined based on the Equation 26 and controlled by FORTRAN calculator block CA-CT-EF-1 varying the input value of the CT-EFT-1 work stream according to the number of necessary fans (63.0 kWh per fan driver).

5.2.7 Water cycles

The water cycle balance consider receive water: from treatment plant (BO-L-1) to process make-up water to deaerator unit (BO-DEA-1) in the 1G CHP/CEST scenarios and 1G-CHP/EBPST scenarios; from treatment plant (PO-L-1 and PO-L-3) to desuperheater units (PO-MIX-1 and PO-MIX-2) in the 1G CHP/CEST scenarios; from treatment plant (CT-L-1) to water-cooling tower basin (CT-MIX-1) of the water-cooling tower system (CT blocks) in the 1G CHP/CEST scenarios.

Process steam/water loses occur due: water evaporation or condensation (PO-BLO-1) in equipments and tube lines (PO-SPL-1), discharging 5.0%$_{w/w}$ of the process steam at 2.5 bar (PO-BLO-1) in the 1G CHP/CEST scenarios and 1G-CHP/EBPST scenarios; treatment of boiler water blowdown discharge 15.0%$_{w/w}$ of the purged water (BD-BLO-1) (recovery and recycle of 85.0%$_{w/w}$ of the water blowdown) 1G CHP/CEST scenarios; treatment of water-cooling tower blowdown discharge 13.0%$_{w/w}$ of the water (recovery and recycle of 87.0%$_{w/w}$ of the water blowdown); water evaporation (CT-EVA-1) in the water-cooling tower (PO-SPL-1) TO ATMOSPHERE discharge 100.0%$_{w/w}$ of the water-stream in the 1G CHP/CEST scenarios; and water drift (CT-DRI-1) in the cooling tower (PO-SPL-1) TO ATMOSPHERE discharge 100.0%$_{w/w}$ of the water-stream in the 1G CHP/CEST scenarios.

As shown in Figure 29, deaerator unit (HR-DEA-1) in the 1G-CHP/EBPST scenarios receive steam: from the flash vessel (BD-FLASH-1) at 1.4 bar (deaerator pressure) and 109.0ºC (BD-G-1), steam at 2.5 bar and 130.0ºC (ST-G-6) from the second extraction (ST-SPL-2) in the 1G CHP/CEST scenarios or from exhaust steam (ST-SPL-2) in the 1G-CHP/EBPST scenarios, pre-heated (temperature depends on the scenario) fresh-water at 1.4 bar (BO-L-3) as make-up water (WATER FROM TREATEMENT PLANT) required in the deaerator unit (BO-DEA-1), water from the 1G sugarcane biorefinery processes at 2.5 bar and 90.0ºC (PO-L-6 and PO-L-7). Also, as shown in Figure 29, deaerator unit (BO-DEA-1) in the 1G-CHP/EBPST scenarios and 1G CHP/CEST scenarios send degassed and conditioned water at 1.4 bar and 105.0ºC to low-temperature economizers (BO-ECO-1) in the solid-fuel fired boiler bottoming-cycle system (BO blocks).

Steam at 2.5 bar and 130.0ºC (ST-SPL-2) from the second extraction (CEST) or from exhaust steam (EBPST) are used into the deaerator as degassing agent, main to remove dissolved O_2 and CO_2 content in the process water cycle by raises the feed-water (make-up water and process water condenser return) temperature to 105.0ºC at 1.4 bar in the deaerator unit (BO-DEA-1).

5.2.8 Make-up water and water treatments

Spreadsheet calculation model is applied to determine the mass flow rate of make-up water is required by the treatment plant (fresh-water use) of the optimized 1G sugarcane biorefinery. Global mass balance of the complete water cycle considering the treatment of the wastewater in conventional treatment plant (not simulated) is estimated according the spreadsheet calculation model of the water cycle (loss, recycle an reuse models).

Two distinct use types are required in the 1G CHP scenarios, classified as:

a) make-up water for water-cooling tower system (only for 1G CHP/CEST systems): fresh-water required by the cooling water cycle, defined by the mass flow rate of the evaporation, drift, and tower basin blowdown losses (not recovered);
b) make-up water for process water cycle: fresh-water required by the process water cycle is defined by mass flow rate of evaporative process and condensation losses in pipeline and equipments, vent streams, blowdown losses, and condensate knock-outs (not recovered);

After the wastewater treatment, the recovered water fraction (recycle/reuse) is considered as "fresh water" (subtracting in the quantity of fresh-water intake) and the water fraction discharged (not recovered) with the impurities in the wastewater treatment plant as "water losses".

The water treatment is simplified by considering the follow categories:

a) make-up raw water treatment: considers only the make-up of fresh-water obtained from the global mass balance of the complete water cycle, taking into account the recycle and reuse of water;
b) cooling water treatment (maintenance): considers the make-up raw water obtained from the mass balance of the water-cooling tower cycle and their water circulating in closed loop-cycle (water maintenance), taking into account the recycle and reuse of water;
c) process water treatment (maintenance): considers the make-up raw water obtained from the mass balance of the water process cycle and their water circulating in closed loop-cycle (water maintenance), taking into account the recycle and reuse of water;

The chemicals compounds and their consumption for treating water are determined by spreadsheet calculation model according to the type of water treatment required (make-up water, process water, cooling water and special water treatments). The water treatment is based on the water treatment processes available in the Ecoinvent 3 library (unit) of the SimaPro®v.7.3.3 software and in estimations for the water treatment plant for sugarcane biorefineries evaluated by the division of AIB of the CTBE/CNPEM.

Table 14 – Aspen Plus®v8.4 simulation parameters of CHP/CEST systems with integral use of available biomass (bagasse and straw) to generate surplus electricity and export to the electric power grid

(continues)

Parameters	CHP/CEST systems						
	SC1	**SC2**	**SC3**	**SC4**	**SC5** (ref)	**SC6**	**SC7**
1G sugarcane biorefinery							
Cane stalks (tonnes/hr) 4.0 Mtc (basis)	503.018	503.018	503.018	503.018	503.018	503.018	503.018
Sugar production (tonnes/hr)	25.559	25.559	25.559	25.559	25.559	25.559	25.559
Anhydrous ethanol production (tonnes/hr)	21.013	21.013	21.013	21.013	21.013	21.013	21.013
Electricity exported to the electric power grid (MWh)	59.089	88.230	90.595	97.007	99.012	97.942	94.998
Installed power generation capacity (MW)	75.879	105.261	107.897	114.630	116.717	115.755	113.320
Consumption of electricity by the 1G biorefinery (MWh)	16.789	17.030	17.302	17.624	17.706	17.813	18.322
Boiler feedstock handling and milling							
Sugarcane bagasse available for use (tonnes/hr)	133.150	133.150	133.150	133.150	133.150	133.150	133.150
Sugarcane straw available for use (tonnes/hr)	42.279	42.279	42.279	42.279	42.279	42.279	42.279
Sugarcane bagasse consumption (tonnes/hr)	126.492	126.492	126.492	126.492	126.492	126.492	126.492
Sugarcane bagasse reserve (tonnes/hr)	6.658	6.658	6.658	6.658	6.658	6.658	6.658
Sugarcane straw consumption (tonnes/hr)	42.279	42.279	42.279	42.279	42.279	42.279	42.279
Sugarcane bagasse moisture content ($\%_{w/w}$)	50.0	50.0	50.0	50.0	50.0	50.0	50. 0
Sugarcane straw moisture content ($\%_{w/w}$)	15.0	15.0	15.0	15.0	15.0	15.0	15.0
Total dry biomass consumption (tonnes/hr) [a]	98.765	98.765	98.765	98.765	98.765	98.765	98.765
Surplus biomass (tonnes/hr) [a]	none	none	none	none	none	none	none
HHV_{AR} of biomass mix (MJ/kg) [a]	11.10	11.10	11.10	11.10	11.10	11.10	11.10
LHV_{AR} of biomass mix (MJ/kg) [a]	9.21	9.21	9.21	9.21	9.21	9.21	9.21
LHV_{db} of biomass mix (MJ/kg) [a]	17.53	17.53	17.53	17.53	17.53	17.53	17.53
Biomass mix moisture ($\%_{w/w}$) [a]	41.28	41.28	41.28	41.28	41.28	41.28	41.28
Electricity required for handling and milling (MWh)	125.072	125.072	125.072	125.072	125.072	125.072	125.072
Solid solid-fuel fired boiler							
Atmospheric air flow to combustion chamber (tonnes/hr)	623264	609.041	595.422	595.422	595.422	595.422	582.095
Oxygen excess ratio ($\%_{w/w}$) [e]	12.00	10.00	8.00	8.00	8.00	8.00	6.00
Boiler combustion temperature (°C)	1522.7	1541.6	1560.0	1560.0	1560.0	1560.0	1578.1
bottom and fly-ashes removal from boiler (tonnes/hr)	4.534	4.534	4.534	4.534	4.533	4.534	4.534

Table 14 – Aspen Plus®v8.4 simulation parameters of CHP/CEST systems with integral use of available biomass (bagasse and straw) to generate surplus electricity and export to the electric power grid

(continue)

Parameter	CHP/CEST						
	SC1	**SC2**	**SC3**	**SC4**	**SC5 (ref)**	**SC6**	**SC7**
Solid solid-fuel fired boiler							
Exhaust-gas temperature (Flue-gas) (ºC)	160.0	160.0	160.0	155.0	150.0	150.0	135.0
Boiler water blowdown (to treatment) (tonnes/hr)	21.522	19.611	19.315	18.900	18.840	18.878	19.218
Steam pressure (bar)	22.0	45.0	65.0	85.0	90.0	96.0	120.0
Steam pressure (bar)	22.0	45.0	65.0	85.0	90.0	96.0	120.0
Steam temperature (ºC)	320.0	450.0	480.0	520.0	530.0	530.0	530.0
Stem generated by the boiler (tonnes/hr)	516.524	470.660	463.554	453.589	452.160	453.060	461.228
Boiler thermal efficiency 1 (%) [b]	86.74	86.79	86.77	87.01	87.27	87.26	88.00
Boiler thermal efficiency 2 (%) [b]	83.24	83.37	83.42	83.65	83.91	83.89	84.68
Condensing-extraction steam turbine (CEST)							
Steam extraction at 6.0 bar (dehydration) (tonnes/hr)	13.708	13.708	13.708	13.708	13.708	13.708	13.708
Steam extraction at 2.5 bar (process) (tonnes/hr)	184.578	184.578	184.578	184.578	184.578	184.578	184.578
Steam at 2.5 bar sent to deaerator (tonnes/hr)	32.162	26.648	25.128	23.555	23.266	23.136	23.013
6.0 bar steam temperature (ºC)	198.3	209.9	206.1	206.6	206.9	205.5	200.8
Electricity required by the 1G biorefinery (MWh)	15.0	15.0	15.0	15.0	15.0	15.0	15.0
Electricity consumed by the CHP/CEST system (MWh)	1.789	2.030	2.302	2.624	2.706	2.813	3.322
CHP/CEST net-electricity efficiency (%) [b]	17.07	23.79	24.33	25.81	26.27	26.03	25.35
CEST net-electricity efficiency (%) [c]	19.68	27.41	28.04	29.66	30.10	29.83	28.80
Make-up water to deaerator unit (with recycle) (kg/hr) [d]	11.792	11.314	11.128	10.961	10.927	10.896	10.795
Multi-cells water-cooling tower							
Number of tower cells required to cool-down water	14	12	11	11	11	11	12
Make-up water (with recycle) (tonnes/hr)	206.001	171.908	169.564	163.371	162.526	163.718	186.647
Water evaporation (tonnes/hr)	184.755	154.178	152.076	146.521	145.764	146.833	154.042
Water drift (tonnes/hr)	18.578	15.503	15.292	14.733	14.657	14.764	15.489
Tower basin blowdown (to treatment) (tonnes/hr)	20.528	17.131	16.897	16.280	16.196	16.315	17.116
Electricity required by fan drivers (kWh)	882	756	693	693	693	693	756

Table 14 – Aspen Plus®v8.4 simulation parameters of CHP/CEST systems with integral use of available biomass (bagasse and straw) to generate surplus electricity and export to the electric power grid

(conclusion)

Water cycle [d]							
Process maintenance (tonnes/hr)	26.213	23.024	21.785	20.673	20.443	20.239	19.569
Cooling water maintenance (tonnes/hr)	223.861	186.812	184.265	177.534	176.617	174.614	186.647
Make-up raw water (tonnes/hr)	217.794	183.222	180.692	174.332	173.453	163.718	182.552

(ref) reference scenario

[a] biomass refers to sugarcane bagasse and sugarcane straw

[b] efficiency based on LHV_{AR} of biomass at 25ºC and 1 atm

[c] efficiency based on useful heat generated by the boiler and transferred to water/steam

[d] only account for the water cycle the CHP/CEST system and the steam (heat) to equipment users in the 1G sugarcane biorefinery

[e] based on oxygen inlet and not in the stoichiometric oxygen for combustion

Table 15 – Aspen Plus$^{®}$v8.4 simulation parameters of CHP/EBPST systems with partial use of available biomass (bagasse and straw) to supply the thermal and electrical energy demands of the 1G sugarcane biorefinery with surplus biomass and electricity

(continues)

Parameter	CHP/EBPST systems						
	SC1 $^{(int)}$	**SC2**	**SC3**	**SC4**	**SC5 $^{(ref)}$**	**SC6**	**SC7**
1G sugarcane biorefinery							
Cane stalks (tonnes/hr) 4.0 Mtc (basis)	503.018	503.018	503.018	503.018	503.018	503.018	503.018
Sugar production (tonnes/hr)	25.559	25.559	25.559	25.559	25.559	25.559	25.559
Anhydrous ethanol (tonnes/hr)	21.013	21.013	21.013	21.013	21.013	21.013	21.013
Electricity exported to the electric power grid (MWh)	3.363	17.437	19.727	23.611	24.624	24.212	22.544
Installed power generation capacity (MW)	18.669	32.927	35.373	39.414	40.465	40.099	38.607
Consumption of electricity by the 1G biorefinery (MWh)	15.306	15.494	15.646	15.802	15.841	15.887	16.063
Boiler feedstock handling and preparation							
Sugarcane bagasse available for use (tonnes/hr)	133.150	133.150	133.150	133.150	133.150	133.150	133.150
Sugarcane straw available for use (tonnes/hr)	42.279	42.279	42.279	42.279	42.279	42.279	42.279
Sugarcane bagasse consumption (tonnes/hr)	81.376	89.069	90.205	92.011	92.233	92.001	90.024
Sugarcane bagasse reserve (tonnes/hr)	6.658	6.658	6.658	6.658	6.658	6.658	6.658
Sugarcane straw consumption (tonnes/hr)	none	none	none	none	none	none	none
Sugarcane bagasse moisture content ($\%_{w/w}$)	50.0	50.0	50.0	50.0	50.0	50.0	50.0
Sugarcane straw moisture content ($\%_{w/w}$)	15.0	15.0	15.0	15.0	15.0	15.0	15.0
Total dry biomass consumption (tonnes/hr) [a]	40.691	44.531	45.108	46.001	46.120	46.004	45.018
Surplus biomass (tonnes/hr) [a]	87.396	79.703	78.567	76.762	76.538	76.771	78.747
HHV_{AR} of biomass mix (MJ/kg) [a]	9.44	9.45	9.45	9.45	9.45	9.45	9.45
LHV_{AR} of biomass mix (MJ/kg) [a]	7.45	7.45	7.45	7.45	7.45	7.45	7.45
LHV_{db} of biomass mix (MJ/kg) [a]	17.51	17.51	17.51	17.51	17.51	17.51	17.51
Biomass mix moisture ($\%_{w/w}$) [a]	50.0	50.0	50.0	50.0	50.0	50.0	50.0
Electricity required for handling and milling (MWh)	none	none	none	none	none	none	none
Solid solid-fuel fired boiler							
Atmospheric air flow to combustion chamber (tonnes/hr)	256.178	274.108	271.491	276.924	277.596	276.896	265.077
Oxygen excess ratio ($\%_{w/w}$) [e]	12.0	10.0	8.0	8.0	8.0	8.0	6.0
Boiler combustion temperature (ºC)	1387.3	1403.4	1419.3	1419.3	1419.3	1419.3	1434.8
Generation of bottom ashes (tonnes/hr)	1.366	1.495	1.514	1.544	1.548	1.544	1.511
Fly-ashes removal by emission control filters (fine matter) (tonnes/hr)	0.420	0.460	0.466	0.475	0.477	0.475	0.465
Exhaust-gas temperature (Flue-gas) (ºC)	160.0	160.0	160.0	155.0	150.0	150.0	135.0

Table 15 – Aspen Plus®v8.4 simulation parameters of CHP/EBPST systems with partial use of available biomass (bagasse and straw) to supply the thermal and electrical energy demands of the 1G sugarcane biorefinery with surplus biomass and electricity

(conclusion)

Parameter	CHP/EBPST systems						
	SC1	SC2	SC3	SC4	SC5 (ref)	SC6	SC7
Solid solid-fuel fired boiler							
Boiler water blowdown (to treatment) (tonnes/hr)	8.459	8.430	8.411	8.396	8.393	8.389	8.373
Steam pressure (bar)	22.0	45.0	65.0	85.0	90.0	96.0	120.0
Steam temperature (ºC)	320.0	450.0	480.0	520.0	530.0	530.0	530.0
Stem generated by the boiler (tonnes/hr)	203.017	202.310	201.871	201.507	201.424	201.326	200.958
Boiler thermal efficiency 1 (%) [b]	86.81	86.80	86.80	87.07	87.31	87.34	88.26
Boiler thermal efficiency 2 (%) [b]	83.16	83.22	83.30	83.54	83.83	83.82	84.77
Extraction back-pressure steam turbine (EBPST)							
Steam extraction at 6.0 bar (dehydration) (tonnes/hr)	13.708	13.708	13.708	13.708	13.708	13.708	13.708
Exhaust steam at 2.5 bar (process) (tonnes/hr)	184.578	184.578	184.578	184.578	184.578	184.578	184.578
Steam at 2.5 bar sent to deaerator (tonnes/hr)	4.730	4.023	3.585	3.220	3.136	3.039	2.672
6.0 bar steam temperature (ºC)	198.3	209.9	206.1	206.6	206.9	205.5	200.8
2.5 bar steam temperature (ºC)	130.0	130.0	130.0	130.0	130.0	130.0	130.0
Electricity required by the 1G biorefinery (MWh)	15.0	15.0	15.0	15.0	15.0	15.0	15.0
Electricity consumed by the CHP/CEST system (MWh)	0.306	0.494	0.646	0.802	0.842	0.887	1.064
CHP/EBPST net-electricity efficiency (%) [b]	10.77	17.39	18.39	20.04	20.52	20.35	19.92
EBPST net-electricity efficiency (%) [c]	12.41	20.03	21.17	23.02	23.49	23.30	22.56
Make-up water to deaerator unit (with recycle) (kg/hr) [d]	10.248	10.136	10.066	10.009	9.996	9.980	9.922
Multi-cells water-cooling tower							
Number of tower cells required to cool-down water	none	none	none	none	none	none	none
Water cycle [d]							
Process maintenance (tonnes/hr)	15.916	15.169	14.707	14.323	14.235	14.132	13.744
Cooling water maintenance (tonnes/hr)	none	none	none	none	none	none	none
Make-up raw water (tonnes/hr)	10.248	10.136	10.066	10.009	9.996	9.980	9.922

(ref) reference scenario (surplus electricity)

(int) reference scenario for surplus biomass and integration with thermochemical routes

[a] biomass refers to bagasse

[b] efficiency based on LHV_{AR} of biomass at 25ºC and 1 atm

[c] efficiency based on useful heat generated by the boiler and transferred to water/steam

[d] only account for the water cycle the CHP/CEST system and the steam (heat) to equipment users in the 1G sugarcane biorefinery

[e] based on oxygen inlet and not in the stoichiometric oxygen for combustion

6 Biomass integrated directly-heated gasifier and internal combustion engine in combined-cycle integrated at an optimized first generation sugarcane biorefinery with annexed ethanol distillery

Biomass integrated biomass gasification with internal combustion engine in combined-cycle (BIG-ICE/CC) system for electrical energy production is an alternative for large power plants, competing with the advanced CHP systems. Biomass-to-electricity is a well-known electricity-generating option in the Brazilian electricity sector playing an important role in the renewable energy sector (Figure 18), accounted for 7.6% of electricity consumption in 2013.

Sugarcane bagasse and straw gasification to produce synthesis gas (combustible gas) and their use in ICEs can provides much more efficient conversion of available biomass into electricity than the traditional efficient CHP/CEST systems (e.g.: CHP/CEST (SC5)) (biomass-combustion to electricity generation), with environmental advantages front the gas-fired power generation sector.

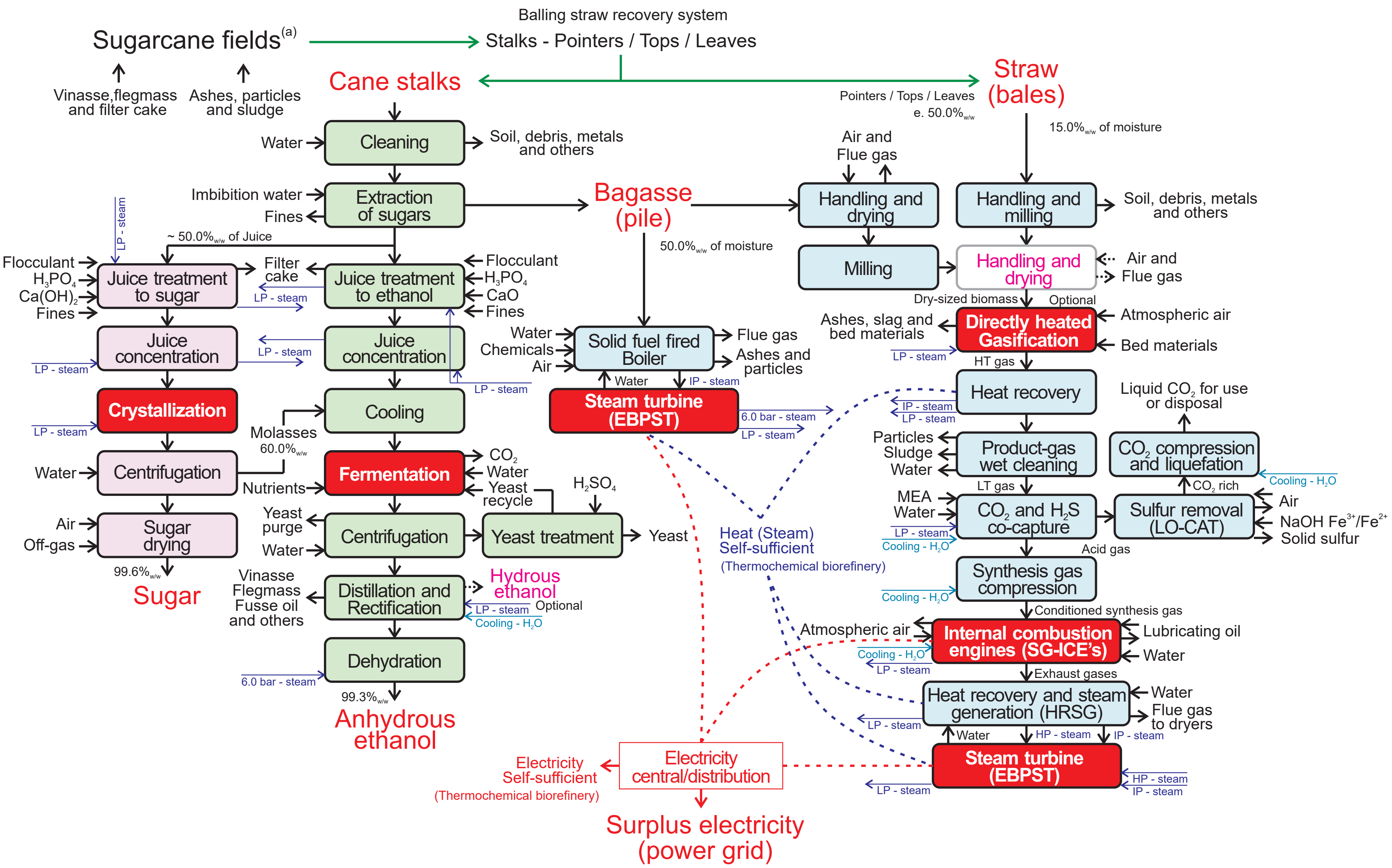
Replacing coal-fired and natural gas-fired plants by BIG-ICE/CC system to export electricity to the power grid can be an alternative to most reduction in the fossil resource dependence (e.g.: natural gas and oil) and in the pollutants emissions, with potential reduction main on climate change (CC) and fossil depletion (FD) impact indicators.

6.1 Scenarios assessed

Two possible thermochemical-biorefinery scenarios applying BIG-ICE/CC system were simulated in Aspen Plus$^{®}$v8.4 process simulation platform and assessed under the scope of VSB tool, taking into account the integral use of available sugarcane bagasse and straw for the efficient production of electricity while supply the thermal and electrical energy required by the thermochemical-biorefinery.

Thermochemical-biorefinery scenarios applying BIG-ICE/CC system are defined in the section 3.4.2 (Biomass integrated directly-heated gasifier and internal combustion engine in combined-cycle). A scheme of the sugar, ethanol, and electricity production from BIG-ICE/CC route integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery is detailed in the Figure 31 for the BIG-ICE/CC scenario 1 (SC1), and in the Figure 32 for BIG-ICE/CC scenario 2 (SC2).

Figure 31 - Flow block diagram of biomass integrated directly-heated gasifier and internal combustion engine in combined-cycle (BIG-ICE/CC) in energy and mass integration mode integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery: Scenario 1 (SC1)



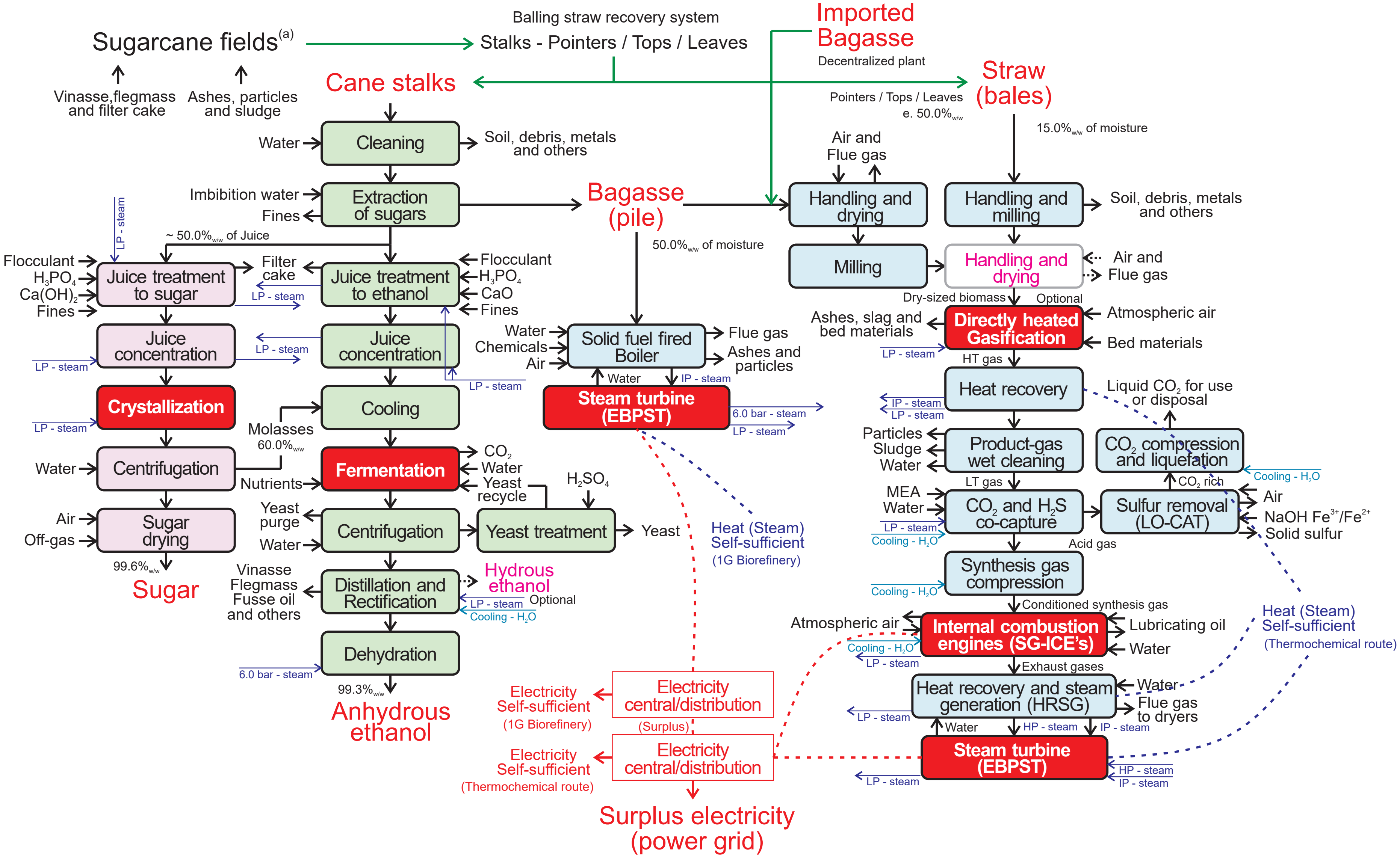


Figure 32 - Flow block diagram of biomass integrated directly-heated gasifier and internal combustion engine in combined-cycle (BIG-ICE/CC) in standalone mode integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery. Scenario 2 (SC2)

BIG-ICE/CC scenarios 1 (SC1) and BIG-ICE/CC scenario 2 (SC2) are integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery according to section 5 (First generation sugarcane biorefinery), and to agricultural and industrial phases of the 1G sugarcane biorefinery assessed by the division of AIB of the CTBE/CNPEM and published – *The Virtual Sugarcane Biorefinery (VSB)*: 2011 Report (BRAZILIAN BIOETHANOL SCIENCE AND TECHNOLOGY LABORATORY, 2012) – and in – Virtual Biorefinery: An Optimization Strategy for Renewable Carbon Valorization (BONOMI et al., 2016).

BIG-ICE/CC route scenarios were implemented in Aspen Plus®v8.4 process simulation platform to evaluate the electricity generation while supply the thermal and electrical energy requirements for the thermochemical-biorefinery. Available sugarcane bagasse and straw are gasified in an atmospheric CFB directly-heated gasifier using atmospheric air and steam gasification agents to produce low-medium LHV synthesis gas. Therefore, is conditioned and then used in multiples single-gas fueled (SG) spark-ignited (SI) internal combustion engine (ICE), with turbo charging system operating according to lean-burn four-stroke Otto-cycle in combined-cycle (CC) mode with steam turbine (ST) system (Rankine-cycle cogeneration system) for thermochemical route-cycles.

Aspen Plus®v8.4 complete flowsheet`s of BIG-ICE/CC detailed scenarios are presented in the APPENDIX A. Figure A15 shows BIG-ICE/CC scenario 1 (SC1), and Figure A16 shows the BIG-ICE/CC scenario 2 (SC2).

6.1.1 Physical properties

The GLOBAL property methods used are ELECNRTL, and RKS-BM.

The local properties method used is: IDEAL for biomass handling and sizing, biomass multi-step dryer and control particulate emissions, and lubricating oil side in the SG-ICE with turbo charging system; RKS-BR for biomass multi-step dryer and control particulate emissions, gasification of biomass in an atmospheric CFB directly-heated gasifier, syngas cooling and heat recovery, CO_2 compression and storage/use, synthesis gas compression (conditioning), SG-ICE with turbo charging system, HRGS system, traditional CHP system applying EBPST system, and for gaseous streams side; ELECNRTL for low-temperature synthesis gas wet cleaning system, and co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution; IAPWS-95 for multi-cells water-cooling tower, Water cycles, BPST and CEST systems for thermochemical route-cycles, traditional CHP system applying EBPST system, for pure water-side streams, and for pure steam-side streams.

Non-conventional solids physical property method used for BAGASSE and STRAW component properties is the HCOALGEN model (general coal models) applying the Mott and Spooner correlation (4 option code) according to section 3.7 (Non-conventional solids physical property methods) for estimate the enthalpy, and COALIGT model for estimate the density.

6.1.2 Available raw biomass

Raw sugarcane bagasse (SUGARCANE BAGASSE) is represented by BAGASSE and SOIL streams according to Table 9, and raw sugarcane straw (SUGARCANE STRAW) is represented by STRAW and TRASH according to Table 9. METAL stream was added to represent the amount of the tramp metals removed by the magnetic head pulleys (inlet-to-outlet model). Others debris were not considered present (to specify removal process) and can be accounted for in the trash fraction (TRASH) as inert material.

Sugarcane straw (SUGARCANE STRAW) is collected from the field (after the sugarcane harvesting) using a baling system (with pre-chopping system). In this system, the straw is sent separately from the cane stalks to the thermochemical-biorefinery. The transport is made using trucks (up to 25 tonnes per vehicle) or road trains (up to 70 tonnes per vehicle). All the BIG-ICE/CC scenarios consider that 50.0%$_{w/w}$ of the total sugarcane straw available is recovered and send to the thermochemical-biorefinery with 15.0%$_{w/w}$ of moisture content (on-site). As the transport vehicle enters the plant, they are weighed and the straw bales are dumped (PR-MIX-3) or removed by adapted cane loaders and stored (PR-MIX-3) as feedstock for further processes.

In the BIG-ICE/CC (SC1), part of available bagasse (BAGASSE) is belt-conveyed directly to the traditional CHP/EBPST system or to bagasse pile (PR-SPL-1) for burning purpose, generating thermal and electrical energy to supply part of the energy required by the 1G sugarcane biorefinery while BIG-ICE/CC route supply the other part. In the BIG-ICE/CC (SC2), part of the available bagasse (SUGARCANE BAGASSE) is burned to generate the thermal and electrical energy to supply all of this energy required by the 1G sugarcane biorefinery. Surplus bagasse (SUGARCANE BAGASSE) from the boiler-pile or directly from the cane mills is conveyed (centralized plant) or transported (decentralized plant) as available feedstock to the BIG-ICE/CC plant together imported bagasse (scale setting).

6.1.3 Biomass handling and sizing

Sugarcane bagasse (SUGARCANE BAGASSE) with 50.0%$_{w/w}$ of moisture content after the cane mills (driver by electrical motors) is transported by a conveyor (screw, drag or belt) to a temporary pile (PR-SPL-1) (feeding or equalization pile) or sent directly to the bagasse flash dryers (DR-DRY-1) by feeder conveyor (PR-MIX-1). In the BIG-ICE/CC (SC1), part is sent to biomass feed drum (PR-MIX-5) in the traditional solid-fuel fired boiler (BO blocks) to burning in the boiler chamber (BO-COMBU).

In the Aspen Plus®v8.4 process model simulation 5.0%$_{w/w}$ of the raw bagasse (BAGASSE) is reserved (PR-SPL-1) in the pile (RESERVE BAGASSE) for brief stops and start-ups. In the BIG-ICE/CC (SC1), part of the raw bagasse (BAGASSE) can be used as received (wet) from the cane mills to be burned in the solid-fuel fired boiler (BO-COMBU). Another part of the raw bagasse (BAGASSE), from the cane mills or temporary bagasse pile (PR-SPL-1) is screw-conveyed (PR-SCR-2) directly to first-stage bagasse flash dryer (DR-DRY-1) to reduce the moisture content before the gross-size reduction stage (PR-CRU-1).

As shown in Figure 33, Aspen Plus®v8.4 flowsheet of the biomass handling and sizing in the BIG-ICE/CC (SC1) with 1G-CHP/EBPST system considers that the raw bagasse (SUGARCANE BAGASSE) wherein the bagasse (SUGARCANE BAGASSE) from the cane mills can be directly belt-conveyed (PR-SCR-8) to boiler fuel feeders. Moreover, the model also consider fed from the temporary bagasse pile (PR-SPL-1) by using a tractor (actual system) to carries part of the bagasse available to the conveyor boiler feed tray (PR-MIX-5).

As shown in Figure 34, Aspen Plus®v8.4 flowsheet of the biomass handling and sizing in the BIG-ICE/CC (SC2) considers that the raw bagasse (BAGASSE) from the cane mills or temporary bagasse pile (PR-SPL-1) are screw-conveyed (PR-SCR-2) directly to first-stage bagasse flash dryer (DR-DRY-1) to reduce the moisture content before the gross-size reduction stage (PR-CRU-1). After the first-stage of drying (DR-DRY-1), the bagasse is belt-conveyed (PR-SCR-1) to a pre-milling bagasse machine (PR-CRU-1) to gross-size reduction. After this stage, the bagasse is classified in a screen-deck solid-solid classifier (PR-CLA-2), the fine fraction is directly screw-conveyed (PR-SCR-2) to bagasse second-flash dryer (DR-DRY-1) and the oversized fraction is recycled and mixed back (PR-MIX-2) for further gross-size reduction cycle in closed-loop at size requirements. Gross-sized and pre-dried bagasse is screw-conveyed (PR-SCR-2) to bagasse second-flash dryer (DR-DRY-1) to reduce the moisture content to 10.0%$_{w/w}$ (dry bagasse) before the fine-size reduction stage (PR-CRU-1).

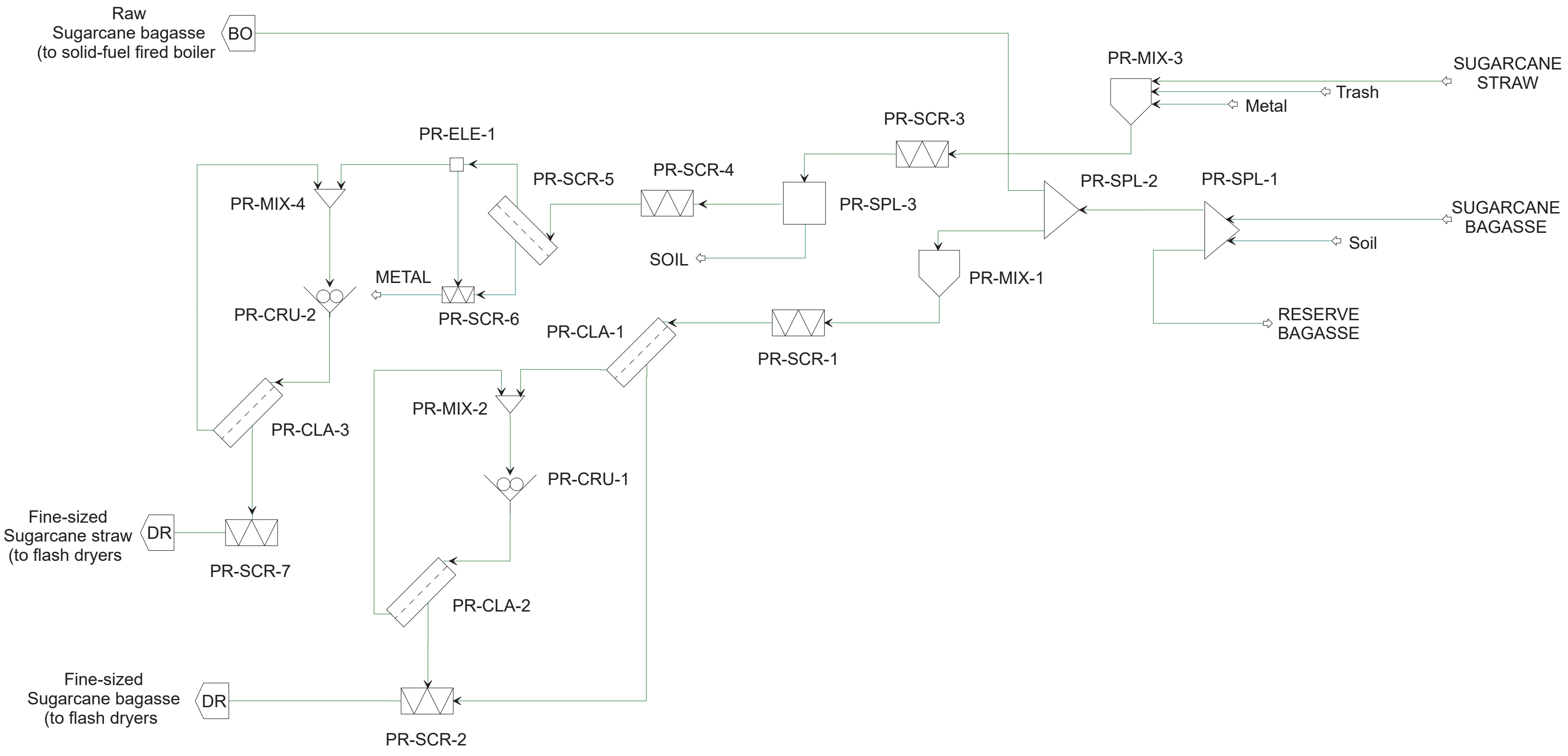


Figure 33 - Aspen Plus® v8.4 flowsheet of the biomass handling and sizing for BIG-ICE/CC (SC1)

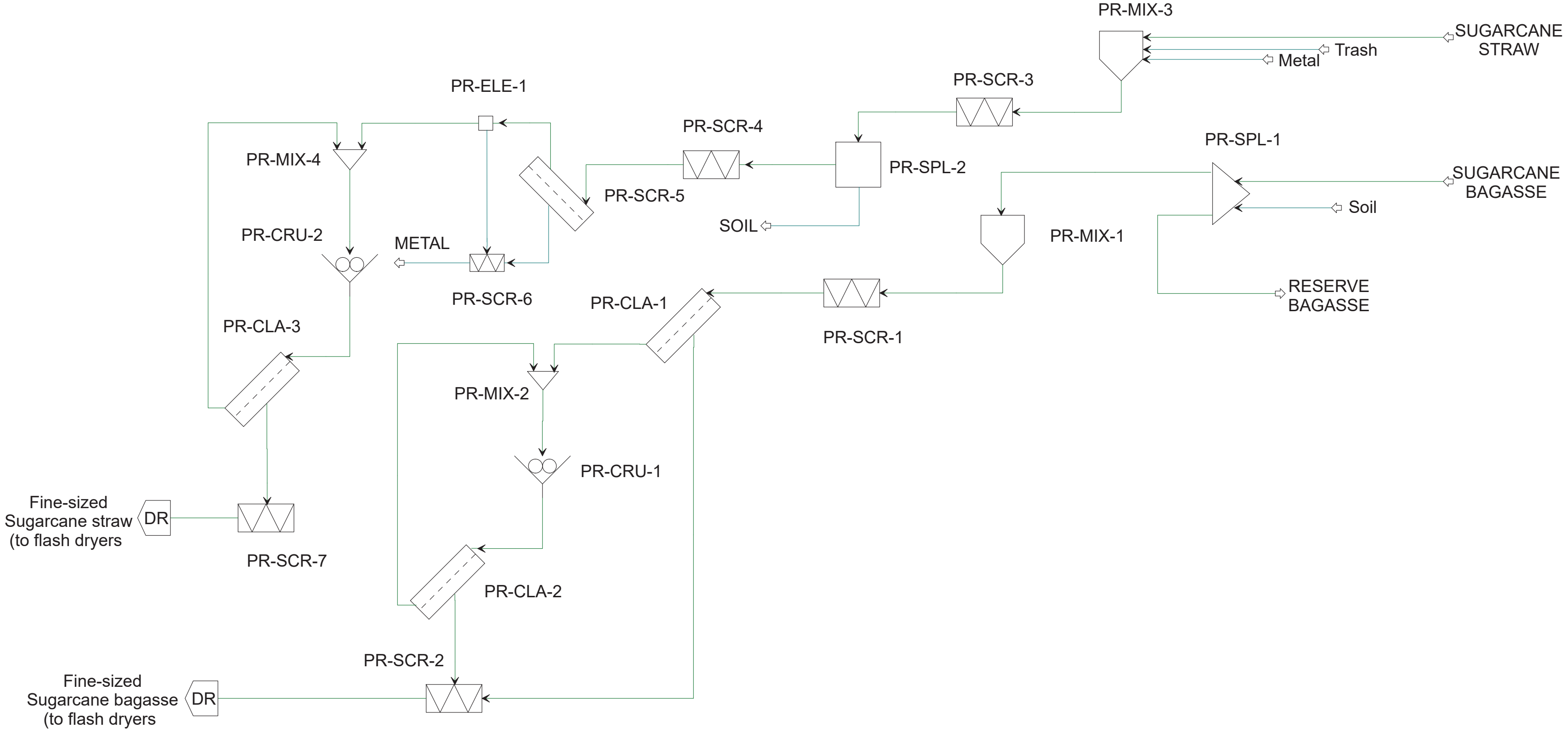


Figure 34 - Aspen Plus® v8.4 flowsheet of the biomass handling and sizing for BIG-ICE/CC (SC2)

As shown in Figure 33, Aspen Plus®v8.4 flowsheet of the simplified aggregated-steps model for the biomass handling and sizing in the BIG-ICE/CC (SC1) and as shown in Figure 34 the Aspen Plus®v8.4 flowsheet of the simplified aggregated-steps model for the biomass handling and sizing in the BIG-ICE/CC (SC2) are compost by: dumper (PR-MIX-3); storage area (PR-MIX-3); temporary bagasse pile (PR-SPL-1 and PR-SPL-3); bagasse pre-milling machine (PR-CRU-1); bagasse fine-size milling machines (DR-CRU-1); straw fine-size cutting-milling machine (DR-CRU-2); pre-sizing bagasse screen-deck solid-solid classifier (PR-CLA-1); bagasse screen-deck solid-solid classifier (PR-CLA-2); straw screen-deck solid-solid classifier (PR-CLA-3); oversized bagasse mixer (PR-MIX-2); unpacking and preparation area (PR-SPL-2); magnetic head pulleys (PR-ELE-1); magnetic separator (PR-SCR-5); screw-conveyor (PR-SCR-7); oversized straw mixer (PR-MIX-4); belt-conveyor (PR-SCR-1); bagasse feeder conveyor (PR-MIX-1); transporter (PR-SCR-3); screw-conveyor (PR-SCR-2); drag-conveyor (PR-SCR-4); screw-conveyor (PR-SCR-6); and screw-conveyor (PR-SCR-7).

This model is an old version when the platform did not own a rigorous modeling of solids drying and grinding processes (currently there are rigorous and phenomenological models). The model does not take into account the phenomenological coupled effects of drying and milling processes in the energy (thermal and electrical) consumption, allowing the multi-stage process may be aggregated into a single block-stage model.

The gross-sized and dried bagasse is belt-conveyed (PR-SCR-1) to pre-sizing classification in a screen-deck solid-solid classifier (PR-CLA-1), being classified according to ideal function for 2.0 mm of cut size (thickness). After, is sent to the fine-size milling machine (PR-CRU-1) to fine-size reduction and classification in a screen-deck solid-solid classifier (PR-CLA-2) according to ideal function for 2.0 mm of cut size (thickness). The fine fraction is screw-conveyed (PR-SCR-2) to gasifier feed drum (DR-MIX-4) and the oversized fraction is recycled and mixed back (PR-MIX-2) for further fine-size reduction cycle.

Aspen Plus®v8.4 process model simulation of the bagasse gross-size milling and fine-size milling machines (DR-CRU-1) are combined in a single-block model. The single block-stage model was developed by using a Crusher solids block to represent the particle diameter reduction to a maximum of 4.0 mm of thickness according to Gates-Gaudin-Schuhmann general cumulative distribution function to avoid 50.0%$_{w/w}$ of the bagasse mass flow rate with more than 2.0 mm of thickness.

The straw bales delivered (STRAW+TRASH+METAL) are transported (PR-SCR-3) to unpacking and preparation area (PR-SPL-2), considering a pre-chopping process in the field by the straw baling machine. The straw bales are unpacked (PR-SPL-2), the over sized or hardest biomass, and heavier particles (rocks) delivered with the straw bales is separated and screwed-out. In these processes is considered removal 50.0%$_{w/w}$ of the soil fraction content in the trash (TRASH), accumulated due to contact with the agricultural land.

The electrical power work required by the bagasse size reduction and handling system is estimated as 22.0 kWh per tonnes of wet bagasse inlet in the sizing system. It is set in bond work index by design specification DS-PR-PC-1. In addition, outlet PSD distribution is determined by Bond's comminution power law and a sizing distribution function.

Unpacked-straw (pre-chopped) is drag-conveyed (PR-SCR-4) to the magnetic separation (PR-SCR-5) (prevent damages) by magnetic head pulleys (PR-ELE-1) to remove the tramp metals (METALS) along with 5.0%$_{w/w}$ of the soil content, its fraction is screwed-out (PR-SCR-6) to final disposal or sent to be recycled (metals). After removal the debris (TRASH) and ferrous metals, the straw is belt-conveyed to a cutting-milling straw machine (PR-CRU-2) to fine-size reduction with size-classification by screen-deck solid-solid classifier (PR-CLA-3) according to ideal function for 2.0 mm of cut size (thickness). The fine fraction is directly screw-conveyed (PR-SCR-7) to straw flash dryer (DR-DRY-2) and the oversized fraction is recycled and mixed back (PR-MIX-4) for further fine-size reduction cycle.

Aspen Plus®v8.4 process model simulation of the straw fine-size cutting-milling machine (DR-CRU-2) was developed by using a Crusher solids block to represent the particle diameter reduction. The model consider a maximum of 4.0 mm of thickness according to Gates-Gaudin-Schuhmann general cumulative distribution function to avoid 50.0%$_{w/w}$ of the straw mass flow rate with more than 2.0 mm of thickness.

The electrical power work required by the straw size reduction and handling system is estimated based on chopper's machines and fine-size cutting-milling processes for sugarcane straw as 8.0 kWh per tonnes of wet straw inlet in the sizing system (after the magnetic head pulleys). It is set in the bond work index using the design specification DS-PR-PC-2. In addition, outlet PSD distribution is determined by Bond's comminution power law and a sizing distribution function.

Sized straw is screw-conveyed (PR-SCR-7) to straw flash dryer (DR-DRY-2). In some cases (dry straw recovery conditions), there may not be need of drying the straw and then this can bypass the straw flash dryer (DR-DRY-2) and be directly belt-conveyed to the gasifier feed drum (DR-MIX-3).

6.1.4 Biomass multi-step dryer and control particulate emissions

The raw moist bagasse is fed by screw-conveyor (PR-SCR-2) into parallel bagasse flash dryer trains (DR-DRY-1). The moisture content is reduced from 50.0%$_{w/w}$ to 10.0%$_{w/w}$ in a multi-steps drying process (DR-DRY-1).

Sized straw with higher-moisture content (considered 15.0%$_{w/w}$), recovered in rain conditions (or which has been humidified) is belt-conveyed to dryer feeder drum and screw-conveyed (PR-SCR-7) to straw flash dryer (DR-DRY-2). Sized straw with lower-moisture content (equal or less than 10.0%$_{w/w}$) obtained on dry straw recovery conditions (not considered in this research Master's degree) bypass the straw flash dryer (DR-DRY-2) and is directly belt-conveyed to the gasifier feed drum (DR-MIX-3).

Figure 35 shows the Aspen Plus®v8.4 flowsheet of the biomass multi-step dryer and control particulate emissions implemented for BIG-ICE/CC (SC1) and for BIG-ICE/CC (SC2).

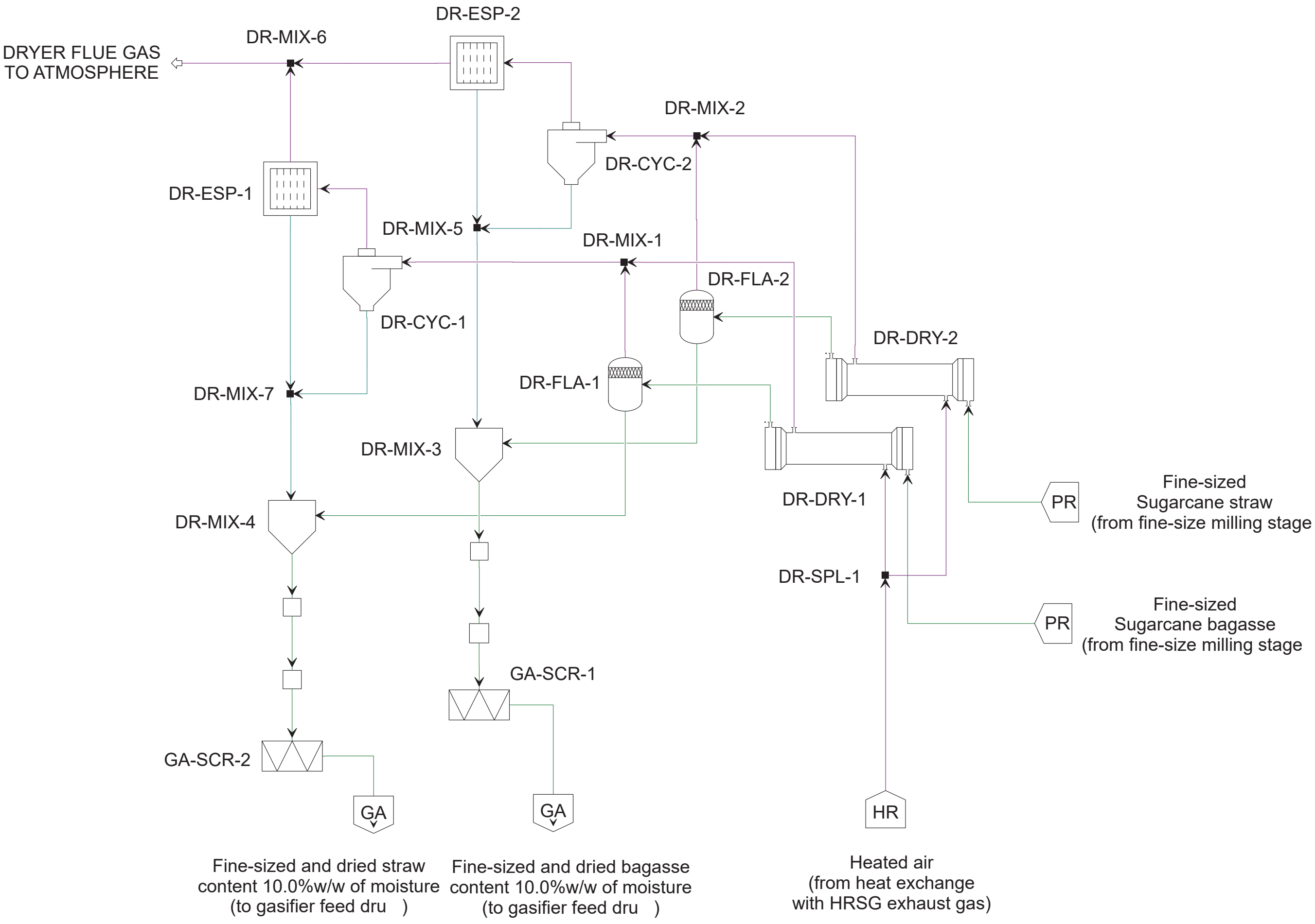


Figure 35 - Aspen Plus®v8.4 flowsheet of the biomass multi-step dryer and control particulate emissions for BIG-ICE/CC (SC1) and for BIG-ICE/CC (SC2)

As shown in Figure 35, Aspen Plus®v8.4 flowsheet of the simplified aggregated-steps model of the biomass multi-step dryer and control particulate emissions in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2) is compost by: first-stage bagasse flash dryer (DR-DRY-1); second-stage bagasse flash dryer (DR-DRY-1); straw flash dryer (DR-DRY-2); advanced blower system (DR-ASP-1); pre-filter unit (DR-FIL-1); bagasse after-dryer single-cyclone (DR-CYC-1); straw after-dryer single-cyclone (DR-CYC-2); bagasse electrostatic precipitator (DR-ESP-1); straw electrostatic precipitator (DR-ESP-1); fine-solids mixer 1 (DR-MIX-7); fine-solids mixer 2 (DR-MIX-8); straw gasifier storage bin (DR-MIX-3); bagasse gasifier storage bin (DR-MIX-4); gaseous mixer 1 (DR-MIX-1); gaseous mixer 2 (DR-MIX-2); flash separator 1 (DR-FLA-1); and flash separator 2 (DR-FLA-2).

Fresh drying air agent (ATMOSPHERIC AIR) is indirect preheated using the dryer humidified exhaust-gas and heated (DR-HEA-1) using only the HRSG flue-gas or a mixture of the HRSG flue-gas with 1G-CHP/EBPST exhaust-gas. In the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2), drying air agent is heated to 120.0ºC.

The hot-air drying agent is forced-injected at atmospheric pressure in the bagasse multi-stage flash dryer (DR-DRY-1) and straw flash dryer (DR-DRY-2) by advanced blower system (DR-ASP-1) modeled by using a Compr pressure changer block according to isentropic method for compressor considering 85.0% isentropic efficiency and 99.0% mechanical efficiency. A pre-filter unit (DR-FIL-1) modeled by using a FabFl solids separator block according to Piecewise separation efficiency in function of the particle diameter of the solids is used to protect the blower and the flash dryers from debris (PARTICLES). The advanced blower system (DR-ASP-1) is used to adjust the mass flow rate of the hot-air drying agent required by the drying process (technical assessment) and equalize the drop pressure of the system to atmospheric discharge condition in the dryer flue-gas (FLUE-GAS FROM STACK).

The multi-step bagasse flash dryer (DR-DRY-1) and the straw flash dryer (DR-DRY-2) is modeled by using a HeatX exchanger block coupled with a Flash2 separator block operating at atmospheric pressure (no pressure drop consideration). The model represents the direct contact of hot-air drying agent with bagasse (DR-FLA-1) and straw (DR-FLA-2), and the resultant thermal and fluid dynamic effects.

The thermal exchange models consider that the biomass heat at saturation temperature (at about 100.0ºC for atmospheric pressure) to liquid-vapor equilibrium phase to separate the moisture content (flash model principles). The direct contact model consider drag $0.2\%_{w/w}$ of the total biomass (daef) fed as biomass fine fibers and $0.1\%_{w/w}$ of the total particles (e.g.: soil and others) as fine particles due the high mass flow rate and the turbulence of the drying air agent. The model also considers that $0.01\%_{w/w}$ of the moisture contained in the biomass is entrained together with the particulate emissions (without energetic consumption to evaporate). Extractives, volatile organic compounds, and the moisture content in the biomass are evaporated according to flash equilibrium model (DR-MIX-1 for bagasse model, and DR-MIX-2 for straw model). Hence, they are emitted to atmosphere together the drying air agent in the dryer flue-gas (FLUE-GAS FROM STACK).

The fine-sized and dried straw (solid phase) content $10.0\%_{w/w}$ of moisture after the straw flash dryer (DR-FLA-2) is belt-conveyed to a gasifier feed drum (DR-MIX-4).

The raw wet bagasse is dried in a first-stage bagasse flash dryer (DR-DRY-1) to reduce the moisture content before the gross-size reduction stage (PR-CRU-1). Lower moisture content easiest the process of gross-size milling (DR-CRU-1), and reduce the thermal energy required by this first-stage, the moisture content level affect the machine performance. After gross-sized, the bagasse is sent back to a second-stage bagasse flash dryer (DR-DRY-1) to reduce the moisture content to 10.0%$_{w/w}$, before the fine-size milling stage. The gross-sized and dried bagasse (solid phase) with 10.0%$_{w/w}$ of moisture content is belt-conveyed to gross-size milling machine (DR-CRU-1) to reduce the size particle at gasifier required level.

The first-stage and second-stage of the bagasse flash dryer (DR-DRY-1) combined in a single-block model, and the straw flash dryer (DR-DRY-2) are modeled by using a HeatX exchanger block and Flash2 separator block. Estimate the thermal energy required by the biomass flash dryers (DR-DRY-1 and DR-DRY-2) to reduce the moisture content of bagasse and straw to 10.0%$_{w/w}$ by using hot-air agent, inlet at 120.0ºC and outlet at about 100.0ºC.

The hot-air mass flow rate is controlled by design specification DS-DR-TG-1 to distribute the air-flow in order to obtain the same outlet temperature (same temperature range) in the dryers (DR-DRY-1 and DR-DRY-2). The design specification DS-DR-FG-1 is used to estimate the thermal energy required by the multi-step bagasse drying process, and the design specification DS-DR-FG-2 is used to estimate the thermal energy required for the straw drying process. The design specification DS-DR-FG-3 is used to control the mass flow rate of fresh-air inlet (ATMOSPHERIC AIR) the dryers, optimizing the dying processes under determined temperature range (120.0ºC~100.0ºC in the air agent side).

The Aspen Plus®v8.4 process model simulation of bagasse flash dryers (DR-DRY-1) and straw flash dryers (DR-DRY-2) overestimates the power consumption because only uses the heat of vaporization of water and sensible heat exchanger according to biomass heat capacity, not taking into account other phenomena. The design specification DS-DR-HD-3 is used to correct the model estimative and approach to the real value demanded by the process, applying 45.0% as reduction factor of thermal energy calculated in the model, this thermal energy is provide by the Heat exchangers block between the HRSG exhaust-gas (HR-HEA-1) and the air agent mass flow rate (DR-HEA-1). The cooled HRSG flue-gas (FLUE-GAS FROM STACK) temperature is controlled and dependent on the exhaust-gas temperature of the subcritical HRSG system (without wet gaseous cleaning system).

Humidified exhaust-gas from first-stage and second-stage bagasse flash dryers (DR-MIX-1) enters in the after-dryer single-cyclone (DR-CYC-1) modeled by using a Cyclone solids separator block to remove the gross particulate content in the dryer humidified exhaust-gas according to Muschelknautz calculation method for a maximum pressure drop of 0.02 bar applying spiral inlet cyclone type. After the dryer single-cyclone (DR-CYC-1), dryer humidified exhaust-gas pass flowing through an electrostatic precipitator (DR-ESP-1) modeled by using ESP solids separator block according to Svarovsky calculation model for vertically mounted collecting plate's model with particles separation efficiency of 95.0% based on the migration velocity and the ratio of precipitation area. Part of the persistent fine particulate matters are removed avoid-reducing their emissions to atmosphere with the dryer's flue-gas (FLUE-GAS FROM STACK).

The dryer humidified exhaust-gas of the straw flash dryers (DR-MIX-2) enters in the after-dryer single-cyclone (DR-CYC-2) modeled by using a Cyclone solids separator block to remove the gross particulate content in the dryer humidified exhaust-gas according to Muschelknautz calculation method for a maximum pressure drop of 0.02 bar applying spiral inlet cyclone type. After the dryer single-cyclone (DR-CYC-2), dryer humidified exhaust-gas pass flowing through an electrostatic precipitator (DR-ESP-2) modeled by using ESP solids separator block according to Svarovsky calculation model for vertically mounted collecting plate's model with particles separation efficiency of 95.0% based on the migration velocity and the ratio of precipitation area. Part of the persistent fine particulate matters are removed avoid-reducing their emissions to atmosphere with the dryer's flue-gas (FLUE-GAS FROM STACK).

Gross and fine particulate matters removed from the dryer humidified exhaust-gas are sent to gasifier storage bin (DR-MIX-3) together the dried and sized sugarcane bagasse and straw (mixed in the feed gasifier drum).

6.1.5 Gasification of biomass in an atmospheric circulating fluidized bed directly-heated gasifier by using atmospheric air and steam gasification agents

The Aspen Plus®v8.4 process model simulation of the gasification of biomass in an atmospheric CFB directly-heated gasifier by using atmospheric air and steam gasification agents is based on zero-dimensional isothermal built-in multi-blocks models (CFB directly-heated gasifier process-zones) in steady state operation mode.

Figure 36 shows the Aspen Plus®v8.4 flowsheet of the gasification of biomass in an atmospheric CFB directly-heated gasifier by using atmospheric air and steam gasification agents for BIG-ICE/CC (SC1) and for BIG-ICE/CC (SC2).

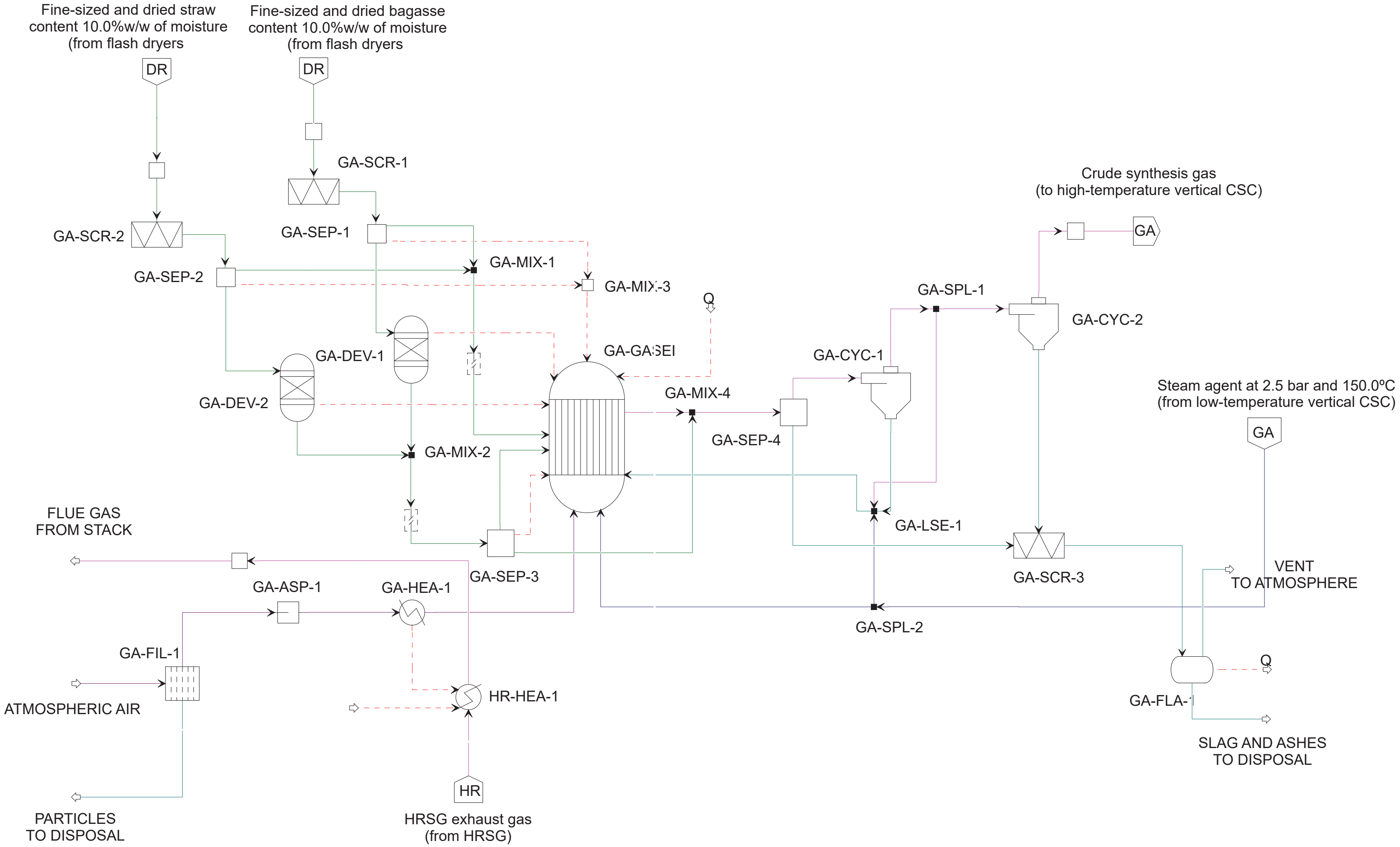


Figure 36 - Aspen Plus® v8.4 flowsheet of the gasification of biomass in an atmospheric CFB directly-heated gasifier by using atmospheric air and steam gasification agents for BIG-ICE/CC (SC1) and for BIG-ICE/CC (SC2)

As shown in Figure 36, Aspen Plus®v8.4 flowsheet of the gasification of biomass in an atmospheric CFB directly-heated gasifier by using atmospheric air and steam agents in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2), the model was developed as built-in multi-blocks and splitted in bagasse and straw feed system, pre-filter unit (GA-FIL-1), advanced blower system (GA-ASP-1), heat exchanger (GA-HEA-1 and HR-HEA-1), and more five basic linked zones to represent the atmospheric CFB directly-heated gasifier: a) drying zone (GA-SEP-1 and GA-SEP-2); b) devolatilization (thermal decomposition) or pyrolysis zone (GA-DEV-1 and GA-DEV-2); c) gasification or reduction zone (GA-GASEI); d) combustion or oxidation zone (GA-GASEI); and e) primary gasifier cyclone (GA-CYC-1).

The model use Mott and Spooner correlation (option code 4) to estimate the heat of combustion and heat of formation, Kirov correlation (option code 1) to estimate the heat capacity. RKS cubic equation of state with BM alpha function property method evaluates the heat transfer between the CFB directly-heated gasifier zones (multi-blocks), as well as heat loss from the gasifier considered by using design specification DS-GA-QL-1.

Dried (10.0$\%_{w/w}$ of moisture content) and sized (less than about 2.0 mm of tickles) sugarcane bagasse and straw, after the multi-steps drying process and control particulate emissions, is belt-conveyed to bagasse storage bin (DR-MIX-4) and straw storage bin (DR-MIX-3). Hence, sugarcane bagasse and straw are lifted from the temporary storage bin and gravimetric fed into the gasifier feed drum (DR-MIX-3).

Sugarcane bagasse and straw (biomass) is horizontally conveyed into the inject screws to introduce the bagasse (GA-SCR-2) and straw (GA-SCR-1) into the gasifier, near the bottom of the CFB gasifier bed. The mass flow rate of sugarcane bagasse and straw inject-screwed into the atmospheric CFB directly-heated gasifier is controlled by the bagasse screw (GA-SCR-2) and straw screw (GA-SCR-1), in each metering bins (DR-MIX-3 and DR-MIX-4).

The Aspen Plus®v8.4 process model simulation of the drying process-zone consider the bagasse (GA-SEP-2) and straw (GA-SEP-1) instantaneous drying process at 150.0ºC vaporizing the moisture content and volatilizing the extractives content in the inlet dried and sized bagasse and straw, which are sent directly to the oxidative and reductive reactions zone (GA-GASEI).

The Aspen Plus®v8.4 process model simulation of the devolatilization process-zone was developed using RYield reactor block to represent the atmospheric decomposition at 500ºC of the BAGASSE non-conventional solids (GA-DEV-2) and the STRAW non-conventional solids (GA-DEV-1) into its ‘constituting’ conventional components (‘ELEMENTS’). The non-conventional solids are converted to form carbon (C), hydrogen (H_2), oxygen (O_2), chlorine (Cl_2), nitrogen oxide (NO), sulfur dioxide (SO_2), and hydrogen sulfide (H_2S) using about 16.67$\%_{w/w}$ of the sulfur (S) content. Salts, minerals, ashes, and soil are specified as inert components in the devolatilization process-zone (bypass).

FORTRAN calculator block CA-GA-CB-2 is used to specify the yield distribution of the bagasse decomposition (GA-DEV-2) in the devolatilization process-zone and the mass flow rate of each constituent component in the outlet stream according to the sugarcane bagasse ultimate analysis (Table 5). FORTRAN calculator block CA-GA-CB-1 is used to specify the yield distribution of the straw decomposition (GA-DEV-1) in the devolatilization process-zone and the mass flow rate of each constituent component in the outlet stream according to the sugarcane straw ultimate analysis (Table 6).

Sep separator block GA-SEP-3 as adjustment model is used to selectively separate specific amounts of char (C) to adjust the carbon conversion efficiency of the atmospheric CFB directly-heated gasifier bypass the carbon around the reaction zones (GA-GASEI) using the design specification DS-GA-FS-1 to control the carbon split fraction to obtain 98.0%$_{w/w}$ of carbon conversion efficiency. The GA-SEP-3 separator block also adjusts and considers a fraction of 10.0%$_{w/w}$ of the salts with potassium and chlorine content as reactive compounds together the integral minerals. The another fraction containing 90.0%$_{w/w}$ of the salts with potassium and chlorine (content in the inlet biomass) is considered as non-reactive compounds and primary bypass the reaction zones (GA-GASEI).

The adjustment model (GA-SEP-3) consider the possibility of the entrained gross-particles (solid fraction) content reactive potassium and chlorine (bed supplementary material linked) captured in the primary gasifier cyclone (GA-CYC-1) return back trough the leg-riser to the gasifier bed (GA-GASEI) as reactive compounds. A small fraction of the fine particles contend the reactive-considered potassium and chlorine leave the primary gasifier cyclone (GA-CYC-1) with gaseous product, linked with the bed materials (not included in the Aspen Plus®v8.4 process model simulation) and in form of oxides sulfates or phosphates (possible products).

Surrounding atmospheric fresh-air (ATMOSPHERIC AIR) is induced by advanced blower system (GA-ASP-1) modeled by using a Compr pressure changer block according to isentropic method for compressor considering 85.0% isentropic efficiency and 99.0% mechanical efficiency, with pre-filter unit (GA-FIL-1) modeled by using a FabFl solids separator block to protect the blower (GA-ASP-1) and the gasifier air distributors (GA-GASEI) from debris (PARTICLES) according to Piecewise separation efficiency in function of the particle diameter of the solids.

Dryer flue-gas is used to preheated (GA-HEA-1) and the HRSG exhaust-gas (HR-HEA-1) is used to heated (GA-HEA-1) the atmospheric fresh-air (ATMOSPHERIC AIR), obtaining hot-air agent at 120.0ºC in the BIG-ICE/CC (SC1) or at 150.0ºC in the BIG-ICE/CC (SC2), before being injected in the atmospheric CFB directly-heated gasifier. The hot-air agent is then injected by primary injection distributor in the bottom of the bed (GA-GASEI) and by secondary distributor air points (close to biomass feed point) in the combustion zone (GA-GASEI).

The quantity of hot-air agent entering into the atmospheric CFB directly-heated gasifier is controlled by the design specification DS-GA-TG-1 varying the mass flow rate of the air agent intake. The hot-air agent required is determined by the thermal energy necessary to the gasification reactions occurs and to the crude synthesis gas leave the atmospheric CFB directly-heated gasifier at 850.0ºC, operational temperature selected for the atmospheric CFB directly-heated gasifier model implemented in this research Master's degree.

In the atmospheric CFB directly-heated gasifier, the combustion in-bed (GA-GASEI) supply the thermal energy required for the endothermic gasification reactions and to heater the material-compounds, the combustion gas products acts as fluidizing bed agent and gasifying agent. The Aspen Plus®v8.4 process model simulation of oxidizing and gasification process-zones in bed and freeboard is modeled using RGibbs reactor block (GA-GASEI) to represent the solid and gaseous reaction according to chemical equilibrium by Gibbs free-energy minimization method. The model consider all components as potential products in products sheet, it is a simple approach to represent the oxidizing and gasification reactions to obtain a crude synthesis gas at 850.0ºC.

Chemical equilibrium by Gibbs free-energy minimization method overestimate the Equivalence rate (ER_{AIR}) and the mass flow rate of CO_2 and H_2O (fraction in the crude synthesis gas), mainly because the model does not predict the reverse water gas shift equilibrium effect and the formation of light hydrocarbons and heavy hydrocarbons, breaking them into simpler forms. The model predicts the formation of more H_2 and less CO than the real process (experimental data). To break the hydrocarbon compounds is required energy, which is supplied by the combustion process (extended) demanding more oxidizing agent and forming consequently more CO_2 and H_2O as a product of combustion.

Steam agent at 2.5 bar and 150.0ºC (fluidization agent) is generated by the low-temperature vertical CSC (GA-CSC-1) in the synthesis gas heat recovery cooling system (second section). $95.0\%_{w/w}$ of the steam agent is injected by the primary and secondary injection distributor in the bed (GA-GASEI) in order to fluidize the bed and promote the gasification reactions (GA-GASEI), and $5.0\%_{w/w}$ of the steam agent in injected in the loop-seal (GA-LSE-1). The ratio of steam agent to dry biomass (bagasse and straw) is calculate by the Equation 7 and controlled by the design specification DS-GA-FG-1 varying the inlet hot water/steam agent mass flow rate to obtain a STBR equal of 0.5, considering the moisture content in the inlet bagasse and straw. The STBR is maintenance in 0.5 due to lack of details for bed fluidization, probably this value will be changed in future rigorous models involving fluid dynamic models, raising the steam mass flow rate to optimize the bed fluidization.

2.0% of the LHV_{db} of the biomass fed is assumed to be lost from the gasifier (GA-GASEI) being controlled by the design specification DS-GA-QL-1 with the aid of parameter calculation blocks (BHV blocks group) implemented.

The gasification of sugarcane bagasse and straw using atmospheric air and steam as gasification agents provides a crude synthesis gas content very-low or insignificant inerter elements present in the surrounding air (N2, Ne, He, Xe, Ar and Kr), water vapor (H_2O), carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), methane (CH_4), hydrogen sulfide (H_2S), hydrogen chlorine (HCl), chlorine (Cl_2), carbonyl sulfide (COS), ammonia (NH_3), nitrogen oxides (NO_x), sulfur oxides (SO_x), and solid particulate matters.

Tar, light hydrocarbons and heavy hydrocarbons is not estimated by the chemical equilibrium applying the Gibbs free-energy minimization method (GA-GASEI), hydrocarbons are converted to simple form as water vapor (H_2O), carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2) and a small fraction of methane (CH_4). Solid particulate matters content bed material, specifics catalytic active materials, unconverted char, coke, ashes content, soil, salts and minerals and others.

The main impurities present in the crude synthesis gas can be ammonia (NH_3), hydrogen sulfide (H_2S), carbonyl sulfide (COS), hydrogen chloride (HCl), chlorine (Cl_2), nitrous oxides (NO_x), sulfur oxides (SO_x), volatile metals, volatile organic compounds, tar and oils (heavy hydrocarbons), fines or submicron particles containing metals and metal salts, unconverted char (C), solid particulates, materials bed particles (not included in the Aspen Plus®v8.4 process model simulation), and others alkali compounds.

Primary gasifier cyclone gas/solid separator (GA-CYC-1) is modeled by using a Cyclone solids separator block as single-cyclone to remove the gross particulate content (ashes, silicates, metal salts, unconverted carbon, bed and additives materials) in the crude synthesis gas according to Muschelknautz calculation method for a maximum pressure drop of 0.012 bar applying spiral inlet cyclone type. The gross-particulate separated from the crude synthesis gas is recycled by the leg-riser back to the gasifier bed (GA-GASEI) to promote second-pass in the reaction zones raising the char conversion (to obtain $98.0\%_{w/w}$ of carbon conversion).

In the Aspen Plus®v8.4 process model simulation is considered that $50.0\%_{w/w}$ of the unconverted char (C) is removed in the gasifier bottom particulate materials discharge system (GA-SEP-4) modeled by using a Sep separator blocks. Another part can be recycled by the primary gasifier cyclone (GA-CYC-1) and a small fraction of fine particles can be dragged by the crude synthesis gas to the secondary multi-cyclone system (GA-CYC-2) according to the primary gasifier cyclone (GA-CYC-1) efficiency and the size of the solid particles (PSD distribution).

The model consider that $0.2\%_{w/w}$ of the crude synthesis gas conventional phase flowing into the primary gasifier cyclone (GA-CYC-1) return back to the reaction zone (GA-GASEI) by the leg-riser together the particles in the loop-seal (GA-LSE-1).

A secondary multi-cyclone system (GA-CYC-2) designed with five cyclones (battery) and modeled by using a Cyclone solids separator block according to Muschelknautz calculation method for a maximum pressure drop of 0.02 bar applying spiral inlet cyclone type removes part of the residual fines-particulate matters that leaving the top of the primary gasifier cyclone (GA-CYC-1). These particles are belt-conveyed and mixed (GA-SCR-3) with the bottom particulate matters removed from the gasifier (GA-SEP-4) to final disposal. The fine particles not recovered in the secondary multi-cyclone system (GA-CYC-2) is removed from the synthesis gas in the low-temperature synthesis gas wet cleaning system.

Bottom particulate matters (e.g.: sand; ash; slag; specifics catalytic active materials; unconverted materials, metal salts; alkali compounds and others) is discharged from the bottom of the gasifier (GA-GASEI), cooled using directly contact water added to avoid dust (consider the heat loss in the GA-FLA-1) by water-cooled screw conveyor (not simulated). The bottom particulate matters are stored together the fines-particulate matters removed in the multi-cyclone system (GA-CYC-2) in the ashes temporary storage bins to humidified ashes/slag (GA-FLA-1) until offloaded for disposal (field disposal together vinasses).

6.1.5.1 Gasifier bed materials

Spreadsheet calculation model is used to determine the quantity of MgO must be present into the gasifier bed (GA-GASEI) and the make-up mass flow rate of MgO necessary to substantially avoid the formation (sequestering potassium) of low-melting point glass-like bed agglomerations (K_2SiO_4). The bed agglomerations were associated to direct adhesion of the bed particles by partly molten fuel ash derived K–Mg phosphates (ashes content) and K-silicates (ashes and soil content) that should result from the interactions with the biomass potassium content. MgO raise the melting point (ternary eutectic form) sequestering potassium avoiding/reducing it to be carried over in the gasifier cyclones (GA-CYC-1) and deposits in the equipment walls.

MgO supplementary bed material load is estimated to be 2.0 mol mass flow rate per mol of reactive potassium inlet into the gasifier (GA-GASEI). MgO is delivered to thermochemical-biorefinery supplies offloading area by truck to storage, a pneumatic line feed the gasifier loop bed media feed bin, which transfers the supplies to the gasifier by screw-conveyor or pneumatic transporter (not included in the Aspen Plus®v8.4 process model simulation).

In the spreadsheet calculation model is considered the olive make-up mass flow rate as being 1.0%$_{w/w}$ of the mass flow rate of dry ash and extractive free (daef) sugarcane bagasse and straw inlet into the gasifier to compensate the olive losses. Olivine recirculate by the primary gasifier cyclone (GA-CYC-1) trough the leg-riser and the major part of the entrained olive is recovered from the crude synthesis gas exiting the gasifier by the secondary multi-cyclone system (GA-CYC-2), only a small part of the olivine as fine particles are dragged and removed in the low-temperature synthesis gas wet cleaning system (losses).

The majority of the bed materials and gross-biomass derived particles are separated in the primary gasifier cyclone (GA-CYC-1) and sent-back (recycled) into the leg-riser and gravity-feed back to the gasifier bed (GA-GASEI) using steam fluidized loop-seal (GA-LSE-1). A secondary multi-cyclone system (GA-CYC-2) removes part of the residual fines-particulate matters that leaving the top of the primary gasifier cyclone (GA-CYC-1), this particles are mixed with the bottom particulate material removed from the gasifier (GA-SEP-4) to final disposal (BED MATERIALS AND ASHES).

The mineral-crystal (iron content) olivine catalyst considered as gasifier bed media is a commercial type olivine catalyst $\alpha\text{-}(Mg_{0.8}Fe_{0.2})_2SiO_4$ delivered to thermochemical-biorefinery supplies offloading area by truck to storage. Pneumatic line fed the gasifier loop bed media feed bin, which transfers the supplies to the gasifier by screw-conveyor or pneumatic transporter (not included in the Aspen Plus$^{®}$v8.4 process model simulation).

Olivine catalyst is used to reduce by about 60.0%$_{w/w}$ of the tar content in the crude synthesis gas produced in the atmospheric CFB directly-heated gasifier (GA-GASEI). Tar abatement increased up to 92.0%$_{w/w}$ when catalytic CF were combined with the bed, not included in the Aspen Plus$^{®}$v8.4 process model simulation due the limitations of the gasification Gibbs equilibrium model, in future works with rigorous model can be considered.

6.1.6 Syngas cooling and heat recovery

The synthesis gas for effective use in SG-ICEs requires the compression of the synthesis gas to low-pressure requirements to improve the volumetric energy density. To compress the synthesis gas is necessary reducing the synthesis gas temperature in order to reduce the consumption of electrical energy and fit the maximum temperature allowed by the compressor.

Hot synthesis gas has a great potential to thermal energy generation (sensible heat) and recovery this heat can increase the process steam production and reduce the stress on the HRSG system in the BIG-ICE/CC route due the largest thermal energy required by the thermochemical-biorefinery.

Figure 37 shows the Aspen Plus$^{®}$v8.4 flowsheet of the syngas cooling and heat recovery for BIG-ICE/CC (SC1), and for BIG-ICE/CC (SC2).

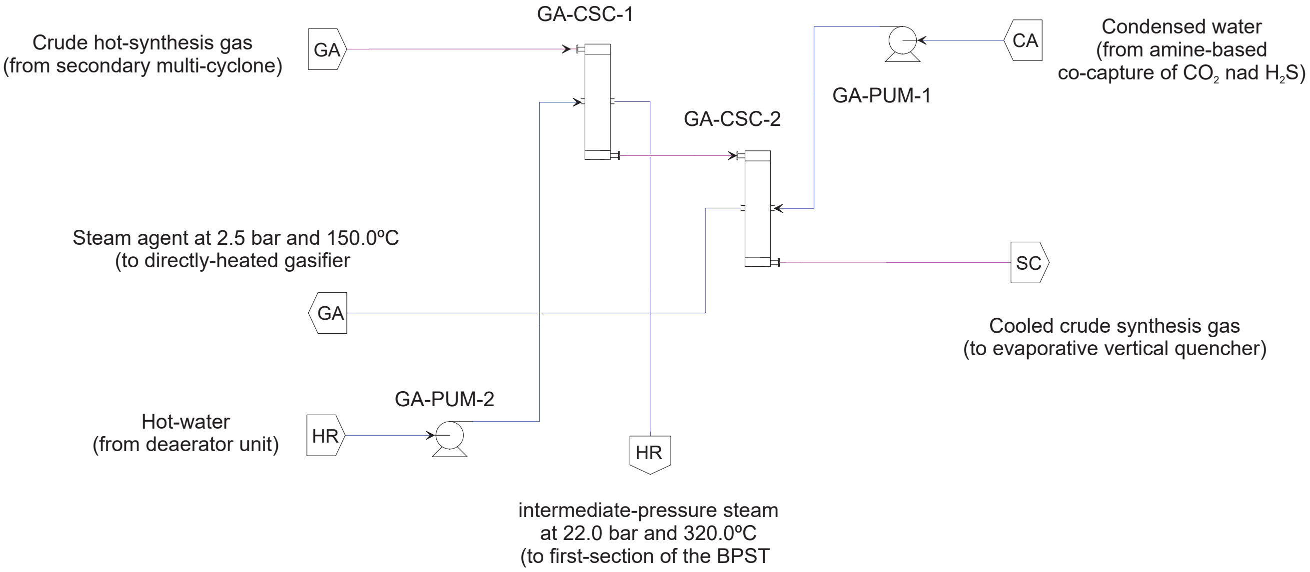


Figure 37 - Aspen Plus®v8.4 flowsheet of the syngas cooling and heat recovery for BIG-

As shown in Figure 37, Aspen Plus®v8.4 flowsheet of the syngas cooling and heat recovery in the BIG-ICE/CC (SC1), and BIG-ICE/CC (SC2) is compost by: high-temperature vertical CSC (GA-CSC-1); low-temperature vertical CSC (GA-CSC-2); water pump 1 (GA-PUM-1); and water pump 2 (GA-PUM-2).

Atmospheric crude hot-synthesis gas that leave the secondary multi-cyclone system (GA-CYC-2) is cooled in two cooling sections generating intermediate-pressure steam by the high-temperature vertical CSC (GA-CSC-1) modeled by using a HeatX exchanger block and low-pressure steam by the low-temperature vertical CSC (GA-CSC-2) modeled by using a HeatX exchanger block, without the catalytic high-performance CF.

The high-temperature vertical CSC (GA-CSC-1) and low-temperature vertical CSC (GA-CSC-2) are modeled using RKS-BM physical property methods to atmospheric crude hot-synthesis gas side, and IAPWS-95 physical property methods to hot water/steam side.

In the BIG-ICE/CC (SC1), and BIG-ICE/CC (SC2), atmospheric crude hot-synthesis gas produced by the atmospheric CFB directly-heated gasifier at 850.0ºC is cooled to about 318.0ºC by the high-temperature vertical CSC (GA-CSC-1). The atmospheric crude hot-synthesis gas at 318.0ºC after the high-temperature vertical CSC (GA-CSC-1) is cooled to about 125.0ºC by the low-temperature vertical CSC (GA-CSC-2).

Deaerated hot process water from deaerator unit (HR-DEA-1) at 1.4 bar and 105.0ºC is pumped (GA-PUM-2) to 22.0 bar before entering into the high-temperature vertical

CSC (GA-CSC-1). The atmospheric crude hot-synthesis gas is cooled in the first-section of (GA-CSC-1) exchange sensible heat to produce intermediate-pressure steam. In the BIG-ICE/CC (SC1), intermediate-pressure steam at 22.0 bar and 320.0ºC is produced and expanded in the first-section of the BPST system (ST blocks) to generate electrical energy. In the BIG-ICE/CC (SC2), intermediate-pressure steam at 22.0 bar and 380.0ºC is produced and expanded in the second-section of the CEST system (ST blocks) to generate electrical energy.

In the BIG-ICE/CC (SC1), and BIG-ICE/CC (SC2), condensed water at about 2.3 bar and 123.0ºC after the stripper reboiler (CA-REB-1) in the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution is after-pumped (GA-PUM-1) to the syngas cooling and heat recovery (GA blocks). In these cases, is used to cool down the synthesis gas, after-generating gasification steam agent at 2.5 bar and 150.0ºC in the low-temperature vertical CSC (GA-CSC-2).

Cooled crude synthesis gas is fed in the evaporative vertical quencher (spray tower) (SC-SCR-1) in the low-temperature synthesis gas wet cleaning system (wet scrubbing unit).

The mass flow rate of deaerated hot process water to intermediate-pressure steam generation is controlled by design specification DS-GA-TL-1 varying the inlet mass flow rate of deaerated hot process water in the high-temperature vertical CSC (GA-CSC-1) coupled with design specification DS-GA-TL-2 which determines the temperature between the high-temperature vertical CSC (GA-CSC-1) and low-temperature vertical CSC (GA-CSC-2) sections.

The mass flow rate of deaerated hot process water to low-pressure steam generation is controlled by design specification DS-GA-FG-1 varying the inlet mass flow rate to produce gasification steam agent at 2.5 bar and 150.0ºC to atmospheric CFB directly-heated gasifier (GA-GASEI and GA-LSE-1). The amount of gasification steam agent is determined by Equation 7 to obtain a STBR of 0.5, considering the moisture present in the biomass-fuel inlet into the gasifier (GA-GASEI).

The catalytic high-performance CF between the high-temperature vertical CSC (GA-CSC-1) and the low-temperature vertical CSC (GA-CSC-2) was not implemented in the Aspen Plus®v8.4 process model simulation of the syngas cooling and heat recovery, due the limitations of the gasification Gibbs equilibrium model (GA-GASEI). The system is mainly used to reform the reminiscent tar and heavy hydrocarbons. Also, can remove part of the particle content in the atmospheric crude synthesis gas. Considering the presence of olivine catalyst in the gasifier bed (GA-GASEI) only traces of tar and heavy hydrocarbons is expected.

6.1.7 Low-temperature synthesis gas wet cleaning system

After the initial particulate removal accomplished by the multi-cyclones system (GA-CYC-2) and the convective indirect cooling of the crude synthesis gas by the syngas cooling and heat recovery an additional cooling step is carried out by wet scrubbing unit (direct water contact cooling).

The low-temperature synthesis gas wet cleaning system (wet scrubbing unit) is used to remove water-soluble contaminants and particles from the synthesis gas including ammonia (NH_3), hydrogen chloride (HCl), sulfur oxides (SO_x), carbonyl sulfide (COS), volatile organic compounds, tar and oils (heavy hydrocarbons), particles containing metals and metal salts, unconverted char (C) solid particulates, materials bed particles (not included in the Aspen Plus®v8.4 process model simulation), and others alkali compounds. Also, remove a small part of hydrogen sulfide (H_2S), nitrous oxides (NO_x), and carbon dioxide (CO_2).

The Aspen Plus®v8.4 process model simulation of the low-temperature synthesis gas wet cleaning system was developed using Electrolyte NRTL physical property methods for liquid phase and RK equation of state for vapor phase (ELECNRTL physical property methods) for electrolytes calculation using true components approach and aqueous activity coefficient basis for Henry components. Aqueous activity coefficient for the supercritical and non-condensable components (e.g.: H_2, O_2, N_2, Ne, He, Ar, Kr, Xe, CO, CO_2, Cl_2, SO_2, NH_3, H_2S, CHN, HCl) selected as Henry components is calculated according to the Henry's law for represent the behavior of dissolved gases, considering the affinity with water and their interaction with other electrolytes presents.

Figure 38 shows the Aspen Plus®v8.4 flowsheet of the low-temperature synthesis gas wet cleaning system for BIG-ICE/CC (SC1) and for BIG-ICE/CC (SC2).

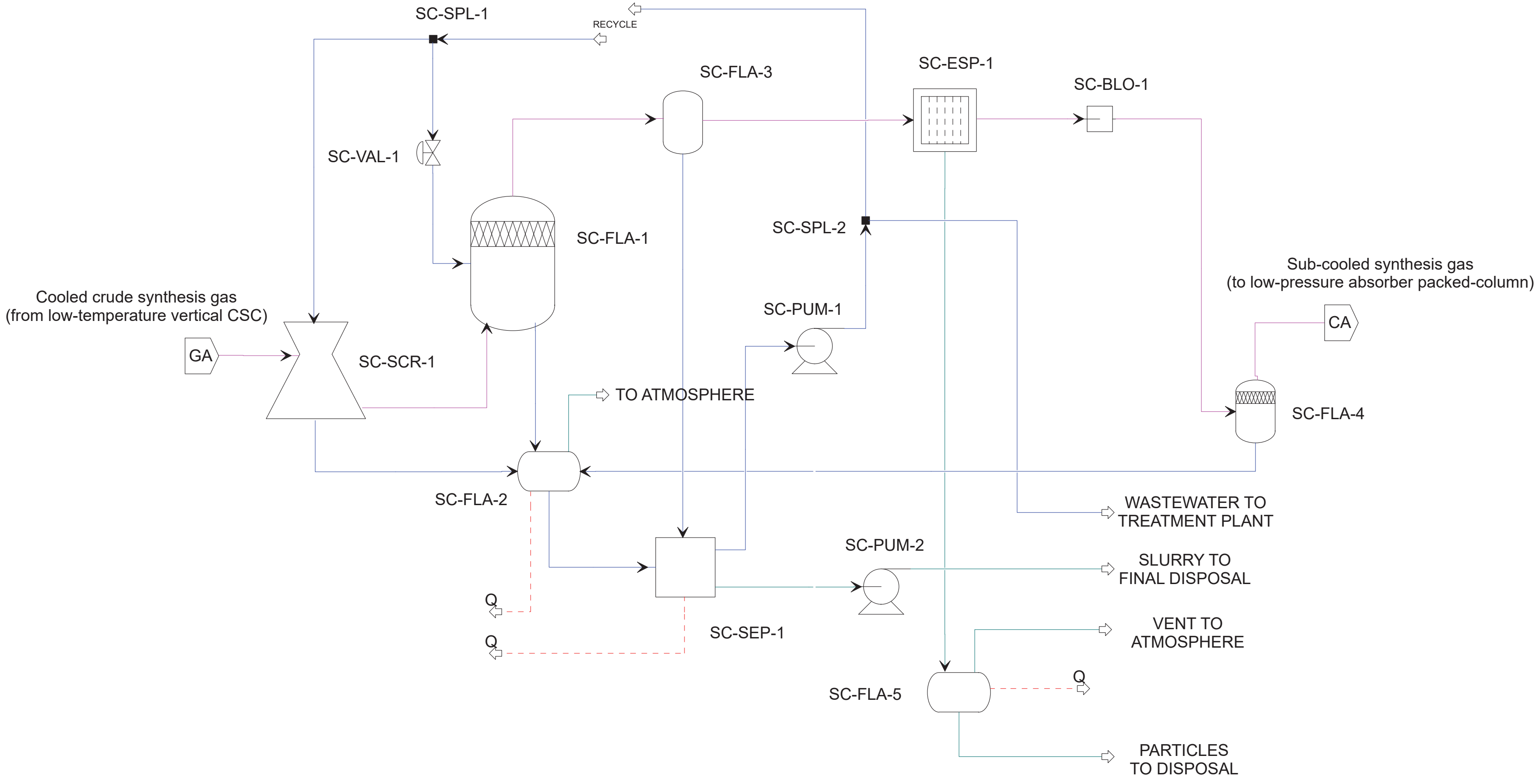


Figure 38 - Aspen Plus® v8.4 flowsheet of the low-temperature synthesis gas wet cleaning system for BIG-ICE/CC (SC1) and for BIG-ICE/CC (SC2)

As shown in Figure 38, Aspen Plus®v8.4 flowsheet of the low-temperature synthesis gas wet cleaning system in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2) is compost by: vertical down-flow water spray quencher (SC-SCR-1); vertical water venturi scrubber (SC-SCR-1); decanter to separate the heavy hydrocarbons from the water (not included in the Aspen Plus®v8.4 process model simulation); water recovery and recycle unit (SC-FLA-2); packet-bed condenser/absorber sub-cooler (SC-FLA-1); mist eliminator (demister) drum (SC-FLA-3); wet electrostatic precipitator (WESP) (SC-ESP-1); blower system (SC-BLO-1); after air cooler (SC-FLA-4); condensate knock-out drum (SC-FLA-4); clarifier and decanter units (SC-FLA-2); sludge setting tank (SC-SEP-2); slurry pump (SC-PUM-2); water pumps (SC-PUM-1); cleaned water recirculation tank (SC-SEP-2); and humidified particles temporary bin (SC-FLA-5).

The interaction of the key components potentially presents in the cooled crude synthesis gas in the presence of pure-water is evaluated in the Aspen Plus®v8.4 process model simulation of the low-temperature synthesis gas wet cleaning system. The model was developed with a chemistry model for specify reactions method applying the Elec Wizard auxiliary tool to generate possible components and reactions for the electrolyte simulation approach. The approach include the salt formation and dissociation reaction in water based on the hydronium ion (H_3O^+) reactions mechanism according to electrolyte solution chemistry (Chemistry ID: CH-SC-SOU) for BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2).

Activity coefficients (GAMUS) of the ionic solutes are based on infinite-dilution condition in pure water (Unsymmetrical) according to standard APV84 chemistry database to determine the parameters of the equilibrium and salt precipitation reactions (equilibrium constants).

The cooled crude synthesis gas at about 125.0ºC and atmospheric pressure from the low-temperature vertical CSC (GA-CSC-2) is down-flow conducted through the vertical water spray quencher (SC-SCR-1) in direct contact with recycled pure-water (without alkali addition) at 25.0ºC injected by 10 spray nozzles with 1.1 mm of diameter and angle of 70.0º. The injected water is vaporized cooling down (pre-cooling chamber) the synthesis gas to saturation conditions at about 100.0ºC (without water condensation) before entering the vertical venturi scrubber (SC-SCR-1) with water loop tar removal system.

The Aspen Plus®v8.4 process model simulation for the vertical water spray quencher (SC-SCR-1) coupled in the vertical venturi scrubber (SC-SCR-1) uses Calvert's calculation method for spray tower designed with separation efficiency of 70.0% in the vertical venturi scrubber (SC-SCR-1). Electrolyte solution chemistry (CH-SC-SOU) is used to estimate the dissolved gases, the electrolytes interactions by salt formation, and dissociation reaction in pure water. The solid particles scrubbed (SC-SCR-1) are removed in the VSscrub solids separator block, the scrubbing liquid phase is removed in the Flash2 separator block (SC-FLA-1) together the condensed phase in the packet-bed condenser/absorber sub-cooler (SC-FLA-1).

The electrolyte solution chemistry model Chemistry ID: CH-SC-SOU implemented in the Aspen Plus®v8.4 process model simulation of the low-temperature synthesis gas wet cleaning system was developed with a CHEMISTRY model.

Chemistry ID: CH-SC-SOU

1	Equilibrium	$2H_2O \leftrightarrow H_3O^+ + OH^-$
2	Equilibrium	$CO_2 + 2H_2O \leftrightarrow H_3O^+ + HCO_3^-$
3	Equilibrium	$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-}$
4	Equilibrium	$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$
5	Equilibrium	$NH_3 + HCO_3^- \leftrightarrow H_2O + NH_2COO^-$
6	Equilibrium	$H_2O + H_2S \leftrightarrow H_3O^+ + HS^-$
7	Equilibrium	$H_2O + HS^- \leftrightarrow H_3O^+ + S^{2-}$
8	Equilibrium	$HCl + H_2O \leftrightarrow H_3O^+ + Cl^-$
9	Equilibrium	$2H_2O + Cl_2 \leftrightarrow HClO + H_3O^+ + Cl^-$
10	Equilibrium	$H_2O + HClO \leftrightarrow H_3O^+ + ClO^-$
11	Equilibrium	$H_2O + H_3PO_4 \leftrightarrow H_3O^+ + H_2PO_4^-$
12	Equilibrium	$H_2O + H_2PO_4^- \leftrightarrow H_3O^+ + HPO_4^{2-}$
13	Equilibrium	$H_2O + HPO_4^{2-} \leftrightarrow H_3O^+ + PO_4^{3-}$
14	Equilibrium	$2H_2O + SO_2 \leftrightarrow H_3O^+ + HSO_3^-$
15	Equilibrium	$H_2O + HSO_3^- \leftrightarrow H_3O^+ + SO_3^{2-}$
16	Equilibrium	$H_2O + CHN \leftrightarrow H_3O^+ + CN^-$
17	Equilibrium	$H_2O + CHN \leftrightarrow H_3O^+ + CN^-$
18	Salt	$NH_4CN \leftrightarrow NH_4^+ + CN^-$
19	Salt	$NH_4HCO_3 \leftrightarrow NH_4^+ + HCO_3^-$
20	Salt	$NH_4HS \leftrightarrow NH_4^+ + HS^-$
21	Salt	$(NH_4)_2SO_3 \leftrightarrow 2NH_4^+ + SO_3^{2-}$
22	Salt	$NH_4HSO_3 \leftrightarrow NH_4^+ + HSO_3^-$
23	Salt	$NH_6PO_4 \leftrightarrow NH_4^+ + H_2PO_4^-$
24	Salt	$(NH_4)_2HPO_4 \leftrightarrow 2NH_4^+ + HPO_4^{2-}$
25	Salt	$(NH_4)_3PO_4 \leftrightarrow 3NH_4^+ + PO_4^{3-}$

Some of the electrolyte and salts formation reactions some reactions may not be favorable and not affecting significantly the concentration of ions in aqueous phase (condensed).

In the vertical venturi scrubber (SC-SCR-1) is collected the gross-particulate according to the aerodynamic size and removed the condensed residual heavy hydrocarbons (e.g.: tar, oils) in the basin (SC-FLA-2) of the venturi scrubber (liquid drain) by the water loop tar removal system (not included in the Aspen Plus®v8.4 process model simulation). The scrubbed liquid with heavy hydrocarbons mixed with water is collected in the basin (SC-FLA-2) and sent to oil/water separator (not included in the Aspen Plus®v8.4 process model simulation) to remove the hydrocarbons from the water by density differences. The liquid hydrocarbons removed is sent to final disposal or sent-back to the gasifier (GA-GASEI), the water phase is recovered and recycle to the venturi scrubber (SC-SCR-1) at 25.0ºC and injected by the spray nozzles in the chamber.

Cleaned water is pumped from the cleaned water recirculation tank (SC-SEP-2) in closed-loop cycle to the packet-bed condenser/absorber sub-cooler (SC-FLA-1). Cooled synthesis gas is then sub-cooled to 45.0ºC being removed $15.0\%_{w/w}$ of the entrained fine-particles by the use of a large amount of recycled-water from the cleaned water recirculation tank (SC-SEP-2) in the packet-bed condenser/absorber sub-cooler (SC-FLA-1).

The Aspen Plus®v8.4 process model simulation consider $0.5\%_{w/w}$ of entrained water to mist eliminator (SC-FLA-3) which is responsible to remove the excess of water content droplets in the sub-cooled synthesis gas at saturation conditions before entering in the WESP (SC-ESP-1).

The amount of cleaned-water recycled to vertical water spray quencher (SC-SCR-1) and to vertical venturi scrubber (SC-SCR-1) is controlled by design specification DS-SC-TG-1 varying the inlet cleaned-water (SC-SPL-1) in order to achieve the saturation condition (cooling).

The amount of cleaned-water recycled to packet-bed condenser/absorber sub-cooler (SC-FLA-1) is controlled by design specification DS-SC-TG-2 varying the inlet cleaned-water (SC-SPL-2) in order to achieve the sub-cooled condition for WESP system (SC-ESP-1), and the synthesis gas temperature required by the low-pressure absorber packed-column (CA-ABS-1) in the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution (CA blocks).

The equilibrium constants for reactions 6 and 7 in CH-SC-SOU are obtained from Austgen et al. (1988) apud Aspen Tech (2013a), as shown in the Table 16 in the section 6.1.8 (Co-capture of CO2 and H2S by using MEA-based aqueous absorbing-solution).

The equilibrium constants (A, B, C and D) for the reactions from 1 to 17 in CH-SC-SOU and the salt precipitation equilibrium constants (A, B, C D and E) for the reactions from 18 to 25 in CH-SC-SOU are obtained from the standard Gibbs free energy from the databank of Aspen Plus®v8.4. The built-in expression for calculating equilibrium constants is used for the reactions from 1 to 17 in CH-SC-SOU electrolyte solution chemistry, according to Equation 27.

$$\ln k_{eq} = A + \frac{B}{T} + C.\ln T + D.T \tag{27}$$

Where, k_{eq} is the equilibrium constant, T is the absolute temperature (K), A, B, C, D is user supplied coefficients.

The built-in expression for calculating salt precipitation equilibrium constants is used for the reactions from 18 to 25 in CH-SC-SOU electrolyte solution chemistry, according to Equation 28.

$$\ln k_{salt} = A + \frac{B}{T} + C.\ln T + D.T \ + E.\left(\frac{P - P_{ref}}{P_{ref}}\right) \tag{28}$$

Considering: $P_{ref} = 1.0\ atmosphere$

Where, k_{salt} is the salt precipitation equilibrium constant, T is the absolute temperature (K), A, B, C, D, E is user supplied coefficients, P_{ref}.is the reference pressure (atm) and P is the absolute pressure (atm)

The ELECNRTL physical property methods is used in the low-temperature synthesis gas wet cleaning system (SC blocks) with the same properties assumption employed in the Aspen Plus®v8.4 process model simulation of the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution (CA blocks), according to Aspen Tech (2013a) apply the standard parameter in the APV84 Aspen Plus®v8.4 database for the Clarke model (VAQCLK) for liquid molar volume with option 1 to use the quadratic mixing rule for solvents, Jones-Dole electrolyte correction model (MUL2JONS) weighted by mass fraction (option code 1) for liquid viscosity model for the solvent (option code 1) using Aspen liquid mixture viscosity (option code 2), Onsager-Samaras model (SIG2ONSG) for liquid surface tension for electrolyte system (option code 1) wit exponent codes -9 in mixing rule, Riedel electrolyte correction model (KL2RDL) for thermal conductivity, Nernst-Hartley model (DL1NST) for binary diffusivity with mixture viscosity weighted by mass fraction (option code 1).

The excess of the wastewater recovered from the basin (SC-FLA-2) of the vertical venturi scrubber (SC-SCR-1), from the cooler condenser basin (SC-FLA-2) and from the mist eliminator (SC-FLA-3) is sent to the clarifier and decanter units (SC-SEP-2) and cleaned water recirculation tank (SC-SEP-2) to remove the sludge and be cooled at ambient conditions. The contend solids and precipitated or dissociated salts is concentrate in the bottom sludge phase and sent to the sludge setting tank (SC-SEP-

2) to be removed and sent of-site to final disposal in the sugarcane field. In the Aspen Plus®v8.4 process model simulation is considered 50.0%$_{w/w}$ of water content in the sludge phase, which can be pumped by slurry pump (SC-PUM-2) to storage tank before send-off the site by tank truck transporter (SLURRY TO DISPOSAL).

The cleaned water from the clarifiers (SC-SEP-2) at quality requirements to be recycled to vertical water spray quencher (SC-SCR-1) and to vertical venturi scrubber (SC-SCR-1) is stored in the cleaned water recirculation tank (SC-SEP-2). The excess of water recovered from the synthesis gas is separate (SC-SPL2) and pumped (SC-PUM-1) to wastewater treatment plant (WASTEWATER TO TREATEMNT PLANT) to be used as make-up water for other processes (loss reduction principles).

In the Aspen Plus®v8.4 process model simulation of the synthesis gas cleaning wet system is considered the WESP (SC-ESP-1) operating at satured synthesis gas conditions (100% relative humidity) to remove the persistent fine-particles (final particles) as additional particulate polishing step. The WESP (SC-ESP-1) is modeled according to Svarovsky calculation model for vertically mounted collecting plate's model with separation efficiency of 92.0% of the particles present in the sub-cooled synthesis gas stream and based on the migration velocity and the ratio of precipitation area.

The persistent fine-particles collected is removed from the basin (SC-ESP-1) and conveyed to be stored into the humidified particles temporary bin (SC-FLA-5) until offloaded (PARTICLES TO DISPOSAL) for the final disposal (field disposal together vinasses and gasifier bottom particulate materials).

Blower system (SC-BLO-1) with induced draft fan is modeled by using a Compr pressure changer block according to isentropic method for compressor considering 85.0% isentropic efficiency and 99.0% mechanical efficiency. The system is used to produce the desired pressure drop across the venturi scrubber system and to equalize the pressure (drop pressure) inducing the synthesis gas flow through the system at desired mass flow rate. After pressurized (SC-BLO-1) the sub-cooled synthesis gas is cooled in the air cooler (SC-FLA-4) and the condensed phase removed in the knock-out drum (SC-FLA-4) back to the cleaned water recirculation tank (SC-SEP-2).

The sub-cooled synthesis gas in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) is sent-ducted to the low-pressure absorber packed-column (CA-ABS-1) in the co-capture of CO_2 and H_2S by using MEA-based absorbing-solution (CA blocks) at temperature of 50.0ºC.

6.1.8 Co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution

Co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution at atmospheric pressure has the potential to capture mainly CO_2 and co-capture H_2S and fractions of carbonyl sulfide (COS), carbonyl disulfide (CS_2), and mercaptans (is not the main goal) removed a lesser extension from the system. The amount of co-captured compounds depends on the mass flow rate of MEA-based aqueous absorbing-solution circulating in the system.

Typical CO_2 and H_2S co-capture system (CA blocks) at atmospheric pressure using $30.0\%_{w/w}$ of conventional MEA in aqueous solution (CA-L-5) is adequate for atmospheric pressure systems (stable at around of 120.0ºC) with lower emissions of degradation products.

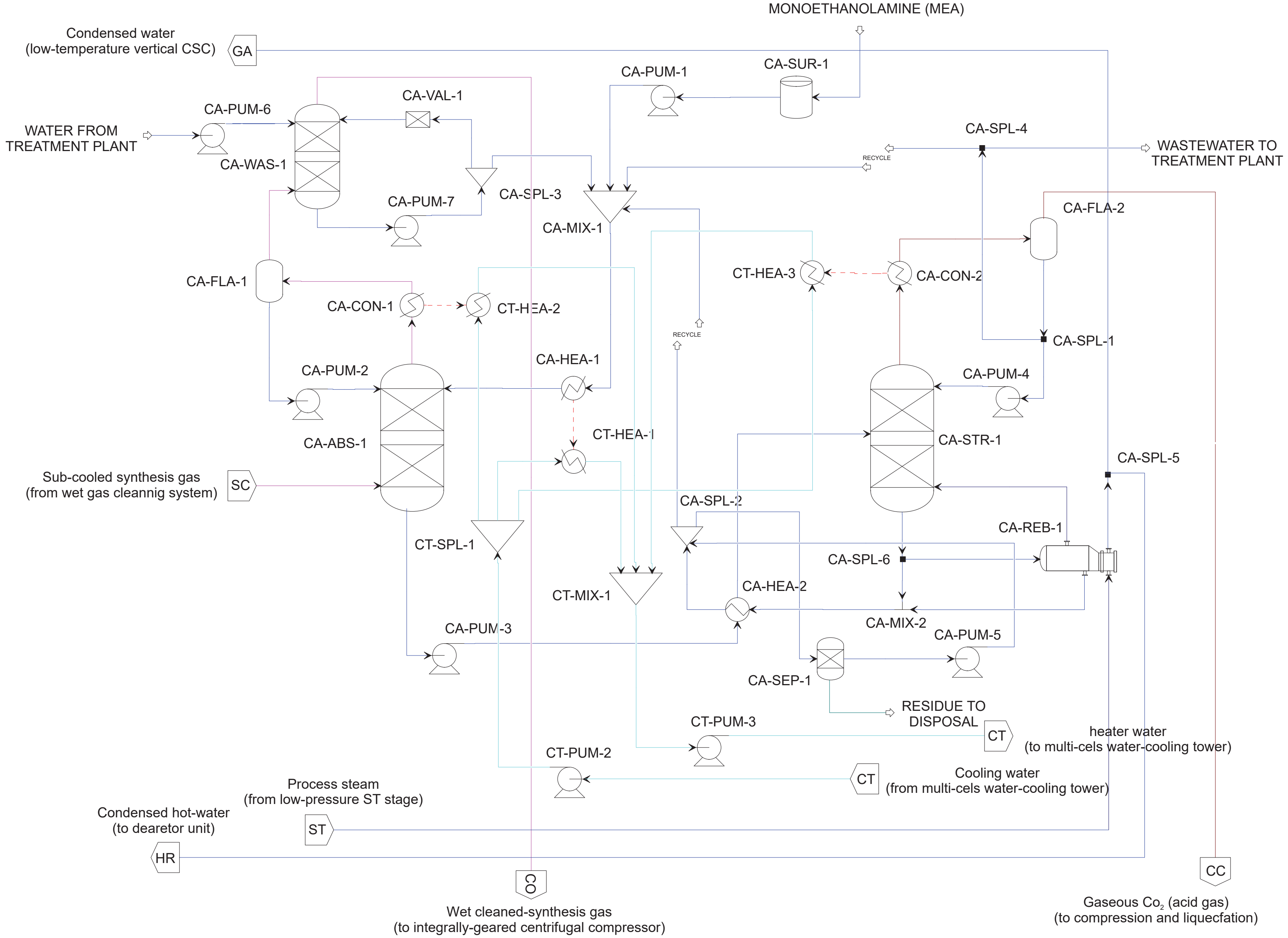
Aspen Plus®v8.4 process model simulation of the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution was employed in order to remove $90.0\%_{w/w}$ of CO_2 content in the synthesis gas increasing the energy density of the synthesis gas (remove the CO_2 as inert gas) as required by the SG-ICEs (downstream process), and to control the atmosphere emissions.

The mixture of CO_2 and amine in water (CO_2-amine-H_2O interaction) is highly non-ideal and the presence of ions and polar molecules in the liquid phase creates significant thermal effects increasing the temperature of the system at point of raise the degradation process of the MEA-based solution employed, the gas phase is lower non-ideal for atmospheric pressure system.

The rigorous Aspen Plus®v8.4 process model simulation of the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution (CA blocks) consider the complete cycle in closed-loop cycle mode with heat integrations. From the model is obtained the rigorous energy balance of the system, and the mass flow rate of process steam (thermal energy) and cooling water required by the system (reboiler and condensers equipments). Rigorous model is essential and indispensable to determine the influence of this system in the thermal energy balance of the integrated processes in the thermochemical-biorefinery.

Figure 39 shows the Aspen Plus®v8.4 flowsheet of the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution ($30.0\%_{w/w}$ of MEA-based aqueous absorbing-solution) for BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2).

Figure 39 - Aspen Plus® v8.4 flowsheet of the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution (30.0%$_{w/w}$ of MEA-based aqueous absorbing-solution) for BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2)



As shown in Figure 39, Aspen Plus®v8.4 process model simulation of the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution (CA blocks) in closed-loop cycle in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2) is compost by: low-pressure absorber packed-column (CA-ABS-1); low-pressure stripper packed-column (CA-STR-1); washer packed-column section (CA-WAS-1); washer water recycle-pump (CA-PUM-7); washer water bleed (CA-SPL-3); cross-solution heat exchanger (CA-HEA-2); mixture tank (CA-MIX-1); amine surge tank (CA-SUR-1); amine supply pump (CA-PUM-1); absorber reflux-pump (CA-PUM-2); desorber reflux pump (CA-PUM-4); absorber condenser (CA-CON-1 and CT-HEA-2); absorber liquid reflux-drum (CA-FLA-1); water purge splitter (CA-SPL-4); striper liquid reflux-drum (CA-FLA-2); stripper condenser (CA-CON-2 and CT-HEA-3); striper water bleed (CA-SPL-1); lean-amine water cooler (CA-HEA-1 and CT-HEA-1); rich-amine pump (CA-PUM-3); carbon-based filter (CA-SEP-1); stripper reboiler (CA-REB-1); amine reclaim (CA-SPL-2); reclaimer recirculation pump (CA-PUM-5); make-up water pump (CA-PUM-6); and cooling water pumps (CT-PUM-2 and CT-PUM-3).

ASPEN Rate-Sep simulation package is used in the low-pressure absorber packed-column (CA-ABS-1), in the low-pressure stripper packed-column (CA-STR-1), and in the washer packed-column section (CA-WAS-1) to non-equilibrium mass transfer rate-based calculations taken in account the mass and heat transfer limitations, liquid and vapor film diffusion, equipment hydrodynamics, and chemical reaction mechanisms.

The rigorous Aspen Plus®v8.4 process model simulation of co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks) consider the complete cycle in closed-loop cycle mode under the steady state operating conditions. The model was developed using Electrolyte NRTL physical property methods for liquid phase and RK equation of state for vapor phase (ELECNRTL physical property methods) for electrolytes calculation using true components approach and aqueous activity coefficient basis for Henry components. The selected components (e.g.: H_2, O_2, N_2, Ne, He, Ar, Kr, Xe, CO, CO_2, Cl_2, NH_3, CHN, HCL, CH_4, NO_x, SO_x) to employ the Henry's law as supercritical and non-condensable components for represent the behavior of dissolved gases according to the affinity with water and their interaction with electrolytes.

The degradation products generated during the solvent degradation process may produce new pollutants, which could be emitted to the atmosphere. Thermal and oxidative degradation, and polymerization reactions, have been considered undergoes thermal degradation temperature limits in presence of dissolved CO2.

Solvent degradation process was simplified in the Aspen Plus process simulation model of the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution (CA blocks), based on mass balance of the system, a representative fraction of the MEA-based aqueous absorbing-solution degraded is removed as input parameters in the carbon-based filter (CA-SEP-1).

The electrolyte solution chemistry model Chemistry ID: CH-CA-MEA implemented in the Aspen Plus®v8.4 process model simulation of the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution was developed with a CHEMISTRY model.

Chemistry ID: CH-CA-MEA

1	Equilibrium	$2H_2O \leftrightarrow H_3O^+ + OH^-$
2	Equilibrium	$CO_2 + 2H_2O \leftrightarrow H_3O^+ + HCO_3^-$
3	Equilibrium	$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-}$
4	Equilibrium	$MEAH^+ + H_2O \leftrightarrow MEA + H_3O^+$
5	Equilibrium	$MEACOO^- + H_2O \leftrightarrow MEA + HCO_3^-$
6	Equilibrium	$H_2O + H_2S \leftrightarrow HS^- + H_3O^+$
7	Equilibrium	$H_2O + HS^- \leftrightarrow S^{2-} + H_3O^+$

The built-in expression for calculating equilibrium constants is used for the reactions from 1 to 7 in CH-CA-MEA electrolyte solution chemistry, according to Equation 29.

$$\ln k_{eq} = A + \frac{B}{T} + C.\ln T + D.T \tag{29}$$

Where, k_{eq} is the equilibrium constant, T is the absolute temperature (K), and A, B, C, D is user supplied coefficients.

Equilibrium constants (Table 16) for the reactions from 1 to 5 in CH-CA-MEA are obtained from the standard Gibbs free energy according to Aspen Tech (2013). The equilibrium constants (Table 16) for reactions 6 and 7 in CH-CA-MEA are obtained from Austgen et al. (1988) apud Aspen Tech (2013a).

The Aspen Plus®v8.4 parameters DGAQFM (DGFORM), DHAQFM (DHFORM) and CPAQ0 (CPIG) used to calculate the standard Gibbs free energy of $MEAH^+$ and $MEACOO^-$ are changed according to estimated by Aspen Tech (2013), parameters for the other components are obtained from the databank of Aspen Plus®v8.4.

Table 16 – Equilibrium constants for CH-CA-MEA standard Gibbs free energy model of the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution

Reaction number	Coefficients				
	A	B	C	D	E
1	132.899	-13445.9	-22.4773	0	0
2	231.465	-12092.1	-36.7816	0	0
3	216.05	-12431.7	-35.4819	0	0
4	-3.03833	-7008.36	0	-0.003135	0
5	-0.52135	-2545.53	0	0	0
6	214.582	-12995.4	-33.5471	0	0
7	-9.74196	-8585.47	0	0	0

Source: Austgen et al. (1988) apud Aspen Tech (2013a)
Note: concentration basis selected by unsymmetric reference state of ions: mole-frac

The reaction model Reaction ID: RE-CA-MEA implemented in the Aspen Plus v8.4 process model simulation of the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution was developed with a REACTIONS model.

Reaction ID: RE-CA-MEA

1	Equilibrium	$H_2O + MEAH^+ \leftrightarrow MEA + H_3O^+$
2	Equilibrium	$2H_2O \leftrightarrow H_3O^+ + OH^-$
3	Equilibrium	$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-}$
4	Kinetic	$CO_2 + OH^- \rightarrow HCO_3^-$
5	Kinetic	$HCO_3^- \rightarrow CO_2 + OH^-$
6	Kinetic	$MEA + CO_2 + H_2O + \rightarrow MEACOO^- + H_3O^+$
7	Kinetic	$MEACOO^- + H_3O^+ \rightarrow MEA + H_2O + CO_2$
8	Equilibrium	$H_2O + H_2S \leftrightarrow HS^- + H_3O^+$
9	Equilibrium	$H_2O + HS^- \leftrightarrow S^{2-} + H_3O^+$

The equilibrium constants for reactions from 1 to 3 in RE-CA-MEA are obtained from the standard Gibbs free energy. The equilibrium constants for reactions 8 and 9 (Table 17) in RE-CA-MEA are the same equilibrium constants for reactions 6 and 7 in CH-CA-MEA.

Table 17 – Equilibrium constants for RE-CA-MEA standard Gibbs free energy model of the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution

Reaction number	Coefficients				
	A	B	C	D	E
8	214.582	-12995.4	-33.5471	0	0
9	-9.74196	-8585.47	0	0	0

Source: Austgen et al. (1988) apud Aspen Tech (2013a)
Note: equilibrium constant basis: mole gamma

The power law reduced expressions is used for the reactions from 4 to 7 in RE-CA-MEA rate-controlled reactions, according to Equation 30.

$$r = kT^n exp\left(-\frac{E}{RT}\right)\prod_{i=1}^{N} C_i^{a_i} \tag{30}$$

Considering: $n = 0$

Where, r is the rate of reaction, k is the pre-exponential factor, T is the absolute temperature (T), n is the temperature exponent, E is the activation energy, R is the universal gas constant, N is the number of components in the reaction, C_i is the concentration of component i, and a_i is the stoichiometric coefficient of component i in the reaction equation.

The kinetic parameters for reactions 4 and 5, in RE-CA-MEA, were obtained from Pinset et al. (1956) apud Aspen Tech (2013a). The kinetic parameters for reactions 6 and 7, in RE-CA-MEA, were obtained from Hikita et al. (1977) apud Aspen Tech (2013a). Table 18 shows the kinetic parameter for the rate-controlled reactions according to Aspen Tech (2013a).

Table 18 - Pre-exponential factor and activation energy kinetic parameters for RE-CA-MEA rate-based model of the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution

Reaction number	Pre-exponential factor	Activation energy (ca/mol)
4	$4.32e^{+13}$	13249
5	$2.38e^{+17}$	29451
6	$9.77e^{+10}$	9855.8
7	$3.23e^{+19}$	15655

Source: Aspen Tech (2013a) and Aspen Plus®v8.4 database APV84 (2015)

The ELECNRTL physical property methods used in the Aspen Plus®v8.4 process model simulation of co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution according to Aspen Tech (2013a) apply Clarke model (VAQCLK) for liquid molar volume using the quadratic mixing rule for solvents (option 1) with interaction parameter VLQKIJ for the quadratic mixing rule between MEA and H_2O from Kapadi et al. (2007) and Clarke model parameter for the main electrolytes.

(MEA-H_2O-CO_2) from Weiland (1996), Jones-Dole electrolyte correction model (MUL2JONS) weighted by mass fraction (option code 1) for liquid viscosity model for the solvent (option code 1) using Aspen liquid mixture viscosity (option code 2) with interaction parameters (MUKIJ and MULIJ) of MEA-H_2O from Kapadi et al. (2002) and Wadi et al. (1995) and Jones-Dole model parameters (IONMUB) from Palaty (1992) and Pac et al. (1984), Onsager-Samaras model (SIG2ONSG) for liquid surface tension for electrolyte system (option code 1) wit exponent codes being -9 in mixing rule, Riedel electrolyte correction model (KL2RDL) for thermal conductivity, Nernst-Hartley model (DL1NST) for binary diffusivity with mixture viscosity weighted by mass fraction (option code 1).

The sub-cooled and satured synthesis gas (CA-G-1) at 50.0ºC and 1.1 bar from the condenser knock-out drum (SC-FLA-4) in the low-temperature synthesis gas wet cleaning system (SC blocks) containing CO_2 and H_2S and others pollutants not removed in the low-temperature wet cleaning steps, fed-enter into the bottom of the low-pressure absorber packed-column (CA-ABS-1) by the blower system (SC-BLO-1). The synthesis gas flow upward through the absorber packet in contact with the down flow MEA-based aqueous absorbing-solution (lean-amine solution) to exit as clean outlet gas at the absorber top stage (CA-ABS-1). The system was designed to removal $90.0\%_{w/w}$ of CO_2 present in sub-cooled synthesis gas with top stage pressure at 1.06 bar and column pressure drop of 0.04 bar, the lean-amine solutions is fed on the top stage and the sub-cooled and satured synthesis gas on the bottom stage (CA-ABS-1).

The MEA considered to forming the absorbing-solution is a commercial type high-concentrate MEA-based solution shipped and delivered to thermochemical-biorefinery supplies offloading area by truck to storage. From the storage tank, high-concentrate MEA-based solution is ducted to the amine surge tank (CA-SUR-1) and pumped by the amine supply pump (CA-PUM-1) to the mixture tank (CA-MIX-1) to be added with the water and lean-amine solution in circulation on closed-loop cycle mode.

Make-up of high-concentrate MEA-based solution added into the system depends on the losses (thermal, oxidative, reclaimed, and entrained-off). The make-up is made from time to time but simulated in the Aspen Plus®v8.4 process model simulation as continues process in steady state mode. The mass flow rate of high concentrate MEA-based solution is controlled by design specification DS-CA-CL-1 varying the mass flow rate inlet the system to maintenance the lean-amine solution content $30.0\%_{w/w}$ of MEA in the inlet stream (CA-L-6) in the top of the low-pressure absorber packed-column (CA-ABS-1). The design specification considers all active MEA ionic forms present in the solution measured by apparent component mass fraction for electrolyte system as property sets.

The lean-amine solution formed in the mixture tank (CA-MIX-1) is cooled by the lean-amine water cooler (CA-HEA-1) passing cooling water (CT-HEA-1) modeled by using a Heater exchanger blocks to maintenance the inlet conditions at 1.06 bar and 40.0ºC. The lean-amine solution with low fraction of CO_2, H_2S, and others pollutants content (e.g.: NH_3, SOx, CHN, COS, hydrocarbons) without degradation products (not included in the Aspen Plus®v8.4 process model simulation) is then fed in the 1º theoretically liquid stage (top column stage) of the low-pressure absorber packed-column (CA-ABS-1).

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-2) to the lean-amine water cooler (CT-HEA-1). The amount of cooling water required is determined and controlled by design specification DS-CA-TL-1 varying the mass flow rate of cooling water passing through the lean-amine water cooler (CT-HEA-1). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

Rigorous Aspen Plus®v8.4 process model simulation of the low-pressure absorber packed-column (CA-ABS-1) was developed using RadFrac columns block on standard convergence mode with reaction model RE-CA-MEA and electrolyte solution chemistry model CH-CA-MEA without in-bed condenser and reboiler. The model was optimized for estimated 20 theoretical stages considering a NORTON IMTP 38.0 mm packing section from 1º to 20º theoretically stages with section packed height and diameter optimized for each system requirements (scenarios dependence) on standards characteristics. The model use rate-based calculation for Mixed flow model without reactions and film resistance in vapor phase, without reactions and with film resistance in liquid phase. Default Aspen Plus®v8.4 packing parameters is applied to calculate pressure drop and liquid holdup by Stichlmair method, to predict the mass transfer coefficient and interfacial area by Onda et al. (1968) correlation, and heat transfer coefficient by Chilton-Colburn (Taylor and Krishna, 1993) method.

The gaseous top-product at about 1.06 bar and 72.0ºC leave from the 1º theoretically vapor stage in the low-pressure absorber packed-column (CA-ABS-1) is cooled to 1.04 bar and 40.0ºC in the absorber condenser (CA-CON-1) by cooling water (CT-HEA-2) modeled by using a Heater exchanger blocks condensing a fraction of the entrained water with MEA.

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-2) to the absorber condenser (CT-HEA-2). The amount of cooling water required is determined and controlled by design specification DS-CA-TL-2 varying the mass flow rate of cooling water passing through the absorber condenser

(CT-HEA-2). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system. The condensed phase formed at 1.04 bar and 40.0ºC is flash-separated in the absorber liquid reflux-drum (CA-FLA-1) modeled by using a Flash2 separator block. The condensate top product from the absorber liquid reflux-drum (CA-FLA-1) is pumped at 1.06 bar and 40.0ºC by the absorber reflux-pump (CA-PUM-2) and refluxed back to the 1º theoretically liquid stage (top column stage) of the low-pressure absorber packed-column (CA-ABS-1).

The gaseous phase from the absorber liquid reflux-drum (CA-FLA-1) is ducted-fed into the bottom of the washer packed-column section (CA-WAS-1) at 1.04 bar and 40.0ºC. The liquid bottom product is obtained at 1.10 bar and about 54.0ºC from the 20º theoretically liquid stage (bottom column stage) in the low-pressure absorber packed-column (CA-ABS-1) as a CO_2 and H_2S rich solution (rich-amine solution) with others pollutants content (e.g.: NH_3, SOx, CHN, COS, hydrocarbons) without degradation products (not included in the Aspen Plus®v8.4 process model simulation). Liquid bottom product is pumped by the rich-amine pump (CA-PUM-3) to the cross-solution heat exchanger (CA-HEA-2).

Make-up water (WATER FROM TREATMENT PLANT) at atmospheric pressure and 25.0ºC from the treatment plant is pumped (CA-PUM-6) at 1.03 bar to the 1º theoretically liquid stage (top column stage) in the washer packed-column section (CA-WAS-1). The water obtained in the bottom of the of the washer packed-column section (CA-WAS-1) is pumped by the washer water recycle-pump (CA-PUM-7) back to the 1º theoretically liquid stage (top column stage) to enter at 1.03 bar and about 37.0ºC in the washer packed-column section (CA-WAS-1). The water mass flow rate of water circulating in close-loop cycle is defined by the parameters of the washer packed-column section (CA-WAS-1), and by the employed temperature limits in the Aspen Plus®v8.4 process model simulation.

Single washer water step as final polishing step reduces the concentration of MEA and others water affinity contaminants in the cleaned synthesis gas.

Rigorous Aspen Plus®v8.4 process model simulation of the washer packed-column section (CA-WAS-1) was developed as a top section of the low-pressure absorber packed-column (CA-ABS-1) using RadFrac columns block on standard convergence mode with reaction model RE-CA-MEA and electrolyte solution chemistry model CH-CA-MEA without in-bed condenser and reboiler. The model was optimized for estimated 5 theoretical stages considering a NORTON IMTP 25.0 mm packing section from 1º to 5º theoretically stages with section packed height and diameter optimized for each system requirements (scenarios dependence) on standards characteristics, and according to diameter of the low-pressure absorber packed-column (CA-ABS-1). The model use rate-based calculation for Mixed flow model without reactions and film resistance in vapor phase, without reactions and with film resistance in liquid phase. Default Aspen Plus®v8.4 packing parameters is applied to calculate pressure drop and liquid holdup by Stichlmair method, to predict the mass transfer coefficient and interfacial area by Onda et al. (1968) correlation, and heat transfer coefficient by Chilton- Colburn (Taylor and Krishna, 1993) method.

A fraction of 0.45% of the circulating water is drained in the washer water bleed (CA-SPL-3) to recovery the concentrate washer-recovered MEA-based aqueous absorbing-solution and removes the dissolved gases (amine contaminated wash water), in closed-loop water cycle. After, drained water is recycled and sends back to mixture tank (CA-MIX-1).

The wet cleaned-synthesis gas (gaseous top-product) from washer packed-column section (CA-WAS-1) at 1.03 bar and about 39.0ºC is ducted to the integrally-geared centrifugal two stages compressor (CO blocks) to conditioning the synthesis gas for effective use as single-gas fuel in the SG-ICEs in CC mode (IC blocks).

Rich-amine solution from the low-pressure absorber packed-column (CA-ABS-1) is sent by rich-amine pump (CA-PUM-3) to cross-solution heat exchanger (CA-HEA-2) modeled by using a HeatX exchanger block for exchange heat (thermal energy recovery) with the lean-amine solution from the low-pressure stripper packed-column (CA-STR-1). Lean-amine solution is cooled from about 121.0ºC to about 62.0ºC, heating the rich-amine from about 54.0ºC to about 105.0ºC. The heated rich-amine solution is fed into the 6º theoretical stage in the low-pressure stripper packed-column (CA-STR-1) on top of the regenerative section. The cooled lean-amine solution is sent to amine reclaimer (CA-SPL-2) or directly back to mixture tank (CA-MIX-1) closing the MEA-based aqueous absorbing-solution cycle.

Rigorous Aspen Plus®v8.4 process model simulation of the low-pressure stripper packed-column (CA-STR-1) was developed using RadFrac columns block on standard convergence mode with reaction model RE-CA-MEA and electrolyte solution chemistry model CH-CA-MEA without in-bed condenser and reboiler. The model was optimized for estimated 25 theoretical stages (5 theoretical stages as washer section) considering a NORTON IMTP 38.0 mm packing section from 1º to 25º theoretically stages with height and diameter for regenerative and washer packed sections optimized for each system requirements (scenarios dependence) on standards characteristics. The model use rate-based calculation for mixed flow model without reactions and film resistance in vapor phase, without reactions and with film resistance in liquid phase. Default Aspen Plus®v8.4 packing parameters is applied to calculate pressure drop and liquid holdup by Stichlmair method, to predict the mass transfer coefficient and interfacial area by Onda et al. (1968) correlation, and heat transfer coefficient by Chilton- Colburn (Taylor and Krishna, 1993) method.

The gaseous top-product containing mainly acid gases (CO_2 and H_2S) at about 1.72 bar and 94.3ºC from the 1º theoretically vapor stage (top column stage) of the low-pressure stripper packed-column (CA-STR-1) is cooled in the stripper condenser (CA-CON-2) passing cooling water (CT-HEA-3) modeled using Heater exchanger blocks. Hence, form-condense 54.0%$_{w/w}$ (model result) of the gaseous top-product on saturation equilibrium conditions.

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-3) to the stripper condenser (CT-HEA-3). The amount of cooling water required is determined and controlled by design specification DS-CA-TL-3 varying the mass flow rate of cooling water passing through the stripper condenser (CT-HEA-3). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

The condensed phase formed at 1.7 bar and 40.0ºC is flash-separated in the striper liquid reflux-drum (CA-FLA-2) modeled by using a Flash2 separator block. A fraction of the condensate top product containing mainly water from the striper liquid reflux-drum (CA-FLA-2) is splitted in the striper water bleed (CA-SPL-1) and sent-recycled back to the mixture tank (CA-MIX-1) as recovered water (recycle) in closed-loop-cycle mode. Another fraction (15.0%$_{w/w}$ by model result) of the condensate top product is pumped at 1.72 bar and 40.0ºC by the desorber reflux pump (CA-PUM-4), and refluxed back to the 1º theoretically liquid stage (internal washer section) in the low-pressure stripper packed-column (CA-STR-1). The excess of water is purged (CA-SPL-4) and sent to wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for reuse as make-up water (WATER FROM TREATMENT).

About 44.0%$_{w/w}$ of gaseous top-product (non-condensed) containing mainly CO_2 and H_2S leaving from the striper liquid reflux-drum (CA-FLA-2) at 1.7 bar and 40.0ºC (saturation condition) is directly sent to be compressed and liquefied by the integrally-geared centrifugal six stages compressor (CC blocks).

The liquid bottom product containing mainly regenerated amine solution at 1.78 bar and about 119.4ºC from the 25º theoretically liquid stage in the regenerative section in the low-pressure stripper packed-column (CA-STR-1) as lean-amine solution is splitted in the lean-amine sump splitter (CA-SPL-6) of the stripper reboiler (CA-REB-1). 95.0%$_{w/w}$ of the bottom liquid product in the sump is fed in the stripper reboiler (CA-REB-1), and 5.0%$_{w/w}$ of the bottom liquid product in the sump is drained as product and mixed in the lean-amine regenerated mixer (CA-MIX-2) with heated bottom liquid phase overflow the baffle.

The reboiler circulation baffle model was developed by using a HeatX exchanger block (CA-REB-1) and by using an FSplit splitter block (CA-SPL-6) to represent the stripper reboiler configured for circulation with baffle.

The bottom liquid product from the lean-amine regenerated mixer (CA-MIX-2) contain regenerated MEA, low fraction of CO_2, H_2S, and others pollutants content (e.g.: NH_3, SOx, CHN, COS, hydrocarbons) without degradation products (not included in the Aspen Plus®v8.4 process model simulation).

The thermal energy required in the stripper reboiler (CA-REB-1) determine the MEA-based aqueous absorbing-solution vaporized in the reboiler, and the regeneration extent trough the low-pressure stripper packed-column (CA-STR-1) to obtain the required capture levels (adjust the required fraction of CO_2 captured to $90\%_{w/w}$ of the inlet).

The thermal energy required by the stripper reboiler (CA-REB-1) in the BIG-ICE/CC (SC1) is supplied by process steam at 2.5 bar and 130.0ºC obtained from the steam exhausted at 2.5 bar from the low-pressure expansion stage in the BPST system for thermochemical route-cycles. The thermal energy required by the stripper reboiler (CA-REB-1) in the BIG-ICE/CC (SC2) is supplied by process steam at 2.5 bar and 130.0ºC obtained from the steam extraction at 2.5 bar (ST-SPL-1) in the CEST system.

The mass flow rate of process steam at 2.5 bar and 130.0ºC required is determined by thermal requirements and exchanger temperature limits (cross-over avoided) in the cycle-system, and controlled by design specification DS-CA-FL-2 varying the mass flow rate of water/steam circulating through the reboiler exchanger cycle.

In the BIG-ICE/CC (SC1), and BIG-ICE/CC (SC2), a fraction of the condensed water after the stripper reboiler (CA-REB-1) is pumped (GA-PUM-1) as conditioned hot water to syngas cooling and heat recovery (GA blocks) to produce the gasification steam agent in the low-temperature vertical CSC (GA-CSC-2). The reminiscent fraction is sent-back (recycle) to the deaerator unit (HR-DEA-1). The splitted hot water for each purpose is controlled by design specification DS-CA-TL-3 varying the mass flow rate of the water based on the quantity of gasification steam agent is required by the atmospheric CFB directly-heated gasifier (GA-GASEI).

The lean-amine solution regenerated from the lean-amine regenerated mixer (CA-MIX-2) is send to be cooled from about 121.0ºC to about 62.0ºC, recovering the heat in the cross-solution heat exchanger (CA-HEA-2). After cooled, the lean-amine solution is sent to the amine reclaimer (CA-SPL-2).

Amine reclaimer (CA-SPL-2) split $0.18\%_{w/w}$ of the lean-amine solution circulating back to low-pressure absorber packed-column (CA-ABS-1). Amine reclaimer (CA-SPL-2) is modeled by using a FSplit splitter block to adjust the amine make-up, and simulate the losses of MEA due the thermal and oxidizing degradation, according to input fraction of components removed in the carbon-based filter (CA-SEP-1) as simplified mode (model artifice). In the carbon-based filter (CA-SEP-1) modeled by using a Sep separator block is considered a loss of $10.0\%_{w/w}$ of the circulating water in the reclaimer cycle, and the downdraft of all dissolved gases and electrolyte entering the filter system (CA-SEP-1).

The lean-amine solution reclaimed is filtered by carbon-based filter (CA-SEP-1) containing activated charcoal medium put on stream at every 3 to 4 weeks of interval (continues stead-state simulated). In this stage, are removed sulphur and nitrogen compounds, amine salts, particles, and degradation products (not included in the Aspen Plus®v8.4 process model simulation), formed over time in the amine cycle in closed loop-cycle mode.

A fraction of the amine reclaimed is recovered in the presence of a strong alkali solution (e.g.: NaOH) and with the application of heat (not included in the Aspen Plus®v8.4 process model simulation). Another fraction, retained and removed by the carbon-based filter (CA-SEP-1) is sent to wastewater treatment plant, and after destined to final disposal (e.g.: landfill) with carbon filter active medium (activated charcoal) (RESIDUE TO DISPOSAL). Recovered amine is sent-back into the amine-lean solution line (CA-SPL-2) by the recirculation pump (CA-PUM-5) together 90.0%$_{w/w}$ of cleaned-water that passes through the carbon-based filter (CA-SEP-1).

6.1.9 Carbon dioxide compression and storage/use

The gaseous CO_2 captured (acid gas) in the BIG-ICE/CC (SC1) and for BIG-ICE/CC (SC2) by the co-capture of CO_2 and H_2S by using amine-based aqueous absorbing-solution (CA blocks) is compressed by the integrally-geared centrifugal six stages compressor (CC blocks) (multiple pinions). The compressed gaseous CO_2 is after-cooled been liquefied producing liquid CO_2 at 30.0ºC and 73.0 bar for further uses. High-pressure liquid pump (CC-PUM-1) is used to adjust the pressure to 150.0 bar (or more) to be injected into the geological formations for permanent storage (CCS).

The Aspen Plus®v8.4 process model simulation of the integrally-geared centrifugal six stages compressor (CC blocks) is based on the Siemens STC-GV integrally-geared centrifugal multi-stages compressor series feature a single-shaft arrangement and configured to allow inter-cooling steps. The Aspen Plus®v8.4 process model simulation of the integrally-geared centrifugal six stages compressor (CC blocks) was developed using Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 83.0% isentropic efficiency (isentropic compression).

Figure 40 shows the Aspen Plus®v8.4 flowsheet of the CO_2 compression and storage/use area for BIG-ICE/CC (SC1) and for BIG-ICE/CC (SC2).

The gaseous top-product containing mainly CO_2 and H_2S from the striper liquid reflux-drum (CA-FLA-2) at 1.7 bar and 40.0ºC (saturation condition) is compressed by the six impellers (CC-COM-1~6). The pressurized gases between the compression stages (CC-COM-1~6) is cooled to 30.0ºC by the water inter-cooler exchangers (CC-1~5) modeled by using a MHeatX exchanger blocks generating condensed phase content water and dissolved gases. The condensed phase is removed in the condenser knock-out drums (CC-FLA-1~5) modeled by using a Flash2 separator block and sent to atmospheric condensate buffer/equalizer tank (CC-FLA-7) modeled by Flash2 separators block at ambient conditions.

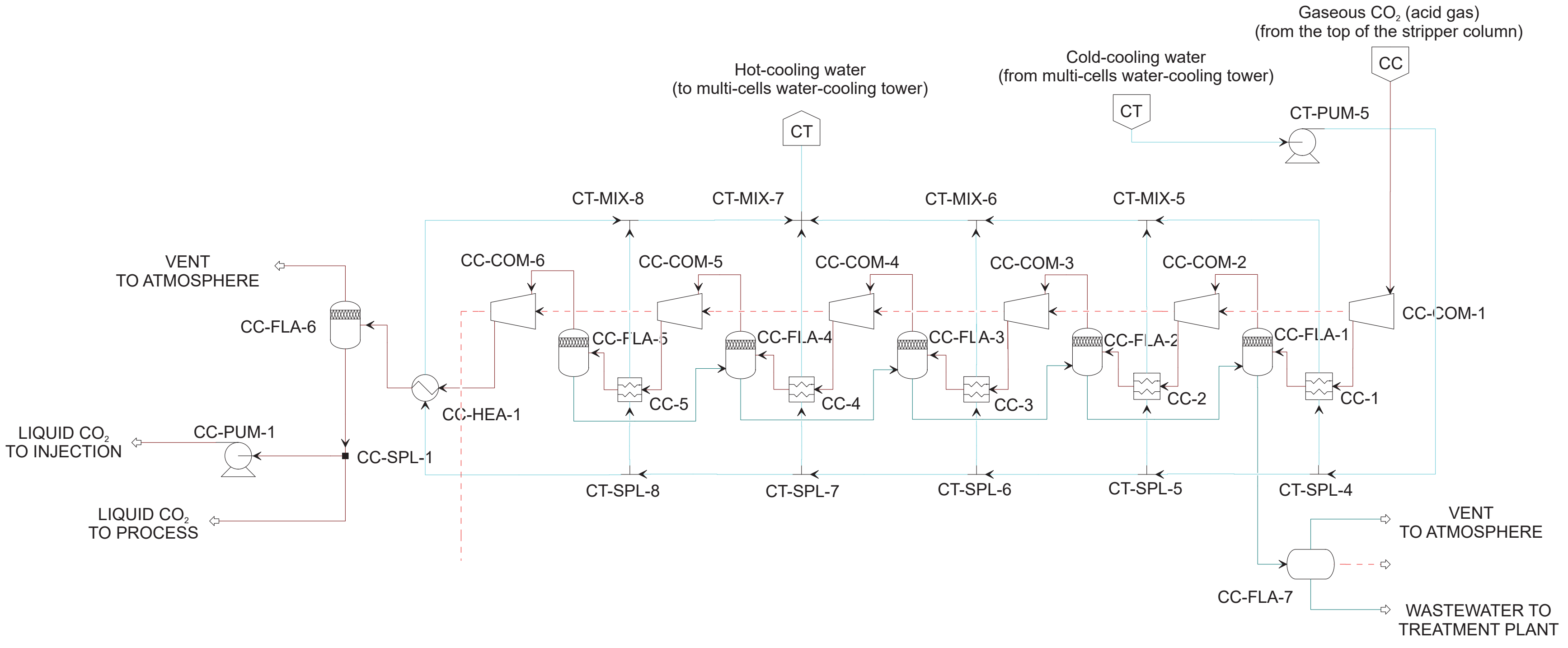


Figure 40 - Aspen Plus® v8.4 flowsheet of the CO_2 compression and storage/use area for BIG-ICE/CC (SC1) and for BIG-ICE/CC (SC2)

As shown in Figure 40, Aspen Plus®v8.4 flowsheet of CO_2 compression and storage/use area in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2) is compost by: integrally-geared centrifugal six stages compressor (CC-COM-1~6); water inter-cooler exchangers (CC-1~5); supercritical liquefactor-cooler (CC-HEA-1); condenser knock-out drum (CC-FLA-5); liquid water pump (CC-PUM-1); high-pressure liquid pump (CC-PUM-1); direct drive permanent magnet motor (mechanical efficiency); degases warm (CC-FLA-6); atmospheric condensate buffer/equalizer tank (CO-FLA-7); high-pressure buffer/equalizer tank (CO-FLA-6); and liquid CO_2 temporary storage tank (CC-SPL-1).

The captured gaseous CO_2 without the presence of H_2S (applying LO-CAT sulfur recovery unit) or the acid gas (technical compressor limits analysis) as leave in the top of the stripper column (CA-FLA-2) flow enters the compressor by the inlet guide (CC-COM-1) to distribute the flow providing a uniform condition in the first-stage impeller (CC-COM-1). The gaseous CO_2 is compressed by the impellers (CC-COM-1~6) modeled by using Compr pressure changer blocks according to rigorous ASME method for isentropic compressor. After the stages of compression (CC-COM-1~6), hot gas ducted-leaving is cooled to 30.0ºC by the water inter-cooler exchangers (CC-1~5) modeled by using MHeatX exchanger blocks generating condensed phase content water and dissolved gasses. Condensed phase is removed in the condenser knock-out drums (CC-FLA-1~5) modeled by using Flash2 separator blocks and sent to atmospheric condensate buffer/equalizer tank (CC-FLA-7) modeled by using a Flash2 separator block at ambient conditions.

Cooled high-pressure gaseous CO_2 at about 73.0 bar and 88.0ºC (supercritical pressure) after the six-stage impeller (CO-COM-6) is cooled to 30.0ºC and liquefied by the supercritical liquefactor-cooler (CC-HEA-1) modeled by using a HeatX exchanger block. Liquid CO_2 is sent to high-pressure buffer/equalizer tank (CO-FLA-6) to remove any non-condensable gases present in the line to atmosphere (VENT TO ATMOSPHERE) coupled with the liquid CO_2 temporary storage tank (CC-SPL-1) to maintenance the liquid phase at 73.0 bar and 30.0CºC.

The liquid CO_2 produce-captured can be send to permanent storage (HIGH-PRESSURE CO_2 TO STORAGE) in geological formations (CCS) (e.g.: aquifers, oil and gas fields, unmineable coal beds) at about 150.0 bar using a high-pressure liquid pump (CC-PUM-1) to compress the liquid CO_2. The liquid CO_2 produce-captured can be send to process use (LIQUID CO_2 TO PROCESS) at adequate conditions required by the downstream process (not included in the model) or by the transportation off-site (e.g.: algae-based liquid biofuels, methanol catalytic synthesis). The use of captured CO_2 is not defined in this research Master`s degree.

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-5) to the water inter-cooler exchangers (CC-1~5) and to the supercritical liquefactor-cooler (CC-HEA-1). The amount of cooling water required is determined and controlled varying the mass flow rate of cooling water flows through the equipment users. The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system. The lubricating oil circuit and the lubricating oil water-cooling system (low make-up and electricity requirements) are suppressed from the Aspen Plus$^{®}$v8.4 process model simulations in this research Master`s degree.

The ambient equalized condensate (CC-FLA-7) is after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

The single shaft and multiple pinions in the integrally-geared centrifugal six stages compressor (CC-COM blocks) is drive by a synchronous direct drive permanent magnet motor modeled by CC-E-6 work stream. The compression stages (impellers) are optimized to obtain the same compression ratio by design specification DS-CC-TR-1 and FORTRAN calculation block CA-CC-TR-2 varying the pressure ratio in the six compression stages (CO-COM blocks). The electrical potential losses by attrite in the mechanical move parts was considered as 1.0% of the mechanical energy required by the stage (99.0% mechanical efficiency).

6.1.10 Synthesis gas compression (conditioning)

The sub-cooled and cleaned synthesis gas obtained in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2) has a lower energetic density (low-medium LHV synthesis gas) compared with natural gas and less than that required by the SG-ICE (developed for natural gas). The synthesis gas produced by the atmospheric CFB directly-heated gasifier using atmospheric air and steam agents is not suitable for efficient use in SG-ICEs developed for natural gas or an equivalent gas with high heating value about 28.0 MJ/Nm^3 (quality of the fuel-gas). To achieve the synthesis gas energy density its is compressed by a integrally-geared centrifugal two stages compressor (CO blocks) until reaching the minimum required for an efficient use (quality requirement) as fuel-gas in SG-ICEs (IC blocks) according to technical parameters and limits of pressure and temperature in the cylinder chambers during the complete four-stroke Otto-cycle.

The Aspen Plus$^{®}$v8.4 process model simulation of the integrally-geared centrifugal two stages compressor (CO-COM blocks) is based on the Siemens STC-GV integrally-geared centrifugal multi-stages compressor series feature a single-shaft arrangement configured to allow inter-cooling and after-cooling steps.

Figure 41 shows the Aspen Plus$^{®}$v8.4 flowsheet of the cleaned synthesis gas compression (conditioning) for BIG-ICE/CC (SC1) and for BIG-ICE/CC (SC2).

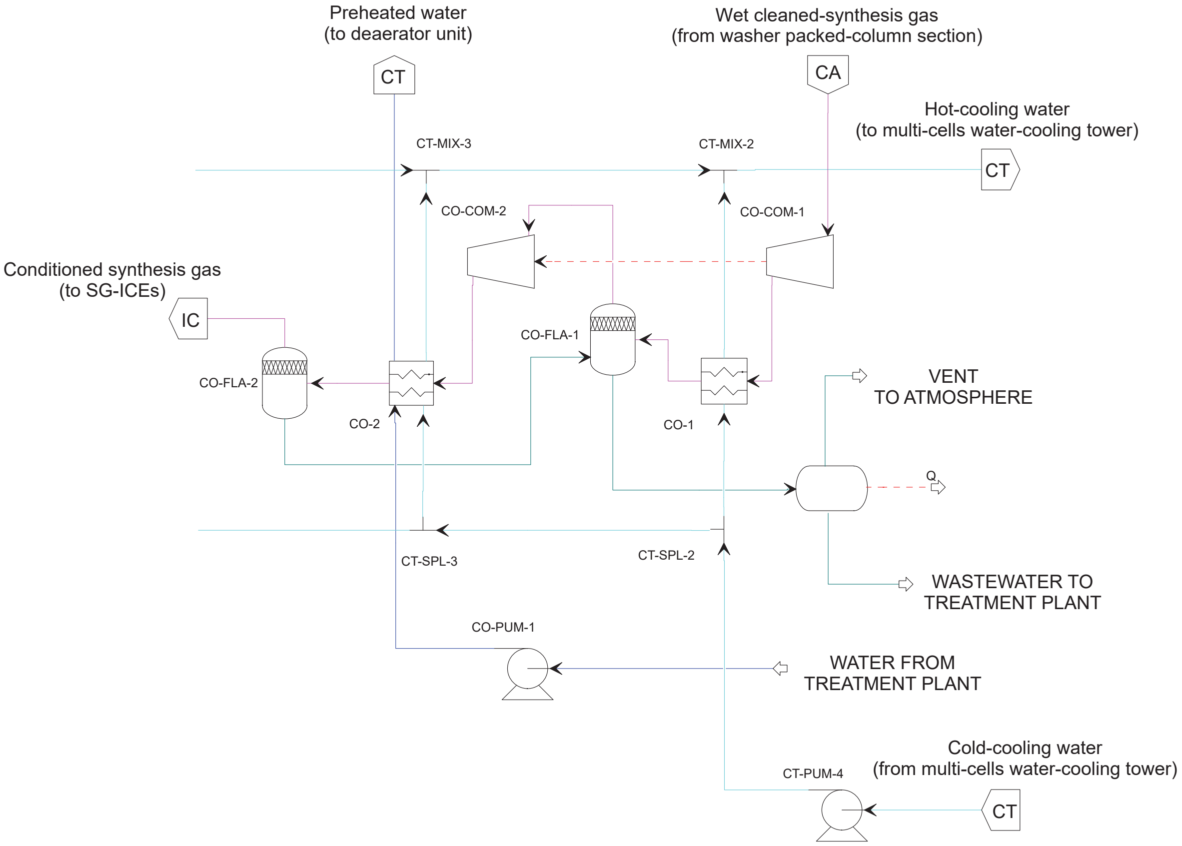


Figure 41 - Aspen Plus®v8.4 flowsheet of the cleaned synthesis gas compression (conditioning) for BICE/CC (SC1) and for BIG-ICE/CC (SC2)

As shown in Figure 41, Aspen Plus®v8.4 flowsheet of the cleaned synthesis gas compression (conditioning) in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2) is compost by: integrally-geared centrifugal two stages compressor (CO-COM-1 and CO-COM-2); water inter-cooler exchange (CO-1); tree-circuits water after-cooler exchange (CO-2); condenser knock-out drums (CO-FLA-1 and CO-FLA-2); atmospheric condensate buffer/equalizer tank (CO-FLA-3); direct drive permanent magnet motor (not included as block); and liquid water pump (CO-PUM-1).

The sub-cooled and cleaned synthesis gas (wet gas) from the 1º theoretically gaseous stage (top column stage) in the washer packed-column section (CA-WAS-1) flow enters the compressor by the inlet guide (CO-COM-1) to distribute the flow providing a uniform condition in the first-stage impeller (CO-COM-1). The sub-cooled and cleaned synthesis gas is compressed to an optimized pressure (OP-CO-PG-1) by the first-stage impeller (CO-COM-1) modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 83.0% isentropic efficiency (isentropic compression).

The synthesis gas after the first-stage of compression (CO-COM-1) ducted-leaving is cooled to 30.0ºC by the water inter-cooler exchanger (CO-1) modeled by using a MHeatX exchanger blocks generating condensed phase content water and dissolved gases. The condensed phase is removed in the condenser knock-out drum (CO-FLA-1) modeled by using a Flash2 separator block and sent to atmospheric condensate buffer/equalizer tank (CO-FLA-3) modeled by using a Flash2 separator block at ambient conditions.

Synthesis gas free of condensate phase enters in the second-stage impeller (CO-COM-2) and is compressed to an optimized pressure (OP-CO-PG-1) to deliver the conditioned synthesis gas at required pressure by the downdraft equipment, the SG-ICEs (IC blocks) require in this case a pressure at about 6.0 bar in their injection system (IC-MIX-1). The second-stage impeller (CO-COM-2) is modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 83.0% isentropic efficiency (isentropic compression).

The synthesis gas after the second-stage of compression (CO-COM-2) ducted-leaving is cooled to 30.0ºC by the water three-circuit after-cooler exchanger (CO-2) modeled by using a MHeatX exchanger block generating condensed phase content water and dissolved gases. The condensed phase is removed in the condenser knock-out drum (CO-FLA-2) modeled by using a Flash2 separator block and sent to atmospheric condensate buffer/equalizer tank (CO-FLA-3) modeled by using a Flash2 separator block at ambient conditions (equalizer).

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-4) to the cooling water circuits in the cooler exchangers (CO-1 and CO-2). The amount of water used to cool-down the synthesis gas is determined and controlled by design specification DS-CO-TL-1 varying the mass flow rate of cooling water passing through the cooling water circuit in the inter-cooler exchanger (CO-1), and by design specification DS-CO-TL-2 varying the mass flow rate of cooling water passing through the cooling water circuit in the water three-circuit after-cooler exchanger (CO-2). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system. The lubricating oil circuit and the lubricating water-cooling system are suppressed from the Aspen Plus$^{®}$v8.4 process model simulations in this research Master`s degree.

Part of the deaerator make-up water (WATER FROM TREATMENT PLANT) at atmospheric pressure and 25.0ºC is pumped at 1.42 bar by the liquid water pump (CO-PUM-1). And, then is preheated at 105ºC passing through the water three-circuit after-cooler exchanger (CO-2), being after sent-fed into the deaerator unit (HR-DEA-1), recovering heat and consequently reducing the low-pressure steam required by the deaerator unit (HR-DEA-1)

The ambient equalized condensate (CO-FLA-3) is after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

The single shaft and pinions with variable speed gears in the integrally-geared centrifugal two stages compressor (CO-COM blocks) is driver by a synchronous direct drive permanent magnet motor modeled by CO-E-2 work stream and optimized to achieve the lowest consumption of electric power energy. The electric power energy consumed is optimize-minimized using optimization model analysis tools OP-CO-PG-1 varying the pressure obtained after the first-stage impeller (CO-COM-1) according with model analysis tools constraint CN-CO-PG-1 ensuring the technical compression fundaments (raise pressure in the next stage). The electrical potential losses by attrite in the mechanical move parts was considered as 1.0% of the mechanical energy required by the stage (99.0% mechanical efficiency).

6.1.11 Single-gas fueled internal combustion engine with turbo charging system

The single-gas fueled internal combustion engine (SG-ICE) with turbo charging system (IC blocks) is based on the Wärtsilä world's largest tri-fuel engine 18V50 operating using only gases as fuel. The engine is modified according to technical data and parameter limits to operate with conditioned synthesis gas for large-scale electricity generation (large-power thermochemical-biorefinery plant) considering the main topics described in the section 4.1.12 (Internal combustion engine).

The Aspen Plus®v8.4 process model simulation of the SG-ICEs (IC blocks) under the steady state operating conditions to represent the complete four-stroke Otto-cycle was developed using RKS-BM physical property methods for the fuel-gas side, IDEAL physical property methods for the liquid lubricating oil side (simplified composition), and IAPWS-95 physical property methods for the cooling water side.

The Aspen Plus®v8.4 process model simulation of the multiples SG-ICEs based on the Wärtsilä engine 18V50SG with turbo charging system consider an electrical energy outputs of about 18.76 MWh per engine at 60 Hz and 514 rpm with efficiency of 48.6% at the generator terminals. The engine operates according to lean-burn process with air-fuel ratio of about 2.07 in CC mode with a simplest intermediate-pressure HRSG system designed to heat recovery and low-pressure steam generation to supply the thermal energy required by the thermochemical-biorefinery.

Figure 42 shows the Aspen Plus®v8.4 flowsheet of the SG-ICEs with turbo charging system under the steady state operating conditions to represent the complete four-stroke Otto-cycle for BIG-ICE/CC (SC1) and for BIG-ICE/CC (SC2).

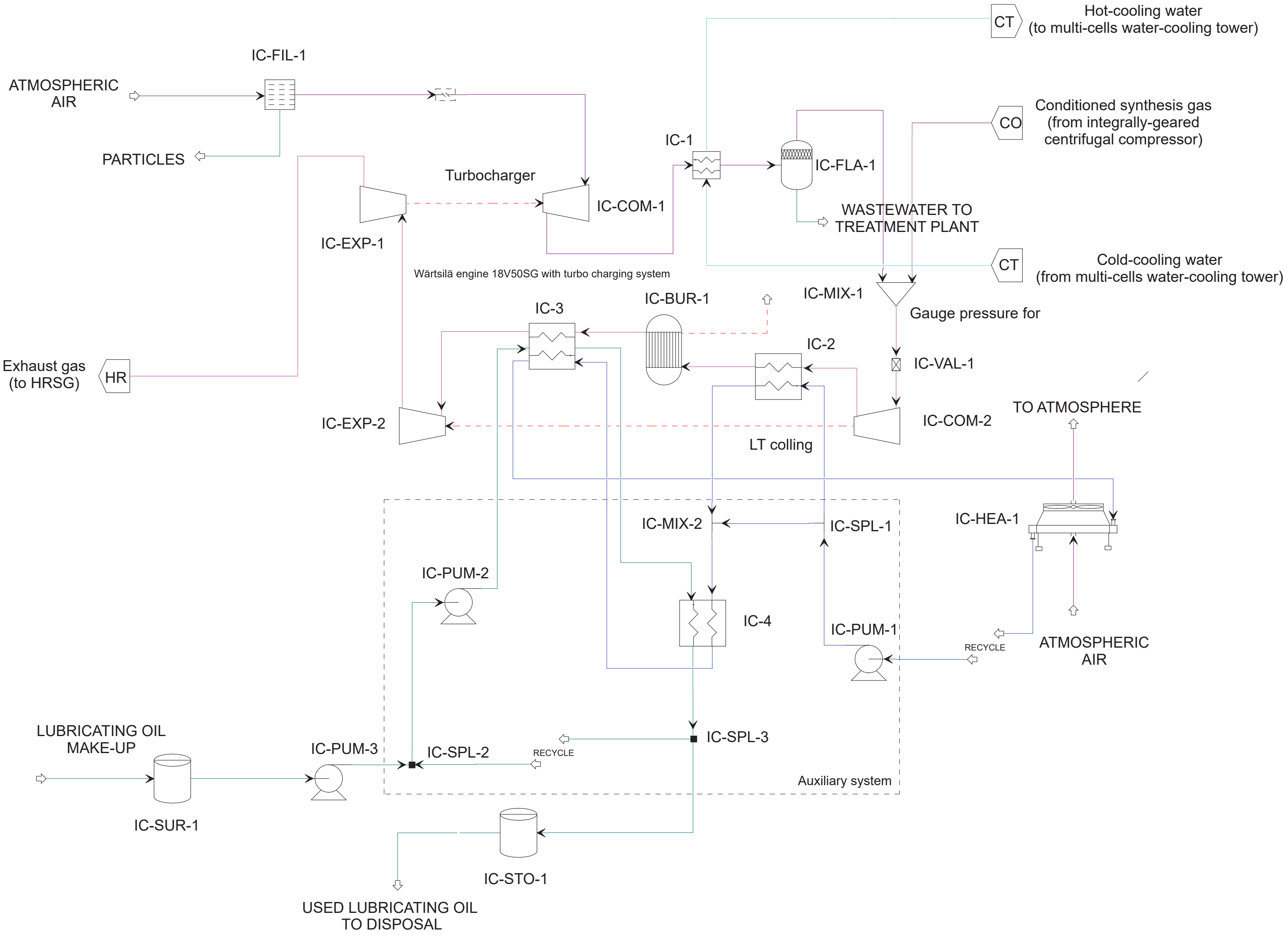


Figure 42 - Aspen Plus® v8.4 flowsheet of the single-gas fueled internal combustion engines with turbo charging system under the steady state operating conditions to represent the complete four-stroke Otto-cycle for BIG-ICE/CC (SC1) and for BIG-ICE/CC (SC2)

As shown in Figure 42, Aspen Plus$^{®}$v8.4 flowsheet of SG-ICEs with turbo charging system in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2) is compost by: air fans (not included in the model); self-cleaning air filter unit (IC-FIL-1); single pipes exhaust (SPEX) turbo charging system with exhaust-gas side expander (IC-EXP-1); and air-side compressor (IC-COM-1); piston chamber and cylinder in compression stoke state (IC-COM-2) and in expansion stoke state (IC-EXP-2); spark plug (IC-BUR-1); chamber in combustion process (IC-BUR-1); condenser knock-out drum (IC-FLA-1); mixture air-fuel pre-chamber (IC-MIX-1); air and fuel injection system (IC-MIX-1); admission gauge valve (IC-VAL-1); high-temperature (HT) cooling water circuits (IC-3); low-temperature (LT) cooling water circuits (IC-2); modified advanced LT and HT cooling water circuits charge air cooler (IC-1); lubricating oil engine circuit (IC-3); indirect contact radiator unit (IC-HEA-1); and auxiliary module.

The auxiliary module is compost by: water circulation pump (IC-PUM-1); lubricating oil cooler (IC-4); lubricating oil circulation pump (IC-PUM-2); lubricating oil make-up pump (IC-PUM-3); lubricating oil surge tank (IC-SUR-1); cooling water splitter (IC-SPL-1); cooling water mixer (IC-MIX-2); filter unit and lubricating oil purge system (IC-SPL-3); used lubricating oil storage tank (IC-STO-1); and lubricating oil mixer (IC-SPL-2).

The SG-ICEs model consider conditioned synthesis gas fed compressed at pressure level (compress-conditioning process) to obtain the fuel-gas quality around 30.0 MJ/m³ (pressurized cubic metric based) in the injection system (IC-MIX-1), according to section 6.1.10 (Synthesis gas compression (conditioning)).

The conditioned synthesis gas (compress-conditioning) at about 30.0 MJ/m³ in the injection system (IC-MIX-1) obtained from the integrally-geared centrifugal two stages compressor (CO blocks) is mixed with charged-pressurized combustion air (oxidant) in a mixture air-fuel pre-chamber (IC-MIX-1) modeled by using a Mixer block.

The combustion air (ATMOSPSHERIC AIR) is taken by air fans from the engine room (surrounding atmospheric air) at atmospheric pressure and 25.0ºC. The air first flow-pass through a self-cleaning air filter unit (IC-FIL-1) modeled by using a Fabric filter solids separator block to remove/reduce contaminants and particulate matter avoiding damages by debris in the SPEX turbocharger air-side compressor (IC-COM-1) and piston chamber (IC-COM-2).

High-efficiency single pipes exhaust (SPEX) turbo charging system designed streamlined with engine exhaust-gas side (expansion) and combustion air-side (compression) to intensify the power output per unit cylinder volume and unit engine. The engine was considered configured for one high-efficiency SPEX turbo charging system per cylinder bank compost by SPEX turbocharger (charged aspiration) air-side compressor (IC-COM-1) modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 97.0% isentropic efficiency, and by SPEX turbocharger exhaust-gas side expander (IC-EXP-1) modeled by using a Compr pressure changer block according to isentropic method for isentropic expansion compressor considering 97.0% isentropic efficiency. The electrical potential losses by attrite in the mechanical move parts was considered as 1.0% of the mechanical energy required by the stage (99.0% mechanical efficiency).

Aspen Plus®v8.4 process model simulation of the high-efficiency SPEX turbo charging system do not consider the injection of fresh-water into the SPEX turbocharger system during operation to cleaning of the SPEX turbocharger air-side compressor (IC-COM-1) and SPEX turbocharger exhaust-gas side expander (IC-EXP-1). The high-efficiency SPEX turbo charging system do not use part of the charged-pressurized combustion air directly into the exhaust-gas manifold (without passing through the engine).

Combustion air inlet the SPEX turbocharger air-side to be charged-compressed (IC-COM-1) at same pressure of the conditioned synthesis gas in the injection system (IC-MIX-1) while in the SPEX turbocharger exhaust-gas side expander (IC-EXP-1) the exhausted gas from the cylinder chamber (IC-EXP-2) is expanded at 1.3 bar and 425.0ºC. The expansion work power is used to compress air in the SPEX turbocharger air-side compressor (IC-COM-1).

In this research Master`s degree the pressure of the conditioned synthesis gas was estimates to achieve the energy density (fuel-gas quality) requirement according to Aspen Plus®v8.4 process model simulations.

The air-fuel ratio is adjusted to lean-burn process at about 2.07 according to Equation 9 or as equivalent by oxygen excess by about 20.0%$_{w/w}$ in excess (inlet/outlet excess) measured (HV-7) in the exhausted gases according to Equation 12. The air-fuel ratio is controlled by design specification DS-IC-FG-1 varying the inlet mass flow rate of combustion air in the system.

The charged-pressurized combustion air leaving at about 234.0ºC after compression process (one-stage model) from the SPEX turbocharger air-side compressor (IC-COM-1) is cooled to 45.0ºC. To cooling, is used cooling water available at 27.0ºC from the first-section of the multi-cells water-cooling tower (CT blocks) into the modified advanced LT and HT cooling water circuits charge air cooler (IC-1) modeled by using a MHeatX exchanger blocks (IC-1), generating condensed phase content water and dissolved gases. The condensed phase is removed in the condenser knock-out drum (IC-FLA-1) modeled by using a Flash2 separator block and send to be after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

The modified advanced LT and HT cooling water circuits charge air cooler (IC-1) is connected to first-section of the multi-cells water-cooling tower (CT blocks) as complementary external cooling system used to reduce the cooling water circulation trough the indirect contact radiator unit (IC-HEA-1). In the Aspen Plus®v8.4 process model simulation was not considered the heat recovery and steam generation from this hot-stream (charged-pressurized combustion air) by an external system. In an optimized and integrated technologies scenario (future studies) can be produced process steam at 2.5 bar and 130.0ºC reducing the stress on the HRSG system.

The amount of cooling water necessary for cooling the charged-pressurized combustion air is determined and controlled by using the CT-SP-3 split fraction varying the mass flow rate of cooling water passing through the charge air cooler (IC-1). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

The conditioned synthesis gas and the charged-pressurized combustion air (oxidant) are mixed in a mixture air-fuel pre-chamber (IC-MIX-1). Hence, then is injected into the top of a cylinder (IC-COM-2) considering a drop pressure of 10.0% of the pressure in the mixture air-fuel pre-chamber (IC-MIX-1) by the injection process through admission gauge valve (IC-VAL-1) modeled by using Valve pressure change block considering only vapor as valid phase. The air-fuel mixture is inject-forced by the admission gauge valve (IC-VAL-1) into the cylinder during the expansion stoke when the piston descend from the top of the cylinder to the bottom of the cylinder (variable pressure not determined).

The gas admission valves (IC-VAL-1) control the correct amount of air-fuel mixture is fed into each cylinder (not include in the Aspen Plus®v8.4 process model simulation) and the cylinder pressure in the top dead center position after the exhaust stroke (IC-COM-2).

The pressure in the top dead center position during the injection of the air-fuel mixture into the cylinder chamber (IC-COM-2) is controlled by design specification IC-PG-2 varying the injection pressure in the valve gauge (IC-VAL-1) coupled with the required pressure in the exhaust stroke (IC-EXP-2). The pressure in the exhaust stroke (IC-EXP-2) is controlled by design specification DS-IC-PG-1 varying the cylinder pressure in the top dead center position on the exhaust stroke (IC-EXP-2). The pressure must expand the exhaust-gas to 1.3 bar and 425.0ºC in the in the SPEX turbocharger exhaust-gas side expander (IC-EXP-1) and be sufficient to perform the air compression in the SPEX turbocharger air-side compressor (IC-COM-1).

The compression stroke in the piston chamber and cylinder in compression stoke state (IC-COM-2) is modeled by using a Compr pressure changer block (IC-COM-2) according to rigorous ASME method for isentropic compressor considering 99.0% isentropic efficiency and 99.0% of mechanical efficiency. The volumetric compression ratio (spark-ignited engines) was fixed at 10:1 considering the technical operational limits of the SG-ICEs based on the Wärtsilä engine 18V50SG with turbo charging system, applicable for efficient operation using low-medium heat values synthesis gas. The volumetric compression ratio is controlled by design specification DS-IC-PG-4 according to low-pressure (model determined) in the top dead center position after the exhaust stroke (IC-COM-2) varying the pressure of the cylinder block (IC-COM-2) to performer the volumetric compression ratio varying the discharge pressure of the block (IC-COM-2). Whereas, estimate the peak-pressure and peak temperature of the air-fuel mixture in the compress stroke before the spark ignition (combustion).

In this research Master`s degree and in the Aspen Plus®v8.4 process model simulation was assumed that the air-fuel mixture does not reach the auto-ignition (pressure and temperature dependence) state during the compression stroke. Determine this point requires experimental data considering the fuel-gas mixture specific composition.

The spark ignition of the lean air-fuel mixture is initiated by a spark plug located in the pre-chamber (not include in the Aspen Plus®v8.4 process model simulation). After the compression stroke (IC-COM-2) and ignition, the in-cylinder chamber in combustion process (IC-BUR-1) modeled by using a RGibbs reactor block, representing the gaseous reaction according to chemical equilibrium by Gibbs free-energy minimization method considering all components as potential products in products sheet, generate a high-peak pressure and a high-peak temperature (technical operational limits).

0.5% of the LHV_{AR} of the conditioned synthesis gas fed is assumed to be lost from the SG-ICEs (IC-BUR-1), being controlled by FORTRAN calculator block CA-IC-QL-1 varying the heat duty in the chamber in combustion process (IC-BUR-1) with the aid of parameter calculation blocks (DHV blocks group) implemented.

The high-peak pressure and a high-peak temperature (IC-BUR-1) is determined considering the isovolumetric combustion in the cylinder chamber (before cylinder-expansion process) obtained from design specification DS-IC-PG-3 varying the pressure (temperature variable) of the RGibbs reactor block (IC-BUR-1) to obtain the same volume in the inlet and outlet streams coupled with FORTRAN calculator block CA-IC-QL-1 (heat losses).

The expansion stroke in the piston chamber and cylinder in expansion stoke state (IC-EXP-2) is modeled by using a Compr pressure changer block (IC-EXP-2) in turbine mode considering 99.0% isentropic efficiency (isentropic expansion) and 99.0% mechanical efficiency. The expansion stroke and the work power generated by the expansion process are controlled by the design specification DS-IC-PG-1 varying the cylinder pressure in the top dead center position in the exhaust stroke (IC-EXP-2).

SG-ICEs exhaust-gas at 1.3 bar and 425.0ºC after expansion in the SPEX turbocharger exhaust-gas side expander (IC-EXP-1) is directly ducted to the conventional low-pressure HRSG simple designed to recover the sensible heat from the exhaust-gas and generate low-pressure steam to be used as thermal energy supply and to be expanded in steam turbines.

The Aspen Plus®v8.4 process model simulation of the advanced cooling water circuits integrate lubricating oil cooler (IC-4) and cooling water internal channels cooler (IC-2 and IC-3) are based on the SG-ICE Wärtsilä 18V50SG. Thus, three separate cooling circuits are considered: the cylinder cooling circuit (jacket); the charge air LT and HT cooling circuits; and the circuit for the lube oil cooler built on the auxiliary module.

The cooling circuits are modified and simplified represented by: HT cooling water circuit (IC-3) (cylinder heads); LT cooling water circuit (IC-2) (cylinder liners); modified advanced LT and HT cooling water circuits charge air cooler (IC-1); and the lubricating oil cooler (IC-4).

The hot water from HT cooling water circuit (IC-3), LT cooling water circuit (IC-2), and the lubricating oil cooler (IC-4) is cooled in a single circuit indirect contact radiator unit (IC-HEA-1). Charged-pressurized combustion air is cooled in the modified advanced LT and HT cooling water circuits charge air cooler (IC-1) by using cooling water from the multi-cells water-cooling tower (CT blocks).

The Aspen Plus®v8.4 process model simulation of the engine auxiliary module consider the use of water circulation pump (IC-PUM-1) to maintenance the required mass flow rate of cooling water circulating in the internal cooling circuits.

Cooling water at 4.0 bar and 30.0ºC after cooled by the indirect contact radiator unit (IC-HEA-1) is pumped to 5.0 bar by the water circulation pump (IC-PUM-1). Part of the cooling water at 5.0 bar and about 30.0ºC is splitted (IC-SPL-1) and sent to the LT cooling water circuit (IC-2) leaving the circuit at 40.0ºC. This heated cooling water is mixed (IC-MIX-2) with another part of the cooling water at 30.0ºC direct pumped (IC-PUM-1) to the lubricating oil cooler (IC-4) modeled by using a MHeatX exchanger block cooling the hot-lubricating oil.

The cooling water at 5.0 bar and about of 68.6ºC after the lubricating oil cooler (IC-4) is sent to the HT cooling water circuit (IC-3) pass-flowing exchanging heat thought the cylinder heads hot-zone. Cooling water after the HT cooling water circuit (IC-3) leaving the cylinder heads at 93.0ºC (hot water) is cooled to 30.0ºC in the indirect contact radiator unit (IC-HEA-1) modeled by using a HeatX exchanger block in closed-loop cycle mode (recycle). Indirect contact radiator unit (IC-HEA-1) cooling the hot water inducing (mechanical propeller drive fans) the surrounding air at ambient conditions (ATMOSPHERIC AIR) passing through the indirect contact surfaces (IC-HEA-1).

The mass flow rate of circulating cooling water is controlled by design specification DS-IC-TG-1 varying the cooling water mass flow rate required to cool-down the lubricating oil and to maintenance the HT cooling water circuit (IC-3) and the LT cooling water circuit (IC-2) to obtain the SG-ICEs exhaust-gas at 1.3 bar and 425.0ºC.

The cooling surrounding air (ATMOSPHERIC AIR) required to maintenance and cool-down the hot water to 30.0ºC (ideal consideration) in the indirect contact radiator unit (IC-HEA-1) is controlled by design specification DS-IC-TG-2 varying the mass flow rate of surrounding air (ATMOSPHERIC AIR) flowing thought the indirect contact radiator unit (IC-HEA-1) to obtain heated used air at 60.0ºC (TO ATMOSPHERE).

The new and renovated lubricating oil (LUBRICATING OIL) is delivered to thermochemical-biorefinery supplies offloading area by truck (tank) to storage tank, from which is transferred to lubricating oil surge tank (IC-SUR-1) to be used as new lubricating oil make-up at atmospheric pressure and 25.0ºC.

The Aspen Plus®v8.4 process model simulation of the engine auxiliary module consider the use of lubricating oil make-up pump (IC-PUM-3) to transfer the new lubricating oil (LUBRICATING OIL) from the storage tank in the thermochemical-biorefinery supplies offloading area to the lubricating oil surge tank (IC-SUR-1).

The lubricating oil make-up at ambient conditions is compress-pumped to 5.0 bar and about 25.0ºC by the lubricating oil make-up pump (IC-PUM-3) and then injected-mixed with the pressurized circulating lubricating oil into the lubricating oil mixer (IC-SPL-2) equalizing the lubricating oil temperature at about 65.0ºC (viscous fluid flow limit).

The SG-ICE requires about 50.0 m^3/hr of lubricating oil per engine circulating in the internal oil channels (IC-3). In order to maintenance the flowing rate, circulating lubricating oil at about 5.0 bar and 65.0ºC from the lubricating oil mixer (IC-SPL-2) is pumped-controlled by the lubricating oil circulation pump (IC-PUM-2), in addition to maintenance the hot-temperature of the lubricating oil above 72.0ºC (degradation limit) ensuring the efficient lubrication of the internal moving mechanical parts.

The lubricating oil at about 5.0 bar and 65.0ºC passing through the internal hot-surfaces on internal moving mechanical parts being heated to 72.0ºC, the acceptable thermal limits for avoid the oil degradation is controlled by the lubricating oil mass flow rate and cooling system limits. Hot lubricating oil at 72.0ºC is cooled down to 67.0ºC pass flowing in the internal channels of the lubricating oil cooler (IC-4). The amount of heat removed by the lubricating oil is determined and controlled by the thermal limits (viscosity and degradation operational limits) and the mass flow rate of the lubricating oil flowing through the system.

The Aspen Plus®v8.4 process model simulation of the lubricating oil cycle consider $0.02\%_{w/w}$ of the circulating lubricating oil as cycle losses (purged), which is removed from the system in the filter unit and lubricating oil purge system (IC-SPL-3) as used lubricating oil. The used lubricating oil is stored in the used lubricating oil storage tank (IC-STO-1) to be after-sent (time-to-time) to treatment or final disposal. Spreadsheet calculation model consider a recovery efficiency of $85.0\%_{w/w}$ of the used lubricating oil sent to treatment unit (not disposal impacts) as renovated lubricating oil and

15.0%$_{w/w}$ sent for the final disposal as hazard waste (USED LUBRICATING OIL TO DISPOSAL).

The make-up of new and renovated lubricant oil (LUBRICATING OIL) is controlled by design specification DS-IC-FL-1 varying the inlet mass flow rate of new and renovated lubricating oil (LUBRICATING OIL) into the system. The make-up is based on the mass flow rate of used lubricating oil purged (USED LUBRICATING OIL TO DISPOSAL) from the system by the filter unit and lubricating oil purge system (IC-SPL-3).

6.1.12 Heat recovery steam generator (HRSG)

The heat recovery steam generators (HRSG) for the combined-cycles and co-generation was simulated based on the horizontal gas-flow drum type aiming primary supply the thermal energy required by the biorefinery-technologies and secondarily generate steam to be expanded in steam turbines system for power generation.

Aspen Plus®v8.4 process model simulation of the staggered exchanger tube banks was developed using RKS-BM physical property methods for the hot exhaust-gas side and IAPWS-95 physical property methods for the water and steam side. The exchanger tube banks are modeled by using HeatX exchanger blocks considering the temperature limits (crossover avoided) between the exchanger tube banks and their influence on the water/steam mass flow rate for each circuit-level.

The arrangement of the exchanger tube banks in the Aspen Plus®v8.4 process model simulation consider the pressure-levels coupled with the temperature approach required per each circuit-level. The quantity of heat recovered is dependent on the heat requirements of the biomass multi-step dryer and control particulate emissions.

Figure 43 shows the Aspen Plus®v8.4 flowsheet of the double pressure circuit-levels HRSG system for BIG-ICE/CC (SC1). Figure 44 shows the Aspen Plus®v8.4 flowsheet of the triple pressure circuit-levels reheated HRSG system for BIG-ICE/CC (SC2).

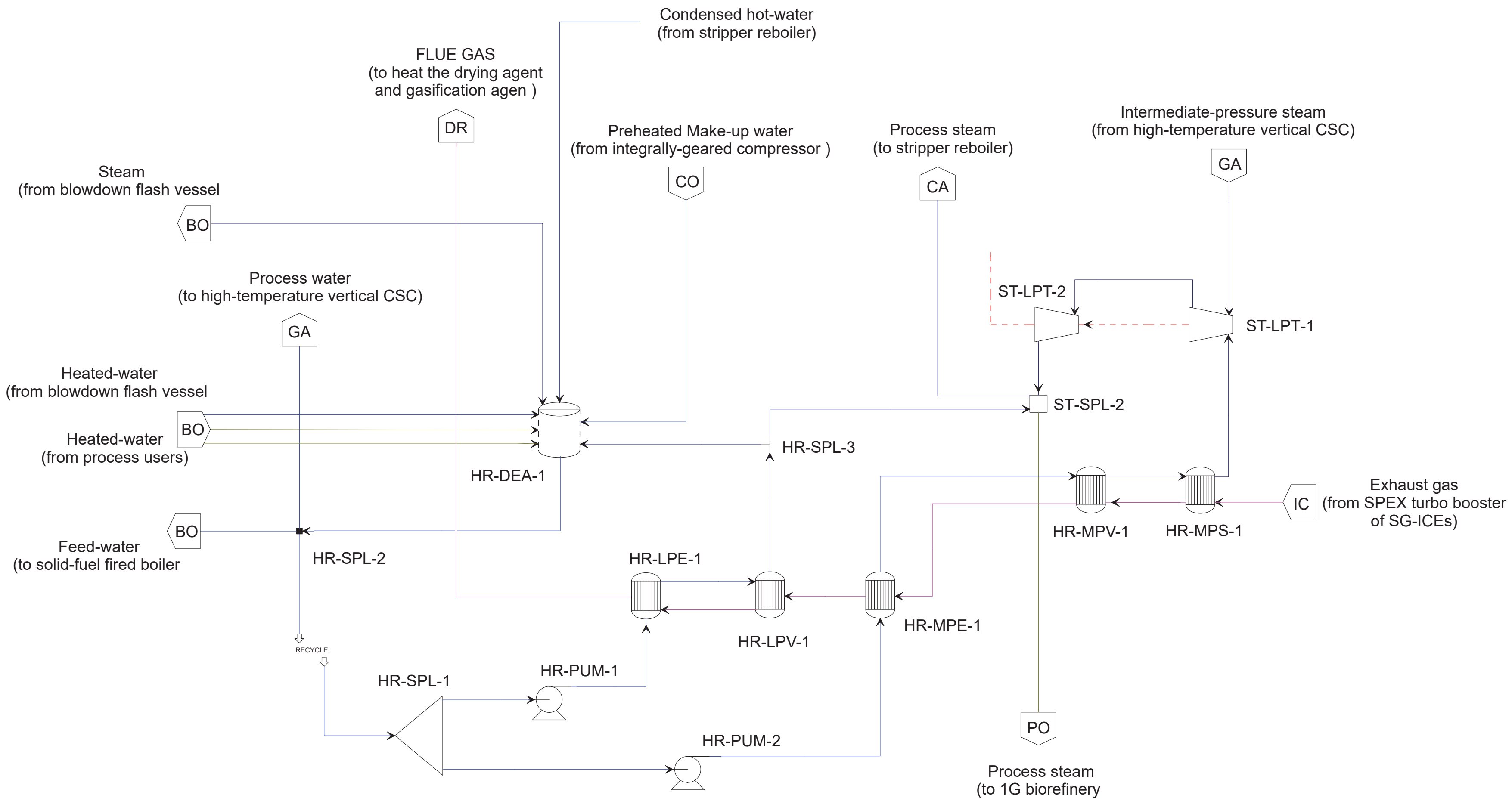


Figure 43 - Aspen Plus® v8.4 flowsheet of the double pressure circuit-levels heat recovery steam generator (HRSG) and back-pressure steam turbine BPST for BIG-ICE/CC (SC1)

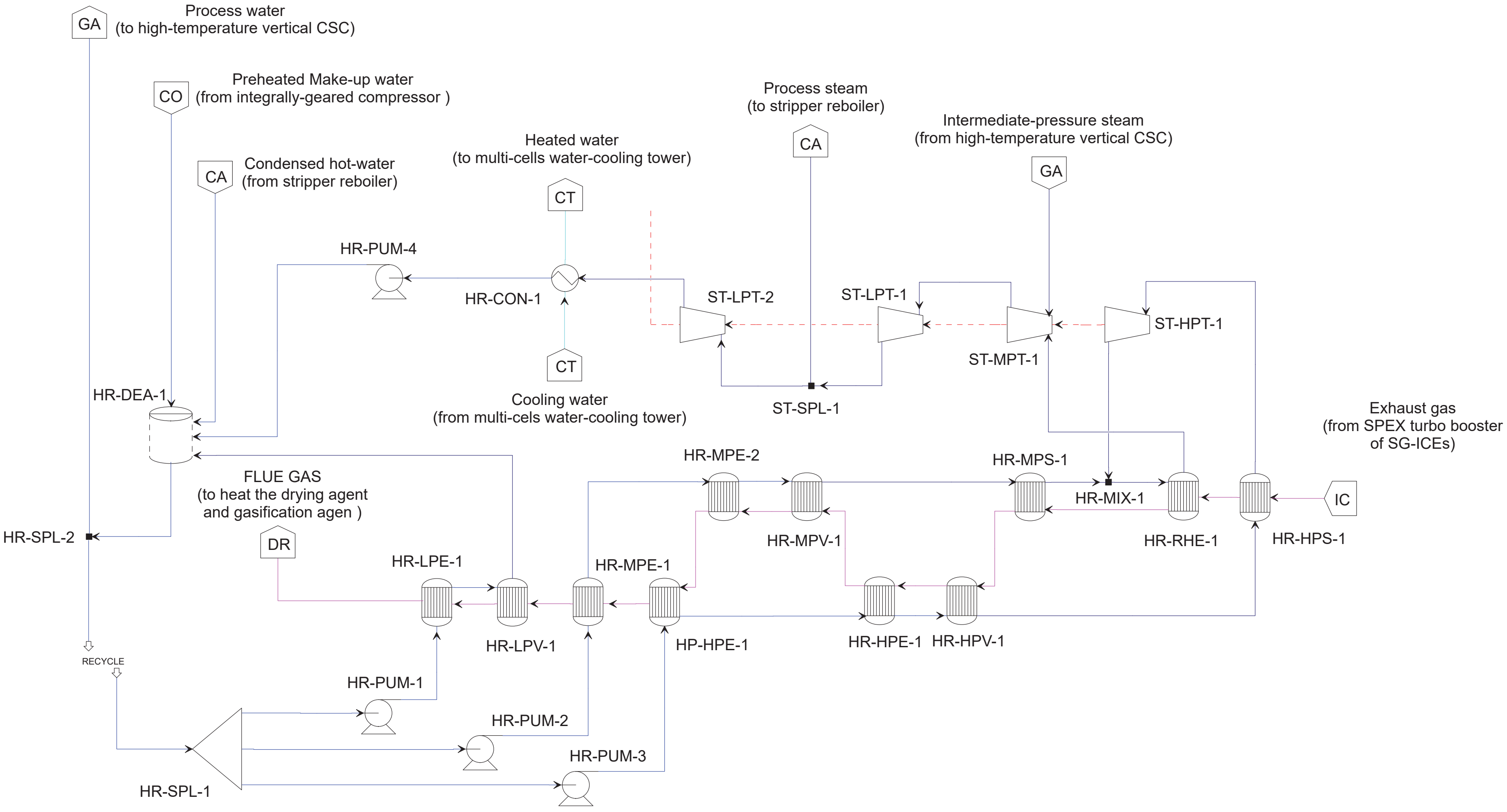


Figure 44 - Aspen Plus® v8.4 flowsheet of the triple pressure circuit-levels reheated heat recovery steam generator (HRSG) and condensing-extraction steam turbine (CEST) for BIG-ICE/CC (SC2)

As shown in Figure 43, Aspen Plus®v8.4 flowsheet of the double pressure circuit-levels HRSG system in the BIG-ICE/CC (SC1) is compost by: LP circuit-level water pump (HR-PUM-1); IP circuit-level water pump (HR-PUM-2); LP economizer bank tubes (HR-LPE-1); LP vaporizer bank tubes (HR-LPV-1); IP economizer bank tubes (HR-MPE-1); IP vaporizer bank tubes (HR-MPV-1); IP superheater bank tubes (HR-MPS-1); deaerator exchanger bank tubes (HR-SPL-3); deaerated hot process water splitter (HR-SPL-1); and LP steam mixer/splitter drum (ST-SPL-2).

The conventional double pressure circuit-levels HRSG system (HR blocks) receive exhaust-gas at 1.3 bar and 425.0ºC, generated after expansion in the high-efficiency SPEX turbo charging system (IC-EXP-1) of the SG-ICEs. In the BIG-ICE/CC (SC1), the intermediate-pressure steam generated by the double pressure circuit-levels HRSG system (HR blocks) is supplied to BPST system (ST blocks) (BC).

The Aspen Plus®v8.4 process model simulation of the horizontal gas-flow drum type HRSG system under consideration in the BIG-ICE/CC (SC1) was designed with customized low-pressure (LP) circuit-level to generate steam at 2.5 bar and 130.0ºC and intermediate-pressure (IP) circuit-level to generate steam at 22.0 bar and 320.0ºC.

In the Aspen Plus®v8.4 process model simulation, the deaerator exchanger bank tubes is considered coupled with the LP circuit-level (HR-LPE-1 and HR-LPV-1) generating steam to deaerator unit (HR-DEA-1) and process steam to supply part of the thermal energy required by the thermochemical-biorefinery (SC1).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 2.5 bar (drum pressure) by the LP circuit-level water pump (HR-PUM-1). The pressure-adequate water is heated to about 127.0ºC (saturated liquid) circulate flowing through the LP economizer bank tubes (HR-LPE-1) and vaporized generating process steam at 2.5 bar and 130.0ºC in the LP vaporizer bank tubes (HR-LPV-1).

Low-pressure steam at 2.5 bar and 130.0ºC destined to the deaerator unit (HR-DEA-1) as degassing agent is used mainly to remove dissolved gasses (e.g.: O_2 and CO_2) by raises the water temperature (make-up water and condensed process water) to generate hot water at 1.4 bar and 105.0ºC in the deaerator unit (HR-DEA-1). The amount of steam at 2.5 bar from the deaerator vaporizer bank tubes (HR-LPV-1) is controlled by design specification DS-HR-TL-1 adjusting the amount of steam fed into the deaerator unit (HR-DEA-1) varying the water/steam mass flow rate estimate-used into the deaerator unit (HR-DEA-1) according to described in the section 6.1.16 (Water cycles).

The amount of process steam at 2.5 bar and 130.0ºC generated in the LP vaporizer bank tubes (HR-LPV-1) is determined by the thermal energy requirements closing the thermal energy balance of the thermochemical-biorefinery (SC1).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 22.0 bar by the IP circuit-level water pump (HR-PUM-2). Circulate-flowing pressurized water is heated to 170.0ºC (hot liquid) in the IP economizer bank tubes (HR-MPE-1). Hence it is vaporized to about 217.0ºC (saturated vapor) in the IP vaporizer bank tubes (HR-MPV-1) passing from liquid to vapor phase, generating saturated steam at 22.0 bar. Saturated steam is superheated to 320.0ºC in the IP superheater bank tubes (HR-MPS-1).

The amount of subcritical superheated steam at 22.0 bar and 320.0ºC generated is determined by heat exchanger surface area required by the IP exchanger tube banks, the temperature limitations (approaches and cross-over) between the tube banks (heating zones) and the technical parameters of the steam turbine under consideration.

Conditioned feed water and steam mass flow rate passing through the IP staggered exchanger tube banks (HR-MP blocks) is controlled by design specification DS-HR-TG-1 varying the mass flow rate of the deaerated feed water circulating in the exchanger tube banks in order to promote efficient heat exchange.

The subcritical steam at 22.0 bar and 320.0ºC is expanded in the intermediate-pressure expansion stage (ST-HPT-2) of the BPST system in the BIG-ICE/CC (SC1), producing electrical power energy according to described in the section 6.1.13 (Steam turbine applied in combined-cycles).

The gases at 1.3 bar and 425.0ºC exhausted from the SPEX turbo charging system (IC-EXP-1) of the SG-ICEs enters the conventional double pressure circuit-levels HRSG system (HR blocks) transfer the sensible heat to the water/steam and exits the HRSG system at atmospheric pressure and 122.0ºC (liquid-gas exchange process zone).

In the BIG-ICE/CC (SC1), the flue-gas at about 122.0ºC after the HRSG system is mixed in the gases mixer (HR-MIX-1) with the flue-gas at 160.0ºC from the traditional 1G-CHP/EBPST system (SC1). The mixed flue-gas at about 135.0ºC is then routed to additional exchanger tube banks (gas-gas exchange process zone) to heat the drying air agent (ATMOSPHERIC AIR) to 120.0ºC. The hot drying air agent supply the thermal energy required and promote the drying process of the biomass in the bagasse flash dryers (DR-DRY-1) and the straw flash dryers (DR-DRY-2).

In the BIG-ICE/CC (SC1), atmospheric air gasification agent at ambient conditions is heated to 130.0ºC (GA-HEA-1) by using the HRSG hot exhaust-gas (HR-HEA-1) before being injected into the atmospheric CFB directly-heated gasifier (GA blocks).

As shown in Figure 44, Aspen Plus®v8.4 flowsheet of the triple pressure circuit-levels reheated HRSG system in the BIG-ICE/CC (SC2) is compost by: LP circuit-level water pump (HR-PUM-1); IP circuit-level water pump (HR-PUM-2); HP circuit-level water pump (HR-PUM-3); LP economizer bank tubes (HR-LPE-1); LP vaporizer bank tubes (HR-LPV-1); IP economizer bank tubes 1 (HR-MPE-1); IP economizer bank tubes 2 (HR-MPE-2); IP vaporizer bank tubes (HR-MPV-1); IP superheater bank tubes (HR-MPS-1); IP reheater bank tubes (HR-RHE-1); HP economizer bank tubes 1 (HR-HPE-1); HP economizer bank tubes 2 (HR-HPE-2); HP vaporizer bank tubes (HR-MPV-1); HP superheater bank tubes (HR-HPS-1); IP steam mixer (HR-MIX-1); and deaerated hot process water splitter (HR-SPL-1).

The conventional triple pressure circuit-levels reheated HRSG system (HR blocks) receive exhaust-gas at 1.3 bar and 425.0ºC generated after expansion in the high-efficiency SPEX turbo charging system (IC-EXP-1) of the SG-ICEs. In the BIG-ICE/CC (SC2), the high-pressure and intermediate-pressure steam generated by the triple pressure circuit-levels reheated HRSG system (HR blocks) is supplied to CEST system (ST blocks).

The Aspen Plus®v8.4 process model simulation of the horizontal gas-flow drum type HRSG system under consideration in the BIG-ICE/CC (SC2) was designed with customized low-pressure (LP) circuit-level to generate steam at 2.5 bar and 130.0ºC, intermediate-pressure (IP) circuit-level to generate steam at 22.0 bar and 331.0ºC, intermediate-pressure (IP) reheater bank tubes (HR-RHE-1) to generate steam at 22.0 bar and 380.0ºC, and high-pressure (HP) circuit-level to generate steam at 45.0 bar and 420.0ºC.

In the Aspen Plus®v8.4 process model simulation, the deaerator exchanger bank tubes is considered as the LP circuit-level (HR-LPE-1 and HR-LPV-1) generating steam at 2.5 bar and 130.0ºC (degassing agent) to be used only in the deaerator unit (HR-DEA-1).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 2.5 bar (drum pressure) by the LP circuit-level water pump (HR-PUM-1). The pressure-adequate water is heated to about 127.0ºC (saturated liquid) circulate flowing through the LP economizer bank tubes (HR-LPE-1) and vaporized generating steam at 2.5 bar and 130.0ºC in the LP vaporizer bank tubes (HR-LPV-1).

Low-pressure steam at 2.5 bar and 130.0ºC destined to the deaerator unit (HR-DEA-1) as degassing agent is used mainly to remove dissolved gasses (e.g.: O_2 and CO_2) by raises the water temperature (make-up water and condensed process water) to generate hot water at 1.4 bar and 105.0ºC in the deaerator unit (HR-DEA-1). The amount of steam at 2.5 bar from the deaerator vaporizer bank tubes (HR-LPV-1) is controlled by design specification DS-HR-TL-1 adjusting the amount of low-pressure steam fed into the deaerator unit (HR-DEA-1) varying the water/steam mass flow rate estimate-used into the deaerator unit (HR-DEA-1) according to described in the section 6.1.16 (Water cycles).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 22.0 bar (drum pressure) by the IP circuit-level water pump (HR-PUM-2). Circulate-flowing pressurized water is heated to 185.0ºC (hot liquid) in the IP economizer bank tubes 1 (HR-MPE-1), and heated to about 217.0ºC (saturated liquid) in the IP economizer bank tubes 2 (HR-MPE-2). Hence it is vaporized to about 217.0ºC (saturated vapor) in the IP vaporizer bank tubes (HR-MPV-1), generating saturated steam at 22.0 bar. The saturated steam is then superheated to 331.0ºC in the IP superheater bank tubes (HR-MPS-1).

The amount of subcritical superheated steam at 22.0 bar and 331.0ºC generated is determined by heat exchanger surface area required by the IP exchanger tube banks, the temperature limitations (approaches and cross-over) between the tube banks (heating zones) and the technical parameters of the steam turbine under consideration.

Conditioned feed water and steam mass flow rate passing through the IP staggered exchanger tube banks (HR-MP blocks) is controlled by design specification DS-HR-TG-2 varying the mass flow rate of the deaerated feed water circulating in the exchanger tube banks in order to promote an efficient heat exchange.

The superheated steam generated in the IP superheater bank tubes (HR-MPS-1) is mixed in the IP steam mixer (HR-MIX-1) with the expanded steam at 22.0 bar and 331.0ºC (intermediate-pressure level), obtained after the expansion of the high-pressure steam at 45.0 bar and 420.0ºC by the high-pressure expansion stage (ST-HPT-1) of the CEST system in the BIG-ICE/CC (SC2). The resultant intermediate-pressure steam is superheated in the IP reheater bank tubes (HR-RHE-1) to generate steam at 22.0 bar and 380.0ºC.

The temperature of the intermediate-pressure steam obtained after the IP superheater bank tubes (HR-MPS-1) is determined by the conditions (temperature and pressure) of the expanded steam obtained after the high-pressure expansion stage (ST-HPT-1) of the CEST system and controlled by design specification DS-HR-TG-1 to obtain the same conditions in the IP steam mixer (HR-MIX-1).

The subcritical steam at 22.0 bar and 380.0ºC is expanded in the intermediate-pressure expansion stage (ST-MPT-1) of the CEST system in the BIG-ICE/CC (SC2), producing electrical power energy according to described in the section6.1.13 (Steam turbine applied in combined-cycles).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 45.0 bar (drum pressure) by the HP circuit-level water pump (HR-PUM-3). Circulate-flowing pressurized water is heated to 195.0ºC (hot liquid) in the HP economizer bank tubes 1 (HR-HPE-1), and heated to about 257.0ºC (saturated liquid) in the HP economizer bank tubes 2 (HR-HPE-2). Hence it is vaporized to about 257.0ºC (saturated vapor) in the HP vaporizer bank tubes (HR-HPV-1) passing from liquid to vapor phase, generating saturated steam at 45.0 bar. The saturated steam is superheated to 420.0ºC in the HP superheater bank tubes (HR-HPS-1).

The amount of subcritical superheated steam at 45.0 bar and 420.0ºC generated is determined by the temperature limitations (approach) between the exchanger tube banks (heating zones) and the technical parameters of the steam turbine under consideration.

Subcritical steam at 45.0 bar and 420.0ºC is expanded in the high-pressure expansion stage (ST-HPT-1) of the CEST system in the BIG-ICE/CC (SC2), producing electrical power energy according to described in the section 6.1.13 (Steam turbine applied in combined-cycles). Expanded steam at 22.0 bar and 331.0ºC is routed and superheated again in the IP reheater bank tubes (HR-RHE-1).

The gases at 1.3 bar and 425.0ºC exhausted from the SPEX turbo charging system (IC-EXP-1) of the SG-ICEs enters the conventional triple pressure circuit-levels HRSG system (HR blocks) transfer the sensible heat to the water/steam and exits the HRSG system at atmospheric pressure and 180.0ºC (liquid-gas exchange process zone).

In the BIG-ICE/CC (SC2), the flue-gas at about 180.0ºC after the HRSG system is directly routed to additional exchanger tube banks (gas-gas exchange process zone) to heat the drying air agent (ATMOSPHERIC AIR) to 120.0ºC. The hot drying air agent supply the thermal energy required and promote the drying process of the biomass in the bagasse flash dryers (DR-DRY-1) and the straw flash dryers (DR-DRY-2).

In the BIG-ICE/CC (SC2), atmospheric air gasification agent at ambient conditions is heated to 150.0ºC (GA-HEA-1) by using the HRSG hot exhaust-gas (HR-HEA-1) before being injected into the atmospheric CFB directly-heated gasifier (GA blocks).

6.1.13 Steam turbine applied in combined-cycles

The Aspen Plus®v8.4 process model simulation of the steam turbine applied in combined-cycles considers conventional subcritical steam turbines, operating in Rankine-cycle mode.

As shown in Figure 43, Aspen Plus®v8.4 flowsheet of the BPST system in the BIG-ICE/CC (SC1) is compost by: intermediate-pressure expansion stage (ST-HPT-2); low-pressure expansion stage (ST-LPT-2); and steam splitter (ST-SPL-2).

The Aspen Plus®v8.4 process model simulation of the BPST (ST blocks) system in the BIG-ICE/CC (SC1) was developed using IAPWS-95 physical property methods considering about 74.55% isentropic efficiency (isentropic expansion). The model considers exhaust-steam at 2.5 bar and 130.0ºC in the low-pressure section (ST-LPT-2).

In the BIG-ICE/CC (SC1), the intermediate-pressure steam at 22.0 bar and 320.0ºC generated in the IP circuit-level (HR-HPS-1) and in the high-temperature vertical CSC (GA-CSC-1) is expanded to 6.0 bar and about 198.3ºC (low-pressure level) by the first-section of the BPST (ST-HPT-2) modeled by using a Compr pressure changer block in turbine model, without intermediate extractions of steam.

The expanded steam is then expanded to 2.5 bar and 130.0ºC (exhaust) by the second-section of the BPST (ST-LPT-2) modeled by using a Compr pressure changer block in turbine model. The exhaust-steam is used as process steam (ST-SPL-2) to supply part of the thermal energy required by 1G-thecnologies (integrated scenario) and part of the thermal energy required by the thermochemical technologies.

As shown in Figure 44, Aspen Plus®v8.4 flowsheet CEST system in the BIG-ICE/CC (SC2) is compost by: high-pressure expansion stage (ST-HPT-1); intermediate-pressure expansion stage (ST-MPT-1); low-pressure expansion stage (ST-LPT-1); condensing expansion stage (ST-LPT-2); steam extraction at 2.5 bar (ST-SPL-1); water-cooled surface condenser (HR-CON-1); and condensed water pump (HR-PUM-4).

The Aspen Plus®v8.4 process model simulation of the CEST (ST blocks) system in the BIG-ICE/CC (SC2) was developed using IAPWS-95 physical property methods considering about 82.08% isentropic efficiency (isentropic expansion).

In the BIG-ICE/CC (SC2), the high-pressure steam at 45.0 bar and 420.0ºC generated in the HP circuit-level (HR-HPS-1) is expanded to 22.0 bar and at about 331.0ºC (intermediate-pressure) by the first-section of the CEST (ST-HPT-1) modeled by using a Compr pressure changer block in turbine model. After expanded, the steam is mixed with intermediate-pressure steam at 22.0 bar and about 331.0ºC generated in the IP circuit-level (HR-MPS-1) of the HRSG system and then reheated to 22.0 bar and 380.0ºC in the reheated exchanger tube banks (HR-RHE-1) in the HRGS intermediate-pressure circuit-level.

Intermediate-pressure steam at 22.0 bar and 380.0ºC generated in the high-temperature vertical CSC (GA-CSC-1) and intermediate-pressure reheated steam are expanded to 6.0 bar and 237.6ºC in the second-section of the CEST (ST-MPT-1) modeled by using a Compr pressure changer block in turbine model. After, the steam at 6.0 bar and 237.6ºC is expanded to 2.5 bar and 158.0ºC in the third section of the CEST (ST-LPT-1) modeled by using a Compr pressure changer block in turbine model. Part of this steam is extracted (ST-SPL-1) to supply part of the thermal energy required by the thermochemical technologies (standalone scenario).

Surplus steam at 2.5 bar and about 158.0ºC from the third section of the CEST (ST-LPT-1) is expanded to 0.11 bar and 48.0ºC by the four section of the CEST (ST-LPT-

2) modeled by using a Compr pressure changer block in turbine model, ensuring that the quality of the steam-exiting a CEST condensing-stage (ST-LPT-2) is greater than 90.0% (technical limit). CEST condensing-stage (ST-LPT-2) is directly connected to water-cooled surface condenser (HR-CON-1) modeled by using a Heater exchanger block. The vacuum-pressure steam exhausted is condensed generating a water condensate (liquid phase) available to be after pumped (HR-PUM-4) back to deaerator unit (HR-DEA-1) in closed-loop cycle.

The electrical potential losses (turbine-mechanical generator) by attrite in the mechanical move parts was considered as 1.0% of the mechanical potential energy produced by the STs (99.0% mechanical efficiency).

6.1.14 Traditional *c*ombined heat and power generation system applying extraction back-pressure steam turbine

In the thermochemical-biorefinery scenario 1 (SC1) and thermochemical-biorefinery scenario 2 (SC2) is considered the optimized 1G sugarcane biorefinery (1G sugarcane biorefinery) with annexed ethanol distillery using a typical solid-fuel fired boiler bottoming-cycle system (grate type) and non-condensing type back-pressure extractive steam turbine (EBPST) operating at 22.0 bar and 320.0ºC (SC1) in Rankine-cycle mode for thermal and electrical energy generation (CHP).

Part of the sugarcane bagasse (SUGARCANE BAGASSE) from mills (without use of straw) as fuel is consumed in the solid-fuel fired boiler bottoming-cycle system, the surplus bagasse (SUGARCANE BAGASSE) and the straw (SUGARCANE STRAW) available is used as feedstock in the self-sufficient in energy terms BIG-ICE/CC route.

In the thermochemical-biorefinery scenario 1 (SC1), traditional 1G-CHP/EBPST (SC1) system supply part of the thermal and electrical energy required by the 1G-thecnologies, another part is supplied by the BIG-ICE/CC (SC1) operating in integrated mode. In the thermochemical-biorefinery scenario 2 (SC2), traditional 1G-CHP/EBPST (SC1) system supply the entire thermal and electrical energy required by the 1G sugarcane biorefinery, BIG-ICE/CC (SC2) operating in standalone mode.

Traditional 1G-CHP/EBPST system (SC1) with surplus biomass is simulated and detailed according to Aspen Plus®v8.4 process model simulation described in the section 5.1 (First generation sugarcane biorefinery with annexed ethanol distillery).

Figure 45 shows the Aspen Plus®v8.4 flowsheet of the 1G-CHP/EBPST (SC1) system for BIG-ICE/CC (SC1).

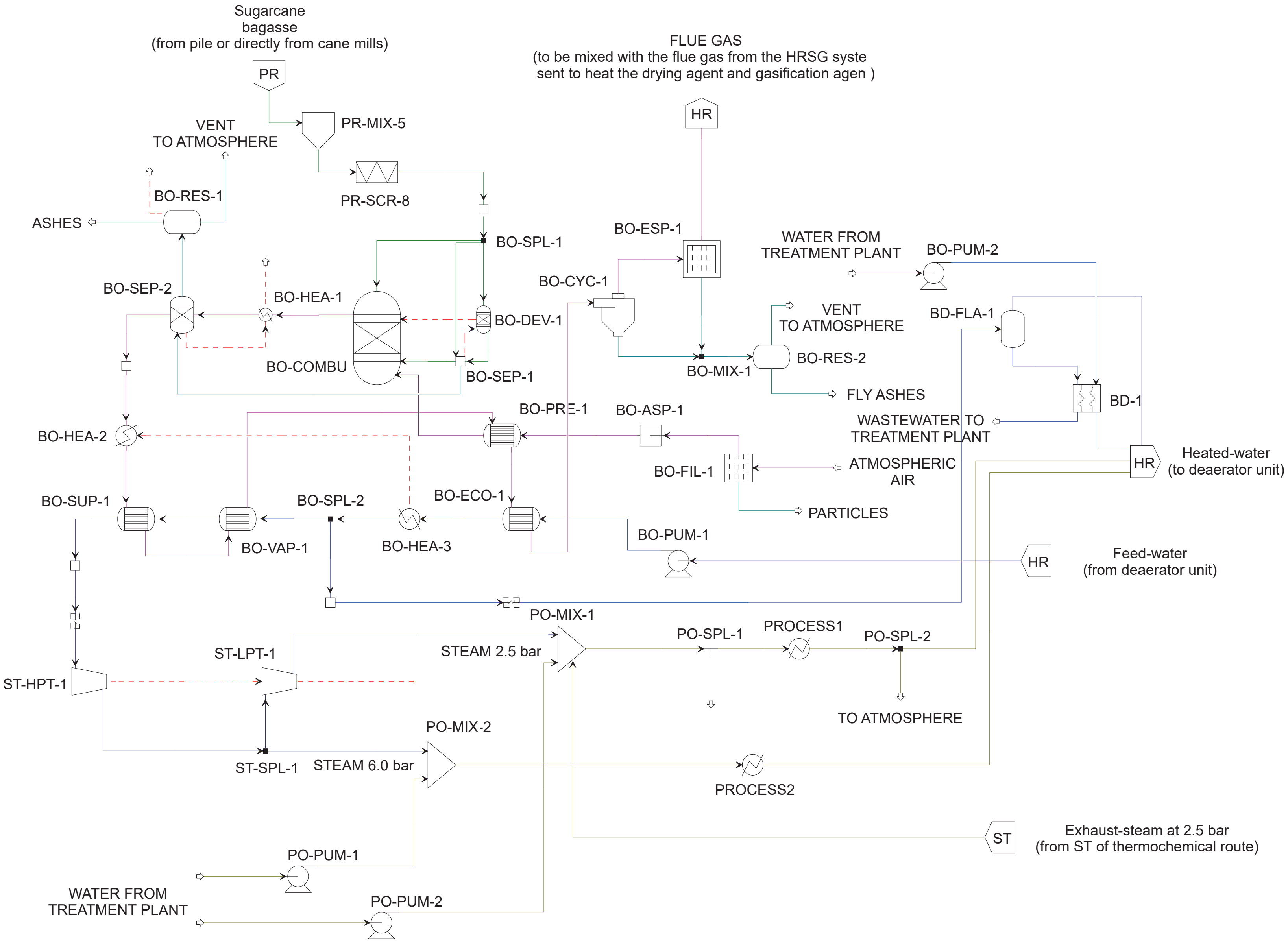


Figure 45 - Aspen Plus® v8.4 flowsheet of the 1G-CHP/EBPST (SC1) system for BIG-ICE/CC (SC1)

As shown in Figure 45, Aspen Plus®v8.4 flowsheet of the 1G-CHP/EBPST (SC1) system in the BIG-ICE/CC (SC1) is compost by: feed tray (PR-MIX-5); conveyor boiler fuel feeders (PR-SCR-8); breakdown RYield reactor block (BO-DEV-1); burner chamber (BO-COMBU); adjust Sep separator block (BO-SEP-1); heat loss adjust Heater exchanger block (BO-HEA-1); wet ashes removal grate system (BO-SEP-2); ashes bins (BO-RES-1); air pre-filter unit (BO-FIL-1); air preheated (BO-PRE-1); advanced blower system (BO-ASP-1); feed-water pump (BO-PUM-1); low-temperature economizers, and high-temperature economizers (BO-ECO-1); radiant heat adjust Heater exchanger block (BO-HEA-2 and BO-HEA-3); evaporator (BO-EVA-1); superheater (BO-SUP-1); saturated water purge (BO-SPL-3); blowdown flash vessel (BD-FLASH-1); multi-cyclone unit (BO-CYC-1); electrostatic precipitator unit (BO-ESP-1); ashes temporary storage bins (BO-RES-2); intermediate-pressure EBPST stage (ST-HPS-1); low-pressure EBPST stage (ST-LPS-1); steam extraction at 6.0 bar (ST-SPL-1); make-up water pump (BO-PUM-2); and blowdown heat recovery exchanger (BD-1).

A fraction of the bagasse from the mills (SUGARCANE BAGASSE) can be directly belt-conveyed to boiler fuel feeders (PR-SCR-8) or carried by tractors (actual system) from the bagasse pile to the conveyor feed tray (PR-MIX-5) to be fed by drum and hydraulic/pneumatic fuel feeders (PR-SCR-8) into the combustion chamber (BO-COMBU).

The Aspen Plus®v8.4 process model simulation of the typical solid-fuel fired boiler use a breakdown RYield reactors type (BO-BEV-1) as a theoretical artifice to simulate the decomposition of the non-conventional solids BAGASSE (BO-DEV-1) into its ‘constituting’ conventional components (‘ELEMENTS’). In the breakdown RYield reactor block (BO-DEV-1) is formed carbon (C), hydrogen (H_2), oxygen (O_2), chlorine (Cl_2), nitrogen oxide (NO) sulfur dioxide (SO_2), and hydrogen sulfide (H_2S) using about 16.67%$_{w/w}$ of the sulfur (S) content. Salts, minerals, ashes, and soil are specified as inert components in the devolatilization process-zone (bypass).

FORTRAN calculator block CA-BO-CS-1 is used to specify the yield distributions and the mass flow rate of each constituent component in the outlet stream according to the bagasse ultimate analysis (Table 5). The blocks BO-SPL-1 and BO-SPL-2 split the volatile material from the biomass and sent directly to the combustor chamber (BO-COMBU).

Sep separators block BO-SEP-1 as adjustment model is used to adjust the biomass conversion, the carbon conversion (CA-BO-XS-1) and the ashes content (solids formation) as bottom ashes (ASHES) or fly-ashes (FLY-ASHES). The amount of bottom ashes (ASHES) and fly-ashes (FLY-ASHES) and hers composition are controlled by BO-SEP-2 block which simulate the grate system and the automatically wet ashes removal system (BO-SEP-2), without considering the water use in the simulation (cleaning grate system). The ashes temporary storage bins (BO-RES-1) consider the heat loss (heat transported with ashes) by natural heat changes with the ambient conditions.

The solid-fuel fired boiler models consider a heat loss (BO-HEA-1) due the surface radiation and convection with to surrounding ambient. The heat loss (BO-HEA-1) is calculated by FORTRAN calculator block CA-BO-QL-1 based on the fraction of the LHV_{db} of the biomass inlet in the boiler, according to Equation 16 detailed in the section 3.9.13 (Heat losses to surrounding ambient).

The Aspen Plus®v8.4 process model simulation of the burner chamber (BO-COMBU) was developed using RGibbs reactor type which uses the Gibbs free energy minimization method, considering all the possible solids emissions (soil and atmosphere) and gaseous emissions (atmosphere). The Gibbs free energy minimization method determines the equilibrium composition of the products resulting from the many reactions that can occur.

The burner chamber (BO-COMBU) model can determine in the gaseous phase the formation of NO_2, N_2O, NO, SO_2, SO_3, NH_3, H_2S, HCL, Cl_2, COS, CHN, volatile organic compounds, and particulate matter formation (salt and solid compounds). Also, can determine in the solid phase (ashes and fly-ashes) the formation of unconverted biomass (BAGASSE and STRAW) and carbon (C), salts and mineral (biomass constitutional content), SiO_2 (biomass ash constitutional content), MgO, CaO, KCl, K_2O, K_3PO_4, and soil. Gibbs free energy minimization method underestimate the formation of S, CaS, and MgS. Sulfur is emitted on gaseous form in Gibbs combustion models (oxidized metals are more stable form).

Combustion air (ATMOSPHERIC AIR) is preheated (BO-PRE-1) and forced-injected in the burner chamber (BO-COMBU) by advanced blower system (BO-ASP-1) with pre-filter unit (BO-FIL-1) to protect the blower and burner from debris (PARTICLES). The amount of air employed is controlled by design specification DS-BO-FG-1 varying the mass flow rate of atmospheric air (ATMOSPHERCI AIR) inlet into the burner chamber (BO-COMBU). The model consider $8.0\%_{w/w}$ as the ratio of the oxygen mass flow rate out off the burner chamber (BO-COMBU) to the oxygen mass flow rate inlet into the burner chamber (BO-COMBU).

The liquid non-saturated feed-water from deaerator unit (HR-DEA-1) at 1.4 bar and 105.0ºC is pumped to 22.0 bar by the feed-water pump (BO-PUM-1) and then fed into the solid-fuel fired boiler tubes banks. Non-saturated feed-water is heated at saturation conditions in the low-temperature and high-temperature economizers (BO-ECO-1) by radiant (BO-HEA-2 and BO-HEA-3) and convective heat (BO-ECO-1), is evaporate to saturated steam in the evaporator (BO-EVA-1) and superheated in the superheater (BO-SUP-1) leaving the boiler at 22.0 bar and 320ºC to be expanded in the EBPST system (ST blocks).

The temperature of the flue-gas after the air pre-heater exchanger (BO-PRE-1) is controlled by design specification DS-BO-FL-1 to be 160.0ºC varying the mass flow rate of the boiler feed-water flowing through the water-side tube bank, coupled with the design specification DS-BO-FG-1 varying the mass flow rate of the atmospheric air inlet into the burner chamber (BO-COMBU) to control the excess air ratio.

4.0%$_{w/w}$ of the saturated water mass flow rate is purged (BO-SPL-3) from the boiler as continue blowdown and then fleshed to 1.4 bar (deaerator pressure) in the blowdown tank (BD-FLASH-1). The vaporized phase is sent to the first deaerator unit (HR-DEA-1) to heat recovery (reducing the amount of steam 2.5 bar used in the deaerator). The liquid phase is cooled to 30.0ºC by the blowdown heat recovery exchanger (BD-1) heating the make-up raw water (WATER FROM TREATMENT PLANT) which is pumped to 1.4 bar by the make-up water pump (BO-PUM-2) to the deaerator unit (HR-DEA-1). Blowdown remove impurities from boiler as dissolved impurities, in the Aspen Plus®v8.4 process model simulation is not considered the presence of impurities. The amount of impurities depends on the fresh-water quality, on make-up water treatment process and maintenance treatment of process water cycle.

In the spreadsheet calculation model of the treatment processes was considered the recovery of 87.0%$_{w/w}$ of the water blowdown according to Equation 25.

Particulate material content in the flue-gas (FLY-ASHES) are reduced by control particulate emissions system applying a multi-cyclone unit (BO-CYC-1) modeled by using a Cyclone solids separator block. The multi-cyclone unit (BO-CYC-1) was designed optimized with 5 cyclones (battery) to remove the gross particulate content in the exhaust-gas according to Muschelknautz calculation method for a maximum pressure drop of 0.01 bar applying spiral inlet cyclones type.

Part of the persistent fine particulate matters after the multi-cyclone unit (BO-CYC-1) is removed by the electrostatic precipitator (DR-ESP-1) modeled by suing a ESP solids separator block according to Svarovsky calculation model for vertically mounted collecting plates model with separation efficiency of 92.0% based on the migration velocity and the ratio of precipitation area. The fly-ashes (FLY AHSES) are stored in the ashes temporary storage bins (BO-RES-2) and mixed with the ASHES to be after-sent to application in the sugarcane crops.

The flue-gas from the boiler system content steam (H_2O), NO_2, N_2O, NO, SO_2, SO_3, NH_3, H_2S, HCL, Cl_2, COS, CHN, volatile organic compounds, and particulate matter (MgO, CaO, KCl, K_2O, K_3PO_4, BIOMASS, C, salts, and mineral) is mixed with the flue-gas from the HRSG system and sent to heat the drying agent and gasification agent (heat recovery).

The Aspen Plus®v8.4 process model simulation of the EBPST (ST blocks) of the 1G-CHP/EBPST (SC1) system in the BIG-ICE/CC (SC1) was developed using IAPWS-95 physical property methods considering about 74.55% isentropic efficiency. The model considers exhaust-steam at 2.5 bar and 130.0ºC in the low-pressure section (ST-LPS-1).

The intermediate-pressure steam at 22.0 bar and 320.0ºC generated in the solid-fuel fired boiler tubes banks is expanded to 6.0 bar and about 198.3ºC by the first-section of the EBPST (ST-HPT-1) modeled by using a Compr pressure changer block in turbine model. After expanded, part of the steam is extracted (ST-SPL-1) to supply part of the thermal energy required by the dehydration ethanol process (1G-thecnologie).

Another part of the steam at 6.0 bar and about 198.3ºC is expanded to 2.5 bar and 130.0ºC in the second-section of the EBPST (ST-MPS-1) modeled by using a Compr pressure changer block in turbine model. The exhaust-steam at 2.5 bar and 130.0ºC is used to supply part of the 1G-thecnologies thermal energy requirements.

The electricity generated by the EBPST (ST blocks) of the 1G-CHP/EBPST (SC1) system in the BIG-ICE/CC (SC1) is used to supply part of electricity required by the 1G sugarcane biorefinery. Another part is supplied by the BIG-ICE/CC route. The electrical potential losses (turbine-mechanical generator) by attrite in the mechanical move parts was considered as 1.0% of the mechanical energy produced by the turbine (99.0% mechanical efficiency).

Spreadsheet calculation considering the wastewater treatment process (WASTEWATER TO TREATMENT PLANT) with a maximum of 85.0%$_{w/w}$ recovery efficiency is used to determine the amount of water (TO WASTEWATER TREATMENT PLANT) is recovered and recycled to the deaerator unit (HR-DEA-1) after treatment as make-up water and the requirements of supplementary fresh-make-up water to close the water balance.

6.1.15 Multi-cells water-cooling tower

The Aspen Plus®v8.4 process model simulation consider modules of draft-packaged water-cooling induced-tower 43.0ºC/30.0ºC/27.0ºC type with capacity for 700.0 m³/hr of water mass flow rate. The model was developed using IAPWS-95 physical property methods for the water-side streams, and RKS cubic equation of state with BM alpha function property method to simulate the air-side streams and the heat transfer between the atmospheric air-side and the water-side in the water tower module (CT-TOW blocks). The heat transfer in the gas-side or liquid-side streams in the cooling water equipment users depends on the physical property methods employed in the area in which they are allocated.

Figure 46 (a) shows the Aspen Plus®v8.4 flowsheet of the first-section of the multi-cells water-cooling tower for BIG-ICE/CC (SC1) and for BIG-ICE/CC (SC2). Figure 46 (b) shows the Aspen Plus®v8.4 flowsheet of the second-section of the multi-cells water-cooling tower for BIG-ICE/CC (SC2).

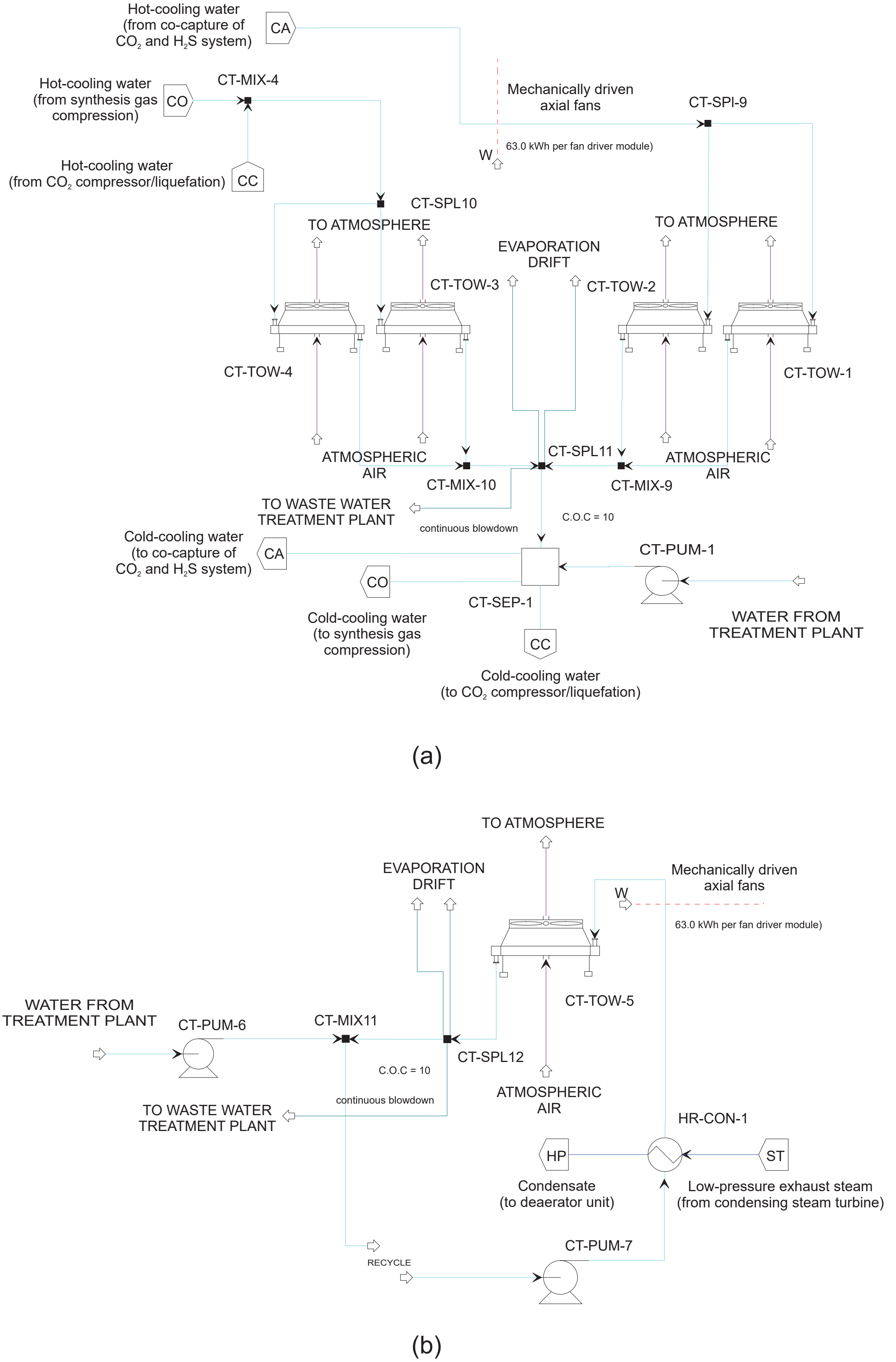


Figure 46 - Aspen Plus$^{®}$v8.4 flowsheet of the multi-cells water-cooling tower for: a) BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2); and b) BIG-ICE/CC (SC2)

As shown in Figure 46 (a), the Aspen Plus®v8.4 flowsheet of the simplified first-section of water-cooling tower system in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2), and as shown in Figure 46 (b), the Aspen Plus®v8.4 flowsheet of the simplified second section water-cooling tower system in the BIG-ICE/CC (SC2), are composts by: pumps (CT-PUM blocks); fans (CT-EFT work streams); water-cooling tower modules (CT-TOW blocks); water-cooling tower basin (CT-SEP blocks); adjust losses (evaporation and drift) and blowdown system (CT-SPL blocks); and spreadsheet calculation of blowdown cycles of concentration (C.O.C) system.

The multi-cells water-cooling tower (CT-blocks) provides cooling water to remove heat and adjust the process temperature to appropriate levels. The cooling water is distributed to the cooling water equipment users in the BIG-ICE/CC scenarios to:

b) condense and cool-down the top gas product from the absorber (CT-HEA-2) an stripper (CT-HEA-3) columns in the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2);
c) cool down the absorber inlet lean amine aqueous solution (CT-HEA-1) in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2);
d) cool-down the synthesis gas in the inter-stages (CO-1 and CO-2) of compression (intercooler and after-cooler) in the integrally-geared two stages centrifugal compressor in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2);
e) cool-down the CO_2 gas in the inter-stages (CO-1~5) of compression in the integrally-geared six stage centrifugal compressor (inter-cooler and after-cooler) and liquefier the captured CO_2 (CC-HEA-1) in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2);
f) cool-down the charged-air in the modified turbocharger after-cooler (IC-1) in the SG-ICEs in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2);
g) condense the low-pressure exhausted steam from the condensing section turbine (CEST) employed in the BIG-ICE/CC (SC2).

The Aspen Plus®v8.4 process model simulation of water-cooling tower system operating in water recirculation mode determine the requirements of cooling water heat exchanger, make-up of recycled and fresh water, water blowdown, and electric motor drives (fan drivers and pumps). In the model are used the standards design equations as defined in the section 3.9.17 (Water-cooling tower) for the modular single fan-cells arrangement operates as staged mode by sections each with variable-frequency drivers.

The ambient condition of the atmospheric surrounding air (ATMOSPHERIC AIR) considered in the Aspen Plus®v8.4 process model simulation is 25.0ºC at atmospheric pressure with relative humidity of 80.0% and web bulb temperature at about 21.3ºC.

Multi-cells water-cooling tower (CT-TOW blocks) is determined based on the cooling capacity of 700 tonnes/hr of hot water per modular cells (CT-TOW blocks) considering mechanical axial propeller single fan-cells counter-flow draft designed (CT-TOW blocks). The numbers of cells and fans are estimated based on the mass flow rate of cooling water circulating in each of the specific sections (first and second sections).

The induced surrounding air exchange convective heat with the hot water in the water-cooling tower (CT-TOW blocks) represented as a simple HeatX exchange block (CT-TOW blocks). The surrounding air is induced upward through the fill (CT-TOW blocks) being heated from 25.0ºC to 40.0ºC. The hot cooling water flow downward through the fill (CT-TOW blocks) been cooled down from 43.0ºC to 30.0ºC. This simple model results in the overestimated amount of air in relation to reality or a more complex model (direct contact model).

In the BIG-ICE/CC (SC1), and BIG-ICE/CC (SC2), the amount of surrounding air flowing through the fill (CT-TOW blocks) of the first-section of the multi-cells water-cooling tower is determined and controlled by design specification DS-CT-FG-1, design specification DS-CT-FG-3, FORTRAN calculator block CA-CT-FG-2, and FORTRAN calculator block CA-CT-FG-4, varying the mass flow rate (CT-AIR streams) of surrounding air passing through the fill (CT-TOW blocks), required to cooling down the hot water.

In the BIG-ICE/CC (SC2), the amount of surrounding air flowing through the fill (CT-TOW blocks) of the second-section of the multi-cells water-cooling tower is determined and controlled by design specification DS-CT-FG-5, varying the mass flow rate (CT-AIR streams) of surrounding air passing through the fill (CT-TOW blocks), required to cooling down the hot water.

Treated fresh and recycled water as make-up water (WATER FROM TREATMENT PLANT) at atmospheric pressure and 25.0ºC is pumped (simplified by one pump) by make-up pump (CT-PUM-1) to the first-section of the multi-cells water-cooling tower and mixed with the down flow cooled-water at 30.0ºC in the water-cooling tower basin (CT-SEP-1). For the second-section of the multi-cells water-cooling tower make-up water (WATER FROM TREATMENT PLANT) is pumped by make-up pump (CT-PUM-6) and mixed with the down flow cooled-water at 30.0ºC in the water-cooling tower basin (CT-MIX-11).

In the BIG-ICE/CC (SC1), and BIG-ICE/CC (SC2), cooling water available at 27.0ºC (heat sink) for the first-section of the multi-cells water-cooling tower is pumped (CT-PUM-2) to Co-capture of CO_2 and H_2S by using MEA-based absorbing-solution, pumped (CT-PUM-3) to synthesis gas integrally-geared multi-stage centrifugal compressor system, and pumped (CT-PUM-5) to CO_2 gas integrally-geared multi-stage centrifugal compressor.

In the BIG-ICE/CC (SC2), cooling water available at 27.0ºC (heat sink) for the second-section of the multi-cells water-cooling tower is pumped (CT-PUM-7) to CEST condenser (HR-CON-1).

The cooling water at 27.0ºC is heated by passing through the user equipments to 43.0ºC (tower design limit), the hot water is duct-sent back to the multi-cells water-cooling tower (CT blocks) and discharged inlet into the cooling tower cells (CT-TOW blocks) at 43.0ºC to be cooled in a water closed-loop cycle system. The amount of water necessary for cooling down the equipments at required levels is determined and controlled by a set of design specification (e.g.: DS-CA-TL-1, DS-CA-TL-2, DS-CA-TL-3, DS-CT-FL-2, DS-CT-FL-3, DS-CT-FL-5, DS-CO-TL-1, DS-CO-TL-2) varying the mass flow rate of cooling water flows through the equipment users. The cooling water is heated at the limit of 43.0ºC (water-cooling tower design) and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

Hot water at 43.0ºC is fed in the first and second sections of multi-cells water-cooling tower (CT-TOW blocks) to be cooled down to 30.0ºC by direct contact in counter-flow with vertically upward induced (mechanical axial propeller fans) surrounding air through the fill (CT-TOW blocks) at atmospheric pressure and 25.0ºC. The model consider relative humidity of 80.0% and web bulb temperature at about 21.3ºC, which results in a range of 13.0ºC and an approach of 8.7ºC.

The Aspen Plus®v8.4 process model simulation of water-cooling tower system considers the water evaporation rate obtained by the Equation 21, and the drift loss rate obtained by the Equation 22. In the BIG-ICE/CC (SC1), and BIG-ICE/CC (SC2), the equations are employed in the CT-SPL-11 for the first-section of the multi-cells water-cooling tower to determine the CT-EVA-1 and CT-DRI-1 streams by using FORTRAN calculator block CA-CT-LL-1. In the BIG-ICE/CC (SC2), the equations are employed in the CT-SPL-12 for the second-section of the multi-cells water-cooling tower to determine the CT-EVA-2 and CT-DRI-2 streams by using FORTRAN calculator block CA-CT-LL-2.

A tower basin blowdown (CT-BLO streams) to remove or reduce the concentration of the impurities is developed in the Aspen Plus®v8.4 process model simulation according to Equation 25 as continuous blowdown system. In the BIG-ICE/CC (SC1), and BIG-ICE/CC (SC2), first-section of the multi-cells water-cooling tower (CT-SPL-12) consider the tower basin blowdown (CT-BLO-1) and blowdown cycles of concentration (C.O.C) determined by using FORTRAN calculator block CA-CT-LL-1 to remove the solids formed (not included in the Aspen Plus®v8.4 process model simulation). In the BIG-ICE/CC (SC2), second-section of the multi-cells water-cooling tower (CT-SPL-12) consider the tower basin blowdown (CT-BLO-2) and blowdown cycles of concentration (C.O.C) determined by using FORTRAN calculator block CA-CT-LL-2 to remove the solids formed (not included in the Aspen Plus®v8.4 process model simulation).

In the BIG-ICE/CC (SC1), and BIG-ICE/CC (SC2), make-up water (WATER FROM TREATMENT PLANT) is pumped by make-up pump (CT-PUM-1) to the first-section of the multi-cells water-cooling tower basin (CT-SEP-1). In the BIG-ICE/CC (SC2), make-up water (WATER FROM TREATMENT PLANT) is pumped by make-up pump (CT-PUM-3) to the second-section of the multi-cells water-cooling tower basin (CT-MIX-11).

The make-up water for the multi-cells water-cooling tower is determined based on the water losses by evaporation (CT-EVA streams), drift (CT-DRI streams), and tower basin blowdown (CT-BLO streams), according to Equation 23.

In this research Master's degree, is considered a recovery of 87.0%$_{w/w}$ of the water blowdown after the treatment as available cooling water to reuse/recycle at 27.0ºC. The amount of water recovered is determined by spreadsheet calculation model of the cooling water treatment process according to Equation 24. The discarded water fraction contains a high concentration of impurities (e.g.: minerals and salts), not included in the Aspen Plus®v8.4 process model simulation.

The electricity required by the large mechanically driven axial fans (CT-EFT work streams) to induce the surrounding air upward through the fill in the cell-tower module (CT-TOW blocks) are estimated of 63.0 kWh per fan driver (module). The total of electricity required by the fan drivers is based on the number of cells (CT-TOW blocks) that compose the multi-cells water-cooling tower. The electricity consumed by the mechanical drivers in the axial fans (CT-EFT work streams) is estimated based on the Equation 26.

In the BIG-ICE/CC (SC1), and BIG-ICE/CC (SC2), the electricity required (CT-EFT-1 work stream) in the first-section of the multi-cells water-cooling tower by the large mechanically driven axial fans (CT-EFT-1 work stream) to induce the surrounding air upward through the fill in the cell-tower module (CT-TOW blocks) is determined and controlled by FORTRAN calculator block CA-CT-EF-1 varying the input value of the CT-EFT-1 work stream according to the number of necessary fans (63.0 kWh per fan driver).

In the BIG-ICE/CC (SC2) the electricity required (CT-EFT-2 work stream) in the second-section of the multi-cells water-cooling tower by the large mechanically driven axial fans (CT-EFT-2 work stream) to induce the surrounding air upward through the fill in the cell-tower module (CT-TOW blocks) is determined and controlled by FORTRAN calculator block CA-CT-EF-2 varying the input value of the CT-EFT-3 work stream according to the number of necessary fans (63.0 kWh per fan driver).

6.1.16 Water cycles

The water cycle balance consider receive water: from treatment plant (BO-L-6) to process make-up water to deaerator unit (HR-DEA-1) in the BIG-ICE/CC (SC1); from treatment plant (CO-L-3) to process make-up water to deaerator unit (HR-DEA-1) in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2); from treatment plant (CA-L-32) to washer packed-column section (CA-WAS-1) in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2); from treatment plant (PO-L-1 and PO-L-3) to desuperheater units (PO-MIX-1 and PO-MIX-2) in the BIG-ICE/CC (SC1); from treatment plant to first-section of (CT-L-1) of water-cooling tower system in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2); and from treatment plant to second section (CT-L-61) of water-cooling tower system (CT-MIX-11) in the BIG-ICE/CC (SC2).

Also, sends wastewater: (BD-BLO-1) from boiler liquid-phase water blowdown (BD-FLA-1) in the BIG-ICE/CC (SC1); to treatment plant (SC-L-12) from the excess of the wastewater recovered in the low-temperature synthesis gas wet cleaning system (SC-SPL-2) in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2); to disposal (SC-SLUR) from the sludge phase (50%$_{w/w}$ of water content) removed in the low-temperature synthesis gas wet cleaning system (SC-SPL-2) in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2); to treatment plant (CA-L-17) from the excess of the wastewater recovered from the striper water bleed (CA-SPL-1) in the co-capture of CO_2 and H_2S by using MEA-based absorbing-solution (CA-SPL-4) in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2); to disposal (CA-L-29) from the reclaimer carbon-based filter (CA-SEP-1) in the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution considered in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2); to treatment plant (CO-BLO-1) from the condenser knock-out drum in the synthesis gas integrally-geared centrifugal two stages compressor (CO-FLA-3) in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2); to treatment plant (IC-BLO-1) from the condenser knock-out drum in the SG-ICEs (IC-FLA-1) in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2); to treatment plant (CC-BLO-1) from the condenser knock-out drum in the CO_2 gas integrally-geared centrifugal six stages compressor (CC-FLA-7) in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2); to treatment plant (CT-BLO-1) from water-cooling tower blowdown (CT-SPL blocks) in the first-section of the multi-cells water-cooling tower in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2); and to treatment plant (CT-BLO-2) from water-cooling tower blowdown (CT-SPL blocks) in the second-section of the multi-cells water-cooling tower in the BIG-ICE/CC (SC2).

Process steam/water losses occur due: water evaporation or condensation (PO-BLO-1) in equipments and tube lines (PO-SPL-1) discharge 5.0%$_{w/w}$ of the process steam at 2.5 bar (PO-BLO-1) in the BIG-ICE/CC (SC1); treatment of boiler water blowdown discharge 15.0%$_{w/w}$ of the purged water (BD-BLO-1) (recovery and recycle of 85.0%$_{w/w}$ of the water blowdown) in the BIG-ICE/CC (SC1); sludge disposal discharge 100.0%$_{w/w}$ of the water content in the sludge phase (SC-SLUR) in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2); treatment of the excess of recovered water in the low-temperature synthesis gas wet cleaning system discharge 5.0%$_{w/w}$ of the water (SC-L-12) (recovery and recycle 95.0%$_{w/w}$ of the recovered water) in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2); treatment of the excess of water recovered in the co-capture of CO_2 and H_2S by using MEA-based solution discharge 15.0%$_{w/w}$ of the water in excess (CA-L-17) (recovery and recycle of 85.0%$_{w/w}$ of the water in excess) in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2); filtered amine residue disposal discharge 100.0%$_{w/w}$ of the water content in the residue fraction (CA-L-29) in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2); treatment of the water from the condenser knock-out drums discharge 5.0%$_{w/w}$ of the water (CO-BLO-1, IC-BLO-1 and CC-BLO-1) (recovery and recycle of 95.0%$_{w/w}$ of the condensed water) in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2); water evaporation (CT-EVA-1) and drift (CT-DRI-1) in the first-section of the water-cooling tower discharge 100.0%$_{w/w}$ of the water-stream in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2); water evaporation (CT-EVA-2) and drift (CT-DRI-2) in the second-section of the water-cooling tower discharge 100.0%$_{w/w}$ of the water-stream in the BIG-ICE/CC (SC2); treatment of the first-section of the water-cooling tower blowdown discharge 13.0%$_{w/w}$ of the purged water (CT-BLO-1) (recovery and recycle of 87.0%$_{w/w}$ of the water blowdown) in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2); and treatment of the second-section of the water-cooling tower blowdown discharge 13.0%$_{w/w}$ of the purged water (CT-BLO-2) (recovery and recycle of 87.0%$_{w/w}$ of the water blowdown) in the BIG-ICE/CC (SC2).

As shown in Figure 43, deaerator unit (HR-DEA-1) in the BIG-ICE/CC (SC1) receive: low-pressure steam from the flash vessel (BD-FLA-1) at 1.4 bar (deaerator pressure) and 109.0ºC (BD-G-1); steam at 2.5 bar and 130.0ºC (HR-G-15) from the HRSG LP circuit-level; pre-heated fresh-water at 1.4 bar and 52.0ºC (BO-L-8) as part of the make-up water (WATER FROM TREATEMENT PLANT) required in the deaerator unit (HR-DEA-1); water from BIG-ICE/CC (SC1) processes at 2.5 bar and at about 124.0ºC (CA-L-23); water from the 1G sugarcane biorefinery processes at 2.5 bar and 90.0ºC (PO-L-7 and PO-L-8); heated make-up raw water (WATER FROM TREATEMENT PLANT) at 1.4 bar and 105.0ºC (HR-L-12) closing the process water loop-cycle. Also, as shown in Figure 43, deaerator unit (HR-DEA-1) in the BIG-ICE/CC (SC1) send degassed and conditioned water at 1.4 bar and 105.0ºC to solid-fuel fired boiler (1G-thecnology) (HR-L-10), to HRSG system (HR-L-9) and to high-temperature vertical CSC (HR-L-11).

As shown in Figure 44, deaerator unit (HR-DEA-1) in the BIG-ICE/CC (SC2) receive: steam at 2.5 bar and 130.0ºC (HR-G-13) from the HRSG LP circuit-level; water from the BIG-ICE/CC (SC2) processes at 2.5 bar and at about 124.0ºC (CA-L-23), condensed exhaust-steam at 1.4 bar and about 48.0ºC (HR-L-14) from the CEST condenser and from the make-up heated fresh-water (WATER FROM TREATEMENT PLANT) at 1.4 bar and 105.0ºC (HR-L-18) closing the process water loop-cycle. Also, as shown in Figure 44, deaerator unit (HR-DEA-1) in the BIG-ICE/CC (SC2) send degassed and conditioned water at 1.4 bar and 105.0ºC to HRSG system (HR-L-16) and to high-temperature vertical CSC (HR-L-17).

The amount of low-pressure steam at 2.5 bar and 130.0ºC from the HRSG LP circuit-level destined to deaerator unit (HR-DEA-1) is determined and controlled by design specification DS-HR-TL-1 varying the water/steam mass flow rate in the HRSG LP circuit-level and estimate-used into the deaerator unit (HR-DEA-1) as degassing agent. Low-pressure steam at 2.5 bar and 130.0ºC is used mainly to remove dissolved O_2 and CO_2 content in the process water cycle by raises the deaerator water temperature (make-up water and process water condenser return) to 1.4 bar and 105.0ºC in the deaerator unit (HR-DEA-1).

In the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2), make-up water supplied to deaerator unit (HR-DEA-1) from the water treatment plant is based on the mass balance of the process steam/water losses and recycled water cycle. The amount of water required in the BIG-ICE/CC (SC1) is determined and controlled by design specification DS-AE-FL-1, design specification DS-HR-FL-1 and design specification DS-HR-FL-3 varying the mass flow rate of water (WATER FROM TREATMENT PLANT) fed into the deaerator unit (HR-DEA-1). The amount of water required in the BIG-ICE/CC (SC2) is determined and controlled by design specification DS-HR-FL-1 and design specification DS-HR-FL-3 varying the mass flow rate of water (WATER FROM TREATMENT PLANT) fed into the deaerator unit (HR-DEA-1)

Make-up water supplied to the water-cooling tower system from the water treatment plant is based on the mass balance of the water-cooling tower system considering losses associated with evaporation, drift and blowdown. In the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2), make-up water supplied (CT-L-1) into the first-section of the water-cooling tower system is controlled by design specification DS-CT-FL-1 varying the mass flow rate of water (WATER FROM TREATMENT PLANT). In the BIG-ICE/CC (SC2), make-up water supplied (CT-L-61) into the second-section of the water-cooling tower system is controlled by design specification DS-CT-FL-4 varying the mass flow rate of water (WATER FROM TREATMENT PLANT).

6.1.17 Make-up water and water treatments

The mass flow rate of make-up water to treatment plant (fresh water) is determined using spreadsheet calculation models by a global mass balance of the complete water cycle considering the treatment of the wastewater in the wastewater treatment plant (not simulated) estimated according the spreadsheet calculation model of the water cycle (losses, recycles an reuse model).

Three distinct use types are required in the BIG-ICE/CC scenarios, classified as:

c) make-up water for water-cooling tower system: fresh-water required by the cooling water cycle is defined by the mass flow rate of the evaporation, drift, and tower basin blowdown losses (not recovered);
d) make-up water for process water cycle: fresh-water required by the process water cycle is defined by the mass flow rate of the evaporative process and condensation losses in pipeline and equipments, by vent streams, blowdown losses, and condensate knock-outs (not recovered);
e) make-up water for SG-ICEs cooling water cycle: fresh-water required by the SG-ICEs advanced cooling water circuits can be defined by the mass flow rate of the evaporative process losses in pipeline and radiator unit.

The recovered water fraction after the wastewater treatment to recycle/reuse is considered as “fresh” water (subtracting in the quantity of fresh-water intake) and the water fraction discharged (not recovered) with the impurities removed in the wastewater treatment process a water losses. The water treatment is simplified by the follow categories:

d) make-up raw water treatment: considers only the make-up of fresh-water obtained from the global mass balance of the complete water cycle, taking into account the recycle and reuse of available water;
e) cooling water treatment (maintenance): considers the make-up raw water obtained from the mass balance of the water tower cycle and the water circulating in the water tower cycle in closed loop-cycle (water maintenance), taking into account the recycle and reuse of available water;
f) process water treatment (maintenance): considers the make-up raw water obtained from the mass balance of the water process cycle and the water circulating in the water process cycle in closed loop-cycle (water maintenance), taking into account the recycle and reuse of available water;
g) cooling water treatment for SG-ICEs (maintenance): considers the make-up raw water obtained from the mass balance of the cooling water circuits and the water circulating in the engine water cycle in closed loop-cycle (water maintenance).

The chemicals compounds and their consumption for treating water are determined by spreadsheet calculation model according to the type of water treatment required (make-up water, process water, cooling water and water special treatment. The water treatment is based on the water treatment processes available in the Ecoinvent 3 library (unit) in SimaPro®v.7.3.3 software and in the water treatment process defined by the division of AIB of the CTBE/CNPEM for the 1G sugarcane biorefinery.

Table 19 – Aspen Plus®v8.4 simulation parameters (input and output) of BIG-ICE/CC routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	BIG-ICE/CC route scenarios	
	SC1	**SC2**
Thermochemical-biorefinery		
Cane stalks (tonnes/hr) 4.0 Mtc (basis)	503.018	503.018
Sugar production (tonnes/hr)	25.559	25.559
Anhydrous ethanol production (tonnes/hr)	21.013	21.013
Electricity exported to the electric power grid (MWh)	120.746	188..979
Installed power generation capacity (MW)	158.786	222.238
Consumption of electricity by the 1G biorefinery (MWh)	38.040	33.255
Available raw biomass [a]		
Sugarcane bagasse available for use (tonnes/hr)	133.150	133.150
Sugarcane straw available for use (tonnes/hr)	42.279	42.279
Sugarcane bagasse imported by the BIG-ICE/CC route (tonnes/hr)	none	87.396
Sugarcane bagasse reserve (tonnes/hr)	6.658	13.316
Sugarcane bagasse moisture content (%)	50.0	50.0
Sugarcane straw moisture content (%)	15.0	15.0
Consumption of sugarcane bagasse by the BIG-ICE/CC route (tonnes/hr)	68.939	126.492
Consumption of sugarcane straw by the BIG-ICE/CC route (tonnes/hr)	42.279	42.279
Consumption of sugarcane bagasse by the 1G-CHP/EBPST system (tonnes/hr)	54.554	81.376
Consumption of sugarcane straw by the 1G-CHP/EBPST system (tonnes/hr)	none	none
Dry biomass consumed in the BIG-GT/CC route (tonnes/hr) [a]	69.985	40.691
Surplus biomass (tonnes/hr) [a]	none	none
LHV_{AR} of bagasse (MJ/kg)	7.45	7.45
LHV_{AR} of straw (MJ/kg)	17.57	17.51
1G sugarcane biorefinery with annexed ethanol distillery (int)		
CHP/ST system type	CHP/EBPST (SC1)	CHP/EBPST (SC1)
Integration type	Integrated	Standalone
Electricity required by the 1G sugarcane biorefinery (MWh)	15.0	15.0
Steam demand at 6.0 bar (dehydration) (tonnes/hr)	14.175	14.175
Steam demand at 2.5 bar (process) (tonnes/hr)	184.945	184.945

Table 19 – **Aspen Plus®v8.4 simulation parameters (input and output) of BIG-ICE/CC routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery**

(continues)

Parameter	**BIG-ICE/CC route scenarios**	
	SC1	**SC2**
Biomass multi-step drying process and control particulate emissions [a]		
Electricity required for sugarcane bagasse handling and milling (MWh)	1.517	2.783
Electricity required for sugarcane straw handling and milling (MWh)	0.334	0.334
Thermal energy required by the biomass dryers (GJ/hr) [a]	470.7	817.03
HHV$_{AR}$ of biomass mix (MJ/kg) [a]	17.02	17.01
LHV$_{AR}$ of biomass mix (MJ/kg) [a]	15.52	15.51
LHV$_{db}$ of biomass mix (MJ/kg) [a]	17.53	17.53
Biomass mix moisture (%) [a]	10.0	10.0
Gasification of biomass in an atmospheric CFB directly-heated gasifier [a]		
Gasification agents	Air / Steam	Air / Steam
Atmospheric air flow into the gasifier (tonnes/hr)	143.482	200.852
Steam at 2.5 bar flow into the gasifier (tonnes/hr)	30.264	42.661
Raw synthesis gas temperature (ºC)	850.0	850.0
Air agent inlet temperature (ºC)	130.0	150.0
Steam agent inlet temperature (ºC)	150.0	150.0
Equivalence ratio (ER$_{AIR}$)	0.359	0.356
Steam-to-biomass ratio (STBR) [a]	0.50	0.50
Carbon conversion (%)	98.0	980
Hydrogen mol flow rate (mol/hr)	2.070,7	2.935,7
Monoxide carbon mol flow rate (mol/hr)	1.394,2	1.975,2
H_2/CO ratio	1.486	1.486
Gasifier cold-gas efficiency (%) [b]	55.62	55.80
Gasifier hot-gas efficiency (%) [b]	91.89	91.94
Synthesis gas flow mass rate (tonnes/hr)	248.654	349.321
HHV$_{db}$ of synthesis gas (MJ/kg)	4.77	4.81
LHV$_{db}$ of synthesis gas (MJ/kg)	4.31	4.35
Generation of bottom particulate materials (tonnes/hr) [h]	3.612	5.135
Olivine mass flow rate – make-up (kg/hr)	699.640	956.649
MgO mass flow rate – make-up (kg/hr)	183.029	250.264
Fines-particulate matters removed by multi-cyclone system (kg/hr)	125.699	193.723

Table 19 – Aspen Plus®v8.4 simulation parameters (input and output) of BIG-ICE/CC routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	BIG-ICE/CC route scenarios	
	SC1	SC2
Syngas cooling and heat recovery		
Intermediate-pressure steam at 23 bar generated by the HT-CSC (tonnes/hr)	77.913	104.120
Intermediate-pressure steam temperature (ºC)	320.0	380.0
Low-pressure steam at 2.5 bar generated by the LT-CSC (tonnes/hr)	30.264	42.661
Low-pressure steam temperature (ºC)	150.0	150.0
Synthesis gas temperature after the HT-CSC (ºC)	318.0	318.0
Synthesis gas temperature after the LT-CSC (ºC)	125.0	125.0
Low-temperature synthesis gas wet cleaning system		
Recirculation of water in spray scrubber (tonnes/h)	3.243	4.562
Recirculation of water in condenser cooler (tonnes/h)	937.390	1316.527
Electricity required by the blower (MWh)	1.551	2.188
Particulate removal by spray scrubber, condenser cooler and venturi system (kg/hr)	73.0	110.0
Persistent fine particles removal by the WESP (kg/hr)	22.0	35.0
Generation of slurry (kg/hr)	174,296	266.119
Excess of water sent off-site to wastewater treatment plant (tonnes/hr)	21.383	30.132
Synthesis gas temperature after the wet cleaning system (ºC)	50.0	50.0
Co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution		
Acid gas removal (captured) (tonnes/hr)	51.810	72.750
CO_2 removal efficiency (%)	90.00	90.00
H_2S content in the acid gas stream ($\%_{mol}$)	0.133	0.100
MEA concentration ($\%_{w/w}$)	30.00	30.00
Consumption of MEA by the system (kg/hr)	87.521	214.059
Lean MEA aqueous absorbing-solution mass flow rate (tonnes/hr) [d]	667000	1030.000
Consumption of thermal energy by the stripper reboiler (GJ/hr)	193.6	267.3
Fresh cool-make-up water to synthesis gas washer (kg/hr)	55.000	100.000
Excess of water sent to wastewater treatment plant (tonnes/hr)	7.618	10.761
Filtered residues sent to wastewater treatment plant and final disposal (kg/hr)	199.810	361.861
Cooling water required by the system (tonnes/hr)	3190.788	4415.864

Table 19 – Aspen Plus®v8.4 simulation parameters (input and output) of BIG-ICE/CC routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	BIG-ICE/CC route scenarios	
	SC1	SC2
CO_2 compression and storage/use (geological storage)		
Pressure required to liquefier CO_2 and to injection (bar)	73.0 / 150.0	73.0 / 150.0
Final generation of liquid CO_2 to injection (reservoir)	50.910	71.490
Number of compression stages (+1 liquid pump stage)	6+1	6+1
Condensed water knock-out to wastewater treatment plant (tonnes/hr)	0.900	1.264
Consumption of electricity to CO_2 compression/liquefaction and injection (MWh)	3.998	5.614
Synthesis gas compression (conditioning)		
Number of compression stages	2	2
Cleaned synthesis gas pressure (bar)	6.0	6.0
Condensed water knock-out to wastewater treatment plant (tonnes/hr)	7.909	11.096
Consumption of electricity by the compressor (MWh) ^{g}	13.743	19.419
Single-fueled internal combustion engine with turbo charging system ^{e} (ICE)		
Number of SG-ICEs in parallel operation	8 unid	11 unid
Cycle-type	Four-stroke Otto-cycle	Four-stroke Otto-cycle
Ignition type	Sparkle-ignition	Sparkle-ignition
Cooling system	Water jacket / Radiator	Water jacket / Radiator
Compression/expansion ratio	10:1	10:1
Turbocharged type	Single pipe exhaust	Single pipe exhaust
Fuel mixture injection system type	Gauge valve	Gauge valve
Auxiliary engine modules	Pumps, coolers and filters	Pumps, coolers and filters
HHV_{AR} of conditioned synthesis gas (MJ/kg)	6.26	5.64
LHV_{AR} of conditioned synthesis gas (MJ/kg)	5.62	6.29
Energy density of the synthesis gas at 6.0 bar (MJ/m³)	29.80	29.99
Energy required by the air turbocharging system (MWh)	20.06	28.46
Engine heat rate (kJ/kWh)	7411.0	7411.0
Grid frequency and engine speed	60 Hz / 514 rpm	60 Hz / 514 rpm
Installed power generation capacity (MW)	135.50	191.58
Engine electrical efficiency at generator terminals (%)	48.6	48.6
Air fuel ratio	2,08	2,10

Table 19 – Aspen Plus®v8.4 simulation parameters (input and output) of BIG-ICE/CC routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	BIG-ICE/CC route scenarios	
	SC1	SC2
Single-fueled internal combustion engine with turbo charging system [e] (ICE)		
Excess of oxygen (%) [c]	25.0	25.0
Fuel inlet pressure (bar)	6.0	6.0
Fuel inlet temperature (ºC) - after conditioning compression	45.0	45.0
Air inlet pressure (bar)	atmospheric	atmospheric
Air pressure after the turbocharger (bar)	6.0	6.0
Fresh air inlet temperature (ºC)	25.0	25.0
Temperature after air turbocharger (ºC)	234.0	234.0
Temperature after air cooler (ºC)	45.0	45.0
Pick-compression pressure (bar)	65.0	65.0
Pick-compression temperature (ºC)	502.0	502.0
Pick-combustion pressure (bar)	155.0	155.0
Pick-combustion temperature (ºC)	1885.0	1888.0
Gauge pressure drop (maximum considered) (bar)	0.6	0.6
Hot water temperature in the HT integrated cooler (ºC)	93.0	93.0
Hot water temperature in the LT integrated cooler (ºC)	40.0	40.0
Lubricating oil mass flow rate trough engines (tonnes/h)	339.997	540.792
Cold-lubricating oil temperature (ºC)	65.0	65.0
Hot-lubricating oil temperature (ºC)	72.0	72.0
Consumption of lubricating oil by system (kg/h) – make-up	78.795	108.158
HT and LT cooling water circulating in the system (tonnes/hr	305.718	449.860
Heat recovery steam generator (HRSG)		
HRSG type	Double-pressure	Triple-pressure reheated
High-pressure steam (bar)	none	45.0
Intermediate-pressure steam (bar)	22.0	23.0
Low-pressure steam (bar)	2.5	2.5
Steam temperature of the high-pressure circuit (ºC)	none	420.0
Steam temperature of the intermediate-pressure circuit (ºC)	320.0	380.0
Steam temperature of the low-pressure circuit (ºC)	130.0	130.0
Steam generation by high-pressure circuit (tonnes/hr)	none	50.000

Table 19 – Aspen Plus®v8.4 simulation parameters (input and output) of BIG-ICE/CC routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	BIG-ICE/CC route scenarios	
	SC1	SC2
Heat recovery steam generator (HRSG)		
Steam generation by intermediate-pressure circuit (tonnes/hr)	31.483	18.862
Steam generation by low-pressure circuit (tonnes/hr)	37.509	2.899
Steam at 2.5 bar sent to deaerator (tonnes/hr)	3.451	2.899
Deaerator temperature (ºC)	105.0	105.0
Deaerator pressure (bar)	1.4	1.4
ICEs exhaust-gas temperature (ºC) – HRSG inlet	425.0	425.0
HRSG flue-gas temperature (ºC)	122.0	180.0
Steam turbine applied in combined-cycles (ST)		
Steam turbine type	BPST *	CEST
High-pressure steam inlet-level (bar)	none	45.0
Intermediate-pressure steam inlet-level (bar)	23.0	23.0
Exhaust steam pressure (bar)	2.5	0.11
High-pressure steam temperature (ºC)	320.0	420.0
Exhaust steam at 2.5 bar sent to thermochemical-biorefinery process (tonnes/hr)	109.396	none
Exhaust steam at 0.11 bar sent to condenser (tonnes/hr)	none	50.993
Steam extraction at 2.5 bar sent to thermochemical-biorefinery process (tonnes/hr)	none	117.990
Steam extraction at 6.0 bar sent to 1G-dehydration system (tonnes/hr)	none	none
Isentropic turbine efficiency (%)	74.55	82.08
Electrical energy generator efficiency (%)	99.0	99.0
Installed power generation capacity (MW)	10.31	27.30
Traditional CHP/EBPST system		
Sugarcane bagasse consumption (tonnes/hr)	54.554	81.376
Sugarcane straw consumption (tonnes/hr)	none	none
Oxygen excess ratio (%$_{w/w}$) [c]	0.08	0.12
Steam pressure (bar)	22.0	22.0
Steam temperature (ºC)	320.0	320.0
Boiler carbon conversion (%$_{w/w}$)	99.0	99.0
Exhaust-gas temperature (Flue-gas) (ºC)	160.0	160.0
Exhaust steam at 2.5 bar sent to 1G sugarcane biorefinery (tonnes/hr)	128.983	184.945

Table 19 – Aspen Plus®v8.4 simulation parameters (input and output) of BIG-ICE/CC routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(conclusion)

Parameter	BIG-ICE/CC route scenarios	
	SC1	SC2
Traditional CHP/EBPST system		
Steam extraction at 6.0 bar sent to 1G-dehydration system (tonnes/hr)	13.707	14.175
Boiler water blowdown (to treatment) (tonnes/hr)	5.943	8.459
Generation of bottom ashes (tonnes/hr)	1.074	1.366
Fly-ashes removal by emission control filters (fine matter) (tonnes/hr)	0.324	0.420
Boiler thermal efficiency 1 (%) [b]	86.22	86.81
Boiler thermal efficiency 2 (%) [b]	82.77	83.16
Steam turbine type	EBPST	EBPST
Exhaust steam at 2.5 bar sent to 1G biorefinery (tonnes/hr)	128.983	184.945
Steam extraction at 6.0 bar sent to 1G-dehydration system (tonnes/hr)	13.707	14.175
Multi-cells water-cooling tower [g]		
Number of sections (sec) (sec)	1 sec	2 sec
Tower cells required - sec 1	8 cells	11 cells
Tower cells required - sec 2	none	3 cells
Make-up water (with recycle) - sec 1 (tonnes/hr)	133.576	185.013
Make-up water (with recycle) - sec 2 (tonnes/hr)	none	40.177
Water evaporation - sec 1 (tonnes/hr)	110.242	152.693
Water evaporation - sec 2 (tonnes/hr)	none	33.158
Water drift - sec 1 (tonnes/hr)	11.085	15.354
Water drift - sec 2 (tonnes/hr)	none	3.334
Tower basin blowdown (to treatment) - sec 1 (tonnes/hr)	12.249	16.966
Tower basin blowdown (to treatment) - sec 2 (tonnes/hr)	none	3.684
Electricity required by driver fans - sec 1 (kWh)	504.0	693.0
Electricity required by fan drivers - sec 2 (kWh)	none	189.0
Water cycles		
Process water/steam maintenance (tonnes/hr)	44.297 **	42.761
Cooling water maintenance (tonnes/hr)	136.466	175.048
Make-up raw water (tonnes/hr)	128.700 **	150.321
Pre-heated fresh-water as deaerator make-up (tonnes/hr)	43.381 **	117.328

Table 19 – Aspen Plus®v8.4 simulation parameters (input and output) of BIG-ICE/CC routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(conclusion)

Parameter	**BIG-ICE/CC route scenarios**	
	SC1	**SC2**
Water cycles		
Generation of deaerated hot process water (tonnes/hr)	295.490 **	171.882
Pre-heated fresh-water as deaerator make-up (tonnes/hr)	43.381 **	117.328
Generation of deaerated hot process water (tonnes/hr)	295.490 **	171.882

(int) reference scenario for surplus biomass and integration with thermochemical routes

[a] biomass refers to sugarcane bagasse and sugarcane straw

[b] efficiency based on LHV_{AR} of fuel at 25ºC and 1 atm

[c] excess based on inlet oxygen and not in the stoichiometric oxygen for combustion

[d] lean MEA aqueous absorbing-solution mass flow rate inlet in the top of the absorber

[e] manufacturer technical data for gas conditions at LHV > 28MJ/Nm³ (ISO 3046)

[f] electricity consumed to compress the synthesis gas can be considered as power loss or an reduction on efficiency in the engine calculus

[g] section 1 (sec1) to cooling compressors systems and CO_2 and H_2S co-capture system, and section 2 (sec 2) to condensing CEST exhaust-steam

[h] considers all solid matters removed, including bed media and catalytic active materials

* steam turbine without steam extractions

** account for water cycle the 1G-CHP/ST system and the steam (heat) to equipment users in the 1G sugarcane biorefinery.

7 Biomass integrated directly-heated gasifier and gas turbine in combined-cycle integrated at an optimized first generation sugarcane biorefinery with annexed ethanol distillery

Biomass integrated gasification with gas turbine in combined-cycle (BIG-GT/CC) system for electrical energy production is an alternative for a large-biomass power plant. Sugarcane bagasse and straw gasification to produce synthesis gas (combustible gas) and their use in a high-efficiency gas turbine cycle (advanced technology) in CC mode can provides much more efficient conversion of available biomass into electricity per unit of consumed biomass than traditional efficient CHP/CEST systems (e.g.: CHP/CEST (SC5)).

Sugarcane bagasse and straw are potential sources aplenty available and accessible in Brazil for electrical energy production by BIG-GT/CC route as an alternative option to reduce the extremely-dependence of Brazilian electricity sector (Figure 18) on hydropower plants (89.0% of the share of all renewables resources of the total electricity final consumption in 2013). Also, can even replace the fossil fuel-powered thermoelectric plants (18.3% of the total electricity final consumption in 2013), changing to a more sustainable resource. Actuality (2015), the sector is on stress by changes in the Brazil’s rainfall systems and by the increasing consumption above the energy supply, gradually becoming more expensive and on a collision course with the Brazilian development and the costs of the human needs.

7.1 Scenarios assessed

Five possible thermochemical-biorefinery scenarios applying BIG-GT/CC system were simulated in Aspen Plus®v8.4 process simulation platform and assessed under the scope of the VSB tool, taking into account the integral use of available sugarcane bagasse and straw for the efficient production of electricity while supply the thermal and electrical energy required by the thermochemical-biorefinery.

Thermochemical-biorefinery scenarios applying BIG-GT/CC system are defined in the section 3.4.3 (Biomass integrated directly-heated gasifier and gas turbine in combined-cycle system). A scheme of the sugar, ethanol, and electricity production from BIG-GT/CC route integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery is detailed in the Figure 47 for BIG-GT/CC scenario 1 (SC1), in the Figure 48 for BIG-GT/CC scenario 2 (SC2), in the Figure 49 for BIG-GT/CC scenario 3 (SC3), in the Figure 50 for BIG-GT/CC for scenario 4 (SC4), and in the Figure 51 for BIG-GT/CC scenario 5 (SC5).

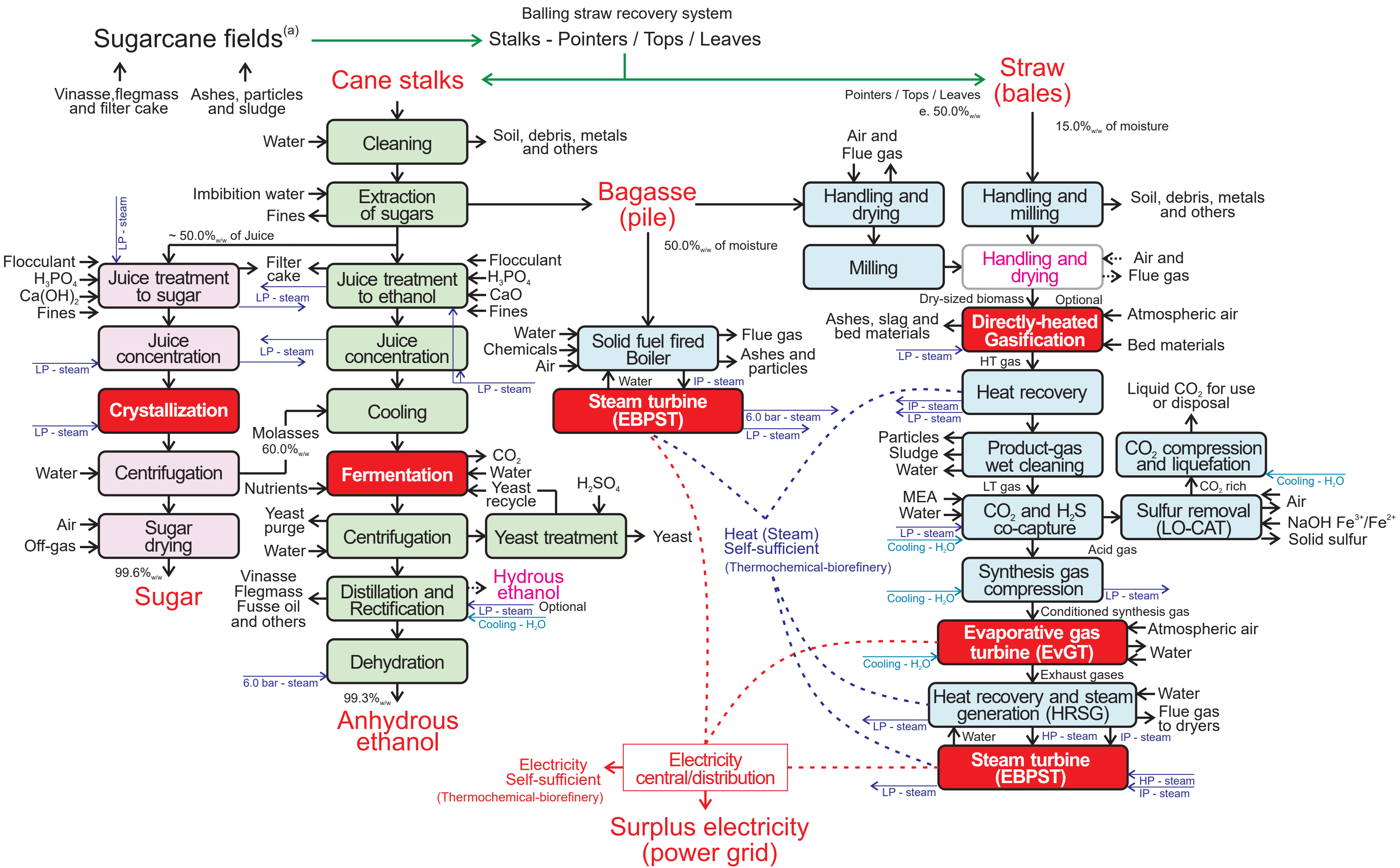
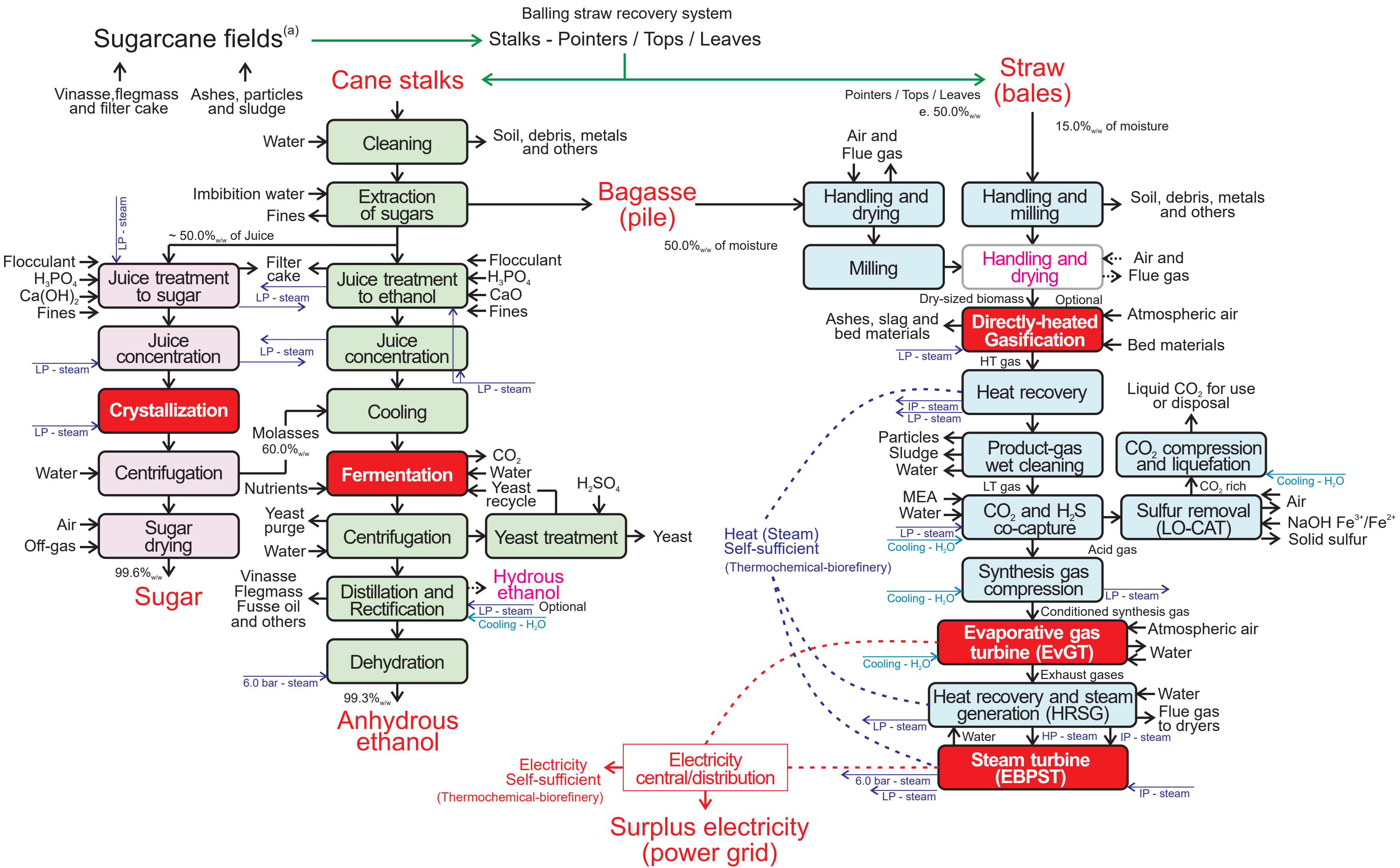


Figure 47 - Flow block diagram of biomass integrated directly-heated gasifier and gas turbine in combined-cycle (BIG-GT/CC) in energy and mass integration mode integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery: Scenario 1 (SC1)

Figure 48 - Flow block diagram of biomass integrated directly-heated gasifier and gas turbine in combined-cycle (BIG-GT/CC) in energy and mass integration mode integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery: Scenario 2 (SC2)



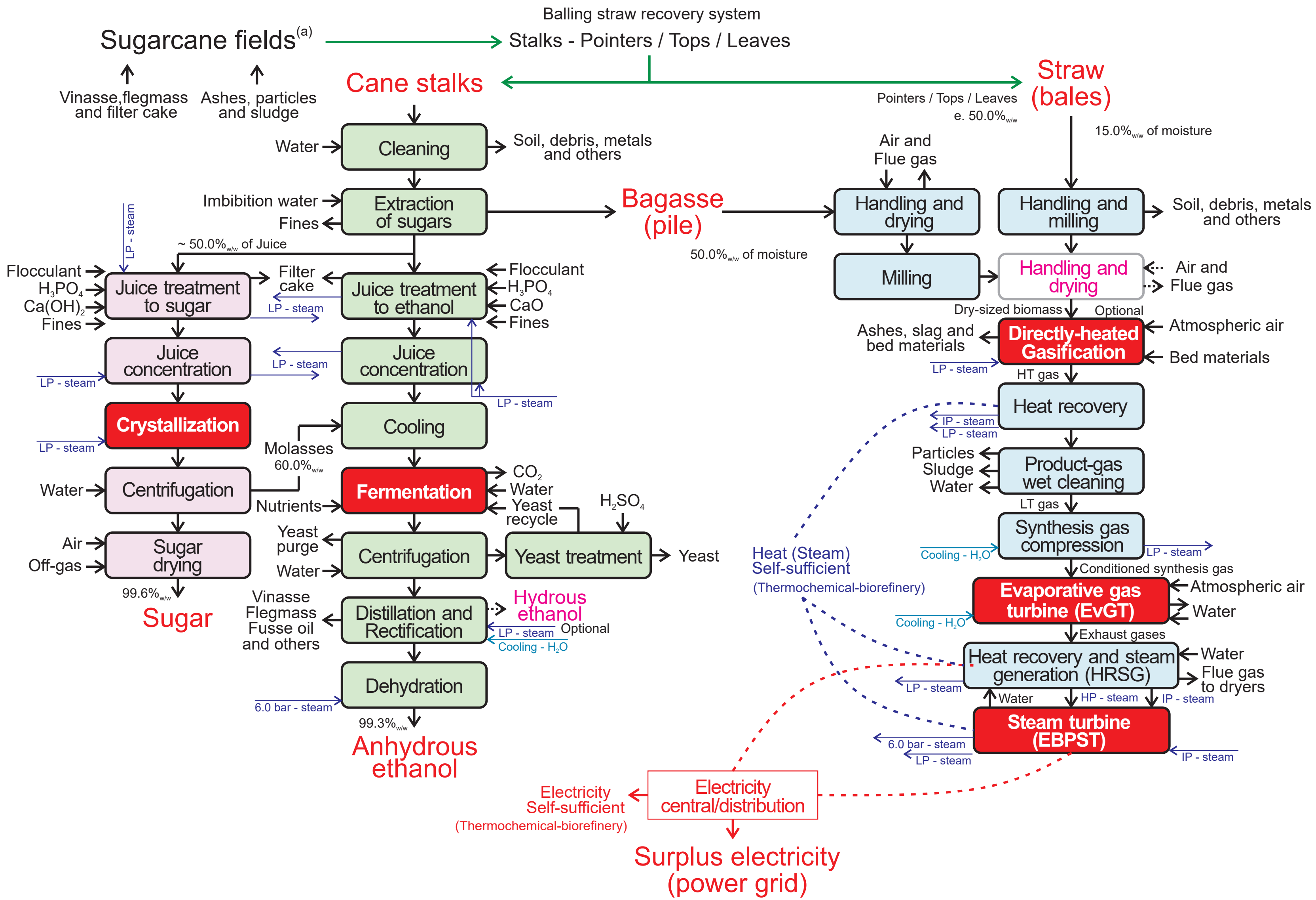


Figure 49 - Flow block diagram of biomass integrated directly-heated gasifier and gas turbine in combined-cycle (BIG-GT/CC) in energy and mass integration mode integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery: Scenario 3 (SC3)

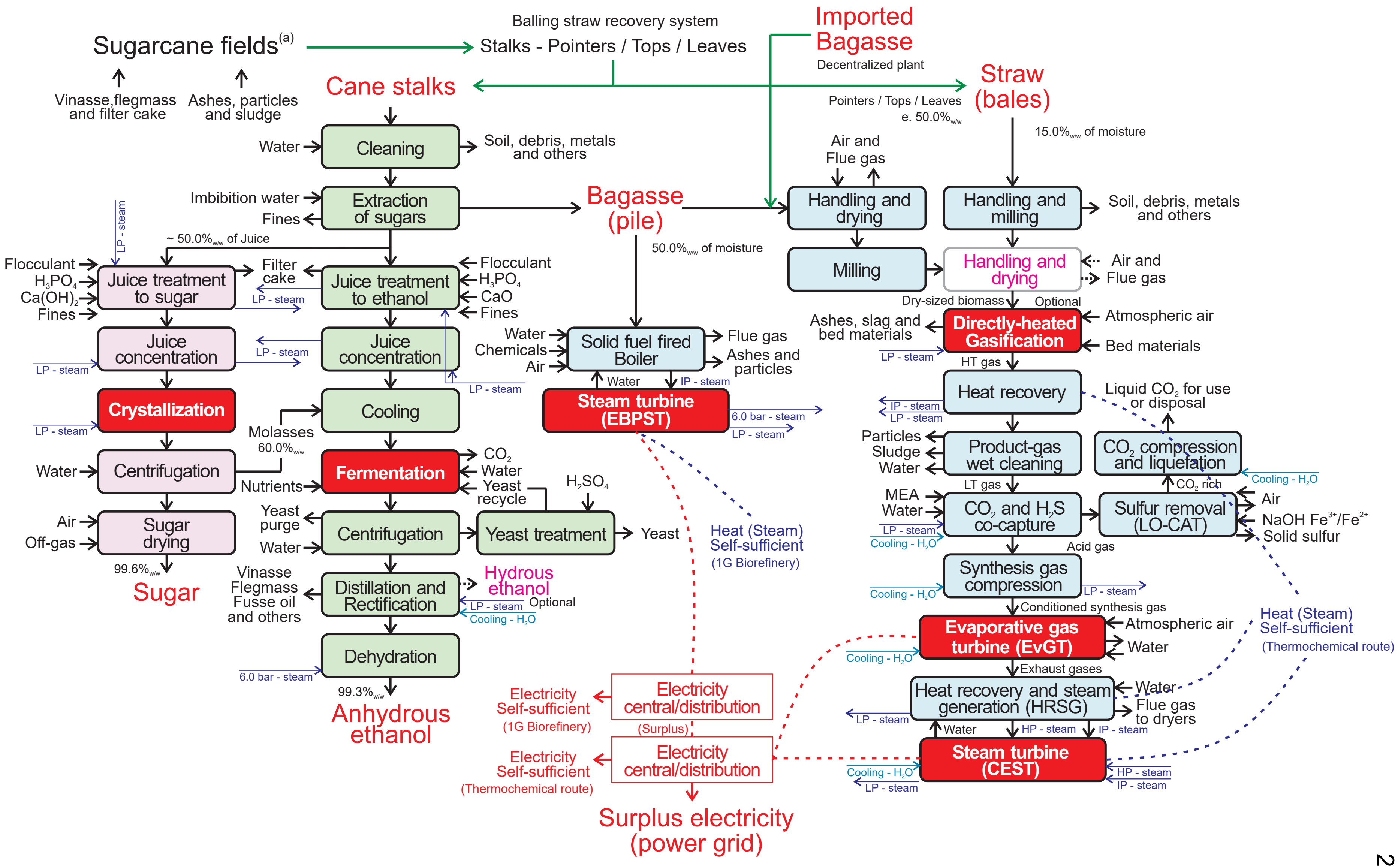
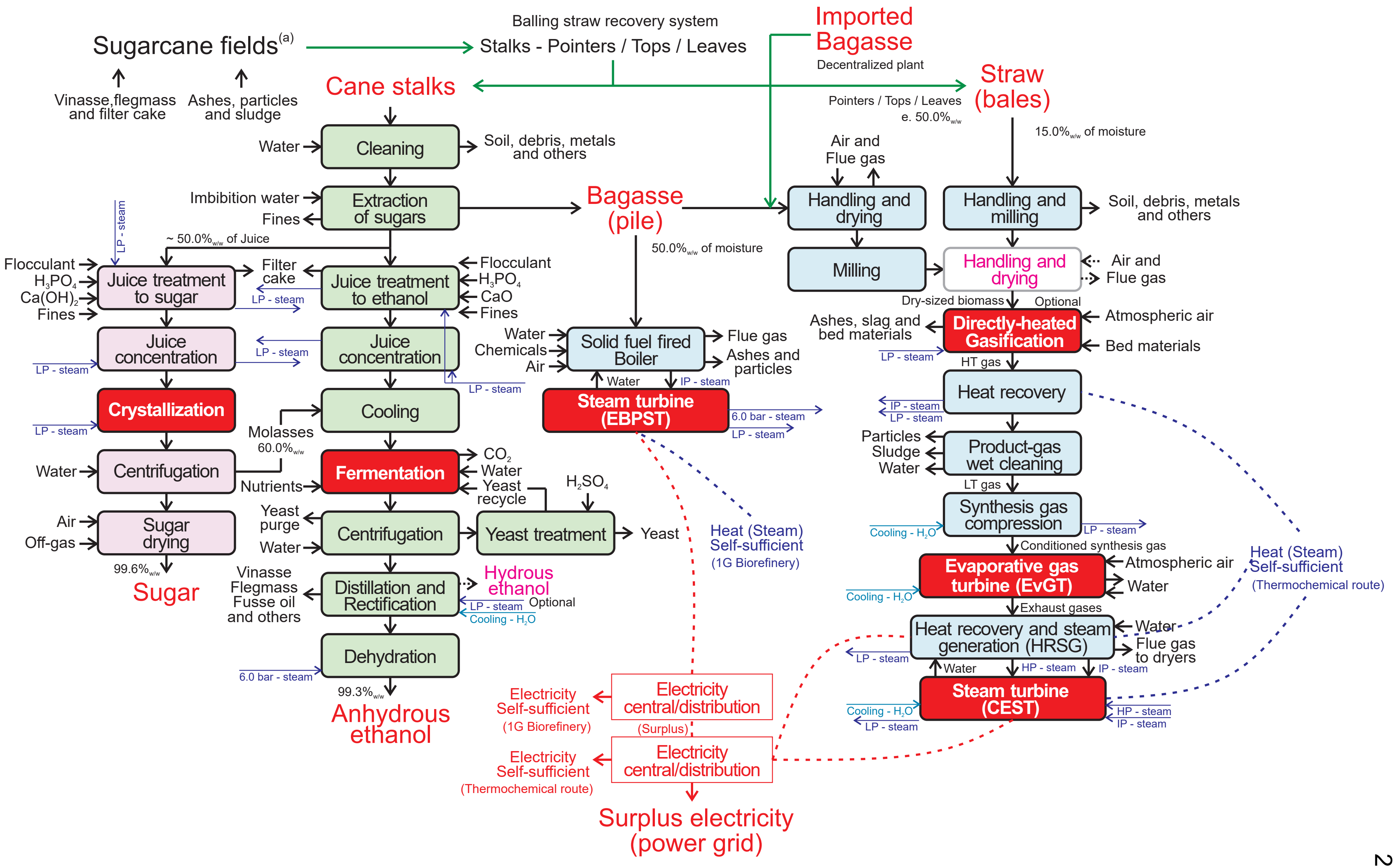


Figure 50 - Flow block diagram of biomass integrated directly-heated gasifier and gas turbine in combined-cycle (BIG-GT/CC) in standalone mode integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery: Scenario 4 (SC4)

Figure 51 - Flow block diagram of biomass integrated directly-heated gasifier and gas turbine in combined-cycle (BIG-GT/CC) in standalone mode integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery: Scenario 5 (SC5)



BIG-GT/CC scenarios 1 (SC1), BIG-GT/CC scenario 2 (SC2), BIG-GT/CC scenario 3 (SC3), BIG-GT/CC scenarios 4 (SC4), and BIG-GT/CC scenarios 5 (SC5) are integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery according to section 5 (First generation sugarcane biorefinery), and to agricultural and industrial phases of the 1G sugarcane biorefinery assessed by the division of AIB of the CTBE/CNPEM and published – *The Virtual Sugarcane Biorefinery (VSB)*: 2011 Report (BRAZILIAN BIOETHANOL SCIENCE AND TECHNOLOGY LABORATORY, 2012) – and in – Virtual Biorefinery: An Optimization Strategy for Renewable Carbon Valorization (BONOMI et al., 2016).

BIG-GT/CC route scenarios were implemented in Aspen Plus®v8.4 process simulation platform to evaluate the electricity generation while supply the thermal and electrical energy requirements for the thermochemical-biorefinery. Available sugarcane bagasse and straw are gasified in an atmospheric CFB directly-heated gasifier using atmospheric air and steam gasification agents to produce low-medium LHV synthesis gas. Therefore, is conditioned and then used in a high-performance sequential combustion full-flow advanced evaporative (humidification tower) gas turbine (EvGT) in combined-cycle (CC) mode with steam turbine (ST) system (Rankine-cycle cogeneration system) for thermochemical route-cycles. The evaporative-class gas turbine cycle-class has dual combustion chamber (reheated), heat recovery intercooler/after-cooler and exhaust-gas heat recovery system (recuperator).

Aspen Plus®v8.4 complete flowsheet`s of BIG-GT/CC detailed scenarios are presented in the APPENDIX A. Figure A17 shows BIG-GT/CC scenario 1 (SC1), Figure A18 shows the BIG-GT/CC scenario 2 (SC2), Figure A19 shows the BIG-GT/CC scenario 3 (SC3), Figure A20 shows the BIG-GT/CC scenario 4 (SC4), and Figure A21 shows the BIG-GT/CC scenario 5 (SC5).

7.1.1 Physical properties

The GLOBAL property methods used are ELECNRTL, and RKS-BM

The local properties method used is: IDEAL for biomass handling and sizing, and biomass multi-step dryer and control particulate emissions; RKS-BR for biomass multi-step dryer and control particulate emissions, gasification of biomass in an atmospheric CFB directly-heated gasifier, syngas cooling and heat recovery, CO_2 compression and storage/use, synthesis gas compression (conditioning), high-performance sequential combustion full-flow advanced EvGT, HRGS system, and traditional CHP system applying EBPST system; ELECNRTL for low-temperature synthesis gas wet cleaning system, and co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution; IAPWS-95 for multi-cells water-cooling tower, water cycles, BPST, EBPST and CEST systems for thermochemical route-cycles, traditional CHP system applying EBPST system, for pure water-side streams, and for pure steam-side streams; and RKS-BM for gaseous streams side.

Non-conventional solids physical property method used for BAGASSE and STRAW component properties is the HCOALGEN model (general coal models) applying the Mott and Spooner correlation (4 option code) according to section 3.7 (Non-conventional solids physical property methods) for estimate the enthalpy, and COALIGT model for estimate the density.

7.1.2 Available raw biomass

Raw sugarcane bagasse (SUGARCANE BAGASSE) is represented by BAGASSE and SOIL streams according to Table 9, and raw sugarcane straw (SUGARCANE STRAW) is represented by STRAW and TRASH according to Table 9. METAL stream was added to represent the amount of the tramp metals removed by the magnetic head pulleys (inlet-to-outlet model). Others debris were not considered present (to specify removal process) and can be accounted for in the trash fraction (TRASH) as inert material.

Sugarcane straw (SUGARCANE STRAW) is collected from the field (after the sugarcane harvesting) using a baling system (with pre-chopping system). In this system, the straw is separately sent from the cane stalks to the thermochemical-biorefinery. The transport is made using trucks (up to 25 tonnes/vehicle) or road trains (up to 70 tonnes/vehicle). All the BIG-GT/CC scenarios consider that $50.0\%_{w/w}$ of the total sugarcane straw available is recovered and send to the thermochemical-biorefinery with $15.0\%_{w/w}$ of moisture content (on-site). As the transport vehicle enters the plant, they are weighed and the straw bales are dumped (PR-MIX-3) or removed by adapted cane loaders and stored (PR-MIX-3) as feedstock for further processes.

In the BIG-GT/CC (SC1), part of available bagasse (BAGASSE) is belt-conveyed directly to the traditional CHP/EBPST system or to bagasse pile (PR-SPL-1) for burning purpose, generating thermal and electrical energy to supply part of the energy required by the 1G sugarcane biorefinery while BIG-GT/CC route supply the another part. In the BIG-GT/CC (SC2) and BIG-GT/CC (SC3), all of the available bagasse (BAGASSE) is belt-conveyed directly to the bagasse flash dryers (DR-DRY-1) in the BIG-GT/CC route or to bagasse pile (PR-SPL-1) as feedstock for further processes. In the BIG-GT/CC (SC4) and BIG-GT/CC (SC5), part of available bagasse (SUGARCANE BAGASSE) is burned to generate the thermal and electrical energy all of this energy required by the 1G sugarcane biorefinery. Surplus bagasse (SUGARCANE BAGASSE) from the boiler-pile or directly from the cane mills is conveyed (centralized plant) or transported (decentralized plant) as available feedstock to the BIG-GT/CC plant together imported bagasse (scale setting).

7.1.3 Biomass handling and sizing

Sugarcane bagasse (SUGARCANE BAGASSE) with 50.0%$_{w/w}$ of moisture content after the cane mills (driver by electrical motors) is transported by a conveyor (screw, drag or belt) to a temporary pile (PR-SPL-1) (feeding or equalization pile) or sent directly to the bagasse flash dryers (DR-DRY-1) by feeder conveyor (PR-MIX-1). In the BIG-GT/CC (SC1), BIG-GT/CC (SC4), and BIG-GT/CC (SC5), part is sent to biomass feed drum (PR-MIX-5) in the traditional solid-fuel fired boiler (BO blocks) to burning in the boiler chamber (BO-COMBU).

As shown in Figure 33, Aspen Plus®v8.4 flowsheet of the simplified aggregated-steps model for the biomass handling and sizing in the BIG-ICE/CC (SC1) is the same model with modified parameters for BIG-GT/CC (SC1), and as shown in Figure 34, Aspen Plus®v8.4 flowsheet of the simplified aggregated-steps model for the biomass handling and sizing in the BIG-ICE/CC (SC2) is the same model with modified parameters for BIG-GT/CC (SC2), for BIG-GT/CC (SC3), for BIG-GT/CC (SC4) and for BIG-GT/CC (SC5). The Aspen Plus®v8.4 flowsheet`s are compost by: dumper (PR-MIX-3); storage area (PR-MIX-3); temporary bagasse pile (PR-SPL-1 and PR-SPL-3); bagasse pre-milling machine (PR-CRU-1); fine-size milling machines (DR-CRU-1); straw fine-size cutting-milling machine (DR-CRU-2); pre-sizing bagasse screen-deck solid-solid classifier (PR-CLA-1); bagasse screen-deck solid-solid classifier (PR-CLA-2); straw screen-deck solid-solid classifier (PR-CLA-3); oversized bagasse mixer (PR-MIX-2); unpacking and preparation area (PR-SPL-2); magnetic head pulleys (PR-ELE-1); magnetic separator (PR-SCR-5); screw-conveyor (PR-SCR-7); oversized straw mixer (PR-MIX-4); belt-conveyor (PR-SCR-1); bagasse feeder conveyor (PR-MIX-1); transporter (PR-SCR-3); screw-conveyed (PR-SCR-2); drag-conveyor (PR-SCR-4); screw-conveyor (PR-SCR-6); and screw-conveyor (PR-SCR-7).

In the Aspen Plus®v8.4 process model simulation 5.0%$_{w/w}$ of the raw bagasse (BAGASSE) is reserved (PR-SPL-1) in the pile (RESERVE BAGASSE) for brief stops and start-up.

In the BIG-GT/CC (SC1), part of the raw bagasse (BAGASSE) can be used as received (wet) from the cane mills to be burned in the solid-fuel fired boiler (BO-COMBU). Another part of the raw bagasse (BAGASSE) from the cane mills or temporary bagasse pile (PR-SPL-1) is screw-conveyed (PR-SCR-2) directly to first-stage bagasse flash dryer (DR-DRY-1) to reduce the moisture content before the gross-size reduction stage (PR-CRU-1).

As shown in Figure 33, Aspen Plus®v8.4 flowsheet of the biomass handling and sizing in the BIG-ICE/CC (SC1), which is the same model with modified parameters in the BIG-GT/CC (SC1) with 1G-CHP/EBPST system wherein the bagasse (SUGARCANE BAGASSE) from the cane mills can be directly belt-conveyed (PR-SCR-8) to boiler fuel feeders. Moreover, the model also consider fed from the temporary bagasse pile (PR-SPL-1) by using a tractor (actual system) to carries part of the bagasse available to the conveyor boiler feed tray (PR-MIX-5).

As shown in Figure 34, Aspen Plus®v8.4 flowsheet of the biomass handling and sizing in the BIG-ICE/CC (SC2), which is the same model with modified parameters for BIG-GT/CC (SC2), for BIG-GT/CC (SC3), for BIG-GT/CC (SC4), and for BIG-GT/CC (SC5) considers that the raw bagasse (BAGASSE) from the cane mills or temporary bagasse pile (PR-SPL-1) are screw-conveyed (PR-SCR-2) directly to first-stage bagasse flash dryer (DR-DRY-1) to reduce the moisture content before the gross-size reduction stage (PR-CRU-1). After the first-stage of drying (DR-DRY-1), the bagasse is belt-conveyed (PR-SCR-1) to a pre-milling bagasse machine (PR-CRU-1) to gross-size reduction. After this stage, the bagasse is classified in a screen-deck solid-solid classifier (PR-CLA-2), the fine fraction is directly screw-conveyed (PR-SCR-2) to bagasse second-flash dryer (DR-DRY-1) and the oversized fraction is recycled and mixed back (PR-MIX-2) for further gross-size reduction cycle in closed-loop at size requirements. Gross-sized and pre-dried bagasse is screw-conveyed (PR-SCR-2) to bagasse second-flash dryer (DR-DRY-1) to reduce the moisture content to 10.0%$_{w/w}$ (dry bagasse) before the fine-size reduction stage (PR-CRU-1).

The gross-sized and dried bagasse is belt-conveyed (PR-SCR-1) to pre-sizing classification in a screen-deck solid-solid classifier (PR-CLA-1), being classified according to ideal function for 2.0 mm of cut size (thickness). After, is sent to the fine-size milling machine (PR-CRU-1) to fine-size reduction and classification in a screen-deck solid-solid classifier (PR-CLA-2) according to ideal function for 2.0 mm of cut size (thickness). The fine fraction is screw-conveyed (PR-SCR-2) to gasifier feed drum (DR-MIX-4) and the oversized fraction is recycled and mixed back (PR-MIX-2) for further fine-size reduction cycle.

Aspen Plus®v8.4 process model simulation of the bagasse gross-size milling and fine-size milling machines (DR-CRU-1) are combined in a single-block model. The single block-stage model was developed by using Crusher solids block to reduce the particle diameter to a maximum of 4.0 mm of thickness according to Gates-Gaudin-Schuhmann general cumulative distribution function to avoid 50.0%$_{w/w}$ of the bagasse mass flow rate with more than 2.0 mm of thickness.

The electrical power work required by the bagasse size reduction and handling system is estimated as 22.0 kWh per tonnes of wet bagasse inlet in the sizing system. It is set in bond work index by design specification DS-PR-PC-1. In addition, outlet PSD distribution is determined by Bond’s comminution power law and a sizing distribution function.

The straw bales delivered (STRAW+TRASH+METAL) are transported (PR-SCR-3) to unpacking and preparation area (PR-SPL-2), considering a pre-chopping process in the field by the straw baling machine. The straw bales are unpacked (PR-SPL-2), the over sized or hardest biomass, and heavier particles (rocks) delivered with the straw bales is separated and screwed-out. In these processes is considered removal 50.0$\%_{w/w}$ of the soil fraction content in the trash (TRASH), accumulated due to contact with the agricultural land.

Unpacked-straw (pre-chopped) is drag-conveyed (PR-SCR-4) to the magnetic separation (PR-SCR-5) (prevent damages) by magnetic head pulleys (PR-ELE-1) to remove the tramp metals (METALS) along with 5.0$\%_{w/w}$ of the soil content, its fraction is screwed-out (PR-SCR-6) to final disposal or send to be recycled (metals). After removal the debris (TRASH) and ferrous metals, the straw is belt-conveyed to a cutting-milling straw machine (PR-CRU-2) to fine-size reduction with size-classification by screen-deck solid-solid classifier (PR-CLA-3) according to ideal function for 2.0 mm of cut size (thickness). The fine fraction is directly screw-conveyed (PR-SCR-7) to straw flash dryer (DR-DRY-2) and the oversized fraction is recycled and mixed back (PR-MIX-4) for further fine-size reduction cycle in closed-loop at size requirements.

Aspen Plus®v8.4 process model simulation of the straw fine-size cutting-milling machine (DR-CRU-2) was developed by using Crusher solids block to represent the particle diameter reduction. The model consider a maximum of 4.0 mm of thickness according to Gates-Gaudin-Schuhmann general cumulative distribution function to avoid 50.0$\%_{w/w}$ of the straw mass flow rate with more than 2.0 mm of thickness.

The electrical power work required by the straw size reduction and handling system is estimated based on chopper's machines and fine-size cutting-milling processes for sugarcane straw as 8.0 kWh per tonnes of wet straw inlet in the sizing system (after the magnetic head pulleys). It is set in the bond work index using the design specification DS-PR-PC-2. In addition, outlet PSD distribution is determined by Bond's comminution power law and a sizing distribution function.

Sized straw is screw-conveyed (PR-SCR-7) to straw flash dryer (DR-DRY-2). In some cases (dry gathering conditions), there may not be need of drying the straw and then this can bypass the straw flash dryer (DR-DRY-2) and be directly belt-conveyed to the gasifier feed drum (DR-MIX-3).

7.1.4 Biomass multi-step dryer and control particulate emissions

The raw moist bagasse is fed by screw-conveyor (PR-SCR-2) into parallel bagasse flash dryer trains (DR-DRY-1). The moisture content is reduced from 50.0%$_{w/w}$ to 10.0%$_{w/w}$ in a multi-steps drying process (DR-DRY-1).

Sized straw with higher-moisture content (considered 15.0%$_{w/w}$), recovered in rain conditions (or which has been humidified) is belt-conveyed to dryer feeder drum and screw-conveyed (PR-SCR-7) to straw flash dryer (DR-DRY-2). The moisture content is reduced from 15.0%$_{w/w}$ to 10.0%$_{w/w}$. Sized straw with lower-moisture content (equal or less than 10.0%$_{w/w}$) obtained on dry straw recovery conditions (not considered in this research Master's degree) bypass the straw flash dryer (DR-DRY-2) and is directly belt-conveyed to the gasifier feed drum (DR-MIX-3).

As shown in Figure 35, Aspen Plus®v8.4 flowsheet of the simplified aggregated-steps model of the biomass multi-step dryer and control particulate emissions in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2) which is the same model with modified parameters for BIG-GT/CC (SC1), for BIG-GT/CC (SC2), for BIG-GT/CC (SC3), for BIG-GT/CC (SC4), and for BIG-GT/CC (SC5) is compost by: first-stage bagasse flash dryer (DR-DRY-1); second-stage bagasse flash dryer (DR-DRY-1); straw flash dryer (DR-DRY-2); advanced blower system (DR-ASP-1); pre-filter unit (DR-FIL-1); bagasse after-dryer single-cyclone (DR-CYC-1); straw after-dryer single-cyclone (DR-CYC-2); bagasse electrostatic precipitator (DR-ESP-1); straw electrostatic precipitator (DR-ESP-1); fine-solids mixer 1 (DR-MIX-7); fine-solids mixer 2 (DR-MIX-8); straw gasifier storage bin (DR-MIX-3); bagasse gasifier storage bin (DR-MIX-4); gaseous mixer 1 (DR-MIX-1); gaseous mixer 2 (DR-MIX-2); flash separator 1 (DR-FLA-1); and flash separator 2 (DR-FLA-2).

Fresh drying air agent (ATMOSPHERIC AIR) is indirect preheated using the dryer humidified exhaust-gas and heated (DR-HEA-1) using only the HRSG flue-gas or a mixture of the HRSG flue-gas with 1G-CHP/EBPST exhaust-gas. In the BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5), drying air agent is heated to 120.0ºC.

The hot-air drying agent is forced-injected at atmospheric pressure in the bagasse multi-stage flash dryer (DR-DRY-1) and straw flash dryer (DR-DRY-2) by advanced blower system (DR-ASP-1) modeled by using a Compr pressure changer block according to isentropic method for compressor considering 85.0% isentropic efficiency and 99.0% mechanical efficiency. A pre-filter unit (DR-FIL-1) modeled by using a FabFl solids separator block according to Piecewise separation efficiency in function of the particle diameter of the solids is used to protect the blower and the flash dryers from debris (PARTICLES). The advanced blower system (DR-ASP-1) is used to adjust the mass flow rate of the hot-air drying agent required by the drying process (technical assessment) and equalize the drop pressure of the system to atmospheric discharge condition in the dryer flue-gas (FLUE-GAS FROM STACK).

The multi-step bagasse flash dryer (DR-DRY-1) and the straw flash dryer (DR-DRY-2) is modeled by using a HeatX exchanger block coupled with a Flash2 separator block operating at atmospheric pressure (no pressure drop consideration). The model represents the direct contact of hot-air drying agent with bagasse (DR-FLA-1) and straw (DR-FLA-2), and the resultant thermal and fluid dynamic effects.

The thermal exchange models consider that the biomass heat at saturation temperature (at about 100.0ºC for atmospheric pressure) to liquid-vapor equilibrium phase to separate the moisture content (flash model principles). The direct contact model consider drag 0.2%$_{w/w}$ of the total biomass (daef) feed as biomass fine fibers and 0.1%$_{w/w}$ of the total particles (e.g.: soil and others) as fine particles due the high mass flow rate and the turbulence of the drying air agent. The model also considers that 0.01%$_{w/w}$ of the moisture contained in the biomass is entrained together with the particulate emissions (without energetic consumption to evaporate).

Extractives, volatile organic compounds, and moisture contents in the biomass are evaporated according to flash equilibrium model (DR-MIX-1 for bagasse model and DR-MIX-2 for straw model). Hence, they are emitted to atmosphere together the drying air agent in the dryer flue-gas (FLUE-GAS FROM STACK).

The fine-sized and dried straw (solid phase) content 10.0%$_{w/w}$ of moisture after the straw flash dryer (DR-FLA-2) is belt-conveyed to a gasifier feed drum (DR-MIX-4).

The raw wet bagasse is dried in a first-stage bagasse flash dryer (DR-DRY-1) to reduce the moisture content before the gross-size reduction stage (PR-CRU-1). Lower moisture content easiest the process of gross-size milling (DR-CRU-1), and reduce the thermal energy required by this first-stage, the moisture content level affect the machine performance. After gross-sized, the bagasse is sent back to a second-stage bagasse flash dryer (DR-DRY-1) to reduce moisture content to 10.0%$_{w/w}$, before the fine-size milling stage. The gross-sized and dried bagasse (solid phase) with 10.0%$_{w/w}$ of moisture content is belt-conveyed to gross-size milling machine (DR-CRU-1) to reduce the size particle at gasifier required level.

The first-stage and second-stage of the bagasse flash dryer (DR-DRY-1) combined in a single-block model and the straw flash dryer (DR-DRY-2) are modeled by using a HeatX exchanger block and Flash2 separator block. Estimate the thermal energy required by the biomass flash driers (DR-DRY-1 and DR-DRY-2) to reduce the moisture content of bagasse and straw to 10.0%$_{w/w}$ by using hot-air agent, inlet at 120.0ºC and outlet at about 100.0ºC.

The hot-air mass flow rate is controlled by design specification DS-DR-TG-1 to distribute the air-flow in order to obtain the same outlet temperature (same temperature range) in the dryers (DR-DRY-1 and DR-DRY-2). The design specification DS-DR-FG-1 is used to estimate the thermal energy required by the multi-step bagasse drying process, and the design specification DS-DR-FG-2 is used to estimate the thermal energy required for the straw drying process. The design specification DS-DR-FG-3 is used to control the mass flow rate of fresh-air inlet (ATMOSPHERIC AIR) the dryers, optimizing the dying processes under determined temperature range (120.0ºC~100.0ºC in the air agent side).

The Aspen Plus®v8.4 process model simulation of bagasse flash dryers (DR-DRY-1) and straw flash dryers (DR-DRY-2) overestimates the power consumption because only uses the heat of vaporization of water and sensible heat exchanger according to biomass heat capacity, not taking into account other phenomena. The design specification DS-DR-HD-3 is used to correct the model estimative and approach to the real value demanded by the process, applying 45.0% as reduction factor of thermal energy calculated in the model, this thermal energy is provide by the Heat exchanger block between the HRSG exhaust-gas (HR-HEA-1) and the air agent mass flow rate (DR-HEA-1). The cooled HRSG flue-gas (FLUE-GAS FROM STACK) temperature is controlled and dependent on the exhaust-gas temperature of the subcritical HRSG system (without wet gaseous cleaning system).

Humidified exhaust-gas from first-stage and second-stage bagasse flash dryers (DR-MIX-1) enters in the after-dryer single-cyclone (DR-CYC-1) modeled by using a Cyclone solids separator block to remove the gross particulate content in the dryer humidified exhaust-gas according to Muschelknautz calculation method for a maximum pressure drop of 0.02 bar applying spiral inlet cyclone type. After the dryer single-cyclone (DR-CYC-1), dryer humidified exhaust-gas pass flowing through an electrostatic precipitator (DR-ESP-1) modeled by using a ESP solids separator block according to Svarovsky calculation model for vertically mounted collecting plates model with separation efficiency of 95.0% based on the migration velocity and the ratio of precipitation area. Part of the persistent fine particulate matters are removed avoid-reducing their emissions to atmosphere with the dryer’s flue-gas (FLUE-GAS FROM STACK).

The dryer humidified exhaust-gas of the straw flash dryers (DR-MIX-2) enters in the after-dryer single-cyclone (DR-CYC-2) modeled by using a Cyclone solids separator block to remove the gross particulate content in the dryer humidified exhaust-gas according to Muschelknautz calculation method for a maximum pressure drop of 0.02 bar applying spiral inlet cyclone type. After the dryer single-cyclone (DR-CYC-2), dryer humidified exhaust-gas pass flowing through an electrostatic precipitator (DR-ESP-2) modeled by using a ESP solids separator block according to Svarovsky calculation model for vertically mounted collecting plates model with separation efficiency of 95.0% based on the migration velocity and the ratio of precipitation area. Part of the persistent fine particulate matters are removed avoid-reducing their emissions to atmosphere with the dryer’s flue-gas (FLUE-GAS FROM STACK).

The gross and fine particulate matters removed from the dryer humidified exhaust-gas are sent to gasifier storage bin (DR-MIX-3) together the dried and sized bagasse and straw (mixed in the feed gasifier drum).

7.1.5 Gasification of biomass in an atmospheric circulating fluidized bed directly-heated gasifier by using atmospheric air and steam gasification agents

The Aspen Plus®v8.4 process model simulation of the gasification of biomass in an atmospheric CFB directly-heated gasifier by using atmospheric air and steam gasification agents is based on zero-dimensional isothermal built-in multi-blocks models (CFB directly-heated gasifier process-zones) in steady state operation mode.

The model use Mott and Spooner correlation (option code 4) to estimate the heat of combustion and heat of formation, Kirov correlation (option code 1) to estimate the heat capacity. RKS cubic equation of state with BM alpha function property method evaluates the heat transfer between the CFB directly-heated gasifier zones (multi-blocks), as well as heat loss from the gasifier considered by using design specification DS-GA-QL-1.

As shown in Figure 36, Aspen Plus®v8.4 flowsheet of the gasification of biomass in an atmospheric CFB directly-heated gasifier by using atmospheric air and steam gasification agents in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2) which is the same model with modified parameters for BIG-GT/CC (SC1), for BIG-GT/CC (SC2), for BIG-GT/CC (SC3), for BIG-GT/CC (SC4), and for BIG-GT/CC (SC5). The model was developed as built-in multi-blocks and splitted in bagasse and straw feed system, pre-filter unit (GA-FIL-1), advanced blower system (GA-ASP-1), heat exchanger (GA-HEA-1 and HR-HEA-1), and more five basic linked zones representing the atmospheric CFB directly-heated gasifier: a) drying zone (GA-SEP-1 and GA-SEP-2); b) devolatilization (thermal decomposition) or pyrolysis zone (GA-DEV-1 and GA-DEV-2); c) gasification or reduction zone (GA-GASEI); and d) combustion or oxidation zone (GA-GASEI); and e) primary gasifier cyclone (GA-CYC-1).

Dried (10.0%$_{w/w}$ of moisture content) and sized (less than about 2.0 mm of tickles) sugarcane bagasse and straw, after the multi-steps drying process and control particulate emissions, is belt-conveyed to bagasse storage bin (DR-MIX-4) and straw storage bin (DR-MIX-3). Hence, sugarcane bagasse and straw are lifted from the temporary storage bin and gravimetric fed into the gasifier feed drum (DR-MIX-3).

Sugarcane bagasse and straw (biomass) is horizontally conveyed into the inject screws to introduce the sugarcane bagasse (GA-SCR-2) and straw (GA-SCR-1) into the gasifier, near the bottom of the CFB gasifier bed. The mass flow rate of sugarcane bagasse and straw inject-screwed into the atmospheric CFB directly-heated gasifier is controlled by the bagasse screw (GA-SCR-2) and straw screw (GA-SCR-1), in each metering bins (DR-MIX-3 and DR-MIX-4).

The Aspen Plus®v8.4 process model simulation of the drying process-zone consider the bagasse (GA-SEP-2) and straw (GA-SEP-1) instantaneous drying process at 150.0ºC vaporizing the moisture content and volatilizing the extractives content in the inlet dried and sized bagasse and straw, which are sent directly to the oxidative and reductive reactions zone (GA-GASEI).

The Aspen Plus®v8.4 process model simulation of the devolatilization process-zone was developed using RYield reactor block to represent the atmospheric decomposition at 500ºC of the BAGASSE non-conventional solids (GA-DEV-2) and the STRAW non-conventional solids (GA-DEV-1) into its 'constituting' conventional components ('ELEMENTS'). The non-conventional solids are converted to form carbon (C), hydrogen (H_2), oxygen (O_2), chlorine (Cl_2), nitrogen oxide (NO), sulfur dioxide (SO_2), and hydrogen sulfide (H_2S) using about 16.67%$_{w/w}$ of the sulfur (S) content. Salts, minerals, ashes, and soil are specified as inert components in the devolatilization process-zone (bypass).

FORTRAN calculator block CA-GA-CB-2 is used to specify the yield distribution of the bagasse decomposition (GA-DEV-2) in the devolatilization process-zone and the mass flow rate of each constituent component in the outlet stream according to the sugarcane bagasse ultimate analysis (Table 5). FORTRAN calculator block CA-GA-CB-1 is used to specify the yield distribution of the straw decomposition (GA-DEV-1) in the devolatilization process-zone and the mass flow rate of each constituent component in the outlet stream according to the sugarcane straw ultimate analysis (Table 6).

Sep separator block GA-SEP-3 as adjustment model is used to selectively separate specific amounts of char (C) to adjust the carbon conversion efficiency of the atmospheric CFB directly-heated gasifier bypass the carbon around the reaction zones (GA-GASEI) using the design specification DS-GA-FS-1 to control the carbon split fraction to obtain 98.0%$_{w/w}$ of carbon conversion efficiency. The GA-SEP-3 separator block also adjusts and considers a fraction of 10.0%$_{w/w}$ of the salts with potassium and chlorine content as reactive compounds together the integral minerals. The another fraction containing 90.0%$_{w/w}$ of the salts with potassium and chlorine (content in the inlet biomass) is considered as non-reactive compounds and primary bypass the reaction zones (GA-GASEI).

The adjustment model (GA-SEP-3) consider the possibility of the entrained gross-particles (solid fraction) content reactive potassium and chlorine (bed supplementary material linked) captured in the primary gasifier cyclone (GA-CYC-1) return back trough the leg-riser to the gasifier bed (GA-GASEI) as reactive compounds. A small fraction of the fine particles contend the reactive-considered potassium and chlorine leave the primary gasifier cyclone (GA-CYC-1) with gaseous product, linked with the bed materials (not included in the Aspen Plus®v8.4 process model simulation) and in form of oxides sulfates or phosphates (possible products).

Surrounding atmospheric fresh-air (ATMOSPHERIC AIR) is induced by advanced blower system (GA-ASP-1) modeled by using a Compr pressure changer block according to isentropic method for compressor considering 85.0% isentropic efficiency and 99.0% mechanical efficiency, with pre-filter unit (GA-FIL-1) modeled by using a FabFl solids separator block to protect the blower (GA-ASP-1) and the gasifier air distributors (GA-GASEI) from debris (PARTICLES) according to Piecewise separation efficiency in function of the particle diameter of the solids.

Dryer flue-gas is used to preheated (GA-HEA-1) and the HRSG exhaust-gas (HR-HEA-1) is used to heated (GA-HEA-1) the atmospheric fresh-air (ATMOSPHERIC AIR), obtaining hot-air agent at 120.0ºC in the BIG-ICE/CC (SC1) or at 150.0ºC in the BIG-ICE/CC (SC2), before being injected in the atmospheric CFB directly-heated gasifier. The hot-air agent is then injected by primary injection distributor in the bottom of the bed (GA-GASEI) and by secondary distributor air points (close to biomass feed point) in the combustion zone (GA-GASEI).

The quantity of hot-air agent entering into the atmospheric CFB directly-heated gasifier is controlled by the design specification DS-GA-TG-1 varying the mass flow rate of the air agent intake. The hot-air agent required is determined by the thermal energy necessary to the gasification reactions occurs and to the crude synthesis gas leave the atmospheric CFB directly-heated gasifier at 850.0ºC, operational temperature selected for the atmospheric CFB directly-heated gasifier model implemented in this research Master’s degree.

In the atmospheric CFB directly-heated gasifier, the combustion in-bed (GA-GASEI) supply the thermal energy required for the endothermic gasification reactions and to heater the material-compounds, the combustion gas products acts as fluidizing bed agent and gasifying agent. The Aspen Plus®v8.4 process model simulation of oxidizing and gasification process-zones in bed and freeboard is modeled using RGibbs reactor block (GA-GASEI) to represent the solid and gaseous reaction according to chemical equilibrium by Gibbs free-energy minimization method. The model consider all components as potential products in products sheet, it is a simple approach to represent the oxidizing and gasification reactions to obtain a crude synthesis gas at 850.0ºC.

Chemical equilibrium by Gibbs free-energy minimization method overestimate the Equivalence rate (ER_{AIR}) and the mass flow rate of CO_2 and H_2O (fraction in the crude synthesis gas), mainly because the model does not predict the reverse water gas shift equilibrium effect and the formation of light hydrocarbons and heavy hydrocarbons, breaking them into simpler forms. The model predicts the formation of more H_2 and less CO than the real process (experimental data). To break the hydrocarbon compounds is required energy, which is supplied by the combustion process (extended) demanding more oxidizing agent and forming consequently more CO_2 and H_2O as a product of combustion.

Steam agent at 2.5 bar and 150.0ºC (fluidization agent) is generated by the low-temperature vertical CSC (GA-CSC-1) in the synthesis gas heat recovery cooling system (second section). 95.0%$_{w/w}$ of the steam agent is injected by the primary and secondary injection distributor in the bed (GA-GASEI) in order to fluidize the bed and promote the gasification reactions (GA-GASEI), and 5.0%$_{w/w}$ of the steam agent in injected in the loop-seal (GA-LSE-1). The ratio of steam agent to dry biomass (bagasse and straw) is calculate by the Equation 7 and controlled by the design specification DS-GA-FG-1 varying the inlet hot water/steam agent mass flow rate to obtain a STBR equal of 0.5, considering the moisture content in the inlet bagasse and straw. The STBR is maintenance in 0.5 due to lack of details for bed fluidization, probably this value will be changed in future rigorous models involving fluid dynamic models, raising the steam mass flow rate to optimize the bed fluidization.

2.0% of the LHV_{db} of the biomass fed is assumed to be lost from the gasifier (GA-GASEI) being controlled by the design specification DS-GA-QL-1 with the aid of parameter calculation blocks (BHV blocks group) implemented.

The gasification of sugarcane bagasse and straw using atmospheric air and steam as gasification agents provides a crude synthesis gas content very-low or insignificant inerter elements present in the surrounding air (N2, Ne, He, Xe, Ar and Kr), water vapor (H_2O), carbon monoxide (CO), hydrogen (H2), carbon dioxide (CO2), methane (CH4), hydrogen sulfide (H_2S), hydrogen chlorine (HCl), chlorine (Cl_2), carbonyl sulfide (COS), ammonia (NH_3), nitrogen oxides (NO_x), sulfur oxides (SO_x), and solid particulate matters.

Tar, light hydrocarbons and heavy hydrocarbons is not estimated by the chemical equilibrium applying the Gibbs free-energy minimization method (GA-GASEI), hydrocarbons are converted to simple form as water vapor (H_2O), carbon monoxide (CO), hydrogen (H2), carbon dioxide (CO2) and a small fraction of methane (CH4). Solid particulate matters content bed material, specifics catalytic active materials, unconverted char, coke, ashes content, soil, salts and minerals and others.

The main impurities present in the crude synthesis gas can be ammonia (NH_3), hydrogen sulfide (H_2S), carbonyl sulfide (COS), hydrogen chloride (HCl), chlorine (Cl_2), nitrous oxides (NO_x), sulfur oxides (SO_x), volatile metals, volatile organic compounds, tar and oils (heavy hydrocarbons), fines or submicron particles containing metals and metal salts, unconverted char (C), solid particulates, materials bed particles (not included in the Aspen Plus®v8.4 process model simulation), and others alkali compounds.

Primary gasifier cyclone gas/solid separator (GA-CYC-1) is modeled by using a Cyclone solids separator block as single-cyclone to remove the gross particulate content (ashes, silicates, metal salts, unconverted carbon, bed and additives materials) in the crude synthesis gas according to Muschelknautz calculation method for a maximum pressure drop of 0.012 bar applying spiral inlet cyclone type. The gross-particulate separated from the crude synthesis gas is recycled by the leg-riser back to the gasifier bed (GA-GASEI) to promote second-pass in the reaction zones raising the char conversion (to obtain $98.0\%_{w/w}$ of carbon conversion).

In the Aspen Plus®v8.4 process model simulation is considered that $50.0\%_{w/w}$ of the unconverted char (C) is removed in the gasifier bottom particulate materials discharge system (GA-SEP-4) modeled by using a Sep separator blocks. Another part can be recycled by the primary gasifier cyclone (GA-CYC-1) and a small fraction of fine particles can be dragged by the crude synthesis gas to the secondary multi-cyclone system (GA-CYC-2) according to the primary gasifier cyclone (GA-CYC-1) efficiency and the size of the solid particles (PSD distribution).

The model consider that $0.2\%_{w/w}$ of the crude synthesis gas conventional phase flowing into the primary gasifier cyclone (GA-CYC-1) return back to the reaction zone (GA-GASEI) by the leg-riser together the particles in the loop-seal (GA-LSE-1).

A secondary multi-cyclone system (GA-CYC-2) designed with five cyclones (battery) and modeled by using a Cyclone solids separator block according to Muschelknautz calculation method for a maximum pressure drop of 0.02 bar applying spiral inlet cyclone type removes part of the residual fines-particulate matters that leaving the top of the primary gasifier cyclone (GA-CYC-1). These particles are belt-conveyed and mixed (GA-SCR-3) with the bottom particulate matters removed from the gasifier (GA-SEP-4) to final disposal. The fine particles not recovered in the secondary multi-cyclone system (GA-CYC-2) is removed from the synthesis gas in the low-temperature synthesis gas wet cleaning system.

Bottom particulate matters (e.g.: sand; ash; slag; specifics catalytic active materials; unconverted materials, metal salts; alkali compounds and others) is discharged from the bottom of the gasifier (GA-GASEI), cooled using directly contact water added to avoid dust (consider the heat loss in the GA-FLA-1) by water-cooled screw conveyor (not simulated). The bottom particulate matters are stored together the fines-particulate matters removed in the multi-cyclone system (GA-CYC-2) in the ashes temporary storage bins to humidified ashes/slag (GA-FLA-1) until offloaded for disposal (field disposal together vinasses).

7.1.5.1 Gasifier bed materials

Spreadsheet calculation model is used to determine the quantity of MgO must be present into the gasifier bed (GA-GASEI) and the make-up mass flow rate of MgO necessary to substantially avoid the formation (sequestering potassium) of low-melting point glass-like bed agglomerations (K_2SiO_4). The bed agglomerations were associated to direct adhesion of the bed particles by partly molten fuel ash derived K–Mg phosphates (ashes content) and K-silicates (ashes and soil content) that should result from the interactions with the biomass potassium content. MgO raise the melting point (ternary eutectic form) sequestering potassium avoiding/reducing it to be carried over in the gasifier cyclones (GA-CYC-1) and deposits in the equipment walls.

MgO supplementary bed material load is estimated to be 2.0 mol mass flow rate per mol of reactive potassium inlet into the gasifier (GA-GASEI). MgO is delivered to thermochemical-biorefinery supplies offloading area by truck to storage, a pneumatic line feed the gasifier loop bed media feed bin, which transfers the supplies to the gasifier by screw-conveyor or pneumatic transporter (not included in the Aspen Plus®v8.4 process model simulation).

In the spreadsheet calculation model is considered the olive make-up mass flow rate as being 1.0%$_{w/w}$ of the mass flow rate of dry ash and extractive free (daef) sugarcane bagasse and straw inlet into the gasifier to compensate the olive losses. Olivine recirculate by the primary gasifier cyclone (GA-CYC-1) trough the leg-riser and the major part of the entrained olive is recovered from the crude synthesis gas exiting the gasifier by the secondary multi-cyclone system (GA-CYC-2), only a small part of the olivine as fine particles are dragged and removed in the low-temperature synthesis gas wet cleaning system (losses).

The majority of the bed materials and gross-biomass derived particles are separated in the primary gasifier cyclone (GA-CYC-1) and sent back (recycled) into the leg-riser and gravity-feed back to the gasifier bed (GA-GASEI) using steam fluidized loop-seal (GA-LSE-1). A secondary multi-cyclone system (GA-CYC-2) removes part of the residual fines-particulate matters that leaving the top of the primary gasifier cyclone (GA-CYC-1), this particles are mixed with the bottom particulate material removed from the gasifier (GA-SEP-4) to final disposal (BED MATERIALS AND ASHES).

The mineral-crystal (iron content) olivine catalyst considered as gasifier bed media is a commercial type olivine catalyst α-$(Mg_{0.8}Fe_{0.2})_2SiO_4$ delivered to thermochemical-biorefinery supplies offloading area by truck to storage. Pneumatic line fed the gasifier loop bed media feed bin, which transfers the supplies to the gasifier by screw-conveyor or pneumatic transporter (not included in the Aspen Plus®v8.4 process model simulation).

Olivine catalyst is used to reduce by about 60.0%$_{w/w}$ of the tar content in the crude synthesis gas produced in the atmospheric CFB directly-heated gasifier (GA-GASEI). Tar abatement increased up to 92.0%$_{w/w}$ when catalytic CF were combined with the bed, not included in the Aspen Plus®v8.4 process model simulation due the limitations of the gasification Gibbs equilibrium model, in future works with rigorous model can be considered.

7.1.6 Syngas cooling and heat recovery

The synthesis gas at low-pressure require compression process to achieve the required pressure of the high-performance sequential combustion full-flow advanced

EvGT. To compress the synthesis gas is necessary reducing the synthesis gas temperature in order to reduce the consumption of electrical energy and fit the maximum temperature allowed by the compressor.

Hot synthesis gas has a great potential to thermal energy generation (sensible heat) and recovery this heat can increase the process steam production and reduce the stress on the HRSG system in the BIG-GT/CC route.

As shown in Figure 37, Aspen Plus®v8.4 flowsheet of the syngas cooling and heat recovery in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2), which is the same model with modified parameters for BIG-GT/CC (SC1), for BIG-GT/CC (SC2), and for BIG-GT/CC (SC4) is compost by: high-temperature vertical CSC (GA-CSC-1); low-temperature vertical CSC (GA-CSC-2); water pump 1 (GA-PUM-1); and water pump 2 (GA-PUM-2).

Atmospheric crude hot-synthesis gas that leave the secondary multi-cyclone system (GA-CYC-2) is cooled in two cooling sections generating intermediate-pressure steam by the high-temperature vertical CSC (GA-CSC-1) modeled by using a HeatX exchanger block and low-pressure steam by the low-temperature vertical CSC (GA-CSC-2) modeled by using a HeatX exchanger block, without the catalytic high-performance CF.

The high-temperature vertical CSC (GA-CSC-1) and low-temperature vertical CSC (GA-CSC-2) are modeled using RKS-BM physical property methods to atmospheric crude hot-synthesis gas side and, IAPWS-95 physical property methods to hot water/steam side.

In the BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4), atmospheric crude hot-synthesis gas produced by the atmospheric CFB directly-heated gasifier at 850.0ºC is cooled to about 318.0ºC by the high-temperature vertical CSC (GA-CSC-1). The atmospheric crude hot-synthesis gas at 318.0ºC after the high-temperature vertical CSC (GA-CSC-1) is cooled to about 125.0ºC by the low-temperature vertical CSC (GA-CSC-2).

Deaerated hot process water from deaerator unit (HR-DEA-1) at 1.4 bar and 105.0ºC is pumped (GA-PUM-2) to 23.0 bar before entering into the high-temperature vertical CSC (GA-CSC-1). The atmospheric crude hot-synthesis gas is cooled in the first-section of (GA-CSC-1) exchange sensible heat to produce intermediate-pressure steam. In the BIG-GT/CC (SC1), intermediate-pressure steam at 23.0 bar and 337.9ºC is produced and expanded in the second-section of the BPST system (ST blocks) to generate electrical energy.

Figure 52 shows the Aspen Plus®v8.4 flowsheet of the syngas cooling and heat recovery for BIG-GT/CC (SC3) and for BIG-GT/CC (SC5), scenarios without co-capture of CO_2 and H_2S by using MEA-based absorbing-solution (CA blocks).

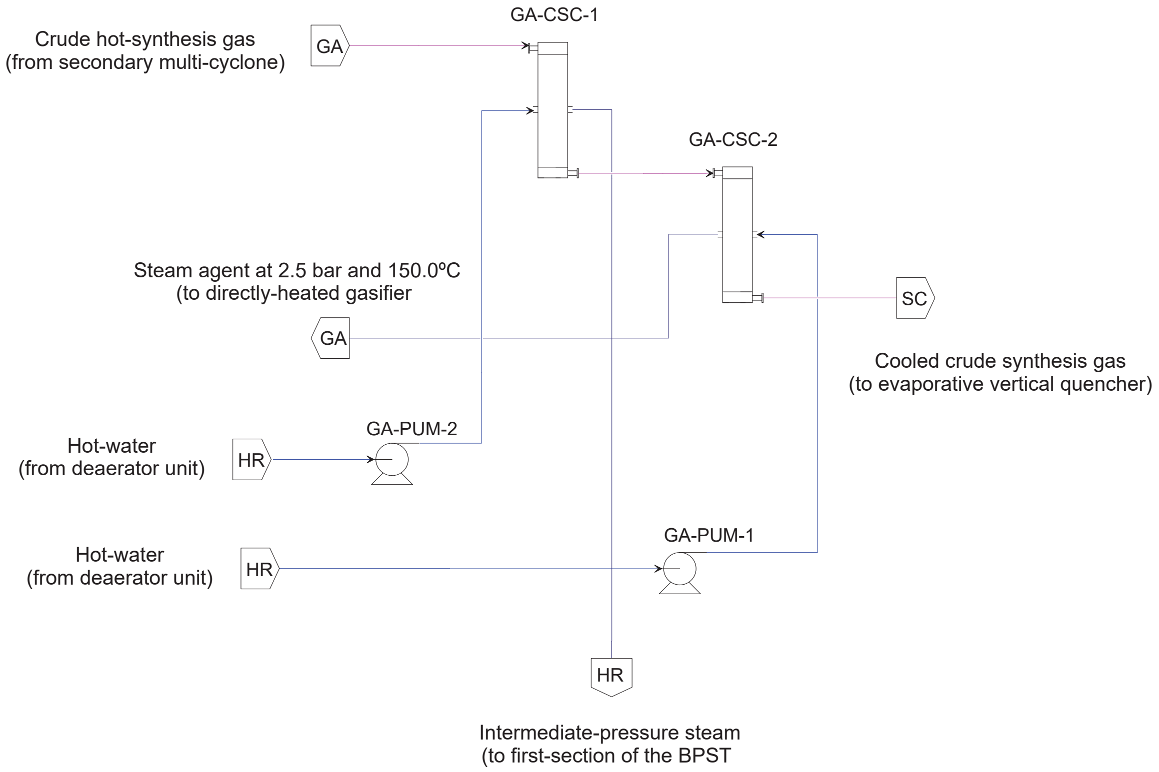


Figure 52 - Aspen Plus®v8.4 flowsheet of the syngas cooling and heat recovery for BIG-GT/CC (SC3) and for BIG-GT/CC (SC5)

As shown in Figure 52, Aspen Plus®v8.4 flowsheet of the syngas cooling and heat recovery in the BIG-GT/CC (SC3) and BIG-GT/CC (SC5) is compost by: high-temperature vertical CSC (GA-CSC-1); low-temperature vertical CSC (GA-CSC-2); water pump 1 (GA-PUM-1); and water pump 2 (GA-PUM-2).

In the BIG-GT/CC (SC3) and BIG-GT/CC (SC5), atmospheric crude hot-synthesis gas produced by the atmospheric CFB directly-heated gasifier at 850.0ºC is cooled to about 321.0ºC by the high-temperature vertical CSC (GA-CSC-1). The atmospheric crude hot-synthesis gas at 321.0ºC after the high-temperature vertical CSC (GA-CSC-1) is cooled to about 120.0ºC by the low-temperature vertical CSC (GA-CSC-2).

In the BIG-GT/CC (SC2), intermediate-pressure steam at 23.0 bar and 337.9ºC is produced and expanded in the second-section of the EBPST system (ST blocks) to generate electrical energy. In the BIG-GT/CC (SC3), intermediate-pressure steam at 23.0 bar and 330.8ºC is produced and expanded in the second-section of the EBPST system (ST blocks) to generate electrical energy. In the BIG-GT/CC (SC4) and BIG-GT/CC (SC5), intermediate-pressure steam at 23.0 bar and 540.0ºC (reheater pipe bank) is produced and expanded in the second-section of the CEST system (ST blocks) to generate electrical energy.

In the BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4), condensed water at about 2.3 bar and 123.0ºC after the stripper reboiler (CA-REB-1) in the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution is after-pumped (GA-PUM-1) to the syngas cooling and heat recovery (GA blocks). In these cases, is used to cool down the synthesis gas, after-generating gasification steam agent at 2.5 bar and 150.0ºC in the low-temperature vertical CSC (GA-CSC-2).

In the BIG-GT/CC (SC3) and BIG-GT/CC (SC5), deaerated hot process water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is pumped to 2.5 bar by the water pump 1 (GA-PUM-1) to the syngas cooling and heat recovery (GA blocks). In these cases, is used to cool down the synthesis gas, after-generating gasification steam agent at 2.5 bar and 150.0ºC in the low-temperature vertical CSC (GA-CSC-2).

Cooled crude synthesis gas is fed in the evaporative vertical quencher (spray tower) (SC-SCR-1) in the low-temperature synthesis gas wet cleaning system (wet scrubbing unit).

The mass flow rate of deaerated hot process water to intermediate-pressure steam generation is controlled by the design specification DS-GA-TL-1 varying the inlet mass flow rate of deaerated hot process water in the high-temperature vertical CSC (GA-CSC-1) coupled with the design specification DS-GA-TL-2 which determines the temperature between the high-temperature vertical CSC (GA-CSC-1) and low-temperature vertical CSC (GA-CSC-2) sections.

The mass flow rate of deaerated hot process water to low-pressure steam generation is controlled by design specification DS-GA-FG-1 varying the inlet mass flow rate to produce gasification steam agent at 2.5 bar and 150.0ºC to atmospheric CFB directly-heated gasifier (GA-GASEI and GA-LSE-1). The amount of gasification steam agent is determined by Equation 7 to obtain a STBR of 0.5, considering the moisture present in the biomass-fuel inlet into the gasifier (GA-GASEI).

The catalytic high-performance CF between the high-temperature vertical CSC (GA-CSC-1) and the low-temperature vertical CSC (GA-CSC-2) was not implemented in the Aspen Plus®v8.4 process model simulation of the syngas cooling and heat recovery, due the limitations of the gasification Gibbs equilibrium model (GA-GASEI). The system is mainly used to reform the reminiscent tar and heavy hydrocarbons. Also, can remove part of the particle content in the atmospheric crude synthesis gas. Considering the presence of olivine catalyst in the gasifier bed (GA-GASEI) only traces of tar and heavy hydrocarbons is expected.

7.1.7 Low-temperature synthesis gas wet cleaning system

After the initial particulate removal accomplished by the multi-cyclones system (GA-CYC-2) and the convective indirect cooling of the crude synthesis gas by the syngas cooling and heat recovery an additional cooling step is carried out by wet scrubbing unit (direct water contact cooling).

The low-temperature synthesis gas wet cleaning system (wet scrubbing unit) is used to remove water-soluble contaminants and particles from the synthesis gas including ammonia (NH_3), hydrogen chloride (HCl), sulfur oxides (SO_x), carbonyl sulfide (COS), volatile organic compounds, tar and oils (heavy hydrocarbons), particles containing metals and metal salts, unconverted char (C) solid particulates, materials bed particles (not included in the Aspen Plus®v8.4 process model simulation), and others alkali compounds. Also, remove a small part of hydrogen sulfide (H_2S), nitrous oxides (NO_x), and carbon dioxide (CO_2).

As shown in Figure 38, Aspen Plus®v8.4 flowsheet of the low-temperature synthesis gas wet cleaning system in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2) which is the same model with modified parameters for BIG-GT/CC (SC1), for BIG-GT/CC (SC2), for BIG-GT/CC (SC3), for BIG-GT/CC (SC4), and for BIG-GT/CC (SC5) is compost by: vertical down-flow water spray quencher (SC-SCR-1); vertical water venturi scrubber (SC-SCR-1); decanter to separate the heavy hydrocarbons from the water (not included in the Aspen Plus®v8.4 process model simulation); water recovery and recycle unit (SC-FLA-2); packet-bed condenser/absorber sub-cooler (SC-FLA-1); mist eliminator (demister) drum (SC-FLA-3); wet electrostatic precipitator (WESP) (SC-ESP-1); blower system (SC-BLO-1); after air cooler (SC-FLA-4); condensate knock-out drum (SC-FLA-4); clarifier and decanter units (SC-FLA-2); sludge setting tank (SC-SEP-2) slurry pump (SC-PUM-2); water pumps (SC-PUM-1); cleaned water recirculation tank (SC-SEP-2); and humidified particles temporary bin (SC-FLA-5).

The Aspen Plus®v8.4 process model simulation of the low-temperature synthesis gas wet cleaning system was developed using Electrolyte NRTL physical property methods for liquid phase, and RK equation of state for vapor phase (ELECNRTL physical property methods) for electrolytes calculation using true components approach and aqueous activity coefficient basis for Henry components. Aqueous activity coefficient for the supercritical and non-condensable components (e.g.: H_2, O_2, N_2, Ne, He, Ar, Kr, Xe, CO, CO_2, Cl_2, SO_2, NH_3, H_2S, CHN, HCl) selected as Henry components is calculated according to the Henry's law for represent the behavior of dissolved gases, according the affinity with water and their interaction with other electrolytes presents.

The interaction of the key components potentially presents in the cooled crude synthesis gas in the presence of pure-water is evaluated in the Aspen Plus®v8.4

process model simulation of the low-temperature synthesis gas wet cleaning system. The model was developed with a chemistry model for specify reactions method applying the Elec Wizard auxiliary tool to generate possible components and reactions for the electrolyte simulation approach. The approach include the salt formation and dissociation reaction in water based on the hydronium ion (H_3O^+) reactions mechanism according to electrolyte solution chemistry (Chemistry ID: CH-SC-SOU) presented in the section 6.1.7 (Low-temperature synthesis gas wet cleaning system), as described for BIG-ICE/CC (SC1) and for BIG-ICE/CC (SC2).

The cooled crude synthesis gas from the low-temperature vertical CSC (GA-CSC-2) is down-flow conducted through the vertical water spray quencher (SC-SCR-1) in direct contact with recycled pure-water (without alkali addition) at 25.0ºC injected by spray nozzles. The injected water is vaporized, cooling down (pre-cooling chamber) the synthesis gas to saturation conditions at about 100.0ºC (without water condensation) before entering the vertical venturi scrubber (SC-SCR-1) with water loop tar removal system.

The Aspen Plus®v8.4 process model simulation for the vertical water spray quencher (SC-SCR-1) coupled in the vertical venturi scrubber (SC-SCR-1) uses Calvert's calculation method for spray tower designed with separation efficiency of 70.0% in the vertical venturi scrubber (SC-SCR-1). Electrolyte solution chemistry (CH-SC-SOU) is used to estimate the dissolved gases, the electrolytes interactions by salt formation, and dissociation reaction in pure water. The solid particles scrubbed (SC-SCR-1) are removed in the VSscrub solids separator block, the scrubbing liquid phase is removed in the Flash2 separator block (SCFLA-1) together the condensed phase in the packet-bed condenser/absorber sub-cooler (SC-FLA-1).

The electrolyte solution chemistry model Chemistry ID: CH-SC-SOU implemented in the Aspen Plus®v8.4 process model simulation of the low-temperature synthesis gas wet cleaning system was developed with a CHEMISTRY model according to section 6.1.7 (Low-temperature synthesis gas wet cleaning system), as described for BIG-ICE/CC (SC1) and for BIG-ICE/CC (SC2).

In the vertical venturi scrubber (SC-SCR-1) is collected the gross-particulate according to the aerodynamic size and removed the condensed residual heavy hydrocarbons (e.g.: tar, oils) in the basin (SC-FLA-2) of the venturi scrubber (liquid drain) by the water loop tar removal system (not included in the Aspen Plus®v8.4 process model simulation). The scrubbed liquid with heavy hydrocarbons mixed with water is collected in the basin (SC-FLA-2) and sent to oil/water separator (not included in the Aspen Plus®v8.4 process model simulation) to remove the hydrocarbons from the water by density differences. The liquid hydrocarbons removed is sent to final disposal or sent-back to the gasifier (GA-GASEI), the water phase is recovered and recycle to the venturi scrubber (SC-SCR-1) at 25.0ºC and injected by spray nozzles in the chamber.

Cleaned water is pumped from the cleaned water recirculation tank (SC-SEP-2) in closed-loop cycle to the packet-bed condenser/absorber sub-cooler (SC-FLA-1). Cooled synthesis gas is then sub-cooled to 45.0ºC being removed 15.0%$_{w/w}$ of the entrained fine-particles. Is used a large amount of recycled-water from the cleaned water recirculation tank (SC-SEP-2) in the packet-bed condenser/absorber sub-cooler (SC-FLA-1).

The Aspen Plus®v8.4 process model simulation consider 0.5%$_{w/w}$ of entrained water to mist eliminator (SC-FLA-3) which is responsible to remove the excess of water content droplets in the sub-cooled synthesis gas at saturation conditions before entering in the WESP (SC-ESP-1).

The amount of cleaned-water recycled to vertical water spray quencher (SC-SCR-1) and to vertical venturi scrubber (SC-SCR-1) is controlled by design specification DS-SC-TG-1 varying the inlet cleaned-water (SC-SPL-1) in order to achieve the saturation condition (cooling).

The amount of cleaned-water recycled to packet-bed condenser/absorber sub-cooler (SC-FLA-1) is controlled by design specification DS-SC-TG-2 varying the inlet cleaned-water (SC-SPL-2) in order to achieve the sub-cooled condition for WESP system (SC-ESP-1), and the synthesis gas temperature required by the low-pressure absorber packed-column (CA-ABS-1) in the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution (CA blocks).

The built-in expression (Equation 2729) for calculating equilibrium constants is used for the reactions from 1 to 17 in CH-SC-SOU electrolyte solution chemistry. The built-in expression (Equation 28) for calculating salt precipitation equilibrium constants is used for the reactions from 18 to 25 in CH-SC-SOU electrolyte solution chemistry.

The ELECNRTL physical property methods is used in the low-temperature synthesis gas wet cleaning system (SC blocks) with the same properties assumption employed in the Aspen Plus®v8.4 process model simulation of the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution (CA blocks). In short, detailed-described in the section 6.1.8 (Co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution), and according to section 6.1.7 (Low-temperature synthesis gas wet cleaning system) described for BIG-ICE/CC (SC1), and for BIG-ICE/CC (SC2).

The excess of the wastewater recovered from the basin (SC-FLA-2) of the vertical venturi scrubber (SC-SCR-1), from the cooler condenser basin (SC-FLA-2) and from the mist eliminator (SC-FLA-3) is sent to the clarifier and decanter units (SC-SEP-2) and cleaned water recirculation tank (SC-SEP-2) to remove the sludge, and be cooled at ambient conditions. The contend solids and precipitated or dissociated salts is concentrate in the bottom sludge phase and sent to the sludge setting tank (SC-SEP-2) to be removed and sent of-site to final disposal in the sugarcane field. In the Aspen Plus®v8.4 process model simulation is considered 50.0%$_{w/w}$ of water content in the sludge phase, which can be pumped by slurry pump (SC-PUM-2) to storage tank before sent of-site by tank truck transporter (SLURRY TO DISPOSAL).

The cleaned water from the clarifiers (SC-SEP-2) at quality requirements to be recycled to vertical water spray quencher (SC-SCR-1) and to vertical venturi scrubber (SC-SCR-1) is stored in the cleaned water recirculation tank (SC-SEP-2). The excess of water recovered from the synthesis gas is separate (SC-SPL2) and pumped (SC-PUM-1) to wastewater treatment plant (WASTEWATER TO TREATEMNT PLANT) to be used as make-up water for other processes (loss reduction principles).

In the Aspen Plus®v8.4 process model simulation of the synthesis gas cleaning wet system is considered the WESP (SC-ESP-1) operating at satured synthesis gas conditions (100% relative humidity) to remove the persistent fine-particles (final particles) as additional particulate polishing step. The WESP (SC-ESP-1) is modeled according to Svarovsky calculation model for vertically mounted collecting plate's model with separation efficiency of 92.0% of the particles present in the sub-cooled synthesis gas stream and based on the migration velocity and the ratio of precipitation area.

The persistent fine-particles collected is removed from the basin (SC-ESP-1) and conveyed to be stored into the humidified particles temporary bin (SC-FLA-5) until offloaded (PARTICLES TO DISPOSAL) for the final disposal (field disposal together vinasses and gasifier bottom particulate materials).

Blower system (SC-BLO-1) with induced draft fan is modeled by using a Compr pressure changer block according to isentropic method for compressor considering 85.0% isentropic efficiency and 99.0% mechanical efficiency. The system is used to produce the desired pressure drop across the venturi scrubber system and to equalize the pressure (drop pressure) inducing the synthesis gas flow through the system at desired mass flow rate. After pressurized (SC-BLO-1) the sub-cooled synthesis gas is cooled in the air cooler (SC-FLA-4) and the condensed phase removed in the knock-out drum (SC-FLA-4) back to the cleaned water recirculation tank (SC-SEP-2).

The sub-cooled synthesis gas in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4) is sent-ducted into the low-pressure absorber packed-column (CA-ABS-1) in the co-capture of CO_2 and H_2S by using MEA-based absorbing-solution (CA blocks) at temperature of 50.0ºC. The sub-cooled synthesis gas in the BIG-GT/CC (SC3) and BIG-GT/CC (SC5) is sent-ducted as partial-cleaned synthesis gas to integrally-geared centrifugal three stages compressor (CO blocks) in the synthesis gas compression (conditioning). The integrally-geared centrifugal three stages compressor (CO blocks) is used to conditioning the sub-cooled and partial-cleaned synthesis gas to be used in the high-performance sequential combustion full-flow advanced EvGT (GT blocks).

7.1.8 Co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution

Amine-based aqueous absorbing-solution for atmospheric pressure systems employing conventional monoethanolamine (MEA) was considered in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4). The sub-cooled synthesis gas in the BIG-GT/CC (SC3) and BIG-GT/CC (SC5) is sent-ducted as partial-cleaned synthesis gas to integrally-geared centrifugal three stages compressor (CO blocks) in the synthesis gas compression (conditioning).

Co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution at atmospheric pressure has the potential to capture mainly CO_2 and co-capture H_2S and fractions of carbonyl sulfide (COS), carbonyl disulfide (CS_2), and mercaptans (is not the main goal) removed a lesser extension from the system. The amount of co-captured compounds depends on the mass flow rate of MEA-based aqueous absorbing-solution circulating in the system.

Typical CO_2 and H_2S co-capture system (CA blocks) at atmospheric pressure using $30.0\%_{w/w}$ of conventional MEA in aqueous solution (CA-L-5) is adequate for atmospheric pressure systems (stable at around of 120.0ºC) with lower emissions of degradation products. Aspen Plus®v8.4 process model simulation of the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution was employed in order to remove $90.0\%_{w/w}$ of CO_2 content in the synthesis gas aiming increase the energy density of the synthesis gas, reducing and controlling atmospheric emissions.

The mixture of CO_2 and amine in water (CO_2-amine-H_2O interaction) is highly non-ideal and the presence of ions and polar molecules in the liquid phase creates significant thermal effects increasing the temperature of the system at point of raise the degradation process of the MEA-based solution employed, the gas phase is lower non-ideal for atmospheric pressure system.

The rigorous Aspen Plus®v8.4 process model simulation of the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution (CA blocks) consider the complete cycle in closed-loop cycle mode with heat integrations. From the model is obtained the rigorous energy balance of the system, and the mass flow rate of process steam (thermal energy) and cooling water required by the system (reboiler and condensers equipments). Rigorous model is essential and indispensable to determine the influence of this system in the thermal energy balance of the integrated processes in the thermochemical-biorefinery.

As shown in Figure 39, Aspen Plus®v8.4 process model simulation of the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution (CA blocks) in closed-loop cycle in the BIG-ICE/CC (SC1), and BIG-ICE/CC (SC2), which is the same model with modified parameters for BIG-GT/CC (SC1), for BIG-GT/CC (SC2), and for BIG-GT/CC (SC4) is compost by: low-pressure absorber packed-column (CA-

ABS-1); low-pressure stripper packed-column (CA-STR-1); washer packed-column section (CA-WAS-1); washer water recycle-pump (CA-PUM-7); washer water bleed (CA-SPL-3); cross-solution heat exchanger (CA-HEA-2); mixture tank (CA-MIX-1), amine surge tank (CA-SUR-1), amine supply pump (CA-PUM-1), absorber reflux-pump (CA-PUM-2); desorber reflux pump (CA-PUM-4); absorber condenser (CA-CON-1 and CT-HEA-2); absorber liquid reflux-drum (CA-FLA-1); water purge splitter (CA-SPL-4); striper liquid reflux-drum (CA-FLA-2); stripper condenser (CA-CON-2 and CT-HEA-3); striper water bleed (CA-SPL-1); lean-amine water cooler (CA-HEA-1 and CT-HEA-1); rich-amine pump (CA-PUM-3); carbon-based filter (CA-SEP-1); stripper reboiler (CA-REB-1); amine reclaimer (CA-SPL-2); reclaimer recirculation pump (CA-PUM-5); make-up water pump (CA-PUM-6); and cooling water pumps (CT-PUM-2 and CT-PUM-3).

ASPEN Rate-Sep simulation package is used in the low-pressure absorber packed-column (CA-ABS-1), in the low-pressure stripper packed-column (CA-STR-1), and in the washer packed-column section (CA-WAS-1) to non-equilibrium mass transfer rate-based calculations taken in account the mass and heat transfer limitations, liquid and vapor film diffusion, equipment hydrodynamics, and chemical reaction mechanisms.

The rigorous Aspen Plus®v8.4 process model simulation of co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks) consider the complete cycle in closed-loop cycle mode under the steady state operating conditions. The model was developed using Electrolyte NRTL physical property methods for liquid phase, and RK equation of state for vapor phase (ELECNRTL physical property methods) for electrolytes calculation using true components approach and aqueous activity coefficient basis for Henry components. The selected components (e.g.: H_2, O_2, N_2, Ne, He, Ar, Kr, Xe, CO, CO_2, Cl_2, NH_3, CHN, HCL, CH_4, NO_x, SO_x) to employ the Henry's law as supercritical and non-condensable components for represent the behavior of dissolved gases according to the affinity with water and their interaction with electrolytes.

The degradation products generated during the solvent degradation process may produce new pollutants, which could be emitted to the atmosphere. Thermal and oxidative degradation, and polymerization reactions, have been considered undergoes thermal degradation temperature limits in presence of dissolved CO2. The degradation process was simplified in the Aspen Plus process simulation model of the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution (CA blocks), based on mass balance of the system, a representative fraction of the MEA-based aqueous absorbing-solution degraded is removed as input parameters in the carbon-based filter (CA-SEP-1).

The electrolyte solution chemistry model Chemistry ID: CH-CA-MEA implemented in the Aspen Plus®v8.4 process model simulation of the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution was developed with a CHEMISTRY model and equilibrium constants for the CH-CA-MEA according to section 6.1.8 (Co-capture of CO2 and H2S by using MEA-based aqueous absorbing-solution).

The built-in expression for calculating equilibrium constants is used for the reactions from 1 to 7 in CH-CA-MEA electrolyte solution chemistry, according to Equation 29.

The Aspen Plus®v8.4 parameters used to calculate the standard Gibbs free energy of $MEAH^+$ and $MEACOO^-$ and the ELECNRTL physical property methods used in the model of co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution are defined and detailed in the section 6.1.8 (Co-capture of CO2 and H2S by using MEA-based aqueous absorbing-solution).

The reaction model Reaction ID: RE-CA-MEA implemented in the Aspen Plus v8.4 process model simulation of the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution was developed with a REACTIONS model and equilibrium constants for the RE-CA-MEA according to section 6.1.8 (Co-capture of CO2 and H2S by using MEA-based aqueous absorbing-solution).

The power law reduced expressions is used for the reactions from 4 to 7 in RE-CA-MEA rate-controlled reactions, according to Equation 30.

The sub-cooled and satured synthesis gas (CA-G-1) at 50.0ºC and 1.1 bar from the condenser knock-out drum (SC-FLA-4) in the low-temperature synthesis gas wet cleaning system (SC blocks) containing CO_2 and H_2S and others pollutants not removed in the low-temperature wet cleaning steps, fed-enter into the bottom of the low-pressure absorber packed-column (CA-ABS-1) by the blower system (SC-BLO-1). The synthesis gas flow upward through the absorber packet in contact with the down flow MEA-based aqueous absorbing-solution (lean-amine solution) to exit as clean outlet gas at the absorber top stage (CA-ABS-1). The system was designed to removal $90.0\%_{w/w}$ of CO_2 present in sub-cooled synthesis gas with top stage pressure at 1.06 bar and column pressure drop of 0.04 bar, the lean-amine solutions is fed on the top stage and the sub-cooled and satured synthesis gas on the bottom stage (CA-ABS-1).

The MEA considered to forming the absorbing-solution is a commercial type high-concentrate MEA-based solution shipped and delivered to thermochemical-biorefinery scenario 1 (SC1), thermochemical-biorefinery scenario 2 (SC2), and thermochemical-biorefinery scenario 4 (SC4) supplies offloading area by truck to storage. From the storage tank, high concentrate MEA-based solution is ducted to the amine surge tank (CA-SUR-1) and pumped by the amine supply pump (CA-PUM-1) to the mixture tank (CA-MIX-1) to be added with the water and lean-amine solution in circulation on closed-loop cycle mode.

Make-up of high-concentrate MEA-based solution added into the system depends on the losses (thermal, oxidative, reclaimed, and entrained-off). The make-up is made from time to time but simulated in the Aspen Plus®v8.4 process model simulation as continues process in steady state mode. The mass flow rate of high concentrate

MEA-based solution is controlled by design specification DS-CA-CL-1 varying the mass flow rate inlet the system to maintenance the lean-amine solution content $30.0\%_{w/w}$ of MEA in the inlet stream (CA-L-6) in the top of the low-pressure absorber packed-column (CA-ABS-1). The design specification considers all active MEA ionic forms present in the solution measured by apparent component mass fraction for electrolyte system as property sets.

The lean-amine solution formed in the mixture tank (CA-MIX-1) is cooled by the lean-amine water cooler (CA-HEA-1) passing cooling water (CT-HEA-1) modeled by using a Heater exchanger blocks to maintenance the inlet conditions at 1.06 bar and 40.0ºC. The lean-amine solution with low fraction of CO_2, H_2S, and others pollutants content (e.g.: NH_3, SOx, CHN, COS, hydrocarbons) without degradation products (not included in the Aspen Plus®v8.4 process model simulation) is then fed in the 1º theoretically liquid stage (top column stage) of the low-pressure absorber packed-column (CA-ABS-1).

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-2) to the lean-amine water cooler (CT-HEA-1). The amount of cooling water required is determined and controlled by design specification DS-CA-TL-1 varying the mass flow rate of cooling water passing through the lean-amine water cooler (CT-HEA-1). The cooling water is heated at the limit of 43.0ºC and duct-sent-back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

Rigorous Aspen Plus®v8.4 process model simulation of the low-pressure absorber packed-column (CA-ABS-1) was developed using RadFrac columns block on standard convergence mode with reaction model RE-CA-MEA and electrolyte solution chemistry model CH-CA-MEA without in-bed condenser and reboiler. The model was optimized for estimated 20 theoretical stages considering a NORTON IMTP 38.0 mm packing section from 1º to 20º theoretically stages with section packed height and diameter optimized for each system requirements (scenarios dependence) on standards characteristics. The model use rate-based calculation for Mixed flow model without reactions and film resistance in vapor phase, without reactions and with film resistance in liquid phase. Default Aspen Plus®v8.4 packing parameters is applied to calculate pressure drop and liquid holdup by Stichlmair method, to predict the mass transfer coefficient and interfacial area by Onda et al. (1968) correlation, and heat transfer coefficient by Chilton-Colburn (Taylor and Krishna, 1993) method.

The gaseous top-product at about 1.06 bar and 72.0ºC leave from the 1º theoretically vapor stage (top column stage) in the low-pressure absorber packed-column (CA-ABS-1) is cooled to 1.04 bar and 40.0ºC in the absorber condenser (CA-CON-1) by cooling water (CT-HEA-2) modeled by using a Heater exchanger blocks condensing a fraction of the entrained water with MEA.

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-2) to the absorber condenser (CT-HEA-2). The amount of cooling water required is determined and controlled by design specification DS-CA-TL-2 varying the mass flow rate of cooling water passing through the absorber condenser (CT-HEA-2). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

The condensed phase formed at 1.04 bar and 40.0ºC is flash-separated in the absorber liquid reflux-drum (CA-FLA-1) modeled by using a Flash2 separator block. The condensate top product from the absorber liquid reflux-drum (CA-FLA-1) is pumped at 1.06 bar and 40.0ºC by the absorber reflux-pump (CA-PUM-2) and refluxed back to the 1º theoretically liquid stage (top column stage) of the low-pressure absorber packed-column (CA-ABS-1).

The gaseous phase from the absorber liquid reflux-drum (CA-FLA-1) is ducted-fed into the bottom of the washer packed-column section (CA-WAS-1) at 1.04 bar and 40.0ºC.

The liquid bottom product is obtained at 1.10 bar and about 54.0ºC from the 20º theoretically liquid stage (bottom column stage) in the low-pressure absorber packed-column (CA-ABS-1) as a CO_2 and H_2S rich solution (rich-amine solution) with others pollutants content (e.g.: NH_3, SOx, CHN, COS, hydrocarbons) without degradation products (not included in the Aspen Plus®v8.4 process model simulation). Liquid bottom product is pumped by the rich-amine pump (CA-PUM-3) to the cross-solution heat exchanger (CA-HEA-2).

Make-up water (WATER FROM TREATMENT PLANT) at atmospheric pressure and 25.0ºC from the treatment plant is pumped (CA-PUM-6) at 1.03 bar to the 1º theoretically liquid stage (top column stage) in the washer packed-column section (CA-WAS-1). The water obtained in the bottom of the of the washer packed-column section (CA-WAS-1) is pumped by the washer water recycle-pump (CA-PUM-7) back to the 1º theoretically liquid stage (top column stage) to enter at 1.03 bar and about 37.0ºC in the washer packed-column section (CA-WAS-1). The water mass flow rate of water circulating in close-loop cycle is defined by the parameters of the washer packed-column section (CA-WAS-1), and by the employed temperature limits in the Aspen Plus®v8.4 process model simulation.

The single washer water step as final polishing step reduces the concentration of MEA and others water affinity contaminants in the cleaned synthesis gas.

Rigorous Aspen Plus®v8.4 process model simulation of the washer packed-column section (CA-WAS-1) was developed as a top section of the low-pressure absorber packed-column (CA-ABS-1) using RadFrac columns block on standard convergence mode with reaction model RE-CA-MEA and electrolyte solution chemistry model CH-CA-MEA without in-bed condenser and reboiler. The model was optimized for estimated 5 theoretical stages considering a NORTON IMTP 25.0 mm packing section from 1º to 5º theoretically stages with section packed height and diameter optimized for each system requirements (scenarios dependence) on standards characteristics, and according to diameter of the low-pressure absorber packed-column (CA-ABS-1). The model use rate-based calculation for Mixed flow model without reactions and film resistance in vapor phase, without reactions and with film resistance in liquid phase. Default Aspen Plus®v8.4 packing parameters is applied to calculate pressure drop and liquid holdup by Stichlmair method, to predict the mass transfer coefficient and interfacial area by Onda et al. (1968) correlation, and heat transfer coefficient by Chilton- Colburn (Taylor and Krishna, 1993) method.

A fraction of 0.45% of the circulating water is drained in the washer water bleed (CA-SPL-3) to recovery the concentrate washer-recovered MEA-based aqueous absorbing-solution and removes the dissolved gases (amine contaminated wash water), in closed-loop water cycle. After, drained water is recycled and sends back to mixture tank (CA-MIX-1).

The wet cleaned-synthesis gas (gaseous top-product) from washer packed-column section (CA-WAS-1) at 1.03 bar and about 39.0ºC is ducted to the integrally-geared centrifugal three stages compressor (CO blocks) to conditioning the synthesis gas for effective use as single-gas fuel in the high-performance sequential combustion full-flow advanced EvGT (GT blocks) operating in CC mode.

Rich-amine solution from the low-pressure absorber packed-column (CA-ABS-1) is send by rich-amine pump (CA-PUM-3) to cross-solution heat exchanger (CA-HEA-2) modeled by using a HeatX exchanger block for exchange heat (thermal energy recovery) with the lean-amine solution from the low-pressure stripper packed-column (CA-STR-1). Lean-amine solution is cooled from about 121.0ºC to about 62.0ºC, heating the rich-amine from about 53.0ºC to about 105.0ºC. The heated rich-amine solution is fed into the 6º theoretical stage in the low-pressure stripper packed-column (CA-STR-1) on top of the regenerative section. The cooled lean-amine solution is send to amine reclaimer (CA-SPL-2) or directly back to mixture tank (CA-MIX-1) closing the MEA-based aqueous absorbing-solution cycle.

Rigorous Aspen Plus®v8.4 process model simulation of the low-pressure stripper packed-column (CA-STR-1) was developed using RadFrac columns block on standard convergence mode with reaction model RE-CA-MEA and electrolyte solution chemistry model CH-CA-MEA without in-bed condenser and reboiler. The model was optimized for estimated 25 theoretical stages (5 theoretical stages as washer section) considering a NORTON IMTP 38.0 mm packing section from 1º to 25º theoretically stages with height and diameter for regenerative and washer packed sections optimized for each system requirements (scenarios dependence) on standards characteristics. The model use rate-based calculation for Mixed flow model without reactions and film resistance in vapor phase, without reactions and with film resistance in liquid phase. Default Aspen Plus®v8.4 packing parameters is applied to calculate pressure drop and liquid holdup by Stichlmair method, to predict the mass transfer coefficient and interfacial area by Onda et al. (1968) correlation, and heat transfer coefficient by Chilton- Colburn (Taylor and Krishna, 1993) method.

The gaseous top-product containing mainly acid gases (CO_2 and H_2S) at about 1.72 bar and 94.3ºC from the 1º theoretically vapor stage (top column stage) of the low-pressure stripper packed-column (CA-STR-1) is cooled in the stripper condenser (CA-CON-2) passing cooling water (CT-HEA-3) modeled using Heater exchanger blocks. Hence, form-condense 54.0$\%_{w/w}$ (model result) of the gaseous top-product (condensate phase) on saturation equilibrium conditions.

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-3) to the stripper condenser (CT-HEA-3). The amount of cooling water required is determined and controlled by design specification DS-CA-TL-3 varying the mass flow rate of cooling water passing through the stripper condenser (CT-HEA-3). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

The condensed phase formed at 1.7 bar and 40.0ºC is flash-separated in the striper liquid reflux-drum (CA-FLA-2) modeled by using a Flash2 separator block. A fraction of the condensate top product containing mainly water from the striper liquid reflux-drum (CA-FLA-2) is splitted in the striper water bleed (CA-SPL-1) and send-recycled back to the mixture tank (CA-MIX-1) as recovered water (recycle) in closed-loop-cycle mode. Another fraction (15.0$\%_{w/w}$ by model result) of the condensate top product is pumped at 1.72 bar and 40.0ºC by the desorber reflux pump (CA-PUM-4) and refluxed back to the 1º theoretically liquid stage (internal washer section) of the low-pressure stripper packed-column (CA-STR-1). The excess of water is purged (CA-SPL-4) and sent to wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for reuse as make-up water (WATER FROM TREATMENT).

About 44.0$\%_{w/w}$ of gaseous top-product (non-condensed) containing mainly CO_2 and H_2S leaving from the striper liquid reflux-drum (CA-FLA-2) at 1.7 bar and 40.0ºC (saturation condition) is directly send to be compressed and liquefied by the integrally-geared centrifugal six stages compressor (CC blocks).

The liquid bottom product containing mainly regenerated amine solution at 1.78 bar and about 119.4ºC from the 25º theoretically liquid stage (bottom column stage) in the regenerative section in the low-pressure stripper packed-column (CA-ABS-1) as lean-amine solution is splitted in the lean-amine sump splitter (CA-SPL-6) of the stripper reboiler (CA-REB-1). 95.0$\%_{w/w}$ of the bottom liquid product in the sump is fed in the stripper reboiler (CA-REB-1), and 5.0$\%_{w/w}$ of the bottom liquid product in the sump is drained as product and mixed in the lean-amine regenerated mixer (CA-MIX-2) with heated bottom liquid phase overflow the baffle.

The reboiler circulation baffle model was developed by using a HeatX exchanger block (CA-REB-1) and by using a FSplit splitter block (CA-SPL-6) to represent the stripper reboiler configured for circulation with baffle.

The bottom liquid product from the lean-amine regenerated mixer (CA-MIX-2) contain regenerated MEA, low fraction of CO_2, H_2S, and others pollutants content (e.g.: NH_3, SOx, CHN, COS, hydrocarbons) without degradation products (not included in the Aspen Plus®v8.4 process model simulation).

The thermal energy for stripper reboiler (CA-REB-1) determine the MEA-based aqueous absorbing-solution vaporized in the reboiler and the regeneration extent trough the low-pressure stripper packed-column (CA-STR-1) to obtain the required capture levels (adjust the required fraction of CO_2 captured to $90\%_{w/w}$ of the inlet).

The thermal energy required by the stripper reboiler (CA-REB-1) in the BIG-GT/CC (SC1) is supplied by process steam at 2.5 bar and 130.0ºC obtained from the steam exhausted at 2.5 bar from the low-pressure expansion stage in the BPST system for thermochemical route-cycles. The thermal energy required by the stripper reboiler (CA-REB-1) in the BIG-GT/CC (SC2) is supplied by process steam at 2.5 bar and 130.0ºC obtained from the steam exhausted at 2.5 bar from the low-pressure expansion stage in the EBPST system for thermochemical route-cycles. The thermal energy required by the stripper reboiler (CA-REB-1) in the BIG-GT/CC (SC4) is supplied by process steam at 2.5 bar and 274.6ºC obtained from the steam extraction at 2.5 bar (ST-SPL-1) in the CEST system.

In the BIG-GT/CC (SC1), and BIG-GT/CC (SC2), the mass flow rate of process steam at 2.5 bar and 130.0ºC, and in the BIG-GT/CC (SC4), the mass flow rate of process steam at 2.5 bar and 274.6ºC, are determined by thermal requirements and exchanger temperature limits (cross-over avoided) in the cycle-system, and controlled by design specification DS-CA-FL-2 varying the mass flow rate of water/steam circulating through the reboiler exchanger cycle.

In the BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4), part of the condensed water after the stripper reboiler (CA-REB-1) is pumped (GA-PUM-1) as conditioned hot water to syngas cooling and heat recovery (GA blocks) to produce the gasification steam agent in the low-temperature vertical CSC (GA-CSC-2). Reminiscent part is sent-back (recycle) to the deaerator unit (HR-DEA-1). The splitted hot water for each purpose is controlled by design specification DS-CA-TL-3 varying the mass flow rate of the water based on the quantity of gasification steam agent is required by the atmospheric CFB directly-heated gasifier (GA-GASEI).

The lean-amine solution regenerated from the lean-amine regenerated mixer (CA-MIX-2) is send to be cooled from about 121.0ºC to about 62.0ºC, recovering the heat in the cross-solution heat exchanger (CA-HEA-2). After cooled, the lean-amine solution is sent to the amine reclaimer (CA-SPL-2).

Amine reclaimer (CA-SPL-2) split 0.18%$_{w/w}$ of the lean-amine solution circulating back to low-pressure absorber packed-column (CA-ABS-1). Amine reclaimer (CA-SPL-2) is modeled by using a FSplit splitter block to adjust the amine make-up, and simulate the losses of MEA due the thermal and oxidizing degradation, according to input fraction of components removed in the carbon-based filter (CA-SEP-1) as simplified mode (model artifice). In the carbon-based filter (CA-SEP-1) modeled by using a Sep separator block is considered a loss of 10.0%$_{w/w}$ of the circulating water in the reclaimer cycle and the downdraft of all dissolved gases and electrolyte entering the filter system (CA-SEP-1).

The lean-amine solution reclaimed is filtered by carbon-based filter (CA-SEP-1) containing activated charcoal medium put on stream at every 3 to 4 weeks of interval (continues stead-state simulated). In this stage, are removed sulphur and nitrogen compounds, amine salts, particles, and degradation products (not included in the Aspen Plus®v8.4 process model simulation), formed over time in the amine cycle in closed loop-cycle mode.

A fraction of the amine reclaimed is recovered in the presence of a strong alkali solution (e.g.: NaOH) and with the application of heat (not included in the Aspen Plus®v8.4 process model simulation). Another fraction, retained and removed by the carbon-based filter (CA-SEP-1) is sent to wastewater treatment plant, and after destined to final disposal (e.g.: landfill) with carbon filter active medium (activated charcoal) (RESIDUE TO DISPOSAL). Recovered amine is sent-back into the amine-lean solution line (CA-SPL-2) by the recirculation pump (CA-PUM-5) together 90.0%$_{w/w}$ of cleaned-water that passes through the carbon-based filter (CA-SEP-1).

7.1.9 Carbon dioxide compression and storage/use

The gaseous CO_2 captured (acid gas) in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4) by the CO_2 and H_2S co-capture system using MEA-based aqueous absorbing-solution (CA blocks) is compressed by the integrally-geared centrifugal six stages compressor (CC blocks) (multiple pinions). The compressed gaseous CO_2 is after-cooled been liquefied producing liquid CO_2 at 30.0ºC and 73.0 bar for further uses. High-pressure liquid pump (CC-PUM-1) is used to adjust the pressure to 150.0 bar (or more) to be injected into the geological formations for permanent storage (CCS).

The Aspen Plus®v8.4 process model simulation of the integrally-geared centrifugal six stages compressor (CC blocks) is based on the Siemens STC-GV integrally-geared centrifugal multi-stages compressor series feature a single-shaft arrangement and configured to allow inter-cooling steps. The Aspen Plus®v8.4 process model simulation of the integrally-geared centrifugal six stages compressor (CC blocks) was developed using Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 83.0% isentropic efficiency (isentropic compression).

As shown in Figure 40, Aspen Plus®v8.4 flowsheet of the CO_2 compression and storage/use area in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2), which is the same model with modified parameters for BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4) is compost by: integrally-geared centrifugal six stages compressor (CC-COM-1~6); water inter-cooler exchangers (CC-1~5); supercritical liquefactor-cooler (CC-HEA-1); condenser knock-out drum (CC-FLA-5); liquid water pump (CC-PUM-1); high-pressure liquid pump (CC-PUM-1); direct drive permanent magnet motor (mechanical efficiency); degases warm (CC-FLA-6); atmospheric condensate buffer/equalizer tank (CO-FLA-7); high-pressure buffer/equalizer tank (CO-FLA-6); and liquid CO_2 temporary storage tank (CC-SPL-1).

The captured gaseous CO_2 without the presence of H_2S (applying LO-CAT sulfur recovery unit) or the acid gas (technical compressor limits analysis) as leave in the top of the stripper column (CA-FLA-2) at 1.7 bar and 40.0ºC (saturation condition) is compressed by the six impellers (CC-COM-1~6). The pressurized gases between the compression stages (CC-COM-1~5) is cooled to 30.0ºC by the water inter-cooler exchangers (CC-1~5) modeled by using a MHeatX exchanger blocks generating condensed phase content water and dissolved gases. The condensed phase is removed in the condenser knock-out drums (CC-FLA-1~5) modeled by using a Flash2 separator block and send to atmospheric condensate buffer/equalizer tank (CC-FLA-7) modeled by Flash2 separators block at ambient conditions.

Cooled high-pressure gaseous CO_2 at about 73.0 bar and 88.0ºC (supercritical pressure) after the six-stage impeller (CO-COM-6) is cooled to 30.0ºC and liquefied by the supercritical liquefactor-cooler (CC-HEA-1) modeled by using a HeatX exchanger block. Liquid CO_2 is sent to high-pressure buffer/equalizer tank (CO-FLA-6) to remove any non-condensable gases present in the line to atmosphere (VENT TO ATMOSPHERE) coupled with the liquid CO_2 temporary storage tank (CC-SPL-1) to maintenance the liquid phase at 73.0 bar and 30.0CºC.

The liquid CO_2 produce-captured can be send to permanent storage (HIGH-PRESSURE CO_2 TO STORAGE) in geological formations (CCS) (e.g.: aquifers, oil and gas fields, unmineable coal beds) at about 150.0 bar using a high-pressure liquid pump (CC-PUM-1) to compress the liquid CO_2. The liquid CO_2 produce-captured can be send to process use (LIQUID CO_2 TO PROCESS) at adequate conditions required by the downstream process (not included in the model) or by the transportation off-site (e.g.: algae-based liquid biofuels, methanol synthesis). The use of captured CO_2 is not defined in this research Master`s degree.

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-5) to the water inter-cooler exchangers (CC-1~5) and to the supercritical liquefactor-cooler (CC-HEA-1). The amount of cooling water required is determined and controlled varying the mass flow rate of cooling water flows through the equipment users. The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system. The lubricating oil circuit and the lubricating oil water-cooling system (low make-up and electricity requirements) are suppressed from the Aspen Plus®v8.4 process model simulations in this research Master`s degree.

The ambient equalized condensate (CC-FLA-7) is after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

The single shaft and multiple pinions in the integrally-geared centrifugal six stages compressor (CC-COM blocks) is drive by a synchronous direct drive permanent magnet motor modeled by CC-E-6 work stream. The compression stages (impellers) are optimized to obtain the same compression ratio by design specification DS-CC-TR-1 and FORTRAN calculation block CA-CC-TR-2 varying the pressure ratio in the six compression stages (CO-COM blocks). The electrical potential losses by attrite in the mechanical move parts was considered as 1.0% of the mechanical energy required by the stage (99.0% mechanical efficiency).

7.1.10 Synthesis gas compression (conditioning)

The sub-cooled and cleaned synthesis gas in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4), or the sub-cooled and partial-cleaned synthesis gas in the BIG-GT/CC (SC3), and BIG-GT/CC (SC5), are compressed by integrally-geared centrifugal three stages compressor (CO blocks). The pressure is set according to the specifications for efficient use in the high-performance sequential combustion full-flow advanced EvGT (GT blocks) operating in CC mode.

The Aspen Plus®v8.4 process model simulation of the integrally-geared centrifugal three stages compressor (CO-COM blocks) is based on the Siemens STC-GV integrally-geared centrifugal multi-stages compressor series feature a single-shaft arrangement and configured to allow inter-cooling steps, without after-cooling step (high-temperature inlet).

Figure 53 shows the Aspen Plus®v8.4 flowsheet of the cleaned synthesis gas compression (conditioning) for BIG-GT/CC (SC1), for BIG-GT/CC (SC2), for BIG-GT/CC (SC3), for BIG-GT/CC (SC4), and for BIG-GT/CC (SC5).

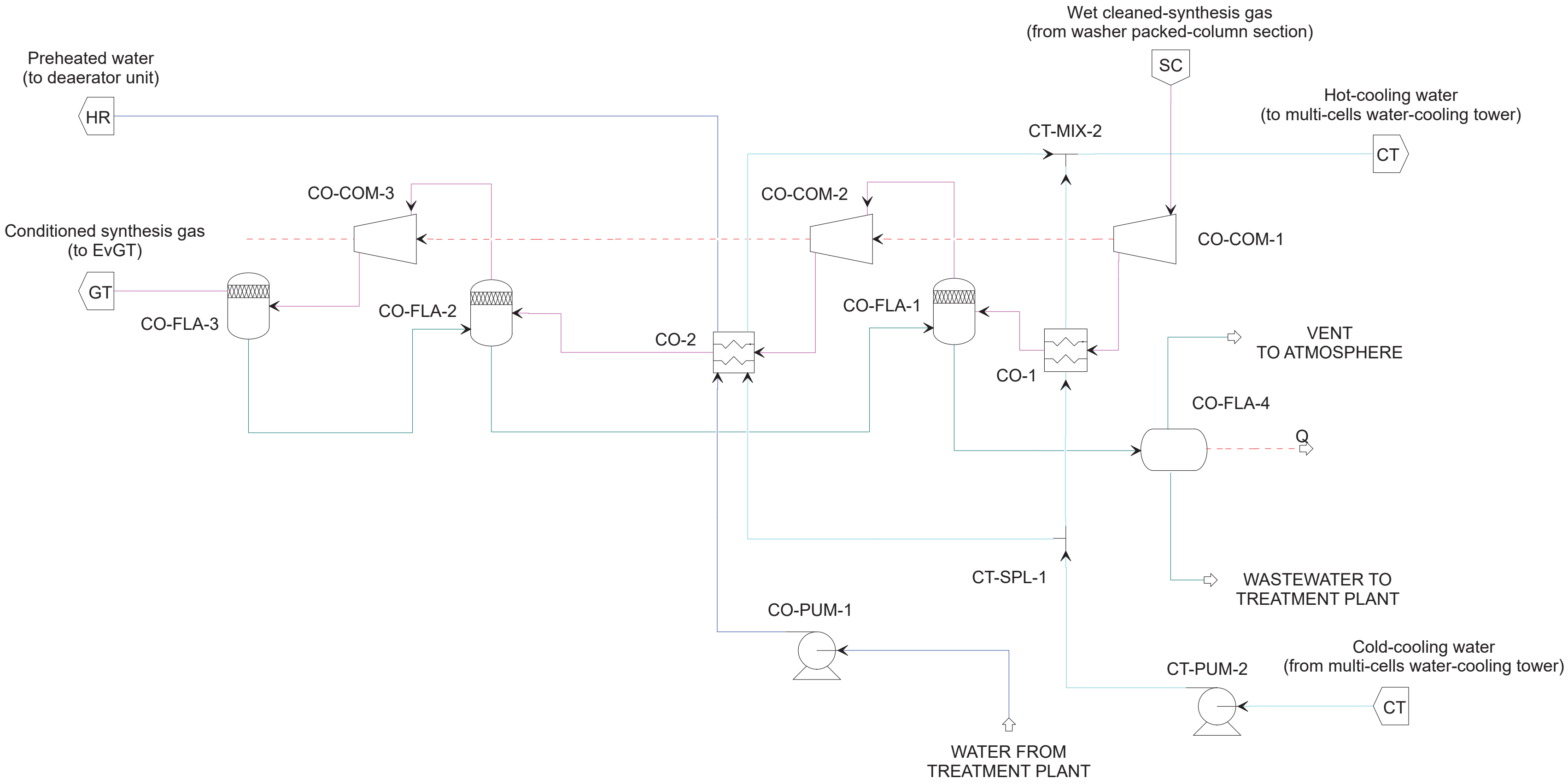


Figure 53 - Aspen Plus® v8.4 flowsheet of the cleaned synthesis gas compression (conditioning) for BIG-GT/CC (SC1), for BIG-GT/CC (SC2), for BIG-GT/CC (SC3), for BIG-GT/CC (SC4), and for BIG-GT/CC (SC5)

As shown in Figure 53, Aspen Plus®v8.4 flowsheet of the cleaned synthesis gas compression (conditioning) in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5) is compost by: integrally-geared centrifugal three stages compressor (CO-COM-1~3); water inter-cooler exchanger (CO-1); three-circuit water inter-cooler exchanger (CO-2); condenser knock-out drums (CO-FLA-1~3); ambient equalized drum (CO-FLA-4); direct drive permanent magnet motor (not included as block); liquid water pump (CO-PUM-1); and cooling water pump (CT-PUM-2 or CT-PUM-4).

The sub-cooled and cleaned synthesis gas (wet gas) comes from the 1º theoretically gaseous stage (top column stage) of washer packed-column section (CA-WAS-1) in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4). The sub-cooled and partial-cleaned synthesis gas comes from the knock-out drum (SC-FLA-4) in the BIG-GT/CC (SC3), and BIG-GT/CC (SC5). The synthesis gas flow enters the compressor by the inlet guide (CO-COM-1) to distribute the flow providing a uniform condition in the first-stage impeller (CO-COM-1). Hence, is compressed to an optimized pressure (OP-CO-PG-1) by the first-stage impeller (CO-COM-1) modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 83.0% isentropic efficiency (isentropic compression).

The synthesis gas after the first-stage of compression (CO-COM-1) ducted-leaving is cooled to 30.0ºC by the water inter-cooler exchanger (CO-1) modeled by using a MHeatX exchanger blocks generating condensed phase content water and dissolved gases. The condensed phase is removed in the condenser knock-out drum (CO-FLA-1) modeled by using a Flash2 separator block and sent to atmospheric condensate buffer/equalizer tank (CO-FLA-4) modeled by using a Flash2 separator block at ambient conditions.

The synthesis gas free of condensate phase enters in the second-stage impeller (CO-COM-2) to be compressed to an optimized pressure (OP-CO-PG-1). The second-stage impeller (CO-COM-2) is modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 83.0% isentropic efficiency (isentropic compression).

After the second-stage of compression (CO-COM-2), the synthesis gas ducted-leaving is cooled to 30.0ºC by the three-circuit water inter-cooler exchanger (CO-2) modeled by using a MHeatX exchanger block generating condensed phase content water and dissolved gases. The condensed phase is removed in the condenser knock-out drum (CO-FLA-2) modeled by using a Flash2 separator block and sent to atmospheric condensate buffer/equalizer tank (CO-FLA-4) modeled by using a Flash2 separator block at ambient conditions (equalizer).

The synthesis gas free of the condensate phase enters in the third-stage impeller (CO-COM-3) and is compressed delivering conditioned synthesis gas at required pressure by the downdraft equipment. High-performance sequential combustion full-flow advanced EvGT (GT blocks) requires a pressure at about 23.0 bar (turbine configuration) in their injection system (GT-SPL-1). The third-stage impeller (CO-COM-3) is modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 83.0% of isentropic efficiency (isentropic compression). The synthesis gas after the third-stage of compression (CO-COM-3) ducted-leaving is not cooled by after-cooler, is directly ducted to buffer/equalizer tank (CO-FLA-3) or condenser knock-out drum (CO-FLA-3) modeled by using a Flash2 separator block as conditioned synthesis gas to be used as fuel-gas in the high-performance sequential combustion full-flow advanced EvGT (GT blocks) operating in CC mode.

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-2 or CT-PUM-4) to the cooling water circuits in the inter-cooler exchangers (CO-1 and CO-2). The amount of water used to cool-down the synthesis gas is determined and controlled by design specification DS-CO-TL-1 varying the mass flow rate of cooling water passing through the water inter-cooler exchanger (CO-1) and by design specification DS-CO-TL-2 varying the mass flow rate of cooling water passing through the cooling water circuit in the three-circuit water inter-cooler exchanger (CO-2). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system. The lubricating oil circuit and the lubricating water-cooling system are suppressed from the Aspen Plus$^{®}$v8.4 process model simulations in this research Master`s degree.

Part of the deaerator make-up water (WATER FROM TREATMENT PLANT) at atmospheric pressure and 25.0ºC is pumped at 1.42 bar by the liquid water pump (CO-PUM-1). And, then is preheated at 105ºC passing through the three-circuit water inter-cooler exchanger (CO-2), being after sent-fed in the deaerator unit (HR-DEA-1), recovering heat and consequently reducing the low-pressure steam required by the deaerator unit (HR-DEA-1).

The ambient equalized condensate (CO-FLA-4) is after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

The single shaft and pinions with variable speed gears in the integrally-geared centrifugal three stages compressor (CO-COM blocks) is driver by a synchronous direct drive permanent magnet motor modeled by CO-E-3 work stream and optimized to achieve the lowest consumption of electric power energy. The electric power energy consumed is optimize-minimized using optimization model analysis tools OP-CO-PG-1 varying the pressure obtained after the first-stage impeller (CO-COM-1) and after the second-stage impeller (CO-COM-2) in combined mode according with model analysis tools constraint CN-CO-PG-1 ensuring the technical compression fundaments (raise pressure in the next stage). The electrical potential losses by attrite in the mechanical move parts was considered as 1.0% of the mechanical energy required by the stage (99.0% mechanical efficiency).

7.1.11 High-performance sequential combustion full-flow evaporative-class gas turbine (EvGT) operating in combined-cycle mode

The Aspen Plus®v8.4 process model simulation of topping Brayton-cycle by the high-performance sequential combustion full-flow advanced EvGT is based on the ALSTOM advanced-class GT24 gas turbine and GE H-class 7HA gas turbines parameters. The model employed assumes that there are not significant design changes when using the conditioned synthesis gas obtained from gasification of sugarcane bagasse and straw by atmospheric CFB directly-heated gasifier.

EvGT or HGT cycle with injection of water by a humidification tower was developed using RKS-BM physical property methods (i.e. density, humidity, enthalpy, and entropy) for air–water mixture side and for synthesis gas side, and IAPWS-95 physical property methods for the cooling water side (exchangers).

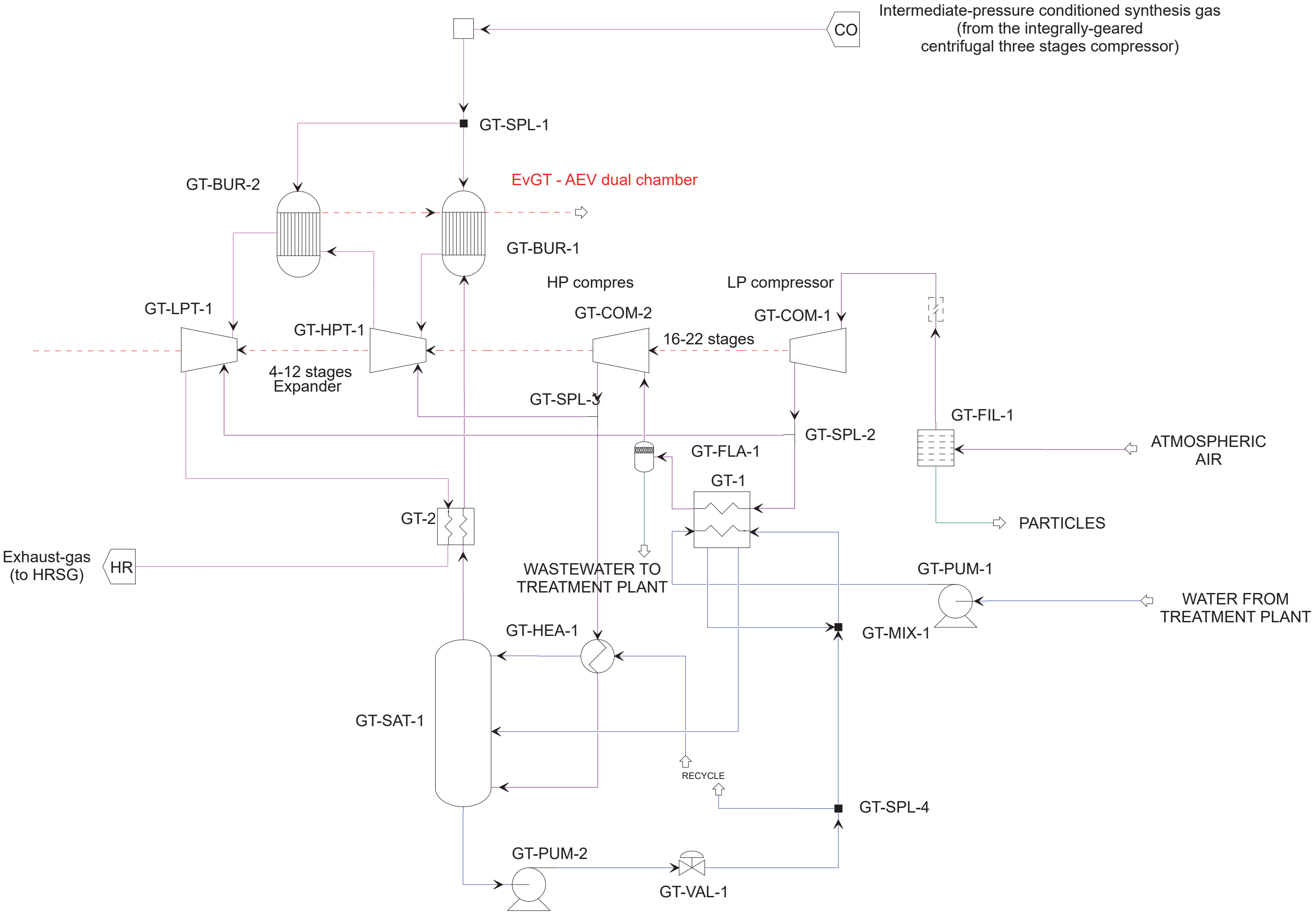
Figure 54 shows the Aspen Plus®v8.4 flowsheet of the high-performance sequential combustion full-flow advanced EvGT for BIG-GT/CC (SC1), for BIG-GT/CC (SC2), for BIG-GT/CC (SC3), for BIG-GT/CC (SC4), and for BIG-GT/CC (SC5).

The combustion air (ATMOSPHERIC AIR) is induced to an air duct from the engine room (surrounding atmospheric air) at atmospheric pressure and 25.0º. The air first pass through the pre-filter and fine-filter self-cleaned unit (GT-FIL-1) modeled by using a Fabric filter solids separator block to remove/reduce contaminants and particulate matter (considered 100.0% of efficiency) avoiding damages by debris (erosion) in the gas turbine internal parts (e.g.: blades, chambers, nozzles, ducts).

Filtered air enter the low-pressure compressor (GT-COM-1) modeled by using a Compr pressure changer block according to rigorous ASME method for polytropic compressor considering 91.0% polytropic efficiency (polytropic compression) to first-section of compression leaving the low-pressure compressor (GT-COM-1) at 4.8 bar and about 215.0ºC. A fraction of this pressurized hot-air is bleed as low-pressure bleed air (GT-SPL-2) for cooling the second-stage fuel nozzle (GT-LPT-1) and blades in the 4-stage low-pressure turbine (GT-LPT-1).

Pressurized hot-air flowing through the third circuit (hot side) of the three-circuit water inter-cooler exchanger (GT-1) in counter-current flow direction, being sub-cooled to about 4.8 bar and 27.0ºC (optimized according to SEV-burner combustion chamber requirements) generating a condensed phase content water and dissolved gases. The condensed phase formed, is removed in the condenser knock-out drum (GT-FLA-1) modeled by using a Flash2 separator block, and is after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

Figure 54 - Aspen Plus® v8.4 flowsheet of the high-performance sequential combustion full-flow advanced EvGT for BIG-GT/CC (SC1), for BIG-GT/CC (SC2), for BIG-GT/CC (SC3), for BIG-GT/CC (SC4), and for BIG-GT/CC (SC5)



As shown in Figure 54. Aspen Plus®v8.4 flowsheet of the high-performance sequential combustion full-flow advanced EvGT in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5) is compost by: low-pressure compressor (GT-COM-1); high-pressure compressor (GT-COM-2); 4-stage low-pressure turbine (GT-LPT-1); high-pressure turbine (GT-HPT-1); three-circuit water inter-cooler exchanger (GT-1); low-pressure bleed air (GT-SPL-2); high-pressure bleed air (GT-SPL-3); EnVironmental (EV) burner (GT-BUR-1); sequential EnVironmental (SEV) burner (GT-BUR-2); first annular combustion chamber (GT-BUR-1); second annular combustion chamber (GT-BUR-2); first-stage fuel nozzle (GT-BUR-1); second-stage fuel nozzle (GT-BUR-2); high-pressure counter-current double-stage humidification packaged-tower (GT-SAT-1); recuperator heat cross-exchanger (GT-2); vortex generators (not included as block); direct drive permanent magnet motor (not included as block); make-up water pump (GT-PUM-1); water mixer (GT-MIX-2); water splitter (GT-SPL-4); gases mixer (GT-MIX-1); buffer/equalizer inlet tank (GT-BUF-1); inlet air pre-filter and fine-filter self-cleaned unit (GT-FIL-1); water inter-cooler exchanger (GT-1); heat recovery after-cooling (GT-HEA-1); high-pressure condensate basin tank (GT-SAT-1); high-pressure recirculation pump (GT-PUM-2); and condenser knock-out drum (GT-FLA-1).

Fresh-water at ambient conditions from treatment plant (WATER FROM TREATMENT PLANT) is pumped to 24.0 bar and about 25.0ºC by make-up water pump (GT-PUM-1) passing-trough the first-circuit of the three-circuit water inter-cooler exchanger (GT-1) modeled by using a MHeatX exchanger block considering a first-circuit (cold side) in counter-current flow direction to achieve sub-cooled conditions in the low-pressure air-side. The pressurized hot water is heated at 23.8 bar and about 61.0ºC, same conditions of the recirculating water.

Recirculaing water obtained from the high-pressure condensate basin tank (GT-SAT-1) in the high-pressure counter-current double-stage humidification packaged-tower (GT-SAT-1), mixed with the pressurized hot water after the first-circuit (same conditions), is pumped to 23.8 bar and about 61.0ºC by recirculating water pumped (GT-PUM-2) passing-trough the second-circuit (cold side) of the three-circuit water inter-cooler exchanger (GT-1). The pressurized hot water is heated at 23.1 bar and 210.0ºC and then fed in the top liquid stage of the high-pressure counter-current double-stage humidification packaged-tower bottom section (GT-SAT-1).

The mass flow rate of make-up water from treatment plant (WATER FROM TREATMENT PLANT) depend on the mass flow rate of water evaporated and entrained with the humidified air leaving on top gaseous stage of the double-stage humidification packaged-tower top section (GT-SAT-1). The mass flow rate of make-up water is controlled by design specification DS-GT-FL-1 varying the inlet water mass flow rate to achieve the temperature required by the double-stage humidification packaged-tower bottom section (GT-SAT-1), and to maintenance the cooling water in closed-loop cycle.

Cooled low-pressure air enter the high-pressure compressor (GT-COM-2) modeled by using a Compr pressure changer block according to rigorous ASME method for polytropic compressor considering 91.0% polytropic efficiency (polytropic compression) to second-section of compression leaving the high-pressure compressor (GT-COM-2) at 23.6 bar and 219.0ºC. A fraction of this pressurized hot-air is bleed off as high-pressure air bleed (GT-SPL-3) for cooling the first-stage fuel nozzle (GT-HPT-1) and blades in the high-pressure turbine (GT-HPT-1).

The mass flow rate of combustion air agent is determined and controlled by the design specification DS-GT-FG-1 varying the intake-air mass flow rate, strongly coupled with design DS-GT-TG-1, design specification DS-GT-PB-1, design specification DS-GT-FG-2, design specification DS-GT-FG-3, FORTRAN calculation block CA-GT-QL-1, and optimization model analysis tools OT-GT-PG-1.

Aspen Plus®v8.4 process simulation simplified model of fuel nozzle and turbine blades cooling systems was developed using FSplit splitter blocks to represent the high-pressure bleed air (GT-SPL-3) for the advanced open loop air-cooled first-stage fuel nozzle (GT-HPT-1) and for blades effusion cooling in the high-pressure turbine (GT-HPT-1). In addition, using FSplit splitter blocks to represent the low-pressure bleed air (GT-SPL-2) for the advanced open loop air-cooled second-stage fuel nozzle (GT-LPT-1) and for blades effusion cooling in the 4-stage low-pressure turbine (GT-LPT-1).

The coolant air mass flow rate bleeds-off is determined in function of the turbine inlet temperature and pressure ratio admitted in the low and high turbine sections of the high-performance sequential combustion full-flow advanced EvGT (GT blocks). In the BIG-GT/CC (SC1), BIG-GT/CC (SC4), and BIG-GT/CC (SC5) with inlet pressure at 23.0 bar and turbine inlet temperature (TIT) of 1600.0ºC consider the low-pressure air bleed off as $5.0\%_{w/w}$ of the exhausted gases per expander sections, cooling air consumption of 0.05 kg of air per kg of exhaust-gas. The mass flow rate of the air bleeds-off is controlled by design specification DS-GT-FG-2 varying the mass flow rate destined to low-pressure bleed air (GT-SPL-2), and by design specification DS-TG-FG-3 varying the mass flow rate destined to high-pressure bleed air (GT-SPL-3). In the BIG-GT/CC (SC2), with inlet pressure at 23.0 bar and TIT of 1300.0ºC is considered the low-pressure air bleed-off as $2.0\%_{w/w}$ of the exhausted gases per expander sections, cooling air consumption of 0.02 kg of air per kg of exhaust-gas. The mass flow rate of the air bleed-off is controlled by design specification DS-GT-FG-2 varying the mass flow rate destined to low-pressure bleed air (GT-SPL-2), and by design specification DS-TG-FG-3 varying the mass flow rate destined to high-pressure bleed air (GT-SPL-3). In the BIG-GT/CC (SC3), with inlet pressure at 23.0 bar and TIT of 1500.0ºC is considered the low-pressure air bleed off as $4.0\%_{w/w}$ of the exhausted gases per expander sections, cooling air consumption of 0.04 kg of air per kg of exhaust-gas. The mass flow rate of the air bleed-off is controlled by design specification DS-GT-FG-2 varying the mass flow rate destined to low-pressure bleed air (GT-SPL-2), and by design specification DS-TG-FG-3 varying the mass flow rate destined to high-pressure bleed air (GT-SPL-3).

The coolant air (bleed air) is guided through the advanced open loop air-cooling internal circuit according to blades effusion cooling method (single-pass or multiple pass circuits) flowing-out together the exhaust-gas (content in excess high combustion oxygen).

High-pressure combustion air, oxidant agent in combustion processes, is cooled to 80.0ºC at 23.6 bar by recirculating water at about 61.0ºC and 23.8 bar in the heat recovery after-cooling (GT-HEA-1) modeled by Heater exchanger blocks using RKS-BM physical property methods to air-water mixture side, and IAPWS-95 physical property methods to water side. The cooled high-pressure combustion air is then injected in bottom of the high-pressure counter-current double-stage humidification packaged-tower (GT-SAT-1).

The water coolant heat recovery fluid (recirculating water) is pumped by the high-pressure recirculation pump (GT-PUM-2) passing-trough the heat recovery after-cooling (GT-HEA-1) being heated to 23.1 bar and 210.0ºC. After heated, is then fed in the top stage of the double-stage humidification packaged-tower top section (GT-SAT-1). The water mass flow rate passing-through the heat recovery after-cooling (GT-HEA-1) is controlled by design specification DS-GT-FL-2 coupled whit the design specification DS-GT-FL-3 varying the amount of water splitted in the water splitter (GT-SPL-4).

Rigorous Aspen Plus®v8.4 process model simulation of the high-pressure counter-current double-stage humidification packaged-tower (GT-SAT-1) was developed using RadFrac columns block on standard convergence mode without in-bed condenser and reboiler. The model was optimized for estimated 5 theoretical stages considering NORTON INTX packing sections with dimension of 6.0 mm and standards characteristics with height and diameter optimized for each system requirements (scenarios dependence). The model use rate-based calculation for Countercurrent flow model without reactions and film resistance in vapor phase, without reactions and with film resistance in liquid phase. Default Aspen Plus®v8.4 packing parameters is applied to predict the mass transfer coefficient and interfacial area by Onda et al. (1968) correlation and heat transfer coefficient by Chilton–Colburn (Taylor and Krishna, 1993) method.

Humidified combustion air at 23.1 bar and 195.0ºC leaving from the 1º theoretically vapor stage (top column stage) in the double-stage humidification packaged-tower top section (GT-SAT-1) is heated by the exhaust-gas from the 4-stage low-pressure turbine (GT-LPT-1) in the recuperator heat cross-exchanger (GT-2).

In the BIG-GT/CC (SC1), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5) the exhaust-gas is cooled down to 1.01 bar and 600.0ºC. In the BIG-GT/CC (SC2), the exhaust-gas is cooled down to 1.01 bar and 715.0ºC. The temperature of the humidified combustion air after the recuperator heat cross-exchanger (GT-2) is determined and controlled by the energy balance (free-degree).

Intermediate-pressure cleaned and conditioned synthesis gas from the synthesis gas compression (conditioning) is fed into the buffer/equalizer inlet tank (CO-FLA-3) as available fuel-gas to be injected in the combustion chambers at about 170.0ºC~180.0ºC and 23.0 bar (scenario conditions dependence). Part of the conditioned synthesis gas is injected in the first annular EV-burner combustion chamber (GT-BUR-1) and another part is injected in the second annular SEV-burner combustion chamber (GT-BUR-2), according to limits in the TIT admitted by the high-performance sequential combustion full-flow advanced EvGT.

Aspen Plus®v8.4 process model simulation of the injection system coupled with the turbine inlet temperature control for the first annular EV-burner combustion chamber (GT-BUR-1) and for the second annular SEV-burner combustion chamber (GT-BUR-2) considers optimized combustion air mass flow rate, optimized discharge pressure (DS-GT-PB-1) of the high-pressure turbine (GT-HPT-1), heat loss from the systems (CA-GT-QL-1), and the fraction of fuel-gas (GT-SPL-1) injected in the first (GT-BUR-1) or second (GT-BUR-2) combustion chamber.

Aspen Plus®v8.4 process model simulation of the first annular combustion chamber (GT-BUR-1) and EV-burner (GT-BUR-1) is represented together the first-stage fuel nozzle (GT-BUR-1) as simple-aggregated model by using a RGibbs reactor block (GT-BUR-1), representing the oxidation and formation gaseous reactions according to chemical equilibrium by Gibbs free-energy minimization method. In the model, was considered all gaseous components expected as potential products.

Aspen Plus®v8.4 process model simulation of the second annular combustion chamber (GT-BUR-2) and SEV-burner (GT-BUR-2) is represented together the second-stage fuel nozzle (GT-BUR-2) as simple-aggregated model by using a RGibbs reactor block (GT-BUR-2), representing the oxidation and formation gaseous reactions according to chemical equilibrium by Gibbs free-energy minimization method. In the model, was considered all gaseous components expected as potential products in products sheet.

Chemical equilibrium by Gibbs free-energy minimization method estimates the maximum of NO_x (e.g.: NO, NO_2, N_2O) and SO_x (SO_2, SO_3), COS and NH_3 from the precursors contained in the synthesis gas and combust-generated in the first annular EV-burner combustion chamber (GT-BUR-1) and in the second annular SEV-burner combustion chamber (GT-BUR-2). The method only consider the effect of temperature and the amount of humidified air injected in the chamber, others effects (emission reduction techniques) are not considered in the Aspen Plus®v8.4 process model simulation (technological designs and arrangement).

The total heat loss from the first annular EV-burner combustion chamber (GT-BUR-1) and the second SEV-burner annular combustion chamber (GT-BUR-2) was considered to be 0.5% of the LHV_{db} of the fuel-gas fed in the high-performance sequential combustion full-flow advanced EvGT (GT blocks). The heat flow-out is controlled by FORTRAN calculator block CA-GT-QL-1 with the aid of parameter calculation blocks (EHV blocks group) implemented.

The mass flow rate of fuel-gas injected in the first annular EV-burner (GT-BUR-1), and consequently the mass flow rate of fuel-gas injected in the second annular SEV-burner combustion chamber (GT-BUR-2) is determined and controlled by DS-GT-TG-1 varying the split fraction (GT-SPL-1) of fuel-gas. In the BIG-GT/CC (SC2), the split fraction (GT-SPL-1) is controlled to obtain TIT of 1300.0ºC. In the BIG-GT/CC (SC3), the split fraction (GT-SPL-1) is controlled to obtain to obtain TIT of 1500.0ºC. In the BIG-GT/CC (SC1), BIG-GT/CC (SC4), and BIG-GT/CC (SC5), the split fraction (GT-SPL-1) is controlled to obtain TIT of 1600.0ºC.

The oxygen consumed in the second annular SEV-burner combustion chamber (GT-BUR-2) pass through the first annular EV-burner combustion chamber (GT-BUR-1) as excess of air. The excess of oxygen mixed with the gaseous combustion products heated in the first chamber (GT-BUR-1) is after-expanded in the high-pressure turbine (GT-HPT-1) modeled by using a Compr pressure changer block in turbine mode considering 94.0% isentropic efficiency model. Gaseous combustion products are expanded to optimized pressure (OP-GT-PG-1) before the second annular SEV-burner combustion chamber (GT-BUR-2).

Part of the fuel-gas is injected through second-stage fuel nozzle (GT-BUR-2) at the cone tip and then into the second annular SEV-burner combustion chamber (GT-BUR-2), being mixed with the expanded gaseous combustion products containing the necessary oxygen to burn-ignite the fuel-gas injected.

The TIT of the second annular SEV-burner combustion chamber (GT-BUR-2) is adjusted by design specification DS-GT-FG-1 varying the mass flow rate of intake-air flowing through the system in excess, according to limits admitted by the high-performance sequential combustion full-flow advanced EvGT. The TIT of the 4-stage low-pressure turbine (GT-LPT-1) is adjusted to be equal to the TIT of the high-pressure turbine (GT-HPT-1).

Gaseous combustion products from the second annular SEV-burner combustion chamber (GT-BUR-2) are expanded to about atmospheric level in the 4-stages low-pressure turbine (GT-LPT-1) modeled by using a Compr pressure changer block in turbine model considering 94.0% isentropic efficiency. The low-pressure gaseous combustion products are cooled in the recuperator heat cross-exchanger (GT-2) heating the humidified air leaving from the top of the double-stage humidification packaged-tower top section (GT-SAT-1). In the BIG-GT/CC (SC2), the cooled low-pressure gaseous are exhausted at 1.01 bar and 715.0ºC being directly fed into the HRSG system. In the BIG-GT/CC (SC1), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5) the cooled low-pressure gaseous are exhausted at 1.01 bar and 600.0ºC being directly fed into the HRSG system.

The single shaft air/hydrogen cooled generator is modeled by GT-E-4 work stream and optimized to produce and export the maximum of electricity to the electric power grid. The electricity generation (GT-E-4 work stream) is optimized by optimization model analysis tools OP-GT-PG-1 varying the pressure obtained after the expansion of the high-pressure combustion product gases in the high-pressure turbine (GT-HPT-1) with model analysis tools constraint CN-GT-TI-1 ensuring the technical temperature and expansion limits.

The sequential combustion process (dual-chamber) offers high gas turbine exhaust conditions allowing achieve the necessary steam generation optimally-adjusting the recuperator heat cross-exchanger (GT-2) output conditions (flexible conditions), closing the thermal energy cycle and energy global-system balances. Changes in the recuperator heat cross-exchanger (GT-2) affect significantly the net-electricity efficiency of the high-performance sequential combustion full-flow advanced EvGT.

7.1.12 Heat recovery steam generator (HRSG)

HRSG for the combined-cycles and co-generation was simulated based on the horizontal gas-flow drum type aiming primary supply the thermal energy required by the biorefinery-technologies and secondarily generate steam to be expanded in steam turbines system for power generation.

Aspen Plus®v8.4 process model simulation of the staggered exchanger tube banks was developed using RKS-BM physical property methods for the hot exhaust-gas side and IAPWS-95 physical property methods for the water and steam side. The exchanger tube banks are modeled by using HeatX exchanger blocks considering the temperature limits (crossover avoided) between the exchanger tube banks and their influence on the water/steam mass flow rate for each circuit-level.

The arrangement of the exchanger tube banks in the Aspen Plus®v8.4 process model simulation consider the pressure-levels coupled with the temperature approach required per each circuit-level. The quantity of heat recovered is dependent on the heat requirements of the biomass multi-step dryer and control particulate emissions.

Figure 55 shows the Aspen Plus®v8.4 flowsheet of the triple pressure circuit-levels HRSG system for BIG-GT/CC (SC1). Figure 56 shows the Aspen Plus®v8.4 flowsheet of the triple pressure circuit-levels HRSG system for BIG-GT/CC (SC2), Figure 57 shows the Aspen Plus®v8.4 flowsheet of the triple pressure circuit-levels HRSG system for BIG-GT/CC (SC3), Figure 58 shows the Aspen Plus®v8.4 flowsheet of the triple pressure circuit-levels reheated HRSG system for BIG-GT/CC (SC4), Figure 59 shows the Aspen Plus®v8.4 flowsheet of the triple pressure circuit-levels reheated HRSG system for BIG-GT/CC (SC5).

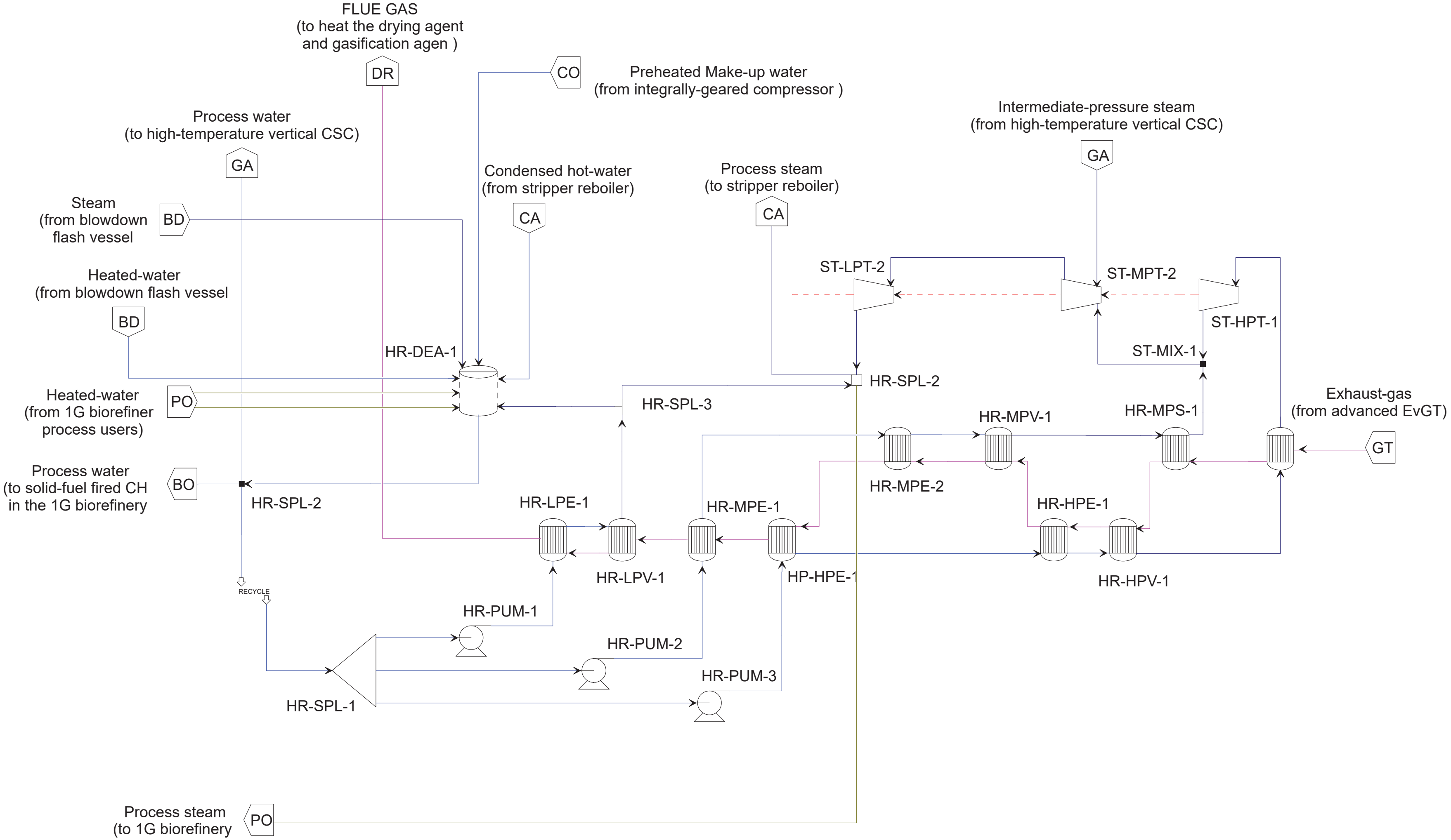


Figure 55 - Aspen Plus® v8.4 flowsheet of the triple pressure circuit-levels Heat recovery steam generator (HRSG) and back-pressure steam turbine system for BIG-GT/CC (SC1)

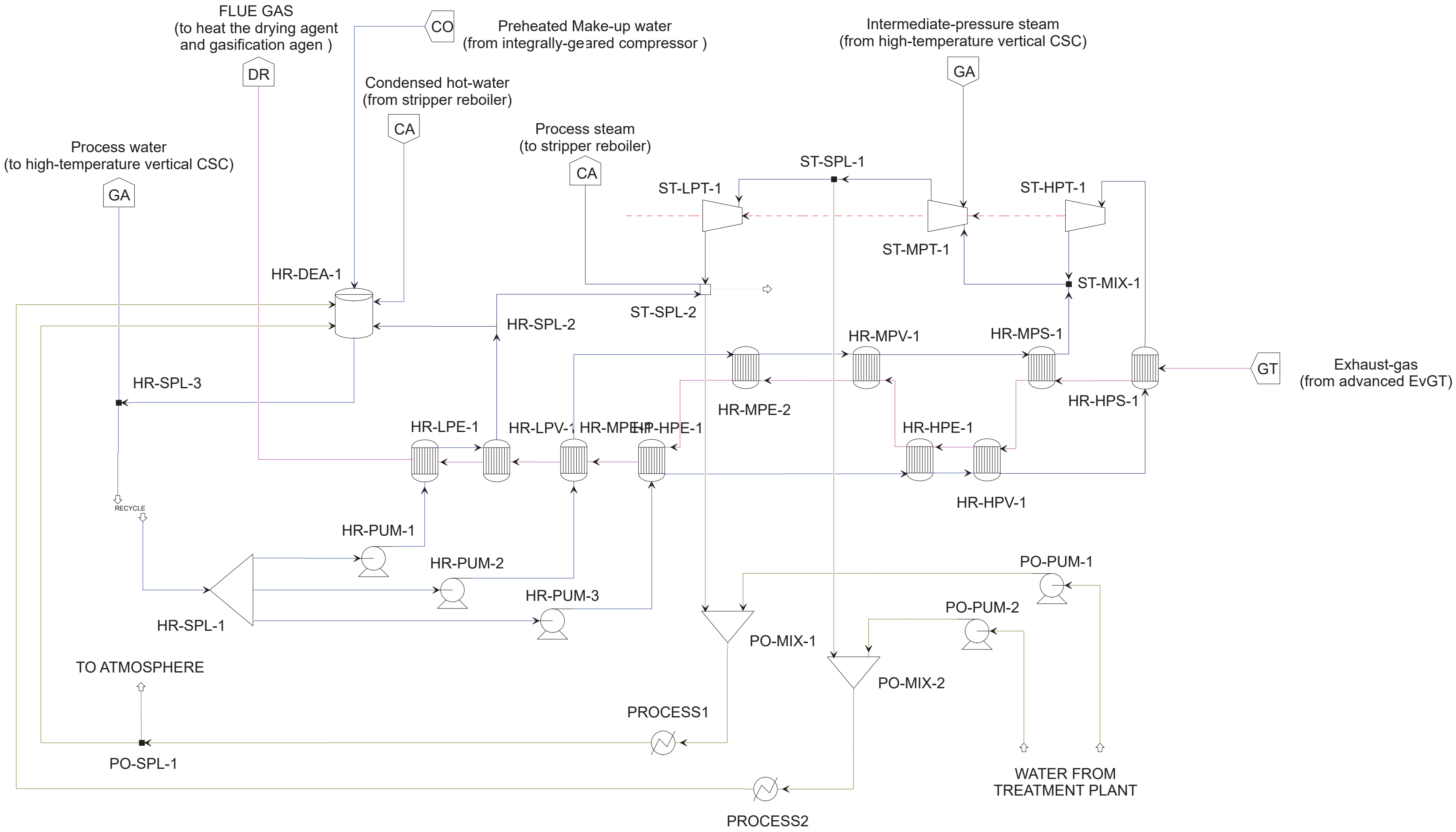


Figure 56 - Aspen Plus® v8.4 flowsheet of the triple pressure circuit-levels Heat recovery steam generator (HRSG) and back-pressure extractive steam turbine system for BIG-GT/CC (SC2)

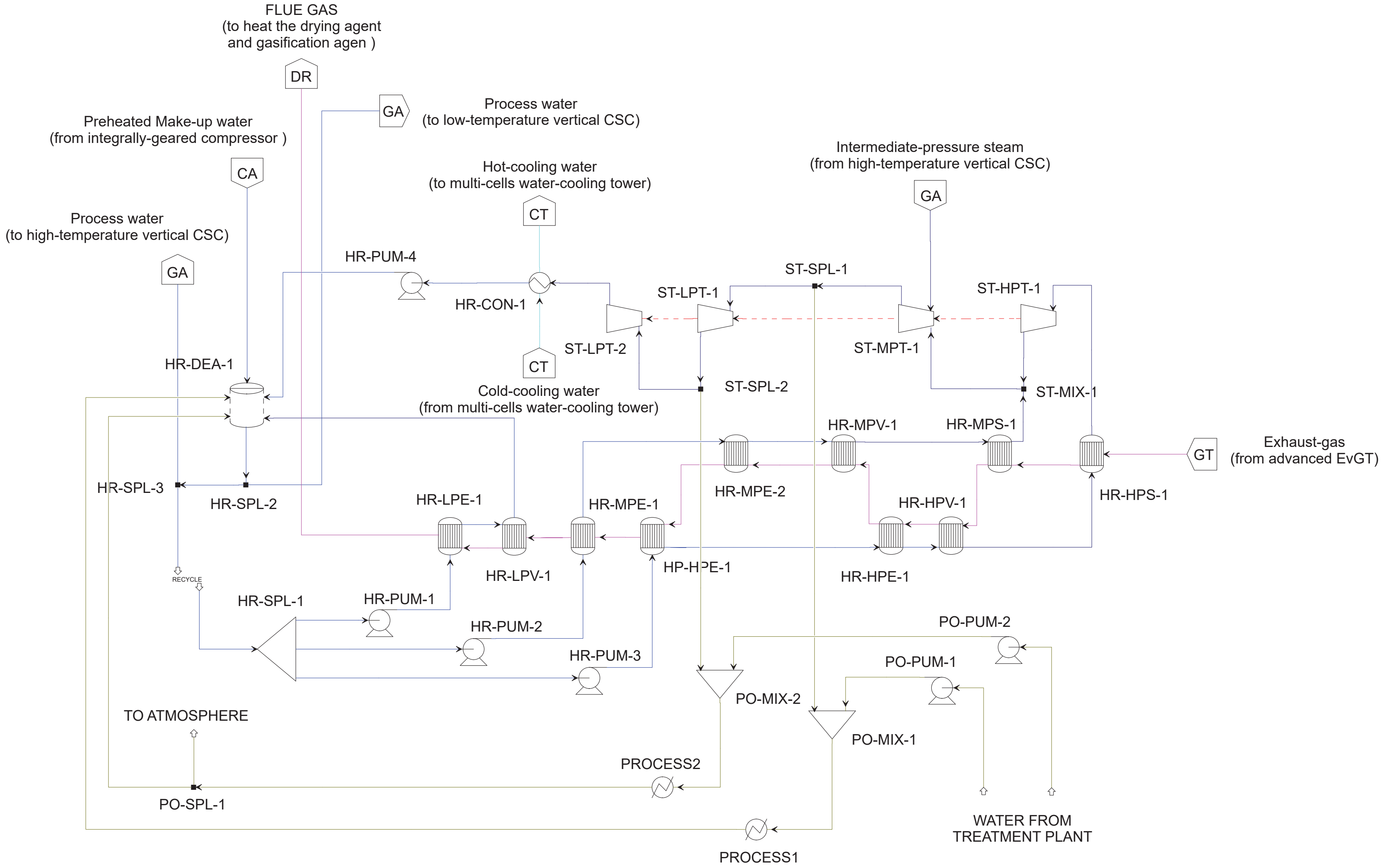


Figure 57 - Aspen Plus® v8.4 flowsheet of the triple pressure circuit-levels Heat recovery steam generator (HRSG) and condensing-extraction steam turbine for BIG-GT/CC (SC3)

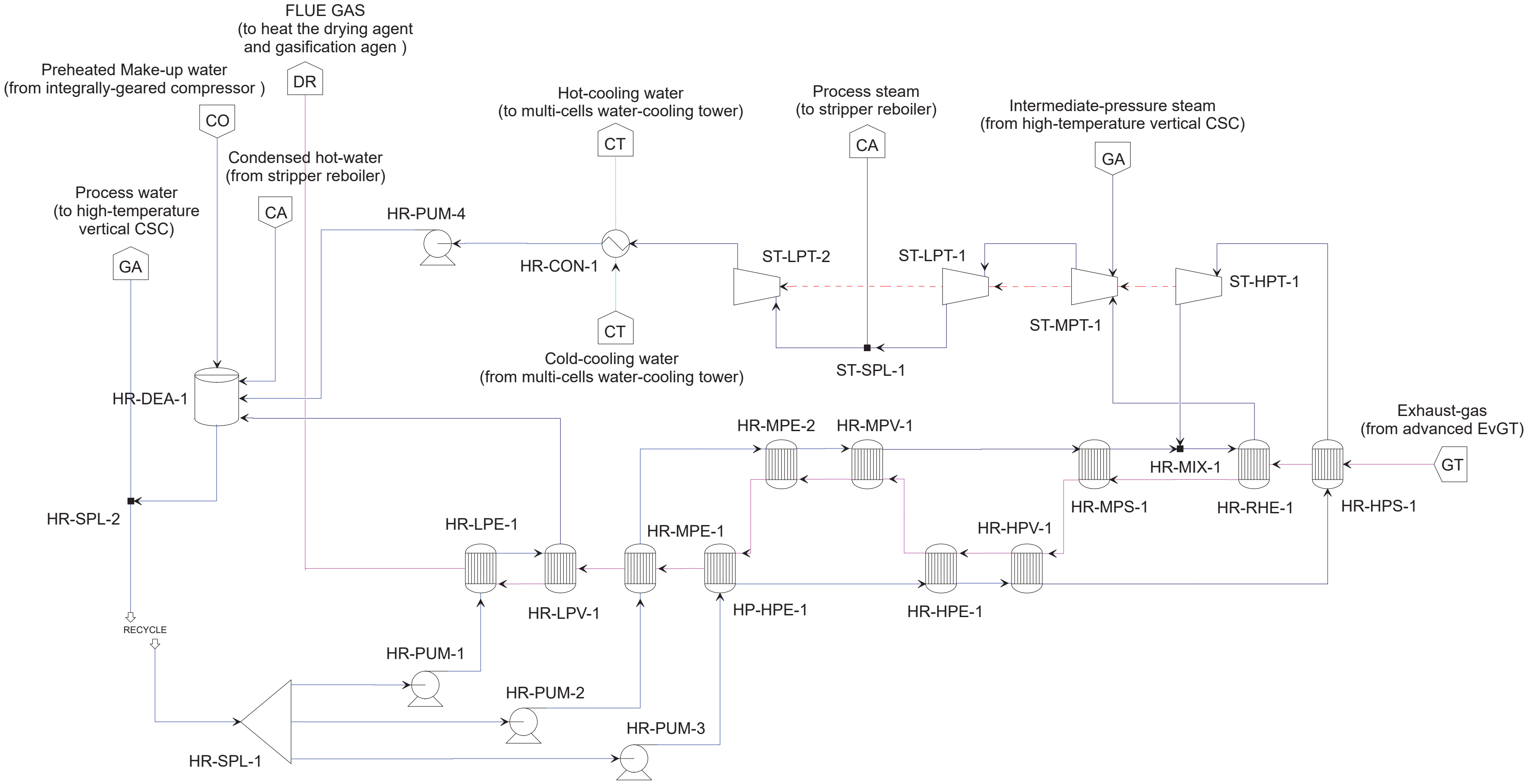


Figure 58 - Aspen Plus® v8.4 flowsheet of the triple pressure circuit-levels reheated Heat recovery steam generator (HRSG) and condensing-extraction steam turbine for BIG-GT/CC (SC4)

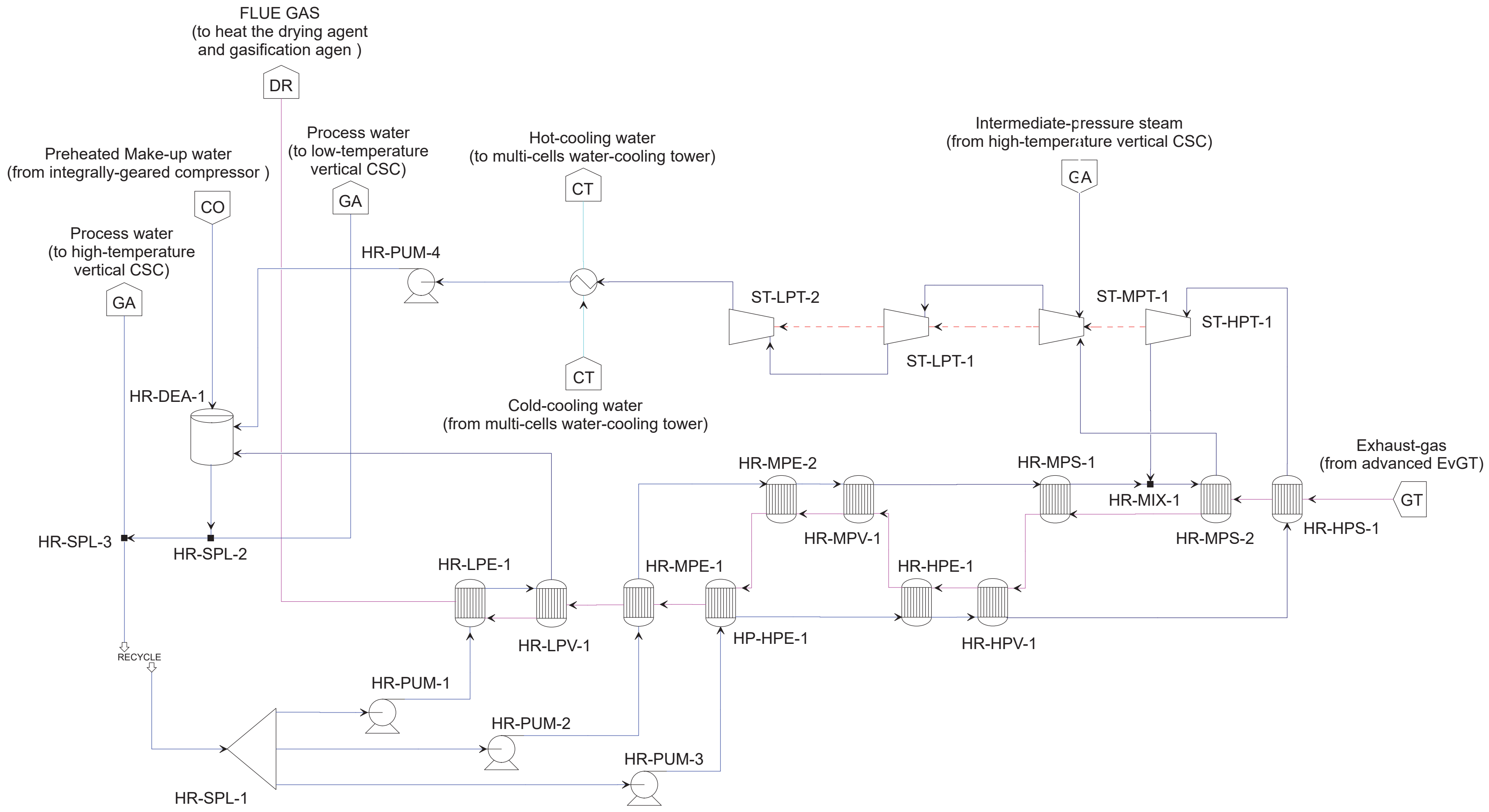


Figure 59 - Aspen Plus® v8.4 flowsheet of the triple pressure circuit-levels reheated Heat recovery steam generator (HRSG) and condensed steam turbine system for BIG-GT/CC (SC5)

As shown in Figure 55, Aspen Plus®v8.4 flowsheet of the triple pressure circuit-levels HRSG system in the BIG-GT/CC (SC1) is compost by: LP circuit-level water pump (HR-PUM-1); IP circuit-level water pump (HR-PUM-2); HP circuit-level water pump (HR-PUM-3); LP economizer bank tubes (HR-LPE-1); LP vaporizer bank tubes (HR-LPV-1); IP economizer bank tubes 1 (HR-MPE-1); IP economizer bank tubes 2 (HR-MPE-2); IP vaporizer bank tubes (HR-MPV-1); IP superheater bank tubes (HR-MPS-1); HP economizer bank tubes 1 (HR-HPE-1); HP economizer bank tubes 2 (HR-HPE-2); HP vaporizer bank tubes (HR-MPV-1); HP superheater bank tubes (HR-HPS-1); steam splitter (HR-SPL-3); deaerator unit (HR-DEA-1); and deaerated hot process water splitter (HR-SPL-1).

The conventional triple pressure circuit-levels HRSG system (HR blocks) receive exhaust-gas at 1.01 bar and 600.0ºC, generated after the recuperator heat cross-exchanger (GT-2) of the high-performance sequential combustion full-flow advanced EvGT. In the BIG-GT/CC (SC1), the high-pressure and intermediate-pressure steam generated by the triple pressure circuit-levels HRSG system (HR blocks) is supplied to BPST system (ST blocks) (BC).

The Aspen Plus®v8.4 process model simulation of the horizontal gas-flow drum type HRSG system under consideration in the BIG-GT/CC (SC1) was designed with customized low-pressure (LP) circuit-level to generate steam at 2.5 bar and 130.0ºC, intermediate-pressure (IP) circuit-level to generate steam at 23.0 bar and 338.0ºC, and high-pressure (HP) circuit-level to generate steam at 45.0 bar and 420.0ºC.

In the Aspen Plus®v8.4 process model simulation, the deaerator exchanger bank tubes is considered coupled with the LP circuit-level (HR-LPE-1 and HR-LPV-1) generating steam to deaerator unit (HR-DEA-1) and process steam to supply part of the thermal energy required by the thermochemical-biorefinery (SC1).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 2.5 bar (drum pressure) by the LP circuit-level water pump (HR-PUM-1). The pressure-adequate water is heated to about 127.0ºC (saturated liquid) circulate flowing through the LP economizer bank tubes (HR-LPE-1) and vaporized generating process steam at 2.5 bar and 130.0ºC in the LP vaporizer bank tubes (HR-LPV-1).

Part of the low-pressure steam at 2.5 bar and 130.0ºC is splitted in the steam splitter (HR-SPL-3) and destined to the deaerator unit (HR-DEA-1) as degassing agent. Low-pressure steam mainly remove dissolved gasses (e.g.: O_2 and CO_2) by raises the water temperature (make-up water and condensed process water) to generate hot water at 1.4 bar and 105.0ºC in the deaerator unit (HR-DEA-1). Another part of the low-pressure steam at 2.5 bar and 130.0ºC splitted in the steam splitter (HR-SPL-3) is destined to supply part of the thermal energy required by the thermochemical-biorefinery (SC1).

The amount of steam at 2.5 bar from the LP vaporizer bank tubes (HR-LPV-1) supplied to deaerator unit (HR-DEA-1) and supplied as process steam to thermochemical-biorefinery (SC1) is controlled by design specification DS-HR-TL-1 varying the water/steam mass flow rate need to close the thermal energy balance of the thermochemical-biorefinery (SC1).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 23.0 bar (drum pressure) by the IP circuit-level water pump (HR-PUM-2). Circulate-flowing pressurized water is heated to about 160.0ºC (hot liquid) in the IP economizer bank tubes 1 (HR-MPE-1), and heated to about 220.0ºC (hot liquid) in the IP economizer bank tubes 2 (HR-MPE-2). Hence, it is vaporized to about 220.0ºC (saturated vapor) in the IP vaporizer bank tubes (HR-MPV-1) passing from liquid to vapor phase, generating saturated steam at 23.0 bar. The saturated steam is superheated to 338.0ºC in the IP superheater bank tubes (HR-MPS-1).

The amount of subcritical superheated steam at 23.0 bar and 338.0ºC generated is determined by heat exchanger surface area required by the IP exchanger tube banks, the temperature limitations (approaches and cross-over) between the tube banks (heating zones), and the technical parameters of the steam turbine under consideration.

Conditioned feed water and steam mass flow rate passing through the IP staggered exchanger tube banks (HR-MP blocks) is controlled by design specification DS-HR-TG-1 varying the mass flow rate of the deaerated feed water circulating in the exchanger tube banks in order to promote efficient heat exchange.

The temperature of the intermediate-pressure steam obtained after the IP superheater bank tubes (HR-MPS-1) is determined by the conditions (temperature and pressure) of the expanded steam obtained after the high-pressure expansion stage (ST-HPT-1) of the BPST system, and controlled by design specification DS-HR-TG-1 to obtain the same conditions in the IP steam mixer (ST-MIX-1).

The subcritical steam at 23.0 bar and 338.0ºC is expanded in the intermediate-pressure expansion stage (ST-MPT-2) of the BPST system in the BIG-GT/CC (SC1), producing electrical power energy according to described in the section 7.1.13 (Steam turbine applied in combined-cycles).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 45.0 bar (drum pressure) by the HP circuit-level water pump (HR-PUM-3). Circulate-flowing pressurized water is heated to about 160.0ºC (hot liquid) in the HP economizer bank tubes 1 (HR-HPE-1), and heated to about 257.0ºC (hot liquid) in the HP economizer bank tubes 2 (HR-HPE-2). Hence, it is vaporized to about 257.0ºC (saturated vapor) in the HP vaporizer bank tubes (HR-HPV-1) passing from liquid to vapor phase, generating saturated steam at 45.0 bar. The saturated steam is superheated to 420.0ºC in the HP superheater bank tubes (HR-HPS-1).

The amount of subcritical superheated steam at 45.0 bar and 420.0ºC generated is determined by the temperature limitations (approach) between the exchanger tube banks (heating zones) and the technical parameters of the steam turbine under consideration.

Conditioned feed water and steam mass flow rate passing through the HP staggered exchanger tube banks (HR-MP blocks) is controlled by the deaerated hot process water splitter (HR-SPL-1) varying the mass flow rate of the deaerated feed water circulating in the exchanger tube banks in order to promote efficient heat exchange.

The subcritical steam at 45.0 bar and 420.0ºC is expanded in the high-pressure expansion stage (ST-HPT-1) of the BPST system in the BIG-GT/CC (SC1), producing electrical power energy according to described in the section 7.1.13 (Steam turbine applied in combined-cycles).

In the BIG-GT/CC (SC1), gases exhausted at 1.01 bar and 600.0ºC from the recuperator heat cross-exchanger (GT-2) of the high-performance sequential combustion full-flow advanced EvGT enters the conventional triple pressure circuit-levels HRSG system (HR blocks) transfer the sensible heat to the water/steam and exits at atmospheric pressure and 152.0ºC (liquid-gas exchange process zone).

The flue-gas at about 152.0ºC after the HRSG system is mixed in the gases mixer (HR-MIX-2) with the flue-gas at 160.0ºC from the traditional 1G-CHP/EBPST system (SC1). The mixed flue-gas at about 153.0ºC is then routed to additional exchanger tube banks (gas-gas exchange process zone) to heat the drying air agent (ATMOSPHERIC AIR) to 120.0ºC. The hot drying air agent supply the thermal energy required and promote the drying process of the biomass in the bagasse flash dryers (DR-DRY-1) and straw flash dryers (DR-DRY-2).

In the BIG-GT/CC (SC1), atmospheric air gasification agent at ambient conditions is heated to 150.0ºC (GA-HEA-1) by using the HRSG hot exhaust-gas (HR-HEA-1) before being injected into the atmospheric CFB directly-heated gasifier (GA blocks).

As shown in Figure 56, Aspen Plus®v8.4 flowsheet of the triple pressure circuit-levels HRSG system in the BIG-GT/CC (SC2) is compost by: LP circuit-level water pump (HR-PUM-1); IP circuit-level water pump (HR-PUM-2); HP circuit-level water pump (HR-PUM-3); LP economizer bank tubes (HR-LPE-1); LP vaporizer bank tubes (HR-LPV-1); IP economizer bank tubes 1 (HR-MPE-1); IP economizer bank tubes 2 (HR-MPE-2); IP vaporizer bank tubes (HR-MPV-1); IP superheater bank tubes (HR-MPS-1); HP economizer bank tubes 1 (HR-HPE-1); HP economizer bank tubes 2 (HR-HPE-2); HP vaporizer bank tubes (HR-MPV-1); HP superheater bank tubes (HR-HPS-1); steam splitter (HR-SPL-2); deaerator unit (HR-DEA-1); and deaerated hot process water splitter (HR-SPL-1).

The conventional triple pressure circuit-levels HRSG system (HR blocks) receive exhaust-gas at 1.01 bar and 715.0ºC, generated after the recuperator heat cross-exchanger (GT-2) of the high-performance sequential combustion full-flow advanced EvGT. In the BIG-GT/CC (SC2), the high-pressure and intermediate-pressure steam generated by the triple pressure circuit-levels HRSG system (HR blocks) is supplied to EBPST system (ST blocks) (BC).

The Aspen Plus®v8.4 process model simulation of the horizontal gas-flow drum type HRSG system under consideration in the BIG-GT/CC (SC2) was designed with customized low-pressure (LP) circuit-level to generate steam at 2.5 bar and 130.0ºC, intermediate-pressure (IP) circuit-level to generate steam at 23.0 bar and 338.0ºC, and high-pressure (HP) circuit-level to generate steam at 45.0 bar and 420.0ºC.

In the Aspen Plus®v8.4 process model simulation, the deaerator exchanger bank tubes is considered coupled with the LP circuit-level (HR-LPE-1 and HR-LPV-1) generating steam to be used in the deaerator unit (HR-DEA-1) and process steam to supply part of the thermal energy required by the thermochemical-biorefinery (SC2).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 2.5 bar (drum pressure) by the LP circuit-level water pump (HR-PUM-1). The pressure-adequate water is heated to about 127.0ºC (saturated liquid) circulate flowing through the LP economizer bank tubes (HR-LPE-1), and vaporized generating process steam at 2.5 bar and 130.0ºC in the LP vaporizer bank tubes (HR-LPV-1).

Part of the low-pressure steam at 2.5 bar and 130.0ºC is splitted in the steam splitter (HR-SPL-3) and destined to the deaerator unit (HR-DEA-1) as degassing agent. Low-pressure steam mainly remove dissolved gasses (e.g.: O_2 and CO_2) by raises the water temperature (make-up water and condensed process water) to generate hot water at 1.4 bar and 105.0ºC in the deaerator unit (HR-DEA-1). Another part of the low-pressure steam at 2.5 bar and 130.0ºC splitted in the steam splitter (HR-SPL-2) is destined to supply part of the thermal energy required by the thermochemical-biorefinery (SC1).

The amount of steam at 2.5 bar from the LP vaporizer bank tubes (HR-LPV-1) supplied to deaerator unit (HR-DEA-1) and supplied as process steam to thermochemical-biorefinery (SC1) is controlled by design specification DS-HR-TL-1 varying the water/steam mass flow rate need to close the thermal energy balance of the thermochemical-biorefinery (SC1).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 23.0 bar (drum pressure) by the IP circuit-level water pump (HR-PUM-2). Circulate-flowing pressurized water is heated to about 180.0ºC (hot liquid) in the IP economizer bank tubes 1 (HR-MPE-1), and heated to about 220.0ºC (hot liquid) in the IP economizer bank tubes 2 (HR-MPE-2). Hence, it is vaporized to about 220.0ºC (saturated vapor) in the IP vaporizer bank tubes (HR-MPV-1) passing from liquid to vapor phase, generating saturated steam at 23.0 bar. The saturated steam is superheated to 338.0ºC in the IP superheater bank tubes (HR-MPS-1).

The amount of subcritical superheated steam at 23.0 bar and 338.0ºC generated is determined by heat exchanger surface area required by the IP exchanger tube banks, the temperature limitations (approaches and cross-over) between the tube banks (heating zones) and the technical parameters of the steam turbine under consideration.

Conditioned feed water and steam mass flow rate passing through the IP staggered exchanger tube banks (HR-MP blocks) is controlled by design specification DS-HR-TG-1 varying the mass flow rate of the deaerated feed water circulating in the exchanger tube banks in order to promote efficient heat exchange.

The temperature of the intermediate-pressure steam obtained after the IP superheater bank tubes (HR-MPS-1) is determined by the conditions (temperature and pressure) of the expanded steam obtained after the high-pressure expansion stage (ST-HPT-1) of the EBPST system, and controlled by design specification DS-HR-TG-1 to obtain the same conditions in the IP steam mixer (ST-MIX-1).

The subcritical steam at 23.0 bar and 338.0ºC is expanded in the intermediate-pressure expansion stage (ST-MPT-1) of the EBPST system in the BIG-GT/CC (SC2), producing electrical power energy according to described in the section 7.1.13 (Steam turbine applied in combined-cycles).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 45.0 bar (drum pressure) by the HP circuit-level water pump (HR-PUM-3). Circulate-flowing pressurized water is heated to about 200.0ºC (hot liquid) in the HP economizer bank tubes 1 (HR-HPE-1), and heated to about 257.0ºC (hot liquid) in the HP economizer bank tubes 2 (HR-HPE-2). Hence, it is vaporized to about 257.0ºC (saturated vapor) in the HP vaporizer bank tubes (HR-HPV-1) passing from liquid to vapor phase, generating saturated steam at 45.0 bar. The saturated steam is superheated to 420.0ºC in the HP superheater bank tubes (HR-HPS-1).

The amount of subcritical superheated steam at 45.0 bar and 420.0ºC generated is determined by the temperature limitations (approach) between the exchanger tube banks (heating zones) and the technical parameters of the steam turbine under consideration.

Conditioned feed water and steam mass flow rate passing through the HP staggered exchanger tube banks (HR-MP blocks) is controlled by the deaerated hot process water splitter (HR-SPL-1) varying the mass flow rate of the deaerated feed water circulating in the exchanger tube banks in order to promote efficient heat exchange.

The subcritical steam at 45.0 bar and 420.0ºC is expanded in the high-pressure expansion stage (ST-HPT-1) of the EBPST system in the BIG-GT/CC (SC2), producing electrical power energy according to described in the section 7.1.13 (Steam turbine applied in combined-cycles).

In the BIG-GT/CC (SC2), gases exhausted at 1.01 bar and 715.0ºC from the recuperator heat cross-exchanger (GT-2) of the high-performance sequential combustion full-flow advanced EvGT enters the conventional double pressure circuit-levels HRSG system (HR blocks) transfer the sensible heat to the water/steam and exits the HRSG system at atmospheric pressure and 131.0ºC (liquid-gas exchange process zone).

The flue-gas at about 131.0ºC after the HRSG system is routed to additional exchanger tube banks (gas-gas exchange process zone) to heat the drying air agent (ATMOSPHERIC AIR) to 120.0ºC. The hot drying air agent supply the thermal energy required and promote the drying process of the biomass in the bagasse flash dryers (DR-DRY-1) and straw flash dryers (DR-DRY-2).

In the BIG-GT/CC (SC2), atmospheric air gasification agent at ambient conditions is heated to 130.0ºC (GA-HEA-1) by using the HRSG hot exhaust-gas (HR-HEA-1) before being injected into the atmospheric CFB directly-heated gasifier (GA blocks).

As shown in Figure 57, Aspen Plus®v8.4 flowsheet of the triple pressure circuit-levels reheated HRSG system in the BIG-GT/CC (SC3) is compost by: LP circuit-level water pump (HR-PUM-1); IP circuit-level water pump (HR-PUM-2); HP circuit-level water pump (HR-PUM-3); LP economizer bank tubes (HR-LPE-1); LP vaporizer bank tubes (HR-LPV-1); IP economizer bank tubes 1 (HR-MPE-1); IP economizer bank tubes 2 (HR-MPE-2); IP vaporizer bank tubes (HR-MPV-1); IP superheater bank tubes (HR-MPS-1); HP economizer bank tubes 1 (HR-HPE-1); HP economizer bank tubes 2 (HR-HPE-2); HP vaporizer bank tubes (HR-MPV-1); HP superheater bank tubes (HR-HPS-1); deaerator unit (HR-DEA-1); and deaerated hot process water splitter (HR-SPL-1).

The conventional triple pressure circuit-levels HRSG system (HR blocks) receive exhaust-gas at 1.01 bar and 600.0ºC generated after the recuperator heat cross-exchanger (GT-2) of the high-performance sequential combustion full-flow advanced EvGT. In the BIG-GT/CC (SC3), the high-pressure and intermediate-pressure steam generated by the triple pressure circuit-levels reheated HRSG system (HR blocks) is supplied to CEST system (ST blocks) (BC).

The Aspen Plus®v8.4 process model simulation of the horizontal gas-flow drum type HRSG system under consideration in the BIG-GT/CC (SC3) was designed with customized low-pressure (LP) circuit-level to generate steam at 2.5 bar and 130.0ºC, intermediate-pressure (IP) circuit-level to produce steam at 23.0 bar and 331.0ºC, and high-pressure (HP) circuit-level to produce steam at 120.0 bar and 540.0ºC.

In the Aspen Plus®v8.4 process model simulation, the deaerator exchanger bank tubes is considered as the LP circuit-level (HR-LPE-1 and HR-LPV-1) generating steam at 2.5 bar and 130.0ºC (degassing agent) to be used only in the deaerator unit (HR-DEA-1).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 2.5 bar (drum pressure) by the LP circuit-level water pump (HR-PUM-1). The pressure-adequate water is heated to about 127.0ºC (saturated liquid) circulate flowing through the LP economizer bank tubes (HR-LPE-1) and vaporized generating process steam at 2.5 bar and 130.0ºC in the LP vaporizer bank tubes (HR-LPV-1).

Low-pressure steam at 2.5 bar and 130.0ºC is destined to the deaerator unit (HR-DEA-1) as degassing agent. Low-pressure steam mainly remove dissolved gasses (e.g.: O_2 and CO_2) by raises the water temperature (make-up water and condensed process water) to generate hot water at 1.4 bar and 105.0ºC in the deaerator unit (HR-DEA-1). The amount of steam at 2.5 bar from the deaerator vaporizer bank tubes (HR-LPV-1) is controlled by design specification DS-HR-TL-1 adjusting the amount of steam fed into the deaerator unit (HR-DEA-1) varying the water/steam mass flow rate estimate-used into the deaerator unit (HR-DEA-1) according to described in the section 7.1.16 (Water cycles).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 23.0 bar (drum pressure) by the IP circuit-level water pump (HR-PUM-2). Circulate-flowing pressurized water is heated to about 170.0ºC (hot liquid) in the IP economizer bank tubes 1 (HR-MPE-1), and heated to about 220.0ºC (hot liquid) in the IP economizer bank tubes 2 (HR-MPE-2). Hence, it is vaporized to about 220.0ºC (saturated vapor) in the IP vaporizer bank tubes (HR-MPV-1) passing from liquid to vapor phase, generating saturated steam at 23.0 bar. The saturated steam is superheated to 331.0ºC in the IP superheater bank tubes (HR-MPS-1).

The amount of subcritical superheated steam at 23.0 bar and 331.0ºC generated is determined by heat exchanger surface area required by the IP exchanger tube banks, the temperature limitations (approaches and cross-over) between the tube banks (heating zones) and the technical parameters of the steam turbine under consideration.

Conditioned feed water and steam mass flow rate passing through the IP staggered exchanger tube banks (HR-MP blocks) is controlled by design specification DS-HR-TG-1 varying the mass flow rate of the deaerated feed water circulating in the exchanger tube banks in order to promote efficient heat exchange.

The temperature of the intermediate-pressure steam obtained after the IP superheater bank tubes (HR-MPS-1) is determined by the conditions (temperature and pressure) of the expanded steam obtained after the high-pressure expansion stage (ST-HPT-1) of the CEST system and controlled by design specification DS-HR-TG-1 to obtain the same conditions in the IP steam mixer (ST-MIX-1).

The subcritical steam at 23.0 bar and 331.0ºC is expanded in the intermediate-pressure expansion stage (ST-MPT-1) of the CEST system in the BIG-GT/CC (SC3), producing electrical power energy according to described in the section 7.1.13 (Steam turbine applied in combined-cycles).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 120.0 bar (drum pressure) by the HP circuit-level water pump (HR-PUM-3). Circulate-flowing pressurized water is heated to about 200.0ºC (hot liquid) in the HP economizer bank tubes 1 (HR-HPE-1), and heated to about 325.0ºC (hot liquid) in the HP economizer bank tubes 2 (HR-HPE-2). Hence, it is vaporized to about 325.0ºC (saturated vapor) in the HP vaporizer bank tubes (HR-HPV-1) passing from liquid to vapor phase, generating saturated steam at 120.0 bar. The saturated steam is superheated to 540.0ºC in the HP superheater bank tubes (HR-HPS-1).

The amount of subcritical superheated steam at 120.0 bar and 540.0ºC generated is determined by the temperature limitations (approach) between the exchanger tube banks (heating zones) and the technical parameters of the steam turbine under consideration.

Conditioned feed water and steam mass flow rate passing through the HP staggered exchanger tube banks (HR-MP blocks) is controlled by the deaerated hot process water splitter (HR-SPL-1) varying the mass flow rate of the deaerated feed water circulating in the exchanger tube banks in order to promote efficient heat exchange.

The subcritical steam at 120.0 bar and 540.0ºC is expanded in the high-pressure expansion stage (ST-HPT-1) of the CEST system in the BIG-GT/CC (SC3), producing electrical power energy according to described in the section 7.1.13 (Steam turbine applied in combined-cycles)

In the BIG-GT/CC (SC3), gases exhausted at 1.01 bar and 600.0ºC from the recuperator heat cross-exchanger (GT-2) of the high-performance sequential combustion full-flow advanced EvGT enters the conventional double pressure circuit-levels HRSG system (HR blocks) transfer the sensible heat to the water/steam and exits the HRSG system at atmospheric pressure and 160.0ºC (liquid-gas exchange process zone).

The flue-gas at about 160.0ºC after the HRSG system is routed to additional exchanger tube banks (gas-gas exchange process zone) to heat the drying air agent (ATMOSPHERIC AIR) to 120.0ºC. The hot drying air agent supply the thermal energy required and promote the drying process of the biomass in the bagasse flash dryers (DR-DRY-1) and the straw flash dryers (DR-DRY-2).

In the BIG-GT/CC (SC3), atmospheric air gasification agent at ambient conditions is heated to 150.0ºC (GA-HEA-1) by using the HRSG hot exhaust-gas (HR-HEA-1) before being injected into the atmospheric CFB directly-heated gasifier (GA blocks).

As shown in Figure 58 for the BIG-GT/CC (SC4), and as shown Figure 59 for the BIG-GT/CC (SC5), Aspen Plus®v8.4 flowsheet of the triple pressure circuit-levels reheated HRSG system are compost by: LP circuit-level water pump (HR-PUM-1); IP circuit-level water pump (HR-PUM-2); HP circuit-level water pump (HR-PUM-3); LP economizer bank tubes (HR-LPE-1); LP vaporizer bank tubes (HR-LPV-1); IP economizer bank tubes 1 (HR-MPE-1); IP economizer bank tubes 2 (HR-MPE-2); IP vaporizer bank tubes (HR-MPV-1); IP superheater bank tubes (HR-MPS-1); IP reheater pipe banks (HR-MPS-2); HP economizer bank tubes 1 (HR-HPE-1); HP economizer bank tubes 2 (HR-HPE-2); HP vaporizer bank tubes (HR-MPV-1); HP superheater bank tubes (HR-HPS-1); IP steam mixer (HR-MIX-1); deaerator unit (HR-DEA-1); deaerator unit (HR-DEA-1); and deaerated hot process water splitter (HR-SPL-1).

The conventional triple pressure circuit-levels HRSG system (HR blocks) receive exhaust-gas at 1.01 bar and 600.0ºC, generated after the recuperator heat cross-exchanger (GT-2) of the high-performance sequential combustion full-flow advanced EvGT. In the BIG-GT/CC (SC4), the high-pressure and intermediate-pressure steam generated by the triple pressure circuit-levels reheated HRSG system (HR blocks) is supplied to CEST system (ST blocks) (BC). In the BIG-GT/CC (SC5), the high-pressure and intermediate-pressure steam generated by the triple pressure circuit-levels reheated HRSG system (HR blocks) is supplied to CST system (ST blocks) (BC).

The Aspen Plus®v8.4 process model simulation of the horizontal gas-flow drum type HRSG system under consideration in the BIG-GT/CC (SC4) and BIG-GT/CC (SC5) was designed with customized low-pressure (LP) circuit-level to generate steam at 2.5 bar and 130.0ºC, intermediate-pressure (IP) circuit-level to generate steam at 23.0 bar and 323.0ºC, intermediate-pressure (IP) reheater bank tubes (HR-MPS-2) to generate steam at 23.0 bar and 540.0ºC, and high-pressure (HP) circuit-level to generate steam at 120.0 bar and 540.0ºC.

In the Aspen Plus®v8.4 process model simulation, the deaerator exchanger bank tubes is considered as the LP circuit-level (HR-LPE-1 and HR-LPV-1) generating steam at 2.5 bar and 130.0ºC (degassing agent) to be used only in the deaerator unit (HR-DEA-1).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 2.5 bar (drum pressure) by the LP circuit-level water pump (HR-PUM-1). The pressure-adequate water is heated to about 127.0ºC (saturated liquid) circulate flowing through the LP economizer bank tubes (HR-LPE-1) and vaporized generating process steam at 2.5 bar and 130.0ºC in the LP vaporizer bank tubes (HR-LPV-1).

Low-pressure steam at 2.5 bar and 130.0ºC is destined to the deaerator unit (HR-DEA-1) as degassing agent. Low-pressure steam mainly remove dissolved gasses (e.g.: O_2 and CO_2) by raises the water temperature (make-up water and condensed process water) to generate hot water at 1.4 bar and 105.0ºC in the deaerator unit (HR-DEA-1). The amount of steam at 2.5 bar from the deaerator vaporizer bank tubes (HR-LPV-1) is controlled by design specification DS-HR-TL-1 adjusting the amount of steam fed into the deaerator unit (HR-DEA-1) varying the water/steam mass flow rate estimate-used into the deaerator unit (HR-DEA-1) according to described in the section 7.1.16 (Water cycles).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 23.0 bar (drum pressure) by the IP circuit-level water pump (HR-PUM-2). Circulate-flowing pressurized water is heated to about 170.0ºC (hot liquid) in the IP economizer bank tubes 1 (HR-MPE-1), and heated to about 220.0ºC (hot liquid) in the IP economizer bank tubes 2 (HR-MPE-2). Hence, it is vaporized to about 220.0ºC (saturated vapor) in the IP vaporizer bank tubes (HR-MPV-1) passing from liquid to vapor phase, generating saturated steam at 23.0 bar. The saturated steam is superheated to 323.0ºC in the IP superheater bank tubes (HR-MPS-1).

The amount of subcritical superheated steam at 23.0 bar and 323.0ºC generated is determined by heat exchanger surface area required by the IP exchanger tube banks, the temperature limitations (approaches and cross-over) between the tube banks (heating zones), and the technical parameters of the steam turbine under consideration.

Conditioned feed water and steam mass flow rate passing through the IP staggered exchanger tube banks (HR-MP blocks) is controlled by design specification DS-HR-TG-1 varying the mass flow rate of the deaerated feed water circulating in the exchanger tube banks in order to promote efficient heat exchange.

The superheated steam generated in the IP superheater bank tubes (HR-MPS-1) is mixed in the IP steam mixer (HR-MIX-1) with the expanded steam at 23.0 bar and 323.0ºC (intermediate-pressure level), obtained after the expansion of the high-pressure steam at 120.0 bar and 540.0ºC by the high-pressure expansion stage (ST-HPT-1) of the CEST system in the BIG-ICE/CC (SC4), or by the high-pressure expansion stage (ST-HPT-1) of the CST system in the BIG-ICE/CC (SC5). The resultant intermediate-pressure steam is superheated in the IP reheater bank tubes (HR-MPS-2) to generate steam at 23.0 bar and 540.0ºC.

The temperature of the intermediate-pressure steam obtained after the IP superheater bank tubes (HR-MPS-1) is determined by the conditions (temperature and pressure) of the expanded steam obtained after the high-pressure expansion stage (ST-HPT-1), and controlled by design specification DS-HR-TG-1 to obtain the same conditions in the IP steam mixer (HR-MIX-1).

In the BIG-GT/CC (SC4), subcritical steam at 23.0 bar and 540.0ºC is expanded in the intermediate-pressure expansion stage (ST-MPT-1) of the CEST system producing electrical power energy according to described in the section 7.1.13 (Steam turbine applied in combined-cycles). In the BIG-GT/CC (SC5), subcritical steam at 23.0 bar and 540.0ºC is expanded in the intermediate-pressure expansion stage (ST-MPT-1) of the CST system producing electrical power energy according to described in the section 7.1.13 (Steam turbine applied in combined-cycles).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 120.0 bar (drum pressure) by the HP circuit-level water pump (HR-PUM-3). Circulate-flowing pressurized water is heated to about 200.0ºC (hot liquid) in the HP economizer bank tubes 1 (HR-HPE-1), and heated to about 325.0ºC (hot liquid) in the HP economizer bank tubes 2 (HR-HPE-2). Hence, it is vaporized to about 325.0ºC (saturated vapor) in the HP vaporizer bank tubes (HR-HPV-1) passing from liquid to vapor phase, generating saturated steam at 120.0 bar. The saturated steam is superheated to 540.0ºC in the HP superheater bank tubes (HR-HPS-1).

The amount of subcritical superheated steam at 120.0 bar and 540.0ºC generated is determined by the temperature limitations (approach) between the exchanger tube banks (heating zones) and the technical parameters of the steam turbine under consideration.

Conditioned feed water and steam mass flow rate passing through the HP staggered exchanger tube banks (HR-MP blocks) is controlled by the deaerated hot process water splitter (HR-SPL-1) varying the mass flow rate of the deaerated feed water circulating in the exchanger tube banks in order to promote efficient heat exchange.

In the BIG-GT/CC (SC4), subcritical steam at 120.0 bar and 540.0ºC is expanded in the high-pressure expansion stage (ST-HPT-1) of the CEST system producing electrical power energy according to described in the section 7.1.13 (Steam turbine applied in combined-cycles). In the BIG-GT/CC (SC5), subcritical steam at 120.0 bar and 540.0ºC is expanded in the high-pressure expansion stage (ST-HPT-1) of the CST system producing electrical power energy according to described in the section 7.1.13 (Steam turbine applied in combined-cycles).

In the BIG-GT/CC (SC4) and BIG-GT/CC (SC5), gases exhausted at 1.01 bar and 600.0ºC from the recuperator heat cross-exchanger (GT-2) of the high-performance sequential combustion full-flow advanced EvGT enters the conventional double pressure circuit-levels HRSG system (HR blocks) transfers sensible heat to the water/steam and exits the HRSG system at atmospheric pressure and 160.0ºC (liquid-gas exchange process zone).

The flue-gas at about 160.0ºC after the HRSG system is routed to additional exchanger tube banks (gas-gas exchange process zone) to heat the drying air agent (ATMOSPHERIC AIR) to 120.0ºC. The hot drying air agent supply the thermal energy required and promote the drying process of the biomass in the bagasse flash dryers (DR-DRY-1) and the straw flash dryers (DR-DRY-2).

In the BIG-GT/CC (SC4) and BIG-GT/CC (SC5), atmospheric air gasification agent at ambient conditions is heated to 150.0ºC (GA-HEA-1) by using the HRSG hot exhaust-gas (HR-HEA-1), before being injected into the atmospheric CFB directly-heated gasifier (GA blocks).

7.1.13 Steam turbine applied in combined-cycles

The Aspen Plus®v8.4 process model simulation of the steam turbine applied in combined-cycles considers conventional subcritical steam turbines driving a generator, operating in Rankine-cycle mode.

The electrical potential losses (turbine-mechanical generator) by attrite in the mechanical move parts was considered as 1.0% of the mechanical potential energy produced by the STs (99.0% mechanical efficiency).

As shown in Figure 55, Aspen Plus®v8.4 flowsheet of the BPST system in the BIG-GT/CC (SC1) is compost by: high-pressure expansion stage (ST-HPT-1); intermediate-pressure expansion stage (ST-MPT-2); low-pressure expansion stage (ST-LPT-2); steam mixer (ST-MIX-1); and steam splitter (ST-SPL-1).

The Aspen Plus®v8.4 process model simulation of the BPST (ST blocks) in the BIG-GT/CC (SC1) was developed using IAPWS-95 physical property methods considering about 79.45% isentropic efficiency (isentropic expansion), obtaining exhaust-steam at 2.5 bar and 130.0ºC in the low-pressure section (ST-LPT-2).

The high-pressure steam at 45.0 bar and 420.0ºC generated in the HP circuit-level (HR-HPS-1) is expanded to 23.0 bar and about 338.0ºC (intermediate-pressure level) by the first-section of the BPST (ST-HPT-1) modeled by using a Compr pressure changer block in turbine model. After expanded, intermediate-pressure steam is mixed (ST-MIX-1) with intermediate-pressure steam at 23.0 bar and about 338.0ºC generated in the IP circuit-level (HR-MPS-1) of the HRSG system and with the intermediate-pressure steam at 23.0 bar and about 338.0ºC generated in the high-temperature vertical CSC (GA-CSC-1).

Intermediate-pressure steam at 23.0 bar and about 338.0ºC is expanded to 6.0 bar and about 205.0ºC by the second-section of the BPST (ST-MPT-2) modeled by using a Compr pressure changer block in turbine model. After, the steam 6.0 bar and about 205.0ºC is expanded to 2.5 bar and 130.0ºC in the third section of the BPST (ST-LPT-2) modeled by using a Compr pressure changer block in turbine model, without intermediate extractions of steam. The exhaust-steam is used as process steam (ST-

SPL-1) to supply part of the thermal energy required by the 1G-thecnologies (integrated scenario) and part of the thermal energy required by the thermochemical technologies.

As shown in Figure 56, the Aspen Plus®v8.4 flowsheet of the EBPST system in the BIG-GT/CC (SC2) is compost by: high-pressure expansion stage (ST-HPT-1); intermediate-pressure expansion stage (ST-MPT-1); low-pressure expansion stage (ST-LPT-1); steam extraction at 6.0 bar (ST-SPL-1), steam mixer (ST-MIX-1); and steam splitter (ST-SPL-2).

The Aspen Plus®v8.4 process model simulation of the EBPST (ST blocks) in the BIG-GT/CC (SC2) was developed using IAPWS-95 physical property methods considering about 79.45% isentropic efficiency (isentropic expansion), obtaining exhaust-steam at 2.5 bar and 130.0ºC in the low-pressure section (ST-LPT-1).

In the BIG-GT/CC (SC2), the high-pressure steam at 45.0 bar and 420.0ºC generated in the HP circuit-level (HR-HPS-1) is expanded to 23.0 bar and about 338.0ºC (intermediate-pressure level) by the first-section of the EBPST (ST-HPT-1) modeled by using a Compr pressure changer block in turbine model. After expanded, the steam is mixed (ST-MIX-1) with intermediate-pressure steam at 23.0 bar and about 338.0ºC generated in the IP circuit-level (HR-MPS-1) of the HRSG system and with the intermediate-pressure steam at 23.0 bar and about 338.0ºC generated in the high-temperature vertical CSC (GA-CSC-1).

Intermediate-pressure steam at 23.0 bar and about 338.0ºC is expanded to 6.0 bar and about 203.0ºC by the second-section of the EBPST (ST-MPT-1) modeled by using a Compr pressure changer block in turbine model. Part of this steam is extracted (ST-SPL-1) as process steam to supply the thermal energy required by the dehydration molecular sieve in the 1G sugarcane biorefinery (integrated scenario).

Surplus steam at 6.0 bar and 203.0ºC from the second-section of the EBPST (ST-MPT-1) is expanded to 2.5 bar and 130.0ºC (exhaust) by the third section of the EBPST (ST-LPT-1) modeled by using a Compr pressure changer block in turbine model.

The exhaust-steam together the steam at 2.5 bar and 130.0ºC from the LP circuit-level (HR-LPV-1) in the HRSG system is used as process steam (ST-SPL-2) to supply the entire 1G-thecnologies thermal energy demand (integrated scenario) and part of the thermal energy required by the thermochemical technologies.

As shown in Figure 57, Aspen Plus®v8.4 flowsheet of the CEST system in the BIG-GT/CC (SC3) is compost by: high-pressure expansion stage (ST-HPT-1); intermediate-pressure expansion stage (ST-MPT-1); low-pressure expansion stage (ST-LPT-1); condensing expansion stage (ST-LPT-2); steam extraction at 6.0 bar (ST-SPL-1); steam extraction at 2.5 bar (ST-SPL-2); water-cooled surface condenser (HR-CON-1); steam mixer (ST-MIX-1); steam splitter (ST-SPL-2); and condensed water pump (HR-PUM-4).

The Aspen Plus$^{®}$v8.4 process model simulation of the CEST (ST blocks) in the BIG-GT/CC (SC3) was developed using IAPWS-95 physical property methods considering about 76.88% isentropic efficiency (isentropic expansion), obtaining extraction-steam at 2.5 bar and 130.0ºC in the low-pressure section (ST-LPT-1).

In the BIG-GT/CC (SC3), the high-pressure steam at 120.0 bar and 540.0ºC generated in the HP circuit-level (HR-HPS-1) is expanded to 23.0 bar and about 331.0ºC (intermediate-pressure level) by the first-section of the CEST (ST-HPT-1) modeled by using a Compr pressure changer block in turbine model. After expanded, intermediate-pressure steam is mixed (ST-MIX-1) with intermediate-pressure steam at 23.0 bar and about 331.0ºC generated in the IP circuit-level (HR-MPS-1) of the HRSG system and with the intermediate-pressure steam at 23.0 bar and about 331.0ºC generated in the high-temperature vertical CSC (GA-CSC-1).

Intermediate-pressure steam at 23.0 bar and about 331.0ºC is expanded to 6.0 bar and about 203.0ºC by the second-section of the CEST (ST-MPT-1) modeled by using a Compr pressure changer block in turbine model. Part of this steam is extracted (ST-SPL-1) as process steam to supply the thermal energy required by the dehydration molecular sieve in the 1G sugarcane biorefinery (integrated scenario).

Surplus steam at 6.0 bar and 203.0ºC from the second-section of the CEST (ST-MPT-1) is expanded to 2.5 bar and 130.0ºC (exhaust) by the third section of the CEST (ST-LPT-1) modeled by using a Compr pressure changer block in turbine model. Part of this steam is extracted (ST-SPL-1) together the steam at 2.5 bar and 130.0ºC from the LP circuit-level (HR-LPV-1) in the HRSG system is used as process steam (ST-SPL-2) to supply the entire 1G-thecnologies thermal energy demand (integrated scenario).

Surplus steam at 2.5 bar and 275.0ºC from the third section of the CEST (ST-LPT-1) is expanded to 0.11 bar and 48.0ºC by the four section of the CEST (ST-LPT-2) modeled by using a Compr pressure changer block in turbine model, ensuring that the quality of the steam-exiting a CEST condensing-stage (ST-LPT-2) is greater than 90.0% (technical limit).

CEST condensing-stage (ST-LPT-2) is directly connected to water-cooled surface condenser (HR-CON-1) modeled by using a Heater exchanger block. The vacuum-pressure steam exhausted is condensed generating a water condensate (liquid phase) available to be after pumped by the condensed water pump (HR-PUM-4) back to deaerator unit (HR-DEA-1) in closed-loop cycle.

As shown in Figure 58, Aspen Plus$^{®}$v8.4 flowsheet of the CEST system in the BIG-GT/CC (SC4) is compost by: high-pressure expansion stage (ST-HPT-1); intermediate-pressure expansion stage (ST-MPT-1); low-pressure expansion stage (ST-LPT-1); condensing expansion stage (ST-LPT-2); steam extraction at 2.5 bar (ST-SPL-1); water-cooled surface condenser (HR-CON-1); and condensed water pump (HR-PUM-4).

The Aspen Plus®v8.4 process model simulation of the CEST (ST blocks) in the BIG-GT/CC (SC4) was developed using IAPWS-95 physical property methods considering about 80.52% isentropic efficiency (isentropic expansion).

In the BIG-GT/CC (SC4), the high-pressure steam at 120.0 bar and 540.0ºC generated in the HP circuit-level (HR-HPS-1) is expanded to 23.0 bar and about 323.0ºC (intermediate-pressure level) by the first-section of the CEST (ST-HPT-1) modeled by using a Compr pressure changer block in turbine model. After expanded, intermediate-pressure steam is mixed with intermediate-pressure steam at 23.0 bar and about 323.0ºC generated in the IP circuit-level (HR-MPS-1) of the HRSG system and then reheated to 23.0 bar and 540.0ºC in the reheated exchanger pipe banks (HR-RHE-1) in the HRGS intermediate-pressure circuit-level.

Intermediate-pressure steam generated in the high-temperature vertical CSC (GA-CSC-1) and the intermediate-pressure reheated steam at 23.0 bar and 540.0ºC are expanded to 6.0 bar and at about 370.0ºC in the second-section of the CEST (ST-MPT-1) modeled by using a Compr pressure changer block in turbine model. After, the steam is expanded to 2.5 bar and 275.0ºC in the third section of the CEST (ST-LPT-1) modeled by using a Compr pressure changer block. Part of this steam is extracted (ST-SPL-1) as process steam to supply part of the thermal energy required by the thermochemical technologies (standalone scenario).

Surplus steam at 2.5 bar and 275.0ºC from the third section of the CEST (ST-LPT-1) is expanded to 0.11 bar and 48.0ºC by the four section of the CEST (ST-LPT-2) modeled by using a Compr pressure changer block in turbine model, ensuring that the quality of the steam-exiting a CEST condensing-stage (ST-LPT-2) is greater than 90.0% (technical limit).

CEST condensing-stage (ST-LPT-2) is directly connected to water-cooled surface condenser (HR-CON-1) modeled by using a Heater exchanger block. The vacuum-pressure steam exhausted is condensed generating a water condensate (liquid phase) available to be after pumped (HR-PUM-4) back to deaerator unit (HR-DEA-1) in closed-loop cycle.

As shown in Figure 59, Aspen Plus®v8.4 flowsheet of the CST system in the BIG-GT/CC (SC5) is compost by: high-pressure expansion stage (ST-HPT-1); intermediate-pressure expansion stage (ST-MPT-1); low-pressure expansion stage (ST-LPT-1); condensing expansion stage (ST-LPT-2); water-cooled surface condenser (HR-CON-1); and condensed water pump (HR-PUM-4).

The Aspen Plus®v8.4 process model simulation of the CST (ST blocks) in the BIG-GT/CC (SC5) was developed using IAPWS-95 physical property methods considering about 80.52% isentropic efficiency (isentropic expansion).

In the BIG-GT/CC (SC5), the high-pressure steam at 120.0 bar and 540.0ºC generated in the HP circuit-level (HR-HPS-1) is expanded to 23.0 bar and about 323.0ºC (intermediate-pressure level) by the first-section of the CST (ST-HPT-1) modeled by using a Compr pressure changer block in turbine model. After expanded, intermediate-pressure steam is mixed with intermediate-pressure steam at 23.0 bar and about 323.0ºC generated in the IP circuit-level (HR-MPS-1) of the HRSG system and then reheated to 23.0 bar and 540.0ºC in the reheated exchanger pipe banks (HR-MPS-2) in the HRGS intermediate-pressure circuit-level.

Intermediate-pressure steam at 23.0 bar and 540.0ºC generated in the high-temperature vertical CSC (GA-CSC-1) and the intermediate-pressure reheated steam at 23.0 bar and 540.0ºC are expanded to 6.0 bar and at about 370.0ºC in the second-section of the CST (ST-MPT-1) modeled by using a Compr pressure changer block in turbine model. After, the steam is expanded to 2.5 bar and 275.0ºC in the third section of the CST (ST-LPT-1) modeled by using a Compr pressure changer block.

The low-pressure steam from the third section of the CEST (ST-LPT-1) is expanded to 0.11 bar and 48.0ºC by the four section of the CEST (ST-LPT-2) modeled by using a Compr pressure changer block in turbine model, ensuring that the quality of the steam-exiting a CEST condensing-stage (ST-LPT-2) is greater than 90.0% (technical limit).

CST condensing-stage (ST-LPT-2) is directly connected to water-cooled surface condenser (HR-CON-1) modeled by using a Heater exchanger block. The vacuum-pressure steam exhausted is condensed generating a water condensate (liquid phase) available to be after pumped (HR-PUM-4) back to deaerator unit (HR-DEA-1) in closed-loop cycle.

7.1.14 Traditional *c*ombined heat and power generation system applying extraction back-pressure steam turbine

In the thermochemical-biorefinery scenario 1 (SC1), thermochemical-biorefinery scenario 4 (SC4), and thermochemical-biorefinery scenario 5 (SC5) is considered the optimized 1G sugarcane biorefinery (1G sugarcane biorefinery) with annexed ethanol distillery using a typical solid-fuel fired boiler bottoming-cycle system (grate type) and non-condensing type extraction back-pressure steam turbine (EBPST) operating at 22.0 bar and 320.0ºC (SC1) in Rankine-cycle mode for thermal and electrical energy generation (CHP).

Part of the sugarcane bagasse (SUGARCANE BAGASSE) from mills (without use of straw) as fuel is consumed in the solid-fuel fired boiler bottoming-cycle system, the surplus bagasse (SUGARCANE BAGASSE) and the straw (SUGARCANE STRAW) available is used as feedstock in the self-sufficient in energy terms BIG-GT/CC route.

In the thermochemical-biorefinery scenario 1 (SC1), traditional 1G-CHP/EBPST (SC1) system supply part of the thermal and electrical energy required by the 1G-thecnologies, another part is supplied by the BIG-GT/CC (SC1) operating in integrated mode. In the thermochemical-biorefinery scenario 4 (SC4) and thermochemical-biorefinery scenario 5 (SC5), traditional 1G-CHP/EBPST (SC1) system supply the entire thermal and electrical energy required by the 1G sugarcane biorefinery, BIG-GT/CC (SC4) and BIG-GT/CC (SC5) operating in standalone mode.

Traditional 1G-CHP/EBPST system (SC1) with surplus biomass is simulated and detailed according to Aspen Plus®v8.4 process model simulation described in the section 5 (First generation sugarcane biorefinery).

As shown in Figure 45, Aspen Plus®v8.4 flowsheet of the 1G-CHP/EBPST (SC1) system in the BIG-ICE/CC (SC1) which is the same model with modified parameters for BIG-GT/CC (SC1) is compost by: feed tray (PR-MIX-5); conveyor boiler fuel feeders (PR-SCR-8); breakdown RYield reactor block (BO-DEV-1); burner chamber (BO-COMBU); adjust Sep separator block (BO-SEP-1); heat loss adjust Heater exchanger block (BO-HEA-1); wet ashes removal grate system (BO-SEP-2); ashes bins (BO-RES-1); air pre-filter unit (BO-FIL-1); air preheated (BO-PRE-1); advanced blower system (BO-ASP-1); feed-water pump (BO-PUM-1); low-temperature economizers and high-temperature economizers (BO-ECO-1); radiant heat adjust Heater exchanger block (BO-HEA-2 and BO-HEA-3); evaporator (BO-EVA-1); superheater (BO-SUP-1); saturated water purge (BO-SPL-3); blowdown flash vessel (BD-FLASH-1); multi-cyclone unit (BO-CYC-1); electrostatic precipitator unit (BO-ESP-1); ashes temporary storage bins (BO-RES-2); intermediate-pressure EBPST stage (ST-HPS-1); low-pressure EBPST stage (ST-LPS-1); steam extraction at 6.0 bar (ST-SPL-1); make-up water pump (BO-PUM-2); and blowdown heat recovery exchanger (BD-1).

A fraction of the bagasse from the mills (SUGARCANE BAGASSE) can be directly belt-conveyed to boiler fuel feeders (PR-SCR-8) or carried by tractors (actual system) from the bagasse pile to the conveyor feed tray (PR-MIX-5) to be fed by drum and hydraulic/pneumatic fuel feeders (PR-SCR-8) into the combustion chamber (BO-COMBU).

The Aspen Plus®v8.4 process model simulation of the typical solid-fuel fired boiler use a breakdown RYield reactors type (BO-BEV-1) as a theoretical artifice to simulate the decomposition of the non-conventional solids BAGASSE (BO-DEV-1) into its ‘constituting’ conventional components (‘ELEMENTS’). In the breakdown RYield reactor block (BO-DEV-1) is formed carbon (C), hydrogen (H_2), oxygen (O_2), chlorine (Cl_2), nitrogen oxide (NO), sulfur dioxide (SO_2), and hydrogen sulfide (H_2S) using about $16.67\%_{w/w}$ of the sulfur (S) content. Salts, minerals, ashes, and soil are specified as inert components in the devolatilization process-zone (bypass).

FORTRAN calculator block CA-BO-CS-1 is used to specify the yield distributions and the mass flow rate of each constituent component in the outlet stream according to the bagasse ultimate analysis (Table 5). The blocks BO-SPL-1 and BO-SPL-2 split the volatile material from the biomass and sent directly to the combustor chamber (BO-COMBU).

Sep separators block BO-SEP-1 as adjustment model is used to adjust the biomass conversion, the carbon conversion (CA-BO-XS-1) and the ashes content (solids formation) as bottom ashes (ASHES) or fly-ashes (FLY-ASHES). The amount of bottom ashes (ASHES) and fly-ashes (FLY-ASHES) and hers composition are controlled by BO-SEP-2 block which simulate the grate system and the automatically wet ashes removal system (BO-SEP-2), without considering the water use in the simulation (cleaning grate system). The ashes temporary storage bins (BO-RES-1) consider the heat loss (heat transported with ashes) by natural heat changes with the ambient conditions.

The solid-fuel fired boiler models consider a heat loss (BO-HEA-1) due the surface radiation and convection with to surrounding ambient. The heat loss (BO-HEA-1) is calculated by FORTRAN calculator block CA-BO-QL-1 based on the fraction of the LHV_{db} of the biomass inlet in the boiler, according to section 3.9.13 (Heat losses to surrounding ambient).

The Aspen Plus®v8.4 process model simulation of the burner chamber (BO-COMBU) was developed using RGibbs reactor type which uses the Gibbs free energy minimization method, considering all the possible solids emissions (soil and atmosphere) and gaseous emissions (atmosphere). The Gibbs free energy minimization method determines the equilibrium composition of the products resulting from the many reactions that can occur. The burner chamber (BO-COMBU) model can determine in the gaseous phase the formation of NO_2, N_2O, NO, SO_2, SO_3, NH_3, H_2S, HCL, Cl_2, COS, CHN, volatile organic compounds, and particulate matter formation (salt and solid compounds). Also, can determine in the solid phase (ashes and fly-ashes) the formation of unconverted biomass (BAGASSE and STRAW) and carbon (C), SiO_2 (biomass constitutional ash content), soil, MgO, CaO, KCl, K_2O, K_3PO_4, salts and mineral (biomass constitutional content). Gibbs free energy minimization method underestimate the formation of CaS, MgS and S. Sulfur is emitted on gaseous form in Gibbs combustion models (oxidized metals are more stable form).

Combustion air (ATMOSPHERIC AIR) is preheated (BO-PRE-1) and forced-injected in the burner chamber (BO-COMBU) by advanced blower system (BO-ASP-1) with pre-filter unit (BO-FIL-1) to protect the blower and burner from debris (PARTICLES). The amount of air employed is controlled by design specification DS-BO-FG-1 varying the mass flow rate of atmospheric air (ATMOSPHERCI AIR) inlet into the burner chamber (BO-COMBU). The model consider $8.0\%_{w/w}$ as the ratio of the oxygen mass flow rate out off the burner chamber (BO-COMBU) to the oxygen mass flow rate inlet into the burner chamber (BO-COMBU).

The liquid non-saturated feed-water from first deaerator unit (HR-DEA-1) at 1.4 bar and 105.0ºC is pumped to 22.0 bar by the feed-water pump (BO-PUM-1) and then fed into the solid-fuel fired boiler pipes banks. Non-saturated feed-water is heated at saturation conditions in the low-temperature and high-temperature economizers (BO-ECO-1) by radiant (BO-HEA-2 and BO-HEA-3) and convective heat (BO-ECO-1), is evaporate to saturated steam in the evaporator (BO-EVA-1) and superheated in the superheater (BO-SUP-1) leaving the boiler at 22.0 bar and 320ºC to be expanded in the EBPST system (ST blocks).

The temperature of the flue-gas after the air pre-heater exchanger (BO-PRE-1) is controlled by design specification DS-BO-FL-1 to be 160.0ºC varying the mass flow rate of the boiler feed-water flowing through the water-side tube bank, coupled with the design specification DS-BO-FG-1 varying the mass flow rate of the atmospheric air inlet into the burner chamber (BO-COMBU) to control the excess air ratio.

4.0%$_{w/w}$ of the saturated water mass flow rate is purged (BO-SPL-3) from the boiler as continue blowdown and then fleshed to 1.4 bar (deaerator pressure) in the blowdown flash vessel (BD-FLASH-1). The vaporized phase is sent to the first deaerator unit (HR-DEA-1) to heat recovery (reducing the amount of steam 2.5 bar used in the deaerator). The liquid phase is cooled to 30.0ºC by the blowdown heat recovery exchanger (BD-1) heating the make-up raw water (WATER FROM TREATMENT PLANT), which is pumped to 1.4 bar by the make-up water pump (BO-PUM-2) to the deaerator unit (HR-DEA-1). Blowdown remove impurities from boiler as dissolved impurities, in the Aspen Plus®v8.4 process model simulation is not considered the presence of impurities. The amount of impurities depends on the fresh-water quality, on make-up water treatment process and maintenance treatment of process water cycle.

In the spreadsheet calculation model of the treatment processes was considered the recovery of 87.0%$_{w/w}$ of the water blowdown according to Equation 24.

Particulate material content in the flue-gas (FLY-ASHES) are reduced by control particulate emissions system applying a multi-cyclone unit (BO-CYC-1) modeled by using a Cyclone solids separator block. The multi-cyclone unit (BO-CYC-1) was designed optimized with 5 cyclones (battery) to remove the gross particulate content in the exhaust-gas according to Muschelknautz calculation method for a maximum pressure drop of 0.01 bar applying spiral inlet cyclones type.

Part of the persistent fine particulate matters after the multi-cyclone unit (BO-CYC-1) is removed by the electrostatic precipitator (DR-ESP-1) modeled by suing a ESP solids separator block according to Svarovsky calculation model for vertically mounted collecting plates model with separation efficiency of 92.0% based on the migration velocity and the ratio of precipitation area. The fly-ashes (FLY AHSES) are stored in the ashes temporary storage bins (BO-RES-2) and mixed with the ASHES to be after-sent to application in the sugarcane crops.

The flue-gas from the boiler system content steam (H_2O), NO_2, N_2O, NO, SO_2, SO_3, NH_3, H_2S, HCL, Cl_2, COS, CHN, volatile organic compounds, and particulate matter (MgO, CaO, KCl, K_2O, K_3PO_4, BIOMASS, C, salts, and mineral) is mixed with the flue-gas from the HRSG system and sent to heat the drying agent and gasification agent (heat recovery).

The Aspen Plus®v8.4 process model simulation of the EBPST (ST blocks) of the 1G-CHP/EBPST (SC1) system in the BIG-GT/CC (SC1) was developed using IAPWS-95 physical property methods considering about 74.55% isentropic efficiency (isentropic expansion). The model considers exhaust-steam at 2.5 bar and 130.0ºC in the low-pressure section (ST-LPS-1).

The intermediate-pressure steam at 22.0 bar and 320.0ºC generated in the solid-fuel fired boiler pipes banks is expanded to 6.0 bar and about 198.3ºC by the first-section of the EBPST (ST-HPT-1) modeled by using a Compr pressure changer block in turbine model. After expanded, part of the steam is extracted (ST-SPL-1) to supply part of the thermal energy required by the dehydration ethanol process (1G-thecnologie).

Another part of the steam at 6.0 bar and about 198.3ºC is expanded to 2.5 bar and 130.0ºC in the second-section of the EBPST (ST-MPS-1) modeled by using a Compr pressure changer block in turbine model. The exhaust-steam at 2.5 bar and 130.0ºC is used to supply part of the 1G-thecnologies thermal energy requirements.

The electricity generated by the EBPST (ST blocks) of the 1G-CHP/EBPST (SC1) system in the BIG-GT/CC (SC1) is used to supply part of electricity required by the 1G sugarcane biorefinery. Another part is supplied by the BIG-GT/CC (SC1). The electrical potential losses (turbine-mechanical generator) by attrite in the mechanical move parts was considered as 1.0% of the mechanical energy produced by the turbine (99.0% mechanical efficiency).

Spreadsheet calculation considering the wastewater treatment process (WASTEWATER TO TREATMENT PLANT) with a maximum of $85.0\%_{w/w}$ recovery efficiency is used to determine the amount of water (TO WASTEWATER TREATMENT PLANT) is recovered and recycled to the deaerator unit (HR-DEA-1) after treatment as make-up water and the requirements of supplementary fresh-make-up water to close the water balance.

7.1.15 Multi-cells water-cooling tower

The Aspen Plus®v8.4 process model simulation consider modules of draft-packaged water-cooling induced-tower 43.0ºC/30.0ºC/27.0ºC type with capacity for 700.0 m³/hr of water mass flow rate. The model was developed using IAPWS-95 physical property methods for the water-side streams, and RKS cubic equation of state with BM alpha function property method to simulate the air-side streams and the heat transfer between the atmospheric air-side and the water-side in the water tower module (CT-TOW blocks). The heat transfer in the gas-side or liquid-side streams in the cooling water equipment users depends on the physical property methods employed in the area in which they are allocated.

The ambient condition of the atmospheric surrounding air (ATMOSPHERIC AIR) considered in the Aspen Plus®v8.4 process model simulation is 25.0ºC at atmospheric pressure with relative humidity of 80.0% and web bulb temperature at about 21.3ºC.

Figure 60 (a) shows the Aspen Plus®v8.4 flowsheet of the first-section of the multi-cells water-cooling tower for BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4). Figure 60 (b) shows the Aspen Plus®v8.4 flowsheet of the first-section of the multi-cells water-cooling tower for BIG-GT/CC (SC3), and BIG-GT/CC (SC5). Figure 61 (a) shows the Aspen Plus®v8.4 flowsheet of the second-section of the multi-cells water-cooling tower for BIG-GT/CC (SC3), and BIG-GT/CC (SC5). Figure 61 (b) shows the Aspen Plus®v8.4 flowsheet of the second-section of the multi-cells water-cooling tower for BIG-GT/CC (SC4).

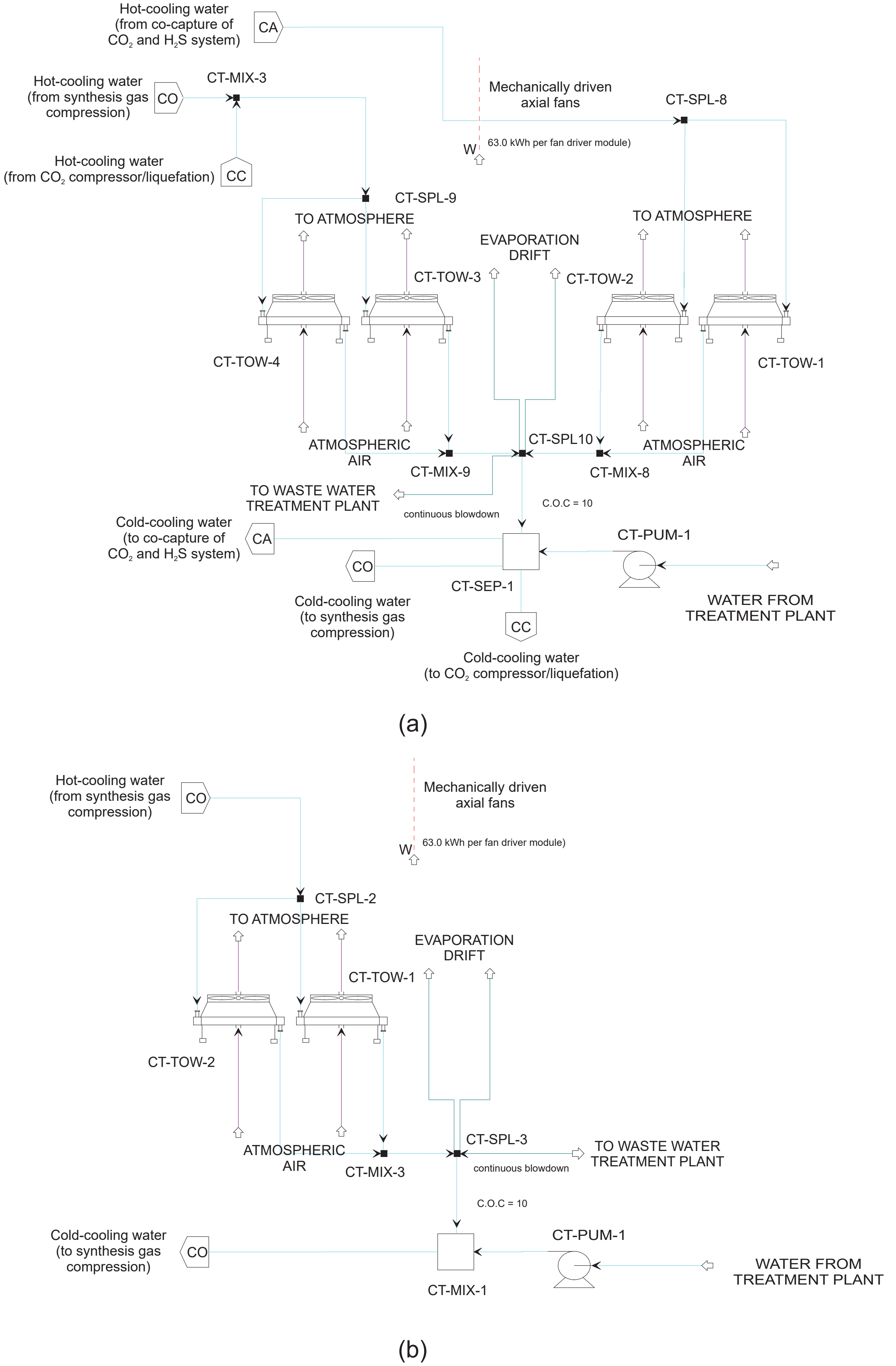
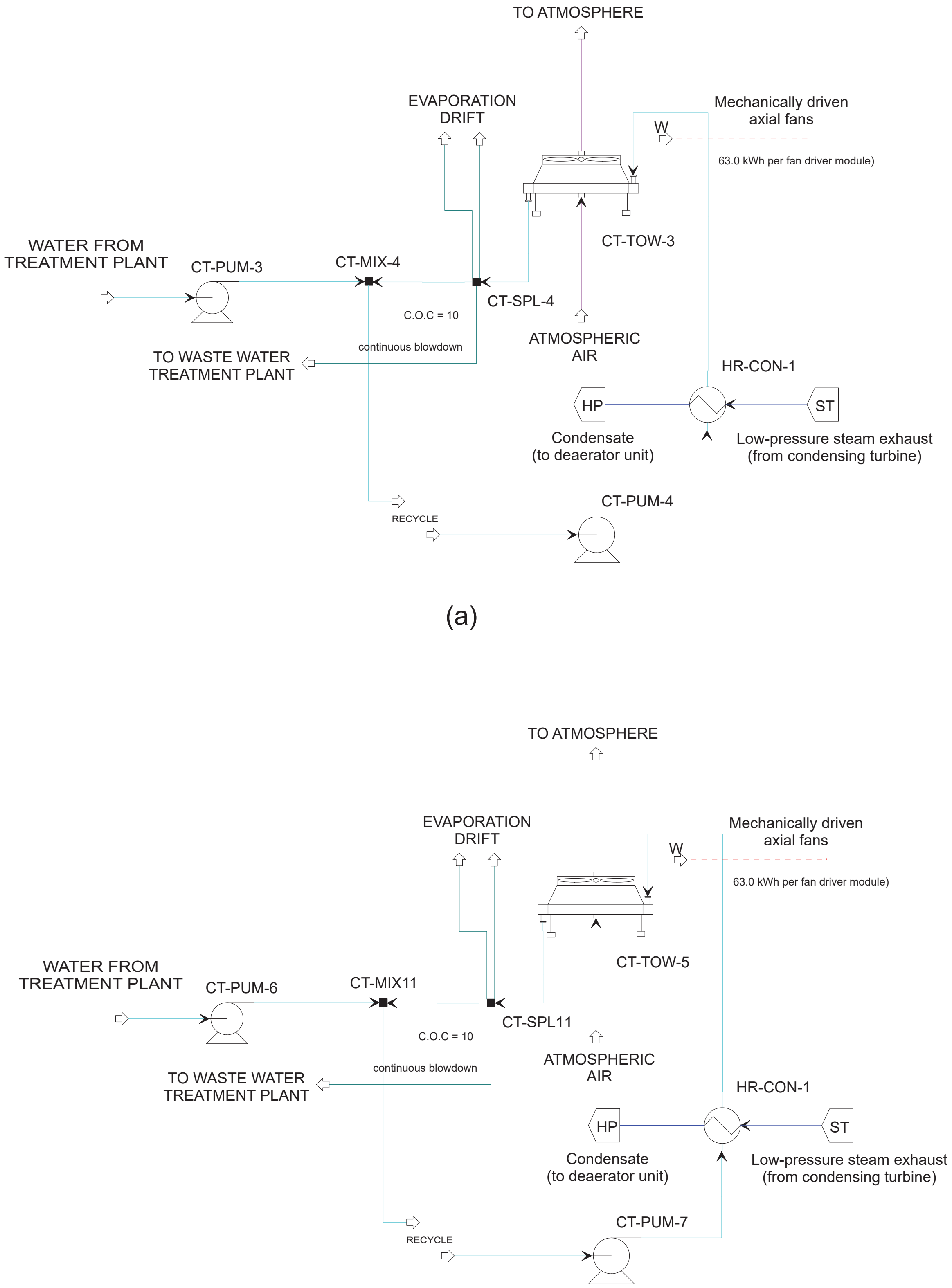


Figure 60 - Aspen Plus®v8.4 flowsheet of the first-section of multi-cells water-cooling tower for: a) BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4); and b) BIG-GT/CC (SC3) and BIG-GT/CC (SC5)



(a)

(b)

Figure 61 - Aspen Plus®v8.4 flowsheet of the second section multi-cells water-cooling tower for: a) BIG-GT/CC (SC3) and BIG-GT/CC (SC5); and b) BIG-GT/CC (SC4)

As shown in Figure 60 (a), Aspen Plus®v8.4 flowsheet of the simplified first-section of the multi-cells water-cooling tower in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4), and as shown in Figure 60 (b), Aspen Plus®v8.4 flowsheet of the simplified first-section of the multi-cells water-cooling tower for BIG-GT/CC (SC3) and BIG-GT/CC (SC5) are composts by: pumps (CT-PUM blocks); fans (CT-EFT streams); water-cooling tower modules (CT-TOW blocks); water-cooling tower basin (CT-SEP blocks); adjust losses (evaporation and drift) and blowdown system (CT-SPL blocks); and spreadsheet calculation of blowdown cycles of concentration (C.O.C) system.

As shown in Figure 61 (a), Aspen Plus®v8.4 flowsheet of the simplified second-section of the multi-cells water-cooling tower in the BIG-GT/CC (SC3) and BIG-GT/CC (SC5), and as shown in Figure 61 (b), Aspen Plus®v8.4 flowsheet of the simplified second-section of the multi-cells water-cooling tower for BIG-GT/CC (SC4) are composts by: pumps (CT-PUM blocks); fans (CT-EFT streams); water-cooling tower modules (CT-TOW blocks); water-cooling tower basin (CT-SEP blocks); adjust losses (evaporation and drift) and blowdown system (CT-SPL blocks); and spreadsheet calculation of blowdown cycles of concentration (C.O.C) system.

The multi-cells water-cooling tower (CT-blocks) provides cooling water to remove heat and adjust the process temperature to appropriate levels. The cooling water is distributed to the cooling water equipment users in the BIG-GT/CC scenarios to:

a) condense and cool-down the top gas product from the absorber (CT-HEA-2) an stripper (CT-HEA-3) columns in the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4);
b) cool down the absorber inlet lean-amine aqueous solution (CT-HEA-1) in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4);
c) cool-down the synthesis gas in the inter-stages (CO-1~3) of compression (intercooler and after-cooler) in the integrally-geared three stage centrifugal compressor in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5);
d) cool-down the CO_2 gas in the inter-stages (CO-1~5) of compression in the integrally-geared six stage centrifugal compressor (intercooler and after-cooler) and liquefier the captured CO_2 (CC-HEA-1) in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4);
e) condense the low-pressure exhausted steam from the condensing section turbine (CEST) employed in the BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5).

The Aspen Plus®v8.4 process model simulation of water-cooling tower system operating in water recirculation mode determine the requirements of cooling water heat exchanger, make-up of recycled and fresh water, water blowdown, and electric motor drives (fan drivers and pumps). In the model are used the standards design equations as defined in the section 3.9.17 (Water-cooling tower) for the modular single fan-cells arrangement operates as staged mode by sections each with variable-frequency drivers.

Multi-cells water-cooling tower (CT-TOW blocks) is determined based on the cooling capacity of 700 tonnes/hr of hot water per modular cells (CT-TOW blocks) considering mechanical axial propeller single fan-cells counter-flow draft designed (CT-TOW blocks). The numbers of cells and fans are estimated based on the mass flow rate of cooling water circulating in each of the specific sections (first and second sections).

The induced surrounding air exchange convective heat with the hot water in the water-cooling tower (CT-TOW blocks) represented as a simple HeateX exchange block (CT-TOW blocks). The surrounding air is induced upward through the fill (CT-TOW blocks) being heated from 25.0ºC to 40.0ºC. The hot cooling water flow downward through the fill (CT-TOW blocks) been cooled down from 43.0ºC to 30.0ºC. This simple model results in the overestimated amount of air in relation to reality or a more complex model (direct contact model).

In the BIG-GT/CC (SC1), BIG-GT/CC (SC2) and BIG-GT/CC (SC4) the amount of surrounding air flowing through the fill (CT-TOW blocks) of the first-section of the multi-cells water-cooling tower is determined and controlled by design specification DS-CT-FG-1, design specification DS-CT-FG-3, FORTRAN calculator block CA-CT-FG-2, and FORTRAN calculator block CA-CT-FG-4, varying the mass flow rate (CT-AIR streams) of the surrounding air passing through the fill (CT-TOW blocks) to cooling down the hot water.

In the BIG-GT/CC (SC3) and BIG-GT/CC (SC5), the amount of surrounding air flowing through the fill (CT-TOW blocks) of the first-section of the multi-cells water-cooling tower is determined and controlled by design specification DS-CT-FG-1, and FORTRAN calculator block CA-CT-FG-2, varying the mass flow rate (CT-AIR streams) of the surrounding air passing through the fill (CT-TOW blocks) to cooling down the hot water.

In the BIG-GT/CC (SC3) and BIG-GT/CC (SC5), the amount of surrounding air flowing through the fill (CT-TOW blocks) of the second-section of the multi-cells water-cooling tower is determined and controlled by design specification DS-CT-FG-3 varying the mass flow rate (CT-AIR streams) of the surrounding air passing through the fill (CT-TOW blocks) to cooling down the hot water.

In the BIG-GT/CC (SC4), the amount of surrounding air flowing through the fill (CT-TOW blocks) of the second-section of the multi-cells water-cooling tower is determined and controlled by design specification DS-CT-FG-5 varying the mass flow rate (CT-AIR streams) of the surrounding air passing through the fill (CT-TOW blocks) to cooling down the hot water.

In the BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5), treated fresh and recycled water as make-up water (WATER FROM TREATMENT PLANT) at atmospheric pressure and 25.0ºC is pumped (simplified by one pump) by make-up pump (CT-PUM-1) to the first-section of the multi-cells water-cooling tower and mixed with the down flow cooled-water at 30.0ºC in the water-cooling tower basin (CT-SEP-1). In the BIG-GT/CC (SC3), make-up water (WATER FROM TREATMENT PLANT) at atmospheric pressure and 25.0ºC is pumped by make-up pump (CT-PUM-4) to the second-section of the multi-cells water-cooling tower and mixed with the down flow cooled-water at 30.0ºC in the water-cooling tower basin (CT-MIX-4). In the BIG-GT/CC (SC4), make-up water (WATER FROM TREATMENT PLANT) at atmospheric pressure and 25.0ºC is pumped by make-up pump (CT-PUM-8) to the second-section of the multi-cells water-cooling tower and mixed with the down flow cooled-water at 30.0ºC in the water-cooling tower basin (CT-MIX-10). In the BIG-GT/CC (SC5), make-up water (WATER FROM TREATMENT PLANT) at atmospheric pressure and 25.0ºC is pumped by make-up pump (CT-PUM-3) to the second-section of the multi-cells water-cooling tower and mixed with the down flow cooled-water at 30.0ºC in the water-cooling tower basin (CT-MIX-4).

In the BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4), cooling water available at 27.0ºC (heat sink) in the first-section of the multi-cells water-cooling tower is pumped (CT-PUM-2) to co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution, pumped (CT-PUM-5) to CO_2 gas integrally-geared multi-stage centrifugal compressor, and pumped (CT-PUM-5) to synthesis gas compression (conditioning). In the BIG-GT/CC (SC3) and BIG-GT/CC (SC5), cooling water available at 27.0ºC (heat sink) in the first-section of the multi-cells water-cooling tower is pumped (CT-PUM-2) to synthesis gas compression (conditioning).

In the BIG-GT/CC (SC3), cooling water available at 27.0ºC (heat sink) for the second-section of the multi-cells water-cooling tower is pumped (CT-PUM-5) to CEST condenser (HR-CON-1). In the BIG-GT/CC (SC4), cooling water available at 27.0ºC (heat sink) for the second-section of the multi-cells water-cooling tower is pumped (CT-PUM-9) to CEST condenser (HR-CON-1). In the BIG-GT/CC (SC5), cooling water available at 27.0ºC (heat sink) for the second-section of the multi-cells water-cooling tower is pumped (CT-PUM-4) to CEST condenser (HR-CON-1)

The cooling water at 27.0ºC is heated by passing through the user equipments to 43.0ºC (tower design limit), the hot water is duct-sent back to the multi-cells water-cooling tower (CT blocks) and discharged inlet into the cooling tower cells (CT-TOW blocks) at 43.0ºC to be cooled in a water closed-loop cycle system. The amount of water necessary for cooling down the equipments at required levels is determined and controlled by a set of design specification (e.g.: DS-CA-TL-1, DS-CA-TL-2, DS-CA-TL-3, DS-CT-FL-2, DS-CT-FL-3, DS-CO-TL-1, DS-CO-TL-2, and DS-CT-FL-5) varying the mass flow rate of cooling water flows through the equipment users. The cooling water is heated at the limit of 43.0ºC (water-cooling tower design) and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

Hot water at 43.0ºC is fed in the first, second, and third sections of multi-cells water-cooling tower (CT-TOW blocks) to be cooled down to 30.0ºC by direct contact in counter-flow with vertically upward induced (mechanical axial propeller fans) surrounding air through the fill (CT-TOW blocks) at atmospheric pressure and 25.0ºC. The model consider relative humidity of 80.0% and web bulb temperature at about 21.3ºC, which results in a range of 13.0ºC and an approach of 8.7ºC.

The Aspen Plus®v8.4 process model simulation of water-cooling tower system considers the water evaporation rate obtained by the Equation 21, and the drift loss rate obtained by the Equation 22. In the BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4), the equations are employed in the CT-SPL-11 for the first-section of the multi-cells water-cooling tower to determine the CT-EVA-1 and CT-DRI-1 streams by using FORTRAN calculator block CA-CT-LL-1. In the BIG-GT/CC (SC3) and BIG-GT/CC (SC5), the equations are employed in the CT-SPL-3 for the first-section of the multi-cells water-cooling tower to determine the CT-EVA-1 and CT-DRI-1 streams by using FORTRAN calculator block CA-CT-LL-1. In the BIG-GT/CC (SC3) and BIG-GT/CC (SC5), the equations are employed in the CT-SPL-4 for the second-section of the multi-cells water-cooling tower to determine the CT-EVA-2 and CT-DRI-2 streams by using FORTRAN calculator block CA-CT-LL-2. In the BIG-GT/CC (SC4), the equations are employed in the CT-SPL-11 for the second-section of the multi-cells water-cooling tower to determine the CT-EVA-2 and CT-DRI-2 streams by using FORTRAN calculator block CA-CT-LL-2.

A tower basin blowdown (CT-BLO streams) to remove or reduce the concentration of the impurities is developed in the Aspen Plus®v8.4 process model simulation according to Equation 25 as continuous blowdown system. In the BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4), first-section of the multi-cells water-cooling tower (CT-SPL-10) considers the tower basin blowdown (CT-BLO-1) and blowdown cycles of concentration (C.O.C) determined by using FORTRAN calculator block CA-CT-LL-1 to remove the solids formed (not included in the Aspen Plus®v8.4 process model simulation).. In the BIG-GT/CC (SC3) and BIG-GT/CC (SC5), first-section of the multi-cells water-cooling tower (CT-SPL-3) considers the tower basin blowdown (CT-BLO-1) and blowdown cycles of concentration (C.O.C) determined by using FORTRAN calculator block CA-CT-LL-1 to remove the solids formed (not included in the Aspen Plus®v8.4 process model simulation). In the BIG-GT/CC (SC3) and BIG-GT/CC (SC5), second-section of the multi-cells water-cooling tower (CT-SPL-4) considers the tower basin blowdown (CT-BLO-2) and blowdown cycles of concentration (C.O.C) determined by using FORTRAN calculator block CA-CT-LL-2 to remove the solids formed (not included in the Aspen Plus®v8.4 process model simulation). In the BIG-GT/CC (SC4), second-section of the multi-cells water-cooling tower (CT-SPL-11) considers the tower basin blowdown (CT-BLO-2) and blowdown cycles of concentration (C.O.C) determined by using FORTRAN calculator block CA-

CT-LL-2 to remove the solids formed (not included in the Aspen Plus®v8.4 process model simulation).

In the BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5), make-up water (WATER FROM TREATMENT PLANT) is pumped by make-up pump (CT-PUM-1) to the first-section of the multi-cells water-cooling tower basin (CT-SEP-1). In the BIG-GT/CC (SC3), make-up water (WATER FROM TREATMENT PLANT) is pumped by make-up pump (CT-PUM-4) to the second-section of the multi-cells water-cooling tower basin (CT-MIX-4). In the BIG-GT/CC (SC4), make-up water (WATER FROM TREATMENT PLANT) is pumped by make-up pump (CT-PUM-8) to the second-section of the multi-cells water-cooling tower basin (CT-MIX-10). In the BIG-GT/CC (SC5), make-up water (WATER FROM TREATMENT PLANT) is pumped by make-up pump (CT-PUM-3) to the second-section of the multi-cells water-cooling tower basin (CT-MIX-4)

The make-up water for the multi-cells water-cooling tower is determined based on the water losses by evaporation (CT-EVA streams), drift (CT-DRI streams), and tower basin blowdown (CT-BLO streams), according to Equation 23.

In this research Master's degree, is considered a recovery of 87.0%$_{w/w}$ of the water blowdown after the treatment as available cooling water to reuse/recycle at 27.0ºC. The amount of water recovered is determined by spreadsheet calculation model of the cooling water treatment process according to Equation 24. The discarded water fraction contains a high concentration of impurities (e.g.: minerals and salts), not included in the Aspen Plus®v8.4 process model simulation.

The electricity required by the large mechanically driven axial fans (CT-EFT work streams) to induce the surrounding air upward through the fill in the cell-tower module (CT-TOW blocks) are estimated of 63.0 kWh per fan driver (module). The total of electricity required by the fan drivers is based on the number of cells (CT-TOW blocks) that compose the multi-cells water-cooling tower. The electricity consumed by the mechanical drivers in the axial fans (CT-EFT work streams) is estimated based on the Equation 26.

In the BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5), the electricity required (CT-EFT-1 work stream) in the first-section of the multi-cells water-cooling tower by the large mechanically driven axial fans (CT-EFT-1 work stream) to induce the surrounding air upward through the fill in the cell-tower module (CT-TOW blocks) is determined and controlled by FORTRAN calculator block CA-CT-EF-1 varying the input value of the CT-EFT-1 work stream according to the number of necessary fans (63.0 kWh per fan driver).

In the BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5), the electricity required (CT-EFT-2 work stream) in the second-section of the multi-cells water-cooling tower by the large mechanically driven axial fans (CT-EFT-2 work stream) to induce the surrounding air upward through the fill in the cell-tower module (CT-TOW blocks) is determined and controlled by FORTRAN calculator block CA-CT-EF-1 varying the input value of the CT-EFT-1 work stream according to the number of necessary fans (63.0 kWh per fan driver).

7.1.16 Water cycles

The water cycle balance consider receive water: from treatment plant (BO-L-6) to process make-up water to deaerator unit (HR-DEA-1) in the BIG-GT/CC (SC1); from treatment plant (CO-L-4) to process make-up water to deaerator unit (HR-DEA-1) in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5); from treatment plant (CA-L-32) to washer packed-column section (CA-WAS-1) in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4); from treatment plant (PO-L-1 and PO-L-3) to desuperheater units (PO-MIX-1 and PO-MIX-2) in the BIG-GT/CC (SC1), BIG-GT/CC (SC2) and BIG-GT/CC (SC3); from treatment plant (GT-L-1) to three-circuit water inter-cooler exchanger (GT-1) in the high-performance sequential combustion full-flow advanced EvGT in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5); from treatment plant (CT-L-1) to first-section of water-cooling tower system in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5); from treatment plant (CT-L-17) to second-section of water-cooling tower system in the BIG-GT/CC (SC3) and BIG-GT/CC (SC5); and from treatment plant (CT-L-57) to second-section of water-cooling tower system in the BIG-GT/CC (SC4).

Also, sends wastewater: to treatment plant (BD-BLO-1) from boiler liquid-phase water blowdown (BD-FLA-1) in the BIG-GT/CC (SC1); to treatment plant (SC-L-12) from the excess of the wastewater recovered in the low-temperature synthesis gas wet cleaning system (SC-SPL-2) in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5); to disposal (SC-SLUR) from the sludge phase (50%$_{w/w}$ of water content) removed in the low-temperature synthesis gas wet cleaning system (SC-SPL-2) in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5); to treatment plant (CA-L-17) from the excess of the wastewater recovered from the striper water bleed (CA-SPL-4) in the co-capture of CO_2 and H_2S by using MEA-based absorbing-solution in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4); to disposal (CA-L-29) from the reclaimer carbon-based filter (CA-SEP-1) in the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4); to treatment plant (CO-BLO-1) from the condenser knock-out drum in the integrally-geared centrifugal three stages compressor (CO-FLA-4) in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5); to treatment plant (GT-

BLO-1) from the condenser knock-out drum (GT-FLA-1) in the high-performance sequential combustion full-flow advanced EvGT in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5); to treatment plant (CC-BLO-1) from the condenser knock-out drum in the CO_2 gas integrally-geared centrifugal six stages compressor (CC-FLA-7) in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4); to treatment plant (CT-BLO-1) from water-cooling tower blowdown (CT-SPL blocks) in the first-section of the multi-cells water-cooling tower in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5); and to treatment plant (CT-BLO-2) from water-cooling tower blowdown (CT-SPL blocks) in the second-section of the multi-cells water-cooling tower in the BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5).

Process steam/water losses occur due: water evaporation or condensation (PO-BLO-1) in equipments and pipe lines (PO-SPL-1 or PO-SPL-2) discharge $5.0\%_{w/w}$ of the process steam at 2.5 bar (PO-BLO-1) in the BIG-GT/CC (SC1), BIG-GT/CC (SC2) and BIG-GT/CC (SC3); treatment of boiler water blowdown discharge $15.0\%_{w/w}$ of the purged water (BD-BLO-1) (recovery and recycle $85.0\%_{w/w}$ of the water blowdown) in the BIG-GT/CC (SC1); sludge disposal discharge $100.0\%_{w/w}$ of the water content in the sludge phase (SC-SLUR) in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5); treatment of the excess of recovered water in the low-temperature synthesis gas wet cleaning system discharge $5.0\%_{w/w}$ of the water (SC-L-12) (recovery and recycle $95.0\%_{w/w}$ of the recovered water) in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5); treatment of the excess of water recovered in the co-capture of CO_2 and H_2S by using MEA-based solution discharge $15.0\%_{w/w}$ of the water in excess (CA-L-17) (recovery and recycle of $85.0\%_{w/w}$ of the water in excess) in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4); filtered amine residue disposal discharge $100.0\%_{w/w}$ of the water content in the residue fraction (CA-L-29) in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), and BIG-GT/CC (SC4); treatment of the water from the condenser knock-out drums discharge $5.0\%_{w/w}$ of the water (CO-BLO-1 and GT-BLO-1 streams) (recovery and recycle of $95.0\%_{w/w}$ of the condensed water) in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5); treatment of the water from the condenser knock-out drum in the CO_2 gas integrally-geared centrifugal six stages compressor (CC-FLA-7) discharge $5.0\%_{w/w}$ of the water (CC-BLO-1) (recovery and recycle of $95.0\%_{w/w}$ of the condensed water) in the BIG-GT/CC (SC1), BIG-GT/CC (SC2) and BIG-GT/CC (SC4); water evaporation (CT-EVA-1) and drift (CT-DRI-1) in the first-section of the water-cooling tower discharge $100.0\%_{w/w}$ of the water-stream in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5); water evaporation (CT-EVA-2) and drift (CT-DRI-2) in the second-section of the water-cooling tower discharge $100.0\%_{w/w}$ of the water-stream in the BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5); treatment of the first-section of the water-cooling tower blowdown discharge $13.0\%_{w/w}$ of the purged water

(CT-BLO-1) (recovery and recycle of 87.0%$_{w/w}$ of the water blowdown) in the BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5); and treatment of the second-section of the water-cooling tower blowdown discharge 13.0%$_{w/w}$ of the purged water (CT-BLO-2) (recovery and recycle of 87.0%$_{w/w}$ of the water blowdown) in the BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5).

As shown in Figure 55, deaerator unit (HR-DEA-1) in the BIG-GT/CC (SC1) receive steam from the flash vessel (BD-FLASH-1) at 1.4 bar (deaerator pressure) and 109.0ºC (BD-G-1), steam at 2.5 bar and 130.0ºC (HR-G-15) from the HRSG LP circuit-level, pre-heated fresh-water at 1.4 bar and 43.0ºC (BO-L-8) as part of the make-up water (WATER FROM TREATEMENT PLANT) required in the deaerator unit (HR-DEA-1), water from the 1G sugarcane biorefinery processes at 2.5 bar and 90.0ºC (PO-L-7 and PO-L-8), water at 2.2 bar and 123.0ºC (CA-L-23) from the stripper reboiler (CA-REB-1) in the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution (CA blocks), and heated make-up raw water (WATER FROM TREATEMENT PLANT) at 1.4 bar and 105.0ºC (HR-L-17) closing the process water loop-cycle. Also, as shown in Figure 55, deaerator unit (HR-DEA-1) in the BIG-GT/CC (SC1) send degassed and conditioned water at 1.4 bar and 105.0ºC to solid-fuel fired boiler (1G-thecnology) (HR-L-15), to HRSG system (HR-L-14), and to high-temperature vertical CSC (HR-L-16).

As shown in Figure 56, deaerator unit (HR-DEA-1) in the BIG-GT/CC (SC2) receive steam at 2.5 bar and 130.0ºC (HR-G-13) from the HRSG LP circuit-level, water from the 1G sugarcane biorefinery processes at 2.5 bar and 90.0ºC (PO-L-7 and PO-L-8), water at 2.2 bar and 123.0ºC (CA-L-23) from the stripper reboiler (CA-REB-1) in the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution (CA blocks); and heated make-up raw water (WATER FROM TREATEMENT PLANT) at 1.4 bar and 105.0ºC (HR-L-16) closing the process water loop-cycle. Also, as shown in Figure 56, deaerator unit (HR-DEA-1) in the BIG-GT/CC (SC2) send degassed and conditioned water at 1.4 bar and 105.0ºC to HRSG system (HR-L-14), and to high-temperature vertical CSC (HR-L-15).

As shown in Figure 57, deaerator unit (HR-DEA-1) in the BIG-GT/CC (SC3) receive steam at 2.5 bar and 130.0ºC (HR-G-12) from the HRSG LP circuit-level, water from the 1G sugarcane biorefinery processes at 2.5 bar and 90.0ºC (PO-L-7 and PO-L-8), heated make-up raw water (WATER FROM TREATEMENT PLANT) at 1.4 bar and 105.0ºC (HR-L-20), and condensed exhaust-steam at 1.4 bar and at about 48.0ºC (HR-L-14) from the CEST condenser closing the process water loop-cycle. Also, as shown in Figure 57, deaerator unit (HR-DEA-1) in the BIG-GT/CC (SC3) send degassed and conditioned water at 1.4 bar and 105.0ºC to HRSG system (HR-L-18) and to high-temperature vertical CSC (HR-L-19).

As shown in Figure 58, deaerator unit (HR-DEA-1) in the BIG-GT/CC (SC4) receive steam at 2.5 bar and 130.0ºC (HR-G-13) from the HRSG LP circuit-level, water at 2.2 bar and 123.0ºC (CA-L-23) from the stripper reboiler (CA-REB-1) in the co-capture of

CO_2 and H_2S by using MEA-based aqueous absorbing-solution (CA blocks), heated make-up raw water (WATER FROM TREATEMENT PLANT) at 1.4 bar and 105.0ºC (HR-L-18), and condensed exhaust-steam at 1.4 bar and at about 48.0ºC (HR-L-14) from the CEST condenser closing the process water loop-cycle. Also, as shown in Figure 58, deaerator unit (HR-DEA-1) in the BIG-GT/CC (SC4) send degassed and conditioned water at 1.4 bar and 105.0ºC to HRSG system (HR-L-16), and to high-temperature vertical CSC (HR-L-17).

As shown in Figure 59, deaerator unit (HR-DEA-1) in the BIG-GT/CC (SC5) receive steam at 2.5 bar and 130.0ºC (HR-G-13) from the HRSG LP circuit-level, heated make-up raw water (WATER FROM TREATEMENT PLANT) at 1.4 bar and 105.0ºC (HR-L-20) and condensed exhaust-steam at 1.4 bar and at about 48.0ºC (HR-L-14) from the CEST condenser closing the process water loop-cycle. Also, as shown in Figure 59, deaerator unit (HR-DEA-1) in the BIG-GT/CC (SC5) sent degassed and conditioned water at 1.4 bar and 105.0ºC to HRSG system (HR-L-18) and to high-temperature vertical CSC (HR-L-19).

The amount of low-pressure steam at 2.5 bar and 130.0ºC from the HRSG LP circuit-level destined to deaerator unit (HR-DEA-1) is determined and controlled by design specification DS-HR-TL-1 varying the water/steam mass flow rate in the HRSG LP circuit-level and estimate-used into the deaerator unit (HR-DEA-1) as degassing agent. Low-pressure steam at 2.5 bar and 130.0ºC is used mainly to remove dissolved O_2 and CO_2 content in the process water cycle by raises the deaerator water temperature (make-up water and process water condenser return) to 1.4 bar and 105.0ºC in the deaerator unit (HR-DEA-1).

In the BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5), the make-up water supply to deaerator unit (HR-DEA-1) from the water treatment plant is based on the mass balance of the process steam/water losses and recycled water cycle. The amount of water required in the BIG-GT/CC (SC2) and BIG-GT/CC (SC4) is determined and controlled by design specification DS-CO-FL-1 and design specification DS-HR-FL-3 varying the mass flow rate of water (WATER FROM TREATMENT PLANT) fed into the deaerator unit (HR-DEA-1). The amount of water required in the BIG-GT/CC (SC3) and BIG-GT/CC (SC5) is determined and controlled by design specification DS-CO-FL-1 and design specification DS-HR-FL-4 varying the mass flow rate of water (WATER FROM TREATMENT PLANT) fed into the deaerator unit (HR-DEA-1). The amount of water required in the BIG-GT/CC (SC1) is determined and controlled by design specification DS-CO-FL-1, design specification DS-HR-FL-1 and controlled by design specification DS-AE-FL-1 varying the mass flow rate of water (WATER FROM TREATMENT PLANT) fed into the deaerator unit (HR-DEA-1).

Make-up water supplied to the water-cooling tower system from the water treatment plant is based on the mass balance of the water-cooling tower system considering losses associated with evaporation, drift, and blowdown. In the BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4), and BIG-GT/CC (SC5), make-up water supplied (CT-L-1) into the first-section of the water-cooling tower system is controlled by design specification DS-CT-FL-1 varying the mass flow rate of water (WATER FROM TREATMENT PLANT). In the BIG-GT/CC (SC3) and BIG-GT/CC (SC5), make-up water supplied (CT-L-17) into the second-section of the water-cooling tower system is controlled by design specification DS-CT-FL-2 varying the mass flow rate of water (WATER FROM TREATMENT PLANT). In the BIG-GT/CC (SC4), make-up water supplied (CT-L-57) into the second-section of the water-cooling tower system is controlled by design specification DS-CT-FL-4 varying the mass flow rate of water (WATER FROM TREATMENT PLANT).

7.1.17 Make-up water and water treatments

The mass flow rate of make-up water to treatment plant (fresh water) is determined using spreadsheet calculation models by a global mass balance of the complete water cycle considering the treatment of the wastewater in the wastewater treatment plant (not simulated), estimated according the spreadsheet calculation model of the water cycle (losses, recycles, and reuse model).

Three distinct use types are required for the BIG-GT/CC scenarios, classified as:

a) make-up water for water-cooling tower system: fresh-water required by the cooling water cycle is defined by the mass flow rate of the evaporation, drift, and tower basin blowdown losses (not recovered water);
b) make-up water for process water cycle: fresh-water required by the process water cycle is defined by the mass flow rate of the evaporative process and condensation losses in pipeline and equipments, by vent streams, blowdown losses, and condensate knock-outs (not recovered);
c) make-up water for high-performance sequential combustion full-flow advanced EvGT water cycle: fresh-water required by the EvGT cooling water circuits and humidifier tower can be defined by the mass flow rate of the evaporative process and the entrained water/vapor in the humidified air destined to the EvGT sequential combustion dual-chambers system.

The recovered water fraction after the wastewater treatment to recycle/reuse is considered as “fresh” water (subtracting in the quantity of fresh-water intake) and the water fraction discharged (not recovered) with the impurities removed in the wastewater treatment process a water losses. The water treatment is simplified by the follow categories:

a) make-up raw water treatment: considers only the make-up of fresh-water obtained from the global mass balance of the complete water cycle, taking into account the recycle and reuse of available water;
b) cooling water treatment (maintenance): considers the make-up raw water obtained from the mass balance of the water tower cycle and the water circulating in the water tower cycle in closed loop-cycle (water maintenance), taking into account the recycle and reuse of available water;
c) process water treatment (maintenance): considers the make-up raw water obtained from the mass balance of the water process cycle and the water circulating in the water process cycle in closed loop-cycle (water maintenance), taking into account the recycle and reuse of available water;
d) cooling water treatment for injection in the high-performance sequential combustion full-flow advanced EvGT: considers make-up raw water obtained from the mass balance of the cooling water circuits, and the water injected by the humidified air in the EvGT sequential combustion dual-chambers system.

The chemicals compounds and their consumption for treating water are determined by spreadsheet calculation model according to the type of water treatment required (make-up water, process water, cooling water and water special treatment. The water treatment is based on the water treatment processes available in the Ecoinvent 3 library (unit) in SimaPro®v.7.3.3 software and in the water treatment process defined by the division of AIB of the CTBE/CNPEM for the 1G sugarcane biorefinery.

Table 20 – Aspen Plus®v8.4 simulation parameters (input and output) of BIG-GT/CC routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	BIG-GT/CC route scenarios				
	SC1	SC2	SC3	SC4	SC5
Thermochemical-biorefinery					
Cane stalks (tonnes/hr) 4.0 Mtc (basis)	503.018	503.018	503.018	503.018	503.018
Sugar production (tonnes/hr)	25.559	25.559	25.559	25.559	25.559
Anhydrous ethanol production (tonnes/hr)	21.013	21.013	21.013	21.013	21.013
Electricity exported to the electric power grid (MWh)	137.084	131.590	170.280	203.439	212.860
Installed power generation capacity (MW)	191.597	189.442	231.855	266.653	274.890
Electricity consumed by the thermochemical-biorefinery (MWh)	54.513	56.221	61.574	63.214	62.031
Available raw biomass [a]					
Sugarcane bagasse available for use (tonnes/hr)	133.150	133.150	133.150	133.150	133.150
Sugarcane straw available for use (tonnes/hr)	42.279	42.279	42.279	42.279	42.279
Sugarcane bagasse imported by the BIG-GT/CC route (tonnes/hr)	none	none	none	87.396	87.396
Sugarcane bagasse reserve (tonnes/hr)	6.658	6.658	6.658	13.316	13.316
Sugarcane bagasse moisture content (%)	50.0	50.0	50.0	50.0	50.0
Sugarcane straw moisture content (%)	15.0	15.0	15.0	15.0	15.0
Consumption of sugarcane bagasse by the BIG-GT/CC route (tonnes/hr)	93.604	126.492	126.492	126.492	126.492
Consumption of sugarcane straw by the BIG-GT/CC route (tonnes/hr)	42.279	42.279	42.279	42.279	42.279
Consumption of sugarcane bagasse by the 1G-CHP/EBPST system (tonnes/hr)	32.888	none	none	81.376	81.376
Consumption of sugarcane straw by the 1G-CHP/EBPST system (tonnes/hr)	none	none	none	none	none
Dry biomass consumed in the BIG-GT/CC route (tonnes/hr) [a]	82.319	98.764	98.764	40.691	40.691
Surplus biomass (tonnes/hr) [a]	none	none	none	none	none
LHV_{AR} of bagasse (MJ/kg)	7.45	7.45	7.45	7.45	7.45
LHV_{AR} of straw (MJ/kg)	17.57	17.57	17.57	17.51	17.51
1G sugarcane biorefinery with annexed ethanol distillery [(int)]					
CHP/ST system type	CHP/EBPST (SC1)	none	none	CHP/EBPST (SC1)	CHP/EBPST (SC1)
Integration type	Integrated	Integrated	Integrated	Standalone	Standalone
Electricity required by the 1G sugarcane biorefinery (MWh)	15.0	15.0	15.0	15.0	15.0
Steam demand at 6.0 bar (dehydration) (tonnes/hr)	14.175	14.175	14.175	14.175	14.175
Steam demand at 2.5 bar (process) (tonnes/hr)	184.945	184.945	184.945	184.945	184.945

Table 20 – Aspen Plus®v8.4 simulation parameters (input and output) of BIG-GT/CC routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	**BIG-GT/CC route scenarios**				
	SC1	**SC2**	**SC3**	**SC4**	**SC5**
Biomass handling and sizing for gasification process					
Electricity required for sugarcane bagasse handling and milling (MWh)	2.059	2.783	2.783	2.783	2.783
Electricity required for sugarcane straw handling and milling (MWh)	0.334	0.334	0.334	0.334	0.334
Biomass multi-step drying process and control particulate emissions [a]					
Thermal energy required by the biomass dryers (GJ/hr) [a]	618.9	817.045	817.033	817.033	817;045
HHV_{AR} of biomass mix (MJ/kg) [a]	17.02	17.01	17.01	17.01	17.01
LHV_{AR} of biomass mix (MJ/kg) [a]	15.52	15.51	15.51	15.51	15.51
LHV_{db} of biomass mix (MJ/kg) [a]	17.53	17.53	17.53	17.53	17.53
Biomass mix moisture (%) [a]	10.00	10.00	10.00	10.00	10.00
Gasification of biomass in an atmospheric CFB directly-heated gasifier [a]					
Gasification agents	Air / Steam	Air / Steam	Air / Steam	Air / Steam	Air / Steam
Atmospheric air flow into the gasifier (tonnes/hr)	167.495	202.280	200.850	200.878	200.841
Steam at 2.5 bar flow into the gasifier (tonnes/hr)	35.579	42.661	42.661	42.661	42.661
Raw synthesis gas temperature (ºC)	850.0	850.0	850.0	850.0	850.0
Air agent inlet temperature (ºC)	150.0	130.0	150.0	150.0	150.0
Steam agent inlet temperature (ºC)	150.0	150.0	150.0	150.0	150.0
Equivalence ratio (ER_{AIR})	0.357	0.359	0.356	0.357	0.357
Steam-to-biomass ratio (STBR)	0.50	0.50	0.50	0.50	0.50
Carbon conversion (%)	98.0	98.0	98.0	98.0	98.0
Hydrogen mol flow rate (mol/hr)	2,447.4	2,923.4	2,936.3	2,935.7	2,936.0
Monoxide carbon mol flow rate (mol/hr)	1,646.7	1,966.9	1,975.4	1,974.8	1,975.4
H_2/CO ratio	1.486	1.486	1.486	1.486	1.486
Gasifier cold-gas efficiency (%) [b]	68.72	68.61	68.74	68.74	68.74
Gasifier hot-gas efficiency (%) [b]	91.92	91.91	91.94	91.94	91.94
Synthesis gas flow mass rate (tonnes/hr)	291.226	350.750	349.320	349.320	349.310
HHV_{db} of synthesis gas (MJ/kg)	4.81	4.78	4.82	4.82	4.82
LHV_{db} of synthesis gas (MJ/kg)	4.34	4.31	4.35	4.35	4.35
Generation of bottom particulate material (tonnes/hr) [f]	4.201	5.135	5.135	5.135	5.135
Olivine mass flow rate - make-up (kg/hr)	822.96	956.649	956.649	956.649	956.649
MgO mass flow rate - make-up (kg/hr)	215.290	250.2641	250.2641	250.2641	250.2641

Table 20 – Aspen Plus® v8.4 simulation parameters (input and output) of BIG-GT/CC routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	BIG-GT/CC route scenarios				
	SC1	SC2	SC3	SC4	SC5
Syngas cooling and heat recovery					
Fines-particulate matters removed by multi-cyclone system (kg/hr)	154.411	194.0651	194.0651	194.0651	194.0651
Intermediate-pressure steam at 23 bar generated by the HT-CSC (tonnes/hr)	89.970	108.366	108.172	92.349	91.943
Intermediate-pressure steam temperature (ºC)	337.9	337.9	330.8	540.0	540.0
Low-pressure steam at 2.5 bar generated by the LT-CSC (tonnes/hr)	35.579	42.661	42.661	42.661	42.661
Low-pressure steam temperature (ºC)	150.0	150.0	150.0	150.0	150.0
Synthesis gas temperature after the HT-CSC (ºC)	318.0	318.0	321.0	318.0	321.0
Synthesis gas temperature after the LT-CSC (ºC)	124.0	124.0	120.0	124.0	120.0
Low-temperature synthesis gas wet cleaning system					
Recirculation of water in spray scrubber (tonnes/h)	3.804	4.482	3.722	4.469	3.721
Recirculation of water in condenser cooler (tonnes/h)	1097.593	1320.775	1291.817	1314.338	1291.734
Electricity required by the blower (MWh)	1.820	2.188	2.183	2.188	2.183
Particulate removal by spray scrubber, condenser cooler and venturi system (kg/hr)	89.0	112.0	112.0	112.0	112.0
Persistent fine particles removal by WESP (kg/hr)	27.0	35.0	35.0	35.0	35.0
Generation of slurry (kg/hr)	221.785	278.593	278.816	278.148	277.767
Excess of water sent off-site to wastewater treatment plant (tonnes/hr)	25.123	30.404	30.110	30.097	29.997
Synthesis gas temperature after the wet cleaning system (ºC)	50.0	50.0	50.0	50.0	50.0
Co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution					
Synthesis gas pressure inlet in the absorber (bar)	1.1	1.1	1.1	1.1	1.1
Pressure of acid gas flow-out the desorber (bar)	1.7	1.7	1.7	1.7	1.7
Acid gas removal (captured) (tonnes/hr)	60.606	73.034	none	72.725	none
CO_2 removal efficiency (%)	90.0	90.0	none	90.0	none
H_2S content in the acid gas stream ($\%_{mol}$)	449 PPM	437 PPM	none	439 PPM	none
MEA concentration ($\%_{w/w}$)	30.0	30.0	none	30.0	none
Consumption of MEA by the system (kg/hr)	154.070	180.354	none	146.1785	none
Lean MEA aqueous absorbing-solution mass flow rate (tonnes/hr) [d]	865.0	1028.0	none	1023.0	none
Consumption of thermal energy by the stripper reboiler (GJ/hr)	223.695	268.525	none	267.229	none
Fresh cool-make-up water to synthesis gas washer (kg/hr)	75.0	100.0	none	100.0	none
Excess of water sent to wastewater treatment plant (tonnes/hr)	8.966	10.754	none	10.859	none
Filtered residues sent to wastewater treatment plant and final disposal (kg/hr)	305.335	357.815	none	355.752	none

Table 20 – Aspen Plus®v8.4 simulation parameters (input and output) of BIG-GT/CC routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	BIG-GT/CC route scenarios				
	SC1	**SC2**	**SC3**	**SC4**	**SC5**
CO_2 compression and storage/use (geological storage)					
Cooling water required by the system (tonnes/hr)	3693.096	4432.860	none	4404.492	none
Pressure required to liquefier CO_2 and to injection (bar)	73.0 / 150.0	73.0 / 150.0	none	73.0 / 150.0	none
Final generation of Liquid CO_2 to injection (reservoir)	59.560	71.766	none	71.470	none
Number of compression stages (+1 liquid pump stage)	6+1	6+1	6+1	6+1	6+1
Condensed water knock-out to wastewater treatment plant (tonnes/hr)	1.045	1.268	none	1.254	none
Consumption of electricity to CO2 compression/liquefaction and injection (MWh)	4.920	5.636	none	5.903	none
Synthesis gas compression (conditioning)					
Number of compression stages	3	3	3	3	3
Cleaned synthesis gas pressure (bar) – to EvGT	23.0	23.0	23.0	23.0	23.0
Condensed water knock-out to wastewater treatment plant (tonnes/hr)	10.585	12.748	24.665	12.576	24.665
Consumption of electricity by the compressor (MWh)	28.153	33.820	38.473	33.748	38.472
Full-flow evaporative advanced class gas turbine (EvGT)					
Gas turbine cycle-type	Evaporative	Evaporative	Evaporative	Evaporative	Evaporative
Operational mode	Combined-cycle	Combined-cycle	Combined-cycle	Combined-cycle	Combined-cycle
Humidification-cycle type	Full-flow	Full-flow	Full-flow	Full-flow	Full-flow
Combustor type	Annular	Annular	Annular	Annular	Annular
Turbine blades cooling system	Bled air points	Bled air points	Bled air points	Bled air points	Bled air points
Ambient temperature (ºC)	25.0	25.0	25.0	25.0	25.0
Ambient pressure (bar)	1.01325	1.01325	1.01325	1.01325	1.01325
Relative humidity in atmospheric air (%)	80.0	80.0	80.0	80.0	80.0
HHV_{AR} of conditioned synthesis gas (MJ/kg)	6.34	6.29	4.80	6.34	4.32
LHV_{AR} of conditioned synthesis gas (MJ/kg)	5.71	5.66	4.32	5.71	4.80
Turbine inlet temperature (ºC) – TIT	1600.0	1300.0	1500.0	1600.0	1600.00
Turbine inlet pressure (bar) - TIP	23.0	23.0	23.0	23.0	23.0
Reheat combustion chamber pressure (bar)	4.84	4.99	4.81	4.77	4.82
Excess of oxygen (%) [c]	23.27	25.93	20.28	23.16	20.35

Table 20 – Aspen Plus®v8.4 simulation parameters (input and output) of BIG-GT/CC routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	BIG-GT/CC route scenarios				
	SC1	SC2	SC3	SC4	SC5
Full-flow evaporative advanced class gas turbine (EvGT)					
Conditioned synthesis gas mass flow rate (tonnes/hr)	185.647	223.507	294.240	222.656	294.232
Synthesis gas fraction flow into reheat combustor (%)	55.16	41.72	57.54	55.4	57.60
Fresh-air mass flow rate (tonnes/hr)	401.238	476.399	460.987	480.784	461.502
Bleed-air coolant mass flow rate (kg of air /kg of inlet gas mass flow rate)	0.05	0.02	0.04	0.05	0.04
Installed power generation capacity (MW)	165.780	167.447	194.050	198.818	193.905
Grid frequency (Hz)	60.0	60.0	60.0	60.0	60.0
Net-electrical efficiency (%) [b]	49.05	41.47	47.59	49.05	47.55
Gross heat rate (kJ/kWh)	7100.0	8398.0	7281.4	7101.6	7287.0
Cooling system type	Closed loop	Closed loop	Closed loop	Closed loop	Closed loop
Air temperature after the intercooler heat exchanger (ºC)	27.0	27.0	27.0	27.0	27.0
Compressed-air temperature inlet the humidifier tower system (ºC)	80.0	80.0	80.0	80.0	80.0
Compressed-air temperature outlet the humidifier tower system (ºC)	195.0	195.0	195.0	195.0	195.0
Mass flow rate of injected water into EvGT by saturated-air flow (tonnes/hr)	31.980	39.827	37.031	38.301	37.072
Hot-water temperature inlet the humidifier tower system (ºC)	210.0	210.0	210.0	210.0	210.0
Temperature of cold-water returning into loop-cycle (ºC)	61.0	61.0	61.0	61.0	61.0
Exhaust-gas mass flow rate (tonnes/hr)	614.452	734.260	787.165	736.456	787.698
Turbine exhaust-gas temperature (ºC)	1056.0	858.0	1005.0	1058.0	1005.0
Exhaust-gas temperature - after the air regenerator heat exchanger (ºC)	600.0	715.0	600.0	600.0	600.0
Heat recovery steam generator (HRSG)					
HRSG type	Triple-pressure	Triple-pressure	Triple-pressure	Triple-pressure reheated	Triple-pressure reheated
High-pressure steam (bar)	45.0	45.0	120.0	120.0	120.0
Intermediate-pressure steam (bar)	23.0	23.0	23.0	23.0	23.0
Low-pressure steam (bar)	2.5	2.5	2.5	2.5	2.5
Steam temperature of the high-pressure circuit (ºC)	420.0	420.0	540.0	540.0	540.0
Steam temperature of the intermediate-pressure circuit (ºC)	337.9	337.9	330.8	540.0	540.0
Steam temperature of the low-pressure circuit (ºC)	130.0	130.0	130.0	130.0	130.0
Steam generation by high-pressure circuit (tonnes/hr)	36.500	37.800	91.000	70.091	75.000
Steam generation by low-pressure circuit (tonnes/hr)	58.787	138.459	10.137	8.273	21.339

Table 20 – Aspen Plus®v8.4 simulation parameters (input and output) of BIG-GT/CC routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	BIG-GT/CC route scenarios				
	SC1	**SC2**	**SC3**	**SC4**	**SC5**
Heat recovery steam generator (HRSG)					
Steam generation by intermediate-pressure circuit (tonnes/hr)	35.615	37.898	44.862	40.976	33.774
Steam at 2.5 bar sent to deaerator (tonnes/hr)	3.704	2.769	10.137	8.273	21.339
Deaerator pressure (bar)	1.4	1.4	1.4	1.4	1.4
Deaerator temperature (ºC)	105.0	105.0	105.0	105.0	105.0
EvGT exhaust-gas temperature (ºC)	600.0	715.0	600.0	600.0	600.0
HRSG flue-gas temperature (ºC)	152.0	131.0	160.0	160.0	160.0
Steam turbine applied in combined-cycles (ST)					
Steam turbine type	BPST *	EBPST	CEST	CEST	CST *
High-pressure steam inlet-level (bar)	45.0	45.0	120.0	120.0	120.0
Intermediate-pressure steam inlet-level (bar)	23.0	23.0	23.0	23.0	23.0
Exhaust steam pressure (bar)	2.5	2.5	0.11	0.11	0.11
High-pressure steam temperature (ºC)	420.0	420.0	540.0	540.0	540.0
Exhaust steam at 2.5 bar to thermochemical-biorefinery (tonnes/hr)	162.086	170.401	none	none	none
Exhaust steam at 0.11 bar to condenser (tonnes/hr)	none	none	45.769	96.824	200.718
Extraction steam at 2.5 bar to thermochemical-biorefinery (tonnes/hr)	none	none	184.579	106.592	none
Steam extraction at 6.0 bar sent to 1G-dehydration system (tonnes/hr)	none	13.662	13.686	none	none
Isentropic turbine efficiency (%)	79.45	79.45	76.88	80.52	80.52
Electrical energy generator efficiency (%)	99.0	99.0	99.0	99.0	99.0
Installed power generation capacity (MW)	18.509	20.365	37.805	49.476	62.625
Traditional CHP/EBPST system					
Sugarcane bagasse consumption (tonnes/hr)	32.888	none	none	81.376	81.376
Exhaust steam mass flow rate at 2.5 bar sent to 1G biorefinery (tonnes/hr)	none	none	none	none	none
Oxygen excess ratio (%$_{w/w}$) [c]	0.08	none	none	0.12	0.12
Steam pressure (bar)	22.0	none	none	22.0	22.0
Steam temperature (ºC)	320.0	none	none	320.0	320.0
Boiler carbon conversion (%$_{w/w}$)	99.0	none	none	99.0	99.0
Exhaust-gas temperature (Flue-gas) (ºC)	160.0	none	none	160.0	160.0
Boiler water blowdown (to treatment) (tonnes/hr)	3.397	none	none	8.459	8.459
Generation of bottom ashes (tonnes/hr)	0.614	none	none	1.366	1.366

Table 20 – Aspen Plus® v8.4 simulation parameters (input and output) of BIG-GT/CC routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continue)

Parameter	BIG-GT/CC route scenarios				
	SC1	**SC2**	**SC3**	**SC4**	**SC5**
Traditional CHP/EBPST system					
Fly-ashes removal by emission control filters (fine matter) (tonnes/hr)	0.186	none	none	0.420	0.420
Boiler thermal efficiency 1 (%) [b]	87.30	none	none	86.81	86.81
Boiler thermal efficiency 2 (%) [b]	83.81	none	none	83.16	83.16
Steam turbine type	BPST *	EBPST	CEST	CEST	CST *
Exhaust steam at 2.5 bar sent to 1G biorefinery (tonnes/hr)	68.803	none	none	184.945	184.945
Steam extraction at 6.0 bar sent to 1G-dehydration system (tonnes/hr)	13.707	none	none	14.175	14.175
Isentropic turbine efficiency (%)	74.55	none	none	74.55	74.55
Electrical energy generator efficiency (%)	99.0	none	none	99.0	99.0
Installed power generation capacity (MW)	7.309	none	none	18.336	18.336
Boiler thermal efficiency 1 (%) [b]	87.30	none	none	86.81	86.81
Boiler thermal efficiency 2 (%) [b]	83.81	none	none	83.16	83.16
Steam turbine type	BPST *	EBPST	CEST	CEST	CST *
Exhaust steam at 2.5 bar sent to 1G biorefinery (tonnes/hr)	68.803	none	none	184.945	184.945
Steam extraction at 6.0 bar sent to 1G-dehydration system (tonnes/hr)	13.707	none	none	14.175	14.175
Isentropic turbine efficiency (%)	74.55	none	none	74.55	74.55
Electrical energy generator efficiency (%)	99.0	none	none	99.0	99.0
Installed power generation capacity (MW)	7.309	none	none	18.336	18.336
Multi-cells water-cooling tower [e]					
Number of sections (sec)	1 sec	1 sec	2 sec	2 sec	2 sec
Tower cells required - sec 1	8 cells	10 cells	4 cells	10 cells	4 cells
Tower cells required - sec 2	none	none	3 cells	6 cells	11 cells
Make-up water (with recycle) - sec 1 (tonnes/hr)	130.900	156.056	52.295	155.942	53.003
Make-up water (with recycle) - sec 2 (tonnes/hr)	none	none	35.647	82.589	171.103
Water evaporation - sec 1 (tonnes/hr)	108.033	128.795	43.160	128.700	43.744
Water evaporation - sec 2 (tonnes/hr)	none	none	29.420	68.161	141.213
Water drift - sec 1 (tonnes/hr)	10.863	12.951	4.340	12.941	4.399
Water drift - sec 2 (tonnes/hr)	none	none	2.958	6.854	14.199
Tower basin blowdown (to treatment) - sec 1 (tonnes/hr)	12.004	14.311	4.796	14.300	4.860
Tower basin blowdown (to treatment) - sec 2 (tonnes/hr)	none	none	3.269	7.573	15.690

Table 20 – Aspen Plus®v8.4 simulation parameters (input and output) of BIG-GT/CC routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(conclusion)

Parameter	BIG-GT/CC route scenarios				
	SC1	SC2	SC3	SC4	SC5
Multi-cells water-cooling tower [e]					
Electricity required by fan drivers - sec 1 (kWh)	504.0	630.0	252.0	630.0	252.0
Electricity required by fan drivers - sec 2 (kWh)	none	none	189.0	315.0	693.0
Water cycles					
Electricity required by fan drivers - sec 2 (kWh)	none	none	189.0	315.0	693.0
Process water/steam maintenance (tonnes/hr)	78.588 **	91.866	88.940	80.962	79.734
Cooling water maintenance (tonnes/hr)	160.491	191.388	92.052	152.388	49.434
Make-up raw water (tonnes/hr)	179.639 **	214.270	89.145	58.512	73.742
Pre-heated fresh-water as deaerator make-up (tonnes/hr)	45.673 **	51.031	51.054	42.661	42.661
Generation of deaerated hot water (tonnes/hr)	305.808 **	322.521	254.171	211.688	222.057

(int) reference scenario for surplus biomass and integration with thermochemical routes

[a] biomass refers to sugarcane bagasse and sugarcane straw

[b] efficiency based on LHV$_{AR}$ of fuel at 25ºC and 1 atm

[c] excess based on inlet oxygen and not in the stoichiometric oxygen for combustion

[d] lean MEA aqueous absorbing-solution mass flow rate inlet in the top of the absorber

[e] section 1 (sec1) to cooling compressors systems and CO_2 and H_2S co-capture system, and section 2 (sec 2) to condensing CEST exhaust-steam

[f] considers all solid matters removed, including bed media and catalytic active materials

* steam turbine without steam extractions

** account for water cycle the 1G-CHP/ST system and the steam (heat) to equipment users in the 1G sugarcane biorefinery.

7.2 Biomass integrated directly-heated gasifier and low-pressure methanol catalytic-synthesis integrated at an optimized first generation sugarcane biorefinery with annexed ethanol distillery

Methanol also named methyl alcohol can be produced from any carbon-containing source (e.g.: fossil raw materials, CO_2, biomass), traditionally produced in large scale from natural gas (methane reforming process) is an important primary chemical in the commodity value-chain in the world. Actually, (2015) is considered the largest feedstock for chemical synthesis of derivatives to a large variety of products or end-uses in many sectors, and to energy feedstock as optional liquid transportation fuel (grade AA).

Biomass integrated directly-heated gasifier and low-pressure methanol catalytic-synthesis (Biomass-to-Methanol) can decentralize and improve the methanol production by using local and renewable resources, diversifying the energetic bio-based products portfolio.

In this research Master`s degree was developed scenarios aiming produce biomass-derived grade AA methanol for end-use as liquid transportation fuel (which is not the Brazilian case). However, the route can be easily operational-modified to produce biomass-derived grade AA in higher degree of purity for chemical use (same equipments), can be used in the Brazil’s biodiesel production chain (increasing its sustainability).

7.2.1 Scenarios assessed

Three possible thermochemical-biorefinery scenarios applying low-pressure methanol catalytic-synthesis (Biomass-to-Methanol) were simulated in Aspen Plus®v8.4 process simulation platform and assessed under the scope of the VSB tool, taking into account the integral use of available sugarcane bagasse and straw for production of methanol while supply the thermal and electrical energy required by the thermochemical-biorefinery.

Thermochemical-biorefinery scenarios applying low-pressure methanol catalytic-synthesis are defined in the section 3.4.4 (Biomass to methanol production by biomass integrated directly-heated gasifier and low-pressure methanol catalytic-synthesis). A scheme of the sugar, ethanol, methanol, and chemicals production from Biomass-to-Methanol route integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery is detailed in the Figure 61 for Biomass-to-Methanol scenario 1 (SC1), in the Figure 62 for Biomass-to-Methanol scenario 2 (SC2), and in the Figure 63 for Biomass-to-Methanol scenario 3 (SC3).

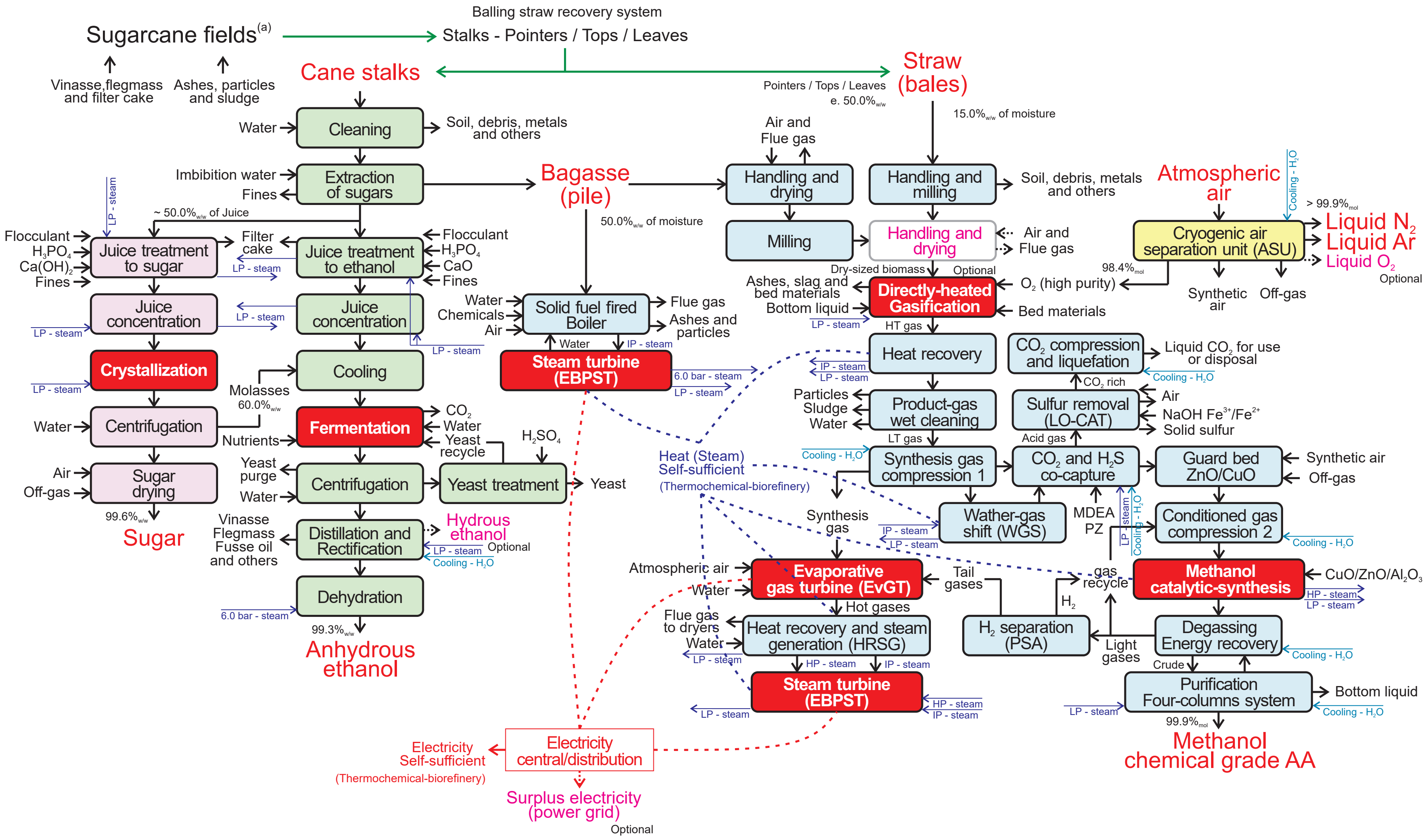
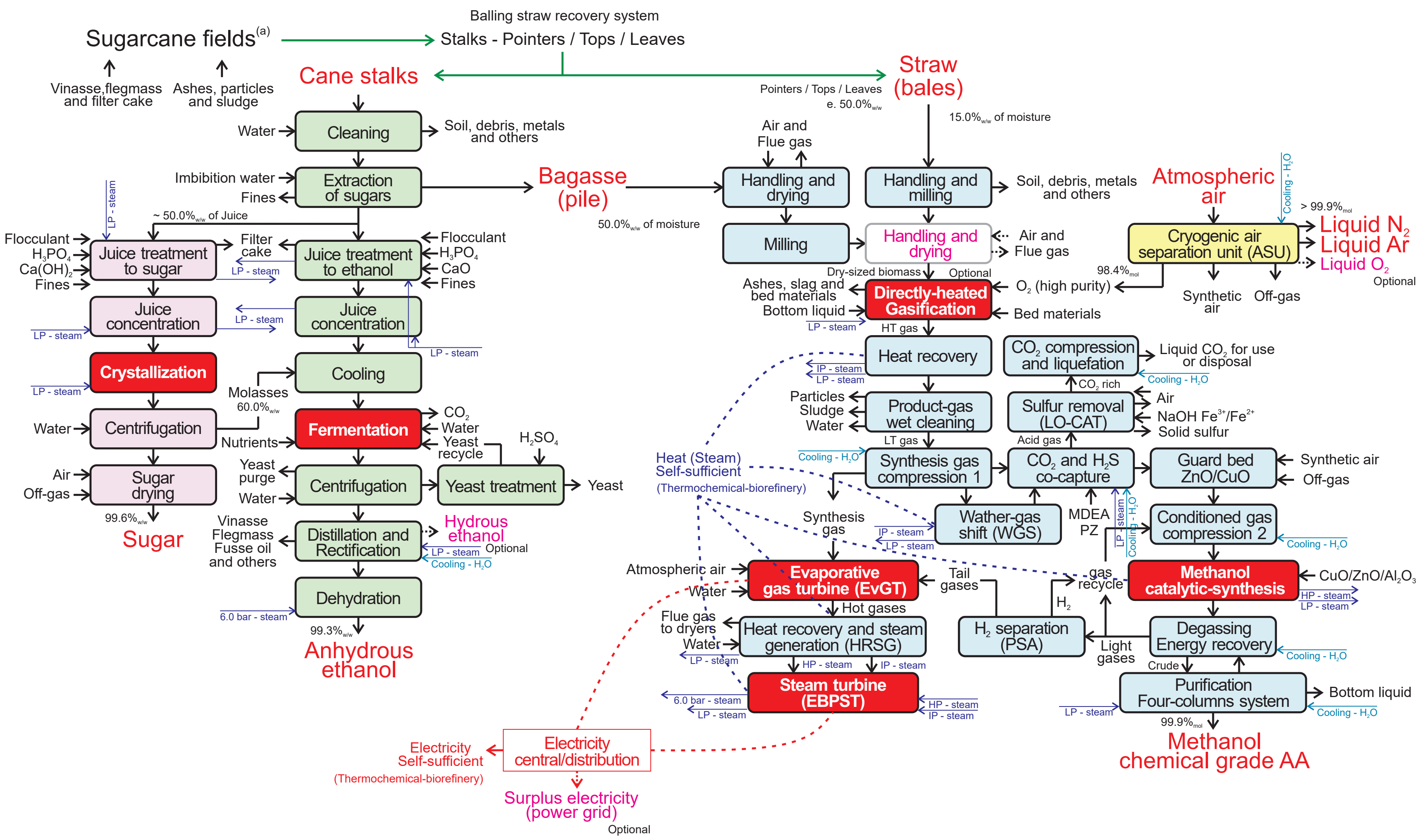


Figure 62 - Flow block diagram of biomass integrated directly-heated gasifier and low-pressure methanol catalytic-synthesis in energy and mass integration mode integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery: Scenario 1 (SC1)

Figure 63 - Flow block diagram of biomass integrated directly-heated gasifier and low-pressure methanol catalytic-synthesis in energy and mass integration mode integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery: Scenario 2 (SC2)



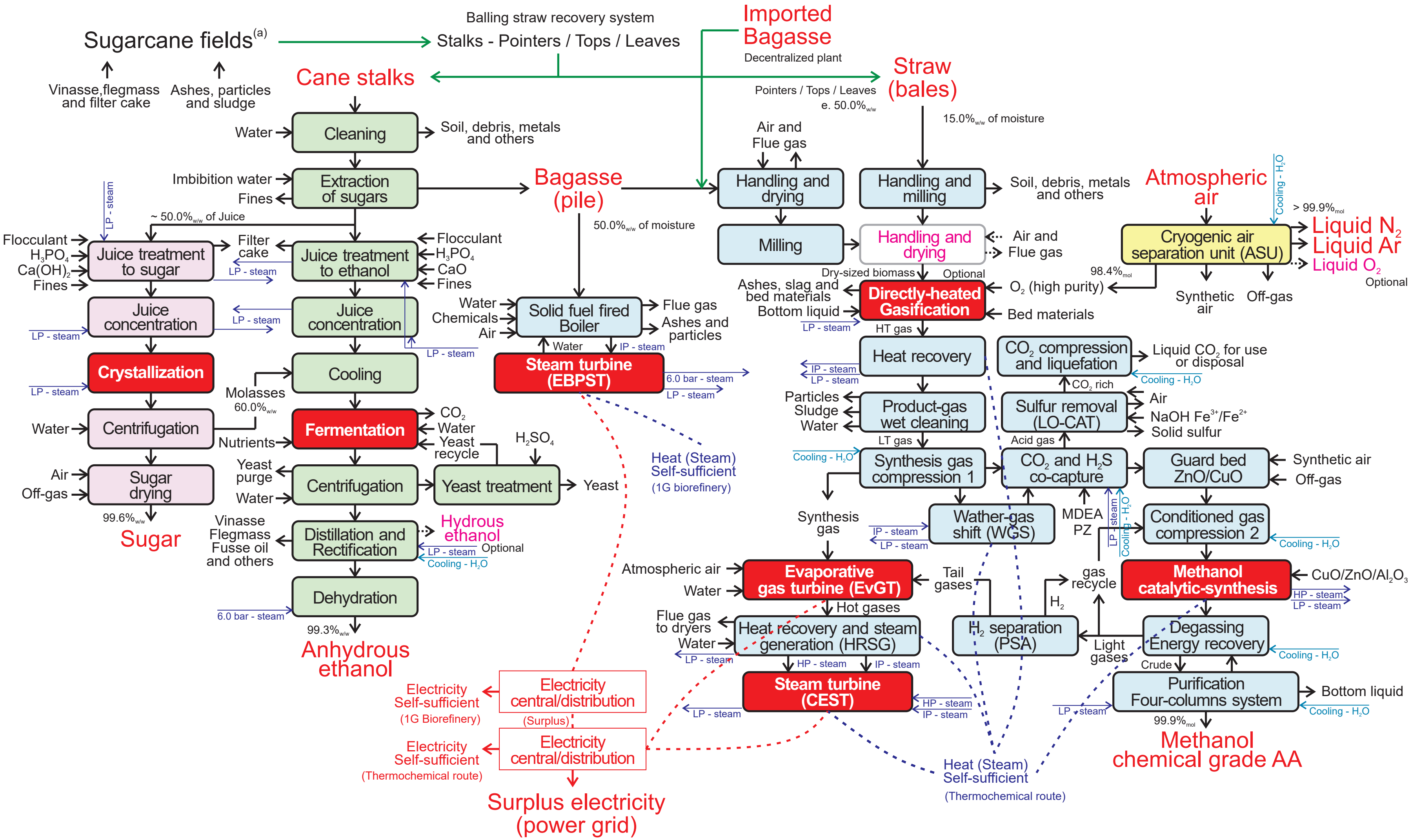


Figure 64 - Flow block diagram of biomass integrated directly-heated gasifier and low-pressure methanol catalytic-synthesis in standalone mode integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery: Scenario 3 (SC3)

Biomass-to-Methanol scenario 1 (SC1), Biomass-to-Methanol scenario 2 (SC2), and Biomass-to-Methanol scenario 3 (SC3) are integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery according to section 5 (First generation sugarcane biorefinery), and to agricultural and industrial phases of the 1G sugarcane biorefinery assessed by the division of AIB of the CTBE/CNPEM and published – *The Virtual Sugarcane Biorefinery (VSB)*: 2011 Report (BRAZILIAN BIOETHANOL SCIENCE AND TECHNOLOGY LABORATORY, 2012) – and in – Virtual Biorefinery: An Optimization Strategy for Renewable Carbon Valorization (BONOMI et al., 2016).

Biomass-to-Methanol route scenarios implemented in Aspen Plus®v8.4 process simulation platform to evaluate the methanol and chemicals production while supply the thermal and electrical energy requirements of the thermochemical-biorefinery. Available sugarcane bagasse and straw are gasified in an atmospheric CFB directly-heated gasifier using high-purity oxygen and steam gasification agents to produce synthesis gas. Therefore, is conditioned and then used in a gas-cooled fixed bed catalytic-synthesis reactor combined in series with a isothermal water-cooled fixed bed catalytic-synthesis reactor (two stages) with loop recycle system for unconverted synthesis gas. In addition, synthesis gas can be directly used in a high-performance sequential combustion full-flow advanced class evaporative (humidification tower) gas turbine (EvGT) in combined-cycle (CC) mode with steam turbine (ST) system (Rankine-cycle cogeneration system).

Aspen Plus®v8.4 complete flowsheet`s of Biomass-to-Methanol detailed scenarios are presented in the APPENDIX A. Figure A22 shows Biomass-to-Methanol scenario 1 (SC1), Figure A23 shows the Biomass-to-Methanol scenario 2 (SC2), and Figure A24 shows the Biomass-to-Methanol scenario 3 (SC3).

7.2.2 Physical properties

The GLOBAL property methods used are ELECNRTL, RKS-BM, and VANL-RK

The local properties method used is: IDEAL for biomass handling and sizing, and biomass multi-step dryer and control particulate emissions; RKS-BM for biomass multi-step dryer and control particulate emissions, gasification of biomass in an atmospheric CFB directly-heated gasifier, syngas cooling and heat recovery, CO_2 compression and storage/use, first-section of synthesis gas compression (conditioning), second-section of synthesis gas compression (conditioning), high-performance sequential combustion full-flow advanced EvGT, HRGS system, traditional CHP system applying EBPST system, low-pressure methanol catalytic-synthesis, HT and LT catalyst WGS reactors at intermediate-pressure level with energy-saving and steam generation, regenerative ZnO/CuO-based guard bed adsorber, energy-saving integrated turbo compressor & expander (turbo booster), hydrogen recovery by four-bed PSA system, and for gaseous streams side; ELECNRTL for low-temperature synthesis gas wet cleaning system, and co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution; NRTL-RK for energy-saving four-column triple-effect methanol distillation system (methanol purification); VANL-RK for double-column cryogenic ASU with high-purity argon recovery; IAPWS-95 for multi-cells water-cooling tower, water cycles, EBPST and CEST systems for thermochemical route-cycles, traditional CHP system applying EBPST system, HT and LT catalyst WGS reactors at intermediate-pressure level with energy-saving and steam generation, low-pressure methanol catalytic-synthesis, for pure water-side streams, and for pure steam-side streams.

Non-conventional solids physical property method used for BAGASSE and STRAW component properties is the HCOALGEN model (general coal models) applying the Mott and Spooner correlation (4 option code) according to section 3.7 (Non-conventional solids physical property methods) for estimate the enthalpy, and COALIGT model for estimate the density.

7.2.3 Available raw biomass

Raw sugarcane bagasse (SUGARCANE BAGASSE) is represented by BAGASSE and SOIL streams according to Table 9, and raw sugarcane straw (SUGARCANE STRAW) is represented by STRAW and TRASH according to Table 9. METAL stream was added to represent the amount of the tramp metals removed by the magnetic head pulleys (inlet-to-outlet model). Others debris were not considered present (to specify removal process) and can be accounted for in the trash fraction (TRASH) as inert material.

Sugarcane straw (SUGARCANE STRAW) is collected from the field (after the sugarcane harvesting) using a baling system (with pre-chopping system). In this system, the straw is separately sent from the cane stalks to the thermochemical-biorefinery. The transport is made using trucks (up to 25 tonnes/vehicle) or road trains (up to 70 tonnes/vehicle). All the Biomass-to-Methanol scenarios consider that 50.0%$_{w/w}$ of the total sugarcane straw available is recovered and sent to the thermochemical-biorefinery with 15.0%$_{w/w}$ of moisture content (on-site). As the transport vehicle enters the plant they are weighed and the straw bales are dumped (PR-MIX-3) or removed by adapted cane loaders and stored (PR-MIX-3) as feedstock for further processes.

In the Biomass-to-Methanol (SC1), part of available bagasse (BAGASSE) is belt-conveyed directly to the traditional CHP/EBPST system or to bagasse pile (PR-SPL-1) for burning purpose, generating thermal and electrical energy to supply part of the energy required by the 1G sugarcane biorefinery while Biomass-to-Methanol route supply the other part. In the Biomass-to-Methanol (SC2), the available bagasse (BAGASSE) is belt-conveyed directly to the bagasse flash dryers (DR-DRY-1) in the Biomass-to-Methanol route or to bagasse pile (PR-SPL-1) as feedstock for further processes. In the Biomass-to-Methanol (SC3), part of available bagasse (SUGARCANE BAGASSE) is burned to generate the thermal and electrical energy to supply all of this energy required by the 1G sugarcane biorefinery. Surplus bagasse (SUGARCANE BAGASSE) from the boiler-pile or directly from the cane mills is conveyed (centralized plant) or transported (decentralized plant) as available feedstock to the Biomass-to-Methanol plant together imported bagasse (scale setting).

7.2.4 Biomass handling and sizing

Sugarcane bagasse (SUGARCANE BAGASSE) at a moisture content of 50.0%$_{w/w}$ after the cane mills (driver by electrical motors) is transported by a conveyor (screw, drag or belt) to a temporary pile (PR-SPL-1) (feeding or equalization pile) or sent directly to the bagasse flash dryers (DR-DRY-1) by feeder conveyor (PR-MIX-1). In the Biomass-to-Methanol (SC1) and Biomass-to-Methanol (SC2), part is sent to biomass feed drum (PR-MIX-5) in the traditional solid-fuel fired boiler (BO blocks) to be burned in the boiler chamber (BO-COMBU).

As shown in Figure 33, Aspen Plus®v8.4 flowsheet of the simplified aggregated-steps model for the biomass handling and sizing for BIG-ICE/CC (SC1) is the same model with modified parameters for Biomass-to-Methanol (SC1), and as shown in Figure 34, Aspen Plus®v8.4 flowsheet of the simplified aggregated-steps model for the biomass handling and sizing for BIG-ICE/CC (SC2) is the same model with modified parameters for Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3). The Aspen Plus®v8.4 flowsheet`s are compost by: dumper (PR-MIX-3); storage area (PR-MIX-3); temporary bagasse pile (PR-SPL-1 and PR-SPL-3); bagasse pre-milling machine (PR-CRU-1); fine-size milling machines (DR-CRU-1); straw fine-size cutting-milling machine (DR-CRU-2); pre-sizing bagasse screen-deck solid-solid classifier (PR-CLA-1); bagasse screen-deck solid-solid classifier (PR-CLA-2); straw screen-deck solid-solid classifier (PR-CLA-3); oversized bagasse mixer (PR-MIX-2); unpacking and preparation area (PR-SPL-2); magnetic head pulleys (PR-ELE-1); magnetic separator (PR-SCR-5); screw-conveyor (PR-SCR-7); oversized straw mixer (PR-MIX-4); belt-conveyor (PR-SCR-1); bagasse feeder conveyor (PR-MIX-1); transporter (PR-SCR-3); screw-conveyor (PR-SCR-2); drag-conveyor (PR-SCR-4); screw-conveyor (PR-SCR-6); and screw-conveyor (PR-SCR-7).

In the Aspen Plus®v8.4 process model simulation 5.0%$_{w/w}$ of the raw bagasse (BAGASSE) is reserved (PR-SPL-1) in the pile (RESERVE BAGASSE) for brief stops and start-up.

In the Biomass-to-Methanol (SC1), part of the raw bagasse (BAGASSE) can be used (or not) as received (wet) from the cane mills to be burned in the solid-fuel fired boiler (BO-COMBU). Another part of the raw bagasse (BAGASSE) from the cane mills or temporary bagasse pile (PR-SPL-1) is screw-conveyed (PR-SCR-2) directly to first-stage bagasse flash dryer (DR-DRY-1) to reduce the moisture content before the gross-size reduction stage (PR-CRU-1).

As shown in Figure 33, Aspen Plus®v8.4 flowsheet of the biomass handling and sizing in the BIG-ICE/CC (SC1), which is the same model with modified parameters in the Biomass-to-Methanol (SC1) with 1G-CHP/EBPST system wherein the bagasse (SUGARCANE BAGASSE) from the cane mills can be directly belt-conveyed (PR-SCR-8) to boiler fuel feeders. Moreover, the model also consider fed from the temporary bagasse pile (PR-SPL-1) by using a tractor (actual system) to carries part of the bagasse available to the conveyor boiler feed tray (PR-MIX-5).

In the Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3), raw bagasse (BAGASSE) from the cane mills or temporary bagasse pile (PR-SPL-1) are screw-conveyed (PR-SCR-2) directly to first-stage bagasse flash dryer (DR-DRY-1) to reduce the moisture content before the gross-size reduction stage (PR-CRU-1). After the first-stage of drying (DR-DRY-1), the bagasse is belt-conveyed (PR-SCR-1) to a pre-milling bagasse machine (PR-CRU-1) to gross-size reduction. After this stage, the bagasse is classified in a screen-deck solid-solid classifier (PR-CLA-2), the fine fraction is directly screw-conveyed (PR-SCR-2) to bagasse second-flash dryer (DR-DRY-1) and the oversized fraction is recycled and mixed back (PR-MIX-2) to further gross-size reduction cycle in closed-loop at size requirements. Gross-sized and pre-dried bagasse is screw-conveyed (PR-SCR-2) to bagasse second-flash dryer (DR-DRY-1) to reduce the moisture content to 10.0%$_{w/w}$ (dry bagasse) before the fine-size reduction stage (PR-CRU-1).

The gross-sized and dried bagasse is belt-conveyed (PR-SCR-1) to pre-sizing classification in a screen-deck solid-solid classifier (PR-CLA-1), being classified according to ideal function for 2.0 mm of cut size (thickness). After, is sent to the fine-size milling machine (PR-CRU-1) to fine-size reduction and classification in a screen-deck solid-solid classifier (PR-CLA-2) according to ideal function for 2.0 mm of cut size (thickness). The fine fraction is screw-conveyed (PR-SCR-2) to gasifier feed drum (DR-MIX-4) and the oversized fraction is recycled and mixed back (PR-MIX-2) for further fine-size reduction cycle.

The raw moist bagasse are screw-conveyed to specific dryer feeder drum, entering by screw-conveyor (PR-SCR-2) into parallel bagasse flash dryer trains (DR-DRY-1) to reduce the moisture content from 50.0%$_{w/w}$ to 10.0%$_{w/w}$ in a multi-steps drying process (DR-DRY-1).

Aspen Plus®v8.4 process model simulation of the bagasse gross-size milling and fine-size milling machines (DR-CRU-1) are combined in a single-block model. The single block-stage model was developed by using Crusher solids block to reduce the particle diameter to a maximum of 4.0 mm of thickness according to Gates-Gaudin-Schuhmann general cumulative distribution function to avoid 50.0%$_{w/w}$ of the bagasse mass flow rate with more than 2.0 mm of thickness.

The electrical power work required by the bagasse size reduction and handling system is estimated as 22.0 kWh per tonnes of wet bagasse inlet in the sizing system. It is set in bond work index by design specification DS-PR-PC-1. In addition, outlet PSD distribution is determined by Bond's comminution power law and a sizing distribution function.

The straw bales delivered (STRAW+TRASH+METAL) are transported (PR-SCR-3) to unpacking and preparation area (PR-SPL-2), considering a pre-chopping process in the field by the straw baling machine. The straw bales are unpacked (PR-SPL-2), the over sized or hardest biomass, and heavier particles (rocks) delivered with the straw bales is separated and screwed-out. In these processes is considered removal 50.0%$_{w/w}$ of the soil fraction content in the trash (TRASH), accumulated due to contact with the agricultural land.

Unpacked-straw (pre-chopped) is drag-conveyed (PR-SCR-4) to the magnetic separation (PR-SCR-5) (prevent damages) by magnetic head pulleys (PR-ELE-1) to remove the tramp metals (METALS) along with 5.0%$_{w/w}$ of the soil content, its fraction is screwed-out (PR-SCR-6) to final disposal or send to be recycled (metals). After removal the debris (TRASH) and ferrous metals, the straw is belt-conveyed to a cutting-milling straw machine (PR-CRU-2) to fine-size reduction with size-classification by screen-deck solid-solid classifier (PR-CLA-3) according to ideal function for 2.0 mm of cut size (thickness). The fine fraction is directly screw-conveyed (PR-SCR-7) to straw flash dryer (DR-DRY-2) and the oversized fraction is recycled and mixed back (PR-MIX-4) for further fine-size reduction cycle in closed-loop at size requirements.

Aspen Plus®v8.4 process model simulation of the straw fine-size cutting-milling machine (DR-CRU-2) was developed by using Crusher solids block to represent the particle diameter reduction. The model consider a maximum of 4.0 mm of thickness according to Gates-Gaudin-Schuhmann general cumulative distribution function to avoid 50.0%$_{w/w}$ of the straw mass flow rate with more than 2.0 mm of thickness.

The electrical power work required by the straw size reduction and handling system is estimated based on chopper's machines and fine-size cutting-milling processes for sugarcane straw as 8.0 kWh per tonnes of wet straw inlet in the sizing system (after the magnetic head pulleys). It is set in the bond work index using the design specification DS-PR-PC-2. In addition, outlet PSD distribution is determined by Bond's comminution power law and a sizing distribution function.

Sized straw is screw-conveyed (PR-SCR-7) to straw flash dryer (DR-DRY-2). In some cases (dry gathering conditions), there may not be need of drying the straw and then this can bypass the straw flash dryer (DR-DRY-2) and be directly belt-conveyed to the gasifier feed drum (DR-MIX-3).

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7.2.5 Biomass multi-step dryer and control particulate emissions

The raw moist bagasse is fed by screw-conveyor (PR-SCR-2) into parallel bagasse flash dryer trains (DR-DRY-1). The moisture content is reduced from 50.0%$_{w/w}$ to 10.0%$_{w/w}$ in a multi-steps drying process (DR-DRY-1).

Sized straw with higher-moisture content (considered 15.0%$_{w/w}$), recovered in rain conditions (or which has been humidified) is belt-conveyed to dryer feeder drum and screw-conveyed (PR-SCR-7) to straw flash dryer (DR-DRY-2). Sized straw with lower-moisture content (equal or less than 10.0%$_{w/w}$) obtained on dry straw recovery conditions (not considered in this research Master's degree) bypass the straw flash dryer (DR-DRY-2) and is directly belt-conveyed to the gasifier feed drum (DR-MIX-3).

As shown in Figure 35, Aspen Plus$^{®}$v8.4 flowsheet of the simplified aggregated-steps model of the biomass multi-step dryer and control particulate emissions in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2), which is the same model with modified parameters for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) is compost by: first-stage bagasse flash dryer (DR-DRY-1); second-stage bagasse flash dryer (DR-DRY-1); straw flash dryer (DR-DRY-2); advanced blower system (DR-ASP-1); pre-filter unit (DR-FIL-1); bagasse after-dryer single-cyclone (DR-CYC-1); straw after-dryer single-cyclone (DR-CYC-2); bagasse electrostatic precipitator (DR-ESP-1); straw electrostatic precipitator (DR-ESP-1); fine-solids mixer 1 (DR-MIX-7); fine-solids mixer 2 (DR-MIX-8); straw gasifier storage bin (DR-MIX-3); bagasse gasifier storage bin (DR-MIX-4); gaseous mixer 1 (DR-MIX-1); gaseous mixer 2 (DR-MIX-2); flash separator 1 (DR-FLA-1); and flash separator 2 (DR-FLA-2).

Fresh drying air agent (ATMOSPHERIC AIR) is indirect preheated using the dryer humidified exhaust-gas and heated (DR-HEA-1) using only the HRSG flue-gas or a mixture of the HRSG flue-gas with 1G-CHP/EBPST exhaust-gas.

The air drying agent is heated to 120.0ºC and then forced-injected at atmospheric pressure in the bagasse multi-stage flash dryer (DR-DRY-1) and straw flash dryer (DR-DRY-2) by advanced blower system (DR-ASP-1) modeled by using a Compr pressure changer block according to isentropic method for compressor considering 85.0% isentropic efficiency and 99.0% mechanical efficiency. A pre-filter unit (DR-FIL-1) modeled by using a FabFl solids separator block according to Piecewise separation efficiency in function of the particle diameter of the solids is used to protect the blower and the flash dryers from debris (PARTICLES). The advanced blower system (DR-ASP-1) is used to adjust the mass flow rate of the hot-air drying agent required by the drying process (technical assessment) and equalize the drop pressure of the system to atmospheric discharge condition in the dryer flue-gas (FLUE-GAS FROM STACK).

The multi-step bagasse flash dryer (DR-DRY-1) and the straw flash dryer (DR-DRY-2) is modeled by using a HeatX exchanger block coupled with a Flash2 separator block operating at atmospheric pressure (no pressure drop consideration). The model represents the direct contact of hot-air drying agent with bagasse (DR-FLA-1) and straw (DR-FLA-2), and the resultant thermal and fluid dynamic effects.

The thermal exchange models consider that the biomass heat at saturation temperature (at about 100.0ºC for atmospheric pressure) to liquid-vapor equilibrium phase to separate the moisture content (flash model principles). The direct contact model consider drag 0.2%$_{w/w}$ of the total biomass (daef) fed as biomass fine fibers and 0.1%$_{w/w}$ of the total particles (e.g.: soil and others) as fine particles due the high mass flow rate and the turbulence of the drying air agent. The model also considers that 0.01%$_{w/w}$ of the moisture contained in the biomass is entrained together with the particulate emissions (without energetic consumption to evaporate). Extractives, volatile organic compounds, and the moisture content in the biomass are evaporated according to flash equilibrium model (DR-MIX-1 for bagasse model, and DR-MIX-2 for straw model). Hence, they are emitted to atmosphere together the drying air agent in the dryer flue-gas (FLUE-GAS FROM STACK).

The fine-sized and dried straw (solid phase) content 10.0%$_{w/w}$ of moisture after the straw flash dryer (DR-FLA-2) is belt-conveyed to a gasifier feed drum (DR-MIX-4).

The raw wet bagasse is dried in a first-stage bagasse flash dryer (DR-DRY-1) to reduce the moisture content before the gross-size reduction stage (PR-CRU-1). Lower moisture content easiest the process of gross-size milling (DR-CRU-1), and reduce the thermal energy required by this first-stage, the moisture content level affect the machine performance. After gross-sized, the bagasse is sent back to a second-stage bagasse flash dryer (DR-DRY-1) to reduce the moisture content to 10.0%$_{w/w}$, before the fine-size milling stage. The gross-sized and dried bagasse (solid phase) with 10.0%$_{w/w}$ of moisture content is belt-conveyed to gross-size milling machine (DR-CRU-1) to reduce the size particle at gasifier required level.

The first-stage and second-stage of the bagasse flash dryer (DR-DRY-1) combined in a single-block model, and the straw flash dryer (DR-DRY-2) are modeled by using a HeatX exchanger block and Flash2 separator block. Estimate the thermal energy required by the biomass flash dryers (DR-DRY-1 and DR-DRY-2) to reduce the moisture content of bagasse and straw to 10.0%$_{w/w}$ by using hot-air agent, inlet at 120.0ºC and outlet at about 100.0ºC.

The hot-air mass flow rate is controlled by design specification DS-DR-TG-1 to distribute the air-flow in order to obtain the same outlet temperature (same temperature range) in the dryers (DR-DRY-1 and DR-DRY-2). The design specification DS-DR-FG-1 is used to estimate the thermal energy required by the multi-step bagasse drying process, and the design specification DS-DR-FG-2 is used to estimate the thermal energy required for the straw drying process. The design specification DS-DR-FG-3 is used to control the mass flow rate of fresh-air inlet (ATMOSPHERIC AIR) the dryers, optimizing the dying processes under determined temperature range (120.0ºC~100.0ºC in the air agent side).

Aspen Plus®v8.4 process model simulation of the bagasse flash dryers (DR-DRY-1) and straw flash dryers (DR-DRY-2) overestimates the power consumption because only uses the heat of vaporization of water and sensible heat exchanger according to biomass heat capacity, not taking into account other phenomena. The design specification DS-DR-HD-3 is used to correct the model estimative and approach to the real value demanded by the process, applying 45.0% as reduction factor of thermal energy calculated in the model, this thermal energy is provide by the Heat exchangers block between the HRSG exhaust-gas (HR-HEA-1) and the air agent mass flow rate (DR-HEA-1). The cooled HRSG flue-gas (FLUE-GAS FROM STACK) temperature is controlled and dependent on the exhaust-gas temperature of the subcritical HRSG system (without wet gaseous cleaning system).

Humidified exhaust-gas from first-stage and second-stage bagasse flash dryers (DR-MIX-1) enters in the after-dryer single-cyclone (DR-CYC-1) modeled by using a Cyclone solids separator block to remove the gross particulate content in the dryer humidified exhaust-gas according to Muschelknautz calculation method for a maximum pressure drop of 0.02 bar applying spiral inlet cyclone type. After the dryer single-cyclone (DR-CYC-1), dryer humidified exhaust-gas pass flowing through an electrostatic precipitator (DR-ESP-1) modeled by using ESP solids separator block according to Svarovsky calculation model for vertically mounted collecting plate’s model with particles separation efficiency of 95.0% based on the migration velocity and the ratio of precipitation area. Part of the persistent fine particulate matters are removed avoid-reducing their emissions to atmosphere with the dryer’s flue-gas (FLUE-GAS FROM STACK).

The dryer humidified exhaust-gas of the straw flash dryers (DR-MIX-2) enters in the after-dryer single-cyclone (DR-CYC-2) modeled by using a Cyclone solids separator block to remove the gross particulate content in the dryer humidified exhaust-gas according to Muschelknautz calculation method for a maximum pressure drop of 0.02 bar applying spiral inlet cyclone type. After the dryer single-cyclone (DR-CYC-2), dryer humidified exhaust-gas pass flowing through an electrostatic precipitator (DR-ESP-2) modeled by using ESP solids separator block according to Svarovsky calculation model for vertically mounted collecting plate’s model with particles separation efficiency of 95.0% based on the migration velocity and the ratio of precipitation area. Part of the persistent fine particulate matters are removed avoid-reducing their emissions to atmosphere with the dryer’s flue-gas (FLUE-GAS FROM STACK).

The gross and fine particulate matters removed from the dryer humidified exhaust-gas are sent to gasifier storage bin (DR-MIX-3) together the dried and sized sugarcane bagasse and straw (mixed in the feed gasifier drum).

7.2.6 Gasification of biomass in an atmospheric circulating fluidized bed directly-heated gasifier by using high-purity oxygen and steam agents

The Aspen Plus®v8.4 process model simulation of the gasification of biomass in an atmospheric CFB directly-heated gasifier by using high-purity oxygen and steam agents is based on zero-dimensional isothermal built-in multi-blocks models (CFB directly-heated gasifier process-zones) in steady state operation mode.

The model use Mott and Spooner correlation (option code 4) to estimate the heat of combustion and heat of formation, Kirov correlation (option code 1) to estimate the heat capacity. RKS cubic equation of state with BM alpha function property method evaluates the heat transfer between the CFB directly-heated gasifier zones (multi-blocks), as well as heat loss from the gasifier considered by using design specification DS-GA-QL-1.

As shown in Figure 36, Aspen Plus®v8.4 flowsheet of the gasification of biomass in a CFB directly-heated gasifier by using atmospheric air and steam agents in the BIG-ICE/CC (SC1), and BIG-ICE/CC (SC2), which is the same model with modified parameters in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), changing the atmospheric air agent for high-purity oxygen agent obtained from the double-column cryogenic ASU with high-purity argon recovery.

Figure 65 shows the Aspen Plus®v8.4 flowsheet of the gasification of biomass in an atmospheric CFB directly-heated gasifier by using high-purity oxygen and steam agents for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3). The model was developed as built-in multi-blocks and splitted in bagasse and straw feed system, gasifier buffer/equalizer tank (GA-BUF-1), advanced blower system (GA-ASP-1), heat exchanger (GA-HEA-1 and HR-HEA-1) and more five basic linked zones representing the atmospheric CFB directly-heated gasifier: a) drying zone (GA-SEP-1 and GA-SEP-2); b) devolatilization (thermal decomposition) or pyrolysis zone (GA-DEV-1 and GA-DEV-2); c) gasification or reduction zone (GA-GASEI); and d) combustion or oxidation zone (GA-GASEI); and e) primary gasifier cyclone (GA-CYC-1).

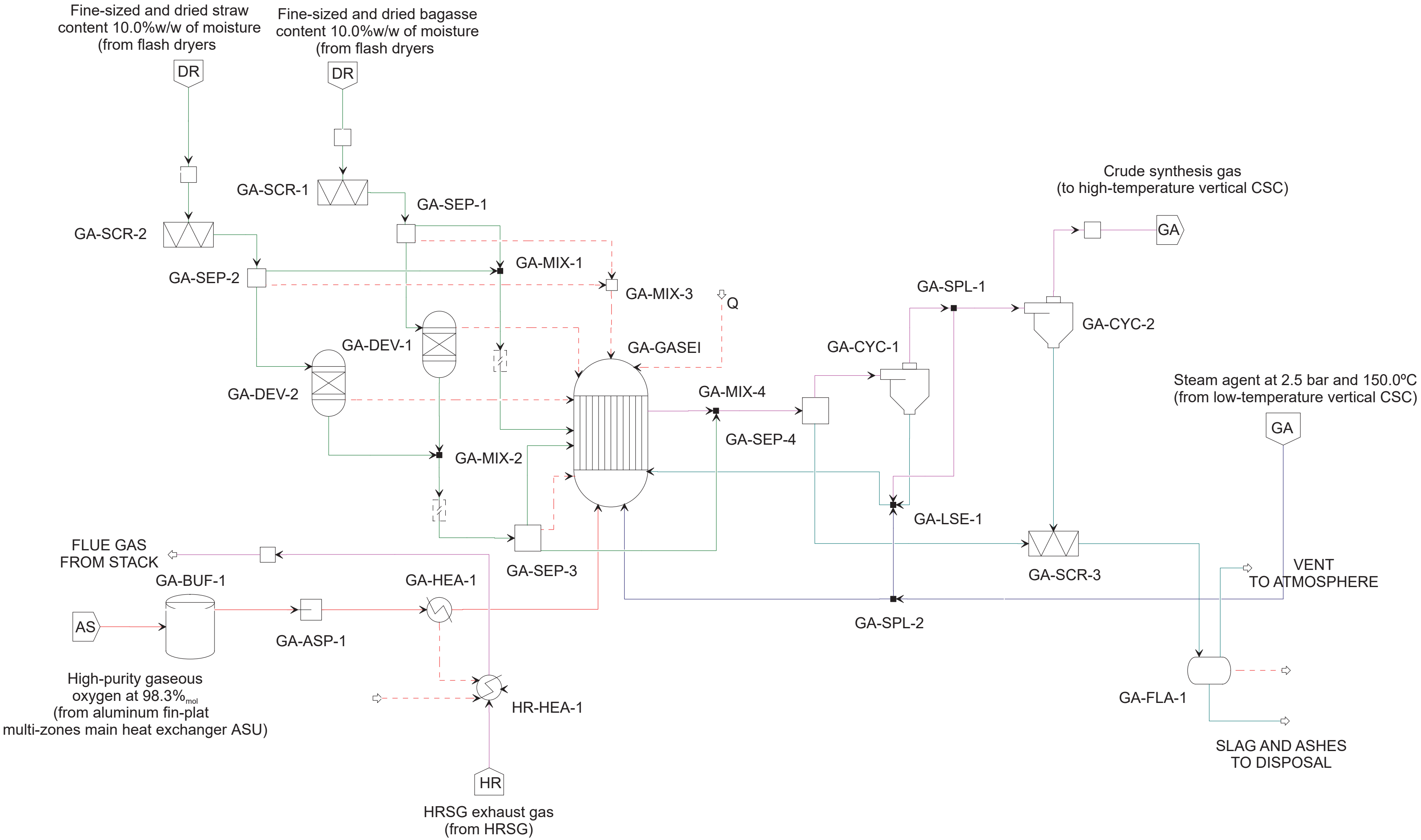


Figure 65 - Aspen Plus® v8.4 flowsheet of the gasification of biomass in an atmospheric CFB directly-heated gasifier by using high-purity oxygen and steam agents for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3)

Dried (10.0%$_{w/w}$ of moisture content) and sized (less than about 2.0 mm of tickles) sugarcane bagasse and straw, after the multi-steps drying process and control particulate emissions, is belt-conveyed to bagasse storage bin (DR-MIX-4) and straw storage bin (DR-MIX-3). Hence, sugarcane bagasse and straw are lifted from the temporary storage bin and gravimetric fed into the gasifier feed drum (DR-MIX-3).

Sugarcane bagasse and straw (biomass) is horizontally conveyed into the inject screws to introduce the sugarcane bagasse (GA-SCR-2) and straw (GA-SCR-1) into the gasifier, near the bottom of the CFB gasifier bed. The mass flow rate of sugarcane bagasse and straw inject-screwed into the atmospheric CFB directly-heated gasifier is controlled by the bagasse screw (GA-SCR-2) and straw screw (GA-SCR-1), in each metering bins (DR-MIX-3 and DR-MIX-4).

Aspen Plus®v8.4 process model simulation of the drying process-zone consider the bagasse (GA-SEP-2) and straw (GA-SEP-1) instantaneous drying process at 150.0ºC vaporizing the moisture content and volatilizing the extractives content in the inlet dried and sized bagasse and straw, which are sent directly to the oxidative and reductive reactions zone (GA-GASEI).

The Aspen Plus®v8.4 process model simulation of the devolatilization process-zone was developed using RYield reactor block to represent the atmospheric decomposition at 500ºC of the BAGASSE non-conventional solids (GA-DEV-2) and the STRAW non-conventional solids (GA-DEV-1) into its ‘constituting’ conventional components (‘ELEMENTS’). The non-conventional solids are converted to form carbon (C), hydrogen (H_2), oxygen (O_2), chlorine (Cl_2), nitrogen oxide (NO), sulfur dioxide (SO_2), and hydrogen sulfide (H_2S) using about 16.67%$_{w/w}$ of the sulfur (S) content. Salts, minerals, ashes, and soil are specified as inert components in the devolatilization process-zone (bypass).

FORTRAN calculator block CA-GA-CB-2 is used to specify the yield distribution of the bagasse decomposition (GA-DEV-2) in the devolatilization process-zone and the mass flow rate of each constituent component in the outlet stream according to the sugarcane bagasse ultimate analysis (Table 5). FORTRAN calculator block CA-GA-CB-1 is used to specify the yield distribution of the straw decomposition (GA-DEV-1) in the devolatilization process-zone and the mass flow rate of each constituent component in the outlet stream according to the sugarcane straw ultimate analysis (Table 6).

Sep separator block GA-SEP-3 as adjustment model is used to selectively separate specific amounts of char (C) to adjust the carbon conversion efficiency of the atmospheric CFB directly-heated gasifier bypass the carbon around the reaction zones (GA-GASEI) using the design specification DS-GA-FS-1 to control the carbon split fraction to obtain 98.0%$_{w/w}$ of carbon conversion efficiency. The GA-SEP-3 separator block also adjusts and considers a fraction of 10.0%$_{w/w}$ of the salts with potassium and chlorine content as reactive compounds together the integral minerals. The another fraction containing 90.0%$_{w/w}$ of the salts with potassium and chlorine (content in the inlet biomass) is considered as non-reactive compounds and primary bypass the reaction zones (GA-GASEI).

The adjustment model (GA-SEP-3) consider the possibility of the entrained gross-particles (solid fraction) content reactive potassium and chlorine (bed supplementary material linked) captured in the primary gasifier cyclone (GA-CYC-1) return back trough the leg-riser to the gasifier bed (GA-GASEI) as reactive compounds. A small fraction of the fine particles contend the reactive-considered potassium and chlorine leave the primary gasifier cyclone (GA-CYC-1) with gaseous product, linked with the bed materials (not included in the Aspen Plus®v8.4 process model simulation) and in form of oxides sulfates or phosphates (possible products).

High-purity oxygen (O_2) agent, at 98.3%$_{mol}$ of purity, is obtained from the double-column cryogenic air separation unit (ASU) with high-purity argon recovery. After the main heat exchanger (AS-2), gaseous high-purity oxygen stream (GA-O2-1) is fed in the gasifier buffer/equalizer tank (GA-BUF-1) at 25.0 ºC and atmospheric pressure (ambient conditions). The high-purity oxygen line contains (model result), on molar percentage basis, $2.597e^{-10}$% of nitrogen (N_2), 98.304% of oxygen (O_2), 1.695% of Argon (Ar), $2.54e^{-23}$% of Neon (Ne), $2.546e^{-20}$% of Helium (He), $4.629e^{-4}$% of Xenon (Xe), $6.053e^{-4}$ of Krypton (Kr).

The oxidizing agent, from the gasifier buffer/equalizer tank (GA-BUF-1), is induced by advanced blower system (GA-ASP-1) modeled by using a Compr pressure changer block according to isentropic method for compressor considering 85.0% isentropic efficiency and 99.0% mechanical efficiency. The high-purity oxygen is preheated (GA-HEA-1) using the dryer flue-gas and heated (GA-HEA-1) using the HRSG exhaust-gas (HR-HEA-1) to obtain 120.0ºC before being injected in the atmospheric CFB directly-heated gasifier in the primary injection distributor in the bottom of the bed (GA-GASEI) an in the secondary distributor points (close to biomass feed point) in the combustion zone (GA-GASEI).

The quantity of high-purity oxygen agent injected into the atmospheric CFB directly-heated gasifier is controlled by the design specification DS-GA-TG-1 coupled with the design specification DS-AS-FG-2 varying the mass flow rate of the high-purity liquid oxygen extracted from the high-pressure packed-column (AS-COL-2). The high-purity oxygen required is determined by the thermal energy necessary to gasification reactions and to crude synthesis gas leaves the atmospheric CFB directly-heated gasifier at 850.0ºC, operational temperature selected for the atmospheric CFB directly-heated gasifier model implemented in this research Master’s degree.

In the atmospheric CFB directly-heated gasifier, the combustion in-bed (GA-GASEI) supply the thermal energy required for the endothermic gasification reactions and to heater the material-compounds, the combustion gas products acts as fluidizing bed agent and gasifying agent. The Aspen Plus®v8.4 process model simulation of oxidizing and gasification process-zones in bed and freeboard is modeled using RGibbs reactor block (GA-GASEI) to represent the solid and gaseous reaction according to chemical equilibrium by Gibbs free-energy minimization method. The model consider all components as potential products in products sheet, it is a simple approach to represent the oxidizing and gasification reactions to obtain a crude synthesis gas at 850.0ºC.

Chemical equilibrium by Gibbs free-energy minimization method overestimate the Equivalence rate (ER_{AIR}) and the mass flow rate of CO_2 and H_2O (fraction in the crude synthesis gas), mainly because the model does not predict the reverse water gas shift equilibrium effect and the formation of light hydrocarbons and heavy hydrocarbons, breaking them into simpler forms. The model predicts the formation of more H_2 and less CO than the real process (experimental data). To break the hydrocarbon compounds is required energy, which is supplied by the combustion process (extended) demanding more oxidizing agent and forming consequently more CO_2 and H_2O as a product of combustion.

Steam agent at 2.5 bar and 150.0ºC (fluidization agent) is generated by the low-temperature vertical CSC (GA-CSC-1) in the synthesis gas heat recovery cooling system (second section). $95.0\%_{w/w}$ of the steam agent is injected by the primary and secondary injection distributor in the bed (GA-GASEI) in order to fluidize the bed and promote the gasification reactions (GA-GASEI), and $5.0\%_{w/w}$ of the steam agent in injected in the loop-seal (GA-LSE-1). The ratio of steam agent to dry biomass (bagasse and straw) is calculate by the Equation 7 and controlled by the design specification DS-GA-FG-1 varying the inlet hot water/steam agent mass flow rate to obtain a STBR equal of 0.5, considering the moisture content in the inlet bagasse and straw. The STBR is maintenance in 0.5 due to lack of details for bed fluidization, probably this value will be changed in future rigorous models involving fluid dynamic models, raising the steam mass flow rate to optimize the bed fluidization.

2.0% of the LHV_{db} of the biomass fed is assumed to be lost from the gasifier (GA-GASEI) being controlled by the design specification DS-GA-QL-1 with the aid of parameter calculation blocks (BHV blocks group) implemented.

The gasification of sugarcane bagasse and straw using high-purity oxygen and steam as gasification agents provides a crude synthesis gas content very-low or insignificant inerter elements present in the surrounding air (N2, Ne, He, Xe, Ar and Kr), water vapor (H_2O), carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), methane (CH_4), hydrogen sulfide (H_2S), hydrogen chlorine (HCl), chlorine (Cl_2), carbonyl sulfide (COS), ammonia (NH_3), nitrogen oxides (NO_x), sulfur oxides (SO_x), and solid particulate matters.

Tar, light hydrocarbons and heavy hydrocarbons is not estimated by the chemical equilibrium applying the Gibbs free-energy minimization method (GA-GASEI), hydrocarbons are converted to simple form as water vapor (H_2O), carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2) and a small fraction of methane (CH_4). Solid particulate matters content bed material, specifics catalytic active materials, unconverted char, coke, ashes content, soil, salts and minerals and others.

The main impurities present in the crude synthesis gas can be ammonia (NH_3), hydrogen sulfide (H_2S), carbonyl sulfide (COS), hydrogen chloride (HCl), chlorine (Cl_2), nitrous oxides (NO_x), sulfur oxides (SO_x), volatile metals, volatile organic compounds, tar and oils (heavy hydrocarbons), fines or submicron particles containing metals and metal salts, unconverted char (C), solid particulates, materials bed particles (not included in the Aspen Plus®v8.4 process model simulation), and others alkali compounds.

Primary gasifier cyclone gas/solid separator (GA-CYC-1) is modeled by using a Cyclone solids separator block as single-cyclone to remove the gross particulate content (ashes, silicates, metal salts, unconverted carbon, bed and additives materials) in the crude synthesis gas according to Muschelknautz calculation method for a maximum pressure drop of 0.012 bar applying spiral inlet cyclone type. The gross-particulate separated from the crude synthesis gas is recycled by the leg-riser back to the gasifier bed (GA-GASEI) to promote second-pass in the reaction zones raising the char conversion (to obtain $98.0\%_{w/w}$ of carbon conversion).

In the Aspen Plus®v8.4 process model simulation is considered that $50.0\%_{w/w}$ of the unconverted char (C) is removed in the gasifier bottom particulate materials discharge system (GA-SEP-4) modeled by using a Sep separator blocks. Another part can be recycled by the primary gasifier cyclone (GA-CYC-1) and a small fraction of fine particles can be dragged by the crude synthesis gas to the secondary multi-cyclone system (GA-CYC-2) according to the primary gasifier cyclone (GA-CYC-1) efficiency and the size of the solid particles (PSD distribution).

The model consider that $0.2\%_{w/w}$ of the crude synthesis gas conventional phase flowing into the primary gasifier cyclone (GA-CYC-1) return back to the reaction zone (GA-GASEI) by the leg-riser together the particles in the loop-seal (GA-LSE-1).

A secondary multi-cyclone system (GA-CYC-2) designed with five cyclones (battery) and modeled by using a Cyclone solids separator block according to Muschelknautz calculation method for a maximum pressure drop of 0.02 bar applying spiral inlet cyclone type removes part of the residual fines-particulate matters that leaving the top of the primary gasifier cyclone (GA-CYC-1). These particles are belt-conveyed and mixed (GA-SCR-3) with the bottom particulate matters removed from the gasifier (GA-SEP-4) to final disposal. The fine particles not recovered in the secondary multi-cyclone system (GA-CYC-2) is removed from the synthesis gas in the low-temperature synthesis gas wet cleaning system.

Bottom particulate matters (e.g.: sand; ash; slag; specifics catalytic active materials; unconverted materials, metal salts; alkali compounds and others) is discharged from the bottom of the gasifier (GA-GASEI), cooled using directly contact water added to avoid dust (consider the heat loss in the GA-FLA-1) by water-cooled screw conveyor (not simulated). The bottom particulate matters are stored together the fines-particulate matters removed in the multi-cyclone system (GA-CYC-2) in the ashes temporary storage bins to humidified ashes/slag (GA-FLA-1) until offloaded for disposal (field disposal together vinasses).

7.2.6.1 Gasifier bed materials

Spreadsheet calculation model is used to determine the quantity of MgO must be present into the gasifier bed (GA-GASEI) and the make-up mass flow rate of MgO necessary to substantially avoid the formation (sequestering potassium) of low-melting point glass-like bed agglomerations (K_2SiO_4). The bed agglomerations were associated to direct adhesion of the bed particles by partly molten fuel ash derived K–Mg phosphates (ashes content) and K-silicates (ashes and soil content) that should result from the interactions with the biomass potassium content. MgO raise the melting point (ternary eutectic form) sequestering potassium avoiding/reducing it to be carried over in the gasifier cyclones (GA-CYC-1) and deposits in the equipment walls.

MgO supplementary bed material load is estimated to be 2.0 mol mass flow rate per mol of reactive potassium inlet into the gasifier (GA-GASEI). MgO is delivered to thermochemical-biorefinery supplies offloading area by truck to storage, a pneumatic line feed the gasifier loop bed media feed bin, which transfers the supplies to the gasifier by screw-conveyor or pneumatic transporter (not included in the Aspen Plus®v8.4 process model simulation).

In the spreadsheet calculation model is considered the olive make-up mass flow rate as being 1.0%$_{w/w}$ of the mass flow rate of dry ash and extractive free (daef) sugarcane bagasse and straw inlet into the gasifier to compensate the olive losses. Olivine recirculate by the primary gasifier cyclone (GA-CYC-1) trough the leg-riser and the major part of the entrained olive is recovered from the crude synthesis gas exiting the gasifier by the secondary multi-cyclone system (GA-CYC-2), only a small part of the olivine as fine particles are dragged and removed in the low-temperature synthesis gas wet cleaning system (losses).

The majority of the bed materials and gross-biomass derived particles are separated in the primary gasifier cyclone (GA-CYC-1) and sent back (recycled) into the leg-riser and gravity-feed back to the gasifier bed (GA-GASEI) using steam fluidized loop-seal (GA-LSE-1). A secondary multi-cyclone system (GA-CYC-2) removes part of the residual fines-particulate matters that leaving the top of the primary gasifier cyclone (GA-CYC-1), this particles are mixed with the bottom particulate material removed from the gasifier (GA-SEP-4) to final disposal (BED MATERIALS AND ASHES).

The mineral-crystal (iron content) olivine catalyst considered as gasifier bed media is a commercial type olivine catalyst α-$(Mg_{0.8}Fe_{0.2})_2SiO_4$ delivered to thermochemical-biorefinery supplies offloading area by truck to storage. Pneumatic line fed the gasifier loop bed media feed bin, which transfers the supplies to the gasifier by screw-conveyor or pneumatic transporter (not included in the Aspen Plus®v8.4 process model simulation).

Olivine catalyst is used to reduce by about 60.0%$_{w/w}$ of the tar content in the crude synthesis gas produced in the atmospheric CFB directly-heated gasifier (GA-GASEI). Tar abatement increased up to 92.0%$_{w/w}$ when catalytic CF were combined with the bed, not included in the Aspen Plus®v8.4 process model simulation due the limitations of the gasification Gibbs equilibrium model, in future works with rigorous model can be considered.

7.2.7 Double-column cryogenic air separation unit with argon side arm column

A double-column cryogenic air separation unit (ASU) with argon side arm column is simulated integrated at a thermochemical-biorefinery to supply the high-purity oxygen required by the directly-heated gasification technology employed to synthesis gas production aiming its utilization for methanol production by low-pressure methanol catalytic-synthesis.

ASU is size-scaled according to the amount of high-purity gaseous oxygen required (considering 5.0%$_{w/w}$ of the high-purity oxygen as reserve in liquid form) in the sugarcane bagasse and straw gasification using atmospheric CFB directly-heated gasifier. Aspen Plus®v8.4 process model simulation is described in the section 7.2.6 (Gasification of biomass in an atmospheric circulating fluidized bed directly-heated gasifier by using high-purity oxygen and steam agents).

Aspen Plus®v8.4 process model simulation of the double-column cryogenic ASU with argon side arm column was developed using Van Laar model for calculates liquid activity coefficients in the property methods and Redlich-Kwong equation-of-state for calculates vapor phase thermodynamic properties.

Double-column cryogenic air separation unit with argon side arm column for the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) is part represent in the Figure 66 showing the Aspen Plus®v8.4 flowsheet of pre-distillation processes used to prepare and adjust the atmospheric air to achieve the cryogenic separation (section 1/3), part in the Figure 67 showing the Aspen Plus®v8.4 flowsheet of cold box section (section 2/3), and part in the Figure 68 showing the Aspen Plus®v8.4 flowsheet of high-pressure double-Claude cycle nitrogen liquefier (section 3/3).

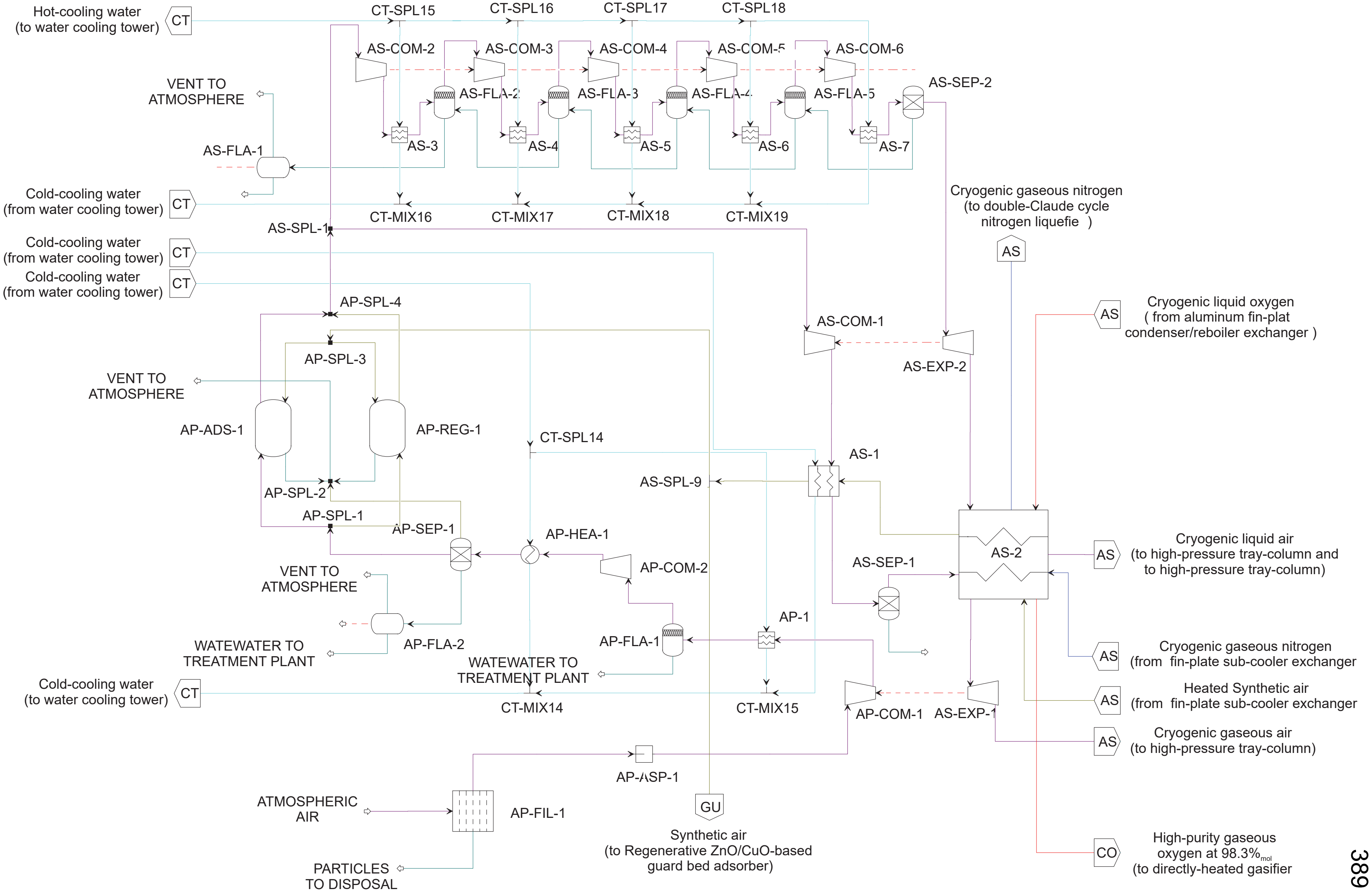


Figure 66 - Aspen Plus® v8.4 flowsheet (section 1/3) of the double-column cryogenic air separation unit with high-purity argon recovery for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3)

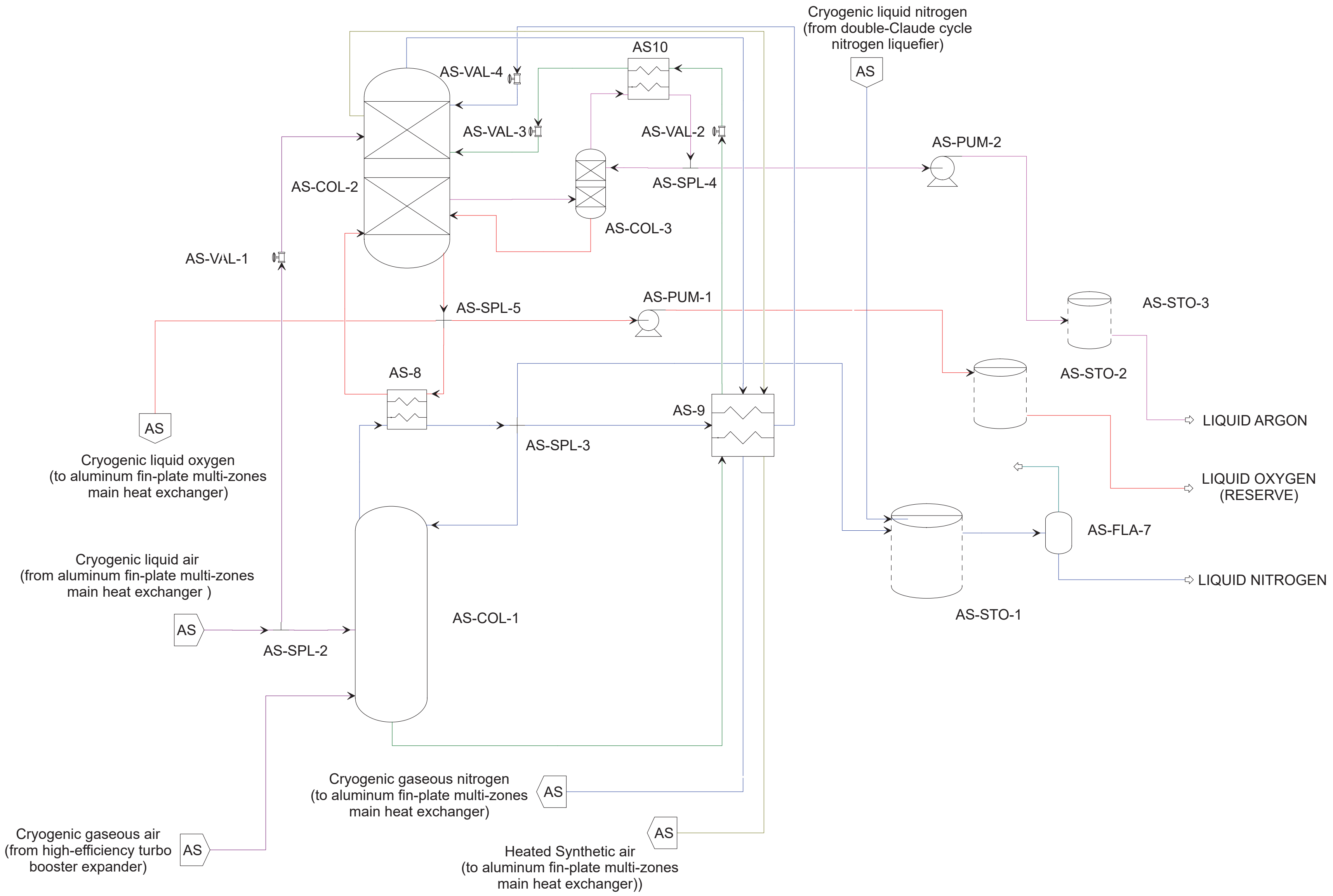


Figure 67 - Aspen Plus® v8.4 flowsheet (section 2/3) of the double-column cryogenic air separation unit with high-purity argon recovery for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3)

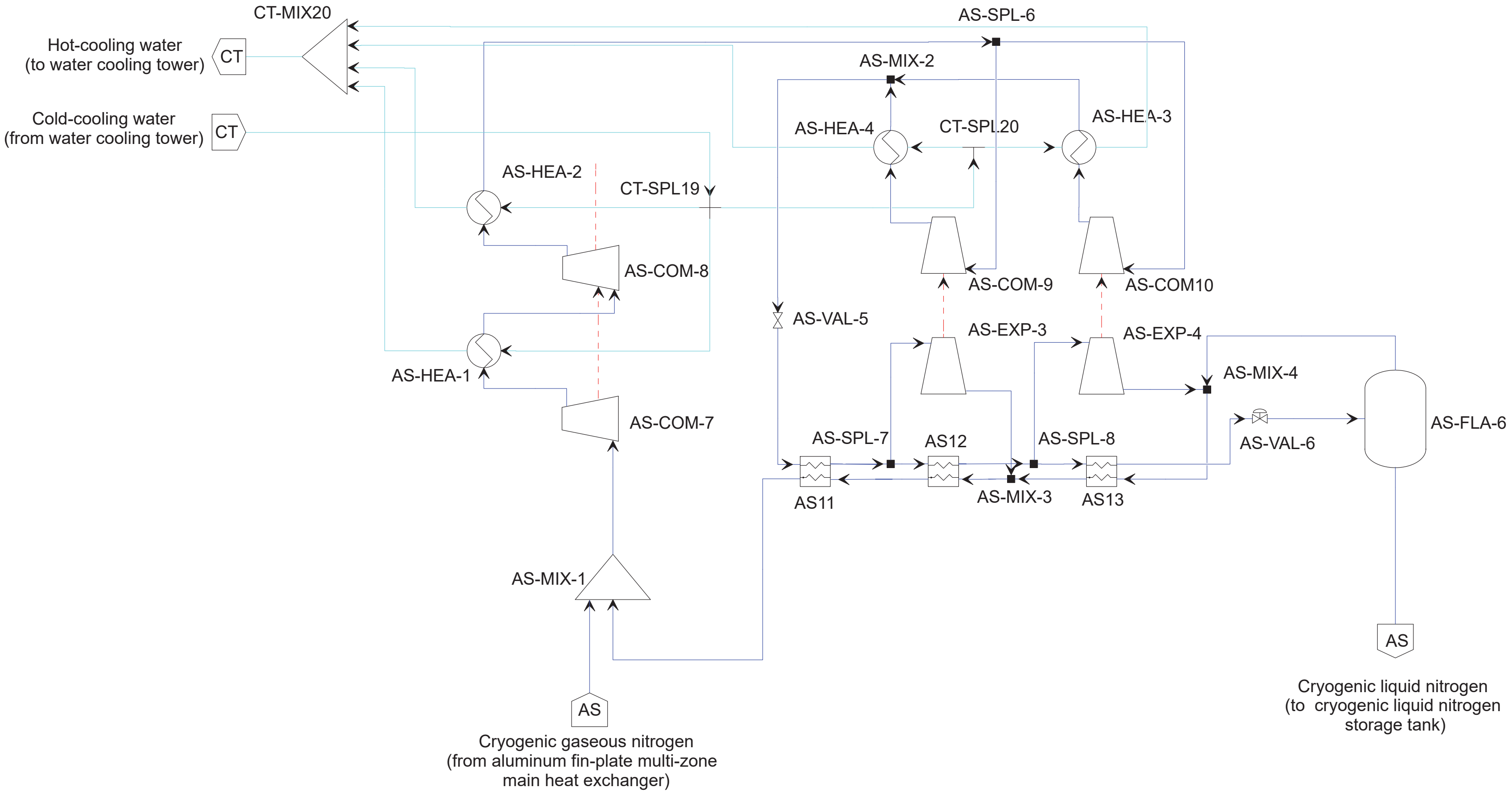


Figure 68 - Aspen Plus® v8.4 flowsheet (section 3/3) of the double-column cryogenic air separation unit with argon side arm column for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3)

As shown in Figure 66, part of the Aspen Plus®v8.4 flowsheet of the pre-distillation processes used to prepare and adjust the atmospheric air to achieve the cryogenic separation (section 1/3) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) is compost by: aluminum fin-plate multi-zones main heat exchanger (AS-2); aluminum fin-plate three-circuit after-cooler exchanger (AS-1); adsorber vessel (AP-ADS-1) (in adsorption-cycle time); regenerative vessel (AP-REG-1) (in regeneration-cycle time); condenser knock-out drum (AP-SEP-1); inlet multi-way valve 1 (AP-SPL-1); inlet multi-way valve 2 (AS-SPL-3); outlet multi-way valve (AP-SPL-4); vent off-gas multi-way valve and silencer (AP-SPL-2); pre-filter unit (AP-FIL-1); advanced blower system (AP-ASP-1); main air compressor (MAC) integrally-geared centrifugal two stages compressor (AP-COM-1 and AP-COM-2) and one stage expander (AS-EXP-1); MAC water after-cooler (AP-HEA-1); MAC condenser knock-out drum (AP-FLA-1); MAC water inter-cooler exchanger (AP-1); atmospheric condensate buffer/equalizer tank (AP-FLA-2); air splitter (AS-SPL-1); booster air compressor (BAC) integrally-geared centrifugal five stages compressor (AS-COM-2~6); BAC water inter-cooler exchangers (AS-3~6); BAC water after-cooler exchanger (AS-7); BAC condenser knock-out drums (CO-FLA-2~5 and AS-SEP-2); condenser knock-out drum (AS-SEP-1); atmospheric condensate buffer/equalizer tank (AP-FLA-1); high-efficiency turbo booster with expander (AS-EXP-2) and compressor (AS-COM-1); and direct drive permanent magnet motors (not included as block).

Aspen Plus®v8.4 process model simulation of the solid and gaseous reaction according to chemical equilibrium by Gibbs free-energy minimization method by using RGibbs reactor block (GA-GASEI) overestimate the equivalence rate (ER_{O2}) than the estimated by rigorous kinetic models or realistic process. Consequently, the ASU is estimated greater than the required for the realistic process (maximum size required).

ASPEN Rate-Sep simulation package is used in the high-pressure tray-column (AS-COL-1), low-pressure multi packed-column (AS-COL-2) and in the argon side arm partitioned packaged-column (AS-COL-3). The package consider non-equilibrium mass transfer rate-based calculations, taken in account the mass and heat transfer limitations, liquid and vapor film diffusion, and equipment fluid dynamic mechanisms.

Surrounding atmospheric fresh-air (ATMOSPHERIC AIR) is induced by advanced blower system (AP-ASP-1) modeled by using a Compr pressure changer block according to isentropic method for compressor considering 85.0% isentropic efficiency and 99.0% mechanical efficiency. A pre-filter unit (AP-FIL-1) is modeled by using a FabFl solids separator block according to Piecewise separation efficiency in function of the particle diameter of the solids to protect the blower (AP-ASP-1) and the MAC integrally-geared centrifugal two stages compressor (AP-COM-1 and AP-COM-2) from debris (PARTICLES).

The amount of atmospheric air processed (plant scale) is defined by the gaseous high-purity oxygen demanded by the atmospheric CFB directly-heated gasifier (CA blocks) avoiding surplus oxygen (avoiding overestimated scale).

Atmospheric air flow enters the MAC integrally-geared centrifugal two stages compressor (AP-COM-1 and AP-COM-2) by the inlet guide (AP-COM-1) to distribute the flow providing a uniform condition in the MAC first-stage impeller (AP-COM-1). Atmospheric air is compressed by the MAC high-efficiency first-stage impeller (AP-COM-1) modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 90.0% isentropic efficiency (isentropic compression).

After the first-stage of compression (AP-COM-1), the compressed air is cooled to 30.0ºC by the MAC water inter-cooler exchanger (AP-1) modeled by using a MHeatX exchanger block generating condensed phase, depending on the air moisture (80.0%$_{w/w}$ considered in the model) and dissolved gases contents. The condensed phase is removed in the condenser knock-out drum (AP-FLA-1) modeled by using a Flash2 separator block and sent to be after-pumped to wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

The air free of the condensate phase enters in the MAC second-stage impeller (AP-COM-2) and is compressed to 5.2 bar and about 122.0ºC by the MAC high-efficiency second-stage impeller (AP-COM-2) modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 90.0% isentropic efficiency (isentropic compression). After the second-stage of compression (AP-COM-2), the compressed air is cooled to 30.0ºC by the MAC water after-cooler exchanger (AP-HEA-1) modeled by using a HeatX exchanger block generating condensed phase content water and dissolved gases. The condensed phase is removed in the MAC condenser knock-out drum (AP-SEP-1) modeled by using a Sep separator block and sent to be after-pumped to wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-9) to the MAC inter-cooler exchanger (AP-1) and to the MAC after-cooler exchanger (AP-HEA-1). The amount of cooling water required is determined and controlled by design specification DS-CT-FL-10 and design specification DS-CT-FL-11, both varying the mass flow rate of cooling water passing through the equipments users. The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

The Aspen Plus®v8.4 process model simulation of the thermal pressure swing adsorption/desorption (TPSA) system was developed in steady-state mode using VANL-RK physical property methods in a simplified model. Flash2 separator blocks represent the pressurized adsorption of impurities (contained in the atmospheric air) in the adsorber vessel (AP-ADS-1) and the atmospheric high-temperature desorption/regeneration process of impurities in the regenerative vessel (AP-RE-1), based on a physical binding of gas molecules to selective adsorbent material layers.

The compressed and cooled air at 5.2 bar and 27.0ºC is supplied to an inlet manifold containing inlet multi-way valve 1 (AS-SPL-1) connected to adsorber vessel (AP-ADS-1) in adsorption-cycle-time and then fed passing the open control inlet multi-way valve 1 (AP-SPL-1) into the adsorber vessel (AP-ADS-1). The compressed air flows through the adsorbing bed material layers using the effect of partial pressure to perform the adsorption cycle (first vessel) in upward direction. Impurities such as H_2O, CO_2, CO, CH_4, and NO_x (e.g.: NO_2, N_2O, and NO) are selectively adsorbed on the surface of the adsorbent material. Purified compressed air from the top of the adsorber vessel (AP-ADS-1) flow-out the TPSA system by the outlet multi-way valve (AP-SPL-4).

After adsorption cycle-time the vessel is depressurized to atmospheric pressure, beginning the desorption/regeneration cycle carried out at low-pressure (atmospheric discharge) in the regenerative vessel (AP-REG-1) (in regeneration cycle-time), on continuous closed-loop cycle mode.

Synthetic air is purged from the low-pressure multi packed-column (AS-COL-2), pre-heated in the aluminum fin-plate multi-circuits main heat exchanger (AS-2), and heated at 1.05 bar and 150.0ºC in the aluminum fin-plate three-circuit after-cooler exchanger (AS-1). Hence, this heated synthetic air is used to regenerate (TPSA) the bed materials in the packaged-layers into the regenerative vessel (GU-REG-1) of the regenerative ZnO/CuO-based guard bed adsorber, and in the regenerative vessel (AP-RE-1) of the double-column cryogenic ASU with high-purity argon recovery system.

Heated low-pressure synthetic air (without impurities) at 1.05 bar and 150.0ºC is part supplied to an inlet manifold containing inlet multi-way valve 2 (AS-SPL-3) connected to regenerative vessel (GU-REG-1) an then feed in the depressurized regenerative vessel (AP-REG-1) passing though the adsorber vessel heating the adsorbing bed material packaged-layers to 150.0ºC. The cycle use the effect of low-pressure and high-temperature to perform the regeneration phase (second vessel), desorbing in a downward direction the impurities adsorbed in the adsorbing bed material surface. Desorbed impurities are being vented to atmosphere by vent off-gas multi-way valve and silencer (AP-SPL-2) together the after-used synthetic air. After the regeneration phase, the regenerative vessel (AP-REG-1) is re-pressurized using purified air and placed on-line for adsorption cycle-time.

The amount of heated low-pressure synthetic air destined to regenerative vessel (AP-REG-1) is determined by the amount of synthetic air purged in the low-pressure multi packed-column (AS-COL-2) and dependent on heated low-pressure synthetic air required by the regenerative vessel (GU-REG-1) in the regenerative ZnO/CuO-based guard bed adsorber. The mass flow rate is controlled by design specification DS-GU-FG-1 varying the mass flow rate of the heated low-pressure synthetic air to regenerative vessel (GU-REG-1) coupled with design specification DS-AS-FG-3 varying the mass splitted (AS-SPL-9).

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), Aspen Plus®v8.4 process model simulation of the low-pressure multi packed-column (AS-COL-2) consider the synthetic air mass flow rate (purge) as $10.0\%_{w/w}$ of the atmospheric air mass flow rate processed by the double-column cryogenic ASU with argon side arm column. Moreover, the mass flow rate is controlled by design specification DS-AS-FG-1 varying the configuration of the synthetic air-side-product stream mass flow rate in the low-pressure multi packed-column (AS-COL-2).

Spreadsheet calculation model of the adsorber (AP-ADS-1) and regenerative (AP-REG-1) vessels consider the especially adsorbent bed material's compost by about $67.0\%_{w/w}$ of SiO_2/Al_2O_3 catalyst layer and $33.0\%_{w/w}$ of Zeolite's catalyst layers. The order of layers is defined from the bottom of the bed (raw atmospheric air entrance) by first layer content SiO_2/Al_2O_3 catalyst and second layer content Zeolite's catalyst family. However, Zeolite's catalyst family is subdivided in layers content 3A Zeolite catalyst and/or 13X Zeolite catalyst. The Zeolite family layer is considered in the spreadsheet calculation model as single layer containing Zeolite catalyst type.

Zeolite's catalyst layers considered in the adsorber (AP-ADS-1) and regenerative (AP-REG-1) vessels are a commercial type 3A Zeolite catalyst and/or 13X Zeolite catalyst. This Zeolite's types are selective for carbonaceous (e.g.: CO, CO_2, and CH_4) and low-selective for NO_x (e.g.: NO_2, N_2O, and NO), being weight loaded considering the saturation ratio limits of $32.0\%_{w/w}$ to adsorbing H_2O and carbonaceous compounds per adsorption cycle. Zeolite's catalyst lifetime is expected to be about 2 year before the necessity of deactivated catalyst to be partial or full discharged and new activity catalyst loaded, deactivated catalyst is sent to regeneration process and/or to final disposal.

SiO_2/Al_2O_3 catalyst layer considered in the adsorber (AP-ADS-1) and regenerative (AP-REG-1) vessels is a commercial type selective for H_2O and carbonaceous (e.g.: CO, CO_2), being weight loaded considering the saturation ratio limits of $50.0\%_{w/w}$ to adsorbing H_20 and $5.0\%_{w/w}$ to adsorbing carbonaceous compounds per adsorption cycle. SiO_2/Al_2O_3 catalyst lifetime is expected to be about 1 year before the necessity of deactivated catalyst to be partial or full discharged and new activity catalyst loaded, deactivated catalyst is sent to regeneration process and/or to final disposal.

The purified pressurized air from the TPSA adsorption/desorption system is separated in two fractions in the air splitter (AS-SPL-1). In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) a fraction of $53.0\%_{w/w}$ is sent to BAC integrally-geared centrifugal five stages compressor (AS-

COM-2~6), and another fraction of 47.0%$_{w/w}$ is sent to turbo booster with expander (AS-EXP-2) and compressor (AS-COM-1) energy save system.

The Aspen Plus®v8.4 process model simulation of the BAC integrally-geared centrifugal five stages compressor (AS-COM-2~6) feature a single-shaft arrangement was developed in steady-state mode using VANL-RK physical property methods for the air-side and IAPWS-95 physical property methods for the water-side. This compressor is compost by BAC integrally-geared centrifugal impeller stages (AS-COM-2~6), BAC water inter-cooler exchangers (AS-3~6), BAC water after-cooler exchanger (AS-7), condenser knock-out drums (AS-FLA-2~5 and AS-SEP-2), direct drive permanent magnet motor (not included in the Aspen Plus®v8.4 process model simulation), and atmospheric condensate buffer/equalizer tank (AS-FLA-1).

Part of the purified pressurized air from the TPSA adsorption/desorption system is compressed to 60.0 bar by the BAC Integrally-geared centrifugal five stages compressor (AS-COM-2~6) modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 83.0% isentropic efficiency (isentropic compression). The compressed air between the BAC-stages is cooled to 30.0ºC by the BAC water inter-cooler exchangers (AS-3~6) and after-cooled to 30.0ºC by the BAC water after-cooler exchanger (AS-7) modeled by using a MHeatX exchanger blocks generating condensed phase content water and dissolved gases. The condensed phase is removed in the condenser knock-out drums (AS-FLA-2~5) modeled by using a Flash2 separator blocks and by Sep separator block (AS-SEP-2), and then sent to atmospheric condensate buffer/equalizer tank (AS-FLA-1) modeled by using a Flash2 separator block at ambient conditions. Then the condensed phase is after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

Sep separator block (AS-SEP-2) is used to remove all of the impurities (simulation artifice) in the Aspen Plus®v8.4 process model simulation before the cryogenic processes leaving only the main key compounds (e.g.: O_2, N_2, Ne, He, Ar, Kr, and Xe).

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM11) to the inter-cooler exchangers (AP-3~7) and to the after-cooler exchanger (AS-7). The amount of cooling water required to cool-down the pressurized-air is determined and controlled by design specification DS-CT-FL-13 varying the mass flow rate of cooling water passing through the equipments users. The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

The single shaft and multiple pinions in the integrally-geared centrifugal five stages compressor (CC-COM blocks) is drive by a synchronous direct drive permanent magnet motor modeled by AS-E-6 work stream and optimized to obtain the same compression ratio in the compression stages by design specification DS-AS-TR-1 and FORTRAN calculation block CA-AS-TR-2 varying the pressure ratio in all of the five compression stages (CO-COM blocks). The electrical potential losses by attrite in the mechanical move parts was considered as 1.0% of the mechanical energy required by the stage (99.0% mechanical efficiency).

Another part of the purified pressurized air from the TPSA adsorption/desorption system is compressed by high-efficiency turbo booster compost by expander (AS-EXP-2) and compressor (AS-COM-1). The turbine side (AS-EXP-2) is modeled by using a Compr pressure changer block in turbine model considering 90.0% isentropic efficiency (isentropic expansion) to represent the expansion from 60.0 bar and 30.0ºC to 5.65 bar and at about -108.0ºC. The compressor side (AS-COM-1) is modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 90.0% isentropic efficiency (isentropic compression) to represent the compression from 5.0 bar and 30.0ºC to about 17.0 bar and 172.0ºC.

After compressed by the high-efficiency turbo booster, the compressed-air is cooled-down to 17.17 bar and 30.0ºC in the aluminum fin-plate three-circuit after-cooler exchanger (AS-1) by cooling water, obtained from the water-cooling tower system at 27.0ºC and pumped (CT-PUM10) through the water-circuit, and by the synthetic air at 1.08 bar and 0.0ºC flowing into gas-circuit. The condensed phase is removed in the condenser knock-out drum (AS-SEP-1) modeled by Sep separator block, used to remove all of the impurities (simulation artifice) in the Aspen Plus®v8.4 process model simulation before the cryogenic processes. Hence, leaving only the main key compounds (e.g.: O_2, N_2, Ne, He, Ar, Kr, and, Xe). The condensate, if there, is after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

Synthetic air, purged from the low-pressure multi packed-column (AS-COL-2), is pre-heated in the aluminum fin-plate multi-zones main heat exchanger (AS-2) and then in the aluminum fin-plate three-circuit after-cooler exchanger (AS-1) is heated from 1.08 bar and 0.0ºC to 1.05 bar and 150.0ºC. Heat is recovered, and the synthetic air conditioned to achieve time-optimized regeneration phase in the regenerative vessel (GU-REG-1) of regenerative ZnO/CuO-based guard bed adsorber, and in the regenerative vessel (AP-RE-1) of double-column cryogenic ASU with high-purity argon recovery.

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM10) to the cooling water circuit in the aluminum fin-plate three-circuit after-cooler exchanger (AS-1). The amount of cooling water required is determined and controlled by design specification DS-CT-FL-12 varying the mass flow rate of cooling water passing through the aluminum fin-plate three-circuit after-cooler exchanger (AS-1). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

Aspen Plus®v8.4 process model simulation of the aluminum fin-plate multi-zones main heat exchanger (AS-2) was developed using VANL-RK physical property methods and modeled by using a MHeatX exchanger block. The exchanger (AS-2) is used to cooling down the compressed air from 17.17 bar and 30.0ºC to about 17.17 bar and -29.0ºC. In addition, to cool down and liquefy (phase change) the expanded air from 5.65 bar and -108.0ºC to about 5.62 bar and -178.0ºC.

To cool down and liquefy the air for distillation process are used gaseous nitrogen product obtained from the 1º theoretically vapor stage (top column stage) of the low-pressure multi-packed column (AS-COL-2) after heat exchanger in the aluminum fin-plate sub-cooler exchanger (AS-9), synthetic air purged from the 22º theoretically gaseous stage in the low-pressure multi-packed column (AS-COL-2) after heat exchanger in the aluminum fin-plate sub-cooler exchanger (AS-9), and liquid oxygen product from the 75º theoretically liquid stage (bottom column stage) of the low-pressure multi-packed column (AS-COL-2). Gaseous nitrogen product is available at about 1.07 bar and -174.2ºC, being heated in the aluminum fin-plate multi-zones main heat exchanger (AS-2) to about 1.05 bar and -67.7ºC. Synthetic air is available at about 1.12 bar and -173.0ºC, being heated in the aluminum fin-plate multi-zones main heat exchanger (AS-2) to about 1.08 bar and 0.0ºC. Liquid oxygen product is available at about 1.30 bar and -180.6ºC, being heated and vaporized (phase change) in the aluminum fin-plate multi-zones main heat exchanger (AS-2) to about 1.01325 bar and 25.0ºC (ambient conditions).

As optional choice, high-purity gaseous nitrogen at 1.05 bar and -67.7ºC (energy economy) is sent to the high-pressure double-Claude cycle nitrogen liquefier (LNG-based nitrogen liquefier) to be liquefied and commercialized as another value-added bio-based product in the product-portfolio of the thermochemical-biorefinery. Even thought, another optional choice is vent to atmosphere in ambient conditions economizing the electricity required by the LNG-based nitrogen liquefiers with possibility to export electricity (equivalent generated) to the electric power grid (flexible configurations) rather than liquid nitrogen.

High-purity gaseous oxygen (O_2) at 98.3%$_{mol}$ is fed into the gasifier buffer/equalizer tank (GA-BUF-1) at 25.0ºC and atmospheric pressure (ambient conditions) and after-used as gasification agent (oxidizing) for gasification of biomass in an atmospheric CFB directly-heated gasifier (CA blocks).

After the aluminum fin-plate multi-zones main heat exchanger (AS-2), the compressed air stream is expanded (AS-EXP-1) from 17.17 bar and -29.0ºC to 5.8 bar and -90.1ºC before to be fed into the high-pressure tray-column (AS-COL-1). The one stage expander (AS-EXP-1) is modeled by using a Compr pressure changer block in turbine model to represent the expansion stage of MAC integrally-geared centrifugal compressor (turbo booster section).

After the aluminum fin-plate multi-zones main heat exchanger (AS-2), the liquefied air at about 5.62 bar and -178.0ºC is separated in two fraction by the liquid air splitter

(AS-SPL-2). Being 50.0%$_{w/w}$ fed into the high-pressure tray-column (AS-COL-1) in the 32º theoretically liquid stage, and another 50.0%$_{w/w}$ fed into the low-pressure multi-packed column (AS-COL-2) in the 23º theoretically liquid stage.

As shown in Figure 67, Aspen Plus®v8.4 flowsheet of the cold box section (section 2/3) in the double-column cryogenic ASU with argon side arm column in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) is compost by: high-pressure tray-column (AS-COL-1); low-pressure multi packaged-column (AS-COL-2); argon side arm partitioned packaged-column (AS-COL-3); aluminum fin-plate sub-cooler exchanger (AS-9); aluminum fin-plate condenser/reboiler exchanger (AS-8); aluminum fin-plate condenser exchanger (AS10); liquid air splitter (AS-SPL-2); cryogenic liquid oxygen pump (AS-PUM-1); cryogenic liquid argon pump (AS-PUM-2); cryogenic liquid nitrogen storage tank (AS-STO-1); cryogenic liquid oxygen storage tank (AS-STO-2); cryogenic liquid argon storage tank (AS-STO-3); anti-flash security valve 1 (AS-VAL-1); anti-flash security valve 2 (AS-VAL-3); anti-flash security valve 3 (AS-VAL-4); adiabatic expansion valve (AS-VAL-2); and vent valve (AS-FLA-7).

After expanded (AS-EXP-1), cryogenic gaseous air at 5.8 bar and at about -90.1ºC is fed in the high-pressure tray-column (AS-COL-1) in the 45º theoretically vapor stage (bottom column stage). In addition, one part of the cryogenic liquid air at about 5.62 bar and -178.0ºC is fed in the high-pressure tray-column (AS-COL-1) in the 32º theoretically liquid stage.

Rigorous Aspen Plus®v8.4 process model simulation of the high-pressure tray-column (AS-COL-1) was developed using VANL-RK physical property methods for RadFrac columns block on cryogenic convergence mode without in-bed condenser and reboiler. The model was optimized for estimated 45 theoretical stages considering a Nutter Float Valve (Aspen96) tray section with two-passes per tray with valve type BDH 14 gauge deck thickness and standards panel A and B with weir height of 30.0 mm and tray diameter of 1.00 m. The model use rate-based calculation for Mixed flow model without reactions in film vapor phase employing vapor and liquid phase film non-ideality corrections. Default Aspen Plus®v8.4 packing parameters is applied to calculate interfacial area and the mass transfer coefficient by Scheffe and Weiland (1987) method, and heat transfer coefficient by Chilton–Colburn (Taylor and Krishna, 1993) method.

The gaseous top-product containing mainly high-purity nitrogen leave at about 5.20 bar and -178.5ºC withdrawn from the 1º theoretically vapor stage (top column stage) in the high-pressure tray-column (AS-COL-1) is cooled and condensate to 5.20 bar and at about -180.5ºC, passing thought the aluminum fin-plate condenser/reboiler exchanger (AS-8) condenser-zone. Part (47.5%$_{w/w}$ by model result) of the high-purity liquid nitrogen return back (as reflux) to the 1º theoretically liquid stage (top column stage) in the high-pressure tray-column (AS-COL-1).

The liquid bottom product containing mainly high-purity liquid oxygen at about 1.30 bar and -180.6ºC from the 75º theoretically liquid stage (bottom column stage) in the low-pressure multi-packed column (AS-COL-2) is used in the aluminum fin-plate condenser/reboiler exchanger (AS-8) into the vaporizer-zone to cool down and condense the gaseous high-purity nitrogen product at about 5.20 bar and -178.5ºC from the 1º theoretically vapor stage (top column stage) in the high-pressure tray-column (AS-COL-1). The amount of liquid bottom product vaporized and sent-flowing upward back trough the multi-packed column (AS-COL-2) is determined by the exchanger temperature limits (cross-over avoided).

A fraction (40.5%$_{w/w}$ by model result) of the high-purity liquid nitrogen is sent to the aluminum fin-plate sub-cooler exchanger (AS-9) and after to the low-pressure column (AS-COL-2). Another reminiscent fraction is withdrawn as high-purity liquid nitrogen product and sent to storage in the cryogenic liquid nitrogen storage tank (AS-STO-1), available as high-purity liquid nitrogen (LIQUID NITROGEN).

The liquid bottom crude product at about 5.80 bar and -171.4ºC containing about 50.4%$_{w/w}$ of liquid nitrogen and 47.1%$_{w/w}$ of liquid oxygen is withdrawn from the 45º theoretically liquid stage (bottom column stage) in the high-pressure tray-column (AS-COL-1). The high-pressure tray-column (AS-COL-1) does not have reboiler, being the bottom liquid Crude product after-sent directly to the aluminum fin-plate sub-cooler exchanger (AS-9).

Another part of the cryogenic liquid air at about 5.62 bar and -178.0ºC from the liquid air splitter (AS-SPL-2) is fed in the low-pressure multi-packed column (AS-COL-2) in the 23º theoretically liquid stage passing before through anti-flash security valve 1 (AS-VAL-1) to avoid the flash-explosion effect adjusting the stream pressure to the tray pressure required. The liquid bottom crude product at about 5.62 bar and -178.0ºC from the aluminum fin-plate condenser exchanger (AS10) is fed in the low-pressure multi-packed column (AS-COL-2) in the 24º theoretically liquid stage passing before through anti-flash security valve 2 (AS-VAL-3) to avoid the flash-explosion effect adjusting the stream pressure to the tray pressure required. The cryogenic liquid nitrogen at about 1.10 bar and -190.4ºC from the aluminum fin-plate sub-cooler exchanger (AS-9) is fed in the low-pressure multi-packed column (AS-COL-2) in the 1º theoretically liquid stage (top column stage) passing before through anti-flash security valve 3 (AS-VAL-4) to avoid the flash-explosion effect adjusting the stream pressure to the tray pressure required. The liquid bottom product at about 1.23 bar and -181.3ºC from the bottom of the argon side arm partitioned packaged-column (AS-COL-3) is fed in the low-pressure multi-packed column (AS-COL-2) in the in the 47º theoretically liquid stage. The bottom product vaporized at 1.30 bar and at about -178.6ºC in the aluminum fin-plate condenser/reboiler exchanger (AS-8) into the reboiler-zone is fed in the low-pressure multi-packed column (AS-COL-2) in the 75º theoretically gaseous stage.

Rigorous Aspen Plus®v8.4 process model simulation of the low-pressure multi packed-column (AS-COL-2) was developed using VANL-RK physical property methods for RadFrac columns block on cryogenic convergence mode without in-bed condenser and reboiler. The model was optimized for estimated 75 theoretical stages divided in three-packaged section: MELLAPAK 170Y packing section from 1º to 23º theoretically stages; MELLAPAK 500Y packing section from 24º to 44º theoretically stages; and MELLAPAK 750Y packing section from 45º to 75º theoretically stages. In this case, the packed column model was developed with packed height of 0.40 m (HETP) per stages and column diameter of 1.80 m on standards characteristics. The model use rate-based calculation for Mixed flow model without reactions and film resistance in vapor phase, without reactions and with film resistance in liquid phase. Default Aspen Plus®v8.4 packing parameters is applied to calculate pressure drop and liquid holdup by Stichlmair method, to predict the mass transfer coefficient and interfacial area by Onda et al. (1968) correlation, and heat transfer coefficient by Chilton- Colburn (Taylor and Krishna, 1993) method.

Synthetic air is withdrawn (purged) at about 1.16 bar and -189.8ºC from the 22º theoretically gaseous stage of the low-pressure multi-packed column (AS-COL-2) to adjust internal column equilibrium and purity of products. The model consider the amount of purged synthetic air as $10.0\%_{w/w}$ of the atmospheric air mass flow rate processed by the double-column cryogenic ASU with argon side arm column, which is controlled by design specification DS-ASFG-1 varying the configuration of stream mass flow rate of the synthetic air-side-product in the low-pressure multi packed-column (AS-COL-2). The purged synthetic air is sent to the aluminum fin-plate sub-cooler exchanger (AS-9).

The gaseous top-product containing mainly gaseous cryogenic nitrogen at about 1.16 bar and -189.8ºC withdrawn from the 1º theoretically vapor stage (top column stage) in the low-pressure multi-packed column (AS-COL-2) is directly sent to the aluminum fin-plate sub-cooler exchanger (AS-9).

Aspen Plus®v8.4 process model simulation of the aluminum fin-plate condenser/reboiler exchanger (AS-8) was developed by using a MHeatX exchanger block representing the integration between the condenser of the high-pressure column (AS-COL-1) and the reboiler of the low-pressure column (AS-COL-2).

The liquid bottom product containing mainly purity oxygen at about 1.30 bar and -180.6ºC from the 75º theoretically liquid stage (bottom column stage) in the low-pressure multi-packed column (AS-COL-2) is heated and vaporized to 1.30 bar and at about -178.6ºC in the aluminum fin-plate condenser/reboiler exchanger (AS-8) into the reboiler-zone. Consequently, the vaporized bottom product flow upward through the packed-column. A fraction of the liquid bottom product vaporized is only the necessary fraction to condense the gaseous top-product from the 1º theoretically vapor stage (top column stage) of the high-pressure tray-column (AS-COL-1), which contain mainly high-purity nitrogen at about 5.20 bar and -178.5ºC, being determined by the exchanger temperature limits (cross-over avoided).

Another fraction of the liquid bottom product containing mainly oxygen from the 75º theoretically liquid stage (bottom column stage) is extracted as product and sent to the aluminum fin-plate multi-zones main heat exchanger (AS-2) as cooling agent. After heated, the gaseous high purity oxygen is sent to the atmospheric CFB directly-heated gasifier (CA blocks) area. The amount of high-purity oxygen produced is controlled by design specification DS-AS-FG-2 and determined by the design specification DS-GA-TG-1 varying the mass flow rate of produced oxygen and by the atmospheric air mass flow rate processed by the double-column cryogenic ASU with argon side arm column.

Another remain fraction (surplus designed) of the liquid bottom product from the low-pressure multi-packed column (AS-COL-2) is extracted as high-purity liquid oxygen product and pumped by cryogenic liquid oxygen pump (AS-PUM-1) to storage in the cryogenic liquid oxygen storage tank (AS-STO-2) as reserve for brief stops and start-up, available as liquid oxygen (LIQUID OXYGEN). The model of the double-column cryogenic ASU with argon side arm column consider a reserve of $5.0\%_{w/w}$, on the liquid form, of the gaseous oxygen produced, which is based on the gaseous oxygen required (bagasse reserve equivalence) by the gasification of biomass in an atmospheric CFB directly-heated gasifier (CA blocks).

Side gaseous cryogenic crude product at about 1.23 bar and -181.3ºC extracted from the 47º theoretically gaseous stage in the low-pressure multi-packed column (AS-COL-2) is fed in the 100º theoretically gaseous stage (bottom column stage) in the argon side arm partitioned packaged-column (AS-COL-3). The amount of side gaseous extracted is determined by the column internal equilibrium and composition of the gaseous phase obtained in the 47º theoretically stage by the ASPEN Rate-Sep simulation package methods. Even thought, it is highly linked with the atmospheric air mass flow rate processed by the double-column cryogenic ASU with argon side arm column and desired purity level of the bottom liquid product obtained in the 75º theoretically liquid stage (bottom column stage) in the low-pressure multi-packed column (AS-COL-2).

Rigorous Aspen Plus®v8.4 process model simulation of the argon side arm partitioned packaged-column (AS-COL-3) was developed using VANL-RK physical property methods for RadFrac columns block on cryogenic convergence mode without in-bed condenser and reboiler. The model was optimized for estimated 100 theoretical stages considering a MELLAPAKPL 452Y packing section from 1º to 100º theoretically stages. The simplified model represents the argon recovery column section and the argon purification section grouped into a single column model considering the packed height of 0.38 m (HETP) per stages and column diameter of 0.70 m on standards characteristics. The model use rate-based calculation for Mixed flow model without reactions and film resistance in vapor phase, without reactions and with film resistance in liquid phase. Default Aspen Plus®v8.4 packing parameters is applied to calculate pressure drop and liquid holdup by Stichlmair method, to predict the mass transfer coefficient and interfacial area by Onda et al. (1968)

correlation, and heat transfer coefficient by Chilton- Colburn (Taylor and Krishna, 1993) method.

The gaseous top-product containing mainly high-purity argon at about 1.22 bar and -184.5ºC from the 1º theoretically vapor stage (top column stage) of the argon side arm partitioned packaged-column (AS-COL-3) is cooled and condensate to 1.22 bar and about -184.5ºC in the aluminum fin-plate condenser exchanger (AS10).

Aspen Plus®v8.4 process model simulation of the aluminum fin-plate condenser exchanger (AS10) was developed using MHeatX exchanger block considering 2 zones in countercurrent mode. High-purity gaseous argon product at about 1.22 bar and -184.1ºC from the 1º theoretically vapor stage (top column stage) of the argon side arm partitioned packaged-column (AS-COL-3) is condensed at about 1.22 bar and -184.5ºC using depressurized sub-cooled bottom liquid Crude product. The depressurized sub-cooled bottom liquid Crude product available at about 1.18 bar and -190.1ºC, after the adiabatic expansion valve (AS-VAL-2), is heated to about 1.17 bar and -188.1ºC.

The largest fraction (98.19$\%_{w/w}$ model result) of the condensate high-purity liquid argon (top product) at 1.22 bar and about -184.5ºC from the aluminum fin-plate condenser exchanger (AS10) is refluxed back into the 1º theoretically liquid stage (top column stage) of the argon side arm partitioned packaged-column (AS-COL-3) to achieve the high-purity level. Another remain fraction (1.81$\%_{w/w}$ model result) is withdrawn as high-purity liquid argon product and pumped by cryogenic liquid argon pump (AS-PUM-2) to storage in the cryogenic liquid argon storage tank (AS-STO-3), hence being available as high-purity liquid argon (LIQUID ARGON) in the product portfolio.

The liquid bottom product at about 1.23 bar and -181.3ºC from the 100º theoretically liquid stage (bottom column stage) of the argon side arm partitioned packaged-column (AS-COL-3) is fed in the low-pressure multi-packed column (AS-COL-2) in the 47º theoretically liquid stage. The amount of liquid bottom product sent-flowing back is determined by ASPEN Rate-Sep simulation package methods and by the amount of high-purity liquid argon refluxed back into the top (argon purity) of the argon side arm partitioned packaged-column (AS-COL-3).

Aspen Plus®v8.4 process model simulation of the aluminum fin-plate sub-cooler exchanger (AS-9) was developed using MHeatX exchanger block considering 4 zones in countercurrent mode.

Bottom liquid Crude product at about 5.80 bar and -171.4ºC from the 45º theoretically liquid stage (bottom column stage) of the high-pressure tray-column (AS-COL-1) is sub-cooled to 5.65 bar and at about -183.8ºC in the aluminum fin-plate sub-cooler exchanger (AS-9). After, is expanded in the adiabatic expansion valve (AS-VAL-2) to 1.18 bar and -190.1ºC before inlet in the aluminum fin-plate condenser exchanger (AS10).

Top high-purity liquid nitrogen product at about 5.20 bar and -180.5ºC from the aluminum fin-plate sub-cooler exchanger (AS-9) is sub-cooled to 5.00 bar and at about -190.5ºC in the aluminum fin-plate sub-cooler exchanger (AS-9). After, is expanded by anti-flash security valve 3 (AS-VAL-4) adjusting the pressure to tray-pressure requirements (1.10 bar and -190.4ºC) before inlet in the 1º theoretically liquid stage (top column stage) of the low-pressure multi packed-column (AS-COL-2).

To sub-cooling the bottom liquid Crude and the top high-purity liquid nitrogen products from the high-pressure tray-column (AS-COL-1) are used gaseous high-purity nitrogen product and synthetic air. Gaseous high-purity nitrogen product is obtained from the 1º theoretically vapor stage (top column stage) in the low-pressure multi-packed column (AS-COL-2) and is available at about 1.10 bar and -194.7ºC. Synthetic air is purged from the 22º theoretically gaseous stage in the low-pressure multi-packed column (AS-COL-2) and is available at about 1.16 bar and -189.8ºC. The gaseous high-purity nitrogen is heated to about 1.07 bar and - 174.2ºC, and the synthetic air is heated to about 1.12 bar and -173.0ºC.

As shown in Figure 68, Aspen Plus®v8.4 flowsheet of the high-pressure double-Claude cycle nitrogen liquefier (section 3/3) in Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) is compost by: water inter-cooler exchanger (AS-HEA-1); water after-cooler exchanger 1 (AS-HEA-2); water after-cooler exchanger 2 (AS-HEA-3); water after-cooler exchanger 3 (AS-HEA-4); high-efficiency centrifugal two stages compressor (AS-COM-7 and AS-COM-8) with first-stage impeller (AS-COM-7) and second-stage impeller (AS-COM-8); splitter 1 (AS-SPL-6); splitter 2 (AS-SPL-7); splitter 3 (AS-SPL-8); mixer 1 (AS-MIX-2); mixer 2 (AS-MIX-3); mixer 3 (AS-MIX-4); first heat exchanger (AS11); second heat exchanger (A12); cold heat exchanger (AS13); warm high-efficiency turbo booster (AS-COM-9 and AS-EXP-3) with centrifugal compressor (AS-COM-9) and expander (AS-EXP-3); cold high-efficiency turbo booster (AS-COM-10 and AS-EXP-4) with centrifugal compressor (AS-COM-10) and expander (AS-EXP-4); recycle mixer (AS-MIX-1); phase separator vessel (AS-FLA-6); and Joule-Thompson valve (AS-VAL-6).

The Aspen Plus®v8.4 process model simulation of the high-pressure double-Claude cycle nitrogen liquefier was developed in steady-state mode using VANL-RK physical property methods for the high-purity nitrogen side, and IAPWS-95 physical property methods for the cooling water side.

Gaseous high-purity nitrogen product at 1.05 bar and about -67.7ºC (compression energy-save) from the aluminum fin-plate multi-zones main heat exchanger (AS-2) sent-enter to the high-pressure double-Claude cycle nitrogen liquefier (LNG-based nitrogen liquefier) in the recycle mixer (AS-MIX-1). Hence, mixed with the heated low-pressure high-purity nitrogen at 1.05 bar and about -28.1ºC recycled back in loop-cycle. The amount of nitrogen recycled is than about 3.6 times the amount of liquefied high-purity nitrogen produced by the high-pressure double-Claude cycle nitrogen liquefier, this amount is determined and controlled by the mass and energy balances.

Gaseous high-purity nitrogen at 1.05 bar and at about 7.0ºC, after mixed, flow enters the high-efficiency centrifugal two stages compressor (AS-COM-7 and AS-COM-8) by the inlet guide (AS-COM-7) to distribute the flow providing a uniform condition in the first-stage impeller (AS-COM-7). This gas is then compressed to optimized pressure level at about 190.0ºC by the first-stage impeller (AS-COM-7), which is modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering about 90.0% isentropic efficiency (isentropic compression) and 99.0% mechanical efficiency.

After the first-stage of compression (AS-COM-7), the compressed gaseous nitrogen is cooled from about 190.0ºC to 40.0ºC without form condensed phase (free of impurities) in the water inter-cooler exchanger (AS-HEA-1) modeled by using a HeatX exchanger block. After cooled, the gas is then compressed in the second-stage impeller (AS-COM-8) to optimized intermediate-pressure level at about 190.0ºC considering about 90.0% of isentropic efficiency (isentropic compression) and 99.0% of mechanical efficiency modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor. After the second-stage of compression (AS-COM-8), the compressed gaseous high-purity nitrogen is cooled from about 190.0ºC to 40.0ºC without condensed phase (free of impurities) in the water after-cooler exchanger 1 (AS-HEA-2) modeled by using a HeatX exchanger blocks.

The pressure levels in the first-stage impeller (AS-COM-7) and second-stage impeller (AS-COM-8) is controlled by design specification DS-AS-PG-1 varying the pressure obtained after the centrifugal compression stages (AS-COM-7 and AS-COM-8), and consequently defining the inter-stage pressure for high-efficiency compression (minimizing the electricity consumption). The cycle pressure is defined by the mass and energy balances in the warm high-efficiency turbo booster (AS-COM-9 and AS-EXP-3) and cold high-efficiency turbo booster (AS-COM-10 and AS-EXP-4) in order to obtain a final-pressure of 40.0 bar after the turbo booster compression steps (AS-COM-9 and AS-COM-10).

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-12) to the cooling water circuit in the inter-cooler exchanger (AS-HEA-1) and to the cooling water circuit in the after-cooler exchanger 1 (AS-HEA-2). The amount of water used to cool-down the gaseous high-purity nitrogen after compression stages is determined and controlled by design specification DS-AS-FL-14 varying the mass flow rate of cooling water passing through the water inter-cooler exchanger (AS-HEA-1), and by design specification DS-AS-FL-15 varying the mass flow rate of cooling water passing through the water after-cooler exchanger 1 (AS-HEA-2). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

The intermediate-pressurized gaseous nitrogen (at about 18.75 bar by model result) and 40.0ºC is separated in two fractions by the splitter 1 (AS-SPL-6). In this case, was considered in the Aspen Plus®v8.4 process model simulation a fraction of 65.0%$_{w/w}$ destined to the cold high-efficiency turbo booster compressor (AS-COM-10), and another fraction of 35.0%$_{w/w}$ destined to the warm high-efficiency turbo booster compressor (AS-COM-9).

The cold booster centrifugal impeller (AS-COM-10) compress the fraction of 65.0%$_{w/w}$ to 40.0 bar and about 123.0ºC modeled by using a Compr pressure changer block (AS-COM-7) according to rigorous ASME method for isentropic compressor considering 92.0% isentropic efficiency (isentropic compression) and 99.0% mechanical efficiency. The warm booster centrifugal impeller (AS-COM-9) compress the another fraction of 35.0%$_{w/w}$ to 40.0 bar and about 123.0ºC (same conditions) modeled by using Compr pressure changer block (AS-COM-7) according to rigorous ASME method for isentropic compressor considering 92.0% isentropic efficiency (isentropic compression) and 99.0% mechanical efficiency.

After the high-efficiency cold booster compression steps (AS-COM-10), the high-pressure gaseous nitrogen is cooled from about 123.0ºC to 30.0ºC, without form condensed phase (free of impurities), in the water after-cooler exchanger 2 (AS-HEA-3) modeled by using a HeatX exchanger block (AS-HEA-1). After the warm booster compression steps (AS-COM-9), the high-pressure gaseous nitrogen is cooled from about 123.0ºC to 30.0ºC, without form condensed phase (free of impurities), in the water after-cooler exchanger 3 (AS-HEA-4) modeled by using a HeatX exchanger blocks (AS-HEA-1).

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-12) to the cooling water circuit in the water after-cooler exchanger 2 (AS-HEA-3) and to the cooling water circuit in the water after-cooler exchanger 3 (AS-HEA-4). The amount of cooling water used to cool-down the high-pressure gaseous high-purity nitrogen after the high-efficiency booster compression stages is determined and controlled by design specification DS-AS-FL-17 varying the mass flow rate of cooling water passing through the water after-cooler exchanger 2 (AS-HEA-3), and by design specification DS-AS-FL-16 varying the mass flow rate of cooling water passing through the water after-cooler exchanger 3 (AS-HEA-4). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

The two fractions of high-pressure and cooled gaseous high-purity nitrogen are mixed in the mixer 1 (AS-MIX-2), and then fed into the sequential cryogenic aluminum fin-plate heat exchangers.

In the hot-side of the first heat exchanger (AS11) modeled by MHeatX exchangers blocks nitrogen at 40.0 bar and 30.0ºC is cooled-down to 40.0 bar and about -5.0ºC by coolant nitrogen in the cold-side. Therefore, coolant nitrogen is heated from 1.05 bar and about -20.0ºC to 1.05 bar and 28.0ºC, hence being leave-recycled back to recycle mixer (AS-MIX-1).

A fraction (about 20.0%$_{w/w}$ by model result) of the cooled high-purity nitrogen is splitted in the splitter 2 (AS-SPL-7) and sent to the warm high-efficiency turbo booster expander (AS-EXP-3) modeled by using a Compr pressure changer block in turbine model considering 92.0% isentropic efficiency and 99.0% mechanical efficiency. The cooled high-purity nitrogen is then expanded from 40.0 bar and -5.0ºC to 1.05 bar and -167.2ºC. After expanded (AS-EXP-3), the gaseous nitrogen is mixed in the mixer 2 (AS-MIX-3) with coolant nitrogen at 1.05 bar and -71.1ºC from the second heat exchanger (A12), and then sent back to the cold-side of the first heat exchanger (AS11).

An fraction (about 80.0%$_{w/w}$ by model result) of the cooled high-purity nitrogen that bypass the warm high-efficiency turbo booster expander (AS-EXP-3) is cooled-down passing through the hot-side of the second heat exchanger (AS12) modeled by MHeatX exchangers blocks. The cooled high-purity nitrogen is sub-cooled from 40.0 bar and at about -5.0ºC to 40.0 bar and at about -70.0ºC by the coolant nitrogen in the cold-side of the second heat exchanger (AS12). Coolant nitrogen is heated from 1.05 bar and about -95.0ºC to 1.05 bar and -20.0ºC leaving to first heat exchanger (AS11).

A optimized fraction of the sub-cooled high-purity nitrogen is splitted in the splitter 3 (AS-SPL-8) and sent to the cold high-efficiency turbo booster expander (AS-EXP-4) modeled by using a Compr pressure changer block in turbine model considering 92.0% isentropic efficiency (isentropic compression) and 99.0% mechanical efficiency. Sub-cooled high-purity nitrogen is expanded from 40.0 bar and -70.0ºC to 1.05 bar and -195.2ºC producing work power for the cold high-efficiency turbo booster compressor (AS-COM-10). The amount of sub-cooled high-purity nitrogen splitted (AS-SPL-8) is controlled by design specification DS-AP-PG-2 varying the mass flow rate of cooled high-purity nitrogen expanded-required to (work power requirements) compress the intermediate-pressure high-purity nitrogen to 40.0 bar and at about 123.0ºC in the cold booster centrifugal high-efficiency compression impeller (AS-COM-10). After expanded, the gaseous high-purity nitrogen is mixed in the mixer 3 (AS-MIX-4) with coolant nitrogen at 1.05 bar and -195.4ºC from the phase separator vessel (AS-FLA-6), and then sent back to the cold-side of the cold heat exchanger (AS13).

Another fraction of sub-cooled high-purity nitrogen, that bypass the cold high-efficiency turbo booster expander (AS-EXP-4), is cooled-down passing through the hot-side of the cold heat exchanger (AS13) modeled by MHeatX exchangers blocks. The sub-cooled high-purity nitrogen is sub-cooled from 40.0 bar and at about -70.0ºC to 40.0 bar and optimized temperature (about -168.2ºC by model result), being liquefied by the gaseous coolant nitrogen in the cold-side of the cold heat exchanger (AS13). Coolant nitrogen is heated from 1.05 bar and at about -195.3ºC to 1.05 bar and about -71.0ºC leaving to the mixer 2 (AS-MIX-3). The outlet-optimized temperature of the high-pressure liquefied nitrogen is determined by design specification DS-AS-VF-1 varying the hot-side temperature in the cold heat exchanger (AS13) in order to obtain vapor fraction of 0.30 after expansion in the Joule-Thompson valve (AS-VAL-6).

Joule-Thompson valve (AS-VAL-6) modeled by Valve pressure changers expand the high-pressure liquefied nitrogen at 40.0 bar and about -168.2ºC to 1.05 bar and about -195.4ºC.

In the Aspen Plus®v8.4 process model simulation, the high-pressure double-Claude cycle is configured in order to obtain $30\%_{w/w}$ of vapor phase and $70\%_{w/w}$ of liquid phase (vapor fraction of 0.30) according to temperature limits between the first heat exchanger (AS11), the second heat exchanger (A12), and the cold heat exchanger (AS13) (crossover avoided). Also, considers the relation between the mass flow rate of the cryogenic gaseous nitrogen recycled as coolant fluid and the consumption of electricity (work power) to re-compress this cryogenic gaseous nitrogen recycled (loop-cycle) as coolant agent. The vapor fraction formed by expansion in the joule-Thompson valve (AS-VAL-6) is controlled by design specification DS-AS-VF-1 varying the hot-side outlet temperature in the cold heat exchanger (AS13).

The liquid and vapor phases from joule-Thompson valve (AS-VAL-6) are flash separated at pressure of 1.05 bar in the phase separator vessel (AS-FLA-6) modeled by using a Flash2 separator block without heat loss (adiabatic flash separation). The vapor phase of high-purity nitrogen is sent-back recycled and mixed in the mixer 3 (AS-MIX-4) with the expanded gaseous high-purity nitrogen at 1.05 bar and at about -195.4ºC (same conditions) from the high-efficiency turbo booster expander (AS-EXP-4). Hence, this resultant stream used in the cold-side of the heater exchangers to cool-down in countercurrent the main stream of high-pressure nitrogen in order to after-obtain the liquefied state.

The liquid phase containing mainly nitrogen is withdrawn from the phase separator vessel (AS-FLA-6) as final high-purity product (LIQUID NITROGEN), and then sent to storage in the cryogenic liquid nitrogen storage tank (AS-STO-1). Where, in this case, is mixed with the high-purity liquid nitrogen obtained as final high-purity product (LIQUID NITROGEN) from the 1º theoretically stage of the high-pressure tray-column (AS-COL-1), after pass flow thought the aluminum fin-plate condenser/reboiler exchanger (AS-8) condenser-zone.

7.2.8 Syngas cooling and heat recovery

The synthesis gas at low-pressure require compression process to achieve the required pressure for effective use in the high-performance sequential combustion full-flow advanced EvGT, in the HT and LT catalyst WGS reactors at intermediate-pressure level with energy-saving, and in the steam generation and low-pressure methanol catalytic-synthesis.

To compress the synthesis gas is necessary reducing the synthesis gas temperature in order to reduce the consumption of electrical energy and fit the maximum temperature allowed by the compressor. Hot synthesis gas has a great potential to thermal energy generation (sensible heat) and recovery this heat can increase the process steam production and reduce the stress on the HRSG system in the Biomass-to-Methanol route.

As shown in Figure 37, Aspen Plus®v8.4 flowsheet of the syngas cooling and heat recovery in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2), which is the same model with modified parameters for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) is compost by: high-temperature vertical CSC (GA-CSC-1); low-temperature vertical CSC (GA-CSC-2); water pump 1 (GA-PUM-1); and water pump 2 (GA-PUM-2).

Atmospheric crude hot-synthesis gas that leave the secondary multi-cyclone system (GA-CYC-2) is cooled in two cooling sections, generating intermediate-pressure steam by the high-temperature vertical CSC (GA-CSC-1) modeled by using a HeatX exchanger block, and low-pressure steam by the low-temperature vertical CSC (GA-CSC-2) modeled by using a HeatX exchanger block, without the catalytic high-performance CF.

The high-temperature vertical CSC (GA-CSC-1) and low-temperature vertical CSC (GA-CSC-2) are modeled using RKS-BM physical property methods to atmospheric crude hot-synthesis gas side, and IAPWS-95 physical property methods to hot water/steam side.

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), atmospheric crude hot-synthesis gas produced by the atmospheric CFB directly-heated gasifier at 850.0ºC is cooled to about 411.0ºC by the high-temperature vertical CSC (GA-CSC-1). The atmospheric crude hot-synthesis gas at 411.0ºC after the high-temperature vertical CSC (GA-CSC-1) is cooled to about 111.0ºC by the low-temperature vertical CSC (GA-CSC-2).

Deaerated hot process water from first deaerator unit (HR-DEA-1) at 1.4 bar and 105.0ºC is pumped (GA-PUM-2) to 23.0 bar before entering into the high-temperature vertical CSC (GA-CSC-1). The atmospheric crude hot-synthesis gas is cooled in the first-section of (GA-CSC-1) exchange sensible heat to produce intermediate-pressure steam. In the Biomass-to-Methanol (SC1), and Biomass-to-Methanol (SC2), intermediate-pressure steam at 23.0 bar and 337.9ºC is produced and expanded in the second-section of the EBPST system (ST blocks) to generate electrical energy. In the Biomass-to-Methanol (SC3), intermediate-pressure steam at 23.0 bar and 450.0ºC (reheater pipe bank) is produced and expanded in the second-section of the CEST system (ST blocks) to generate electrical energy.

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), condensed water at 2.3 bar and 109.0ºC after the stripper reboiler (CA-REB-1) in the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution is after-pumped (GA-PUM-1) to the syngas cooling and heat recovery (GA blocks). In these cases, is used to cool down the synthesis gas, after-generating gasification steam agent at 2.5 bar and 150.0ºC in the low-temperature vertical CSC (GA-CSC-2).

Cooled crude synthesis gas is fed in the evaporative vertical quencher (spray tower) (SC-SCR-1) in the low-temperature synthesis gas wet cleaning system (wet scrubbing unit).

The mass flow rate of deaerated hot process water to intermediate-pressure steam generation is controlled by design specification DS-GA-TL-1 varying the inlet mass flow rate of deaerated hot process water in the high-temperature vertical CSC (GA-CSC-1) coupled with design specification DS-GA-TL-2 that determines the temperature between the high-temperature vertical CSC (GA-CSC-1) and low-temperature vertical CSC (GA-CSC-2) sections.

The mass flow rate of deaerated hot process water to low-pressure steam generation is controlled by design specification DS-GA-FG-1 varying the inlet mass flow rate to produce gasification steam agent at 2.5 bar and 150.0ºC to atmospheric CFB directly-heated gasifier (GA-GASEI and GA-LSE-1). The amount of gasification steam agent is determined by Equation 7 to obtain a STBR of 0.5, considering the moisture present in the biomass-fuel inlet into the gasifier (GA-GASEI).

The catalytic high-performance CF between the high-temperature vertical CSC (GA-CSC-1) and the low-temperature vertical CSC (GA-CSC-2) was not implemented in the Aspen Plus®v8.4 process model simulation of the syngas cooling and heat recovery, due the limitations of the gasification Gibbs equilibrium model (GA-GASEI). The system is mainly used to reform the reminiscent tar and heavy hydrocarbons. Also, can remove part of the particle content in the atmospheric crude synthesis gas. Considering the presence of olivine catalyst in the gasifier bed (GA-GASEI) only traces of tar and heavy hydrocarbons is expected.

7.2.9 Low-temperature synthesis gas wet cleaning system

After the initial particulate removal accomplished by the multi-cyclones system (GA-CYC-2) and the convective indirect cooling of the crude synthesis gas by the syngas cooling and heat recovery an additional cooling step is carried out by wet scrubbing unit (direct water contact cooling).

The low-temperature synthesis gas wet cleaning system (wet scrubbing unit) is used to remove water-soluble contaminants and particles from the synthesis gas including ammonia (NH_3), hydrogen chloride (HCl), sulfur oxides (SO_x), carbonyl sulfide (COS), volatile organic compounds, tar and oils (heavy hydrocarbons), particles containing metals and metal salts, unconverted char (C) solid particulates, materials bed particles (not included in the Aspen Plus®v8.4 process model simulation), and others alkali compounds. Also, remove a small part of hydrogen sulfide (H_2S), nitrous oxides (NO_x), and carbon dioxide (CO_2).

As shown in Figure 38, Aspen Plus®v8.4 flowsheet of the low-temperature synthesis gas wet cleaning system in the BIG-ICE/CC (SC1), and BIG-ICE/CC (SC2), which is the same model with modified parameters for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2); and Biomass-to-Methanol (SC3) is compost by: vertical down-flow water spray quencher (SC-SCR-1); vertical water venturi scrubber (SC-SCR-1); decanter to separate the heavy hydrocarbons from the water (not included in the Aspen Plus®v8.4 process model simulation); water recovery and recycle unit (SC-FLA-2); packet-bed condenser/absorber sub-cooler (SC-FLA-1); mist eliminator (demister) drum (SC-FLA-3); wet electrostatic precipitator (WESP) (SC-ESP-1); blower system (SC-BLO-1); after air cooler (SC-FLA-4); condensate knock-out drum (SC-FLA-4); clarifier and decanter units (SC-FLA-2); sludge setting tank (SC-SEP-2) slurry pump (SC-PUM-2); water pumps (SC-PUM-1); cleaned water recirculation tank (SC-SEP-2); and humidified particles temporary bin (SC-FLA-5).

The Aspen Plus®v8.4 process model simulation of the low-temperature synthesis gas wet cleaning system was developed using Electrolyte NRTL physical property methods for liquid phase, and RK equation of state for vapor phase (ELECNRTL physical property methods) for electrolytes calculation using true components approach and aqueous activity coefficient basis for Henry components. Aqueous activity coefficient for the supercritical and non-condensable components (e.g.: H_2, O_2, N_2, Ne, He, Ar, Kr, Xe, CO, CO_2, Cl_2, SO_2, NH_3, H_2S, CHN, HCl) selected as Henry components is calculated according to the Henry's law for represent the behavior of dissolved gases, according the affinity with water and their interaction with other electrolytes presents.

The interaction of the key components potentially presents in the cooled crude synthesis gas in the presence of pure-water is evaluated in the Aspen Plus®v8.4 process model simulation of the low-temperature synthesis gas wet cleaning system. The model was developed with a chemistry model for specify reactions method applying the Elec Wizard auxiliary tool to generate possible components and reactions for the electrolyte simulation approach. The approach include the salt formation and dissociation reaction in water based on the hydronium ion (H_3O^+) reactions mechanism according to electrolyte solution chemistry (Chemistry ID: CH-SC-SOU) presented in the section 6.1.7 (Low-temperature synthesis gas wet cleaning system), as described for BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2).

The cooled crude synthesis gas from the low-temperature vertical CSC (GA-CSC-2) is down-flow conducted through the vertical water spray quencher (SC-SCR-1) in direct contact with recycled pure-water (without alkali addition) at 25.0ºC injected by spray nozzles. The injected water is vaporized, cooling down (pre-cooling chamber) the synthesis gas to saturation conditions at about 100.0ºC (without water condensation) before entering the vertical venturi scrubber (SC-SCR-1) with water loop tar removal system.

The Aspen Plus®v8.4 process model simulation for the vertical water spray quencher (SC-SCR-1) coupled in the vertical venturi scrubber (SC-SCR-1) uses Calvert's calculation method for spray tower designed with separation efficiency of 70.0% in the vertical venturi scrubber (SC-SCR-1). Electrolyte solution chemistry (CH-SC-SOU) is used to estimate the dissolved gases, the electrolytes interactions by salt formation, and dissociation reaction in pure water. The solid particles scrubbed (SC-SCR-1) are removed in the VSscrub solids separator block, the scrubbing liquid phase is removed in the Flash2 separator block (SCFLA-1) together the condensed phase in the packet-bed condenser/absorber sub-cooler (SC-FLA-1).

The electrolyte solution chemistry model Chemistry ID: CH-SC-SOU implemented in the Aspen Plus®v8.4 process model simulation of the low-temperature synthesis gas wet cleaning system was developed with a CHEMISTRY model according to section 6.1.7 (Low-temperature synthesis gas wet cleaning system) as described for BIG-ICE/CC (SC1), and BIG-ICE/CC (SC2).

In the vertical venturi scrubber (SC-SCR-1) is collected the gross-particulate according to the aerodynamic size, and removed the condensed residual heavy hydrocarbons (e.g.: tar, oils) in the basin (SC-FLA-2) of the venturi scrubber (liquid drain) by the water loop tar removal system (not included in the Aspen Plus®v8.4 process model simulation). The scrubbed liquid with heavy hydrocarbons mixed with water is collected in the basin (SC-FLA-2) and sent to oil/water separator (not included in the Aspen Plus®v8.4 process model simulation) to remove the hydrocarbons from the water by density differences. The liquid hydrocarbons removed is sent to final disposal or sent-back to the gasifier (GA-GASEI), the water phase is recovered and recycle to the venturi scrubber (SC-SCR-1) at 25.0ºC and injected by spray nozzles in the chamber.

Cleaned water is pumped from the cleaned water recirculation tank (SC-SEP-2) in closed-loop cycle to the packet-bed condenser/absorber sub-cooler (SC-FLA-1). Cooled synthesis gas is then sub-cooled to 45.0ºC, being removed 15.0%$_{w/w}$ of the entrained fine-particles. Is used a large amount of recycled-water from the cleaned water recirculation tank (SC-SEP-2) in the packet-bed condenser/absorber sub-cooler (SC-FLA-1).

The Aspen Plus®v8.4 process model simulation consider 0.5%$_{w/w}$ of entrained water to mist eliminator (SC-FLA-3), which is responsible to remove the excess of water content droplets in the sub-cooled synthesis gas at saturation conditions before entering in the WESP (SC-ESP-1).

The amount of cleaned-water recycled to vertical water spray quencher (SC-SCR-1) and to vertical venturi scrubber (SC-SCR-1) is controlled by design specification DS-SC-TG-1 varying the inlet cleaned-water (SC-SPL-1) in order to achieve the saturation condition (cooling).

The amount of cleaned-water recycled to packet-bed condenser/absorber sub-cooler (SC-FLA-1) is controlled by design specification DS-SC-TG-2 varying the inlet cleaned-water (SC-SPL-2) in order to achieve the sub-cooled condition for WESP system (SC-ESP-1), and the synthesis gas temperature required by the low-pressure absorber packed-column (CA-ABS-1) in the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks).

The built-in expression (Equation 27) for calculating equilibrium constants is used for the reactions from 1 to 17 in CH-SC-SOU electrolyte solution chemistry. The built-in expression (Equation 28) for calculating salt precipitation equilibrium constants is used for the reactions from 18 to 25 in CH-SC-SOU electrolyte solution chemistry.

The ELECNRTL physical property methods is used in the low-temperature synthesis gas wet cleaning system (SC blocks) with the same properties assumption employed in the Aspen Plus®v8.4 process model simulation of the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks). In short, detailed-described in the section 7.2.12 (Co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution), and according to section 6.1.7 (Low-temperature synthesis gas wet cleaning system) described for BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2).

The excess of the wastewater recovered from the basin (SC-FLA-2) of the vertical venturi scrubber (SC-SCR-1), from the cooler condenser basin (SC-FLA-2) and from the mist eliminator (SC-FLA-3) is sent to the clarifier and decanter units (SC-SEP-2) and cleaned water recirculation tank (SC-SEP-2) to remove the sludge, and be cooled at ambient conditions. The contend solids and precipitated or dissociated salts is concentrate in the bottom sludge phase and sent to the sludge setting tank (SC-SEP-2) to be removed and sent of-site to final disposal in the sugarcane field. In the Aspen Plus®v8.4 process model simulation is considered $50.0\%_{w/w}$ of water content in the sludge phase, which can be pumped by slurry pump (SC-PUM-2) to storage tank before sent of-site by tank truck transporter (SLURRY TO DISPOSAL).

The cleaned water from the clarifiers (SC-SEP-2) at quality requirements to be recycled to vertical water spray quencher (SC-SCR-1) and to vertical venturi scrubber (SC-SCR-1) is stored in the cleaned water recirculation tank (SC-SEP-2). The excess of water recovered from the synthesis gas is separate (SC-SPL2) and pumped (SC-PUM-1) to wastewater treatment plant (WASTEWATER TO TREATEMNT PLANT) to be used as make-up water for other processes (loss reduction principles).

In the Aspen Plus®v8.4 process model simulation of the synthesis gas cleaning wet system is considered the WESP (SC-ESP-1) operating at satured synthesis gas conditions (100% relative humidity) to remove the persistent fine-particles (final particles) as additional particulate polishing step. The WESP (SC-ESP-1) is modeled according to Svarovsky calculation model for vertically mounted collecting plate's model with separation efficiency of 92.0% of the particles present in the sub-cooled synthesis gas stream and based on the migration velocity and the ratio of precipitation area.

The persistent fine-particles collected is removed from the basin (SC-ESP-1) and conveyed to be stored into the humidified particles temporary bin (SC-FLA-5) until offloaded (PARTICLES TO DISPOSAL) for the final disposal (field disposal together vinasses and gasifier bottom particulate materials).

Blower system (SC-BLO-1) with induced draft fan is modeled by using a Compr pressure changer block according to isentropic method for compressor considering 85.0% isentropic efficiency and 99.0% mechanical efficiency. The system is used to produce the desired pressure drop across the venturi scrubber system and to equalize the pressure (drop pressure) inducing the synthesis gas flow through the system at desired mass flow rate. After pressurized (SC-BLO-1) the sub-cooled synthesis gas is cooled in the air cooler (SC-FLA-4) and the condensed phase removed in the knock-out drum (SC-FLA-4) back to the cleaned water recirculation tank (SC-SEP-2).

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), the sub-cooled synthesis gas is sent-ducted as partial-cleaned synthesis gas to integrally-geared centrifugal three stages compressor (CO blocks) in the first-section of synthesis gas compression (conditioning). The integrally-geared centrifugal three stages compressor (CO blocks) is used to conditioning the sub-cooled and partial-cleaned synthesis gas to be used in the high-performance sequential combustion full-flow advanced EvGT (GT blocks), and in the HT and LT catalyst WGS reactors (WS blocks) at intermediate-pressure level with energy-saving and steam generation.

7.2.10 First-section of synthesis gas compression (conditioning)

The sub-cooled and partial-cleaned synthesis gas obtained in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) is compressed by integrally-geared centrifugal three stages compressor (CO blocks) to an intermediate pressure, between the pressure level of the gasifier and of the low-pressure methanol catalytic-synthesis.

The intermediate-pressure level can be optimized (not included in the Aspen Plus®v8.4 process model simulation) to efficient use in the high-performance sequential combustion full-flow advanced EvGT (GT blocks) operating in CC mode, in the HT and LT catalyst WGS reactors (WG blocks), and in the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks).

The Aspen Plus®v8.4 process model simulation of the integrally-geared centrifugal three stages compressor (CO-COM blocks) is based on the Siemens STC-GV integrally-geared centrifugal multi-stages compressor series feature a single-shaft arrangement and configured to allow inter-cooling steps.

Figure 69 shows the Aspen Plus®v8.4 flowsheet of the first-section of synthesis gas compression (conditioning) for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3).

The sub-cooled and partial-cleaned synthesis gas from the knock-out drum (SC-FLA-4) of the low-temperature synthesis gas wet cleaning system in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), flow enters the compressor by the inlet guide (CO-COM-1) to distribute the flow providing a uniform condition in the first-stage impeller (CO-COM-1). Hence, is compressed to an optimized pressure (OP-CO-PG-1) by the first-stage impeller (CO-COM-1) modeled by using a Compr pressure changer block (CO-COM-1) according to rigorous ASME method for isentropic compressor considering 83.0% isentropic efficiency (isentropic compression).

The synthesis gas after the first-stage of compression (CO-COM-1) ducted-leaving is cooled to 30.0ºC by the tree-circuits water inter-cooler exchanger (CO-1) modeled by using a MHeatX exchanger block generating condensed phase content water and dissolved gases. The condensed phase is removed in the condenser knock-out drum (CO-FLA-1) modeled by using a Flash2 separator block, and sent to atmospheric condensate buffer/equalizer tank (CO-FLA-4) modeled by using a Flash2 separator block at ambient conditions.

The synthesis gas free of condensate phase enters in the second-stage impeller (CO-COM-2) to be compressed to an optimized pressure (OP-CO-PG-1). The second-stage impeller (CO-COM-2) is modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 83.0% isentropic efficiency (isentropic compression).

After the second-stage of compression (CO-COM-2), the synthesis gas ducted-leaving is cooled to 30.0ºC by the three-circuit water inter-cooler exchanger (CO-2) modeled by using a MHeatX exchanger block generating condensed phase content water and dissolved gases. The condensed phase is removed in the condenser knock-out drum (CO-FLA-2) modeled by using a Flash2 separator block, and sent to atmospheric condensate buffer/equalizer tank (CO-FLA-4) modeled by using a Flash2 separator block at ambient conditions (equalizer).

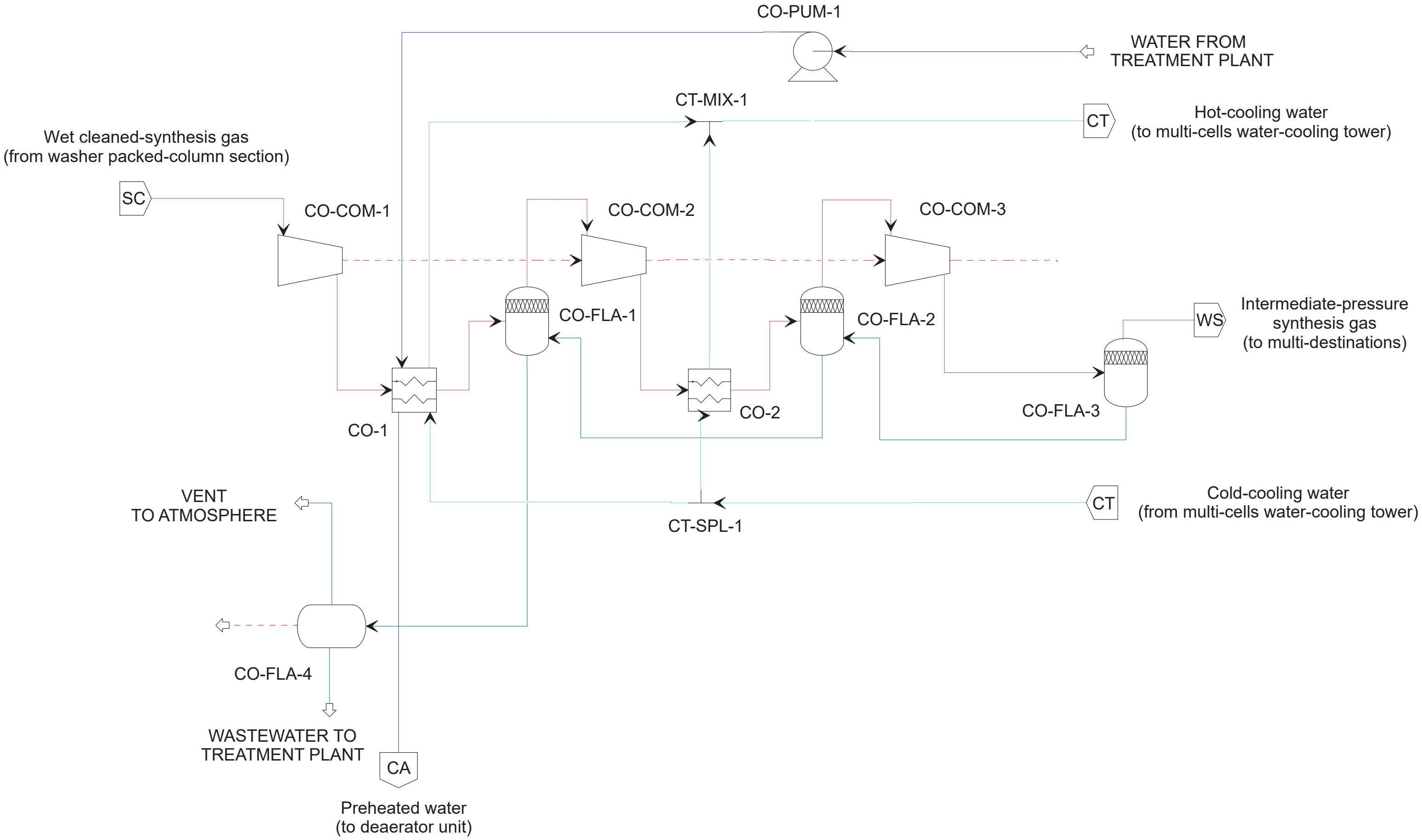


Figure 69 - Aspen Plus® v8.4 flowsheet of the first-section of synthesis gas compression (conditioning) by integrally-geared centrifugal three stages compressor for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3)

As shown in Figure 69, Aspen Plus$^{®}$v8.4 flowsheet of the first-section of synthesis gas compression (conditioning) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) is compost by: integrally-geared centrifugal three stages compressor (CO-COM-1~3); tree-circuits water inter-cooler exchanger (CO-1); water inter-cooler exchanger (CO-2); condenser knock-out drums (CO-FLA-1~3); direct drive permanent magnet motor (not included as block); atmospheric condensate buffer/equalizer tank (CO-FLA-4); and liquid water pump (CO-PUM-1).

The synthesis gas free of the condensate phase enters in the third-stage impeller (CO-COM-3) and is compressed delivering conditioned synthesis gas at required pressure by the downdraft equipment. High-performance sequential combustion full-flow advanced EvGT (GT blocks) requires a pressure at about 23.0 bar (turbine configuration) in their injection system (GT-SPL-1). The third-stage impeller (CO-COM-3) is modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 83.0% of isentropic efficiency (isentropic compression). The synthesis gas after the third-stage of compression (CO-COM-3) ducted-leaving is not cooled by after-cooler, is directly ducted to buffer/equalizer tank (CO-FLA-3) or condenser knock-out drum (CO-FLA-3) modeled by using a Flash2 separator block as conditioned synthesis gas to be used as fuel-gas in the high-performance sequential combustion full-flow advanced EvGT (GT blocks) operating in CC mode.

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-4) to the cooling water circuits in the inter-cooler exchangers (CO-1 and CO-2). The amount of water used to cool-down the synthesis gas is determined and controlled by design specification DS-CO-TL-1 varying the mass flow rate of cooling water passing through the cooling water circuit in the three-circuit water inter-cooler exchanger (CO-1), and by design specification DS-CO-TL-2 varying the mass flow rate of cooling water passing through the water inter-cooler exchanger (CO-2). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system. The lubricating oil circuit and the lubricating water-cooling system are suppressed from the Aspen Plus$^{®}$v8.4 process model simulations in this research Master`s degree.

Part of the deaerator make-up water (WATER FROM TREATMENT PLANT) at atmospheric pressure and 25.0ºC is pumped at 1.42 bar by the liquid water pump (CO-PUM-1). And, then is preheated at 105ºC passing through the three-circuit water inter-cooler exchanger (CO-1), being after sent-fed in the deaerator unit (HR-DEA-1), recovering heat and consequently reducing the low-pressure steam required by the deaerator unit (HR-DEA-1).

The ambient equalized condensate (CO-FLA-4) is after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

The single shaft and pinions with variable speed gears in the integrally-geared centrifugal three stages compressor (CO-COM blocks) is driver by a synchronous direct drive permanent magnet motor modeled by CO-E-3 work stream and optimized to achieve the lowest consumption of electric power energy. The electric power energy consumed is optimize-minimized using optimization model analysis tools OP-CO-PG-1 varying the pressure obtained after the first-stage impeller (CO-COM-1) and after the second-stage impeller (CO-COM-2) in combined mode according with model analysis tools constraint CN-CO-PG-1 ensuring the technical compression fundaments (raise pressure in the next stage). The electrical potential losses by attrite in the mechanical move parts was considered as 1.0% of the mechanical energy required by the stage (99.0% mechanical efficiency).

7.2.11 Synthesis gas destinations (split)

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), synthesis gas at intermediate-pressure from the condenser knock-out drum (CO-FLA-3) in the first-section of synthesis gas compression (conditioning) (CO blocks) is separated in three streams by the intermediate-pressure synthesis gas splitter (WS-SPL-1).

A fraction of the intermediate-pressure synthesis gas is directly sent to high-performance sequential combustion full-flow advanced EvGT (GT blocks). Another fraction of the intermediate-pressure synthesis gas to HT and LT catalyst WGS reactors (WS blocks) at intermediate-pressure level with energy-saving and steam generation to adjust the quality of the synthesis gas required by the low-pressure methanol catalytic-synthesis. The reminiscent fraction of the intermediate-pressure synthesis gas bypass the catalyst WGS reactors and is directly sent to the energy-saving and steam generation section (WS blocks) before fed-enter the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks).

7.2.12 Co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution

PZ/MDEA blend-based aqueous absorbing-solution for intermediate-pressure systems in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), consider the use of PZ/MDEA blend absorbing-solution with 5.0%$_{w/w}$ of piperazine (PZ) and 30.0%$_{w/w}$ of methyl-diethanolamine (MDEA) in aqueous solution.

Aspen Plus$^{®}$v8.4 process model simulation of the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA-L-5) at intermediate-pressure with lower emissions of degradation products is considered in order to remove 96.0%$_{w/w}$ of CO_2 content in the synthesis gas (to achieve the requirement for low-pressure methanol catalytic-synthesis).

The PZ/MDEA blend-based aqueous absorbing-solution has the potential to capture mainly CO_2 and co-capture H_2S and fractions of carbonyl sulfide (COS), carbonyl disulfide (CS_2), and mercaptans (is not the main goal) removed a lesser extension from the system. The amount of co-captured compounds depends on the PZ/MDEA-based aqueous absorbing-solution mass flow rate circulating in the system.

The mixture of CO_2 and amines in water (CO_2-amines-H_2O interaction) is highly non-ideal, and the presence of ions and polar molecules in the liquid phase creates significant thermal effects, increasing the temperature of the system at point of raise the degradation process of the PZ/MDEA blend-based aqueous absorbing-solution employed.

The model consider the heat integrations to obtain the rigorous energy balance of the system, and the mass flow rate of process steam (thermal energy) and cooling water required by the system (reboiler and condensers equipments). The rigorous model is essential and indispensable to determine the influence of this system in the thermal energy balances of the integrated processes in the thermochemical-biorefinery.

Figure 70 shows the Aspen Plus$^{®}$v8.4 flowsheet of the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (5.0%$_{w/w}$ of PZ and 30.0%$_{w/w}$ of MDEA aqueous blend absorbing-solution) for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3).

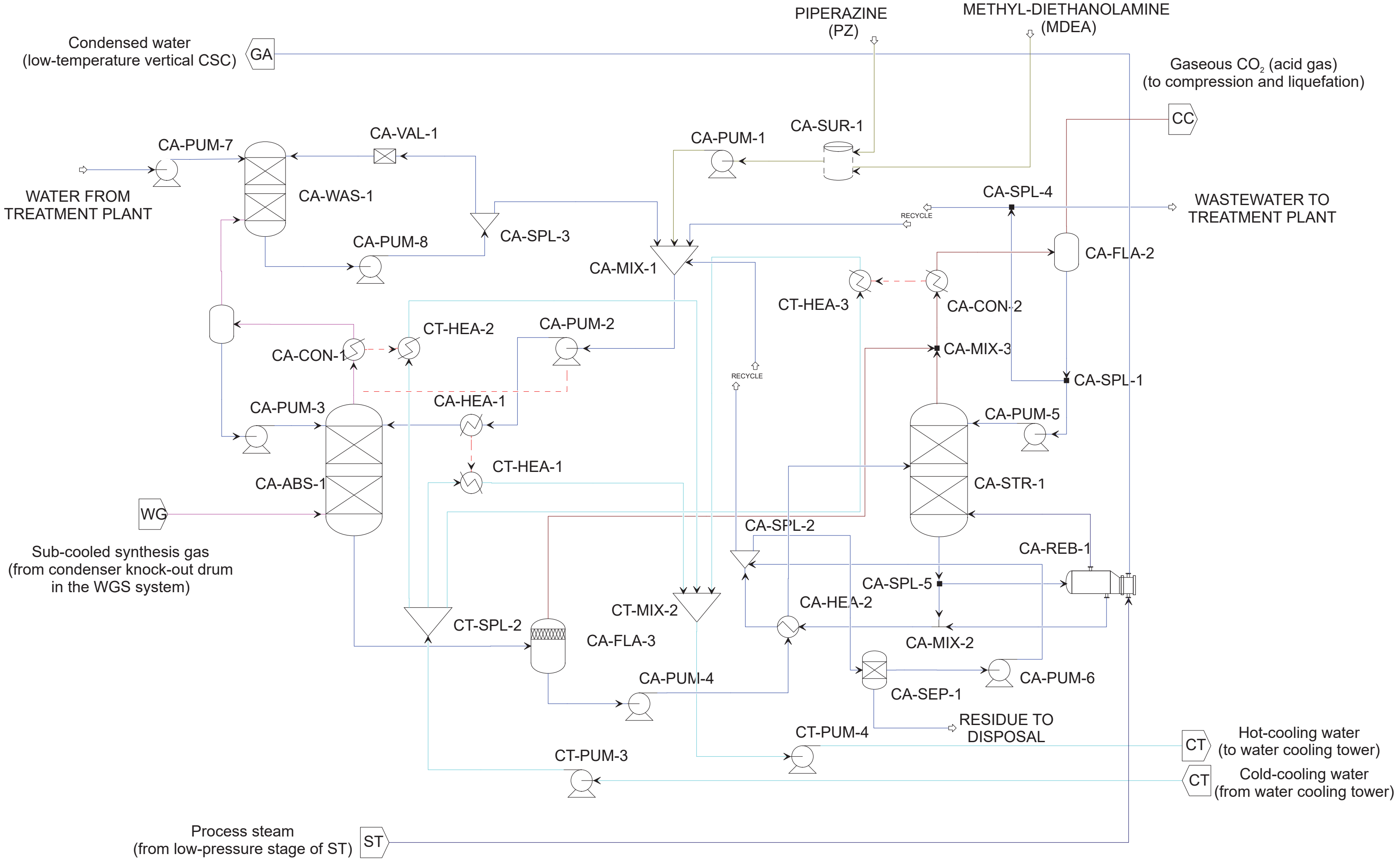


Figure 70 - Aspen Plus® v8.4 flowsheet of the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution ($5.0\%_{w/w}$ of PZ and $30.0\%_{w/w}$ of MDEA aqueous blend absorbing-solution) for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3)

As shown in Figure 70, co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks) in closed-loop cycle in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) is compost by: intermediate-pressure absorber tray-column (CA-ABS-1); low-pressure stripper packed-column (CA-STR-1); washer packed-column section (CA-WAS-1); washer water recycle-pump (CA-PUM-8); washer water bleed (CA-SPL-3); rich-amine flash vessel (CA-FLA-3); gaseous mixer (CA-MIX-3); cross-solution heat exchanger (CA-HEA-2); mixture tank (CA-MIX-1); amine surge tank (CA-SUR-1); amine supply pump (CA-PUM-1); lean-amine pump (CA-PUM-2); absorber reflux-pump (CA-PUM-3); desorber reflux pump (CA-PUM-5); absorber condenser (CA-CON-1 and CT-HEA-2); absorber liquid reflux-drum (CA-FLA-1); water purge splitter (CA-SPL-4); striper liquid reflux-drum (CA-FLA-2); stripper condenser (CA-CON-2 and CT-HEA-3); striper water bleed (CA-SPL-1); lean-amine water cooler (CA-HEA-1 and CT-HEA-1); rich-amine pump (CA-PUM-4); carbon-based filter (CA-SEP-1); stripper reboiler (CA-REB-1); lean-amine sump splitter (CA-SPL-5); amine reclaimer (CA-SPL-2); reclaimer recirculation pump (CA-PUM-6); lean-amine regenerated mixer (CA-MIX-2); make-up water pump (CA-PUM-7); and cooling water pumps (CT-PUM-3 and CT-PUM-4).

The rigorous Aspen Plus®v8.4 process model simulation of co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks) consider the complete cycle in closed-loop cycle mode with heat integrations under the steady state operating conditions. The model was developed using Electrolyte NRTL physical property methods for liquid phase, and RK equation of state for vapor phase (ELECNRTL physical property methods) for electrolytes calculation using true components approach and aqueous activity coefficient basis for Henry components. The selected components (e.g.: H_2, O_2, N_2, Ne, He, Ar, Kr, Xe, CO, CO_2, Cl_2, NH_3, CHN, HCL, CH4, NO_x, SO_x) to employ the Henry's law as supercritical and non-condensable components for represent the behavior of dissolved gases according to the affinity with water and their interaction with electrolytes.

ASPEN Rate-Sep simulation package is used in the intermediate-pressure absorber tray-column (CA-ABS-1), in the low-pressure stripper packed-column (CA-STR-1), and in the washer packed-column section (CA-WAS-1) to non-equilibrium mass transfer rate-based calculations taken in account the mass and heat transfer limitations, liquid and vapor film diffusion, equipment hydrodynamics and chemical reaction mechanisms.

The electrolyte solution chemistry model Chemistry ID: CH-CA-PZMDE implemented in the Aspen Plus®v8.4 process model simulation of the co-capture of CO_2 and H_2S by using PZ/MDEA bleed-based aqueous absorbing-solution was developed with a CHEMISTRY model.

Chemistry ID: CH-CA-PZMDE

1	Equilibrium	$2H_2O \leftrightarrow H_3O^+ + OH^-$
2	Equilibrium	$CO_2 + 2H_2O \leftrightarrow H_3O^+ + HCO_3^-$
3	Equilibrium	$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-}$
4	Equilibrium	$PZH^+ + H_2O \leftrightarrow PZ + H_3O^+$
5	Equilibrium	$PZ + HCO_3^- \leftrightarrow PZCOO^- + H_2O$
6	Equilibrium	$HPZCOO + H_2O \leftrightarrow PZCOO^- + H_3O^+$
7	Equilibrium	$PZCOO^- + HCO_3^- \leftrightarrow PZ(COO^-)_2 + H_2O$
8	Equilibrium	$MDEAH^+ + H_2O \leftrightarrow MDEA + H_3O^+$
9	Equilibrium	$H_2O + H_2S \leftrightarrow HS^- + H_3O^+$
10	Equilibrium	$H_2O + HS^- \leftrightarrow S^{2-} + H_3O^+$

The built-in expression for calculating equilibrium constants is used for the reactions from 1 to 10 in CH-CA-PZMDE electrolyte solution chemistry, according to Equation 31.

$$\ln k_{eq} = A + \frac{B}{T} + C.\ln T + D.T + E.\left(\frac{P - P_{ref}}{P_{ref}}\right) \tag{31}$$

Where, k_{eq} is the equilibrium constant, T is the absolute temperature (K), A, B, C, D, E is user supplied coefficients, P_{ref}.is the reference pressure (atm), and P is the absolute pressure (atm)

The Aspen Plus®v8.4 parameters DGAQFM (DGFORM), DHAQFM (DHFORM) and CPAQ0 (CPIG) used to calculate the standard Gibbs free energy of $MDEAH^+$, PZH^+, $PZCOO^-$, $PZ(COO^-)_2$ and HPZCOO are changed according to estimated by Aspen Tech (2012), parameters for the other components are obtained from the databank of Aspen Plus®v8.4.

The equilibrium constants (standard defined) for the reactions from 1 to 8 in CH-CA-PZMDE are obtained from the standard Gibbs free energy according to Aspen Tech (2012, 2013b). The equilibrium constants (Table 21) for reactions 9 and 10 in CH-CA-PZMDE are obtained from Austgen et al. (1988) apud Aspen Tech (2013a).

Table 21 - Equilibrium constants for CH-CA-PZMDE standard Gibbs free energy model of the co-capture of CO_2 and H_2S by using PZ/MDEA bleed-based aqueous absorbing-solution

Reaction number	Coefficients				
	A	**B**	**C**	**D**	**E**
9	214.582	-12995.4	-33.5471	0	0
10	-9.74196	-8585.47	0	0	0

Source: Austgen et al. (1988) apud Aspen Tech (2013a)
Note: concentration basis selected by unsymmetric reference state of ions: mole-frac

The reaction model Reaction ID: RE-CA-PZMDE implemented in the Aspen Plus®v8.4 process model simulation of the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution was developed with a REACTIONS model.

Reaction ID: RE-CA-PZMDE

1 Equilibrium $2H_2O \leftrightarrow H_3O^+ + OH^-$
2 Equilibrium $HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-}$
3 Equilibrium $PZH^+ + H_2O \leftrightarrow PZ + H_3O^+$
4 Equilibrium $HPZCOO + H_2O \leftrightarrow PZCOO^- + H_3O^+$
5 Equilibrium $MDEAH^+ + H_2O \leftrightarrow MDEA + H_3O^+$
6 Equilibrium $H_2O + H_2S \leftrightarrow HS^- + H_3O^+$
7 Equilibrium $H_2O + HS^- \leftrightarrow S^{2-} + H_3O^+$
8 Kinetic $CO_2 + OH^- \rightarrow HCO_3^-$
9 Kinetic $HCO_3^- \rightarrow CO_2 + OH^-$
10 Kinetic $PZ + CO_2 + H_2O \rightarrow PZCOO^- + H_3O^+$
11 Kinetic $PZCOO^- + HCO_3^- \rightarrow PZ + CO_2 + H_2O$
12 Kinetic $PZCOO^- + CO_2 + H_2O \rightarrow PZ(COO^-)_2 + HCO_3^-$
13 Kinetic $PZ(COO^-)_2 + HCO_3^- \rightarrow PZCOO^- + CO_2 + H_2O$
14 Kinetic $MDEA + CO_2 + H_2O \leftrightarrow MDEAH^+ + H_3O^+$
15 Kinetic $MDEAH^+ + H_3O^+ \rightarrow MDEA + CO_2 + H_2O$

The equilibrium constants for reactions from 1 to 5 in RE-CA-PZMDE are obtained from the standard Gibbs free energy. The equilibrium constants for reactions 6 and 7 in RE-CA-PZMDE are the same equilibrium constants for reactions 9 and 10 in CH-CA-PZMDE (Table 21).

The power law reduced expression is used for the reactions from 8 to 15 in RE-CA-PZMDE rate-controlled reactions, according to Equation 30 or Equation 32.

$$r = kT^{n} exp\left(-\frac{E}{RT}\right) \prod_{i=1}^{N} C_i^{a_i} \tag{32}$$

Considering: $n = 0$

Where, r is the rate of reaction, k is the pre-exponential factor, T is the absolute temperature (T), n is the temperature exponent, E is the activation energy, R is the universal gas constant, N is the number of components in the reaction, C_i is the concentration of component i, and a_i is the stoichiometric coefficient of component i in the reaction equation.

The kinetic parameters for reactions 8 and 9, in RE-CA-PZMDE, were obtained from Pinset et al. (1956) apud Aspen Tech (2013a). The kinetic parameters for reactions 10 to 13, in RE-CA-PZMDE, were obtained from Bishnoi and Rochelle (200, 2002) apud Aspen Tech (2013b). Moreover, the kinetic parameters for reactions 14 and 15, in RE-CA-PZMDE, were obtained from Rinker et al. (1997) apud Aspen Tech (2013b). Table 22 shows the kinetic parameters for the rate-controlled reactions according to Aspen Tech (2013b).

Table 22 - Pre-exponential factor and activation energy kinetic parameters for RE-CA-MEA rate-based model of the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution

Reaction number	Pre-exponential factor	Activation energy (ca/mol)
8	$4.32e^{+13}$	13249
9	$2.38e^{+17}$	29451
10	$4.14e^{+10}$	8038.3
11	$7.94e^{+21}$	15758
12	$3.62e^{+10}$	8038.3
13	$5.56e^{+25}$	18372
14	$2.22e^{+7}$	9029
15	$1.06e^{+16}$	25424

Source: Aspen Tech (2013b) and Aspen Plus®v8.4 database APV84 (2015)

The ELECNRTL physical property methods used in the Aspen Plus®v8.4 process model simulation of co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution according to Aspen Tech (2013b) apply Clarke model (VAQCLK) for liquid molar volume using the quadratic mixing rule for solvents (option 1) with interaction parameter VLQKIJ for the quadratic mixing rule between MDEA and H_2O from Bernal-Garcia et al. (2003) and VLQKIJ for the quadratic mixing rule between PZ and H_2O from Arunkumar and Syamalendu (2006), the Clarke model parameter for the main electrolytes (MDEA-H_2O-CO_2) from Weiland (1998), Jones-Dole electrolyte correction model (MUL2JONS) weighted by mass fraction (option code 1) for liquid viscosity model for the solvent (option code 1) using Aspen liquid mixture viscosity (option code 2) with interaction parameters (MUKIJ and MULIJ) of MDEA-H_2O from Teng et al. (1994) and Jones-Dole model parameters (IONMUB) from Weiland (1998), and interaction parameters (MUKIJ and MULIJ) of PZ-H_2O are left to be defaulted at zero. Onsager-Samaras model (SIG2ONSG) for liquid surface tension for electrolyte system (option code 1) wit exponent codes being -9 in mixing rule, Riedel electrolyte correction model (KL2RDL) for thermal conductivity, Nernst-Hartley model (DL1NST) for binary diffusivity with mixture viscosity weighted by mass fraction (option code 1).

The degradation products generated during the solvent degradation process may produce new pollutants, which could be emitted to the atmosphere. Thermal and oxidative degradation, and polymerization reactions, have been considered undergoes thermal degradation temperature limits in presence of dissolved CO2. The degradation process was simplified in the Aspen Plus process simulation model of the co-capture of CO_2 and H_2S by using PZ/MDEA bleed-based aqueous absorbing-solution (CA blocks), based on mass balance of the system, a representative fraction of the PZ/MDEA blend-based aqueous absorbing-solution depredated is removed as input parameters in the carbon-based filter (CA-SEP-1).

The intermediate-pressure synthesis gas (WS-G-16) at 40.0ºC and 1.1 bar from the condenser knock-out drum (WS-FLA-1) in the catalyst WGS reactors at intermediate-pressure level with energy-saving and steam generation (WS blocks) containing manly CO_2 and H_2S, and others pollutants not removed in the low-temperature wet cleaning steps, fed-enter into the bottom of the intermediate-pressure absorber tray-column (CA-ABS-1). The synthesis gas flow upward through the tray stages in contact with the down flow PZ/MDEA blend-based aqueous absorbing-solution (lean-amine solution) to exit as clean outlet gas at the absorber top stage (CA-ABS-1). The system was designed to removal $96.0\%_{w/w}$ of CO_2 present in intermediate-pressure synthesis gas with top stage pressure at 21.6 bar and column pressure drop of 0.4 bar, the lean-amine solutions is fed on the top stage and the intermediate-pressure synthesis gas on the bottom stage (CA-ABS-1).

The PZ and MDEA considered to forming the absorbing-solution is a commercial type high-concentrate MDEA-based solution and crystal-PZ (hydrated or anhydrous) shipped and delivered to thermochemical-biorefinery supplies offloading area by truck. From the storage tank, high-concentrate MDEA-based solution is ducted to the amine surge tank (CA-SUR-1) and pumped by the amine supply pump (CA-PUM-1) to the mixture tank (CA-MIX-1). Crystal-PZ is sent to mixture stirred-tank (not included in the Aspen Plus®v8.4 process model simulation) to be diluted and mixed with the MDEA-based solution to be after added with the lean-amine solution in circulation on closed-loop cycle mode.

Make-up of high concentrate MDEA-based solution and crystal-PZ added into the system depends on the losses (thermal, oxidative, reclaimed, and entrained-off). The make-up is made from time to time but simulated in the Aspen Plus®v8.4 process model simulation as continues process in steady state mode. The mass flow rate of high concentrate MDEA-based solution is controlled by design specification DS-CA-CL-1 varying the mass flow rate inlet the system to maintenance the lean-amine solution content $30.0\%_{w/w}$ of MDEA in the inlet stream (CA-L-7) in the top of the intermediate-pressure absorber tray-column (CA-ABS-1). The design specification considers all active MDEA ionic forms present in the solution measured by apparent component mass fraction for electrolyte system as property sets. The mass flow rate of crystal-PZ is controlled by design specification DS-CA-CL-2 varying the mass flow rate inlet the system to maintenance the lean-amine solution content $5.0\%_{w/w}$ of PZ in the inlet stream (CA-L-7) in the top of the intermediate-pressure absorber tray-column (CA-ABS-1). The design specification considers all active PZ ionic forms present in the solution measured by apparent component mass fraction for electrolyte system as property sets.

The lean-amine solution formed in the mixture tank (CA-MIX-1) is pumped to 21.8 bar by the lean-amine pump (CA-PUM-2), and cooled in the lean-amine water cooler (CA-HEA-1) passing cooling water (CT-HEA-1) modeled by using a Heater exchanger blocks to maintenance the inlet conditions at 21.6 bar and 40.0ºC. The lean-amine solution with low fraction of CO_2, H_2S, and others pollutants content (e.g.: NH_3, SOx, CHN, COS, hydrocarbons) without degradation products (not included in the Aspen Plus®v8.4 process model simulation) is then feed in the 1° theoretically liquid stage (top column stage) of the intermediate-pressure absorber tray-column (CA-ABS-1).

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-3) to the lean-amine water cooler (CT-HEA-1). The amount of cooling water required is determined and controlled by design specification DS-CA-TL-1 varying the mass flow rate of cooling water passing through the lean-amine water cooler (CT-HEA-1). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

Rigorous Aspen Plus®v8.4 process model simulation of the intermediate-pressure absorber tray-column (CA-ABS-1) was developed using RadFrac columns block on standard convergence mode with reaction model RE-CA-PZMED and electrolyte solution chemistry model CH-CA-PZMDE without in-bed condenser and reboiler. The model was optimized for estimated 20 theoretical stages considering a Glitsch Ballast (Glitsch6) tray section with valve type V-1 12 gauge deck thickness and panel weir height of 40.0 mm with height and diameter optimized for each system requirements (scenarios dependence) on standards characteristics. The model use rate-based calculation for Mixed flow model without reactions and film resistance in vapor phase, without reactions and with film resistance in liquid phase. Default Aspen Plus®v8.4

tray parameters is applied to calculate liquid holdup, interfacial area and to predict the mass transfer coefficient by Scheffe and Weiland (1987) method, and heat transfer coefficient by Chilton–Colburn (Taylor and Krishna, 1993) method.

The gaseous top-product at about 21.6 bar and 55.0ºC leave from the 1º theoretically vapor stage (top column stage) in the intermediate-pressure absorber tray-column (CA-ABS-1) is cooled to 21.4 bar and 40.0ºC in the absorber condenser (CA-CON-1) passing cooling water (CT-HEA-2) modeled by using a Heater exchanger blocks condensing a fraction of the entrained water with PZ/MDEA.

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-3) to the absorber condenser (CT-HEA-2). The amount of cooling water required is determined and controlled by design specification DS-CA-TL-2 varying the mass flow rate of cooling water passing through the absorber condenser (CT-HEA-2). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

The condensed phase formed at 21.4 bar and 40.0ºC is flash-separated in the absorber liquid reflux-drum (CA-FLA-1) modeled by using a Flash2 separator block. The condensate top product from the absorber liquid reflux-drum (CA-FLA-1) is pumped at 21.6 bar and 40.0ºC by the absorber reflux-pump (CA-PUM-3) and refluxed back to the 1º theoretically liquid stage (top column stage) of the intermediate-pressure absorber tray-column (CA-ABS-1).

The gaseous phase from the absorber liquid reflux-drum (CA-FLA-1) is ducted-fed into the bottom of the washer packed-column section (CA-WAS-1) at 21.4 bar and 40.0ºC.

The liquid bottom product is obtained at 22.0 bar and about 96.0ºC from the 20º theoretically liquid stage (bottom column stage) of the intermediate-pressure absorber tray-column (CA-ABS-1) as a CO_2 and H_2S rich solution (rich-amine solution) with others pollutants content (e.g.: NH_3, SOx, CHN, COS, hydrocarbons) without degradation products (not included in the Aspen Plus®v8.4 process model simulation). Liquid bottom product is flashed in the rich-amine flash vessel (CA-FLA-3) modeled by using a Flash2 separator block, when the pressure of the rich-amine solution is reduced from 22.0 bar to 1.72 bar, and then after-pumped by the rich-amine pump (CA-PUM-4) to the cross-solution heat exchanger (CA-HEA-2). Rich-amine flash vessel (CA-FLA-3) remove part of the dissolved gases presents in the rich-amine solution according to vapor-liquid equilibrium for ELECNRTL physical properties.

Make-up water (WATER FROM TREATMENT PLANT) at atmospheric pressure and 25.0ºC from the treatment plant is pumped (CA-PUM-7) at 21.0 bar to the 1º theoretically liquid stage (top column stage) of the washer packed-column section (CA-WAS-1). The water obtained in the bottom of the of the washer packed-column section (CA-WAS-1) is pumped by the washer water recycle-pump (CA-PUM-8) back to the 1º theoretically liquid stage (top column stage) to enter at 21.0 bar and about 37.0ºC in the washer packed-column section (CA-WAS-1). The water mass flow rate of water circulating in close-loop cycle is defined by the parameters of the washer packed-column section (CA-WAS-1), and by the employed temperature limits in the Aspen Plus®v8.4 process model simulation.

The single washer water step as final polishing step reduces the concentration of PZ, MDEA, and others water affinity contaminants in the cleaned synthesis gas.

Rigorous Aspen Plus®v8.4 process model simulation of the washer packed-column section (CA-WAS-1) was developed as a top section of the absorber tray-column (CA-ABS-1) using RadFrac columns block on standard convergence mode with reaction model RE-CA-PZMDE and electrolyte solution chemistry model CH-CA-PZMDE without in-bed condenser and reboiler. The model was optimized for estimated 5 theoretical stages considering NORTON IMTP 38.0 mm packing section from 1º to 5º theoretically stages with section packed height and diameter optimized for each system requirements (scenarios dependence) on standards characteristics, and according to diameter of the intermediate-pressure absorber tray-column (CA-ABS-1). The model use rate-based calculation for Mixed flow model without reactions and film resistance in vapor phase, without reactions and with film resistance in liquid phase. Default Aspen Plus®v8.4 packing parameters is applied to calculate pressure drop and liquid holdup by Stichlmair method, to predict the mass transfer coefficient and interfacial area by Onda et al. (1968) correlation, and heat transfer coefficient by Chilton-Colburn (Taylor and Krishna, 1993) method.

A fraction of 0.45% of the circulating water is drained in the washer water bleed (CA-SPL-3) to recovery the concentrate washer-recovered PZ/MDEA blend-based aqueous absorbing-solution and removes dissolved gases (amine contaminated wash water), in closed-loop water cycle. After, drained water is recycled and sends back to mixture tank (CA-MIX-1).

The wet cleaned-synthesis gas (gaseous top-product) from washer packed-column section (CA-WAS-1) at 21.0 bar and about 36.6ºC is ducted to the regenerative ZnO/CuO-based guard bed adsorber (GU blocks).

Rich-amine solution from the rich-amine flash vessel (CA-FLA-3) is sent by rich-amine pump (CA-PUM-4) to cross-solution heat exchanger (CA-HEA-2) modeled by using a HeatX exchanger block for exchange heat (thermal energy recovery) with the lean-amine solution from the low-pressure stripper packed-column (CA-STR-1). Lean-amine solution is cooled from about 122.0ºC to about 44.0ºC, heating the rich-amine from about 36.6ºC to about 108.0ºC. The heated rich-amine solution is fed into the 6º theoretical stage in the low-pressure stripper packed-column (CA-STR-1) on top of the regenerative section. The cooled lean-amine solution is sent to amine reclaimer (CA-SPL-2) or directly back to mixture tank (CA-MIX-1) closing the PZ/MEA blend-based aqueous absorbing-solution cycle.

Rigorous Aspen Plus®v8.4 process model simulation of the low-pressure stripper packed-column (CA-STR-1) was developed using RadFrac columns block on standard convergence mode with reaction model RE-CA-PZMDE and electrolyte solution chemistry model CH-CA-PZMDE without in-bed condenser and reboiler. The model was optimized for estimated 25 theoretical stages (5 theoretical stages as washer section) considering a NORTON IMTP 38.0 mm packing section from 1º to 25º theoretically stages with height and diameter for regenerative and washer packed sections optimized for each system requirements (scenarios dependence) on standards characteristics. The model use rate-based calculation for Mixed flow model without reactions and film resistance in vapor phase, without reactions and with film resistance in liquid phase. Default Aspen Plus®v8.4 packing parameters is applied to calculate pressure drop and liquid holdup by Stichlmair method, to predict the mass transfer coefficient and interfacial area by Onda et al. (1968) correlation, and heat transfer coefficient by Chilton- Colburn (Taylor and Krishna, 1993) method.

The gaseous top-product containing mainly acid gases (CO_2 and H_2S) at about 1.72 bar and 115.6ºC from the 1º theoretically vapor stage (top column stage) of the low-pressure stripper packed-column (CA-STR-1) is mixed with the fleshed gases at about 1.72 bar and 36.6ºC from the rich-amine flash vessel (CA-FLA-3). After mixed, the gases are then cooled in the stripper condenser (CA-CON-2) passing cooling water (CT-HEA-3) modeled by Heater exchanger's blocks. Hence, form-condense 54.0$\%_{w/w}$ (model result) of the gaseous top-product (condensate phase) on saturation equilibrium conditions.

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-3) to the stripper condenser (CT-HEA-3). The amount of cooling water required is determined and controlled by design specification DS-CA-TL-3 varying the mass flow rate of cooling water passing through the stripper condenser (CT-HEA-3). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

The condensed phase formed at 1.7 bar and 40.0ºC is flash-separated in the striper liquid reflux-drum (CA-FLA-2) modeled by using a Flash2 separator block. A fraction of the condensate top product containing mainly water from the striper liquid reflux-drum (CA-FLA-2) is splitted in the striper water bleed (CA-SPL-1) and sent-recycled back to the mixture tank (CA-MIX-1) as recovered water (recycle) in closed-loop-cycle mode. Another fraction (20.0$\%_{w/w}$ by model result) of the condensate top product is pumped at 1.72 bar and about 40.0ºC by the desorber reflux pump (CA-PUM-5) and refluxed back to the 1º theoretically liquid stage (internal washer section) of the low-pressure stripper packed-column (CA-STR-1). The excess of water, if there is, can be sent to wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for reuse as make-up water (WATER FROM TREATMENT). In the Biomass-to-Methanol scenarios, this is not the case (recycled in the system).

About 44.0%$_{w/w}$ of gaseous top-product (non-condensed) containing mainly CO_2 and H_2S leaving from the striper liquid reflux-drum (CA-FLA-2) at 1.7 bar and 40.0ºC (saturation condition) is directly sent to be compressed and liquefied by the integrally-geared centrifugal six stages compressor (CC blocks).

The liquid bottom product containing mainly regenerated amine solution at 1.78 bar and about 118.2ºC from the 25º theoretically liquid stage (bottom column stage) in the regenerative section of the low-pressure stripper packed-column (CA-ABS-1) as lean-amine solution is splitted in the lean-amine sump splitter (CA-SPL-5) of the stripper reboiler (CA-REB-1). 80.0%$_{w/w}$ of the bottom liquid product in the sump is fed in the stripper reboiler (CA-REB-1), and 20.0%$_{w/w}$ of the bottom liquid product in the sump is drained as product and mixed in the lean-amine regenerated mixer (CA-MIX-2) with heated bottom liquid phase overflow the baffle.

The reboiler circulation baffle model was developed by using a HeatX exchanger block (CA-REB-1) and by using a FSplit splitter block (CA-SPL-5) to represent the stripper reboiler configured for circulation with baffle.

The bottom liquid product from the lean-amine regenerated mixer (CA-MIX-2) contain regenerated MDEA and PZ, low fraction of CO_2, H_2S, and others pollutants content (e.g.: NH_3, SOx, CHN, COS, hydrocarbons) without degradation products (not included in the Aspen Plus®v8.4 process model simulation).

The thermal energy for stripper reboiler (CA-REB-1) determine the PZ/MDEA blend-based aqueous absorbing-solution vaporized in the reboiler and the regeneration extent trough the low-pressure stripper packed-column (CA-STR-1) to obtain the required capture levels (adjust the required fraction of CO_2 captured to 96%$_{w/w}$ of the inlet).

The thermal energy required by the stripper reboiler (CA-REB-1), in the Biomass-to-Methanol (SC1), and Biomass-to-Methanol (SC2), is supplied by process steam at 2.5 bar and 130.0ºC part generated in the low-pressure vaporizer (WS-HEA-2) of the catalyst WGS system, and another part obtained from the steam exhausted at 2.5 bar from the low-pressure expansion stage of the steam turbine applied in CCs. The thermal energy required by the stripper reboiler (CA-REB-1) in the Biomass-to-Methanol (SC3), is supplied by process steam at 2.5 bar and 130.0ºC part generated in the low-pressure vaporizer (WS-HEA-2) of the catalyst WGS system, and part obtained from the steam extraction at 2.5 bar (ST-SPL-1) from the CEST system.

The mass flow rate of process steam at 2.5 bar and 130.0ºC required is determined by thermal requirements and exchanger temperature limits (cross-over avoided) in the cycle-system, and controlled by design specification DS-CA-FL-2 varying the mass flow rate of water/steam circulating through the reboiler exchanger cycle.

In the Biomass-to-Methanol (SC1), and Biomass-to-Methanol (SC2), a fraction of the condensed water after the stripper reboiler (CA-REB-1) is pumped (GA-PUM-1) as conditioned hot water to syngas cooling and heat recovery (GA blocks) to produce the gasification steam agent in the low-temperature vertical CSC (GA-CSC-2). The reminiscent fraction is sent-back (recycle) to the first deaerator unit (HR-DEA-1). In the Biomass-to-Methanol (SC2), all of the condensed water after the stripper reboiler (CA-REB-1) is ducted to hot water reservoir (HR-TAN-1). After, this is pumped (GA-PUM-1) together the deaerated hot process water from the first deaerator unit (HR-DEA-1) as conditioned hot water to syngas cooling and heat recovery (GA blocks) to produce the gasification steam agent in the low-temperature vertical CSC (GA-CSC-2).

The lean-amine solution regenerated from the lean-amine regenerated mixer (CA-MIX-2) is send to be cooled from about 122.0ºC to about 44.0ºC, recovering the heat in the cross-solution heat exchanger (CA-HEA-2). After cooled, the lean-amine solution is sent to the amine reclaimer (CA-SPL-2).

Amine reclaimer (CA-SPL-2) split 0.18$\%_{w/w}$ of the lean-amine solution circulating back to absorber tray-column (CA-ABS-1). Amine reclaimer (CA-SPL-2) is modeled by using a FSplit splitter block to adjust the amine make-up, and simulate the losses of PZ and MDEA due the thermal and oxidizing degradation, according to input fraction of components removed in the carbon-based filter (CA-SEP-1) as simplified mode (model artifice). In the carbon-based filter (CA-SEP-1) modeled by using a Sep separator block is considered a loss of 10.0$\%_{w/w}$ of the circulating water in the reclaimer cycle, and the downdraft of all dissolved gases and electrolyte entering the filter system (CA-SEP-1).

The lean-amine solution reclaimed is filtered by carbon-based filter (CA-SEP-1) containing activated charcoal medium put on stream at every 3 to 4 weeks of interval (continues stead-state simulated). In this stage, are removed sulphur and nitrogen compounds, amine salts, particles, and degradation products (not included in the Aspen Plus®v8.4 process model simulation), formed over time in the amine cycle in closed loop-cycle mode.

A fraction of the amine reclaimed is recovered in the presence of a strong alkali solution (e.g.: NaOH) and with the application of heat (not included in the Aspen Plus®v8.4 process model simulation). Another fraction, retained and removed by the carbon-based filter (CA-SEP-1) is sent to wastewater treatment plant, and after destined to final disposal (e.g.: landfill) with carbon filter active medium (activated charcoal) (RESIDUE TO DISPOSAL). Recovered amine is sent-back into the amine-lean solution line (CA-SPL-2) by the recirculation pump (CA-PUM-5) together 90.0$\%_{w/w}$ of cleaned-water that passes through the carbon-based filter (CA-SEP-1).

MDEA-based aqueous absorbing-solution and PZ-based aqueous absorbing-solution are a solvent with high resistance to oxidative and thermal degradation in intermediate-pressure systems, different from the MEA-based aqueous absorbing-solution that can undergo extensive degradation effect due to the internal temperatures reached in the absorber column (CA-ABS-1). Based systems on PZ/MDEA blend-based aqueous absorbing-solution can be used to compact the CO2 absorption/desorption system, reducing the thermal energy required (steam process) by the stripper reboiler (CA-REB-1) in the regeneration process.

7.2.13 Carbon dioxide compression and storage/use

The gaseous CO_2 captured (acid gas) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) in the co-capture of CO_2 and H_2S by using amine-based aqueous absorbing-solution (CA blocks) is compressed by the integrally-geared centrifugal six stages compressor (CC blocks) (multiple pinions). The compressed gaseous CO_2 is after-cooled, been liquefied producing liquid CO_2 at 30.0ºC and 73.0 bar for further uses. High-pressure liquid pump (CC-PUM-1) is used to adjust the pressure to 150.0 bar (or more) to be injected into the geological formations for permanent storage (CCS).

The Aspen Plus®v8.4 process model simulation of the integrally-geared centrifugal six stages compressor (CC blocks) is based on the Siemens STC-GV integrally-geared centrifugal multi-stages compressor series feature a single-shaft arrangement and configured to allow inter-cooling steps. The Aspen Plus®v8.4 process model simulation of the integrally-geared centrifugal six stages compressor (CC blocks) was developed using Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 83.0% isentropic efficiency (isentropic compression).

Figure 71 shows the Aspen Plus®v8.4 flowsheet of the CO_2 compression and storage/use area for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3).

The captured gaseous CO_2 without the presence of H_2S (applying LO-CAT sulfur recovery unit) or the acid gas (technical compressor limits analysis) as leave in the top of the stripper column (CA-FLA-2) flow enters the compressor by the inlet guide (CC-COM-1) to distribute the flow providing a uniform condition in the first-stage impeller (CC-COM-1). The gaseous CO_2 at 1.7 bar and 40.0ºC (saturation condition) is compressed to about 78.0 bar and 93.0ºC (supercritical pressure) by the impellers (CC-COM-1~6) modeled by using Compr pressure changer blocks according to rigorous ASME method for isentropic compressor.

After the stages of compression (CC-COM-1~6), hot gas ducted-leaving is cooled to 30.0ºC by the water inter-cooler exchangers (CC-1~5) modeled by using MHeatX exchanger blocks, generating condensed phase content water and dissolved gasses. Condensed phase is removed in the condenser knock-out drums (CC-FLA-1~5) modeled by using Flash2 separator blocks and sent to atmospheric condensate buffer/equalizer tank (CC-FLA-7) modeled by using a Flash2 separator block at ambient conditions.

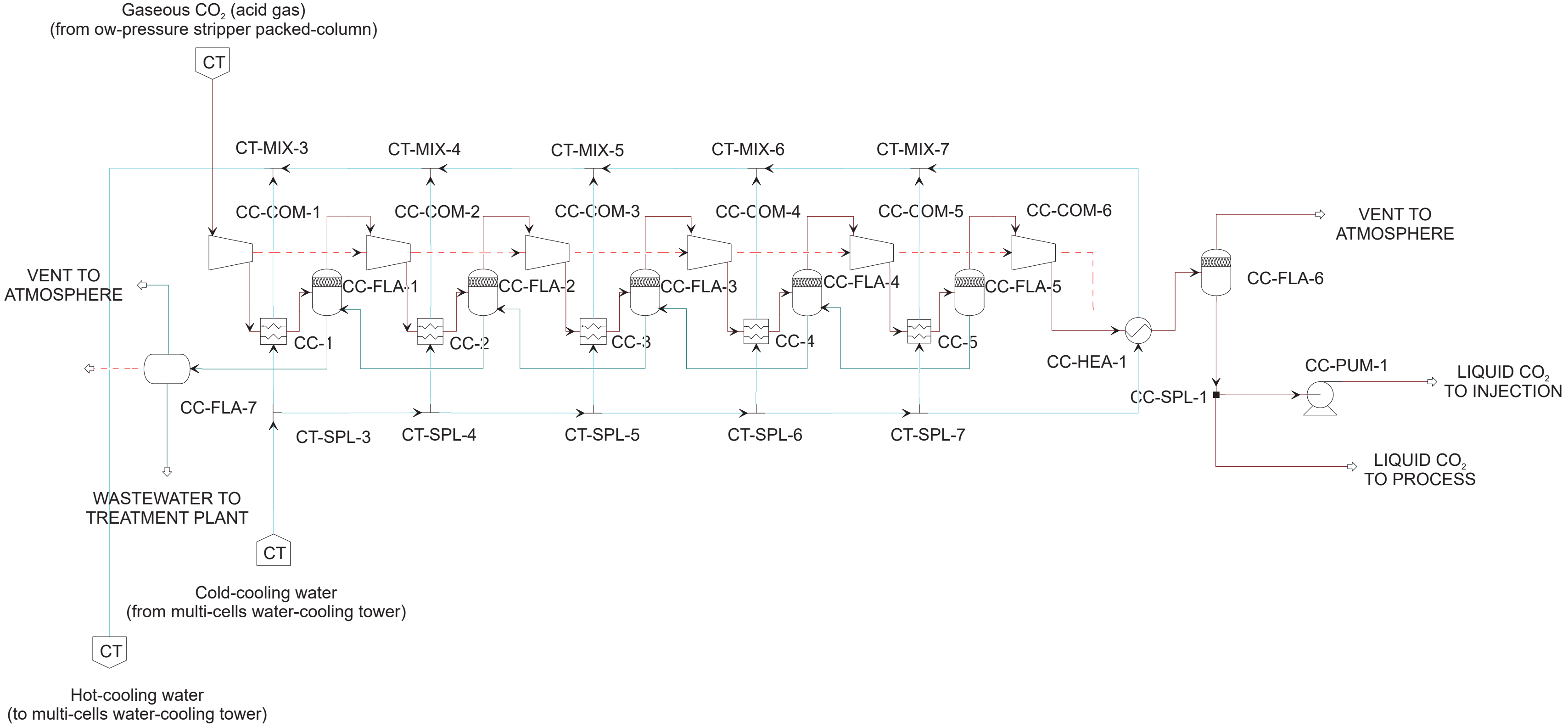


Figure 71 - Aspen Plus® v8.4 flowsheet of the CO_2 compression and storage/use area for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3)

As shown in Figure 71, Aspen Plus®v8.4 flowsheet of the CO_2 compression and storage/use area in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) is compost by: integrally-geared centrifugal six stages compressor (CC-COM-1~6); water inter-cooler exchangers (CC-1~5); supercritical liquefactor-cooler (CC-HEA-1); condenser knock-out drum (CC-FLA-5); liquid water pump (CC-PUM-1); high-pressure liquid pump (CC-PUM-1); direct drive permanent magnet motor (mechanical efficiency); degases warm (CC-FLA-6); atmospheric condensate buffer/equalizer tank (CO-FLA-7); high-pressure buffer/equalizer tank (CO-FLA-6); and liquid CO_2 temporary storage tank (CC-SPL-1).

After the six-stage impeller (CO-COM-6), cooled high-pressure gaseous CO_2 is sub-cooled to about 78.0 bar and 30.0ºC, and liquefied by the supercritical liquefactor-cooler (CC-HEA-1) modeled by using a HeatX exchanger block. Liquid CO_2 is sent to high-pressure buffer/equalizer tank (CO-FLA-6) to remove any non-condensable gases present in the line to atmosphere (VENT TO ATMOSPHERE).

The liquid CO_2 produce-captured can be send to permanent storage (HIGH-PRESSURE CO_2 TO STORAGE) in geological formations (CCS) (e.g.: aquifers, oil and gas fields, unmineable coal beds) at about 150.0 bar, by using a high-pressure liquid pump (CC-PUM-1) to compress the liquid CO_2. The liquid CO_2 produce-captured can be send to process use (LIQUID CO_2 TO PROCESS) at adequate conditions required by the downstream process (not included in the model) or by the transportation off-site (e.g.: algae-based liquid biofuels, methanol synthesis). The use of the captured CO_2 is not defined in this research Master`s degree.

The ambient equalized condensate (CC-FLA-7) is after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-5) to the water inter-cooler exchangers (CC-1~5) and to the supercritical liquefactor-cooler (CC-HEA-1). The amount of cooling water required is determined and controlled varying the mass flow rate of cooling water flows through the equipment users. The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system. The lubricating oil circuit and the lubricating oil water-cooling system are suppressed from the Aspen Plus®v8.4 process model simulations in this research Master`s degree.

The single shaft and multiple pinions in the integrally-geared centrifugal six stages compressor (CC-COM blocks) is drive by a synchronous direct drive permanent magnet motor modeled by CC-E-6 work stream. The compression stages (impellers) are optimized to obtain the same compression ratio by design specification DS-CC-TR-1 and FORTRAN calculation block CA-CC-TR-2 varying the pressure ratio of the six compression stages (CO-COM blocks). The electrical potential losses by attrite in the mechanical move parts was considered as 1.0% of the mechanical energy required by the stage (99.0% mechanical efficiency).

7.2.14 Water-gas-shift reactors

Water-gas-shift (WGS) reaction as described in the section 4.1.16 (Water-gas-shift (WGS) and reverse Water-gas-shift (RWGS) reaction) is carried out as direct-direction reaction mode according to Chemical equation c.8 to increase the H_2 yield (content) in the intermediate-pressure synthesis gas before the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks).

High-temperature (HT) catalyst WGS reactor (WS-HTR-1) followed by a low-temperature (LT) catalyst WGS reactor (WS-LTR-1) with intercooling stage are implemented in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) before the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks).

The Aspen Plus$^{®}$v8.4 process model simulation of the gasification of biomass in a CFB directly-heated gasifier by using high-purity oxygen and steam agents according to section 7.2.6 (Gasification of biomass in an atmospheric circulating fluidized bed directly-heated gasifier by using high-purity oxygen and steam agents) applying the chemical equilibrium by Gibbs free-energy minimization approach overestimates the water gas shift equilibrium effect and the formation of light hydrocarbons and heavy hydrocarbons. The gasification model breaking the higher molecular compounds into simpler forms, according to this model is formed more H_2 and less CO than the predicted by rigorous kinetic models. However, it is not sufficient to obtain the hydrogen to carbon oxides - $(H_2\text{-}CO_2)/(CO+CO_2)$ ratio - required by the low-pressure methanol catalyst-synthesis, there is needed to use a catalyst WGS system operating in direct direction reaction mode.

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) is used only with the objective to adjusts the ratio of hydrogen to carbon oxides - $(H_2\text{-}CO_2)/(CO+CO_2)$ ratio –, but it can also be used to provide more H_2 than necessary for the low-pressure methanol catalytic-synthesis (ME blocks) intended it to increase the energy density of the fuel-gas available to burn in the high-performance sequential combustion full-flow advanced EvGT, without requiring significant changes in the turbine design.

Figure 72 shows the Aspen Plus$^{®}$v8.4 flowsheet of the high-temperature and low-temperature catalyst water-gas-shift reactors at intermediate-pressure level with energy-saving and steam generation for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3).

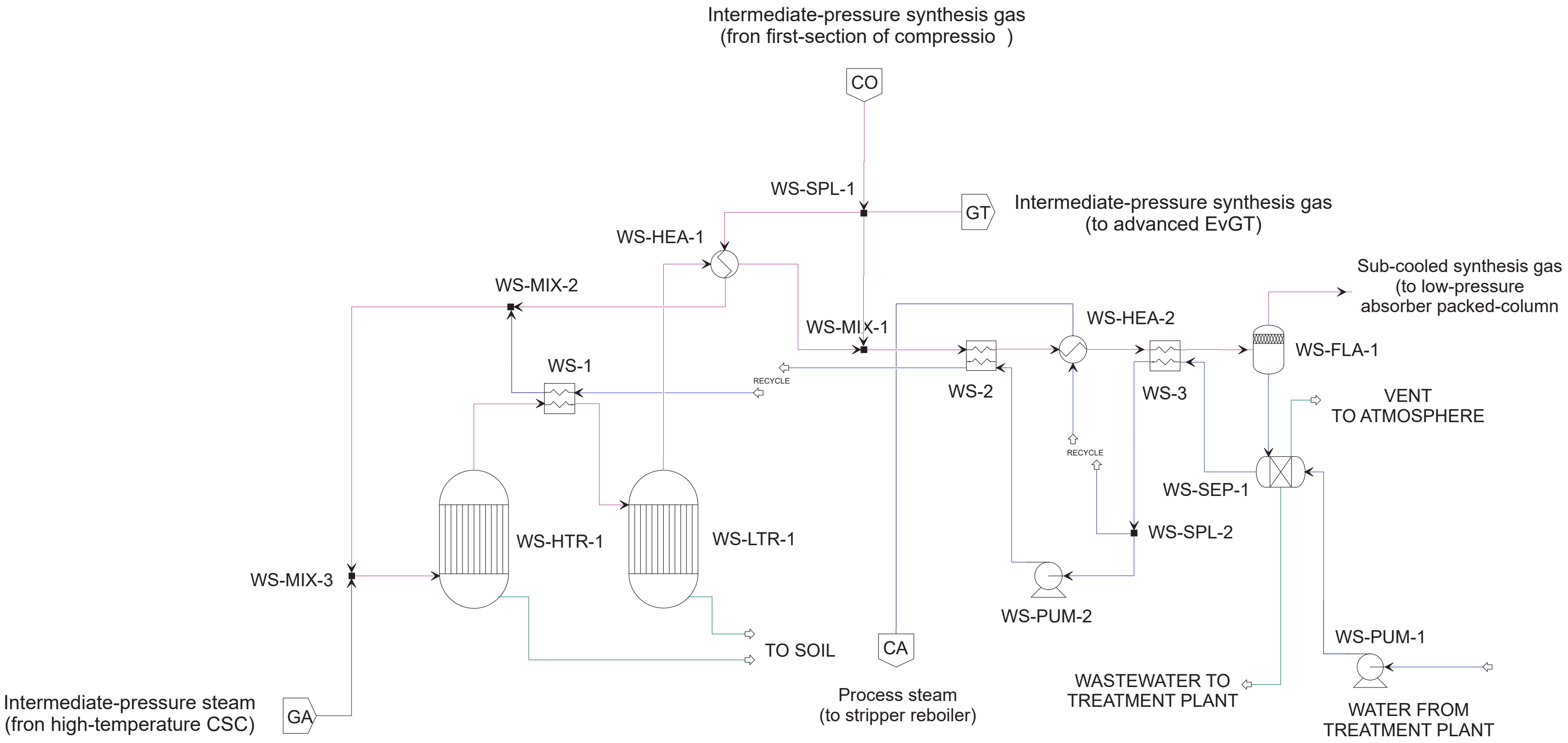


Figure 72 - Aspen Plus® v8.4 flowsheet of the high-temperature and low-temperature catalyst water-gas-shift reactors at intermediate-pressure level with energy-saving and steam generation for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3)

As shown in Figure 72, Aspen Plus®v8.4 flowsheet of the high-temperature and low-temperature catalyst water-gas-shift reactors at intermediate-pressure level with energy-saving and steam generation for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) is compost by: HT catalyst WGS reactor (WS-HTR-1); LT catalyst WGS reactor (WS-LTR-1); cross-gaseous heat exchanger (WS-HEA-1); HT after-cooler (WS-1); intermediate-pressure synthesis gas splitter (WS-SPL-1); intermediate-pressure synthesis gas mixer (WS-MIX-1); steam-gases mixer (WS-MIX-2); and steam mixer and injection (WS-MIX-3). Also, shows the Aspen Plus®v8.4 flowsheet of the energy-saving and steam generation compost by: fresh-water pump (WS-PUM-1); condensed water recovery and recycle system (WS-SEP-1); intermediate-pressure water pump (WS-PUM-2); high-temperature cooler (WS-2); low-temperature cooler (WS-3); low-pressure vaporizer (WS-HEA-2); low-pressure process steam mixer (WS-MIX-4); and condenser knock-out drum (WS-FLA-1).

The WGS reaction adjusts the ratio of hydrogen to carbon oxides - $(H_2-CO_2)/(CO+CO_2)$ ratio – or referred just as stoichiometric number (SN) by adding steam to the catalyst WGS reactors shifting the reaction balance to raise the hydrogen content-fraction at optimal level for the methanol synthesis in the low-pressure methanol catalytic-synthesis (ME blocks) to obtain higher methanol yields.

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) the synthesis gas at intermediate-pressure from the condenser knock-out drum (CO-FLA-3) in the first-section of synthesis gas compression (conditioning) (CO blocks) is separated in the intermediate-pressure synthesis gas splitter (WS-SPL-1) to be used in the catalyst WGS reactors.

The fraction of the intermediate-pressure synthesis gas is before pre-heated in the cross-gaseous heat exchanger (WS-HEA-1) modeled by using a HeatX exchanger block cooling down the product gas from the LT catalyst WGS reactor (WS-LTR-1), recovering energy. The temperature was optimized to obtain the required inlet temperature and the ratio of steam to carbon monoxide – H_2O/CO ratio – in the HT catalyst WGS reactor (WS-HTR-1) and is controlled by design specification DS-WS-RST-1 varying the temperature of synthesis gas obtained after the cross-gaseous heat exchanger (WS-HEA-1) coupled with the design specification DS-WS-TG-1 and dependent on the design specification DS-WS-TG-2.

After pre-heated the intermediate-pressure synthesis gas is mixed (WS-MIX-2) with superheated steam at same pressure level obtained from the HT after-cooler (WS-1) modeled by using a MHeatX exchanger block. The product gas from the HT catalyst WGS reactor (WS-HTR-1) is cooled down to 22.3 bar and 230.0ºC (catalyst temperature limit) before inlet in the LT catalyst WGS reactor (WS-LTR-1), recovering the energy and economizing intermediate-pressure steam obtained from the high-temperature vertical CSC (GA-CSC-1) and used in the catalyst WGS reactors. The amount of water used to cool down the product gas from the HT catalyst WGS reactor (WS-HTR-1) is determined and controlled by design specification DS-WS-TG-

2 varying the mass flow rate of water passing through the HT after-cooler (WS-1) limited to achieve the Synthesis gas inlet temperature in the LT catalyst WGS reactor (WS-LTR-1).

Part of the intermediate-pressure steam produced in the high-temperature vertical CSC (GA-CSC-1) is splitted (GA-SPL-3) and mixed (WS-MIX-3) with the pre-heated intermediate-pressure synthesis gas. In the Biomass-to-Methanol (SC1) and Biomass-to-Methanol (SC2) is produced intermediate-pressure steam at 23.0 bar and 337.9ºC. In the Biomass-to-Methanol (SC3) is produced intermediate-pressure steam at 23.0 bar and 450.0ºC (reheater pipe bank).

The intermediate-pressure steam is used to heat the inlet gases in the HT catalyst WGS reactor (WS-HTR-1) achieving the temperature for reaction in the HT catalyst WGS reactor (WS-HTR-1). Also is used to achieve the stoichiometric molar ratio of steam to carbon monoxide – H_2O/CO ratio – to 4 times the carbon monoxide content in the inlet stream (WS-G-7). The amount of intermediate-pressure steam required is determined and controlled by design specification DS-WS-TG-1 varying the intermediate-pressure steam mass flow rate splitted (GA-SPL-3).

The Aspen Plus®v8.4 process model simulation of HT catalyst WGS reactor (WS-HTR-1) was developed by using a REquil reactor block to represent the water-gas-shift reaction (Chemical equation c.8) according to Gibbs free-energy approach to chemical equilibrium and constants restricted by chemical equilibrium temperature approach. In the Biomass-to-Methanol (SC1) and Biomass-to-Methanol (SC2) the HT catalyst WGS reactor (WS-HTR-1) operates at 23.0 bar and 300.0ºC and in the Biomass-to-Methanol (SC3) at 23.0 bar and 350.0ºC, limited by the intermediate-pressure steam generated in the high-temperature vertical CSC (GA-CSC-1).

The Aspen Plus®v8.4 process model simulation of LT catalyst WGS reactor (WS-LTR-1) was developed by using a REquil reactor block to represent the water-gas-shift reaction (Chemical equation c.8) according to Gibbs free-energy approach to chemical equilibrium and constants restricted by chemical equilibrium temperature approach. In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) the LT catalyst WGS reactor (WS-LTR-1) operates at 22.5 bar and 230.0ºC, limited by the $Zn\text{-}CuO/Al_2O_3$ catalyst operational temperature (low-temperature catalyst).

After the LT catalyst WGS reactor (WS-LTR-1), intermediate-pressure synthesis gas at about 22.5 bar and 247.0ºC in the Biomass-to-Methanol (SC1) and Biomass-to-Methanol (SC2), and at about 22.5 bar and 254.0ºC in the Biomass-to-Methanol (SC3) is cooled in the cross-gaseous heat exchanger (WS-HEA-1) to obtain the optimized inlet temperature and the ratio of steam to carbon monoxide in the HT catalyst WGS reactor (WS-HTR-1) according to design specification DS-WS-RST-1. The intermediate-pressure synthesis gas is mixed back with the synthesis gas bypass fraction from the intermediate-pressure synthesis gas splitter (WS-SPL-1) in the intermediate-pressure synthesis gas mixer (WS-MIX-1), obtaining synthesis gas at about 22.0 bar and 187.0 ºC.

Spreadsheet calculation models are used to determine the quantity of Zn-CuO/Al_2O_3 catalyst must be loaded into LT catalyst WGS reactor (WS-LTR-1) and the quantity of Fe_2O_3/Cr_2O_3 MgO catalyst must be loaded into HT catalyst WGS reactor (WS-HTR-1). ZnO-based catalyst can be added in the HT catalyst WGS reactor (WS-HTR-1) to protect the low activity Zn-CuO/Al_2O_3 catalyst from poisons such as sulphur and chlorine compounds. On the other hand, Fe_2O_3/Cr_2O_3 MgO catalyst is not particularly sensitive to sulphur poisoning, relatively slow sintering still causes a decrease in activity of the catalyst.

Fe_2O_3/Cr_2O_3 MgO catalyst considered in the HT catalyst WGS reactor (WS-HTR-1) is a commercial type high activity catalyst content 92.0$\%_{w/w}$ of Fe_2O_3, 6.0$\%_{w/w}$ of Cr_2O_3 and 2.0$\%_{w/w}$ of MgO. The Fe_2O_3/Cr_2O_3 MgO catalyst is weight loaded to obtain 20.0 kg of Fe_2O_3/Cr_2O_3 MgO catalyst per kmol of CO flowing through the system. Fe_2O_3/Cr_2O_3 MgO catalyst lifetime is expected to be about 4 years before the necessity of deactivated catalyst being partial or full discharged and new activity catalyst be loaded, deactivated catalyst is sent to be regenerated and/or to final disposal.

Zn-CuO/Al_2O_3 catalyst considered in the LT catalyst WGS reactor (WS-LTR-1) is a commercial type low activity catalyst content 20.0$\%_{w/w}$ of Al_2O_3, 47.0$\%_{w/w}$ of ZnO and 33.0$\%_{w/w}$ of CuO. The Zn-CuO/Al_2O_3 catalyst is weight loaded to obtain 20.0 kg of Zn-CuO/Al_2O_3 catalyst per kmol of CO flowing in the system. Zn-CuO/Al_2O_3 catalyst lifetime is expected to be about 2 years before the necessity of deactivated catalyst being partial or full discharged and new activity catalyst loaded, deactivated catalyst is sent to be regenerated and/or to final disposal.

The hot intermediate-pressure synthesis gas enriched with hydrogen enters in the energy-saving and steam generation section to be sub-cooled to 40.0ºC generating steam at low-pressure level. All of the amount of steam generated is used as process steam destined to stripper reboiler (CA-REB-1) in the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks) and hot-liquid water to be used to cooling down the product gas from the HT catalyst WGS reactor (WS-HTR-1) to 22.3 bar and 230.0ºC (catalyst temperature limit) before inlet in the LT catalyst WGS reactor (WS-LTR-1).

In the high-temperature cooler (WS-2) modeled by using a MHeatX exchanger block the pressurized water at about 23.4 bar and 47.0ºC is heated generating hot-liquid water at about 175.0ºC controlled by design specification DS-WS-FL-2 varying the synthesis gas outlet temperature in the low-pressure vaporizer (WS-HEA-2) closing the energy balance. The design specification aims the maximum recovery efficiency according to temperature limits between the cooling/heating steps.

In the low-pressure vaporizer (WS-HEA-2) modeled by using a HeatX exchanger block (WS-HEA-2) heat is recovered to generate low-pressure steam raising the supply and reducing the stress on the HRSG system (HR blocks). Process steam at 2.5 bar and 130.0ºC is generated and sent to steam-gases mixer (WS-MIX-2). This low-pressure steam generated is mixed with the low-pressure steam from the steam turbine applied in combined-cycles used in the stripper reboiler (CA-REB-1) in the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks) as thermal energy utility.

The low-pressure steam generated in the low-pressure vaporizer (WS-HEA-2) is used in the stripper reboiler (CA-REB-1) in the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks) as thermal energy utility. The amount of low-pressure steam at 2.5 bar and 130.0ºC generated depend on the energy balance and is controlled by design specification DS-WS-FL-2 coupled with design specification DS-WS-FL-1 varying the water/steam mass flow rate through the low-pressure vaporizer (WS-HEA-2) according to temperature limits between the exchangers and the heat available to recovery.

The intermediate-pressure synthesis gas is sub-cooled in the low-temperature cooler (WS-3) modeled by using a MHeatX exchanger block reducing the temperature to 22.0 bar and 40.0ºC generating condensed phase content water and dissolved gases. The condensed phase formed is removed in the condenser knock-out drum (WS-FLA-1) modeled by using a Flash2 separator block and sent to the condensed water recovery and recycle system (WS-SEP-1). The sub-cooled synthesis gas is ducted and then fed into the bottom of the intermediate-pressure absorber tray-column (CA-ABS-1) in the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution.

Condensed water at 22.0 bar and 40.0ºC is fleshed to 2.8 bar removing part of the dissolved gases in the condensed water recovery and recycle system (WS-SEP-1) and is after-sent to basin water tank (WS-SEP-1). 10.0%$_{w/w}$ of the condensed water is purged together 50.0%$_{w/w}$ of the impurities contained in the condensate as basin blowdown. The purged condensate is sent to wastewater treatment plant when 95.0%$_{w/w}$ of the water is recovered and mixed with make-up raw water at 25.0ºC pumped (CT-PUM-1) from treatment plant (WATER FROM TREATMENT PLANT) to water recirculation tank (WS-SEP-1).

The amount of make-up raw water (WATER FROM TREATMENT PLANT) required by the energy-saving and steam generation section is controlled by design specification DS-WS-FL-3 varying the mass flow rate of water inlet in the system to maintenance the steam generation and replace the blowdown losses.

7.2.15 Regenerative metallic oxides-based guard bed adsorber

In this research Master's degree is considered removal the sulfur and chlorine reminiscent poisoning content in the synthesis gas with potential to poisoning the $CuO/ZnO/Al_2O_3$ low-active catalyst bed by using a combinations of ZnO and CuO catalyst sorbents in a regenerative guard bed absorber before the low-pressure methanol catalytic-synthesis.

The Aspen Plus®v8.4 process model simulation of the regenerative ZnO/CuO-based guard bed adsorber for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) was developed in steady-state mode using RKS-BM physical property methods without adsorbing and regenerative reactions (simplified model).

Figure 73 shows the Aspen Plus®v8.4 flowsheet of the regenerative Metallic oxides-based guard bed adsorber for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3).

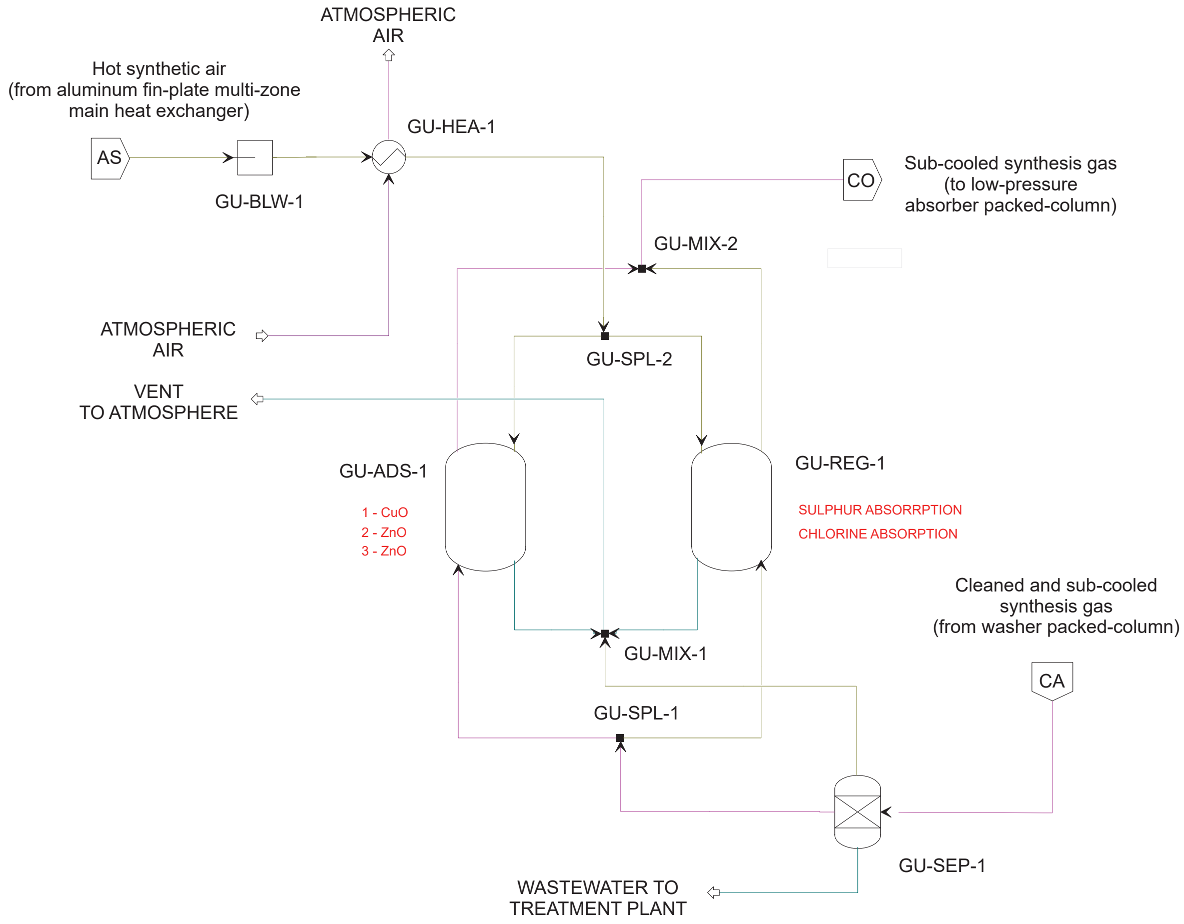


Figure 73 - Aspen Plus®v8.4 flowsheet of the regenerative Metallic oxides-based guard bed adsorber for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3)

As shown in Figure 73 the Aspen Plus®v8.4 flowsheet of the regenerative Metallic oxides-based guard bed adsorber in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) is compost by adsorber vessel (GU-ADS-1) (in adsorption cycle-time), regenerative vessel (GU-RE-1) (in regeneration cycle-time), condenser knock-out drum (GU-SEP-1), high-pressure blower system (GU-BLW-1), atmospheric air after-cooler (GU-HEA-1), inlet multi-way valve 1 (GU-SPL-1), inlet multi-way valve 2 (GU-SPL-2), outlet multi-way valve (GU-MIX-2) and vent off-gas multi-way valve (GU-MIX-1).

The adsorber catalyst bed material in the spreadsheet calculation model of the regenerative ZnO/CuO-based guard bed adsorber consider the bed content 70.0%$_{w/w}$ of ZnO and 30.0%$_{w/w}$ of CuO disposed in defined layers with ZnO catalyst in the bottom layer to adsorb in first time sulfur poisoning compounds (e.g.: H_2S, COS, and SO_x) with final polishing by the CuO catalyst in the top layer guaranteeing lower sulphur and chlorines poisoning in the synthesis gas. A fraction of the bottom layer act as ZnO-based chloride trap removing part of the chlorine compounds (e.g.: HCl and Cl_2) reminiscent in the cleaned and sub-cooled synthesis gas.

The main reactions considered in the interaction between the synthesis gas and the ZnO catalyst layer and CuO catalyst layer are defined and detailed in the section 4.1.17 (Regenerative guard bed adsorbers) represent by the Chemical equations c.9, c.10, c.11 and c.12, and the competitive side-reaction by the Chemical equation c.13.

The Aspen Plus®v8.4 process model simulation in steady-state mode of the adsorbing and regenerative reactions in the ZnO catalyst layer and CuO catalyst layer consider only the atomic balance in the system based on the spreadsheet calculation model to determine the amount of ZnO and CuO catalysts must be loaded into the two vessels.

Cleaned and sub-cooled synthesis gas from the top of the washer packed-column section (CA-WAS-1) in the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks) is supplied into condenser knock-out drum (GU-SEP-1) modeled by using a Sep separator block. The model considers removal 80.0%$_{w/w}$ of the water content in the sub-cooled synthesis gas on liquid form as condensate. This block also is used as simulation artifice for remove together the condensate all of the PZ and MDEA entrained from the washer packed-column section (CA-WAS-1). The ambient equalized condensate (GU-SEP-1) is after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

From the condenser knock-out drums (GU-SEP-1) the cleaned and sub-cooled synthesis gas is fed by inlet multi-way valve 1 (GU-SPL-1) into the adsorber vessel (GU-ADS-1) modeled by using a Flash2 separator block to obtain the mass balance without bed material reactions. The adsorber vessel (GU-ADS-1) model consider the intermediate-pressure synthesis gas at 21.0 bar and about 37.0ºC (can be heated to increase the catalyst activity) flowing through the ZnO catalyst layer and CuO catalyst layer.

Cleaned synthesis gas flow-off the absorber vessel (GU-ADS-1) in the regenerative ZnO/CuO-based guard bed adsorber system by outlet multi-way valve (GU-MIX-2). Cleaned synthesis gas is after-sent directly to the second-section of synthesis gas compression (conditioning) by integrally-geared centrifugal two stages compressor (CO blocks).

The Aspen Plus®v8.4 process model simulation and the spreadsheet calculation model of the regenerative ZnO/CuO-based guard bed adsorber consider that 3.0%$_{w/w}$ of the CO_2, 2.0%$_{w/w}$ of the NO_x and 10.0%$_{w/w}$ of the NH_3 flowing through the adsorbed are removed from the system in the regeneration cycle together 99.0% of the sulfur content (e.g.: H_2S and SO_x), 80.0%$_{w/w}$ of the chlorine content (e.g.: HCl, and HClO) and 95.0%$_{w/w}$ of the Cl_2.

In the Aspen Plus®v8.4 process model simulation of the oxygen-regeneration cycles is considered the use of the synthetic air (similar to atmospheric air) purged from the low-pressure multi packed-column (AS-COL-2) in the double-column cryogenic ASU. Synthetic air has similar composition to the surrounding atmospheric air however without the presence of pollutants (e.g.: CO_2 CH_4 and NO_x) normally presents in the surrounding atmospheric air (ATMOSPHERIC AIR) aiming maintain activity through many regeneration cycles considered to improve the sulfur and chlorine poisoning adsorption.

The synthetic air is pre-heated in the aluminum fin-plate multi-zones main heat exchanger (AS-2) and heated in the aluminum fin-plate three-circuit after-cooler exchanger (AS-1) to 1.05 bar and 150.0ºC. Part of this synthetic air is splitted (AS-SPL-9) and used to achieve time-optimized regeneration phase in the regenerative vessel (GU-REG-1) in the regenerative ZnO/CuO-based guard bed adsorber.

The conditioned synthetic air is induced and compressed to 5.0 bar and about 409.2ºC by the blower system (GU-BLW-1) modeled by using a Compr pressure changer block according to isentropic method for compressor considering 85.0% isentropic efficiency and 99.0% mechanical efficiency.

The spreadsheet calculation model determines the amount of regenerative conditioned synthetic air mass flow rate is required in the regeneration-cycle. The model consider the limits per pass of 0.01 g of sulfur content per g of ZnO catalyst, 0.05 g of CO_2 per g of ZnO catalyst and 0.02 g of HCl per g of CuO catalyst, and the saturation limits (very low activity catalyst) of 0.15 g of sulfur content per g of ZnO catalyst, 0.30 g of CO_2 per g of ZnO catalyst and 0.1 g of HCl per g of CuO catalyst.

The mass flow rate of the synthetic air to regenerate the ZnO/CuO-based guard bed is controlled by design specification DS-GU-FG-1 varying the mass flow rate of the synthetic gas passing thought the regenerative vessel (GU-REG-1) coupled with design specification DS-AS-FG-3 varying the heated synthetic air mass fraction splitted (AS-SPL-9).

The blower system (GU-BLW-1) force the synthetic air through the atmospheric air after-cooler (GU-HEA-1) to be cooled to 5.0 bar and 350.0ºC by atmospheric air. The conditioned synthetic air is then fed by inlet multi-way valve 2 (GU-SPL-2) in the regenerative vessel (GU-REG-1) (in regeneration cycle-time) modeled by using a Flash2 separator block to obtain the mass balance without bed material reactions. Sorbent bed material ZnO catalyst layer and CuO catalyst layer is regenerated to maintain activity through regenerative-cycles removing the adsorbed contaminants from the catalyst.

Metal sulfides formed in the ZnO catalyst layer and CuO catalyst layer are regenerated to oxides and byproducts contain gaseous sulfur and chlorine, according to Chemical equations c.15, c.16 and c.17 by partial oxidation, to Chemical equations c.18 and c.19 by total oxidation (in presence of oxygen), and by catalytic reaction in presence of water according to Chemical equations c.20 and c.21. Side-reactions forming sulfates occurs in lower extension according to Chemical equations c.22 and c.23. The sulfate forms are non-reactive with respect to the desulphurization reactions in the conditions employed during the regenerative-cycle, and thus there is a loss of active material. Reactions are defined and detailed in the section 4.1.17 (Regenerative guard bed adsorbers).

The remaining sulfur content (H_2S and COS) is reduced to an acceptable level which is measured in the inlet stream of the gas-cooled fixed bed catalytic-synthesis reactor (ME-REA-1). For this type of catalyst selected for methanol synthesis by low-pressure methanol catalyst-synthesis the sulfur compounds required level should remain below 1.0 ppm (theoretical limit) in molar basis. Chlorines and nitrous oxides are reduced to traces level (not significant content) in the model (at ppb level).

Chlorines and nitrous oxides are reduced to traces level (not significant content) and CO_2 is removed mainly by the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks) and regenerative ZnO/CuO-based guard bed adsorber to the maximum acceptable level by the low-pressure methanol process to about $10.0\%_{w/w}$ equivalent to about $2.7\%_{mol}$ measured in the inlet stream of the gas-cooled fixed bed catalytic-synthesis reactor (ME-REA-1).

ZnO catalyst is weight loaded to obtain 0.01 g of sulfur adsorber per g of ZnO catalyst (0.15 g of sulfur saturation limit) and CuO catalyst is weight loaded to obtain 0.03 g of chlorine adsorber per g of ZnO and CuO catalyst (0.05 g of chlorine saturation limit).

The lifetime depends on the regeneration cycle and due the significant presence of sulfur and chlorine compounds in the biomass processed by the thermochemical-biorefinery. ZnO catalyst and CuO catalyst considered in the regenerative ZnO/CuO-based guard bed adsorber are a commercial type catalyst considering a catalyst lifetime expected to be about 1 year before the necessity of deactivated catalyst be partial or full discharged and new activity catalyst be loaded, deactivated catalyst is sent to be regenerated and/or to final disposal.

The hot synthetic gas with the potential pollutants (poisoning) removed from the vessel in the regeneration-cycle is emitted to atmosphere (VENT TO ATMOSPHERE) by the vent off-gas multi-way valve (GU-MIX-1).

7.2.16 Second-section of synthesis gas compression (conditioning)

The Aspen Plus$^{®}$v8.4 process model simulation of the integrally-geared centrifugal three stages compressor (CO-COM blocks) is based in the Siemens STC-GV integrally-geared centrifugal multi-stages compressor series feature a single-shaft arrangement configured to allow inter-cooling step.

Figure 74 shows the Aspen Plus$^{®}$v8.4 flowsheet of the second-section of synthesis gas compression (conditioning) for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3).

The synthesis gas at intermediate-pressure destined to methanol production in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) is compressed by integrally-geared centrifugal three stages compressor (CO blocks) to compress the intermediate-pressure synthesis and the unconverted light-gas recycled back to the methanol synthesis (third stage) at pressure requirements to use in the low-pressure methanol catalytic-synthesis. Recycled hydrogen from the hydrogen recovery by four-bed PSA system is added to intermediate-pressure synthesis gas before the second-section of synthesis gas compression.

The intermediate-pressure synthesis gas mixed with the recycled hydrogen in the gases mixer (CO-MIX-1) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) flow enters the compressor by the inlet guide (CO-COM-4) to distribute the flow providing a uniform condition in the first-stage impeller (CO-COM-4), the synthesis gas is compressed by the first-stage impeller (CO-COM-4) to an optimized pressure ratio considering 83.0% isentropic efficiency (isentropic compression) modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor.

The synthesis gas after the first-stage of compression (CO-COM-4) ducted-leaving is cooled to 30.0ºC by the water inter-cooler exchanger (CO-3) modeled by using a MHeatX exchanger block (CO-3) condensed phase content water and dissolved gases if formed is removed in the condenser knock-out drum (CO-FLA-5) modeled by using a Flash2 separator block (CO-FLA-5) and sent to atmospheric condensate buffer/equalizer tank (CO-FLA-7) modeled by using a Flash2 separator block (CO-FLA-7) at ambient conditions.

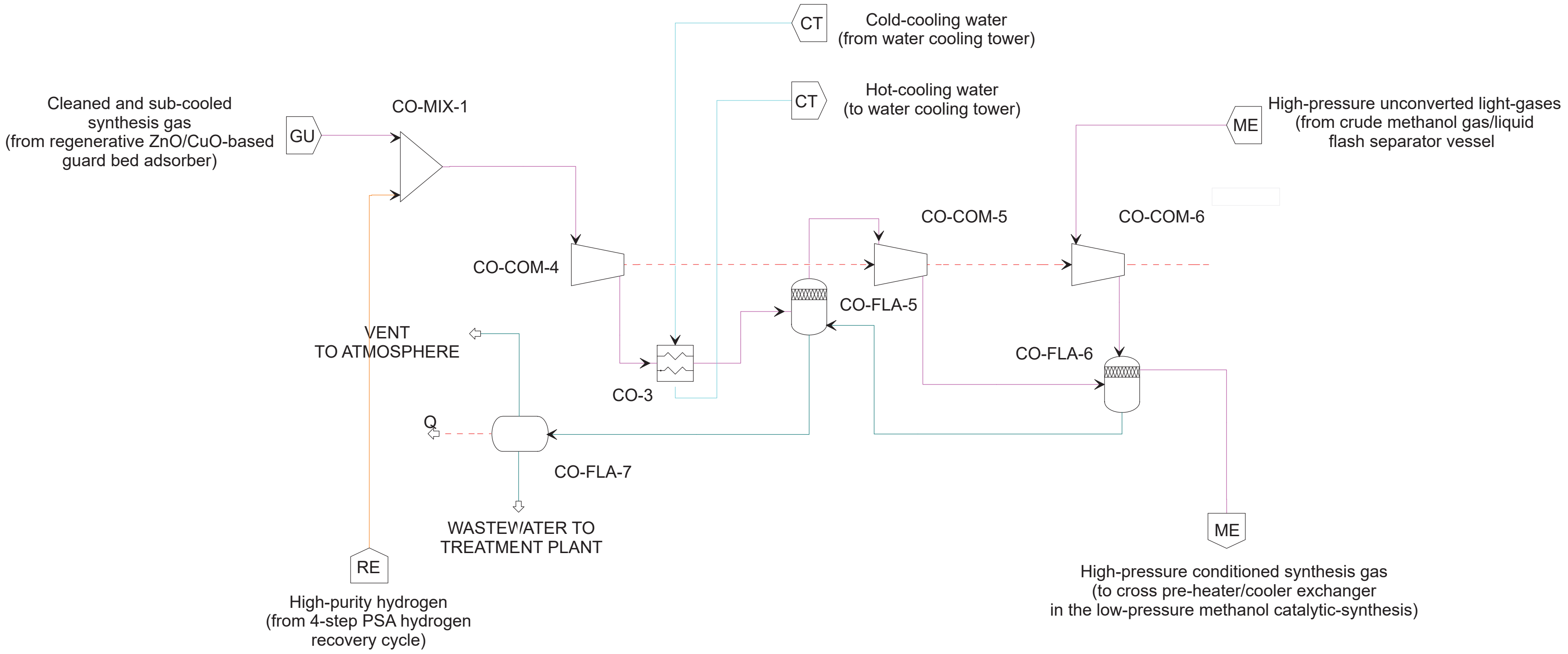


Figure 74 - Aspen Plus® v8.4 flowsheet of the second-section of synthesis gas compression (conditioning) by integrally-geared centrifugal three stages compressor for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3)

As shown in Figure 74 the Aspen Plus®v8.4 flowsheet of the second-section of synthesis gas compression (conditioning) for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) is compost by: integrally-geared centrifugal three stages compressor (CO-COM-4~6) when the third stage is the integrated recycle compressor (CO-COM-6), water inter-cooler exchanger (CO-3), gases mixer (CO-MIX-1), condenser knock-out drum (CO-FLA-5), condenser knock-out drum (CO-FLA-6), direct drive permanent magnet motor (not included as block) and atmospheric condensate buffer/equalizer tank (CO-FLA-7).

After the regenerative ZnO/CuO-based guard bed adsorber system the intermediate-pressure synthesis gas mixed with the recycled unconverted light-gas flow enters the compressor by the inlet guide (CO-COM-4) to distribute the flow providing a uniform condition in the first-stage impeller (CO-COM-4). The synthesis gas is compressed to an optimized pressure ratio (CA-CO-TR-1) by the first-stage impeller (CO-COM-4) modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 83.0% isentropic efficiency (isentropic compression).

The synthesis gas after the first-stage of compression (CO-COM-4) ducted-leaving is cooled to 30.0ºC by the water inter-cooler exchanger (CO-3) modeled by MHeatX exchangers blocks. Condensed phase content water and dissolved gases if formed is removed in the condenser knock-out drum (CO-FLA-5) modeled by using a Flash2 separator block and sent to atmospheric condensate buffer/equalizer tank (CO-FLA-7) modeled by using a Flash2 separator block at ambient conditions.

The synthesis gas free of the condensate phase enters in the second-stage impeller (CO-COM-5) and is compressed to an optimized pressure ratio (CA-CO-TR-1) modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 83.0% isentropic efficiency (isentropic compression). The synthesis gas after the second-stage of compression (CO-COM-5) ducted-leaving is not cooled by after-cooler and is ducted directly to buffer/equalizer tank (CO-FLA-6) or condenser knock-out drum (CO-FLA-6) modeled by using a Flash2 separator block.

Not cooled synthesis gas is compressed by the high-efficiency turbo booster compressor (CO-COM-6) resulting in outlet synthesis gas at high-temperature (within the range allowed) after compression. The heat exchanged between the crude high-temperature gaseous product formed and the synthesis gas is reduced increasing the amount of heat available to generate process steam (thermal energy supply) at the cost of increasing the consumption of electric power energy in the high-efficiency turbo booster (CO-COM-6 and LG-EXP-3). The energy required is supplied without additional cost by the expansion of the high-pressure unconverted light-gas from about 46.0 bar to 25.0 bar (intermediate-pressure) in the high-efficiency turbo booster expander (LG-EXP-3).

After the high-efficiency turbo booster compressor (CO-COM-6) the unconverted synthesis gas (light-gas) at about 51.0 bar is directly feed without cooling-step to buffer/equalizer tank (CO-FLA-6) modeled by using a Flash2 separator block.

The compression stage of the high-efficiency turbo booster (CO-COM-6) is modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 90.0% isentropic efficiency. The high-efficiency turbo booster (CO-COM-6 and LG-EXP-3) is detailed in the section 7.2.19 (Energy-saving integrated turbo compressor & expander (turbo booster)).

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-6) to the inter-cooler exchanger (CO-3). The amount of cooling water required is determined and controlled by design specification DS-CO-TL-3 varying the cooling water mass flow rate through the water inter-cooler exchanger (CO-1). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system. The lubricating oil circuit and the lubricating water-cooling system are suppressed from the Aspen Plus®v8.4 process model simulations in this research Master`s degree.

The ambient equalized condensate (CO-FLA-7) if formed is after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

The compression process is optimized by FORTRAN calculator block CA-CO-TR-1 varying the pressure ratio of the compression stages (CO-COM blocks) coupled with the maximum of energy recovered by the high-efficiency turbo booster expander (LG-EXP-3). The integrally-geared centrifugal two stages compressor (CO-COM blocks) is driver by a synchronous direct drive permanent magnet motor modeled by CO-E-7 work stream. The electric power energy consumed by the integrally-geared centrifugal two stages compressor (CO-COM blocks) is optimize-minimized by FORTRAN calculator block CA-CO-TR-1 varying the pressure ratio of the compression stages coupled with the maximum of expansion work-energy recovered by the high-efficiency turbo booster expander (LG-EXP-3). The electrical potential losses by attrite in the mechanical move parts was considered as 1.0% of the mechanical energy required by the stage (99.0% mechanical efficiency).

The unconverted light-gas recycled back to low-pressure methanol catalytic-synthesis enters in the third-stage impeller (CO-COM-6) and is compressed to the conditioned synthesis gas at required pressure by the downdraft equipment, the low-pressure methanol catalytic-synthesis (ME blocks) require in this case a pressure at about 51.0 bar as inlet pressure in the gas-cooled fixed bed catalytic-synthesis reactor (ME-REA-1), the third-stage impeller (CO-COM-6) considering 83.0% isentropic efficiency (isentropic compression) is modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor. The re-pressurized unconverted light-gas after the third-stage of compression (CO-COM-

6) ducted-leaving is not cooled by after-cooler being ducted directly to buffer/equalizer tank (CO-FLA-6) or condenser knock-out drum (CO-FLA-6) modeled by using a Flash2 separator block (CO-FLA-6) and mixed with the conditioned synthesis gas from the second-stage of compression. Condensed phase content water and dissolved gases if formed is removed in the condenser knock-out drum (CO-FLA-6) modeled by using a Flash2 separator block (CO-FLA-6) and sent to atmospheric condensate buffer/equalizer tank (CO-FLA-7).

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-6) to the inter-cooler exchanger (CO-3), the quantity of cooling water required is controlled by design specification DS-CO-TL-3 varying the cooling water mass flow rate through the water inter-cooler exchanger (CO-1) to leaving at 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system. The lubricating oil circuit and the lubricating water-cooling system are suppressed from the Aspen Plus®v8.4 process model simulations in this research Master`s degree.

The ambient equalized condensate (CO-FLA-7) if formed is after-pumped to the water treatment plant (WASTEWATER TO TREATMENT PLANT) to treatment for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

The integrally-geared centrifugal three stages compressor (CO-COM blocks) is driver by a synchronous direct drive permanent magnet motor modeled by CO-E-8 work stream and optimized to obtain the same compression ratio to compress the intermediate-pressure synthesis gas and the unconverted light-gas at about 51.0 bar by design specification DS-CO-TR-1 and FORTRAN calculator block CA-CO-TR-2 varying the pressure ratio in the three compression stages (CO-COM blocks). The electrical potential losses by attrite in the mechanical move parts was considered as 1.0% of the mechanical energy required by the stage (99.0% mechanical efficiency).

7.2.17 Hydrogen separation by four-bed pressure swing adsorption (PSA) system

The Aspen Plus®v8.4 process model simulation of the four-bed PSA system (RE blocks) consider a short-cycles system based on a physical binding of gas molecules to selective adsorbent material layers, working at constant temperature (ambient temperature). The system use the effect of alternating pressure and partial pressure to perform the adsorption and desorption cycle-times (phases), carried out at intermediate-pressure and four basic process steps (adsorption, depressurization, regeneration and re-pressurization) in continuous closed-loop cycle phases (8 time-cycle steps).

The Aspen Plus®v8.4 process model simulation of the hydrogen separation by four-bed PSA system was developed in steady-state mode using RKS-BM physical property methods in a simplified model applying Sep separator blocks to represent the pressure swing adsorption cycle and obtain the mass balance estimation for the high-purity hydrogen recovery system without the influence of the cycle-time, normally a short cycle-time lasts about 650 seconds.

Figure 75 shows the Aspen Plus®v8.4 flowsheet of the hydrogen separation by four-bed PSA system for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3).

The fraction of unconverted light-gas, that is not recycled back to low-pressure methanol catalytic-synthesis (ME-SPL2 and PU-FLA-1), enter in the light-gas condenser knock-out drum (RE-FLA-1) modeled by using a Flash2 separator block. The condensed phase formed content water and dissolved gases is removed and sent to condensate mixer (RE-MIX-1) to be after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

The intermediate-pressure light-gas then enter (RE-FLA-1) guided by inlet multi-way valve skids (RE-V-1, RE-V-2 and RE-V-3) in the pressure swing adsorption cycle compost by four basic process steps: adsorption; depressurization; regeneration; re-pressurization. First flows through the adsorber vessels (first vessel) in an upward direction.

Impurities such as H_2O, heavy hydrocarbons, light hydrocarbons, aromatic compounds, nitrogen compounds, CO_2, CO, CH_4 and H_2S are selectively adsorbed on the surface of the adsorbent. After the adsorption cycle-time this vessel (first vessel) stops and the new adsorption cycle-time is initiated in other conditioned vessel (second vessel) in closed-loop cycle.

The regeneration phase starts after the adsorption cycle-time depressurizing the vessel (first vessel) in counter-current. On depressurizing cycle-time the gases content in the vessel is transferred and used to pressurize other vessel (fourth vessel) after regenerated, closing the cycle.

The desorbed impurities leave at the bottom of the vessel (third vessel) flowing guided by outlet multi-way valve skids (RE-V-4, RE-V-5 and RE-V-6) to the off-gas system (RE-FLA-2).

Spreadsheet calculation model is used to determine the amount of specific Zeolite's catalyst, activated charcoal catalyst and SiO_2/Al_2O_3 catalyst must be loaded into adsorber vessels (RE-ADS-1~4) to adsorbing the impurities according to characteristically adsorption-saturation limits on the individually selected adsorbent materials.

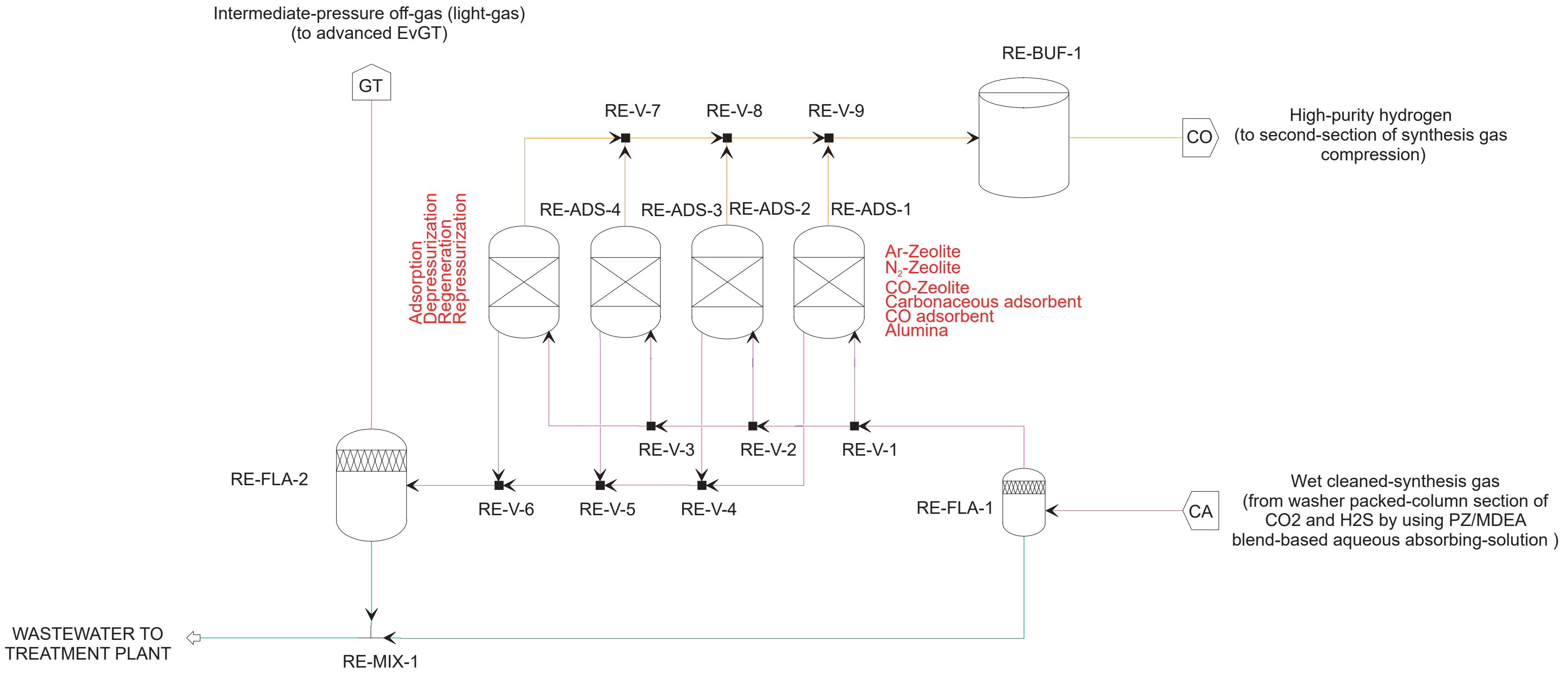


Figure 75 - Aspen Plus® v8.4 flowsheet of the hydrogen separation by four-bed PSA system for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3)

As shown in Figure 75, Aspen Plus®v8.4 flowsheet of the hydrogen separation by four-bed PSA system for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3) is compost by: adsorber vessel 1 (RE-ADS-1); adsorber vessel 2 (RE-ADS-2); adsorber vessel 3 (RE-ADS-3); adsorber vessel 4 (RE-ADS-4); inlet multi-way valve skids (RE-V-1; RE-V-2 and RE-V-3); outlet multi-way valve skids (RE-V-4; RE-V-5; RE-V-6; RE-V-7; RE-V-8; and RE-V-9); light-gas condenser knock-out drum (RE-FLA-1); buffer/equalizer hydrogen tank (RE-BUF-1); off-gas condenser knock-out drum (RE-FLA-2) and condensate mixer (RE-MIX-1).

High-purity hydrogen exits at the top of the adsorber vessel 1 (RE-ADS-1) guided by outlet multi-way valve skids (RE-V-7, RE-V-8, and RE-V-9) to the buffer/equalizer hydrogen tank (RE-BUF-1). The recovered hydrogen is used in the PSA internal-cycle and supplied back to integrally-geared centrifugal three stages compressor (CO-COM blocks) and then to the low-pressure methanol catalytic-synthesis to adjust-maintenance the ratio of hydrogen to carbon oxides - (H_2-CO_2)/(CO+CO_2) ratio – reducing the fraction of CO converted in the catalyst WGS reactors, that are also used to adjust the ratio in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3).

Intermediate-pressure off-gas (light-gas) from the PSA hydrogen separation cycle (RE-ADS blocks) enter in off-gas condenser knock-out drum (RE-FLA-2) modeled by using a Flash2 separator block. The condensed phase formed content water and dissolved gases is removed and sent to condensate mixer (RE-MIX-1) to be after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

Off-gas or light-gas after the off-gas condenser knock-out drum (RE-FLA-2) is sent to the gases mixer (GT-MIX-1) to be used as fuel-gas in the high-performance sequential combustion full-flow advanced EvGT (GT blocks). The light-gas stream-line is mixed (RE-MIX-1) together the tail-gas and a fraction of the crude intermediate-pressure synthesis gas.

Spreadsheet calculation model of the adsorber vessel's bed consider the adsorbent bed material's compost by 60.0%$_{w/w}$ of Zeolite's catalyst layers, 35.0%$_{w/w}$ of activated charcoal catalyst layer and 5.0%$_{w/w}$ of SiO_2/Al_2O_3 catalyst layer. The order of layers is defined from the bottom of the bed (raw light-gas entrance) by first layer content SiO_2/Al_2O_3 catalyst, second layer content activated charcoal catalyst and a third layer content the Zeolite's catalyst family subdivided in layers content 5A Zeolite catalyst, CaX Zeolite catalyst, VSA6 Zeolite catalyst and 13X Zeolite catalyst. The Zeolite family layer is considered in the spreadsheet calculation model as single layer containing Zeolite catalyst type.

Zeolite's catalyst layers in the adsorber vessels (RE-ADS-1~4) are considered as commercial type 5A Zeolite catalyst and CaX Zeolite catalyst selective for N_2 and NO_x (e.g.: NO_2, N_2O and NO), VSA6 Zeolite catalyst selective for carbonaceous (e.g.: CO, CO_2 and CH_4) and 13X Zeolite catalyst selective for CO_2, H_2S and aromatic compounds. Zeolite's catalyst, weight loaded considering the capacity limits of 20.0%$_{w/w}$ to adsorbing H_2O, 80.0%$_{w/w}$ to adsorbing H_2S and 60.0%$_{w/w}$ to adsorbing carbonaceous compounds content in the light-gas. Zeolite's catalyst lifetime is expected to be about 2 years before the necessity of deactivated catalyst being partial or full discharged and new activity catalyst loaded, deactivated catalyst is sent to be regenerated and/or to final disposal.

SiO_2/Al_2O_3 catalyst layer in the adsorber vessels (RE-ADS-1~4) is considered as commercial type selective for H_2O and carbonaceous (e.g.: CO, CO_2). SiO_2/Al_2O_3 catalyst, weight loaded considering the capacity limits of 50.0%$_{w/w}$ to adsorbing H_20 and 5.0%$_{w/w}$ to adsorbing carbonaceous compounds content in the light-gas. Catalyst lifetime is expected to be about 1 year before the necessity of deactivated catalyst being partial or full discharged and new activity catalyst loaded, deactivated catalyst is sent to be regenerated and/or to final disposal.

Activated charcoal catalyst layer in the adsorber vessels (RE-ADS-1~4) is considered as commercial type selective for H_2O and carbonaceous (e.g.: CO, CO_2, CH_4 and light hydrocarbons) weight loaded considering the capacity limits of 30.0%$_{w/w}$ to adsorbing H_20 20.0%$_{w/w}$ to adsorbing H_2S, and 35.0%$_{w/w}$ to adsorbing carbonaceous compounds content in the light-gas. Catalyst lifetime is expected to be about 1 year before the necessity of deactivated catalyst being partial or full discharged and new activity catalyst loaded, deactivated catalyst is sent to be regenerated and/or to final disposal.

7.2.18 Low-pressure methanol catalytic-synthesis

The Aspen Plus®v8.4 process model simulation of the low-pressure methanol catalytic-synthesis is based on the quasi-isothermal Lurgi MegaMethanol® two-step synthesis process (methanol synthesis in water-cooled reactor combined with gas-cooled reactor) and high-active commercial $CuO/ZnO/Al_2O_3$ catalysts for low-temperature methanol catalyst-synthesis (advanced catalyst).

In this process concept the synthesis gas is first used as cooling agent on the tube side of the gas-cooled reactor (first reactor) combined in series with a water-cooled reactor (second reactor), when the preheated gas is converted under near-isothermal conditions, while the heat of reaction is utilized for the production of satured steam.

The Aspen Plus®v8.4 process model simulation of the low-pressure methanol catalytic-synthesis for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) is based on the Chemical equation c.27 (CO hydrogenation), Chemical equation c.28 (CO_2 hydrogenation) and Chemical equation c.8 for WGS reaction applying the Graaf, Stamhuis and Beenackers (1988) kinetic model according to section 4.1.19 (Low-pressure methanol catalytic-synthesis).

To simulate the low-pressure methanol catalytic-synthesis reactor in steady state operation mode was considered the plug flow type-reactor (RPlug) in the Aspen Plus®v8.4 process model simulation applying the rigorously RPlug models based on kinetic reactions applying the Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic expression for methanol synthesis according to section 4.1.19 (Low-pressure methanol catalytic-synthesis).

Figure 76 shows the Aspen Plus®v8.4 flowsheet of the low-pressure methanol catalytic-synthesis for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3).

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), the high-pressure unconverted synthesis gas (light-gas) after the high-efficiency turbo booster compressor (CO-COM-6) is feed-mixed with conditioned synthesis gas in the buffer/equalizer tank (CO-FLA-6) and recycled back to low-pressure methanol catalytic-synthesis.

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), high-purity hydrogen from the buffer/equalizer hydrogen tank (RE-BUF-1) is recycled back and mixed with the intermediate-pressure synthesis gas in the gases mixer (CO-MIX-1) to adjust-maintenance the ratio of hydrogen to carbon oxides - $(H_2\text{-}CO_2)/(CO+CO_2)$ ratio.

The Aspen Plus®v8.4 process model simulation of the low-pressure methanol catalytic-synthesis for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) consider the stoichiometric number (S_1) of the synthesis gas inlet the gas-cooled fixed bed catalytic-synthesis reactor (ME-REA-1) equal to 2.0 (Equation 19) as described in the section 3.9.16 (Hydrogen to carbon ratios) according to 4.1.19 (Low-pressure methanol catalytic-synthesis).

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), conditioned synthesis gas at 51.0 bar and low-temperature is heated in the cross pre-heater/cooler exchanger (ME-1) to 130.0ºC before enters the gas-cooled fixed bed catalytic-synthesis reactor (ME-REA-1) by the high-temperature and high-pressure crude gas product from the gas-cooled fixed bed catalytic-synthesis reactor (ME-REA-1). In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), high-temperature and high-pressure crude gas product at 180.0ºC and about 47.0 bar is cooled by the conditioned synthesis gas in the cross pre-heater/cooler exchanger (ME-1) to intermediate-temperature.

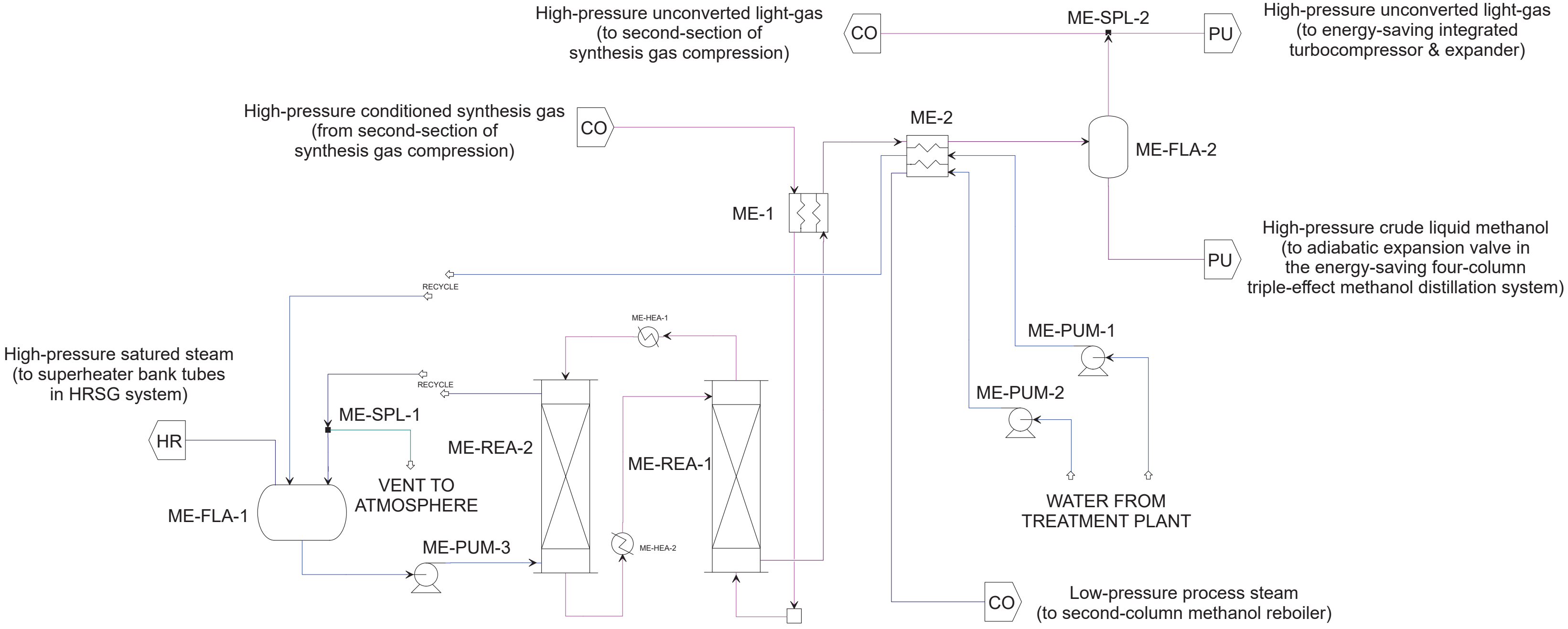


Figure 76 - Aspen Plus® v8.4 flowsheet of the low-pressure methanol catalytic-synthesis by combining gas-cooled fixed bed catalytic-synthesis reactor with isothermal water-cooled fixed bed catalytic-synthesis reactor for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3)

As shown in Figure 76, Aspen Plus®v8.4 flowsheet of the low-pressure methanol catalytic-synthesis for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3) is compost by: gas-cooled fixed bed catalytic-synthesis reactor (ME-REA-1); isothermal water-cooled fixed bed catalytic-synthesis reactor (ME-REA-2); high-pressure steam drum (ME-FLA-1); steam drum vent valve (ME-SPL-1); steam drum water circulation pump (ME-PUM-3); cross pre-heater/cooler exchanger (ME-1); low-temperature water cooler (ME-2); make-up water pump (ME-PUM-1); water circulation pump (ME-PUM-2); high-pressure gas/liquid flash phase separator vessel (ME-FLA-2); recycle splitter (ME-SPL-2); adiabatic expansion valve 1 (PU-VAL-1); adiabatic expansion valve 2 (PU-VAL-2); and crude methanol gas/liquid flash separator vessel (PU-FLA-1).

The Aspen Plus®v8.4 process model simulation of the low-pressure methanol catalytic-synthesis was developed using RKS-BM physical property methods for the gas side-streams and IAPWS-95 physical property methods for the steam/water side-streams (exchangers).

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), conditioned synthesis gas at 51.0 bar and 130.0ºC enters the first reactor, gas-cooled fixed bed catalytic-synthesis reactor (ME-REA-1), a fraction of the gases reacts in the low-activity $CuO/ZnO/Al_2O_3$ catalyst-bed to form methanol according to modified Graaf, Stamhuis and Beenackers (1988) kinetic model (for low-activity catalysts).

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), the high-pressure gas product at about 47.0 bar and 265.0ºC from the second reactor, isothermal water-cooled fixed bed catalytic-synthesis reactor (ME-REA-2), is used as cooling agent on the tube side of the gas-cooled fixed bed catalytic-synthesis reactor (ME-REA-1), being cooled to 180.0ºC and after sent to the cross pre-heater/cooler exchanger (ME-1). In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), the heat of the methanol synthesis reactions (exothermic reactions) in the gas-cooled fixed bed catalytic-synthesis reactor (ME-REA-1) and the heat changed between the reactor media and the high pressure gas product (cooling agent) that comes from the isothermal water-cooled fixed bed catalytic-synthesis reactor (ME-REA-2) increase the temperature of the conditioned synthesis gas (partial reacted) before the isothermal water-cooled fixed bed catalytic-synthesis reactor (ME-REA-2) to about 210.0ºC at 50.0 bar.

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), partial reacted and heated synthesis gas enter the second reactor, isothermal water-cooled fixed bed catalytic-synthesis reactor (ME-REA-2), a major fraction of the gases reacts in the in the high-activity $CuO/ZnO/Al_2O_3$ catalyst-bed to form methanol according to modified Graaf, Stamhuis and Beenackers (1988) kinetic model (for high-activity catalysts).

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), high-pressure saturated water from the high-pressure steam drum (ME-FLA-1) is used to control the temperature of the isothermal water-cooled fixed bed catalytic-synthesis reactor (ME-REA-2) at 265.0ºC. The high-pressure saturated water is pumped from the high-pressure steam drum (ME-FLA-1) by the steam drum water circulation pump (ME-PUM-3) at 47.0 bar and 258.0ºC passing through the tube side of the isothermal water-cooled fixed bed catalytic-synthesis reactor (ME-REA-2) removing the heat released by the methanol synthesis reactions (exothermic reactions) generating high-pressure satured steam at about same conditions 46.0 bar and 258.0ºC. In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), the high-pressure satured steam is send back to the high-pressure steam drum (ME-FLA-1) maintaining the temperature and pressure of the drum (ME-FLA-1), a fraction of 2.0% of the steam generated is considered as losses, being vented to atmosphere (TO ATMOSPHERE) by the steam drum vent valve (ME-SPL-1).

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), the high-pressure satured steam at 46.0 bar and 258.0ºC generated in the high-pressure steam drum (ME-FLA-1) is sent to the horizontal gas-flow drum type HRSG system (HR blocks) to be mixed in the high-pressure steam mixer (HR-MIX-1 or HR-MIX-2) with the steam vaporized by the HP vaporizer bank tubes (HR-HPV-1). After the mixer, high-pressure saturated steam at about 45.0 bar and 257.0ºC is superheated to 420.0ºC in the HP superheater bank tubes (HR-HPS-1) and sent to the ST to generate electricity in the high-pressure expansion stage (ST blocks).

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), the high-pressure crude gas product at intermediate-temperature after the cross pre-heater/cooler exchanger (ME-1) is cooled to 50.0ºC at 45.5 bar in the low-temperature water cooler (ME-2) by the low-temperature and low-pressure water-circuit and by the low-temperature high-pressure water-circuit. In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), the heat recovered is used to generate pre-heated make-up water to high-pressure steam drum (ME-FLA-1) and low-pressure process steam at 2.5 bar and 130.0ºC to supply all of the thermal energy required by the energy-saving four-column triple-effect methanol distillation system (PU blocks).

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), make-up water (WATER FROM TREATMENT PLANT) is pumped to 46.0 bar by the make-up water pump (ME-PUM-1) passing thought the low-temperature water cooler (ME-2) before enter the high-pressure steam drum (ME-FLA-1) as pre-heated high-pressure make-up water. The amount of make-up water used to cool down the crude gas product at intermediate-temperature from cross pre-heater/cooler exchanger (ME-1) in the low-temperature water cooler (ME-2) is determined and controlled varying the mass flow rate of water passing through the low-temperature water cooler (ME-2) limited by the high-pressure crude gas product temperature of 50.0ºC needed before the high-pressure gas/liquid flash phase separator vessel (ME-FLA-2), by the mass flow rate of water required in the high-pressure steam drum (ME-FLA-1) as make-up, and by the energy balance which define the inlet temperature of the make-up water in the high-pressure steam drum (ME-FLA-1) that is pre-heated in the low-temperature water cooler (ME-2).

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), The amount of low-pressure process steam at 2.5 bar and 130.0ºC generated in the low-temperature water cooler (ME-2) is determined and controlled by design specification DS-PU-FL-2 varying the mass flow rate of deaerated water passing through the low-temperature water cooler (ME-2) that is required to generate steam to supply all of the thermal energy required by the energy-saving four-column triple-effect methanol distillation system (PU blocks).

The low-temperature and high-pressure crude gas product at 45.5 bar and 50.0ºC forming two phases, the liquid phase and gaseous phases is separated in the high-pressure gas/liquid flash phase separator vessel (ME-FLA-2).

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), the gaseous phase, high-pressure unconverted light-gas (unconverted synthesis gas) at about 45.5 bar and 50.0ºC from the high-pressure gas/liquid flash phase separator vessel (ME-FLA-2) is splitted in the recycle splitter (ME-SPL-2), being one fraction recycled back to the low-pressure methanol catalytic-synthesis (feed-mixed with conditioned synthesis gas) passing before thought the high-efficiency turbo booster compressor (CO-COM-6) to adjust the pressure (pressure drop), an another fraction considered as purge-gas used in the high-efficiency turbo booster centrifugal expander (PU-EXP-1) in order to produce the work power (PU-E-1) required to compress the tail-gas in the high-efficiency turbo booster centrifugal compressor (PU-COM-1) and after used to obtain the hydrogen required to adjust the - $(H_2-CO_2)/(CO+CO_2)$ ratio - passing thought the four-bed PSA system (RE blocks).

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), the liquid phase, high-pressure crude liquid methanol at about 45.5 bar and 50.0ºC from the high-pressure gas/liquid flash phase separator vessel (ME-FLA-2) is sent to the crude methanol gas/liquid flash separator vessel (PU-FLA-1) in the energy-saving integrated turbo compressor & expander (turbo booster) removing dissolved gases at intermediate-pressure before the enters in the energy-saving four-column triple-effect methanol distillation system (methanol purification).

Spreadsheet calculation models are used to determine the quantity of $CuO/ZnO/Al_2O_3$ catalysts must be loaded into gas-cooled fixed bed catalytic-synthesis reactor (ME-REA-1) and isothermal water-cooled fixed bed catalytic-synthesis reactor (ME-REA-2). The catalyst of the gas-cooled fixed bed catalytic-synthesis reactor (ME-REA-1) can be the partial used catalyst discharged (low-activity) from the water-cooled fixed bed catalytic-synthesis reactor (ME-REA-2).

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3), the $CuO/ZnO/Al_2O_3$ catalyst considered in the gas-cooled fixed bed catalytic-synthesis reactor (ME-REA-1) and isothermal water-cooled fixed bed catalytic-synthesis reactor (ME-REA-2) is a commercial type high activity catalyst considering content 62.0%$_{w/w}$ of CuO, 30.0%$_{w/w}$ of ZnO and 8.0%$_{w/w}$ of Al_2O_3. The $CuO/ZnO/Al_2O_3$ catalyst is weight loaded considering the productivity of 200 g of crude methanol per kg of catalyst per hour (STY). $CuO/ZnO/Al_2O_3$ catalyst lifetime is expected to be about 4 years before the necessity of deactivated catalyst be partial or full discharged and new activity catalyst be loaded, deactivated catalyst is send to be regenerated and/or to final disposal.

7.2.19 Energy-saving integrated turbo compressor & expander (turbo booster)

Part of the unconverted light-gas leaving on the top of the high-pressure gas/liquid flash phase separator vessel (LG-FLA-1) at about 45.5 bar and 50.0ºC is splitted in the recycle splitter (ME-SPL-2) and recycled back to low-pressure methanol catalytic-synthesis (ME blocks). Another part of the unconverted light-gas at about 45.5 bar and 50.0ºC can be expanded to intermediate pressure level providing useful work-energy before being sent to hydrogen recovery by four-bed PSA system (RE blocks) and then to high-performance sequential combustion full-flow advanced EvGT (GT blocks).

The expansion work-energy is used to compress the tail-gas from the crude methanol forerun degassing first tray-column (PU-COL-1) from low-pressure level to intermediate-pressure level by using a high-efficiency turbo booster centrifugal compressor (PU-COM-1). The compressed tail-gas is mixed with the off-gas from the hydrogen recovery by four-bed PSA system (RE blocks) and with the intermediate-pressure synthesis gas from the intermediate-pressure synthesis gas splitter (WS-SPL-1) and then used as fuel-gas in the high-performance sequential combustion full-flow advanced EvGT.

Aspen Plus$^{®}$v8.4 process model simulation of the energy-saving integrated turbo compressor & expander (turbo booster) was developed using RKS-BM physical property methods and NRTL-RK physical property methods (change point).

Figure 77 shows the Aspen Plus$^{®}$v8.4 flowsheet of the energy-saving integrated turbo compressor & expander (turbo booster) for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3).

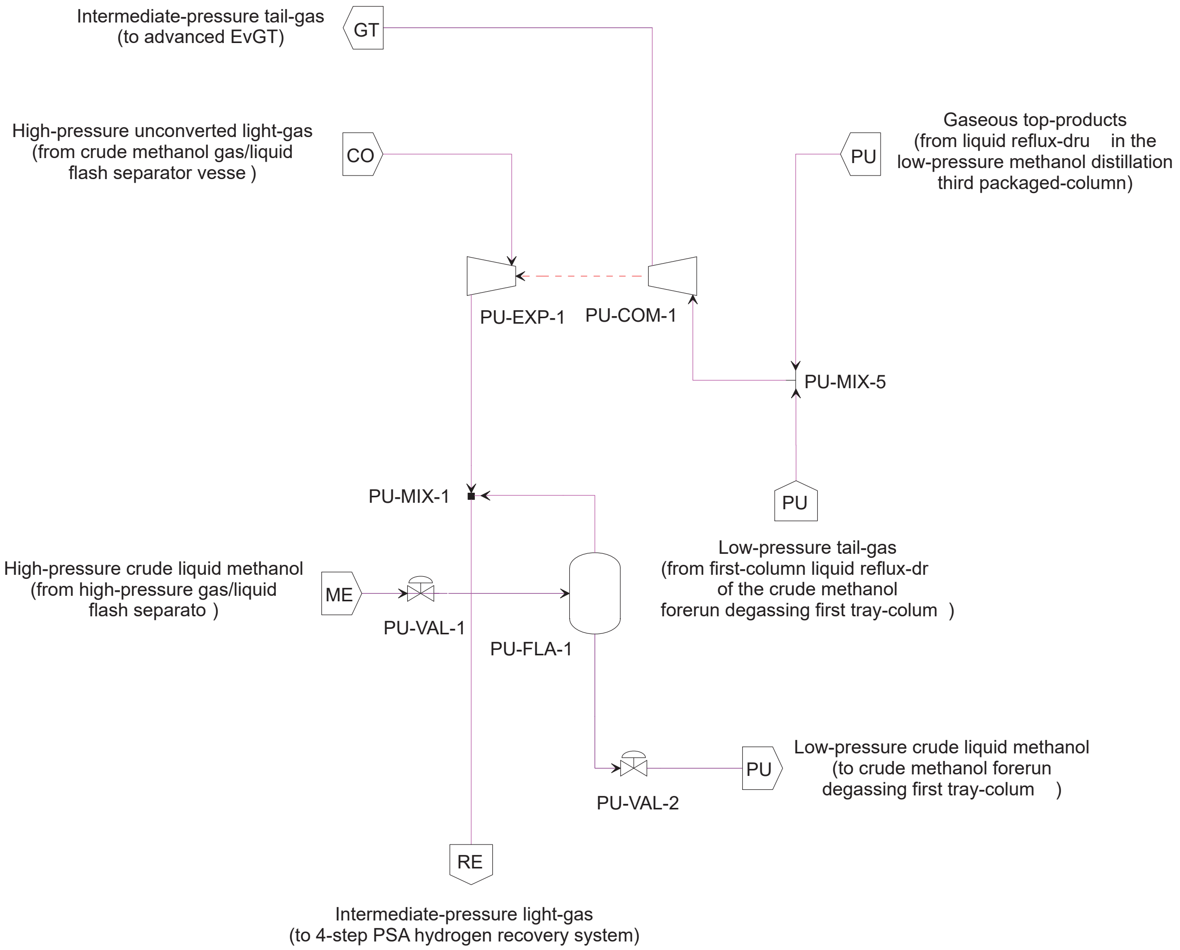


Figure 77 - Aspen Plus®v8.4 flowsheet of the energy-saving integrated turbo compressor & expander (turbo booster) for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3)

As shown in Figure 77, Aspen Plus®v8.4 flowsheet of the of the energy-saving integrated turbo compressor & expander (turbo booster) for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) is compost by: adiabatic expansion valve 1 (PU-VAL-1); adiabatic expansion valve 2 (PU-VAL-2); crude methanol gas/liquid flash separator vessel (PU-FLA-1); gases mixer (PU-MIX-1); light-gas recycle splitter (ME-SPL-2) and high-efficiency turbo booster (PU-COM-1 and PU-EXP-1) with centrifugal compressor (PU-COM-1); and expander (PU-EXP-1).

Aspen Plus®v8.4 process model simulation of the energy-saving integrated turbo compressor & expander (turbo booster) and the efficient use of the high-pressure unconverted light-gas consider optimized fractions of the light-gas splitted in the light-gas recycle splitter (ME-SPL-2) modeled by using a FSplit splitter block. An optimized fraction of the unconverted light-gas is recycled back to achieve a high overall conversion in the low-pressure methanol catalytic-synthesis (ME blocks). The required pressure level by the low-pressure methanol catalytic-synthesis (ME blocks) is adjusted by the integrated recycle compressor (CO-COM-6). Another optimized fraction of unconverted light-gas considered as purge-gas from the high-pressure gas/liquid flash phase separator vessel (ME-FLA-2) is used in the high-efficiency turbo booster centrifugal expander (PU-EXP-1) in order to produce the work power (PU-E-1) required to compress the tail-gas in the high-efficiency turbo booster centrifugal compressor (PU-COM-1) at pressure level of the high-performance sequential combustion full-flow advanced EvGT (GT blocks).

The high-pressure unconverted light-gas at 45.5 bar and 50.0ºC splitted in the light-gas recycle splitter (ME-SPL-2) is compressed to 51.0 bar and about 63.0ºC by the integrated recycle compressor (CO-COM-6) modeled by using a Compr pressure changer block as the third stage of synthesis gas compression according to rigorous ASME method for isentropic compressor considering 90.0% isentropic efficiency (isentropic compression). The high-pressure unconverted light-gas is mixed back to the synthesis gas main stream into the condenser knock-out drum (CO-FLA-6).

High-pressure crude liquid methanol at about 45.5 bar and 50.0ºC from the high-pressure gas/liquid flash phase separator vessel (ME-FLA-2) is expanded to 25.0 bar in the adiabatic expansion valve 1 (PU-VAL-1) modeled by using a Valve pressure changer block. The small fraction of gaseous phase formed in the expansion process is separated in the crude methanol gas/liquid flash separator vessel (PU-FLA-1).

The tail-gas at 1.2 bar and about 35.0ºC from the first-column liquid reflux-drum (PU-FLA-2) in the crude methanol forerun degassing first tray-column (PU-COL-1) is compressed to 23.5 bar and about 304.0ºC (single compression stage) by high-efficiency turbo booster centrifugal compressor (PU-COM-1) modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 90.0% isentropic efficiency (isentropic compression), allowing its use as fuel-gas in the high-performance sequential combustion full-flow advanced EvGT (GT blocks).

The fractions of the high-pressure unconverted light-gas at about 45.5 bar and 50.0ºC destined to low-pressure methanol catalytic-synthesis (ME blocks) and to the hydrogen recovery by four-bed PSA system (RE blocks) is optimized varying the split fraction configuration in the light-gas recycle splitter (ME-SPL-2) considering the expanded conditions of the light-gas and the work power required to compress the tail-gas at intermediate-pressure level closing the mass and energy balances.

After expanded to intermediate-pressure level in the adiabatic expansion valve 1 (PU-VAL-1) the unconverted light-gas from the crude methanol gas/liquid flash separator vessel (PU-FLA-1) is mixed in the gases mixer (PU-MIX-1) with the intermediate-pressure level unconverted light-gas obtained after expansion process in the high-efficiency turbo booster expander (PU-EXP-1). The resultant mix-stream is sent to hydrogen recovery by four-bed PSA system (RE blocks).

Intermediate-pressure crude liquid methanol from the crude methanol gas/liquid flash separator vessel (PU-FLA-1) is expanded in the adiabatic expansion valve 2 (PU-VAL-2) modeled by using a Valve pressure changer block to low-pressure level. The low-pressure methanol is then fed in the crude methanol forerun degassing first tray-column (PU-COL-1)

7.2.20 Energy-saving four-column triple-effect methanol distillation system (methanol purification)

The crude methanol obtained from the low-pressure methanol catalytic-synthesis is distillated in the four-column heat integrated distillation columns train in sequential multi-effect arrangement to obtain grade AA methanol.

The distillation is carried out by using a methanol forerun degassing tray-column (first column) at low-pressure level, an intermediate-pressure methanol distillation tray-column (second column), a low-pressure methanol distillation packaged-column (third-column) and a recovery methanol distillation packaged-column (fourth column).

Grade AA methanol is intended for use as bio-based liquid fuel being only required remove the non-condensable gases (e.g.: H_2, O_2, N_2, Ar, Xe, Kr, CO, CO_2, CH_4, light hydrocarbons, heavy hydrocarbons and the reminiscent impurities as COS, SO_X, NO_x, NH_3, H_2S, CHN and others) and H_2O from the obtained liquid Crude methanol.

The Aspen Plus®v8.4 process model simulation of the energy-saving four-column triple-effect methanol distillation system (methanol purification) was developed in steady-state mode using NRTL-RK physical property methods for the main processes (methanol content) and IAPWS-95 physical property methods for the steam/water side in the heater exchangers.

Figure 78 shows the Aspen Plus®v8.4 flowsheet of the energy-saving four-column triple-effect methanol distillation system (methanol purification) for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3).

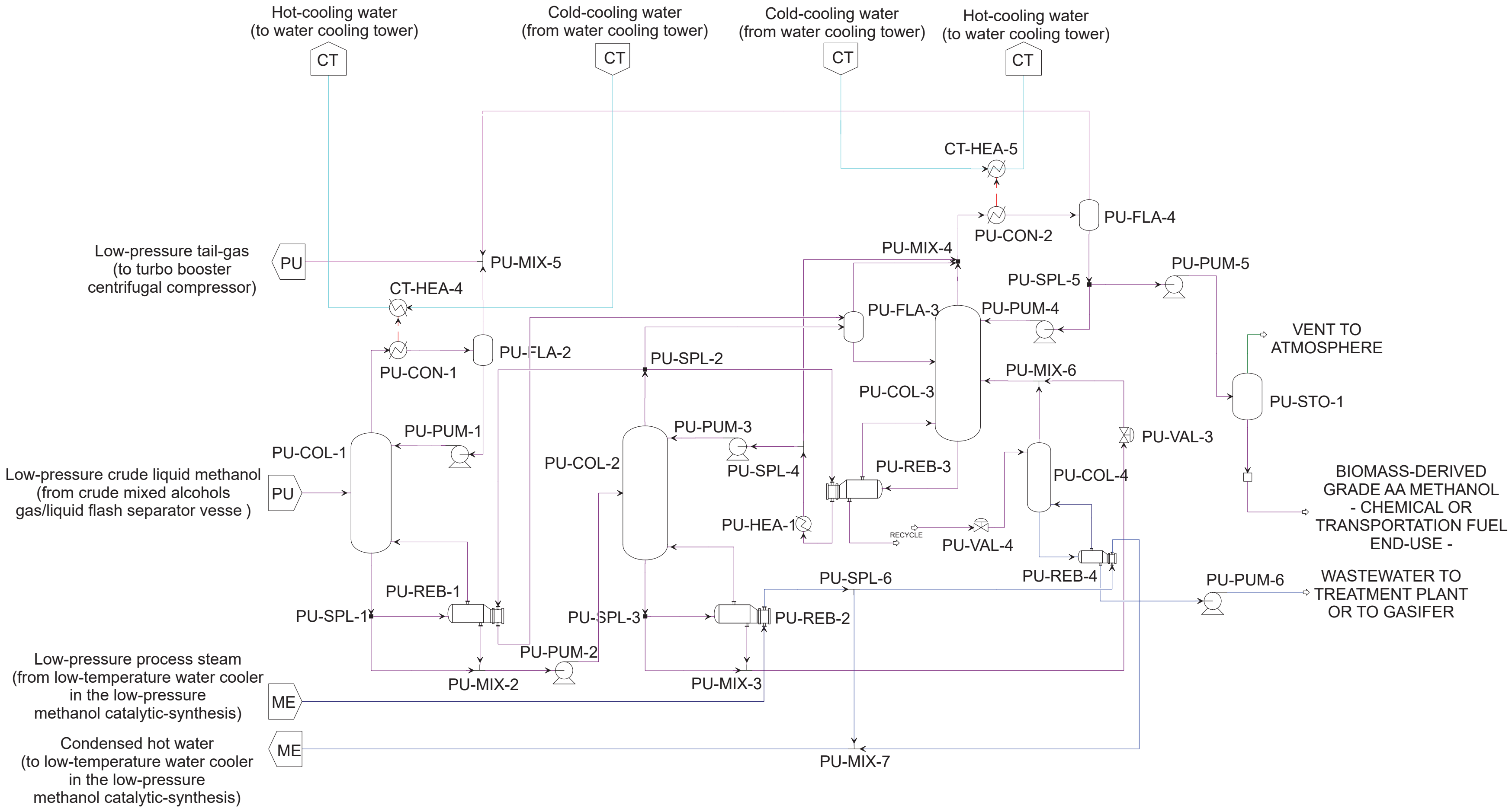


Figure 78 - Aspen Plus® v8.4 flowsheet of the energy-saving four-column triple-effect methanol distillation system (methanol purification) for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3)

As shown in Figure 78 the Aspen Plus®v8.4 flowsheet of the of the energy-saving four-column triple-effect methanol distillation system (methanol purification) for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) is compost by: intermediate-pressure methanol distillation second tray-column (PU-COL-2); low-pressure methanol distillation third packaged-column (PU-COL-3); recovery methanol distillation fourth packaged-column (PU-COL-4); crude methanol forerun degassing first tray-column (PU-COL-1); first-column reflux pump 1 (PU-PUM-1); second-column reflux pump 2 (PU-PUM-3); third-column reflux pump 3 (PU-PUM-4); crude methanol pump (PU-PUM-2); first-column partial condenser (PU-CON-1 and CT-HEA-4); third-column partial condenser (PU-CON-2 and CT-HEA-5); first-column liquid reflux-drum (PU-FLA-2); third-column liquid reflux-drum (PU-FLA-4); tail-gas mixer (PU-MIX-5); integrated first-column methanol distillation reboiler/condenser (PU-REB-1); second-column methanol reboiler (PU-REB-2); integrated third-column methanol reboiler/condenser (PU-REB-3); integrated fourth-column methanol distillation reboiler (PU-REB-4); crude methanol sump splitter (PU-SPL-1); crude methanol mixer (PU-MIX-2); gaseous methanol splitter (PU-SPL-2); methanol sump splitter (PU-SPL-3); methanol mixer 1 (PU-MIX-3); adiabatic expansion valve 1 (PU-VAL-3); adiabatic expansion valve 2 (PU-VAL-4); bottom product pump (PU-PUM-6); methanol storage tank (PU-STO-1); grade AA methanol pump (PU-PUM-5); liquid grade AA methanol splitter (PU-SPL-5); methanol mixer 2 (PU-MIX-6); methanol mixer 3 (PU-MIX-4); flash phase separator and pressure equalizer vessel (PU-FLA-3); liquid splitter (PU-SPL-4); condensate water mixer (PU-MIX-7); and condensate water splitter (PU-SPL-6).

Intermediate-pressure crude liquid methanol from the crude methanol gas/liquid flash separator vessel (PU-FLA-1) is expanded in the adiabatic expansion valve 2 (PU-VAL-2) modeled by using a Valve pressure changer block to 1.056 bar (tray-pressure) and at about 47.7ºC and then fed in the 6º theoretically stage of the crude methanol forerun degassing first tray-column (PU-COL-1).

Crude methanol forerun degassing first tray-column (PU-COL-1) remove the non-condensable gases (e.g.: H_2, O_2, N_2, Ar, Xe, Kr, CO, CO_2, CH_4, light hydrocarbons, heavy hydrocarbons and the reminiscent impurities as COS, SO_X, NO_x, NH_3, H_2S, CHN and others) content in the crude liquid methanol.

Rigorous Aspen Plus®v8.4 process model simulation of the crude methanol forerun degassing first tray-column (PU-COL-1) was developed using RadFrac column block on standard convergence mode without in-bed condenser and reboiler. The model was optimized for estimated 20 theoretical stages considering Bubble cap (Aspen90) tray section with one-pass per tray with cap diameter of 76.2 mm and standards panel A with weir height of 30.0 mm and tray diameter of 0.80 m. The model use rate-based calculation for mixed flow model without reactions and film resistance in vapor phase, without reactions and with film resistance in liquid phase, and employing vapor and liquid phase film non-ideality corrections. Default Aspen Plus®v8.4 tray parameters is applied to calculate interfacial area by AIChE (1958) method, to predict the mass transfer coefficient by Scheffe and Weiland (1987) method, and heat transfer coefficient by Chilton–Colburn (Taylor and Krishna, 1993) method.

The gaseous top-product at about 1.4 bar and 54.1ºC leave from the 1º theoretically vapor stage (top column stage) in the crude methanol forerun degassing first tray-column (PU-COL-1) is cooled in the first-column partial condenser (PU-CON-1) by water-cooling (PU-HEA-5) modeled by using a Heater exchanger block. The condensed phase formed at 1.2 bar and 35.0ºC is flash-separated in the first-column liquid reflux-drum (PU-FLA-2) modeled by using a Flash2 separator block form-condensing about 30.0%$_{w/w}$ (model result) of the gaseous top-product (condensate phase) in saturation equilibrium conditions.

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-7) to the first-column partial condenser (CT-HEA-4). The amount of cooling water required is determined and controlled by design specification DS-PU-FL-3 varying the mass flow rate of cooling water passing through the first-column partial condenser (CT-HEA-4). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

The condensed phase formed at 1.2 bar and 35.0ºC containing mainly CH_3OH and H_2O from the first-column liquid reflux-drum (PU-FLA-2) modeled by using a Flash2 separator block is pumped at 1.4 bar and 35.0ºC by the first-column reflux pump 1 (PU-PUM-1) and refluxed back to the 1º theoretically liquid stage (top column stage) in the crude methanol forerun degassing first tray-column (PU-COL-1).

About 70.0%$_{w/w}$ of gaseous top-product (non-condensed) containing mainly CO_2 (less than 10.0%$_{w/w}$ is combustible) leaving from the first-column liquid reflux-drum (PU-FLA-2) at 1.2 bar and 35.0ºC as tail-gas is sent to be compressed in the high-efficiency turbo booster centrifugal compressor (PU-COM-1) and after-fed as fuel-gas in the high-performance sequential combustion full-flow advanced EvGT (GT blocks).

The liquid bottom product containing degassed crude mixed alcohols at 1.8 bar and about 80.0ºC from the 20º theoretically liquid stage (bottom column stage) in the crude mixed alcohols forerun degassing first tray-column (PU-COL-1) is splitted in the crude methanol sump splitter (PU-SPL-1) in the integrated first-column methanol distillation reboiler/condenser (PU-REB-1).

The reboiler circulation baffle model was developed using HeatX exchanger block to generate liquid and vapor products in the cold side and by using a FSplit splitter block (PU-SPL-1) to drain part of the liquid bottom product (without heat). 12.0%$_{w/w}$ of the liquid phase from the crude methanol sump splitter (PU-SPL-1) is fed in the reboiler feed section and 88.0%$_{w/w}$ of the liquid phase from the crude methanol sump splitter (PU-SPL-1) is drained as overflow bottom liquid degassed crude product.

In the integrated first-column methanol distillation reboiler/condenser (PU-REB-1) section the bottom product from the sump is heated and vaporized considering 90.0%$_{w/w}$ of the liquid phase vaporized at 1.8 bar and 79.7ºC flowing upward back trough the tray-column (PU-COL-1). Another 10.0%$_{w/w}$ overflowing the baffle as heated bottom liquid degassed crude product. The amount of bottom product vaporized in the distillation first-column reboiler (PU-REB-1) is determined according the gaseous content in the bottom liquid degassed crude product and the entrained liquid phase (alcohols) formed in the first-column liquid reflux-drum (PU-FLA-2).

The thermal energy required to heat and vaporize the bottom liquid product in the integrated first-column methanol distillation reboiler/condenser (PU-REB-1) is supplied by the gaseous top-product (purified methanol) at 6.5 bar and 119.3ºC from the intermediate-pressure methanol distillation second tray-column (PU-COL-2) which is condensed passing the integrated first-column methanol distillation reboiler/condenser (PU-REB-1) to 6.2 bar and 117.5ºC (vapor fraction of 0.0).

The fraction-amount of gaseous top-product at 6.5 bar and 119.3ºC obtained from the top of the intermediate-pressure methanol distillation second tray-column (PU-COL-2) destined to the integrated first-column methanol distillation reboiler/condenser (PU-REB-1) is determined by thermal requirements and exchanger temperature limits (cross-over avoided) and controlled by design specification DS-PU-TG-1 varying the mass flow rate of the gaseous top-product circulating through the reboiler exchanger cycle (heat and cool down cycle) in closed-cycle mode.

Bottom liquid degassed crude product from the crude methanol mixer (PU-MIX-2) is pumped by the crude methanol pump (PU-PUM-2) to 6.6 bar (tray-pressure) and about 80.0ºC and then fed in the 10º theoretically liquid stage of the intermediate-pressure methanol distillation second tray-column (PU-COL-2) to be purified.

Rigorous Aspen Plus®v8.4 process model simulation of the intermediate-pressure methanol distillation second tray-column (PU-COL-2) was developed using RadFrac column block on standard convergence mode without in-bed condenser and reboiler. The model was optimized for estimated 55 theoretical stages considering Glitsch Ballast (Aspen90) tray section with one-pass per tray with valve type V-4 12 gauge deck thickness and standards panel A with weir height of 38.0 mm and tray diameter of 1.70 m. The model use rate-based calculation for mixed flow model without reactions and film resistance in vapor phase, without reactions and with film resistance in liquid phase, and employing vapor and liquid phase film non-ideality corrections. Default Aspen Plus®v8.4 tray parameters is applied to calculate interfacial area and to predict the mass transfer coefficient by Scheffe and Weiland (1987) method, and heat transfer coefficient by Chilton–Colburn (Taylor and Krishna, 1993) method.

The gaseous top-product at about 6.5 bar and 119.3ºC leave from the 1º theoretically vapor stage (top column stage) in the intermediate-pressure methanol distillation second tray-column (PU-COL-2) is spitted in three fraction in the gaseous methanol splitter (PU-SPL-2) being one fraction destined to the integrated first-column methanol distillation reboiler/condenser (PU-REB-1), another fraction to the integrated third-column methanol reboiler/condenser (PU-REB-3) and the surplus fraction to the flash phase separator and pressure equalizer vessel (PU-FLA-3) as gaseous top-product.

10.0%$_{w/w}$ of the condensate top-product after the integrated third-column methanol reboiler/condenser (PU-REB-3) is splitted in the liquid splitter (PU-SPL-4) and pumped to 6.5 bar and 117.6ºC by second-column reflux pump 2 (PU-PUM-3) and then refluxed back to the 1º theoretically liquid stage (top column stage) in the intermediate-pressure methanol distillation second tray-column (PU-COL-2). The other 90.0%$_{w/w}$ fraction is sent directly to the third-columns partial condenser (PU-CON-2 and CT-HEA-5) to be condensed as final product grade AA methanol.

The liquid bottom product containing mainly CH_3OH and H_2O at about 7.0 bar and 122.0ºC from the 55º theoretically liquid stage (bottom column stage) in the intermediate-pressure methanol distillation second tray-column (PU-COL-2) is splitted in the methanol sump splitter (PU-SPL-3) in the second-column methanol reboiler (PU-REB-2).

The reboiler circulation baffle model was developed using HeatX exchanger block (PU-REB-2) and FSplit splitter block (PU-SPL-3). 95.0%$_{w/w}$ of the liquid phase from the methanol sump splitter (PU-SPL-3) is feed in the reboiler feed section and 5.0%$_{w/w}$ of the liquid phase from the methanol sump splitter (PU-SPL-3) is drained as overflow bottom liquid product. In the second-column methanol reboiler (PU-REB-2) section the bottom product from the sump is heated and vaporized considering 90.0%$_{w/w}$ of the liquid phase vaporized at 7.0 bar and at about 122.1ºC flowing upward back trough the tray-column (PU-COL-2). Another 10.0%$_{w/w}$ overflowing the baffle as heated bottom liquid degassed crude product. The amount of bottom product vaporized in the second-column methanol reboiler (PU-REB-2) are determined according to desired methanol purity (final purity) and to mass and energy balances in the system considering the integration between the condenser and reboiler exchangers.

The liquid bottom product from the methanol mixer 1 (PU-MIX-3) is sent to the adiabatic expansion valve 1 (PU-VAL-3) to adjust the pressure to 1.46 bar (tray pressure) at about 74.3ºC and then is mixed in the methanol mixer 2 (PU-MIX-6) with the gaseous top-product from the 1º theoretically vapor stage (top column stage) of the recovery methanol distillation fourth packaged-column (PU-COL-4). The mixed stream is then fed in the 45º theoretically on-stage of the low-pressure methanol distillation third packaged-column (PU-COL-3).

The thermal energy required to heat and vaporize the bottom liquid product in the second-column methanol reboiler (PU-REB-2) is supplied by the process steam at 2.5 bar and 130.0ºC generated in the low-temperature water cooler (ME-2) in the low-pressure methanol catalytic-synthesis (ME blocks) being condensate at 2.2 bar and 123.0ºC. In the condensate water splitter (PU-SPL-6) 30.0%$_{w/w}$ of the condensed water is sent directly back to low-temperature water cooler (ME-2) and 70.0%$_{w/w}$ (more than sufficient) pass through the integrated fourth-column methanol distillation reboiler (PU-REB-4) heating/vaporizing the bottom liquid product of the recovery methanol distillation fourth packaged-column (PU-COL-4) before to be vaporized again in closed-loop cycle (losses not included in the Aspen Plus®v8.4 process model simulation).

The mass flow rate of process steam at 2.5 bar and 130.0ºC required by the second-column methanol reboiler (PU-REB-2) is determined by thermal requirements and exchanger temperature limits (cross-over avoided) in the cycle-system and controlled by design specification DS-PU-FL-1 coupled with the design specification DS-PU-FL-2 varying the mass flow rate of the water/steam circulating through the exchangers cycle (heat and cool down cycle) in closed-cycle mode.

The condensed top-product after the integrated first-column methanol distillation reboiler/condenser (PU-REB-1) and after the integrated third-column methanol reboiler/condenser (PU-REB-3) together the surplus fraction gaseous top-product at about 6.5 bar and 119.3ºC from the gaseous methanol splitter (PU-SPL-2) are sent to the flash phase separator and pressure equalizer vessel (PU-FLA-3) to be depressurized to 1.43 bar (tray pressure) generating vapor and liquid phases. The vapor phase is mixed in the methanol mixer 3 (PU-MIX-4) together with the gaseous methanol top-product from the low-pressure methanol distillation third packaged-column (PU-COL-3) and then sent directly to the third-columns partial condenser (PU-CON-2 and CT-HEA-5). The liquid phase is drained and fed into the 40º theoretically liquid stage of the low-pressure methanol distillation third packaged-column (PU-COL-3) to be purified.

Rigorous Aspen Plus®v8.4 process model simulation of the low-pressure methanol distillation third packaged-column (PU-COL-3) was developed using RadFrac column block on standard convergence mode without in-bed condenser and reboiler. The model was optimized for estimated 70 theoretical stages considering Glitsch Ballast (Aspen90) tray section with one-pass per tray with valve type V-4 10 gauge deck thickness and standards panel A with weir height of 38.0 mm and tray diameter of 1.20 m. The model use rate-based calculation for mixed flow model without reactions and film resistance in vapor phase, without reactions and with film resistance in liquid phase, and employing vapor and liquid phase film non-ideality corrections. Default Aspen Plus®v8.4 tray parameters is applied to calculate interfacial area and to predict the mass transfer coefficient by Scheffe and Weiland (1987) method, and heat transfer coefficient by Chilton–Colburn (Taylor and Krishna, 1993) method.

The gaseous top-product containing high purity methanol (grade AA) at about 1.2 bar and 69.2ºC from the 1º theoretically vapor stage (top column stage) in the low-pressure methanol distillation third packaged-column (PU-COL-3) is mixed in the methanol mixer 3 (PU-MIX-4) with the gaseous methanol top-product from the flash phase separator and pressure equalizer vessel (PU-FLA-3) and with the condensed methanol from the liquid splitter (PU-SPL-4) not refluxed back to the intermediate-pressure methanol distillation second tray-column (PU-COL-2). This product mixture is cooled in the first-column total condenser (PU-CON-2) by cooling water (CT-HEA-5) modeled by using a Heater exchanger block form-condensing 100.0%$_{w/w}$ of the gaseous top-product at 1.1 bar and 40.0ºC. If there is gaseous formation, these are flash-separated in the third-column liquid reflux-drum (PU-FLA-4) modeled by using a Flash2 separator block and sent to be mixed in the tail-gas mixer (PU-MIX-5) with the tail-gas obtained from the first-column liquid reflux-drum (PU-FLA-2).

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-7) to the third-column partial condenser (CT-HEA-5). The amount of cooling water required is determined and controlled by design specification DS-PU-FL-4 varying the mass flow rate of cooling water passing through the third-column partial condenser (PU-CON-2). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

Condensed top-product grade AA methanol at 1.1 bar and 40.0ºC from the third-column liquid reflux-drum (PU-FLA-4) is splitted in two fractions in the liquid grade AA methanol splitter (PU-SPL-5). 3.0%$_{w/w}$ of the liquid grade AA methanol is pumped to 1.2 bar and about 40.0ºC by third-column reflux pump 3 (PU-PUM-4) and refluxed back to the 1º theoretically liquid stage (top column stage) in the low-pressure methanol distillation third packaged-column (PU-COL-3). 97.0%$_{w/w}$ of the liquid grade AA methanol is pumped by the grade AA methanol pump (PU-PUM-5) to the methanol storage tank (PU-STO-1) as final product, available as liquid grade AA methanol at ambient conditions (GRADE AA METHANOL).

The liquid bottom product containing mainly CH_3OH and H_2O with only insignificantly traces of dissolved gases (e.g.: NH_3, SOx, CO, H_2S, H_2, CHN, COS, hydrocarbons and air elements) at about 1.6 bar and 79.2ºC from the 70º theoretically liquid stage (bottom column stage) in the low-pressure methanol distillation third packaged-column (PU-COL-3) is heated at 1.6 bar and 83.0ºC in the integrated third-column methanol reboiler/condenser (PU-REB-3).

The reboiler circulation baffle was developed using HeatX exchanger block (PU-REB-3) to represent the distillation third-column reboiler configured for circulation without baffle. The bottom liquid product is heated being about 97.0%$_{w/w}$ vaporized at 2.58 bar and at about 104.1ºC flowing upward back trough the packaged-column (PU-COL-3).

Another 3.0%$_{w/w}$ of the bottom liquid product is drained (liquid phase) from the sump content mainly H_2O with methanol (equilibrium mixture) and traces of heavy hydrocarbons (fusel oil). The kinetic rigorous Aspen Plus®v8.4 process model simulation employed does not consider the formation of higher-molecular alcohols or heavy hydrocarbons. In a real process these heavy components (higher-molecular alcohols and fusel oil) can be extracted in the bottom packaged-stages as side-product. The methanol content in this side-product is recovered in the recovery methanol distillation fourth packaged-column (PU-COL-4) and the reminiscent water and hydrocarbons compounds are sent back to the atmospheric CFB directly-heated gasifier (not included in the Aspen Plus®v8.4 process model simulation) or sent to treatment and final disposal as hazard waste (WASTEWATER TO TREATMENT PLANT).

The thermal energy required to heat and vaporize the bottom liquid product in the integrated third-column methanol reboiler/condenser (PU-REB-3) is supplied by the gaseous top-product at about 6.5 bar and 119.3ºC leave from the 1º theoretically vapor stage (top column stage) in the intermediate-pressure methanol distillation second tray-column (PU-COL-2). The gaseous top-product is cooled down to saturation conditions at 6.2 bar and about 117.6ºC for it to be used back as liquid reflux in the intermediate-pressure methanol distillation second tray-column (PU-COL-2).

The fraction-amount of gaseous top-product at 6.5 bar and 119.3ºC obtained from the top of the intermediate-pressure methanol distillation second tray-column (PU-COL-2) destined to the integrated third-column methanol reboiler/condenser (PU-REB-3) is determined by thermal requirements and exchanger temperature limits (cross-over avoided) and controlled by gaseous methanol splitter (PU-SPL-2) block fraction input varying the mass flow rate of the gaseous top-product circulating through the reboiler exchanger cycle (heat and cool down cycle) in closed-cycle mode.

The bottom liquid product at 1.46 bar and at about 83.0ºC from the integrated third-column methanol reboiler/condenser (PU-REB-3) compost basically by 34.8%$_{mol}$ of H_2O and 65.2%$_{mol}$ of CH_3OH is fed in the 1º theoretically liquid stage (top column stage) of the recovery methanol distillation fourth packaged-column (PU-COL-4).

Rigorous Aspen Plus®v8.4 process model simulation of the recovery methanol distillation fourth packaged-column (PU-COL-4) was developed using RadFrac column block on standard convergence mode without in-bed condenser and reboiler. The model was optimized for estimated 15 theoretical stages considering a NORTON IMTP 16 mm packing section from 1º to 15º theoretically stages with section packed height of 5.00 m and diameter of 013 m on standards characteristics. The model use rate-based calculation for mixed flow model without reactions and film resistance in vapor phase, without reactions and with film resistance in liquid phase, and employing vapor and liquid phase film non-ideality corrections. Default Aspen Plus®v8.4 packing parameters is applied to calculate interfacial area and the mass transfer coefficient by Onda et al. (1968) correlation, and heat transfer coefficient by Chilton–Colburn (Taylor and Krishna, 1993) method.

The gaseous top-product at about 1.46 bar and 80.6ºC leaving from the 1º theoretically vapor stage (top column stage) in the recovery methanol distillation fourth packaged-column (PU-COL-4) is mixed in the methanol mixer 2 (PU-MIX-6) with the bottom liquid product from the second-column methanol reboiler (PU-REB-2) and then fed in the 45º theoretically on-stage of the low-pressure methanol distillation third packaged-column (PU-COL-3).

Bottom liquid product at about 1.5 bar and 113.5ºC leave from the 15º theoretically liquid stage (bottom column stage) in the recovery methanol distillation fourth packaged-column (PU-COL-4) is heated/vaporized at 1.5 bar and 113.5ºC in the integrated fourth-column methanol distillation reboiler (PU-REB-4).

The reboiler circulation baffle model was developed using HeatX exchanger block (DS-REB-2) to represent the integrated fourth-column methanol distillation reboiler (PU-REB-4) configured for circulation without baffle. The bottom liquid product is heated being $80.0\%_{w/w}$ vaporized at 1.5 bar and 113.5ºC flowing upward back trough the packaged-column (PU-COL-4). $20.0\%_{w/w}$ of the bottom liquid product formed is drained from the sump of the integrated fourth-column methanol distillation reboiler (PU-REB-4).

The bottom liquid product contains H_2O, heavy hydrocarbons (fusel oil) and traces of CH_3OH (not recycled) in this Aspen Plus®v8.4 process model simulation is considered to final disposal or to treatment as hazard waste (WASTEWATER TO TREATMENT PLANT) being pumped-out the system by bottom product pump (PU-PUM-6).

The thermal energy required to heat and vaporize the bottom liquid product in the integrated fourth-column methanol distillation reboiler (PU-REB-4) is supplied by part of the condensed hot water ($70.0\%_{w/w}$ splitted) at 2.2 bar and 123.0ºC from the condensate water splitter (PU-SPL-6) generated in the second-column methanol reboiler (PU-REB-2) before being sent to be vaporized again in closed-loop cycle (losses not included in the Aspen Plus®v8.4 process model simulation) in the low-temperature water cooler (ME-2).

7.2.21 High-performance sequential combustion full-flow evaporative-class gas turbine (EvGT) operating in combined-cycle mode

The Aspen Plus®v8.4 process model simulation of topping Brayton-cycle by the high-performance sequential combustion full-flow advanced EvGT is based on the ALSTOM advanced-class GT24 gas turbine and GE H-class 7HA gas turbines parameters. The model employed assumes that there are not significant design changes when using the conditioned synthesis gas obtained from gasification of sugarcane bagasse and straw by atmospheric CFB directly-heated gasifier.

EvGT or HAT cycle with injection of water by a humidification tower was developed using RKS-BM physical property methods (i.e. density, humidity, enthalpy and entropy) for the air–water mixtures side and for the synthesis gas side, and using IAPWS-95 physical property methods for the cooling water side (exchangers).

As shown in Figure 54 the Aspen Plus®v8.4 flowsheet of the high-performance sequential combustion full-flow advanced EvGT for BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4) and BIG-GT/CC (SC5) which is the same model with modified parameters for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3) is compost by: low-pressure compressor (GT-COM-1); high-pressure compressor (GT-COM-2); 4-stage low-pressure turbine (GT-LPT-1); high-pressure turbine (GT-HPT-1); three-circuit water inter-cooler exchanger (GT-1); low-pressure bleed air (GT-SPL-2); high-pressure bleed air (GT-SPL-3); EnVironmental (EV) burner (GT-BUR-1); sequential EnVironmental (SEV) burner (GT-BUR-2); first annular combustion chamber (GT-BUR-1); second annular combustion chamber (GT-BUR-2); first-stage fuel nozzle (GT-BUR-1); second-stage fuel nozzle (GT-BUR-2); high-pressure counter-current double-stage humidification packaged-tower (GT-SAT-1); recuperator heat cross-exchanger (GT-2); vortex generators (not included as block); direct drive permanent magnet motor (not included as block); make-up water pump (GT-PUM-1); water mixer (GT-MIX-2); water splitter (GT-SPL-4); gases mixer (GT-MIX-1); buffer/equalizer inlet tank (GT-BUF-1); inlet air pre-filter and fine-filter self-cleaned unit (GT-FIL-1); water inter-cooler exchanger (GT-1); heat recovery after-cooling (GT-HEA-1); high-pressure condensate basin tank (GT-SAT-1); high-pressure recirculation pump (GT-PUM-2) and condenser knock-out drum (GT-FLA-1).

Surrounding atmospheric air (ATMOSPHERIC AIR) at ambient conditions of 1.01325 bar and 25.0ºC are induced to an air duct and then to the pre-filter and fine-filter self-cleaned unit (GT-FIL-1) modeled by using a Fabric filter solids separator block to remove/reduce contaminants and particulate matter (considered 100.0% of efficiency) avoiding damages by debris (erosion) in the gas turbine internal parts (e.g.: blades, chambers, nozzles, ducts).

Filtered air enter the low-pressure compressor (GT-COM-1) modeled by using a Compr pressure changer block according to rigorous ASME method for polytropic compressor considering 91.0% polytropic efficiency (polytropic compression) to first-section of compression leaving the low-pressure compressor (GT-COM-1) at 4.8 bar and about 215.0ºC. A fraction of this pressurized hot-air is bleed as low-pressure bleed air (GT-SPL-2) for cooling the second-stage fuel nozzle (GT-LPT-1) and blades in the 4-stage low-pressure turbine (GT-LPT-1).

Pressurized hot-air flowing through the third circuit (hot side) of the three-circuit water inter-cooler exchanger (GT-1) in counter-current flow direction being sub-cooled to about 4.8 bar and 27.0ºC (optimized according to SEV-burner combustion chamber requirements) generating a condensed phase content water and dissolved gases. The condensed phase formed is removed in the condenser knock-out drum (GT-FLA-

1) modeled by using a Flash2 separator block and is after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

Fresh-water at ambient conditions from treatment plant (WATER FROM TREATMENT PLANT) is pumped to 24.0 bar and about 25.0ºC by make-up water pump (GT-PUM-1) passing-trough the first-circuit of the three-circuit water inter-cooler exchanger (GT-1) modeled by using a MHeatX exchanger block considering a first-circuit (cold side) in counter-current flow direction to achieve sub-cooled conditions in the low-pressure air-side. The pressurized hot water is heated at 23.8 bar and about 61.0ºC, same conditions of the recirculating water.

Recirculating water at about 23.8 bar and 61.0ºC obtained from the high-pressure condensate basin tank (GT-SAT-1) in the high-pressure counter-current double-stage humidification packaged-tower (GT-SAT-1) mixed with the pressurized hot water after the first-circuit (same conditions) is pumped to 23.8 bar and about 61.0ºC by recirculating water pumped (GT-PUM-2) passing-trough the second-circuit (cold side) of the three-circuit water inter-cooler exchanger (GT-1). The pressurized hot water is heated at 23.1 bar and 210.0ºC and then fed in the top liquid stage of the high-pressure counter-current double-stage humidification packaged-tower bottom section (GT-SAT-1).

The mass flow rate of make-up water from treatment plant (WATER FROM TREATMENT PLANT) depend on the mass flow rate of water evaporated and entrained with the humidified air leaving on top gaseous stage of the double-stage humidification packaged-tower top section (GT-SAT-1). The mass flow rate of make-up water is controlled by design specification DS-GT-FL-1 varying the inlet water mass flow rate to achieve the temperature required by the double-stage humidification packaged-tower bottom section (GT-SAT-1) and to maintenance the cooling water in closed-loop cycle.

Cooled low-pressure air enter the high-pressure compressor (GT-COM-2) modeled by using a Compr pressure changer block according to rigorous ASME method for polytropic compressor considering 91.0% polytropic efficiency (polytropic compression) to second-section of compression leaving the high-pressure compressor (GT-COM-2) at 23.6 bar and 219.0ºC. A fraction of this pressurized hot-air is bleed off as high-pressure air bleed (GT-SPL-3) for cooling the first-stage fuel nozzle (GT-HPT-1) and blades in the high-pressure turbine (GT-HPT-1).

The mass flow rate of combustion air agent is determined and controlled by the design specification DS-GT-FG-1 varying the intake-air mass flow rate strongly coupled with design DS-GT-TG-1, design specification DS-GT-PB-1, design specification DS-GT-FG-2, design specification DS-GT-FG-3, FORTRAN calculation block CA-GT-QL-1 and optimization model analysis tools OT-GT-PG-1.

Aspen Plus®v8.4 process simulation simplified model of fuel nozzle and turbine blades cooling systems was developed using FSplit splitter blocks to represent the high-pressure bleed air (GT-SPL-3) for the advanced open loop air-cooled first-stage fuel nozzle (GT-HPT-1) and for blades effusion cooling in the high-pressure turbine (GT-HPT-1), and to represent the low-pressure bleed air (GT-SPL-2) for the advanced open loop air-cooled second-stage fuel nozzle (GT-LPT-1) and for blades effusion cooling in the 4-stage low-pressure turbine (GT-LPT-1).

The coolant air mass flow rate bleed of is determined in function of the turbine inlet temperature and pressure ratio admitted in the low and high turbine sections of the high-performance sequential combustion full-flow advanced EvGT (GT blocks). In the Biomass-to-Methanol (SC1) and Biomass-to-Methanol (SC3) with inlet pressure at 23.0 bar and TIT of 1500.0ºC consider the low-pressure air bleed off as 4.0%$_{w/w}$ of the exhausted gases per expander sections, cooling air consumption of 0.04 kg of air per kg of exhaust-gas. The mass flow rate of the air bleed off is controlled by design specification DS-GT-FG-2 varying the mass flow rate destined to low-pressure bleed air (GT-SPL-2) and by design specification DS-TG-FG-3 varying the mass flow rate destined to high-pressure bleed air (GT-SPL-3). In the Biomass-to-Methanol (SC2) with inlet pressure at 23.0 bar and TIT of 1350.0ºC is considered the low-pressure air bleed off as 2.5%$_{w/w}$ of the exhausted gases per expander sections, cooling air consumption of 0.025 kg of air per kg of exhaust-gas. The mass flow rate of the air bleed off is controlled by design specification DS-GT-FG-2 varying the mass flow rate destined to low-pressure bleed air (GT-SPL-2) and by design specification DS-TG-FG-3 varying the mass flow rate destined to high-pressure bleed air (GT-SPL-3).

The coolant air (bleed air) is guided through the advanced open loop air-cooling internal circuit according to blades effusion cooling method (single-pass or multiple pass circuits) flowing-out together the exhaust-gas (high combustion oxygen content in excess).

High-pressure combustion air destined as oxidant for combustion processes is cooled to 80.0ºC at 23.6 bar by recirculating water at about 61.0ºC and 23.8 bar in the heat recovery after-cooling (GT-HEA-1) modeled by Heater exchanger blocks using RKS-BM physical property methods to air-water mixture side and IAPWS-95 physical property methods to water side. The cooled high-pressure combustion air is then injected in bottom of the high-pressure counter-current double-stage humidification packaged-tower (GT-SAT-1).

The water coolant heat recovery fluid (recirculating water) is heated in the heat recovery after-cooling (GT-HEA-1) to 23.1 bar and 210.0ºC and then fed in the top stage of the double-stage humidification packaged-tower top section (GT-SAT-1). The water mass flow rate passing-through the heat recovery after-cooling (GT-HEA-1) is controlled by design specification DS-GT-FL-2 coupled whit the design specification DS-GT-FL-3 varying the amount of water splitted in the water splitter (GT-SPL-4) pumped by the high-pressure recirculation pump (GT-PUM-2) passing-trough the heat recovery after-cooling (GT-HEA-1).

Rigorous Aspen Plus®v8.4 process model simulation of the high-pressure counter-current double-stage humidification packaged-tower (GT-SAT-1) was developed using RadFrac columns block on standard convergence mode without in-bed condenser and reboiler. The model was optimized for estimated 5 theoretical stages considering NORTON INTX packing sections with dimension of 6.0 mm and standards characteristics with height and diameter optimized for each system requirements (scenarios dependence). The model use rate-based calculation for Countercurrent flow model without reactions and film resistance in vapor phase and liquid phases. Default Aspen Plus®v8.4 packing parameters is applied to predict the mass transfer coefficient and interfacial area by Onda et al. (1968) correlation, and heat transfer coefficient by Chilton–Colburn (Taylor and Krishna, 1993) method.

Humidified combustion air at 23.1 bar and 195.0ºC leaving from the 1º theoretically vapor stage (top column stage) in the double-stage humidification packaged-tower top section (GT-SAT-1) is heated by the exhaust-gas from the 4-stage low-pressure turbine (GT-LPT-1) in the recuperator heat cross-exchanger (GT-2).

In the Biomass-to-Methanol (SC1) and Biomass-to-Methanol (SC3) the exhaust-gas is cooled down to 1.01 bar and 600.0ºC. In the Biomass-to-Methanol (SC2) the exhaust-gas is cooled down to 1.01 bar and 750.0ºC. The temperature of the humidified combustion air after the recuperator heat cross-exchanger (GT-2) is determined and controlled by the energy balance (free-degree).

Intermediate-pressure cleaned synthesis gas from the intermediate-pressure synthesis gas splitter (WS-SPL-1), off-gas from the light-gas condenser knock-out drum (RE-FLA-1) non-recycled after the hydrogen recovery by four-bed PSA system and tail-gas from crude methanol forerun degassing first tray-column (PU-COL-1) are mixed in the gases mixer (GT-MIX-1).

The mixture of gases is fed in the buffer/equalizer inlet tank (GT-BUF-1) as available fuel-gas to be injected in the combustion chambers at about 165.0ºC~170.0ºC (scenario conditions dependence) and 23.0 bar. Part of the conditioned synthesis gas is injected in the first annular EV-burner combustion chamber (GT-BUR-1) and another part is injected in the second annular SEV-burner combustion chamber (GT-BUR-2) according to limits in the TIT admitted by the high-performance sequential combustion full-flow advanced EvGT.

Aspen Plus®v8.4 process model simulation of the injection system coupled with the turbine inlet temperature control for the first annular EV-burner combustion chamber (GT-BUR-1) and for the second annular SEV-burner combustion chamber (GT-BUR-2) consider the optimized combustion air mass flow rate, the optimized discharge pressure (DS-GT-PB-1) of the high-pressure turbine (GT-HPT-1), the heat loss from the systems (CA-GT-QL-1) and the fraction of fuel-gas (GT-SPL-1) injected in the first (GT-BUR-1) or second (GT-BUR-2) combustion chamber.

Aspen Plus®v8.4 process model simulation of the first annular combustion chamber (GT-BUR-1) and EV-burner (GT-BUR-1) is represented together the first-stage fuel nozzle (GT-BUR-1) as simple-aggregated model by using a RGibbs reactor block (GT-BUR-1) to represent the oxidizing gaseous and formation reactions according to chemical equilibrium by Gibbs free-energy minimization method. In the model was considered all gaseous components expected as potential products in products sheet.

Aspen Plus®v8.4 process model simulation of the second annular combustion chamber (GT-BUR-2) and SEV-burner (GT-BUR-2) is represented together the second-stage fuel nozzle (GT-BUR-2) as simple-aggregated model by using a RGibbs reactor block (GT-BUR-2) to represent the gaseous oxidation and formation reactions according to chemical equilibrium by Gibbs free-energy minimization method. In the model was considered all gaseous components expected as potential products in products sheet.

Chemical equilibrium by Gibbs free-energy minimization method estimates the maximum of NO_x (e.g.: NO, NO_2, N_2O) and SO_x (SO_2, SO_3, CO_S) and NH_3 from the precursors contained in the synthesis gas and combust-generated in the first annular EV-burner combustion chamber (GT-BUR-1) and in the second annular SEV-burner combustion chamber (GT-BUR-2). The method only consider the effect of temperature and the amount of humidified air injected in the chamber, others effect is not considered in the Aspen Plus®v8.4 process model simulation.

The total heat loss from the first annular EV-burner combustion chamber (GT-BUR-1) and from the second SEV-burner annular combustion chamber (GT-BUR-2) was considered to be 0.5% of the LHV_{db} of the fuel-gas fed in the high-performance sequential combustion full-flow advanced EvGT (GT blocks). The heat flow-out is controlled by FORTRAN calculator block CA-GT-QL-1 with the aid of parameter calculation blocks (EHV blocks group) implemented.

The mass flow rate of fuel-gas injected in the first annular EV-burner combustion chamber (GT-BUR-1) and consequently the mass flow rate of fuel-gas injected in the second annular SEV-burner combustion chamber (GT-BUR-2) is determined and controlled by DS-GT-TG-1 varying the split fraction (GT-SPL-1) of fuel-gas to obtain TIT of 1350.0ºC in the Biomass-to-Methanol (SC2) and to obtain TIT of 1500.0ºC in the Biomass-to-Methanol (SC1) and Biomass-to-Methanol (SC3).

The oxygen consumed in the second annular SEV-burner combustion chamber (GT-BUR-2) pass through the first annular EV-burner combustion chamber (GT-BUR-1) as excess of air. The excess of oxygen mixed with the gaseous combustion products heated in the first chamber (GT-BUR-1) is after-expanded in the high-pressure turbine (GT-HPT-1) modeled by using a Compr pressure changer block in turbine mode considering 94.0% isentropic efficiency model. Gaseous combustion products are expanded to optimized pressure (OP-GT-PG-1) before the second annular SEV-burner combustion chamber (GT-BUR-2).

Part of the fuel-gas is injected through second-stage fuel nozzle (GT-BUR-2) at the cone tip and then into the second annular SEV-burner combustion chamber (GT-BUR-2) being mixed with the expanded gaseous combustion products containing the necessary oxygen to burn-ignite the fuel-gas injected.

The TIT of the second annular SEV-burner combustion chamber (GT-BUR-2) is adjusted by design specification DS-GT-FG-1 varying the mass flow rate of intake-air flowing through the system in excess, according to limits admitted by the high-performance sequential combustion full-flow advanced EvGT. The TIT of the 4-stage low-pressure turbine (GT-LPT-1) is adjusted to be equal to the TIT of the high-pressure turbine (GT-HPT-1).

Gaseous combustion products from the second annular SEV-burner combustion chamber (GT-BUR-2) are expanded to atmospheric level in the 4-stages low-pressure turbine (GT-LPT-1) modeled by using a Compr pressure changer block in turbine model considering 94.0% isentropic efficiency. The low-pressure gaseous combustion products are cooled in the recuperator heat cross-exchanger (GT-2) heating the humidified air leaving from the top of the double-stage humidification packaged-tower top section (GT-SAT-1). In the Biomass-to-Methanol (SC2) the cooled low-pressure gaseous are exhausted at 1.01 bar and 745.0ºC being directly fed into the HRSG system. In the Biomass-to-Methanol (SC1) and Biomass-to-Methanol (SC3) the cooled low-pressure gaseous are exhausted at 1.01 bar and 600.0ºC being directly fed into the HRSG system.

The single shaft air/hydrogen cooled generator is modeled by GT-E-4 work stream and optimized to produce and export the maximum of electricity to the electric power grid. The electricity generation (GT-E-4 work stream) is optimized by optimization model analysis tools OP-GT-PG-1 varying the pressure obtained after the expansion of the high-pressure combustion product gases in the high-pressure turbine (GT-HPT-1) with model analysis tools constraint CN-GT-TI-1 ensuring the technical temperature and expansion limits.

The sequential combustion process (dual-chamber) offers high gas turbine exhaust conditions allowing achieve the necessary steam generation optimally-adjusting the recuperator heat cross-exchanger (GT-2) output conditions (flexible conditions), closing the thermal energy cycle and energy global-system balances. Changes in the recuperator heat cross-exchanger (GT-2) affect significantly the net-electricity efficiency of the high-performance sequential combustion full-flow advanced EvGT.

7.2.22 Heat recovery steam generator (HRSG)

The HRSG for the combined-cycles and co-generation was simulated based on the horizontal gas-flow drum type aiming primary supply the thermal energy required by the biorefinery-technologies and secondarily generate steam to be expanded in steam turbines system for power generation.

Aspen Plus®v8.4 process model simulation of the staggered exchanger tube banks was developed using RKS-BM physical property methods for the hot exhaust-gas side and IAPWS-95 physical property methods for the water and steam side. The exchanger tube banks are modeled by using HeatX exchanger blocks considering the temperature limits (crossover avoided) between the exchanger tube banks and their influence on the water/steam mass flow rate for each circuit-level.

The arrangement of the exchanger tube banks in the Aspen Plus®v8.4 process model simulation consider the pressure-levels coupled with the temperature approach required per each circuit-level. The quantity of heat recovered is dependent on the heat requirements of the biomass multi-step dryer and control particulate emissions.

Figure 79 shows the Aspen Plus®v8.4 flowsheet of the triple pressure circuit-levels HRSG system for Biomass-to-Methanol (SC1). Figure 80 shows the Aspen Plus®v8.4 flowsheet of the triple pressure circuit-levels HRSG system for Biomass-to-Methanol (SC2). Figure 81 shows the Aspen Plus®v8.4 flowsheet of the triple pressure circuit-levels reheated HRSG system for Biomass-to-Methanol (SC3).

The conventional triple pressure circuit-levels HRSG system (HR blocks) receive exhaust-gas at 1.01 bar and 600.0ºC generated after the recuperator heat cross-exchanger (GT-2) of the high-performance sequential combustion full-flow advanced EvGT. In the Biomass-to-Methanol (SC1), the high-pressure and intermediate-pressure steam generated by the triple pressure circuit-levels HRSG system (HR blocks) is supplied to BPST system (ST blocks) (BC).

The Aspen Plus®v8.4 process model simulation of the horizontal gas-flow drum type HRSG system under consideration in the Biomass-to-Methanol (SC1) was designed with customized low-pressure (LP) circuit-level to produce steam at 2.5 bar and 130.0ºC, intermediate-pressure (IP) circuit-level to produce steam at 23.0 bar and 338.0ºC, and high-pressure (HP) circuit-level to produce steam at 45.0 bar and 420.0ºC.

In the Aspen Plus®v8.4 process model simulation, the deaerator exchanger bank tubes is considered coupled with the LP circuit-level (HR-LPE-1 and HR-LPV-1) producing steam to deaerator unit (HR-DEA-1) and process steam to supply part of the thermal energy required by the thermochemical-biorefinery (SC1).

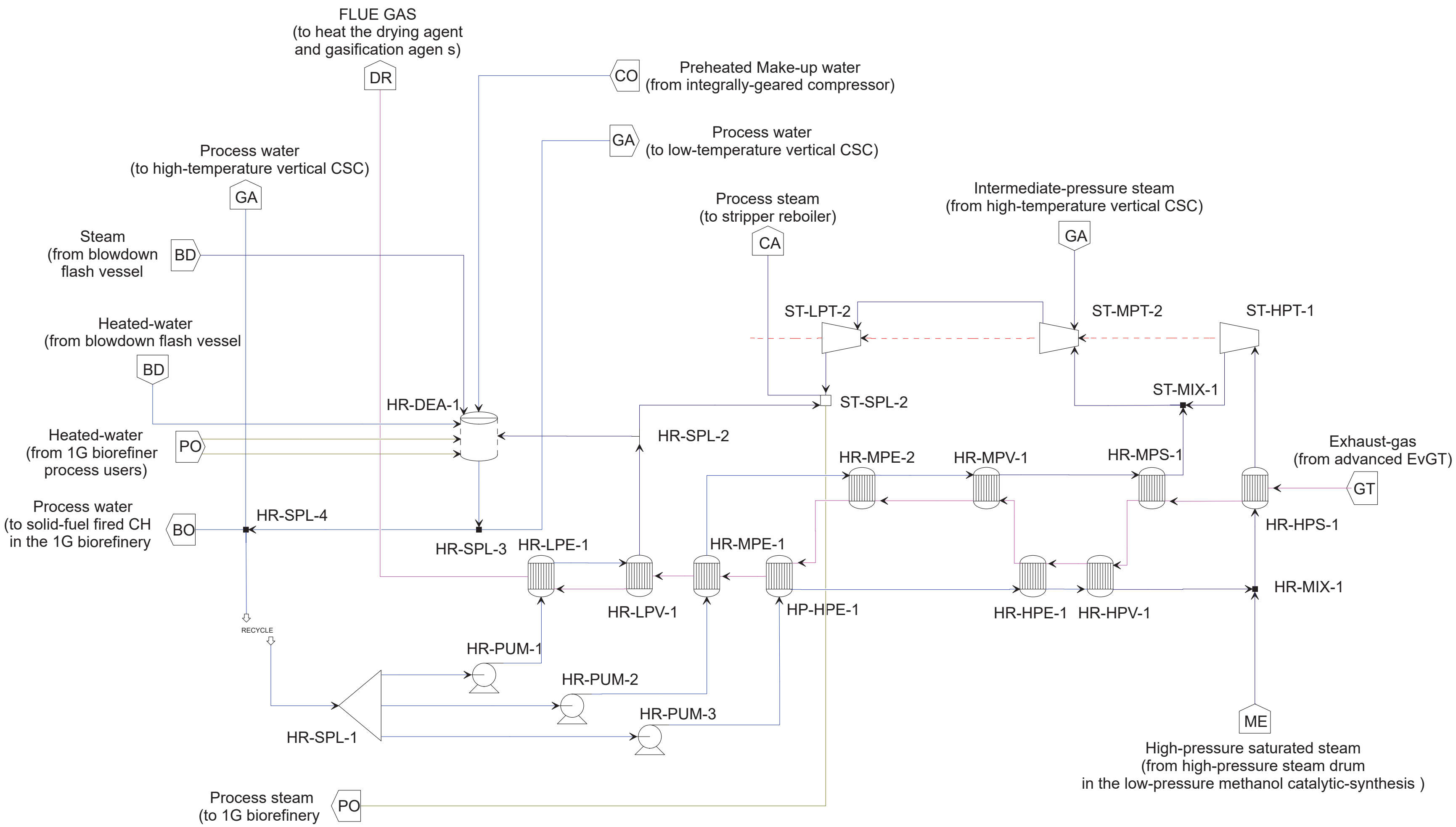
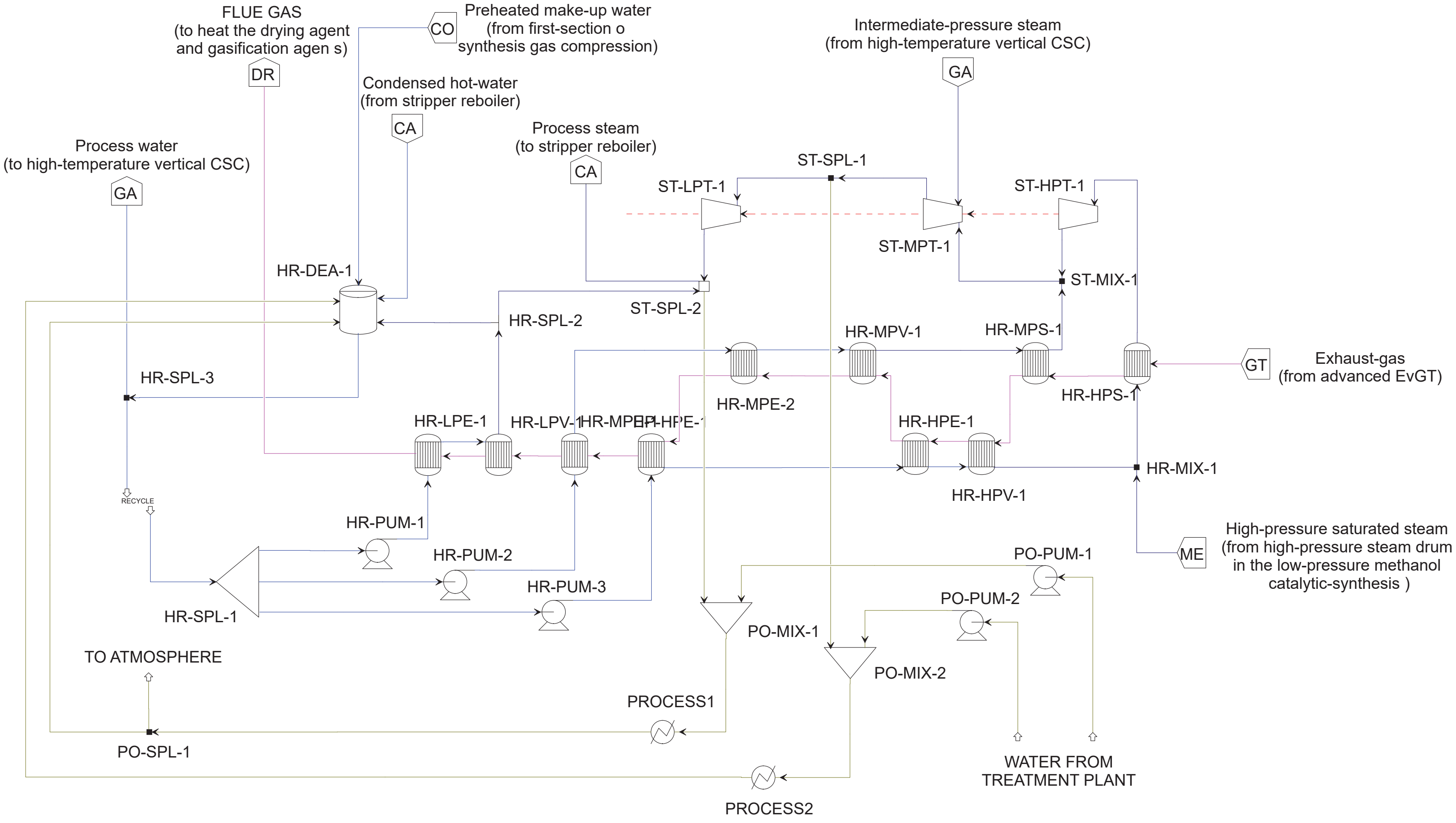


Figure 79 - Aspen Plus® v8.4 flowsheet of the triple pressure circuit-levels Heat recovery steam generator (HRSG) and back-pressure steam turbine system for Biomass-to-Methanol (SC1)

Figure 80 - Aspen Plus$^{®}$ v8.4 flowsheet of the triple pressure circuit-levels Heat recovery steam generator (HRSG) and extraction back-pressure steam turbine for Biomass-to-Methanol (SC2)



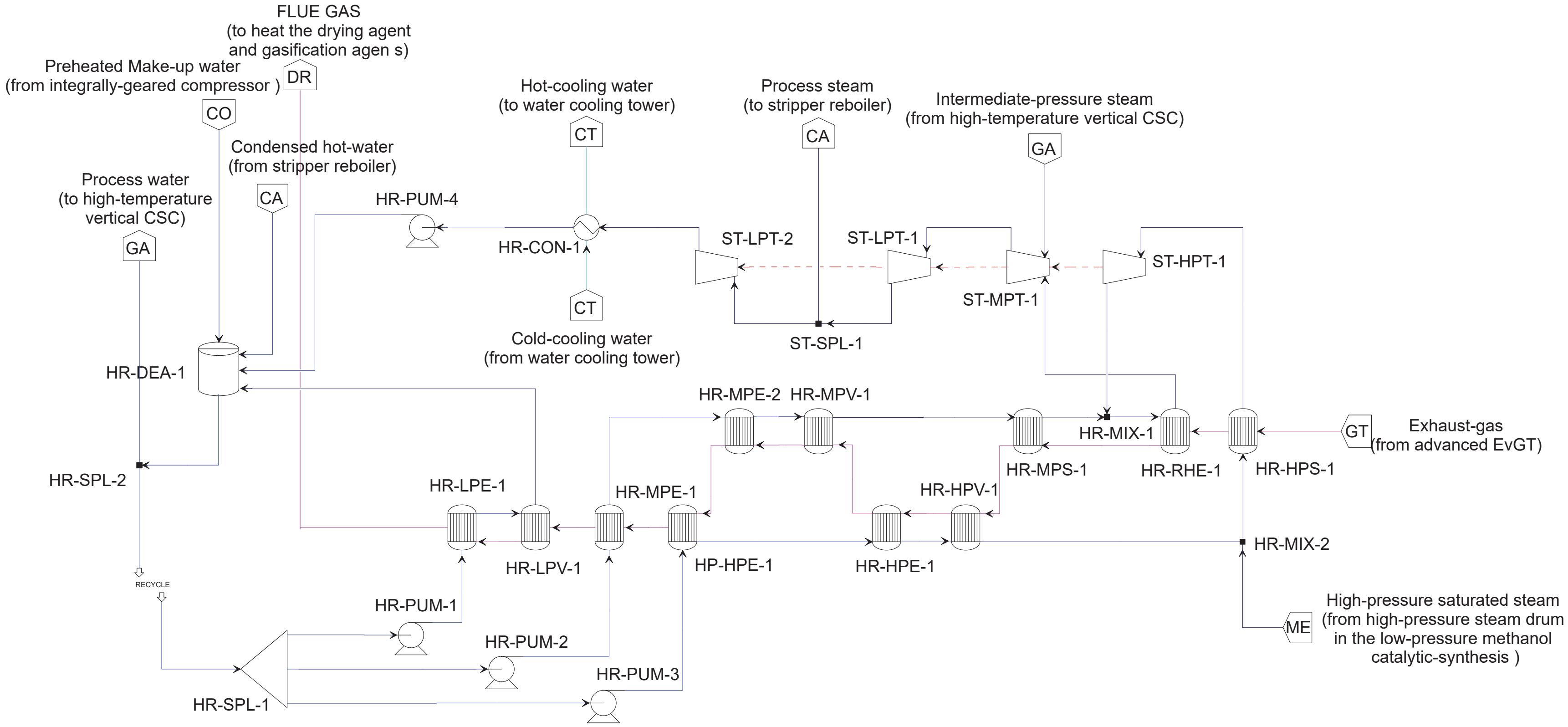


Figure 81 - Aspen Plus® v8.4 flowsheet of the triple pressure circuit-levels reheated Heat recovery steam generator (HRSG) and condensing-extraction steam turbine for Biomass-to-Methanol (SC3)

As shown in Figure 79, Aspen Plus®v8.4 flowsheet of the triple pressure circuit-levels HRSG system in the Biomass-to-Methanol (SC1) is compost by: LP circuit-level water pump (HR-PUM-1); IP circuit-level water pump (HR-PUM-2); HP circuit-level water pump (HR-PUM-3); LP economizer bank tubes (HR-LPE-1); LP vaporizer bank tubes (HR-LPV-1); IP economizer bank tubes 1 (HR-MPE-1); IP economizer bank tubes 2 (HR-MPE-2); IP vaporizer bank tubes (HR-MPV-1); IP superheater bank tubes (HR-MPS-1); HP economizer bank tubes 1 (HR-HPE-1); HP economizer bank tubes 2 (HR-HPE-2); HP vaporizer bank tubes (HR-MPV-1); HP superheater bank tubes (HR-HPS-1); steam splitter (HR-SPL-2); high-pressure steam mixer (HR-MIX-1); deaerator unit (HR-DEA-1); and deaerated hot process water splitter (HR-SPL-1).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 2.5 bar (drum pressure) by the LP circuit-level water pump (HR-PUM-1). The pressure-adequate water is heated to about 127.0ºC (saturated liquid) circulate flowing through the LP economizer bank tubes (HR-LPE-1) and vaporized producing process steam at 2.5 bar and 130.0ºC in the LP vaporizer bank tubes (HR-LPV-1).

Part of the low-pressure steam at 2.5 bar and 130.0ºC is splitted in the steam splitter (HR-SPL-2) and destined to the deaerator unit (HR-DEA-1) as degassing agent. Low-pressure steam mainly remove dissolved gasses (e.g.: O_2 and CO_2) by raises the water temperature (make-up water and condensed process water) to produce hot water at 1.4 bar and 105.0ºC in the deaerator unit (HR-DEA-1). Another part of the low-pressure steam at 2.5 bar and 130.0ºC splitted in the steam splitter (HR-SPL-2) is destined to supply part of the thermal energy required by the thermochemical-biorefinery (SC1).

The amount of steam at 2.5 bar from the LP vaporizer bank tubes (HR-LPV-1) supplied to deaerator unit (HR-DEA-1) and supplied as process steam to thermochemical-biorefinery (SC1) is controlled by design specification DS-HR-TL-1 varying the water/steam mass flow rate need to close the thermal energy balance of the thermochemical-biorefinery (SC1).

Part of conditioned feed water at 1.4 bar and 105.0ºC from the deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 23.0 bar (drum pressure) by the IP circuit-level water pump (HR-PUM-2). Circulate-flowing pressurized water is heated to about 170.0ºC (hot liquid) in the IP economizer bank tubes 1 (HR-MPE-1), and heated to about 220.0ºC (hot liquid) in the IP economizer bank tubes 2 (HR-MPE-2). Hence it is vaporized to about 220.0ºC (saturated vapor) in the IP vaporizer bank tubes (HR-MPV-1) passing from liquid to vapor phase, generating saturated steam at 23.0 bar. The saturated steam is superheated to 338.0ºC in the IP superheater bank tubes (HR-MPS-1).

The amount of subcritical superheated steam at 23.0 bar and 338.0ºC generated is determined by heat exchanger surface area required by the IP exchanger tube banks, the temperature limitations (approaches and cross-over) between the tube banks (heating zones) and the technical parameters of the steam turbine under consideration.

Conditioned feed water and steam mass flow rate passing through the IP staggered exchanger tube banks (HR-MP blocks) is controlled by design specification DS-HR-TG-1 varying the mass flow rate of the deaerated feed water circulating in the exchanger tube banks in order to promote efficient heat exchange.

The temperature of the intermediate-pressure steam obtained after the IP superheater bank tubes (HR-MPS-1) is determined by the conditions (temperature and pressure) of the expanded steam obtained after the high-pressure expansion stage (ST-HPT-1) of the BPST system and controlled by design specification DS-HR-TG-1 to obtain the same conditions in the IP steam mixer (ST-MIX-1).

The subcritical steam at 23.0 bar and 338.0ºC is expanded in the intermediate-pressure expansion stage (ST-MPT-2) of the BPST system in the Biomass-to-Methanol (SC1), producing electrical power energy according to described in the section 7.2.23 (Steam turbine applied in combined-cycles).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 45.0 bar (drum pressure) by the HP circuit-level water pump (HR-PUM-3). Circulate-flowing pressurized water is heated to about 200.0ºC (hot liquid) in the HP economizer bank tubes 1 (HR-HPE-1) and heated to about 257.0ºC (hot liquid) in the HP economizer bank tubes 2 (HR-HPE-2). Hence it is vaporized to about 257.0ºC (saturated vapor) in the HP vaporizer bank tubes (HR-HPV-1) passing from liquid to vapor phase, generating saturated steam at 45.0 bar.

High-pressure saturated steam at 45.0 bar and about 257.0ºC (satured condition) generated in the high-pressure steam drum (ME-FLA-1) in the low-pressure methanol catalytic-synthesis (ME blocks) is mixed in the high-pressure steam mixer (HR-MIX-1 or HR-MIX-2) with the steam vaporized by the HP vaporizer bank tubes (HR-HPV-1). After the mixer, high-pressure saturated steam is superheated to 420.0ºC in the HP superheater bank tubes (HR-HPS-1).

The amount of subcritical superheated steam at 45.0 bar and 420.0ºC generated depends on the amount of steam generated in the high-pressure steam drum (ME-FLA-1), on the temperature limitations (approach) between the exchanger tube banks (heating zones), and on technical parameters of the steam turbine under consideration.

Conditioned feed water and steam mass flow rate passing through the HP staggered exchanger tube banks (HR-MP blocks) is controlled by the deaerated hot process water splitter (HR-SPL-1) varying the mass flow rate of the deaerated feed water circulating in the exchanger tube banks in order to promote efficient heat exchange.

The subcritical steam at 45.0 bar and 420.0ºC is expanded in the high-pressure expansion stage (ST-HPT-1) of the BPST system in the Biomass-to-Methanol (SC1), producing electrical power energy according to described in the section 7.2.23 (Steam turbine applied in combined-cycles).

In the Biomass-to-Methanol (SC1), gases exhausted at 1.01 bar and 600.0ºC from the recuperator heat cross-exchanger (GT-2) of the high-performance sequential combustion full-flow advanced EvGT enters the conventional triple pressure circuit-levels HRSG system (HR blocks) transfer the sensible heat to the water/steam and exits at atmospheric pressure and 122.0ºC (liquid-gas exchange process zone).

The flue-gas at about 122.0ºC after the HRSG system is mixed in the gases mixer (HR-MIX-2) with the flue-gas at 160.0ºC from the traditional 1G-CHP/EBPST system (SC1). The mixed flue-gas at about 135.0ºC is then routed to additional exchanger tube banks (gas-gas exchange process zone) to heat the drying air agent (ATMOSPHERIC AIR) to 120.0ºC. The hot drying air agent supply the thermal energy required and promote the drying process of the biomass in the bagasse flash dryers (DR-DRY-1) and the straw flash dryers (DR-DRY-2).

In the Biomass-to-Methanol (SC1), high-purity oxygen (O_2) gasification agent from gasifier buffer/equalizer tank (GA-BUF-1) at ambient conditions is heated to 120.0ºC (GA-HEA-1) by using the HRSG hot exhaust-gas (HR-HEA-1) before being injected into the atmospheric CFB directly-heated gasifier (GA blocks).

As shown in Figure 80, Aspen Plus®v8.4 flowsheet of the triple pressure circuit-levels HRSG system in the Biomass-to-Methanol (SC2) is compost by: LP circuit-level water pump (HR-PUM-1); IP circuit-level water pump (HR-PUM-2); HP circuit-level water pump (HR-PUM-3); LP economizer bank tubes (HR-LPE-1); LP vaporizer bank tubes (HR-LPV-1); IP economizer bank tubes 1 (HR-MPE-1); IP economizer bank tubes 2 (HR-MPE-2); IP vaporizer bank tubes (HR-MPV-1); IP superheater bank tubes (HR-MPS-1); HP economizer bank tubes 1 (HR-HPE-1); HP economizer bank tubes 2 (HR-HPE-2); HP vaporizer bank tubes (HR-MPV-1); HP superheater bank tubes (HR-HPS-1); steam splitter (HR-SPL-2); high-pressure steam mixer (HR-MIX-1); deaerator unit (HR-DEA-1); and deaerated hot process water splitter (HR-SPL-1).

The conventional triple pressure circuit-levels HRSG system (HR blocks) receive exhaust-gas at 1.01 bar and 745.0ºC generated after the recuperator heat cross-exchanger (GT-2) of the high-performance sequential combustion full-flow advanced EvGT. In the Biomass-to-Methanol (SC2), the high-pressure and intermediate-pressure steam generated by the triple pressure circuit-levels HRSG system (HR blocks) is supplied to EBPST system (ST blocks) (BC).

The Aspen Plus®v8.4 process model simulation of the horizontal gas-flow drum type HRSG system under consideration in the Biomass-to-Methanol (SC2) was designed with customized low-pressure (LP) circuit-level to produce steam at 2.5 bar and 130.0ºC, intermediate-pressure (IP) circuit-level to produce steam at 23.0 bar and

338.0ºC, and high-pressure (HP) circuit-level to produce steam at 45.0 bar and 420.0ºC.

In the Aspen Plus®v8.4 process model simulation, the deaerator exchanger bank tubes is considered coupled with the LP circuit-level (HR-LPE-1 and HR-LPV-1) producing steam to deaerator unit (HR-DEA-1) and process steam to supply part of the thermal energy required by the thermochemical-biorefinery (SC2).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 2.5 bar (drum pressure) by the LP circuit-level water pump (HR-PUM-1). The pressure-adequate water is heated to about 127.0ºC (saturated liquid) circulate flowing through the LP economizer bank tubes (HR-LPE-1) and vaporized producing process steam at 2.5 bar and 130.0ºC in the LP vaporizer bank tubes (HR-LPV-1).

Part of the low-pressure steam at 2.5 bar and 130.0ºC is splitted in the steam splitter (HR-SPL-2) and destined to the deaerator unit (HR-DEA-1) as degassing agent. Low-pressure steam mainly remove dissolved gasses (e.g.: O_2 and CO_2) by raises the water temperature (make-up water and condensed process water) to produce hot water at 1.4 bar and 105.0ºC in the deaerator unit (HR-DEA-1). Another part of the low-pressure steam at 2.5 bar and 130.0ºC splitted in the steam splitter (HR-SPL-2) is destined to supply part of the thermal energy required by the thermochemical-biorefinery (SC2).

The amount of steam at 2.5 bar from the LP vaporizer bank tubes (HR-LPV-1) supplied to deaerator unit (HR-DEA-1) and supplied as process steam to thermochemical-biorefinery (SC1) is controlled by design specification DS-HR-TL-1 varying the water/steam mass flow rate need to close the thermal energy balance of the thermochemical-biorefinery (SC2).

Part of conditioned feed water at 1.4 bar and 105.0ºC from the deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 23.0 bar (drum pressure) by the IP circuit-level water pump (HR-PUM-2). Circulate-flowing pressurized water is heated to about 175.0ºC (hot liquid) in the IP economizer bank tubes 1 (HR-MPE-1), and heated to about 220.0ºC (hot liquid) in the IP economizer bank tubes 2 (HR-MPE-2). Hence it is vaporized to about 220.0ºC (saturated vapor) in the IP vaporizer bank tubes (HR-MPV-1) passing from liquid to vapor phase, generating saturated steam at 23.0 bar. The saturated steam is superheated to 338.0ºC in the IP superheater bank tubes (HR-MPS-1).

The amount of subcritical superheated steam at 23.0 bar and 338.0ºC generated is determined by heat exchanger surface area required by the IP exchanger tube banks, the temperature limitations (approaches and cross-over) between the tube banks (heating zones) and the technical parameters of the steam turbine under consideration.

Conditioned feed water and steam mass flow rate passing through the IP staggered exchanger tube banks (HR-MP blocks) is controlled by design specification DS-HR-TG-1 varying the mass flow rate of the deaerated feed water circulating in the exchanger tube banks in order to promote efficient heat exchange.

The temperature of the intermediate-pressure steam obtained after the IP superheater bank tubes (HR-MPS-1) is determined by the conditions (temperature and pressure) of the expanded steam obtained after the high-pressure expansion stage (ST-HPT-1) of the BPST system and controlled by design specification DS-HR-TG-1 to obtain the same conditions in the IP steam mixer (ST-MIX-1).

The subcritical steam at 23.0 bar and 338.0ºC is expanded in the intermediate-pressure expansion stage (ST-MPT-2) of the EBPST system in the Biomass-to-Methanol (SC2), producing electrical power energy according to described in the section 7.2.23 (Steam turbine applied in combined-cycles).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 45.0 bar (drum pressure) by the HP circuit-level water pump (HR-PUM-3). Circulate-flowing pressurized water is heated to about 200.0ºC (hot liquid) in the HP economizer bank tubes 1 (HR-HPE-1) and heated to about 257.0ºC (hot liquid) in the HP economizer bank tubes 2 (HR-HPE-2). Hence it is vaporized to about 257.0ºC (saturated vapor) in the HP vaporizer bank tubes (HR-HPV-1) passing from liquid to vapor phase, generating saturated steam at 45.0 bar.

High-pressure saturated steam at 45.0 bar and about 257.0ºC (satured condition) generated in the high-pressure steam drum (ME-FLA-1) in the low-pressure methanol catalytic-synthesis (ME blocks) is mixed in the high-pressure steam mixer (HR-MIX-1) with the steam vaporized by the HP vaporizer bank tubes (HR-HPV-1). After the mixer, high-pressure saturated steam is superheated to 420.0ºC in the HP superheater bank tubes (HR-HPS-1).

The amount of subcritical superheated steam at 45.0 bar and 420.0ºC generated depends on the amount of steam generated in the high-pressure steam drum (ME-FLA-1), on the temperature limitations (approach) between the exchanger tube banks (heating zones), and on technical parameters of the steam turbine under consideration.

Conditioned feed water and steam mass flow rate passing through the HP staggered exchanger tube banks (HR-MP blocks) is controlled by the deaerated hot process water splitter (HR-SPL-1) varying the mass flow rate of the deaerated feed water circulating in the exchanger tube banks in order to promote efficient heat exchange.

The subcritical steam at 45.0 bar and 420.0ºC is expanded in the high-pressure expansion stage (ST-HPT-1) of the EBPST system in the Biomass-to-Methanol (SC2), producing electrical power energy according to described in the section 7.2.23 (Steam turbine applied in combined-cycles).

In the Biomass-to-Methanol (SC2), gases exhausted at 1.01 bar and 745.0ºC from the recuperator heat cross-exchanger (GT-2) of the high-performance sequential combustion full-flow advanced EvGT enters the conventional triple pressure circuit-levels HRSG system (HR blocks) transfer the sensible heat to the water/steam and exits at atmospheric pressure and 127.0ºC (liquid-gas exchange process zone).

The flue-gas at about 127.0ºC after the HRSG system is routed to additional exchanger tube banks (gas-gas exchange process zone) to heat the drying air agent (ATMOSPHERIC AIR) to 120.0ºC. The hot drying air agent supply the thermal energy required and promote the drying process of the biomass in the bagasse flash dryers (DR-DRY-1) and the straw flash dryers (DR-DRY-2).

In the Biomass-to-Methanol (SC2), high-purity oxygen (O_2) gasification agent from gasifier buffer/equalizer tank (GA-BUF-1) at ambient conditions is heated to 120.0ºC (GA-HEA-1) by using the HRSG hot exhaust-gas (HR-HEA-1) before being injected into the atmospheric CFB directly-heated gasifier (GA blocks).

As shown in Figure 81, Aspen Plus®v8.4 flowsheet of the triple pressure circuit-levels reheated HRSG system in the Biomass-to-Methanol (SC3) is compost by: LP circuit-level water pump (HR-PUM-1); IP circuit-level water pump (HR-PUM-2); HP circuit-level water pump (HR-PUM-3); LP economizer bank tubes (HR-LPE-1); LP vaporizer bank tubes (HR-LPV-1); IP economizer bank tubes 1 (HR-MPE-1); IP economizer bank tubes 2 (HR-MPE-2); IP vaporizer bank tubes (HR-MPV-1); IP superheater bank tubes (HR-MPS-1); IP reheater pipe banks (HR-RHE-1); HP economizer bank tubes 1 (HR-HPE-1); HP economizer bank tubes 2 (HR-HPE-2); HP vaporizer bank tubes (HR-MPV-1); HP superheater bank tubes (HR-HPS-1); IP steam mixer (HR-MIX-1); high-pressure steam mixer (HR-MIX-2); deaerator unit (HR-DEA-1); and deaerated hot process water splitter (HR-SPL-1).

The conventional triple pressure circuit-levels HRSG system (HR blocks) receive exhaust-gas at 1.01 bar and 600.0ºC generated after the recuperator heat cross-exchanger (GT-2) of the high-performance sequential combustion full-flow advanced EvGT. In the Biomass-to-Methanol (SC3), the high-pressure and intermediate-pressure steam generated by the triple pressure circuit-levels reheated HRSG system (HR blocks) is supplied to CEST system (ST blocks) (BC).

The Aspen Plus®v8.4 process model simulation of the horizontal gas-flow drum type HRSG system under consideration in the Biomass-to-Methanol (SC3) was designed with customized low-pressure (LP) circuit-level to produce steam at 2.5 bar and 130.0ºC, intermediate-pressure (IP) circuit-level to produce steam at 23.0 bar and 338.0ºC, intermediate-pressure (IP) reheater bank tubes (HR-RHE-1) to produce steam at 23.0 bar and 450.0ºC, and high-pressure (HP) circuit-level to produce steam at 45.0 bar and 450.0ºC.

In the Aspen Plus®v8.4 process model simulation, the deaerator exchanger bank tubes is considered as the LP circuit-level (HR-LPE-1 and HR-LPV-1) producing steam at 2.5 bar and 130.0ºC (degassing agent) to be used only in the deaerator unit (HR-DEA-1).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 2.5 bar (drum pressure) by the LP circuit-level water pump (HR-PUM-1). The pressure-adequate water is heated to about 127.0ºC (saturated liquid) circulate flowing through the LP economizer bank tubes (HR-LPE-1) and vaporized producing process steam at 2.5 bar and 130.0ºC in the LP vaporizer bank tubes (HR-LPV-1).

Low-pressure steam at 2.5 bar and 130.0ºC is destined to the deaerator unit (HR-DEA-1) as degassing agent. Low-pressure steam mainly remove dissolved gasses (e.g.: O_2 and CO_2) by raises the water temperature (make-up water and condensed process water) to produce hot water at 1.4 bar and 105.0ºC in the deaerator unit (HR-DEA-1). The amount of steam at 2.5 bar from the deaerator vaporizer bank tubes (HR-LPV-1) is controlled by design specification DS-HR-TL-1 adjusting the amount of steam fed into the deaerator unit (HR-DEA-1) varying the water/steam mass flow rate estimate-used into the deaerator unit (HR-DEA-1) according to described in the section 7.2.26 (Water cycles).

Part of conditioned feed water at 1.4 bar and 105.0ºC from the deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 23.0 bar (drum pressure) by the IP circuit-level water pump (HR-PUM-2). Circulate-flowing pressurized water is heated to about 185.0ºC (hot liquid) in the IP economizer bank tubes 1 (HR-MPE-1), and heated to about 220.0ºC (hot liquid) in the IP economizer bank tubes 2 (HR-MPE-2). Hence it is vaporized to about 220.0ºC (saturated vapor) in the IP vaporizer bank tubes (HR-MPV-1) passing from liquid to vapor phase, generating saturated steam at 23.0 bar. The saturated steam is superheated to 365.0ºC in the IP superheater bank tubes (HR-MPS-1).

The amount of subcritical superheated steam at 23.0 bar and 365.0ºC generated is determined by heat exchanger surface area required by the IP exchanger tube banks, the temperature limitations (approaches and cross-over) between the tube banks (heating zones) and the technical parameters of the steam turbine under consideration.

Conditioned feed water and steam mass flow rate passing through the IP staggered exchanger tube banks (HR-MP blocks) is controlled by design specification DS-HR-TG-1 varying the mass flow rate of the deaerated feed water circulating in the exchanger tube banks in order to promote efficient heat exchange.

The superheated steam produced in the IP superheater bank tubes (HR-MPS-1) is mixed in the IP steam mixer (HR-MIX-1) with the expanded steam at 23.0 bar and 365.0ºC (intermediate-pressure level), obtained after the expansion of the high-pressure steam at 45.0 bar and 450.0ºC by the high-pressure expansion stage (ST-HPT-1) of the CEST system in the Biomass-to-Methanol (SC3). The resultant intermediate-pressure steam is superheated in the IP reheater bank tubes (HR-RHE-1) to produce steam at 23.0 bar and 450.0ºC.

The temperature of the intermediate-pressure steam obtained after the IP superheater bank tubes (HR-MPS-1) is determined by the conditions (temperature and pressure) of the expanded steam obtained after the high-pressure expansion stage (ST-HPT-1) of the CEST system and controlled by design specification DS-HR-TG-1 to obtain the same conditions in the IP steam mixer (HR-MIX-1).

The subcritical steam at 23.0 bar and 338.0ºC is expanded in the intermediate-pressure expansion stage (ST-MPT-2) of the CEST system in the Biomass-to-Methanol (SC3), producing electrical power energy according to described in the section 7.2.23 (Steam turbine applied in combined-cycles).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 45.0 bar (drum pressure) by the HP circuit-level water pump (HR-PUM-3). Circulate-flowing pressurized water is heated to about 200.0ºC (hot liquid) in the HP economizer bank tubes 1 (HR-HPE-1) and heated to about 257.0ºC (hot liquid) in the HP economizer bank tubes 2 (HR-HPE-2). Hence it is vaporized to about 257.0ºC (saturated vapor) in the HP vaporizer bank tubes (HR-HPV-1) passing from liquid to vapor phase, generating saturated steam at 45.0 bar.

High-pressure saturated steam at 45.0 bar and about 257.0ºC (satured condition) generated in the high-pressure steam drum (ME-FLA-1) in the low-pressure methanol catalytic-synthesis (ME blocks) is mixed in the high-pressure steam mixer (HR-MIX-2) with the steam vaporized by the HP vaporizer bank tubes (HR-HPV-1). After the mixer, high-pressure saturated steam is superheated to 450.0ºC in the HP superheater bank tubes (HR-HPS-1).

The amount of subcritical superheated steam at 45.0 bar and 450.0ºC generated depends on the amount of steam generated in the high-pressure steam drum (ME-FLA-1), on the temperature limitations (approach) between the exchanger tube banks (heating zones), and on technical parameters of the steam turbine under consideration.

Conditioned feed water and steam mass flow rate passing through the HP staggered exchanger tube banks (HR-MP blocks) is controlled by the deaerated hot process water splitter (HR-SPL-1) varying the mass flow rate of the deaerated feed water circulating in the exchanger tube banks in order to promote efficient heat exchange.

The subcritical steam at 45.0 bar and 450.0ºC is expanded in the high-pressure expansion stage (ST-HPT-1) of the CEST system in the Biomass-to-Methanol (SC3), producing electrical power energy according to described in the section 7.2.23 (Steam turbine applied in combined-cycles).

In the Biomass-to-Methanol (SC3), gases exhausted at 1.01 bar and 600.0ºC from the recuperator heat cross-exchanger (GT-2) of the high-performance sequential combustion full-flow advanced EvGT enters the conventional triple pressure circuit-levels HRSG system (HR blocks) transfer the sensible heat to the water/steam and exits at atmospheric pressure and 130.0ºC (liquid-gas exchange process zone).

The flue-gas at about 130.0ºC after the HRSG system is routed to additional exchanger tube banks (gas-gas exchange process zone) to heat the drying air agent (ATMOSPHERIC AIR) to 120.0ºC. The hot drying air agent supply the thermal energy required and promote the drying process of the biomass in the bagasse flash dryers (DR-DRY-1) and the straw flash dryers (DR-DRY-2).

In the Biomass-to-Methanol (SC3), high-purity oxygen (O_2) gasification agent from gasifier buffer/equalizer tank (GA-BUF-1) at ambient conditions is heated to 120.0ºC (GA-HEA-1) by using the HRSG hot exhaust-gas (HR-HEA-1) before being injected into the atmospheric CFB directly-heated gasifier (GA blocks).

7.2.23 Steam turbine applied in combined-cycles

The Aspen Plus®v8.4 process model simulation of the steam turbine applied in combined-cycles considers conventional subcritical steam turbines operating in Rankine-cycle mode.

As shown in Figure 79, Aspen Plus®v8.4 flowsheet of the BPST system in the Biomass-to-Methanol (SC1) is compost by: high-pressure expansion stage (ST-HPT-1); intermediate-pressure expansion stage (ST-MPT-2); low-pressure expansion stage (ST-LPT-2); steam mixer (ST-MIX-1); and steam splitter (ST-SPL-2).

The Aspen Plus®v8.4 process model simulation of the BPST (ST blocks) in the Biomass-to-Methanol (SC1) was developed using IAPWS-95 physical property methods considering about 79.45% isentropic efficiency (isentropic expansion). The model considers exhaust-steam at 2.5 bar and 130.0ºC in the low-pressure section (ST-LPT-2).

The high-pressure steam at 45.0 bar and 420.0ºC generated in the HP circuit-level (HR-HPS-1) is expanded to 23.0 bar and about 338.0ºC (intermediate-pressure level) by the first-section of the BPST (ST-HPT-1) modeled by using a Compr pressure changer block in turbine model. After expanded the steam is mixed (ST-MIX-1) with intermediate-pressure steam at 23.0 bar and about 338.0ºC generated in the IP circuit-level (HR-MPS-1) of the HRSG system and with the intermediate-pressure steam at 23.0 bar and about 338.0ºC generated in the high-temperature vertical CSC (GA-CSC-1).

The intermediate-pressure steam is expanded to 6.0 bar and about 205.0ºC by the second-section of the BPST (ST-MPT-2) modeled by using a Compr pressure changer block in turbine model and then to 2.5 bar and 130.0ºC in the third section of the BPST (ST-LPT-2) modeled by using a Compr pressure changer block in turbine model, without intermediate extractions of steam. The exhaust-steam is used as process steam to supply part of the thermal energy required by the 1G-thecnologies (integrated scenario) and part of the thermal energy required by the thermochemical technologies.

As shown in Figure 80, Aspen Plus®v8.4 flowsheet of the EBPST system in the Biomass-to-Methanol (SC2) is compost by: high-pressure expansion stage (ST-HPT-1); intermediate-pressure expansion stage (ST-MPT-1); the low-pressure expansion stage (ST-LPT-1); steam extraction at 6.0 bar (ST-SPL-1); steam mixer (ST-MIX-1); and steam splitter (ST-SPL-2)

The Aspen Plus®v8.4 process model simulation of the EBPST (ST blocks) in the Biomass-to-Methanol (SC2) was developed using IAPWS-95 physical property methods considering about 79.45% isentropic efficiency (isentropic expansion). The model considers exhaust-steam at 2.5 bar and 130.0ºC in the low-pressure section (ST-LPT-1).

The high-pressure steam at 45.0 bar and 420.0ºC generated in the HP circuit-level (HR-HPS-1) is expanded to 23.0 bar and about 338.0ºC (intermediate-pressure level) by the first-section of the EBPST (ST-HPT-1) modeled by using a Compr pressure changer block in turbine model. After expanded the steam is mixed (ST-MIX-1) with intermediate-pressure steam at 23.0 bar and about 345.9ºC generated in the IP circuit-level (HR-MPS-1) of the HRSG system and with the intermediate-pressure steam at 23.0 bar and about 345.9ºC generated in the high-temperature vertical CSC (GA-CSC-1).

The intermediate-pressure steam is expanded to 6.0 bar and about 203.0ºC by the second-section of the EBPST (ST-MPT-1) modeled by using a Compr pressure changer block in turbine model. Part of this steam is extracted (ST-SPL-1) as process steam to supply the thermal energy required by the dehydration molecular sieve in the 1G sugarcane biorefinery (integrated scenario).

Surplus steam at 6.0 bar and 205.0ºC from the second-section of the EBPST (ST-MPT-1) is expanded to 2.5 bar and 130.0ºC (exhaust) by the third section of the EBPST (ST-LPT-1) modeled by using a Compr pressure changer block in turbine model. The exhaust-steam together the steam at 2.5 bar and 130.0ºC from the LP circuit-level (HR-LPV-1) in the HRSG system is used as process steam (ST-SPL-2) to supply the entire 1G-thecnologies thermal energy demand (integrated scenario) and part of the thermal energy required by the thermochemical technologies.

As shown in Figure 81, Aspen Plus®v8.4 flowsheet of the CEST system in the Biomass-to-Methanol (SC3) is compost by: high-pressure expansion stage (ST-HPT-

1); intermediate-pressure expansion stage (ST-MPT-1); low-pressure expansion stage (ST-LPT-1); condensing expansion stage (ST-LPT-2); steam extraction at 6.0 bar (ST-SPL-1); steam extraction at 2.5 bar (ST-SPL-2); water-cooled surface condenser (HR-CON-1); and condensed water pump (HR-PUM-4).

The Aspen Plus®v8.4 process model simulation of the CEST (ST blocks) in the Biomass-to-Methanol (SC3) was developed using IAPWS-95 physical property methods considering about 80.52% isentropic efficiency (isentropic expansion).

The high-pressure steam at 120.0 bar and 540.0ºC generated in the HP circuit-level (HR-HPS-1) is expanded to 23.0 bar and about 323.0ºC (intermediate-pressure level) by the first-section of the CEST (ST-HPT-1) modeled by using a Compr pressure changer block in turbine model. After expanded the steam is mixed with intermediate-pressure steam at 23.0 bar and about 323.0ºC generated in the IP circuit-level (HR-MPS-1) of the HRSG system and then reheated to 23.0 bar and 540.0ºC in the reheated exchanger pipe banks (HR-RHE-1) in the HRGS intermediate-pressure circuit-level.

The intermediate-pressure steam generated in the high-temperature vertical CSC (GA-CSC-1) and the intermediate-pressure reheated steam at 23.0 bar and 540.0ºC are expanded to 6.0 bar and at about 294.0ºC in the second-section of the CEST (ST-MPT-1) modeled by using a Compr pressure changer block in turbine model and then to 2.5 bar and 275.0ºC in the third section of the CEST (ST-LPT-1) modeled by using a Compr pressure changer block. Part of this steam is extracted (ST-SPL-1) as process steam to supply part of the thermal energy required by the thermochemical technologies (standalone scenario).

Surplus steam at 2.5 bar and 275.0ºC from the third section of the CEST (ST-LPT-1) is expanded to 0.11 bar and 48.0ºC by the four section of the CEST (ST-LPT-2) modeled by using a Compr pressure changer block in turbine model, ensuring that the quality of the steam-exiting a CEST condensing-stage (ST-LPT-2) is greater than 90.0% (technical limit).

CEST condensing-stage (ST-LPT-2) is directly connected to water-cooled surface condenser (HR-CON-1) modeled by using a Heater exchanger block. The vacuum-pressure steam exhausted is condensed generating a water condensate (liquid phase) available to be after pumped (HR-PUM-4) back to deaerator unit (HR-DEA-1) in closed-loop cycle.

The electrical potential losses (turbine-mechanical generator) by attrite in the mechanical move parts was considered as 1.0% of the mechanical potential energy produced by the STs (99.0% mechanical efficiency).

7.2.24 Traditional combined heat and power generation system applying extraction back-pressure steam turbine

In the thermochemical-biorefinery scenario 1 (SC1) and thermochemical-biorefinery scenario 3 (SC3) is considered the optimized 1G sugarcane biorefinery (1G sugarcane biorefinery) with annexed ethanol distillery using a typical solid-fuel fired boiler bottoming-cycle system (grate type) and non-condensing type extraction back-pressure steam turbine (EBPST) operating at 22.0 bar and 320.0ºC (SC1) in Rankine-cycle mode for thermal and electrical energy generation (CHP). Part of the sugarcane bagasse (SUGARCANE BAGASSE) from mills (without use of straw) as fuel is consumed in the solid-fuel fired boiler bottoming-cycle system, the surplus bagasse (SUGARCANE BAGASSE) and the straw (SUGARCANE STRAW) available is used as feedstock in the self-sufficient in energy terms Biomass-to-Methanol route.

In the thermochemical-biorefinery scenario 1 (SC1) the traditional 1G-CHP/EBPST (SC1) system supply part of the thermal and electrical energy required by the 1G-thecnologies, another part is supplied by the Biomass-to-Methanol (SC1) operating in integrated mode. In the thermochemical-biorefinery scenario 3 (SC3) the traditional 1G-CHP/EBPST (SC1) system supply the entire thermal and electrical energy required by the 1G sugarcane biorefinery, Biomass-to-Methanol (SC3) operating in standalone mode.

Traditional 1G-CHP/EBPST system (SC1) with surplus biomass is simulated and detailed according to Aspen Plus®v8.4 process model simulation described in the section 5 (First generation sugarcane biorefinery)

As shown in Figure 45 the Aspen Plus®v8.4 flowsheet of the 1G-CHP/EBPST (SC1) system for BIG-ICE/CC (SC1) which is the same model with modified parameters for Biomass-to-Methanol (SC1) is compost by: feed tray (PR-MIX-5); conveyor boiler fuel feeders (PR-SCR-8); breakdown RYield reactor block (BO-DEV-1); burner chamber (BO-COMBU); adjust Sep separator block (BO-SEP-1); heat loss adjust Heater exchanger block (BO-HEA-1); wet ashes removal grate system (BO-SEP-2); ashes bins (BO-RES-1); air pre-filter unit (BO-FIL-1); air preheated (BO-PRE-1); advanced blower system (BO-ASP-1); feed-water pump (BO-PUM-1); low-temperature economizers and high-temperature economizers (BO-ECO-1); radiant heat adjust Heater exchanger block (BO-HEA-2 and BO-HEA-3); evaporator (BO-EVA-1); superheater (BO-SUP-1); saturated water purge (BO-SPL-3); blowdown flash vessel (BD-FLASH-1); multi-cyclone unit (BO-CYC-1); electrostatic precipitator unit (BO-ESP-1); ashes temporary storage bins (BO-RES-2); intermediate-pressure EBPST stage (ST-HPS-1); low-pressure EBPST stage (ST-LPS-1); steam extraction at 6.0 bar (ST-SPL-1); make-up water pump (BO-PUM-2); and blowdown heat recovery exchanger (BD-1).

A fraction of the bagasse from the mills (SUGARCANE BAGASSE) can be directly belt-conveyed to boiler fuel feeders (PR-SCR-8) or carried by tractors (actual system) from the bagasse pile to the conveyor feed tray (PR-MIX-5) to be fed by drum and hydraulic/pneumatic fuel feeders (PR-SCR-8) into the combustion chamber (BO-COMBU).

The Aspen Plus®v8.4 process model simulation of the typical solid-fuel fired boiler use a breakdown RYield reactors type (BO-BEV-1) as a theoretical artifice to simulate the decomposition of the non-conventional solids BAGASSE (BO-DEV-1) into its ‘constituting’ conventional components (‘ELEMENTS’) including carbon (C), hydrogen (H_2), oxygen (O_2), chlorine (Cl_2), nitrogen oxide (NO) sulfur dioxide (SO_2) and hydrogen sulfide (H_2S) using about $16.67\%_{w/w}$ of the sulfur (S) content. Salts, minerals, ashes and soil are specified as inert components in the devolatilization process-zone (bypass).

FORTRAN calculator block CA-BO-CS-1 is used to specify the yield distributions and the mass flow rate of each constituent component in the outlet stream according to the bagasse ultimate analysis (Table 5). The blocks BO-SPL-1 and BO-SPL-2 split the volatile material from the biomass and sent directly to the combustor chamber (BO-COMBU).

Sep separators block BO-SEP-1 as adjustment model is used to adjust the biomass conversion, the carbon conversion (CA-BO-XS-1) and the ashes content (solids formation) as bottom ashes (ASHES) or fly-ashes (FLY-ASHES). The amount of bottom ashes (ASHES) and fly-ashes (FLY-ASHES) and hers composition are controlled by BO-SEP-2 block which simulate the grate system and the automatically wet ashes removal system (BO-SEP-2), without considering the water use in the simulation (cleaning grate system). The ashes temporary storage bins (BO-RES-1) consider the heat loss (heat transported with ashes) by natural heat changes with the ambient conditions.

The solid-fuel fired boiler models consider a heat loss (BO-HEA-1) due the surface radiation and convection with to surrounding ambient. The heat loss (BO-HEA-1) is calculated by FORTRAN calculator block CA-BO-QL-1 based on the fraction of the LHV_{db} of the biomass inlet in the boiler, according to Equation 16 detailed in the section 3.9.13 (Heat losses to surrounding ambient).

The Aspen Plus®v8.4 process model simulation of the burner chamber (BO-COMBU) was developed using RGibbs reactor type which uses the Gibbs free energy minimization method, considering all the possible solids emissions (soil and atmosphere) and gaseous emissions (atmosphere). The Gibbs free energy minimization method determines the equilibrium composition of the products resulting from the many reactions that can occur. The burner chamber (BO-COMBU) model can determine in the gaseous phase the formation of NO_2, N_2O, NO, SO_2, SO_3, NH_3, H_2S, HCL, Cl_2, COS, CHN, volatile organic compounds, and particulate matter formation (salt and solid compounds), and in the solid phase (ashes and fly-ashes) the formation of unconverted biomass (BAGASSE and STRAW) and carbon (C), SiO_2 (biomass constitutional ash content), soil, MgO, CaO, KCl, K_2O, K_3PO_4, salts and mineral (biomass constitutional content). The Gibbs free energy minimization method cannot estimate the formation of CaS, MgS and S, sulfur content being emitted on gaseous forms in Gibbs combustion models (oxidized metals are more stable form).

Combustion air (ATMOSPHERIC AIR) is preheated (BO-PRE-1) and forced-injected in the burner chamber (BO-COMBU) by advanced blower system (BO-ASP-1) with pre-filter unit (BO-FIL-1) to protect the blower and burner from debris (PARTICLES). The amount of air employed is controlled by design specification DS-BO-FG-1 varying the mass flow rate of atmospheric air (ATMOSPHERCI AIR) inlet into the burner chamber (BO-COMBU). The model consider $8.0\%_{w/w}$ as the ratio of the oxygen mass flow rate out off the burner chamber (BO-COMBU) to the oxygen mass flow rate inlet into the burner chamber (BO-COMBU).

The liquid non-saturated feed-water from first deaerator unit (HR-DEA-1) at 1.4 bar and 105.0ºC is pumped-compressed to 22.0 bar by the feed-water pump (BO-PUM-1) and then fed into the solid-fuel fired boiler pipes banks. Non-saturated feed-water is heated at saturation conditions in the low-temperature and high-temperature economizers (BO-ECO-1) by radiant (BO-HEA-2 and BO-HEA-3) and convective heat (BO-ECO-1), is evaporate to saturated steam in the evaporator (BO-EVA-1) and superheated in the superheater (BO-SUP-1) leaving the boiler at 22.0 bar and 320ºC to be expanded in the EBPST system (ST blocks).

The temperature of the flue-gas after the air pre-heater exchanger (BO-PRE-1) is controlled by design specification DS-BO-FL-1 to be 160.0ºC varying the mass flow rate of the boiler feed-water flowing through the water-side pipe bank coupled with the design specification DS-BO-FG-1 varying the mass flow rate of the atmospheric air inlet into the burner chamber (BO-COMBU) to control the excess air ratio.

$4.0\%_{w/w}$ of the saturated water mass flow rate is purged (BO-SPL-3) from the boiler as continue water blowdown and fleshed to 1.4 bar (deaerator pressure) in the blowdown flash vessel (BD-FLASH-1). The vaporized phase is sent to the first deaerator unit (HR-DEA-1) to heat recovery (reducing the amount of steam 2.5 bar used in the deaerator). The liquid phase is cooled to 30.0ºC by the blowdown heat recovery exchanger (BD-1) heating the make-up raw water (WATER FROM TREATMENT PLANT) which is pumped to 1.4 bar by the make-up water pump (BO-PUM-2) to the first deaerator unit (HR-DEA-1). Water blowdown removal impurities from boiler as dissolved impurities, in the Aspen Plus®v8.4 process model simulation is not considered the presence of impurities. The amount of impurities depends on the fresh-water quality, on make-up water treatment process and maintenance treatment of process water cycle.

In the spreadsheet calculation model of the treatment processes was considered the recovery of $87.0\%_{w/w}$ of the water blowdown according to Equation 24.

Particulate material content in the flue-gas (FLY-ASHES) are reduced by control particulate emissions system applying a multi-cyclone unit (BO-CYC-1) modeled by using a Cyclone solids separator block. The multi-cyclone unit (BO-CYC-1) was designed optimized with 5 cyclones (battery) to remove the gross particulate content in the exhaust-gas according to Muschelknautz calculation method for a maximum pressure drop of 0.01 bar applying spiral inlet cyclones type.

Part of the persistent fine particulate matters after the multi-cyclone unit (BO-CYC-1) is removed by the electrostatic precipitator (DR-ESP-1) modeled by suing a ESP solids separator block according to Svarovsky calculation model for vertically mounted collecting plates model with separation efficiency of 92.0% based on the migration velocity and the ratio of precipitation area. The fly-ashes (FLY AHSES) are stored in the ashes temporary storage bins (BO-RES-2) and mixed with the ASHES to be after-sent to application in the sugarcane crops.

The flue-gas from the boiler system content steam (H_2O), NO_2, N_2O, NO, SO_2, SO_3, NH_3, H_2S, HCL, Cl_2, COS, CHN, volatile organic compounds, and particulate matter (MgO, CaO, KCl, K_2O, K_3PO_4, BIOMASS, C, salts and mineral) is mixed with the flue-gas from the HRSG system and sent to heat the drying agent and gasification agent (heat recovery).

The Aspen Plus®v8.4 process model simulation of the EBPST (ST blocks) of the 1G-CHP/EBPST (SC1) system in the Biomass-to-Methanol (SC1) was developed using IAPWS-95 physical property methods considering about 74.55% isentropic efficiency (isentropic expansion). The model considers exhaust-steam at 2.5 bar and 130.0ºC in the low-pressure section (ST-LPS-1).

The intermediate-pressure steam at 22.0 bar and 320.0ºC generated in the solid-fuel fired boiler pipes banks is expanded to 6.0 bar and about 198.3ºC by the first-section of the EBPST (ST-HPT-1) modeled by using a Compr pressure changer block in turbine model. After expanded a part of the steam is extracted (ST-SPL-1) to supply part of the thermal energy required by the dehydration ethanol process (1G-thecnologie).

Another part of the steam at 6.0 bar and about 198.3ºC is expanded to 2.5 bar and 130.0ºC in the second-section of the EBPST (ST-MPS-1) modeled by using a Compr pressure changer block in turbine model. The exhaust-steam at 2.5 bar and 130.0ºC is used to supply part of the 1G-thecnologies thermal energy requirements.

The electricity generated by the EBPST (ST blocks) of the 1G-CHP/EBPST (SC1) system in the Biomass-to-Methanol (SC1) is used to supply part of electricity required by the 1G sugarcane biorefinery. Another part is supplied by the Biomass-to-Methanol route. The electrical potential losses (turbine-mechanical generator) by attrite in the mechanical move parts was considered as 1.0% of the mechanical energy produced by the turbine (99.0% mechanical efficiency).

Spreadsheet calculation considering the wastewater treatment process (WASTEWATER TO TREATMENT PLANT) with a maximum of 85.0%$_{w/w}$ recovery efficiency is used to determine the amount of water (TO WASTEWATER TREATMENT PLANT) is recovered and recycled to the deaerator unit (HR-DEA-1) after treatment as make-up water and the requirements of supplementary fresh-make-up water to close the water balance.

7.2.25 Multi-cells water-cooling tower

The Aspen Plus®v8.4 process model simulation consider modules of draft-packaged water-cooling induced-tower 43.0ºC/30.0ºC/27.0ºC type with capacity for 700.0 m³/hr of water mass flow rate. The model was developed using IAPWS-95 physical property methods for the water-side streams and RKS cubic equation of state with BM alpha function property method to simulate the air-side streams and the heat transfer between the atmospheric air-side and the water-side in the water tower module (CT-TOW blocks). The heat transfer in the gas-side or liquid-side streams in the cooling water equipment users depends on the physical property methods employed in the area in which they are allocated.

The multi-cells water-cooling tower (CT-blocks) provides cooling water to remove heat and adjust the process temperature to appropriate levels. The cooling water is distributed to the cooling water equipment users in the Biomass-to-Methanol scenarios to:

a) condense and cool-down the top gas product from the absorber (CT-HEA-2) an stripper (CT-HEA-3) columns in the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3);
b) cool down the absorber inlet lean amine aqueous solution (CT-HEA-1) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3);
c) cool-down the sub-cooled and partial-cleaned synthesis gas in the inter-stages (CO-1 and CO-2) of the first-section of compression (intercooler) by integrally-geared three stages centrifugal compressor in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3);
d) cool-down the cleaned synthesis gas in the inter-stage (CO-3) of the second-section of compression (intercooler) by integrally-geared two stages centrifugal compressor in Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3);
e) cool-down the CO_2 gas in the inter-stages (CO-1~5) of compression in the integrally-geared six stage centrifugal compressor (inter-cooler and after-

cooler) and liquefier the captured CO_2 (CC-HEA-1) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3);

f) condense and cool-down the top gaseous product from the first tray-column (degases) in the three-column double-effect alcohols distillation system (CT-HEA-4) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3);

g) condense and cool-down the top gas product from the low-pressure column (purification) in the energy-saving four-column triple-effect methanol distillation system (methanol purification) for grade AA methanol (CT-HEA-5) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3);

h) cool-down the atmospheric air in the inter-stage (AP-1) and after-stage (AP-HEA-1) (intercooler and after-cooler) of the integrally-geared two stages centrifugal compressor (MAC) in Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3);

i) cool-down the atmospheric air in the inter-stages (AS-3~6) and after-stage (AS-7) of (intercooler and after-cooler) of the integrally-geared six stages centrifugal compressor (BAC) in Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3);

j) cool-down the atmospheric air in the after-stage (AS-1) (after-cooler) of the high-efficiency turbo booster in Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3);

k) cool-down the high-purity gaseous nitrogen (N_2) in the inter-stages (AS-HEA-1~4) of the gaseous compression side (intercooler) in the high-pressure double-Claude cycle nitrogen liquefier Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3);

l) condense the low-pressure exhausted steam from the condensing section turbine (CEST) employed in the Biomass-to-Methanol (SC3).

The Aspen Plus$^{®}$v8.4 process model simulation of water-cooling tower system operating in water recirculation mode determine the requirements of cooling water heat exchanger, make-up of recycled and fresh water, water blowdown, and electric motor drives (fan drivers and pumps). In the model are used the standards design equations as defined in the section 3.9.17 (Water-cooling tower) for the modular single fan-cells arrangement operates as staged mode by sections each with variable-frequency drivers.

Figure 82 shows the Aspen Plus$^{®}$v8.4 flowsheet of the first-section of the multi-cells water-cooling tower for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3). Figure 83 (a) shows the Aspen Plus$^{®}$v8.4 flowsheet of the second-section of the multi-cells water-cooling tower for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3). Figure 83 (b) shows the Aspen Plus$^{®}$v8.4 flowsheet of the third section of the multi-cells water-cooling tower for Biomass-to-Methanol (SC3).

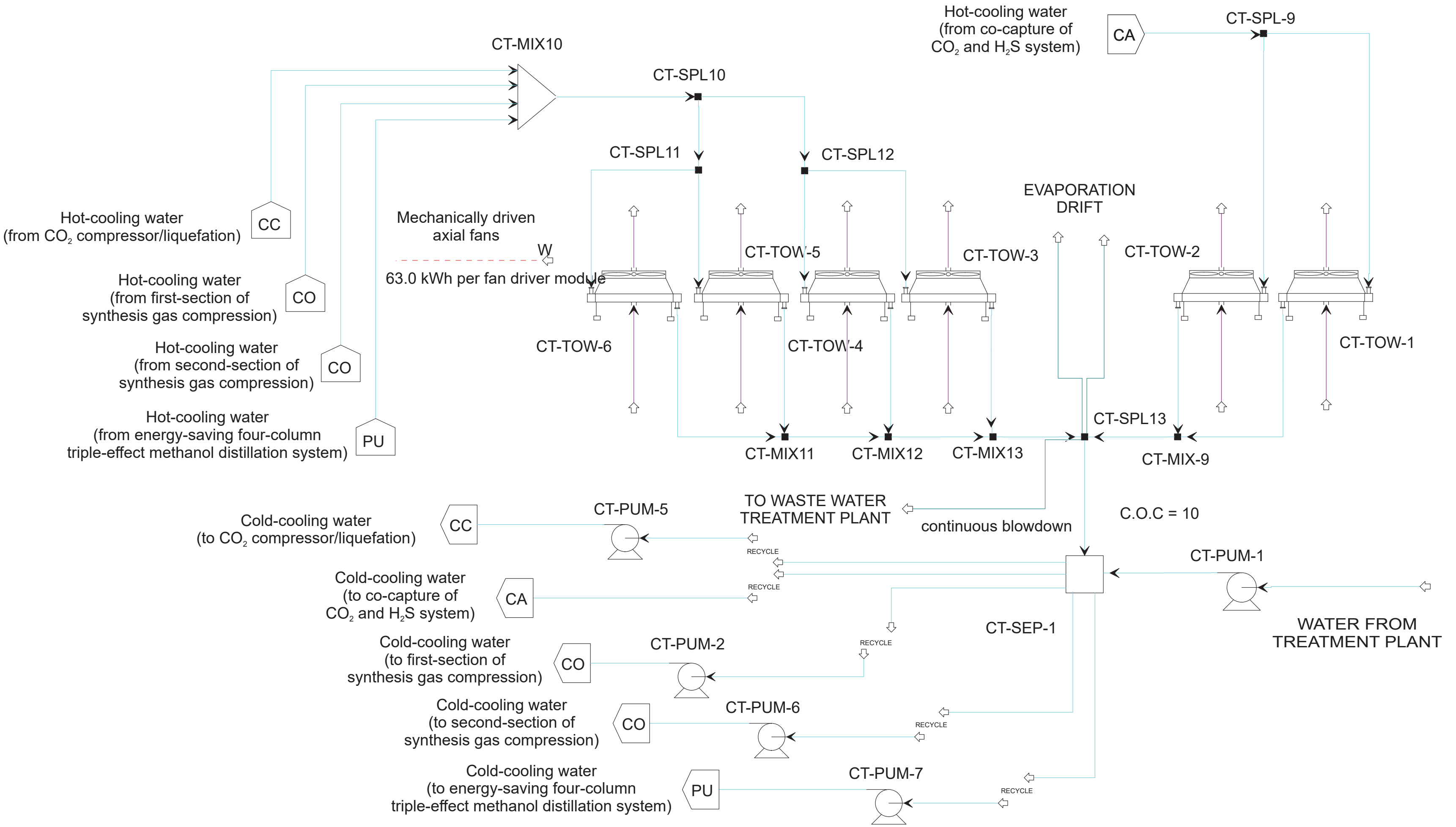
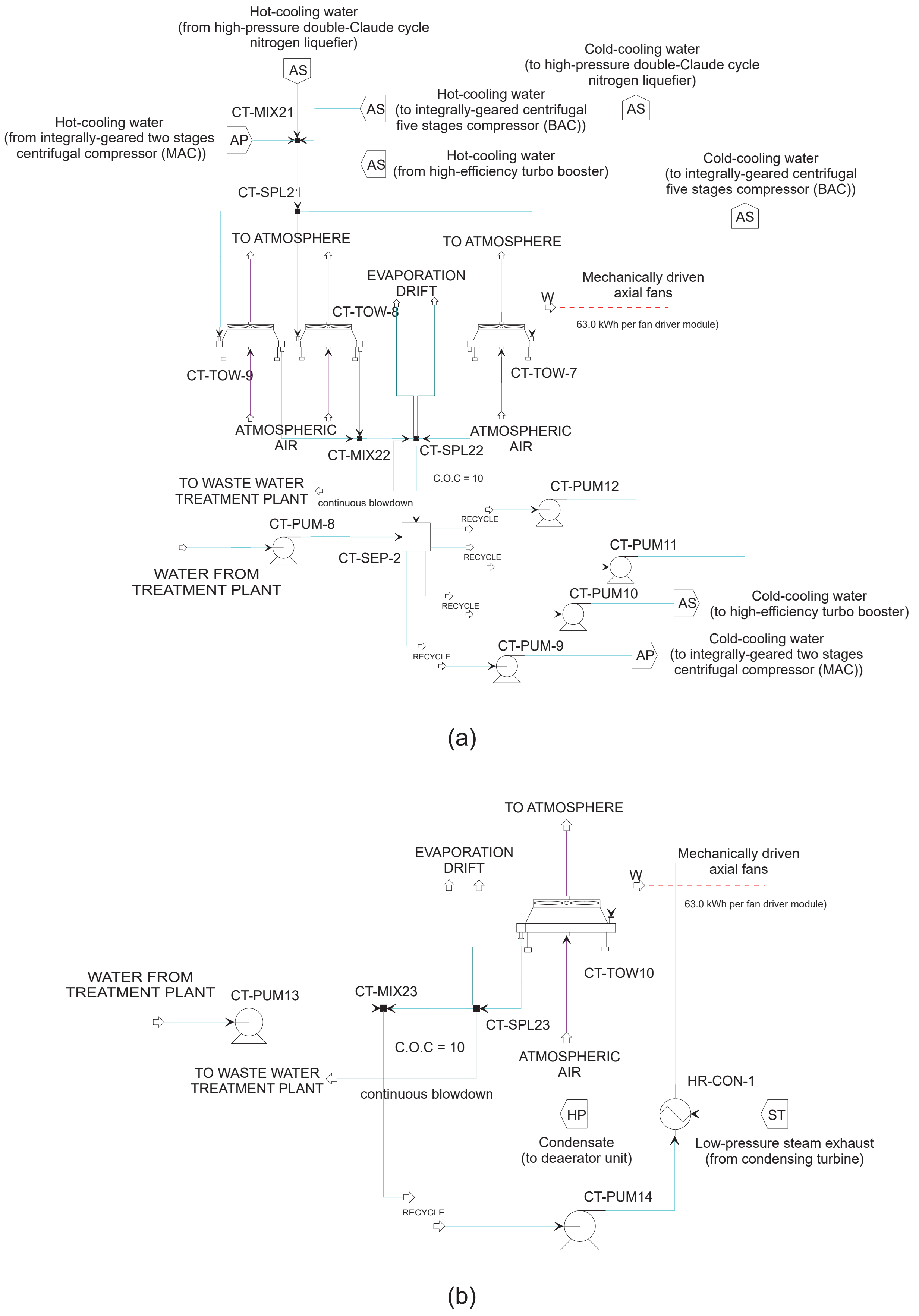


Figure 82 - Aspen Plus® v8.4 flowsheet of the first-section of multi-cells water-cooling tower for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3)



(a)

(b)

Figure 83 - Aspen Plus®v8.4 flowsheet of the multi-cells water-cooling tower for: a) second section for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC4); and b) third section for Biomass-to-Methanol (SC3)

Aspen Plus$^{®}$v8.4 flowsheet of the simplified first-section of (Figure 82) and simplified second section (Figure 83 (a)) of the multi-cells water-cooling tower for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and simplified third section (Figure 83 (b)) of the multi-cells water-cooling tower for Biomass-to-Methanol (SC3) are composts by: pumps (CT-PUM blocks); fans (CT-EFT streams); water-cooling tower modules (CT-TOW blocks); water-cooling tower basin (CT-SEP blocks); adjust losses (evaporation and drift); and blowdown system (CT-SPL blocks) and spreadsheet calculation of blowdown cycles of concentration (C.O.C) system.

The ambient condition of the atmospheric surrounding air (ATMOSPHERIC AIR) considered in the Aspen Plus$^{®}$v8.4 process model simulation is 25.0ºC at atmospheric pressure with relative humidity of 80.0% and web bulb temperature at about 21.3ºC.

The induced surrounding air exchange convective heat with the hot water in the water-cooling tower (CT-TOW blocks) represented as a simple HeatX exchange block (CT-TOW blocks). The surrounding air is induced upward through the fill (CT-TOW blocks) being heated from 25.0ºC to 40.0ºC. The hot cooling water flow downward through the fill (CT-TOW blocks) been cooled down from 43.0ºC to 30.0ºC.

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) the amount of surrounding air flowing through the fill (CT-TOW blocks) of the first-section of the multi-cells water-cooling tower is determined and controlled by design specification DS-CT-FG-1, design specification DS-CT-FG-2, FORTRAN calculator block CA-CT-FG-4 and FORTRAN calculator block CA-CT-FG-5 varying the mass flow rate (CT-AIR streams) of the surrounding air passing through the fill (CT-TOW blocks) to cooling down the hot water.

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3) the amount of surrounding air flowing through the fill (CT-TOW blocks) of the second-section of the multi-cells water-cooling tower is determined and controlled by design specification DS-CT-FG-3 and FORTRAN calculator block CA-CT-FG-6 varying the mass flow rate (CT-AIR streams) of the surrounding air passing through the fill (CT-TOW blocks) to cooling down the hot water.

In the Biomass-to-Mixed alcohols (SC3) the amount of surrounding air flowing through the fill (CT-TOW blocks) of the third section of the multi-cells water-cooling tower is determined and controlled by design specification DS-CT-FG-7 varying the mass flow rate (CT-AIR streams) of the surrounding air passing through the fill (CT-TOW blocks) to cooling down the hot water.

Treated fresh and recycled water as make-up water (WATER FROM TREATMENT PLANT) at atmospheric pressure and 25.0ºC is pumped (simplified by one pump) by make-up pump (CT-PUM-1) to the first-section of the multi-cells water-cooling tower and mixed with the down flow cooled-water at 30.0ºC in the water-cooling tower basin (CT-SEP-1). For the second-section of the multi-cells water-cooling tower make-up water (WATER FROM TREATMENT PLANT) is pumped by make-up pump (CT-PUM-8) and mixed with the down flow cooled-water at 30.0ºC in the water-cooling tower basin (CT-SEP-2).

For the third section of the multi-cells water-cooling tower in the Biomass-to-Methanol (SC3) make-up water (WATER FROM TREATMENT PLANT) is pumped by make-up pump (CT-PUM-13) and mixed with the down flow cooled-water at 30.0ºC in the water-cooling tower basin (CT-MIX-23).

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3) the cooling water available at 27.0ºC (heat sink) for the first-section of the multi-cells water-cooling tower is pumped (CT-PUM-2) to first-section of synthesis gas compression (conditioning), pumped (CT-PUM-3) to co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution, pumped (CT-PUM-5) to CO_2 gas integrally-geared multi-stage centrifugal compressor, pumped (CT-PUM-6) to second-section of synthesis gas compression (conditioning) and pumped (CT-PUM-7) to energy-saving four-column triple-effect methanol distillation system for grade AA methanol.

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3) the cooling water available at 27.0ºC (heat sink) for the second-section of the multi-cells water-cooling tower is pumped (CT-PUM-9) to integrally-geared two stages centrifugal compressor (MAC), pumped to (CT-PUM-10) high-efficiency turbo booster, pumped (CT-PUM-11) to integrally-geared centrifugal five stages compressor (BAC), pumped (CT-PUM-12) to high-pressure double-Claude cycle nitrogen liquefier.

In the Biomass-to-Methanol (SC3) the cooling water available at 27.0ºC (heat sink) for the third section of the multi-cells water-cooling tower is pumped (CT-PUM-14) to CEST condenser.

The cooling water at 27.0ºC is heated by passing through the user equipments to 43.0ºC (tower design limit), the hot water is duct-sent back to the multi-cells water-cooling tower (CT blocks) and discharged inlet into the cooling tower cells (CT-TOW blocks) at 43.0ºC to be cooled in a water closed-loop cycle system. The amount of water necessary for cooling down the equipments at required levels is determined and controlled by a set of design specification (e.g.: DS-CA-TL-1, DS-CA-TL-2, DS-CA-TL-3, DS-CO-TL-1, DS-CO-TL-2, DS-CO-TL-3, DS-PU-FL-3, DS-CT-FL-10, DS-CT-FL-11, DS-CT-FL-12, DS-CT-FL-13, DS-CT-FL-14, DS-CT-FL-15, DS-CT-FL-16, DS-CT-FL-17, DS-CT-FL-19) varying the mass flow rate of cooling water flows through the equipment users. The cooling water is heated at the limit of 43.0ºC (water-cooling tower design) and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

Hot water at 43.0ºC is fed in the first, second and third sections of multi-cells water-cooling tower (CT-TOW blocks) to be cooled down to 30.0ºC by direct contact in counter-flow with vertically upward induced (mechanical axial propeller fans) surrounding air through the fill (CT-TOW blocks) at atmospheric pressure and 25.0ºC. The model consider relative humidity of 80.0% and web bulb temperature at about 21.3ºC, which results in a range of 13.0ºC and an approach of 8.7ºC.

The Aspen Plus®v8.4 process model simulation of water-cooling tower system considers the water evaporation rate obtained by the Equation 21 and the drift loss rate obtained by the Equation 22. In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3) the equations is employed in the CT-SPL-13 for the first-section of the multi-cells water-cooling tower to determine the CT-EVA-1 and CT-DRI-1 streams by using FORTRAN calculator block CA-CT-LL-1 and in the CT-SPL-22 for the second-section of the multi-cells water-cooling tower to determine the CT-EVA-2 and CT-DRI-2 streams by using FORTRAN calculator block CA-CT-LL-2. In the Biomass-to-Methanol (SC3) the equations is employed in the CT-SPL-23 for the third section of the multi-cells water-cooling tower to determine the CT-EVA-3 and CT-DRI-3 streams by using FORTRAN calculator block CA-CT-LL-3.

A tower basin blowdown (CT-BLO streams) to remove or reduce the concentration of the impurities is developed in the Aspen Plus®v8.4 process model simulation according to Equation 25 as continuous blowdown system. In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3) the first-section of the multi-cells water-cooling tower (CT-SPL-13) consider the tower basin blowdown (CT-BLO-1) and blowdown cycles of concentration (C.O.C) determined by using FORTRAN calculator block CA-CT-LL-1 to remove the solids formed (not included in the Aspen Plus®v8.4 process model simulation). In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3) the second-section of the multi-cells water-cooling tower (CT-SPL-22) consider the tower basin blowdown (CT-BLO-2) and blowdown cycles of concentration (C.O.C) determined by using FORTRAN calculator block CA-CT-LL-2 to remove the solids formed (not included in the Aspen Plus®v8.4 process model simulation). In the Biomass-to-Methanol (SC3) the third section of the multi-cells water-cooling tower (CT-SPL-23) consider the tower basin blowdown (CT-BLO-3) and blowdown cycles of concentration (C.O.C) determined by using FORTRAN calculator block CA-CT-LL-3 to remove the solids formed (not included in the Aspen Plus®v8.4 process model simulation).

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3) the make-up water (WATER FROM TREATMENT PLANT) is pumped by make-up pump (CT-PUM-1) to the first-section of the multi-cells water-cooling tower basin (CT-SEP-1) and is pumped by make-up pump (CT-PUM-8) to the second-section of the multi-cells water-cooling tower basin (CT-SEP-2). In the Biomass-to-Methanol (SC3) is pumped by make-up pump (CT-PUM-13) to the third section of the multi-cells water-cooling tower basin (CT-MIX-23).

The make-up water for the multi-cells water-cooling tower is determined based on the water losses by evaporation (CT-EVA streams), drift (CT-DRI streams), and tower basin blowdown (CT-BLO streams), according to Equation 23.

In this research Master's degree is considered a recovery of 87.0%$_{w/w}$ of the water blowdown after the treatment as available cooling water to reuse/recycle at 27.0ºC. The amount of water recovered is determined by spreadsheet calculation model of the cooling water treatment process according to Equation 24. The discarded water fraction contains a high concentration of impurities (e.g.: minerals and salts), not included in the Aspen Plus$^{®}$v8.4 process model simulation.

The electricity required by the large mechanically driven axial fans (CT-EFT work streams) to induce the surrounding air upward through the fill in the cell-tower module (CT-TOW blocks) are estimated of 63.0 kWh per fan driver (module). The total of electricity required by the fan drivers is based on the number of cells (CT-TOW blocks) that compose the multi-cells water-cooling tower. The electricity consumed by the mechanical drivers in the axial fans (CT-EFT work streams) is estimated based on the Equation 26.

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3) the electricity required (CT-EFT-1 work stream) in the first-section of the multi-cells water-cooling tower by the large mechanically driven axial fans (CT-EFT-1 work stream) to induce the surrounding air upward through the fill in the cell-tower module (CT-TOW blocks) is determined and controlled by FORTRAN calculator block CA-CT-EF-1 varying the input value of the CT-EFT-1 work stream according to the number of necessary fans (63.0 kWh per fan driver).

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3) the electricity required (CT-EFT-2 work stream) in the second-section of the multi-cells water-cooling tower by the large mechanically driven axial fans (CT-EFT-2 work stream) to induce the surrounding air upward through the fill in the cell-tower module (CT-TOW blocks) is determined and controlled by FORTRAN calculator block CA-CT-EF-2 varying the input value of the CT-EFT-2 work stream according to the number of necessary fans (63.0 kWh per fan driver).

In the Biomass-to-Methanol (SC3) the electricity required (CT-EFT-3 work stream) in the third section of the multi-cells water-cooling tower by the large mechanically driven axial fans (CT-EFT-3 work stream) to induce the surrounding air upward through the fill in the cell-tower module (CT-TOW blocks) is determined and controlled by FORTRAN calculator block CA-CT-EF-3 varying the input value of the CT-EFT-3 work stream according to the number of necessary fans (63.0 kWh per fan driver).

7.2.26 Water cycles

The water cycle balance consider receive water: from treatment plant (BO-L-6) to process make-up water to deaerator unit (HR-DEA-1) in the Biomass-to-Methanol (SC1); from treatment plant (CO-L-4) to process make-up water to deaerator unit (HR-DEA-1) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); from treatment plant (CA-L-32) to washer packed-column section (CA-WAS-1) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); from treatment plant (WS-L-2) to energy-saving and steam generation system in the HT and LT catalyst WGS reactors at intermediate-pressure level considered in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); from treatment plant (PO-L-1 and PO-L-3) to desuperheater units (PO-MIX-1 and PO-MIX-2) in the Biomass-to-Methanol (SC1) and Biomass-to-Methanol (SC2); from treatment plant (GT-L-1) to three-circuit water inter-cooler exchanger (GT-1) in the high-performance sequential combustion full-flow advanced EvGT in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); from treatment (ME-L-1) plant to low-temperature cooler in the low-pressure methanol catalyst-synthesis (ME-2) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); from treatment plant to first-section of (CT-L-1) and to second section (CT-L-78) of water-cooling tower system in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); and from treatment plant to third section (CT-L-135) of water-cooling tower system in the Biomass-to-Methanol (SC3).

Also, sends wastewater: to treatment plant (BD-BLO-1) from boiler liquid-phase water blowdown (BD-FLA-1) in the Biomass-to-Methanol (SC1); to treatment plant (SC-L-12) from the excess of the wastewater recovered in the low-temperature synthesis gas wet cleaning system (SC-SPL-2) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); to disposal (SC-SLUR) from the sludge phase ($50\%_{w/w}$ of water content) removed in the low-temperature synthesis gas wet cleaning system (SC-SPL-2) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); to disposal (CA-L-28) from the reclaimer carbon-based filter (CA-SEP-1) in the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); to treatment plant (CO-BLO-1) from the condenser knock-out drum in the first-section of the synthesis gas compression in the integrally-geared centrifugal three stages compressor (CO-FLA-4) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Mixed alcohols (SC3); to treatment plant (CO-BLO-2) from the condenser knock-out drum in the second-section of the synthesis gas compression in the integrally-geared centrifugal three stages compressor (CO-FLA-7) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol

(SC3); to treatment plant (WS-BLO-3) from condensed water recovery and recycle system in the energy-saving and steam generation system in the HT and LT catalyst WGS reactors at intermediate-pressure level (WS-SEP-1) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); to treatment plant (GT-BLO-2) from the condenser knock-out drum (GT-FLA-1) in the high-performance sequential combustion full-flow advanced EvGT in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); to treatment plant (GT-BLO-1) from the buffer/equalizer inlet tank (GT-BUF-1) in the high-performance sequential combustion full-flow advanced EvGT in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); to treatment plant (CC-BLO-1) from the condenser knock-out drum in the CO_2 gas integrally-geared centrifugal six stages compressor (CC-FLA-7) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); to treatment plant (CT-BLO-1) from water-cooling tower blowdown (CT-SPL blocks) in the first-section of the multi-cells water-cooling tower in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); to treatment plant (CT-BLO-2) from water-cooling tower blowdown (CT-SPL blocks) in the second-section of the multi-cells water-cooling tower in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); to treatment plant (CT-BLO-3) from water-cooling tower blowdown (CT-SPL blocks) in the third section of the multi-cells water-cooling tower in the Biomass-to-Methanol (SC3); to treatment plant (GU-BLO-1) from condenser knock-out drum in the regenerative ZnO/CuO-based guard bed adsorber (GU-SEP-1) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); to treatment plant (RE-BLO-1) from condenser knock-out drums in the hydrogen recovery by four-bed PSA system (RE-MIX-1) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); to treatment plant (AP-BLO-1) from condenser knock-out drum in the integrally-geared two stages centrifugal compressor (MAC) (AP-FLA-1) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); to treatment plant (AP-BLO-2) from condenser knock-out drum in the integrally-geared two stages centrifugal compressor (MAC) (AP-FLA-2) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); to treatment plant (AS-BLO-2) from condenser knock-out drum in the integrally-geared six stages centrifugal compressor (BAC) (AS-FLA-1) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); and to treatment plant (AS-BLO-1) from condenser knock-out drum after the high-efficiency turbo booster compressor (AS-COM-1) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3).

Process steam/water losses occur due: water evaporation or condensation (PO-BLO-1) in equipments and pipe lines (PO-SPL-1) discharge $5.0\%_{w/w}$ of the process steam at 2.5 bar (PO-BLO-1) in the Biomass-to-Methanol (SC1); water evaporation (ME-VEN-1) in equipments and pipe lines (ME-SPL-1) discharge $2.0\%_{w/w}$ of the high-pressure steam (ME-SPL-1) generated in the high-pressure steam drum (ME-FLA-1) of the isothermal water-cooled fixed bed catalytic-synthesis reactor in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); treatment of boiler water blowdown discharge 15.0%$_{w/w}$ of the purged water (BD-BLO-1) (recovery and recycle of 85.0%$_{w/w}$ of the water blowdown) in the Biomass-to-Methanol (SC1); sludge disposal discharge 100.0%$_{w/w}$ of the water content in the sludge phase (SC-SLUR) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); treatment of the excess of recovered water in the low-temperature synthesis gas wet cleaning system discharge 5.0%$_{w/w}$ of the water (SC-L-12) (recovery and recycle 95.0%$_{w/w}$ of the recovered water) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); filtered amine residue disposal discharge 100.0%$_{w/w}$ of the water content in the residue fraction (CA-L-29) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); treatment of the water from the condenser knock-out drums discharge 5.0%$_{w/w}$ of the water (CO-BLO-1, CO-BLO-2, WS-BLO-1, WS-BLO-2, WS-BLO-3, GU-BLO-1, RE-BLO-1, CC-BLO-1, GT-BLO-1, GT-BLO-2, AP-BLO-1, AP-BLO-2, AS-BLO-1, and AS-BLO-2 streams) (recovery and recycle of 95.0%$_{w/w}$ of the condensed water) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); water evaporation (CT-EVA-1) and drift (CT-DRI-1) in the first-section of the water-cooling tower discharge 100.0%$_{w/w}$ of the water-stream in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); water evaporation (CT-EVA-2) and drift (CT-DRI-2) in the second-section of the water-cooling tower discharge 100.0%$_{w/w}$ of the water-stream in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); water evaporation (CT-EVA-3) and drift (CT-DRI-3) in the third-section of the water-cooling tower discharge 100.0%$_{w/w}$ of the water-stream in the Biomass-to-Methanol (SC3); treatment of the first-section of the water-cooling tower blowdown discharge 13.0%$_{w/w}$ of the purged water (CT-BLO-1) (recovery and recycle of 87.0%$_{w/w}$ of the water blowdown) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); treatment of the second-section of the water-cooling tower blowdown discharge 13.0%$_{w/w}$ of the purged water (CT-BLO-2) (recovery and recycle of 87.0%$_{w/w}$ of the water blowdown) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3); treatment of the third-section of the water-cooling tower blowdown discharge 13.0%$_{w/w}$ of the purged water (CT-BLO-3) (recovery and recycle of 87.0%$_{w/w}$ of the water blowdown) in the Biomass-to-Methanol (SC3).

As shown in Figure 79 the deaerator unit (HR-DEA-1) in the Biomass-to-Methanol (SC1) receive low-pressure steam from the flash vessel (BD-FLA-1) at 1.4 bar (deaerator pressure) and 109.0ºC (BD-G-1), steam at 2.5 bar and 130.0ºC (HR-G-15) from the HRSG LP circuit-level, pre-heated fresh-water at 1.4 bar and 43.0ºC (BO-L-8) as part of the make-up water (WATER FROM TREATEMENT PLANT) required in the deaerator unit (HR-DEA-1), water from the 1G sugarcane biorefinery processes at 2.5 bar and 90.0ºC (PO-L-7 and PO-L-8), and heated make-up raw water (WATER FROM TREATEMENT PLANT) at 1.4 bar and 105.0ºC (HR-L-13) closing the process water loop-cycle. Also as shown in Figure 79 the deaerator unit (HR-DEA-1) in the Biomass-to-Methanol (SC1) sends degassed and conditioned water at 1.4 bar and 105.0ºC to solid-fuel fired boiler (1G-thecnology) (HR-L-21), to HRSG system (HR-L-17), to high-temperature vertical CSC (HR-L-17) and to low-temperature vertical CSC (HR-L-15).

As shown in Figure 80, the deaerator unit (HR-DEA-1) in the Biomass-to-Methanol (SC2) receive steam at 2.5 bar and 130.0ºC (HR-G-13) from the HRSG LP circuit-level, water from the 1G sugarcane biorefinery processes at 2.5 bar and 90.0ºC (PO-L-6 and PO-L-7), and heated make-up raw water (WATER FROM TREATEMENT PLANT) at 1.4 bar and 105.0ºC (HR-L-13) closing the process water loop-cycle. Also, as shown in Figure 80, the deaerator unit (HR-DEA-1) in the Biomass-to-Methanol (SC2) sends degassed and conditioned water at 1.4 bar and 105.0ºC to HRSG system (HR-L-17), to high-temperature vertical CSC (HR-L-18) and to low-temperature vertical CSC (HR-L-15).

As shown in Figure 81, the deaerator unit (HR-DEA-1) in the Biomass-to-Methanol (SC3) receive steam at 2.5 bar and 130.0ºC (HR-G-13) from the HRSG LP circuit-level, heated make-up raw water (WATER FROM TREATEMENT PLANT) at 1.4 bar and 105.0ºC (HR-L-15), and condensed exhaust-steam at 1.4 bar and at about 48.0ºC (HR-L-14) from the CEST condenser closing the process water loop-cycle. Also, as shown in Figure 81, the deaerator unit (HR-DEA-1) in the Biomass-to-Methanol (SC3) sends degassed and conditioned water at 1.4 bar and 105.0ºC to HRSG system (HR-L-17), to high-temperature vertical CSC (HR-L-18) and to low-temperature vertical CSC (HR-L-19).

The amount of low-pressure steam at 2.5 bar and 130.0ºC from the HRSG LP circuit-level destined to deaerator unit (HR-DEA-1) is determined and controlled by design specification DS-HR-TL-1 varying the water/steam mass flow rate in the HRSG LP circuit-level and estimate-used into the deaerator unit (HR-DEA-1) as degassing agent. Low-pressure steam at 2.5 bar and 130.0ºC is used mainly to remove dissolved O_2 and CO_2 content in the process water cycle by raises the deaerator water temperature (make-up water and process water condenser return) to 1.4 bar and 105.0ºC in the deaerator unit (HR-DEA-1).

In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3) the make-up water supply to the deaerator unit (HR-DEA-1) from the water treatment plant is based on the mass balance of the process steam/water losses and recycled water cycle. The amount of water required in the Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3) is determined and controlled by design specification DS-CO-FL-1 and design specification DS-HR-FL-1 varying the mass flow rate of water (WATER FROM TREATMENT PLANT) fed into the first deaerator unit (HR-DEA-1). The amount of water required in the Biomass-to-Methanol (SC1) is determined and controlled by design specification DS-CO-FL-1, design specification DS-HR-FL-1 and controlled by design specification DS-AE-FL-1 varying the mass flow rate of water (WATER FROM TREATMENT PLANT) fed into the deaerator unit (HR-DEA-1).

Make-up water supply to the water-cooling tower system from the water treatment plant is based on the mass balance of the water-cooling tower system considering losses associated with evaporation, drift and blowdown. In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3) the make-up water fed (CT-L-1) into the first-section of the water-cooling tower system is controlled by design specification DS-CT-FL-1 varying the mass flow rate of water (WATER FROM TREATMENT PLANT). In the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3) the make-up water fed (CT-L-78) into the second-section of the water-cooling tower system is controlled by design specification DS-CT-FL-6 varying the mass flow rate of water (WATER FROM TREATMENT PLANT). In the Biomass-to-Methanol (SC3) the make-up water fed (CT-L-138) into the third section of the water-cooling tower system is controlled by design specification DS-CT-FL-18 varying the mass flow rate of water (WATER FROM TREATMENT PLANT)

7.2.27 Make-up water and water treatments

The mass flow rate of make-up water to treatment plant (fresh water) is determined using spreadsheet calculation models by a global mass balance of the complete water cycle considering the treatment of the wastewater in the wastewater treatment plant (not simulated) estimated according the spreadsheet calculation model of the water cycle (losses, recycles an reuse model).

Three distinct use types are required for the Biomass-to-Methanol scenarios, classified as:

f) make-up water for water-cooling tower system: fresh-water required by the cooling water cycle is defined by the mass flow rate of the evaporation, drift, and tower basin blowdown losses (not recovered);
g) make-up water for process water cycle: fresh-water required by the process water cycle is defined by the mass flow rate of the evaporative process and condensation losses in pipeline and equipments, by vent streams, blowdown losses and condensate knock-outs (not recovered);
h) make-up water for high-performance sequential combustion full-flow advanced EvGT water cycle: fresh-water required by the EvGT cooling water circuits and humidifier tower can be defined by the mass flow rate of the evaporative process and entrained vapor in the humidified air in the dual-chamber system;
i) make-up water for high-pressure steam generation drum: fresh-water required by the isothermal water-cooled fixed bed catalytic-synthesis reactor cooling

water circuit can be defined by the mass flow rate of the high-pressure steam generated off-drum at saturation conditions and the steam vent-losses in the high-pressure steam generation drum.

The recovered water fraction after the wastewater treatment to recycle/reuse is considered as “fresh” water (subtracting in the quantity of fresh-water intake) and the water fraction discharged (not recovered) with the impurities removed in the wastewater treatment process a water losses. The water treatment is simplified by the follow categories:

h) make-up raw water treatment: considers only the make-up of fresh-water obtained from the global mass balance of the complete water cycle, taking into account the recycle and reuse of available water;
i) cooling water treatment (maintenance): considers the make-up raw water obtained from the mass balance of the water tower cycle and the water circulating in the water tower cycle in closed loop-cycle (water maintenance), taking into account the recycle and reuse of available water;
j) process water treatment (maintenance): considers the make-up raw water obtained from the mass balance of the water process cycle and the water circulating in the water process cycle in closed loop-cycle (water maintenance), taking into account the recycle and reuse of available water;
k) cooling water treatment for water injection in the EvGT sequential burning chambers: considers the make-up raw water obtained from the mass balance of the cooling water circuits and the water injected by the humidified air in the EvGT sequential burning chambers.

The chemicals compounds and their consumption for treating water are determined by spreadsheet calculation model according to the type of water treatment required (make-up water, process water, cooling water and water special treatment. The water treatment is based on the water treatment processes available in the Ecoinvent 3 library (unit) in SimaPro$^{®}$v.7.3.3 software and in the water treatment process defined by the division of AIB of the CTBE/CNPEM for the 1G sugarcane biorefinery.

Table 23 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Methanol routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	**Biomass-to-Methanol route scenarios**		
	SC1	**SC2**	**SC3**
Thermochemical-biorefinery			
Cane stalks (tonnes/hr) 4.0 Mtc (basis)	503.018	503.018	503.018
Sugar production (tonnes/hr)	25.559	25.559	25.559
Anhydrous ethanol production (tonnes/hr)	21.013	21.013	21.013
Grade AA methanol production (tonnes/hr)	25.688	24.287	37.898
High-purity liquid argon production (tonnes/hr)	0.643	0.788	0.788
High-purity liquid nitrogen production (tonnes/hr)	107.201	130.921	130.921
Electricity exported to the electric power grid (MWh)	none	none	none
Installed power generation capacity (MW)	95.829	112.511	115.989
Electricity consumed by the thermochemical-biorefinery (MWh) [m]	95.829	112.511	115.989
Available raw biomass [a]			
Sugarcane bagasse available for use (tonnes/hr)	133.150	133.150	133.150
Sugarcane straw available for use (tonnes/hr)	42.279	42.279	42.279
Sugarcane bagasse imported (tonnes/hr)	none	none	87.396
Sugarcane bagasse reserve (tonnes/hr)	6.658	6.658	13.316
Sugarcane bagasse moisture content (%)	50.0	50.0	50.0
Sugarcane straw moisture content (%)	15.0	15.0	15.0
Consumption of sugarcane bagasse in the Biomass-to-Methanol route (tonnes/hr)	90.063	126.492	126.492
Consumption of sugarcane straw in the Biomass-to-Methanol route (tonnes/hr)	42.279	42.279	42.279
Consumption of sugarcane bagasse in the 1G-CHP/EBPST system (tonnes/hr)	36.430	none	81.376
Consumption of sugarcane straw in the 1G-CHP/EBPST system (tonnes/hr)	none	none	none
Dry biomass consumed in the Biomass-to-Methanol route (tonnes/hr) [a]	80.548	98.764	98.764
Surplus biomass (tonnes/hr) [a]	none	none	none
LHV_{AR} of bagasse (MJ/kg)	7.45	7.45	7.45
LHV_{AR} of straw (MJ/kg)	17.57	17.57	17.51
1G sugarcane biorefinery with annexed ethanol distillery (int)			
CHP/ST system	CHP/EBPST (SC1)	none	CHP/EBPST (SC1)
Integration mode	Integrated	Integrated	Standalone
Electricity required by the 1G sugarcane biorefinery (MWh)	15.0	15.0	15.0

Table 23 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Methanol routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Methanol route scenarios		
	SC1	**SC2**	**SC3**
1G sugarcane biorefinery with annexed ethanol distillery [(int)]			
Steam demand at 6.0 bar (dehydration) (tonnes/hr)	14.175	14.175	14.175
Steam demand at 2.5 bar (process) (tonnes/hr)	184.945	184.945	184.945
Biomass handling and sizing for gasification process			
Electricity required for sugarcane bagasse handling and milling (MWh)	1.981	2.783	2.783
Electricity required for sugarcane straw handling and milling (MWh)	0.334	0.344	0.344
Biomass multi-step dryer and control particulate emissions [a]			
Thermal energy required by the biomass dryers (GJ/hr) [a]	600.7	820.5	820.5
HHV_{AR} of biomass mix (MJ/kg) [a]	17.02	17.02	17.02
LHV_{AR} of biomass mix (MJ/kg) [a]	15.52	15.51	15.51
LHV_{db} of biomass mix (MJ/kg) [a]	17.53	17.53	17.53
Biomass mix moisture (%) [a]	10.0	10.0	10.0
Gasification of biomass in an atmospheric CFB directly-heated gasifier [a]			
Gasification agents	Oxygen / Steam	Oxygen / Steam	Oxygen / Steam
High-purity oxygen to gasifier (tonnes/hr)	31.741	38.883	38.883
Steam at 2.5 bar flow into the gasifier (tonnes/hr)	34.816	42.661	42.661
Raw synthesis gas temperature (ºC)	850.0	850.0	850.0
Oxygen agent inlet temperature (ºC)	120.0	120.0	120.0
Steam agent inlet temperature (ºC)	150.0	150.0	150.0
Equivalence ratio (ER_{O2})	0.297	0.297	0.297
Steam-to-biomass ratio (STBR)	0.50	0.50	0.50
Carbon conversion (%)	98.0	98.0	98.0
Hydrogen mol flow rate (mol/hr)	2,613.5	3.203,9	3,197.4
Monoxide carbon mol flow rate (mol/hr)	1,793.4	2,198.4	2,193.5
H_2/CO ratio	1.457	1.457	1.457
Gasifier cold-gas efficiency (%) [b]	76.31	76.32	76.32
Gasifier hot-gas efficiency (%) [b]	91.74	91.76	91.76
Synthesis gas flow mass rate (tonnes/hr)	152.762	187.303	187.304
HHV_{db} of synthesis gas (MJ/kg)	11.14	11.14	11.14

Table 23 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Methanol routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Methanol route scenarios		
	SC1	SC2	SC3
Gasification of biomass in an atmospheric CFB directly-heated gasifier [a]			
LHV_{db} of synthesis gas (MJ/kg)	10.06	10.06	10.06
Generation of bottom particulate material (tonnes/hr) [f]	4.309	5.040	5.040
Olivine mass flow rate - make-up (kg/hr)	805.260	956.649	956.649
MgO mass flow rate - make-up (kg/hr)	210.660	250.2641	250.2641
Fines-particulate matters removed by multi-cyclone system (kg/hr)	114.685	144,529	144,531
Syngas cooling and heat recovery			
Intermediate-pressure steam at 23 bar generated by the HT-CSC (tonnes/hr)	48.444	59.424	54.311
Intermediate-pressure steam temperature (ºC)	337.9	337.9	450.0
Low-pressure steam at 2.5 bar generated by the LT-CSC (tonnes/hr)	34.816	42.661	42.661
Low-pressure steam temperature (ºC)	150.0	150.0	150.0
Synthesis gas temperature after the HT-CSC (ºC)	411.0	411.0	411.0
Synthesis gas temperature after the LT-CSC (ºC)	111.0	111.0	111.0
Low-temperature synthesis gas wet cleaning system			
Recirculation of water in spray scrubber (tonnes/h)	1.094	1.341	1.341
Recirculation of water in condenser cooler (tonnes/h)	970.772	1190.606	1190.610
Electricity required by the blower (MWh)	1.025	1.257	1.257
Particulate removal by spray scrubber, condenser cooler and venturi system (kg/hr)	46.0	63.0	63.0
Persistent fine particles removal by WESP (kg/hr)	15.0	21.0	21.0
Generation of slurry (kg/hr)	566.355	710.219	710.219
Excess of water sent off-site to wastewater treatment plant (tonnes/hr)	27.186	33.314	33.379
Synthesis gas temperature after the wet cleaning system (ºC)	50.0	50.0	50.0
Synthesis gas compression (conditioning)			
Number of compression sections (sec)	2	2	2
Number of compression stages - sec 1	3	3	3
Number of compression stages - sec 2	2	2	2
Pressure of the cooled synthesis gas to HT-WGS / LT-WGS and EvGT (bar)	24.0	24.0	24.0
Pressure of the conditioned synthesis gas to methanol synthesis (bar)	51.0	51.0	51.0
Synthesis gas mass flow rate to compress - sec 1 (tonnes/hr)	124.972	153.207	153.207

Table 23 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Methanol routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Methanol route scenarios		
	SC1	SC2	SC3
Synthesis gas compression (conditioning)			
Synthesis gas mass flow rate to compress - sec 2 (tonnes/hr)	29.279	27.723	43.314
Condensed water knock-out to wastewater treatment plant - sec 1 (tonnes/hr)	11.568	14.181	14.180
Condensed water knock-out to wastewater treatment plant - sec 2 (tonnes/hr)	none	none	none
Electricity required to cooled-synthesis gas compression - sec 1 (MWh)	18.143	22.241	22.241
Electricity required to synthesis gas final compression - sec 2 (MWh)	2.081	2.032	3.073
Destination of the intermediate-pressure synthesis gas [i]			
Fraction destined to catalyst WGS system for adjust the hydrogen carbon ratio for low-pressure methanol catalytic-synthesis (%)	9.17	7.02	10.93
Fraction destined directly to EvGT for thermal and electrical energy supply (%) [g]	43.90	56.70	32.40
Fraction destined directly to CO_2 and H_2S co-capture system (%) [h]	46.93	36.28	56.67
HT and LT catalyst WGS reactors at intermediate-pressure level			
Catalyst type for HT catalyst WGS reactor	Fe_2O_3/Cr_2O_3 MgO	Fe_2O_3/Cr_2O_3 MgO	Fe_2O_3/Cr_2O_3 MgO
Catalyst type for LT catalyst WGS reactor	Zn-CuO/Al_2O_3	Zn-CuO/Al_2O_3	Zn-CuO/Al_2O_3
Mass of Fe_2O_3/Cr_2O_3 MgO catalyst load (tonnes)	2.849	2.673	3.943
Mass of Zn-CuO/Al_2O_3 catalyst load (tonnes)	0.761	0.714	1.531
Fe_2O_3/Cr_2O_3 MgO catalyst lifetime (low activity) (years)	4	4	4
Zn-CuO/Al_2O_3 catalyst lifetime (low activity) (years)	2	2	2
HT-WGS reactor nominal temperature (ºC)	300.0	300.0	350.0
LT-WGS reactor nominal temperature (ºC)	230.0	230.0	230.0
Synthesis gas pressure inlet into the WGS system (bar)	23.0	23.0	23.0
Steam to carbon monoxide molar ratio	4	4	4
Consumption of the intermediate-pressure steam by the reactors (tonnes/hr)	8.399	7.882	11.205
Intermediate-pressure steam temperature (ºC)	337.9	337.9	450.0
WGS energy-saving and steam generation			
Mass flow rate of recovered water by cooling/condensing vapor content in the main gas stream (tonnes/hr)	8.970	8.418	13.120
Make-up raw water to cooling and recovery heat system (tonnes/hr)	11.425	10.763	17.792
Water blowdown to wastewater treatment plant (tonnes/hr)	2.041	1.919	3.093

Table 23 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Methanol routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Methanol route scenarios		
	SC1	SC2	SC3
WGS energy-saving and steam generation			
Steam generation in low-pressure circuit (tonnes/hr)	14.972	14.089	21.805
Temperature of low-pressure steam generated (bar)	130.0	130.0	130.0
Pressure of the low-pressure steam generated - for use as process steam (bar)	2.5	2.5	2.5
Steam generation in intermediate-pressure circuit - to WGS system (tonnes/hr)	3.381	3.173	6.012
Temperature of the intermediate-pressure steam generated - to WGS system (bar)	420.0	420.0	420.0
Pressure of the intermediate-pressure steam generated - to WGS system (bar)	23.0	23.0	23.0
Synthesis gas temperature inlet the system	186.0	186.0	187.0
Synthesis gas temperature outlet the system	40.0	40.0	40.0
Co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution			
Synthesis gas pressure inlet in the absorber (bar)	22.0	22.0	22.0
Pressure of acid gas flow-out the desorber (bar)	1.7	1.7	1.7
Acid gas removal (captured) (tonnes/hr)	37.886	35.800	55.850
CO_2 removal efficiency (%)	96.0	96.0	96.0
H_2S content in the acid gas stream ($\%_{mol}$)	145 PPM	152 PPM	289 PPM
MDEA concentration ($\%_{w/w}$)	30.0	30.0	30.0
PZ concentration ($\%_{w/w}$)	5.0	5.0	5.0
Consumption of MDEA (kg/hr)	150.707	142.632	222.237
Consumption of PZ (kg/hr)	25.116	24.423	38.755
Lean MDEA/PZ aqueous solution mass flow rate (tonnes/hr) [d]	279.600	263.948	411.649
Consumption of thermal energy by the stripper reboiler (GJ/hr)	53.103	43.490	78.096
Fresh cool-make-up water to synthesis gas washer (kg/hr)	732.0	690.0	1075.0
Excess of water sent to wastewater treatment plant (tonnes/hr)	none	none	none
Filtered residues sent to wastewater treatment plant and final disposal (kg/hr)	231.608	219.57	341.648
Cooling water required by the system (tonnes/hr)	769.831	628.074	1132.189
CO_2 compression and storage/use (geological storage)			
Pressure required to liquefier CO_2 and to injection (bar)	78.0 / 150.0	75.0 / 150.	75.0 / 150.
Final generation of liquid CO_2 to injection (reservoir)	37.198	35.149	54.835

Table 23 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Methanol routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Methanol route scenarios		
	SC1	**SC2**	**SC3**
CO_2 compression and storage/use (geological storage)			
Number of compression stages (+1 liquid pump stage)	6+1	6+1	6+1
Condensed water knock-out to wastewater treatment plant (tonnes/hr)	0.688	0.650	1.015
Consumption of electricity to CO_2 compression/liquefaction and injection (MWh)	3.169	2.995	4.673
Regenerative ZnO/CuO-based guard bed adsorber system			
Adsorbed compounds (reduction)	H_2S; COS;SO_x; NO_x;HCl;Cl_2;CO_2	H_2S; COS;SO_x; NO_x;HCl;Cl_2;CO_2	H_2S; COS;SO_x; NO_x;HCl;Cl_2;CO_2
Catalyst bed fraction to remove selectively sulfur compounds	70% of ZnO	70% of ZnO	70% of ZnO
Catalyst bed fraction to remove selectively chlorine compounds	30% of CuO	30% of CuO	30% of CuO
ZnO/CuO catalyst lifetime (low activity) (years)	1 / 1	1 / 1	1 / 1
Mass of ZnO catalyst load (tonnes)	5.111	5.042	5.615
Mass of CuO catalyst load (tonnes)	2.190	2.161	2.406
Adsorption temperature (adsorber) (ºC)	38.0	38.0	38.0
Desorption temperature (desorber) (ºC)	350.0	350.0	350.0
Adsorption pressure (adsorber) (ºC)	22.0	22.0	22.0
Desorption pressure (desorber) (ºC)	5.0	5.0	5.0
Mass flow rate of synthetic air from ASU to partial catalyst bed regeneration (kg/hr) [j]	336.324	318.872	444.5
Desorber flue-gas mass flow rate (kg/hr)	422.663	400.362	565.604
Condensed water mass flow rate knock-out to wastewater treatment plant (kg/hr)	119.637	113.197	176.715
Capture efficiency of sulfur compounds (%)	99.0	99.0	99.0
Capture efficiency of chlorine compounds (%)	80.0 / 95.0	80.0 /95.0	80.0 /95.0
Capture efficiency of nitrogen compounds (%)	2.0	2.0	2.0
CO_2 removal efficiency (%)	3.0	3.0	3.0
Hydrogen separation by four-bed PSA system			
Operational mode	Differential loading pressure	Differential loading pressure	Differential loading pressure
Number of process steps	four-bed process	four-bed process	four-bed process
Adsorbed compounds [k]	Low polarity	Low polarity	Low polarity
Zeolite catalyst bed fraction (%)	60.0	60.0	60.0

Table 23 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Methanol routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Methanol route scenarios		
	SC1	**SC2**	**SC3**
Hydrogen separation by four-bed PSA system			
Alumina catalyst bed fraction (%)	5.0	5.0	5.0
Charcoal catalyst bed fraction (%)	35.0	35.0	35.0
Zeolite/Al_2O_3/Charcoal catalyst bed materials lifetime (low activity) (years)	2 / 1 / 1	2 / 1 / 1	2 / 1 / 1
Mass of Zeolite catalyst load (tonnes)	2.996	2.911	4.654
Mass of alumina catalyst load (tonnes)	0.248	0.241	0.386
Mass of charcoal catalyst load (tonnes)	1.743	1.694	2.708
Adsorption pressure (bar)	22.0	22.0	22.0
Desorption and regeneration pressure (bar)	5.0	5.0	5.0
Hydrogen recovery efficiency (%)	98.0	98.0	98.0
Pressurized light-gas inlet mass flow rate (tonnes/hr)	2.621	2.512	3.993
Recovered hydrogen mass flow rate (tonnes/hr)	0.266	0.246	0.132
Light-gas outlet mass flow rate (tonnes/hr) - to EvGT	2.266	2.183	3.471
Condensed water mass flow rate knock-out to wastewater treatment plant (kg/hr)	89.0	84.0	132.0
Low-pressure methanol catalytic-synthesis			
Catalytic-synthesis type	Two-steps	Two-steps	Two-steps
Catalytic-reactor type	Sequential double reactors	Sequential double reactors	Sequential double reactors
First reactor cooling mode	Gas-cooled	Gas-cooled	Gas-cooled
Second reactor cooling mode=type	Water-cooled	Water-cooled	Water-cooled
Commercial catalyst type	Methanol synthesis catalyst	Methanol synthesis catalyst	Methanol synthesis catalyst
Catalyst series	$CuO/ZnO/Al_2O_3$	$CuO/ZnO/Al_2O_3$	$CuO/ZnO/Al_2O_3$
$CuO/ZnO/Al_2O_3$ catalyst lifetime (years)	2 / 2 (4)	2 / 2 (4)	2 / 2 (4)
Mass of $CuO/ZnO/Al_2O_3$ catalyst load per reactor (tonnes)	126.052	133.292	196.660
Crude methanol productivity (g/kg_{cat} /hr)	200.0	200.0	200.0
Synthesis gas inlet temperature in the gas-cooled reactor (ºC)	130.0	130.0	130.0
Synthesis gas inlet temperature in the water-cooled reactor (ºC)	210.0	210.0	210.0
Synthesis gas inlet pressure in the gas-cooled reactor (ºC)	50.0	50.0	50.0
Temperature of the raw gas products after the water-cooled reactor (ºC)	265.0	265.0	265.0

Table 23 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Methanol routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Methanol route scenarios		
	SC1	SC2	SC3
Low-pressure methanol catalyst-synthesis			
Hydrogen to carbon ratio (SN_R) / (H_2-CO_2)/(CO+CO_2) ratio	2.00	2.00	2.00
Multi-pass CO conversion (%)	85.29	84.79	84.18
Multi-pass H_2 conversion (%)	73.97	74.55	74.04
Inlet mass flow rate of conditioned synthesis gas in the gas-cooled reactor (tonnes/hr)	37.713	35.717	56.166
Mass flow rate of crude methanol produced at 46 bar (tonnes/hr)	26.688	25.240	39.366
Raw gas products condense pressure (bar)	46.0	46.0	46.0
Raw gas products condense temperature (ºC)	50.0	50.0	50.0
Fraction of unconverted synthesis gas after gas/liquid separation (light-gas) (%)	50.62	51.33	51.00
Unconverted gas mass flow rate (tonnes/hr)	11.024	10.477	16.800
Fraction of the unconverted gas recycled back to methanol synthesis (%)	76.50	76.30	76.50
Unconverted gases purge-recycled to energy and hydrogen recovery (tonnes/hr)	2.591	2.483	3.984
Saturated water and steam drum pressure (bar)	45.0	45.0	45.0
Temperature of the high-pressure saturated steam generated (ºC)	257.7	257.7	257.7
High-pressure saturated steam mass flow rate (tonnes/hr)	18.704	18.457	30.803
Pressure of the low-pressure steam generated (bar)	2.5	2.5	2.5
Temperature of the low-pressure steam generated (ºC)	130.0	130.0	130.0
Low-pressure steam mass flow rate (tonnes/hr)	12.300	11.626	18.143
Energy-saving four-column triple-effect methanol distillation system			
Distillation columns layout	Four-column	Four-column	Four-column
Methanol quality	Grade AA	Grade AA	Grade AA
Methanol purity ($\%_{w/w}$)	99.93	99.93	99.93
First- column	Stabilizer degassing	Stabilizer degassing	Stabilizer degassing
Second-column	High-pressure	High-pressure	High-pressure
Third column	Low-pressure	Low-pressure	Low-pressure
Four column	Recovery	Recovery	Recovery
Number of stages in the degassing column	20	20	20
Number of stages of the high-pressure column	55	55	55
Number of stages of the low-pressure column	70	70	70

Table 23 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Methanol routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Methanol route scenarios		
	SC1	SC2	SC3
Energy-saving four-column triple-effect methanol distillation system			
Number of stages in the recovery column	15	15	15
Pressure in the top of the first- column (bar)	1.40	1.40	1.40
Pressure in the top of the second-column (bar)	6.50	6.50	6.50
Pressure in the top of the third column (bar)	1.20	1.20	1.20
Pressure in the top of the four column (bar)	1.46	1.46	1.46
Temperature of the top-product in the first-column (ºC)	35.0	35.0	35.0
Temperature of the top-product in the second-column (ºC)	119.3	119.3	119.3
Temperature of the top-product in the third-column (ºC)	40.0	40.0	40.0
Temperature of the top-product in the four-column (ºC)	83.1	83.1	83.1
Crude methanol mass flow rate (tonnes/hr)	26.658	25.211	39.321
Mass flow rate of light-end gases (tail-gas) from degassing column (tonnes/hr)	0.946	0.920	1.388
Mass flow rate of water content hydrocarbons (kg/hr)	24.0	21.0	35.0
Grade AA methanol mass flow rate (tonnes/hr)	25.688	24.287	37.898
First-column reboiler duty (GJ/hr)	3.61	3.41	5.32
Second-column reboiler duty (GJ/hr)	27.13	25.64	40.02
Third-column reboiler duty (GJ/hr)	7.93	7.51	11.70
Four-column reboiler duty (GJ/hr)	0.23	0.20	0.33
Low-pressure steam consumption (tonnes/hr)	12.300	11.626	18.143
Cooling water consumption (tonnes/hr)	420.984	397.829	621.194
Full-flow evaporative advanced class gas turbine (EvGT)			
Gas turbine cycle-type	Evaporative	Evaporative	Evaporative
Operational mode	Combined-cycle	Combined-cycle	Combined-cycle
Humidification-cycle type	Full-flow	Full-flow	Full-flow
Combustor type	Annular	Annular	Annular
Turbine blades cooling system	Bled air points	Bled air points	Bled air points
Ambient temperature (ºC)	25.0	25.0	25.0
Ambient pressure (bar)	1.01325	1.01325	1.01325
Relative humidity in atmospheric air (%)	80.0	80.0	80.0
HHV_{AR} of conditioned synthesis gas (MJ/kg)	10.75	10.90	10.52

Table 23 – Aspen Plus® v8.4 simulation parameters (input and output) of Biomass-to-Methanol routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Methanol route scenarios		
	SC1	SC2	SC3
Full-flow evaporative advanced class gas turbine (EvGT)			
LHV_{AR} of conditioned synthesis gas (MJ/kg)	9.71	9.84	9.52
Turbine inlet temperature (ºC)	1500.0	1350.0	1500.0
Turbine inlet pressure (bar)	23.0	23.0	23.0
Reheat combustion chamber pressure (bar)	4.81	4.37	4.79
Excess of oxygen (%) [c]	37.53	33.46	37.41
Conditioned fuel-gas mass flow rate (tonnes/hr)	52.997	81.913	49.904
Fraction of fuel-gas to reheat combustion (%)	47.36	40.96	47.58
Fresh-air mass flow rate (tonnes/hr)	231.247	336.514	212.884
Bleed-air coolant mass flow rate (kg of air /kg of inlet gas mass flow rate)	0.040	0.025	0.040
Installed power generation capacity (MW)	75.747	101.548	69.908
Grid frequency (Hz)	60.0	60.0	60.0
Net-electrical efficiency (%) [b]	46.91	40.13	40.13
Gross heat rate (kJ/kWh)	6793.0	7937.6	6793.2
Cooling system type	Closed loop	Closed loop	Closed loop
Air temperature after the intercooler heat exchanger (ºC)	27.0	27.0	27.0
Compressed-air temperature inlet the humidifier tower system (ºC)	80.0	80.0	80.0
Compressed-air temperature outlet the humidifier tower system (ºC)	195.0	195.0	195.0
Exhaust-gas mass flow rate (tonnes/hr)	300.530	442.634	277.781
Turbine exhaust-gas temperature (ºC)	1009.0	932.0	1009.0
Exhaust-gas temperature - after the air regenerator heat exchanger (ºC)	600.0	745.0	600.0
Mass flow rate of injected water into EvGT by saturated-air flow (tonnes/hr)	18.889	28.072	17.386
Hot-water temperature inlet the humidifier tower system (ºC)	210.0	210.0	210.0
Temperature of cold-water returning into loop-cycle (ºC)	61.0	61.0	61.0
Heat recovery steam generator (HRSG)			
HRSG type	Triple-pressure	Triple-pressure	Triple-pressure reheated
High-pressure steam (bar)	45.0	45.0	45.0
Intermediate-pressure steam (bar)	23.0	23.0	23.0
Low-pressure steam (bar)	2.5	2.5	2.5

Table 23 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Methanol routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Methanol route scenarios		
	SC1	SC2	SC3
Heat recovery steam generator (HRSG)			
Steam temperature of the high-pressure circuit (ºC)	420.0	420.0	450.0
Steam temperature of the intermediate-pressure circuit (ºC)	337.9	337.9	450.0
Steam temperature of the low-pressure circuit (ºC)	130.0	130.0	130.0
Steam generation by high-pressure circuit (tonnes/hr)	20.300	13.250	20.136
Steam generation by intermediate-pressure circuit (tonnes/hr)	20.306	13.597	17.136
Steam generation by low-pressure circuit (tonnes/hr)	23.492	112.277	10.365
Steam at 2.5 bar sent to deaerator (tonnes/hr)	5.827	5.258	10.365
Deaerator temperature (ºC)	105.0	105.0	105.0
Deaerator pressure (bar)	1.4	1.4	1.4
EvGT exhaust-gas temperature (ºC)	600.0	745.0	600.0
HRSG flue-gas temperature (ºC)	122.0	127.0	130.0
Steam turbine applied in combined-cycles (ST)			
Steam turbine type	BPST *	EBPST	CEST
High-pressure steam inlet-level (bar)	45.0	45.0	45.0
Intermediate-pressure steam inlet-level (bar)	23.0	23.0	23.0
Exhaust steam pressure (bar)	2.5	2.5	2.5
High-pressure steam temperature (ºC)	420.0	420.0	450.0
Exhaust steam at 2.5 bar to thermochemical-biorefinery (tonnes/hr)	99.355	83.183	none
Exhaust steam at 0.11 bar to condenser (tonnes/hr)	none	none	97.511
Extraction steam at 2.5 bar to thermochemical-biorefinery (tonnes/hr)	none	none	13.670
Steam extraction at 6.0 bar sent to 1G-dehydration system (tonnes/hr)	none	13.662	none
Isentropic turbine efficiency (%)	79.45	79.45	80.52
Electrical energy generator efficiency (%)	99.0	99.0	99.0
Installed power generation capacity (MW)	12.031	10.963	27.719
Traditional CHP/EBPST system			
Sugarcane bagasse consumption (tonnes/hr)	36.430	none	81.376
Exhaust steam at 2.5 bar sent to 1G biorefinery (tonnes/hr)	none	none	none
Oxygen excess ratio (%$_{w/w}$) [c]	0.08	none	0.12

Table 23 – Aspen Plus® v8.4 simulation parameters (input and output) of Biomass-to-Methanol routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Methanol route scenarios		
	SC1	**SC2**	**SC3**
Traditional CHP/EBPST system			
Steam pressure (bar)	22.0	none	22.0
Steam temperature (ºC)	320.0	none	320.0
Boiler carbon conversion (%$_{w/w}$)	99.0	none	99.0
Exhaust-gas temperature (Flue-gas) (ºC)	160.0	none	160.0
Boiler water blowdown (to treatment) (tonnes/hr)	3.766	none	8.459
Fly-ashes removal by emission control filters (fine matter) (tonnes/hr)	0.215	none	0.420
Generation of bottom ashes (tonnes/hr)	0.670	none	1.366
Boiler thermal efficiency 1 (%) [b]	86.34	none	86.81
Boiler thermal efficiency 2 (%) [b]	82.90	none	83.16
Steam turbine type	EBPST	none	EBPST
Exhaust steam at 2.5 bar sent to 1G biorefinery (tonnes/hr)	76.685	none	184.945
Steam extraction at 6.0 bar sent to 1G-dehydration system (tonnes/hr)	13.707	none	13.707
Isentropic turbine efficiency (%)	74.55	none	74.55
Electrical energy generator efficiency (%)	99.0	none	99.0
Installed power generation capacity (MW)	12.031	none	27.808
Double-column cryogenic ASU with high-purity argon recovery			
Air separation unit principle	Cryogenic liquefaction	Cryogenic liquefaction	Cryogenic liquefaction
Number of stages of the high-pressure column	45	45	45
Number of stages of the low-pressure column	75	75	75
Number of stages in the argon side arm double-column (by-partitioned)	100	100	100
High-pressure column design	Trays/float valve	Trays–float valve	Trays–float valve
Low-pressure column design	3-Pack/Mellapak	3-Pack/Mellapak	3-Pack/Mellapak
Argon side arm partitioned-column design	Pack/MellapakPl	Pack/MellapakPl	Pack/MellapakPl
High-purity argon production mode	Rectification	Rectification	Rectification
Adsorption/desorption system design	TPSA 2 vessels	TPSA 2 vessels	TPSA 2 vessels
Adsorption pressure (bar) and temperature (ºC)	5.0 / 30.0	5.0 / 30.0	5.0 / 30.0
Desorption pressure (bar) and temperature (ºC)	1.01 / 150.0	1.01 / 150.0	1.01 / 150.0
Mass of Zeolite catalyst load (tonnes)	7.208	8.822	8.822

Table 23 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Methanol routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues

Parameter	Biomass-to-Methanol route scenarios		
	SC1	**SC2**	**SC3**
Double-column cryogenic ASU with high-purity argon recovery			
Mass of alumina catalyst load (tonnes)	14.696	17.987	17.987
Zeolite/Al_2O_3 catalyst bed materials lifetime (low activity) (years)	2 / 1	2 / 1	2 / 1
Pressure in the top of the high-pressure column (bar)	5.20	5.20	5.20
Pressure in the top of the low-pressure column (bar)	1.22	1.22	1.22
Temperature in the top of the high-pressure column (ºC)	-178.5	-178.5	-178.5
Temperature in the top of the low-pressure column (ºC)	-194.7	-194.7	-194.7
Number of zones in the plate main heat exchanger	6	6	6
Number of zones in the plate sub-cooler exchanger	4	4	4
Plate condenser/reboiler mode	Energy-saving	Energy-saving	Energy-saving
Nitrogen liquefier type	High-pressure	High-pressure	High-pressure
Nitrogen liquefaction cycle	Double-Claude	Double-Claude	Double-Claude
Nominal pressure of the nitrogen liquefier (bar)	40.0	40.0	40.0
Number of stages of the main air compressor (MAC)	1	1	1
Number of stages of the booster air compressor (BAC)	5	5	5
Atmospheric air mass flow rate (tonnes/hr) [I]	161.812	198.050	198.050
High-purity liquid argon production (tonnes/hr)	0.643	0.788	0.788
High-purity liquid nitrogen production (tonnes/hr)	107.201	130.921	130.921
Mass flow rate of liquid oxygen as reserve (tonnes/hr)	1.576	1.934	1.933
Mass flow rate of gaseous oxygen sent to gasifier (tonnes/hr)	31.741	38.883	38.883
Purity of liquid argon obtained at plant ($\%_{mol}$)	99.7	99.7	99.7
Purity of liquid nitrogen obtained at plant ($\%_{mol}$)	99.1	99.1	99.1
Purity of oxygen obtained at plant ($\%_{mol}$)	98.3	98.3	98.3
Mass flow rate of synthetic air gas vent stream from low-pressure column (tonnes/hr)	16.181	19.805	19.805
Mass flow rate of purge gas from desorption column (tonnes/hr)	17.454	21.456	21.330
Consumption of electricity by inlet-air blower (MWh)	0.525	0.643	0.643
First energy-saving turbo booster (MWh)	1.213	1.485	1.485
Second energy-saving turbo booster (MWh)	3.014	3.689	3.689
Consumption of electricity by integrated main air compressor (MWh)	4.245	5.195	5.195
Consumption of electricity by booster air compressor (MWh)	3.656	4.475	4.475

Table 23 – Aspen Plus® v8.4 simulation parameters (input and output) of Biomass-to-Methanol routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(conclusion)

Parameter	Biomass-to-Methanol route scenarios		
	SC1	SC2	SC3
Double-column cryogenic ASU with high-purity argon recovery			
Consumption of electricity by high-pressure nitrogen liquefier (MWh) [m]	43.284	52.870	52.947
Total of electricity required by ASU plant (MWh)	52.030	63.629	63.707
Cooling water consumption by MAC (tonnes/hr)	208.396	254.988	255.075
Cooling water consumption by BAC (tonnes/hr)	208.497	255.159	255.159
Cooling water consumption by high-pressure nitrogen liquefier (tonnes/hr)	2774.279	3388.277	3393.817
Condensed water mass flow rate knock-out to wastewater treatment plant (kg/hr)	401.741	491.711	491.711
Multi-cells water-cooling tower [e]			
Number of sections (sec)	2	2	3
Tower cells required - sec 1	4 cells	4 cells	6 cells
Tower cells required - sec 2	5 cells	7 cells	7 cells
Tower cells required - sec 3	none	none	5 cells
Make-up water (with recycle) - sec 1 (tonnes/hr)	63.594	63.834	87.830
Make-up water (with recycle) - sec 2 (tonnes/hr)	83.366	101.857	101.993
Make-up water (with recycle) - sec 3 (tonnes/hr)	none	none	79.859
Water evaporation - sec 1 (tonnes/hr)	52.485	52.683	72.487
Water evaporation - sec 2 (tonnes/hr)	68.803	84.064	84.176
Water evaporation - sec 3 (tonnes/hr)	none	none	65.909
Water drift - sec 1 (tonnes/hr)	5.278	5.297	7.289
Water drift - sec 2 (tonnes/hr)	6.918	8.453	8.464
Water drift - sec 3 (tonnes/hr)	none	none	6.627
Tower basin blowdown (to treatment) - sec 1 (tonnes/hr)	5.832	5.854	8.054
Tower basin blowdown (to treatment) - sec 2 (tonnes/hr)	7.645	9.340	9.353
Tower basin blowdown (to treatment) - sec 3 (tonnes/hr)	none	none	7.323
Electricity required by fan drivers - sec 1 (kWh)	252.0	252.0	378.0
Electricity required by driver fans- sec 2 (kWh)	315.0	441.0	441.0
Electricity required by driver fans- sec 3 (kWh)	none	none	315.0
Water cycles			
Process water/steam maintenance (tonnes/hr)	72.039 **	85.7716 **	69.226
Cooling water maintenance (tonnes/hr)	173.764	199.328	206.573

Table 23 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Methanol routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(conclusion)

Parameter	Biomass-to-Methanol route scenarios		
	SC1	SC2	SC3
Water cycles			
Make-up raw water (tonnes/hr)	188.843 [**]	219.756 [**]	208.179
Pre-heated fresh-water as deaerator make-up (tonnes/hr)	20.883 [**]	26.361 [**]	1.258
Generation of deaerated hot water (tonnes/hr)	217.380 [**]	221.492 [**]	109.134

(int) reference scenario for surplus biomass and integration with thermochemical routes

[a] biomass refers to sugarcane bagasse and sugarcane straw

[b] efficiency based on LHV_{AR} of fuel at 25ºC and 1 atm

[c] excess based on inlet oxygen and not in the stoichiometric oxygen for combustion

[d] lean MDEA/PZ aqueous absorbing-solution mass flow rate inlet in the top of the absorber

[e] section 1 (sec1) to cooling compressors systems and co-capture of CO_2 and H_2S system, section 2 (sec2) to cooling ASU compressors systems, and section 3 (sec 3) to condensing CEST exhaust-steam

[f] considers all solid matters removed, including bed media and catalytic active materials

[g] synthesis gas without passing through the CO_2 and H_2S co-capture system

[h] sent together with the synthesis gas resultant from the catalyst WGS reactors

[i] synthesis gas after the compression-section 1

[j] synthetic air without impurities from ASU vent stream (similar to air composition) used in the catalyst regeneration processes, represented as continuous mass flow rate (simplified form) considering the adsorption/desorption cycle time.

[k] non-adsorbable molecules as N_2, CO, CO_2, hydrocarbons and water vapor

[l] considers all air fractions (e.g.: N_2, O2, Ne, He, Ar, Xe, Kr)

[m] considers the consumption of electricity by the liquefaction process of nitrogen. If the nitrogen is emitted to atmosphere, will be electricity surplus to electric power grid.

* steam turbine without steam extractions

** account for water cycle the 1G-CHP/ST system and the steam (heat) to equipment users in the 1G sugarcane biorefinery.

8 Biomass integrated directly-heated gasifier and mixed alcohols catalyst-synthesis integrated at an optimized first generation sugarcane biorefinery with annexed ethanol distillery

Second generation (2G) ethanol (E2G) as renewable liquid transportation fuel in Brazil, from sugarcane bagasse and straw can be competitively produced by biochemical or thermochemical conversion routes in sugarcane biorefineries (new generation).

The new generation of sugarcane biorefinery plants to be built and the future expansions of existing plants to supply the growing demand for sugar, liquid biofuels, and/or electricity also must take into consideration the more stringent global environmental standards, the scarcity of fossil resources, and the necessity of occupy arable land to supply the growing demand for food's.

Biomass integrated directly-heated gasifier and mixed alcohols catalyst-synthesis (Biomass-to-Mixed alcohols) aimed at production of ethanol (anhydrous form) have a great potential to be the sustainable future technology. In order to increase the productive capacity and efficiency of the sugarcane biorefinery without increasing the sugarcane agricultural land occupation (ALO), reducing the environmental impacts in the supply chain.

8.1 Scenarios assessed

Three possible thermochemical-biorefinery scenarios applying mixed alcohols catalyst-synthesis (Biomass-to-Mixed alcohols) were simulated in Aspen Plus$^{®}$v8.4 process simulation platform and assessed under the scope of the VSB tool, taking into account the integral use of available sugarcane bagasse and straw for the efficient production of ethanol while supply the thermal and electrical energy required by the thermochemical-biorefinery.

Thermochemical-biorefinery scenarios applying mixed alcohols catalyst-synthesis are defined in the section 3.4.5 (Biomass to mixed alcohols production by biomass integrated directly-heated gasifier and mixed alcohols catalyst-synthesis). A scheme of the sugar, ethanol, mixed higher-molecular alcohols, and chemicals production from Biomass-to-Mixed alcohols route integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery is detailed in the Figure 84 for Biomass-to-Mixed alcohols scenario 1 (SC1), in the Figure 85 for Biomass-to-Mixed alcohols scenario 2 (SC2), and in the Figure 86 for Biomass-to-Mixed alcohols scenario 3 (SC3).

Figure 84 - Flow block diagram of biomass integrated directly-heated gasifier and mixed alcohols catalyst-synthesis in energy and mass integration mode integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery: Scenario 1 (SC1)

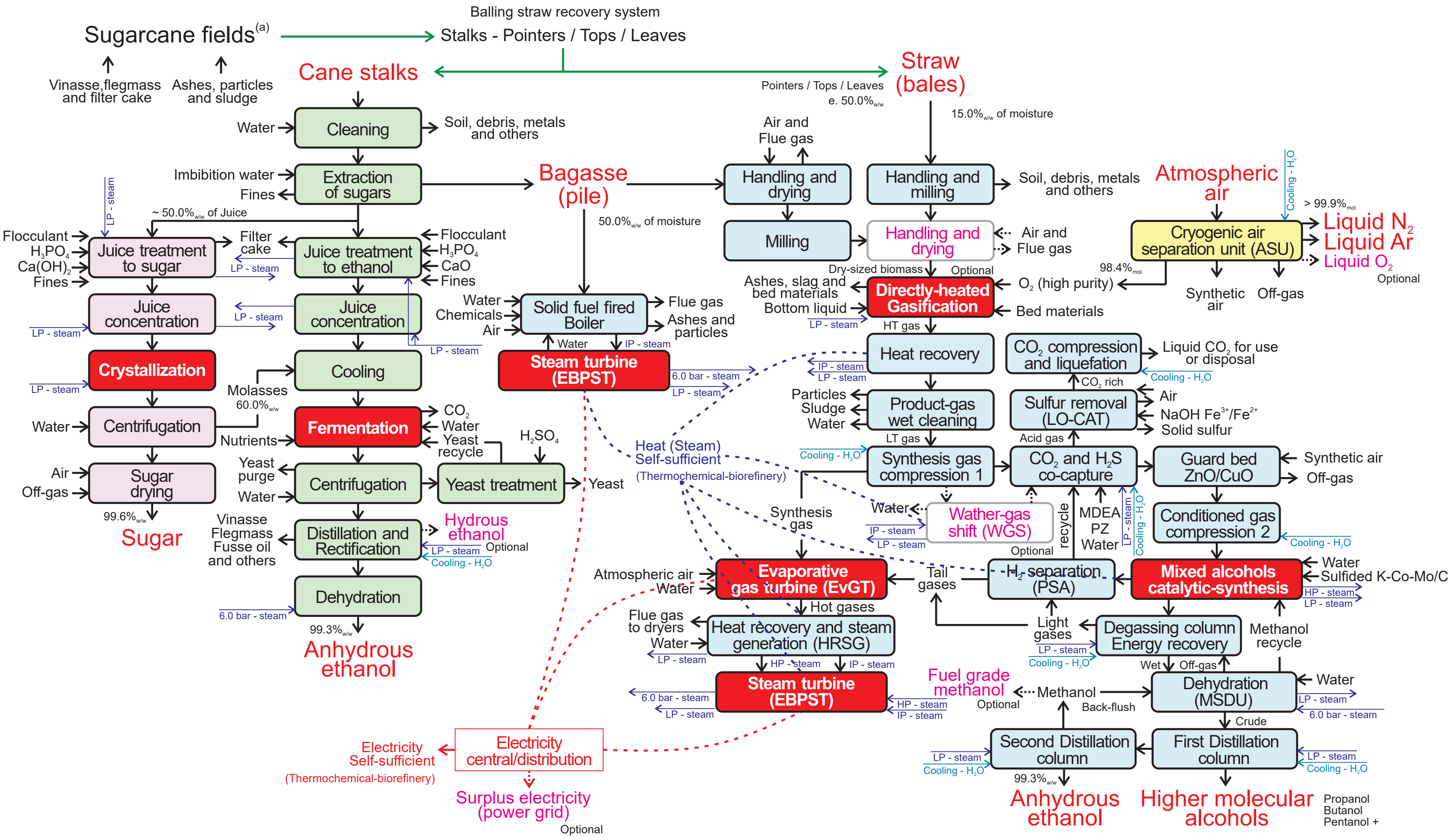
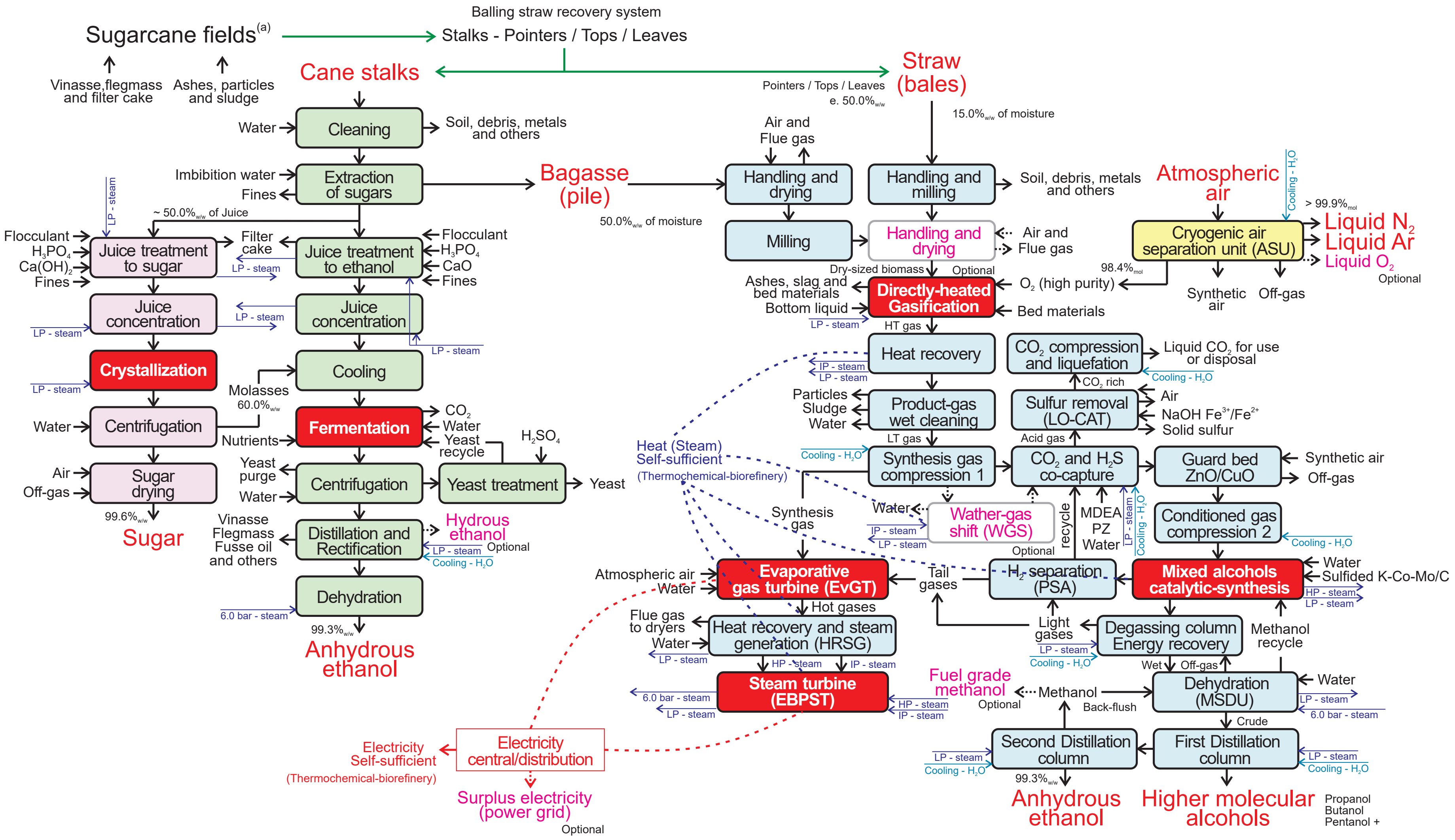


Figure 85 - Flow block diagram of biomass integrated directly-heated gasifier and mixed alcohols catalyst-synthesis in energy and mass integration mode integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery: Scenario 2 (SC2)



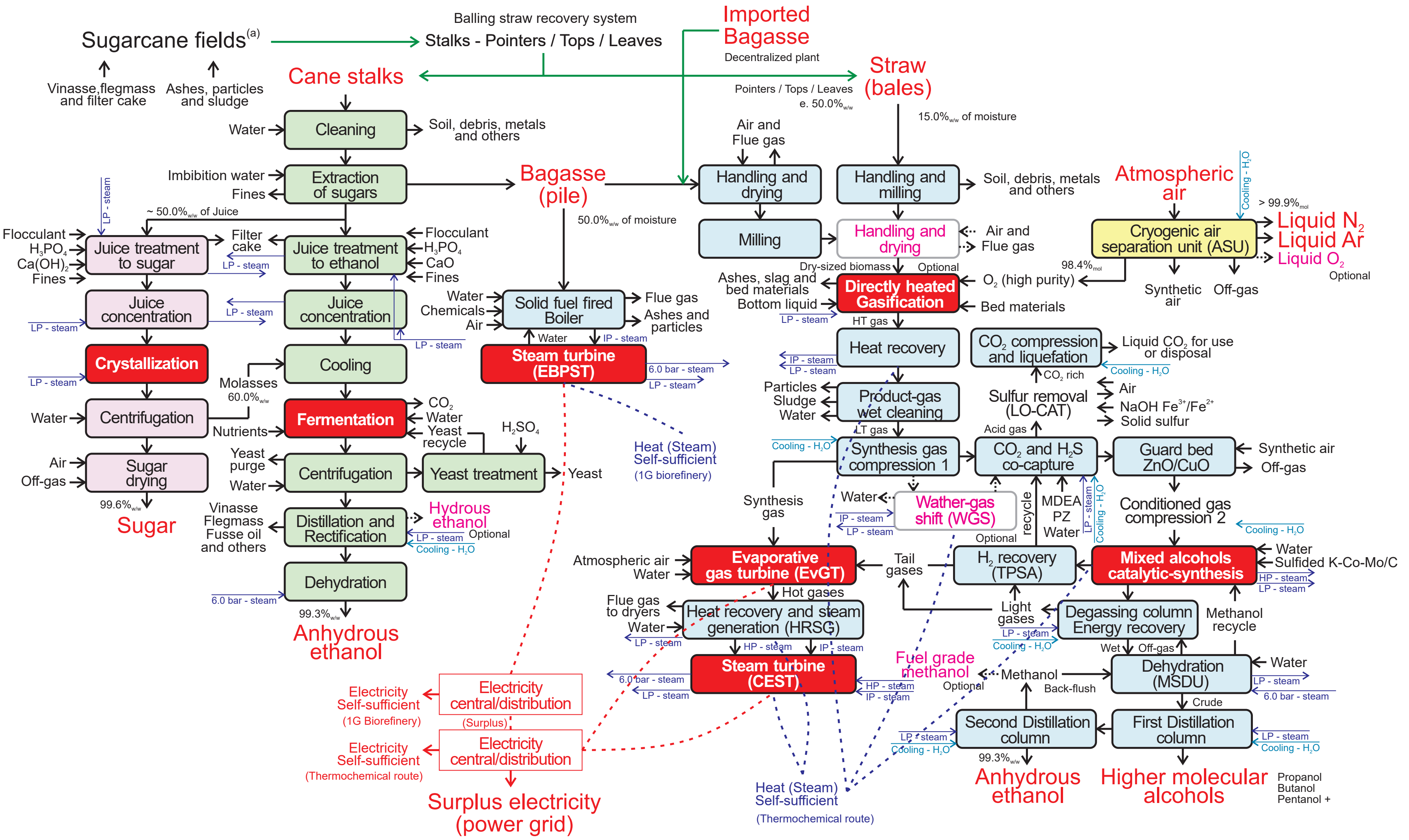


Figure 86 - Flow block diagram of biomass integrated directly-heated gasifier and mixed alcohols catalyst-synthesis in standalone mode integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery: Scenario 3 (SC3)

Biomass-to-Mixed alcohols scenario 1 (SC1), Biomass-to-Mixed alcohols scenario 2 (SC2), and Biomass-to-Mixed alcohols scenario 3 (SC3) are integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery according to section 5 (First generation sugarcane biorefinery), and to agricultural and industrial phases of the 1G sugarcane biorefinery assessed by the division of AIB of the CTBE/CNPEM and published – *The Virtual Sugarcane Biorefinery (VSB)*: 2011 Report (BRAZILIAN BIOETHANOL SCIENCE AND TECHNOLOGY LABORATORY, 2012) – and in – Virtual Biorefinery: An Optimization Strategy for Renewable Carbon Valorization (BONOMI et al., 2016).

Biomass-to-Mixed alcohols route scenarios implemented in Aspen Plus®v8.4 process simulation platform to evaluate the ethanol, mixed higher-molecular alcohols, and chemicals production while supply the thermal and electrical energy requirements of thermochemical-biorefinery. Available sugarcane bagasse and straw are gasified in an atmospheric CFB directly-heated gasifier using high-purity oxygen and steam gasification agents to produce synthesis gas. Therefore, is conditioned and then used in the isothermal water-cooled fixed bed synthesis $KCoMoS_2/C$ (Sulfided Co-K-Mo/C) catalyst reactor with loop recycle system for unconverted synthesis gas (light-gas) and distillated methanol (ratification). Also, can be directly used in a high-performance advanced class evaporative (humidification tower) gas turbine (EvGT) in combined-cycle (CC) mode with steam turbine (ST) system (Rankine-cycle cogeneration system) for thermochemical route-cycles.

Aspen Plus®v8.4 complete flowsheet`s of Biomass-to-Mixed alcohols detailed scenarios are presented in the APPENDIX A. Figure A25 shows Biomass-to-Mixed alcohols scenario 1 (SC1), Figure A26 shows the Biomass-to-Mixed alcohols scenario 2 (SC2), and Figure A27 shows the Biomass-to-Mixed alcohols scenario 3 (SC3).

8.1.1 Physical properties

The GLOBAL property methods used are ELECNRTL, RKS-BM, and VANL-RK

The local properties method used is: IDEAL for biomass handling and sizing, and biomass multi-step dryer and control particulate emissions; RKS-BM for biomass multi-step dryer and control particulate emissions, gasification of biomass in an atmospheric CFB directly-heated gasifier, syngas cooling and heat recovery, CO_2 compression and storage/use, first-section of synthesis gas compression (conditioning), second-section of synthesis gas compression (conditioning), high-performance sequential combustion full-flow advanced EvGT, HRGS system, traditional CHP system applying EBPST system, mixed alcohols catalyst-synthesis, HT and LT catalyst WGS reactors at intermediate-pressure level with energy-saving and steam generation, regenerative ZnO/CuO-based guard bed adsorber, energy-saving integrated turbo compressor & expander (turbo booster), hydrogen recovery by four-bed PSA system, and for gaseous streams side; ELECNRTL for low-temperature synthesis gas wet cleaning system, and co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution; NRTL-RK for three-column double-effect alcohols distillation system (ethanol purification), and Zeolite-based MSDU for mixed alcohols; VANL-RK for double-column cryogenic ASU with high-purity argon recovery; IAPWS-95 for multi-cells water-cooling tower, water cycles, EBPST and CEST systems for thermochemical route-cycles, traditional CHP system applying EBPST system, HT and LT catalyst WGS reactors at intermediate-pressure level with energy-saving and steam generation, direct-contact desuperheater units, mixed alcohols catalyst-synthesis, for pure water-side streams, and for pure steam-side streams.

Non-conventional solids physical property method used for BAGASSE and STRAW component properties is the HCOALGEN model (general coal models) applying the Mott and Spooner correlation (4 option code) according to section 3.7 (Non-conventional solids physical property methods) for estimate the enthalpy, and COALIGT model for estimate the density.

8.1.2 Available raw biomass

Raw sugarcane bagasse (SUGARCANE BAGASSE) is represented by BAGASSE and SOIL streams according to Table 9Table 9, and raw sugarcane straw (SUGARCANE STRAW) is represented by STRAW and TRASH according to Table 9. METAL stream was added to represent the amount of the tramp metals removed by the magnetic head pulleys (inlet-to-outlet model). Others debris were not considered present (to specify removal process) and can be accounted for in the trash fraction (TRASH) as inert material.

Sugarcane straw (SUGARCANE STRAW) is collected from the field (after the sugarcane harvesting) using a baling system (with pre-chopping system). In this system, the straw is separately sent from the cane stalks to the thermochemical-biorefinery. The transport is made using trucks (up to 25 tonnes/vehicle) or road trains (up to 70 tonnes/vehicle). All the Biomass-to-Mixed alcohols scenarios consider that $50.0\%_{w/w}$ of the total sugarcane straw available is recovered and sent to the thermochemical-biorefinery with $15.0\%_{w/w}$ of moisture content (on-site). As the transport vehicle enters the plant they are weighed and the straw bales are dumped (PR-MIX-3) or removed by adapted cane loaders and stored (PR-MIX-3) as feedstock for further processes.

In the Biomass-to-Mixed alcohols (SC1), part of available bagasse (BAGASSE) is belt-conveyed directly to the traditional CHP/EBPST system or to bagasse pile (PR-SPL-1) for burning purpose, generating thermal and electrical energy to supply part of the energy required by the 1G sugarcane biorefinery while Biomass-to-Mixed alcohols route supply the other part. In the Biomass-to-Mixed alcohols (SC2), the available bagasse (BAGASSE) is belt-conveyed directly to the bagasse flash dryers (DR-DRY-1) in the Biomass-to-Mixed alcohols route or to bagasse pile (PR-SPL-1) as feedstock for further processes. In the Biomass-to-Mixed alcohols (SC3), part of available bagasse (SUGARCANE BAGASSE) is burned to generate the thermal and electrical energy to supply all of this energy required by the 1G sugarcane biorefinery. Surplus bagasse (SUGARCANE BAGASSE) from the boiler-pile or directly from the cane mills is conveyed (centralized plant) or transported (decentralized plant) as available feedstock to the Biomass-to-Mixed alcohols plant together imported bagasse (scale setting).

8.1.3 Biomass handling and sizing

Sugarcane bagasse (SUGARCANE BAGASSE) at a moisture content of 50.0%$_{w/w}$ after the cane mills (driver by electrical motors) is transported by a conveyor (screw, drag or belt) to a temporary pile (PR-SPL-1) (feeding or equalization pile) or sent directly to the bagasse flash dryers (DR-DRY-1) by feeder conveyor (PR-MIX-1) or in the Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC2) to biomass feed drum (PR-MIX-5) in the traditional solid-fuel fired boiler (BO blocks) to be burned in the boiler chamber (BO-COMBU).

As shown in Figure 33 the Aspen Plus®v8.4 flowsheet of the simplified aggregated-steps model for the biomass handling and sizing in the BIG-ICE/CC (SC1) is the same model with modified parameters in the Biomass-to-Mixed alcohols (SC1) and as shown in Figure 34 the Aspen Plus®v8.4 flowsheet of the simplified aggregated-steps model for the biomass handling and sizing in the BIG-ICE/CC (SC2) is the same model with modified parameters in the Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3). The Aspen Plus®v8.4 flowsheet`s are compost by dumper (PR-MIX-3), storage area (PR-MIX-3), temporary bagasse pile (PR-SPL-1 and PR-SPL-3), bagasse pre-milling machine (PR-CRU-1), fine-size milling machines (DR-CRU-1), straw fine-size cutting-milling machine (DR-CRU-2), pre-sizing bagasse screen-deck solid-solid classifier (PR-CLA-1), bagasse screen-deck solid-solid classifier (PR-CLA-2), straw screen-deck solid-solid classifier (PR-CLA-3), oversized bagasse mixer (PR-MIX-2), unpacking and preparation area (PR-SPL-2), magnetic head pulleys (PR-ELE-1), magnetic separator (PR-SCR-5), screw-conveyor (PR-SCR-7), oversized straw mixer (PR-MIX-4), belt-conveyor (PR-SCR-1), bagasse feeder conveyor (PR-MIX-1), transporter (PR-SCR-3), screw-conveyed (PR-SCR-2), drag-conveyor (PR-SCR-4), screw-conveyor (PR-SCR-6) and screw-conveyor (PR-SCR-7).

The Aspen Plus®v8.4 process model simulation considers 5.0%$_{w/w}$ of the raw wet bagasse (BAGASSE) reserved in the pile (RESERVE BAGASSE) for brief stops and start-up.

In the Biomass-to-Mixed alcohols (SC1) a part of the raw bagasse (BAGASSE) can be used (or not) as received (wet) from the cane mills to be burned in the solid-fuel fired boiler (BO-COMBU) and another part from the cane mills or temporary bagasse pile (PR-SPL-1) is screw-conveyed (PR-SCR-2) directly to first-stage bagasse flash dryer (DR-DRY-1) to reduce the moisture content before the gross-size reduction stage (PR-CRU-1).

As shown in Figure 33 the Aspen Plus®v8.4 flowsheet of the biomass handling and sizing in the BIG-ICE/CC (SC1) which is the same model with modified parameters in the Biomass-to-Mixed alcohols (SC1) with 1G-CHP/EBPST system wherein the bagasse (SUGARCANE BAGASSE) from the cane mills can be directly belt-conveyed (PR-SCR-8) to boiler fuel feeders or from the pile using a tractor (actual system) to carries part of the bagasse available to the conveyor boiler feed tray (PR-MIX-5).

In the Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) raw bagasse (BAGASSE) from the cane mills or temporary bagasse pile (PR-SPL-1) are screw-conveyed (PR-SCR-2) directly to first-stage bagasse flash dryer (DR-DRY-1) to reduce the moisture content before the gross-size reduction stage (PR-CRU-1). After the first-stage of drying (DR-DRY-1), the bagasse is belt-conveyed (PR-SCR-1) to a pre-milling bagasse machine (PR-CRU-1) to gross-size reduction. After this stage, the bagasse is classified in a screen-deck solid-solid classifier (PR-CLA-2), the fine fraction is directly screw-conveyed (PR-SCR-2) to bagasse second-flash dryer (DR-DRY-1) and the oversized fraction is recycled and mixed back (PR-MIX-2) to further gross-size reduction cycle in closed-loop at size requirements. Gross-sized and pre-dried bagasse is screw-conveyed (PR-SCR-2) to bagasse second-flash dryer (DR-DRY-1) to reduce the moisture content to 10.0%$_{w/w}$ (dry bagasse) before the fine-size reduction stage (PR-CRU-1).

The gross-sized and dried bagasse is belt-conveyed (PR-SCR-1) to pre-sizing classification in a screen-deck solid-solid classifier (PR-CLA-1) and after to the fine-size milling machine (PR-CRU-1) and classification in a screen-deck solid-solid classifier (PR-CLA-2) according to ideal function for 2.0 mm of cut size (thickness). The fine fraction is screw-conveyed (PR-SCR-2) to gasifier feed drum (DR-MIX-4) and the oversized fraction is recycled and mixed back (PR-MIX-2) for further fine-size reduction cycle in closed-loop at size requirements.

Aspen Plus®v8.4 process model simulation of the bagasse gross-size milling and fine-size milling machines (DR-CRU-1) are combined in a single-block model developed by using a Crusher solids block to represent the particle diameter reduction to a maximum of 4.0 mm of thickness and according to Gates-Gaudin-Schuhmann general cumulative distribution function to avoid 50.0%$_{w/w}$ of the bagasse mass flow rate with more than 2.0 mm of thickness.

The electrical power work required by the bagasse size reduction and handling system is estimated as 22.0 kWh per tonnes of wet bagasse inlet in the sizing system. It is set in bond work index by design specification DS-PR-PC-1. In addition, outlet PSD distribution is determined by Bond's comminution power law and a sizing distribution function.

The straw bales delivered (STRAW+TRASH+METAL) are transported (PR-SCR-3) to unpacking and preparation area (PR-SPL-2), considering the pre-chopping process in the field by the straw baling machine. Straw bales are unpacked (PR-SPL-2) and the over sized, hardest biomass and heavier particles (rocks) delivered with the straw bales is separated and screwed-out. In these processes is considered a removal of 50.0%$_{w/w}$ of the soil fraction content in the trash (TRASH), accumulated due to contact with the agricultural land.

Unpacked-straw (pre-chopped) is drag-conveyed (PR-SCR-4) to the magnetic separation (PR-SCR-5) (prevent damages) by magnetic head pulleys (PR-ELE-1) to remove the tramp metals (METALS) along with 5.0%$_{w/w}$ of the soil content, its fraction is screwed-out (PR-SCR-6) to final disposal or send to be recycled (metals). After removal the debris (TRASH) and ferrous metals the straw is belt-conveyed to a cutting-milling straw machine (PR-CRU-2) to fine-size reduction with size-classification by screen-deck solid-solid classifier (PR-CLA-3) according to ideal function for 2.0 mm of cut size (thickness). The fine fraction is directly screw-conveyed (PR-SCR-7) to straw flash dryer (DR-DRY-2) and the oversized fraction is recycled and mixed back (PR-MIX-4) for further fine-size reduction cycle in closed-loop at size requirements.

Aspen Plus®v8.4 process model simulation of the straw fine-size cutting-milling machine (DR-CRU-2) was developed by using a Crusher solids block to represent the particle diameter reduction to a maximum of 4.0 mm of thickness and according to Gates-Gaudin-Schuhmann general cumulative distribution function to avoid 50.0%$_{w/w}$ of the straw mass flow rate with more than 2.0 mm of thickness.

The electrical power work required by the straw size reduction and handling system is estimated based on chopper's machines and fine-size cutting-milling processes for sugarcane straw as 8.0 kWh per tonnes of wet straw inlet in the sizing system (after the magnetic head pulleys). It is set in the bond work index using the design specification DS-PR-PC-2. In addition, outlet PSD distribution is determined by Bond's comminution power law and a sizing distribution function.

Sized straw is screw-conveyed (PR-SCR-7) to straw flash dryer (DR-DRY-2). In some cases (dry straw recovery conditions) there may not be need of drying the straw and then this can bypass the straw flash dryer (DR-DRY-2) and be directly belt-conveyed to the gasifier feed drum (DR-MIX-3).

8.1.4 Biomass multi-step dryer and control particulate emissions

Raw moist bagasse are screw-conveyed to specific dryer feeder drum, entering by screw-conveyor (PR-SCR-2) into parallel bagasse flash dryer trains (DR-DRY-1) to reduce the moisture content from 50.0%$_{w/w}$ to 10.0%$_{w/w}$ in a multi-steps drying process (DR-DRY-1).

Sized straw with higher-moisture content (considered 15.0%$_{w/w}$), recovered in rain conditions (or which has been humidified) is belt-conveyed to dryer feeder drum and screw-conveyed (PR-SCR-7) to straw flash dryer (DR-DRY-2) to reduce the moisture content to 10.0%$_{w/w}$. Sized straw with lower-moisture content (equal or less than 10.0%$_{w/w}$) obtained on dry straw recovery conditions (not considered in this research Master's degree) bypass the straw flash dryer (DR-DRY-2) and is directly belt-conveyed to the gasifier feed drum (DR-MIX-3).

As shown in Figure 35, Aspen Plus$^{®}$v8.4 flowsheet of the simplified aggregated-steps model of the biomass multi-step dryer and control particulate emissions in the BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2) which is the same model with modified parameters in the Biomass-to-Mixed alcohols (SC1); Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) is compost by: first-stage bagasse flash dryer (DR-DRY-1); second-stage bagasse flash dryer (DR-DRY-1); straw flash dryer (DR-DRY-2); advanced blower system (DR-ASP-1); pre-filter unit (DR-FIL-1); bagasse after-dryer single-cyclone (DR-CYC-1); straw after-dryer single-cyclone (DR-CYC-2); bagasse electrostatic precipitator (DR-ESP-1); straw electrostatic precipitator (DR-ESP-1); fine-solids mixer 1 (DR-MIX-7); fine-solids mixer 2 (DR-MIX-8); straw gasifier storage bin (DR-MIX-3); bagasse gasifier storage bin (DR-MIX-4); gaseous mixer 1 (DR-MIX-1); gaseous mixer 2 (DR-MIX-2); flash separator 1 (DR-FLA-1); and flash separator 2 (DR-FLA-2).

Fresh drying air agent (ATMOSPHERIC AIR) is indirect preheated using the dryer humidified exhaust-gas and heated using only the HRSG flue-gas or a mixture of the HRSG flue-gas with 1G-CHP/EBPST exhaust-gas.

Hot-air drying agent at 120.0ºC is forced-injected at atmospheric pressure in the bagasse multi-stage flash dryer (DR-DRY-1) and straw flash dryer (DR-DRY-2) by advanced blower system (DR-ASP-1) modeled by using a Compr pressure changer block according to isentropic method for compressor considering 85.0% isentropic efficiency and 99.0% mechanical efficiency. A pre-filter unit (DR-FIL-1) modeled by using a FabFl solids separator block according to Piecewise separation efficiency in function of the particle diameter of the solids is used to protect the blower and the flash dryers from debris (PARTICLES). The advanced blower system (DR-ASP-1) is used to adjust the mass flow rate of the hot-air drying agent required by the drying process (technical assessment) and equalize the drop pressure of the system to atmospheric discharge condition in the dryer flue-gas (FLUE-GAS FROM STACK).

The multi-step bagasse flash dryer (DR-DRY-1) and the straw flash dryer (DR-DRY-2) is modeled by using a HeatX exchanger block coupled with a Flash2 separator block operating at atmospheric pressure (no pressure drop consideration) to model the direct contact of hot-air drying agent with bagasse (DR-FLA-1) and straw (DR-FLA-2) and the resultant thermal and fluid dynamic effects.

The thermal exchange models consider that the biomass heat at saturation temperature (at about 100.0ºC for atmospheric pressure) to liquid-vapor equilibrium phase to separate the moisture content (flash model principles). The direct contact model consider drag 0.2%$_{w/w}$ of the total biomass (daef) feed as biomass fine fibers and 0.1%$_{w/w}$ of the total particles (e.g.: soil and others) as fine particles due the high mass flow rate and the turbulence of the drying air agent. The model also considers that 0.01%$_{w/w}$ of the moisture contained in the biomass is entrained together with the particulate emissions (without energetic consumption to evaporate).

Extractives, volatile organic compounds, and the moisture content in the biomass are evaporated according to flash equilibrium model (DR-MIX-1 for bagasse model and DR-MIX-2 for straw model) and emitted to the atmosphere together the drying air agent in the dryer flue-gas (FLUE-GAS FROM STACK).

The fine-sized and dried straw (solid phase) content 10.0%$_{w/w}$ of moisture after the straw flash dryer (DR-FLA-2) is belt-conveyed to a gasifier feed drum (DR-MIX-4).

The raw wet bagasse is dried in a first-stage bagasse flash dryer (DR-DRY-1) to reduce the moisture content before the gross-size reduction stage (PR-CRU-1) to facilitate the process of gross-size milling (DR-CRU-1) and reduce the thermal energy required by this first-stage, after gross-sized the bagasse is sent back to a second-stage bagasse flash dryer (DR-DRY-1) to reduce moisture content to 10.0%$_{w/w}$ before the fine-size milling stage. The gross-sized and dried bagasse (solid phase) with 10.0%$_{w/w}$ of moisture content is belt-conveyed to gross-size milling machine (DR-CRU-1) to reduce the size particle at gasifier required level.

The first-stage and second-stage of the bagasse flash dryer (DR-DRY-1) combined in a single-block model and the straw flash dryer (DR-DRY-2) are modeled by using a HeatX exchanger block and Flash2 separator block to estimate the thermal energy required to reduce the bagasse and straw moisture content to 10.0%$_{w/w}$ using hot-air agent inlet at 120.0ºC and outlet at about 100.0ºC from the biomass flash driers (DR-DRY-1 and DR-DRY-2).

The hot-air mass flow rate is controlled by the design specification DS-DR-TG-1 to distribute the air flow in order to obtain the same outlet temperature (same temperature range) in the dryers (DR-DRY-1 and DR-DRY-2), the design specification DS-DR-FG-1 is used to estimate the thermal energy required for the multi-step bagasse drying process and the DS-DR-FG-2 is used to estimate the thermal energy required for the straw drying process. DS-DR-FG-3 is used to control the fresh-air mass flow rate inlet (ATMOSPHERIC AIR) in the system to optimized necessary mass flow rate for the dying processes occurs under the determined temperature range (120.0ºC~100.0ºC in the air agent side).

The Aspen Plus®v8.4 process model simulation bagasse flash dryers (DR-DRY-1) and straw flash dryers (DR-DRY-2) overestimates the power consumption because only uses the heat of vaporization of water and sensible heat exchanger according to biomass heat capacity, not taking into account other phenomena. The design specification DS-DR-HD-3 is used to correct the model estimative and approach the real value demanded by the process, applying 45.0% as reduction factor of thermal energy calculated in the model, this thermal energy is provide by the Heat exchangers block between the HRSG exhaust-gas (HR-HEA-1) and the air agent mass flow rate (DR-HEA-1). The cooled HRSG flue-gas (FLUE-GAS FROM STACK) temperature is controlled and dependent on the exhaust-gas temperature of the subcritical HRSG system (without wet gaseous cleaning system).

Humidified exhaust-gas from first-stage and second-stage bagasse flash dryers (DR-MIX-1) enters in the after-dryer single-cyclone (DR-CYC-1) modeled by using a Cyclone solids separator block to remove the gross particulate content in the dryer humidified exhaust-gas according to Muschelknautz calculation method for a maximum pressure drop of 0.02 bar applying spiral inlet cyclone type, and then in an electrostatic precipitator (DR-ESP-1) modeled by using a ESP solids separator block to reduce the persistent fine particulate matters and theirs emissions to atmosphere in the dryers flue-gas (FLUE-GAS FROM STACK) according to Svarovsky calculation model for vertically mounted collecting plates model with separation efficiency of 95.0% of the particles presents in the dryer humidified exhaust-gas stream based on the migration velocity and the ratio of precipitation area.

The dryer humidified exhaust-gas of the straw flash dryers (DR-MIX-2) enters in the after-dryer single-cyclone (DR-CYC-2) modeled by using a Cyclone solids separator block to remove the gross particulate content in the dryer humidified exhaust-gas according to Muschelknautz calculation method for a maximum pressure drop of 0.02 bar applying spiral inlet cyclone type, and then in an electrostatic precipitator (DR-ESP-2) modeled by using a ESP solids separator block to reduce the persistent fine particulate matters and theirs emissions to atmosphere in the dryers flue-gas (FLUE-GAS FROM STACK) according to Svarovsky calculation model for vertically mounted collecting plates model with separation efficiency of 95.0% of the particles presents in the dryer humidified exhaust-gas stream based on the migration velocity and the ratio of precipitation area.

The gross and fine particulate matters removed from the dryer humidified exhaust-gas are sent to gasifier storage bin (DR-MIX-3) together the dried and sized bagasse and straw (mixed in the feed gasifier drum).

8.1.5 Gasification of biomass in an atmospheric circulating fluidized bed directly-heated gasifier by using high-purity oxygen and steam agents

The Aspen Plus®v8.4 process model simulation of the gasification of biomass in an atmospheric CFB directly-heated gasifier by using high-purity oxygen and steam agents is based on zero-dimensional isothermal built-in multi-blocks models (CFB directly-heated gasifier process-zones) in steady state operation mode. The model use Mott and Spooner correlation (option code 4) to estimate the heat of combustion and heat of formation, Kirov correlation (option code 1) to estimate the heat capacity, and RKS cubic equation of state with BM alpha function property method to simulate the heat transfer between the CFB directly-heated gasifier zones (multi-blocks) and the heat loss from the gasifier.

As shown in Figure 65 the Aspen Plus®v8.4 flowsheet of the gasification of biomass in a CFB directly-heated gasifier by using high-purity oxygen and steam agents in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3) which is the same model with modified parameters for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) has been developed as built-in multi-blocks and splitted in bagasse and straw feed system, gasifier buffer/equalizer tank (GA-BUF-1), advanced blower system (GA-ASP-1), heat exchanger (GA-HEA-1 and HR-HEA-1) and more five basic linked zones representing the atmospheric CFB directly-heated gasifier: a) drying zone (GA-SEP-1 and GA-SEP-2); b) devolatilization (thermal decomposition) or pyrolysis zone (GA-DEV-1 and GA-DEV-2); c) gasification or reduction zone (GA-GASEI); and d) combustion or oxidation zone (GA-GASEI); and e) primary gasifier cyclone (GA-CYC-1).

Dried (10.0%$_{w/w}$ of moisture content) and sized (less than about 2.0 mm of tickles) sugarcane bagasse and straw after the multi-steps drying process and control particulate emissions is belt-conveyed to bagasse storage bin (DR-MIX-4) and straw storage bin (DR-MIX-3), the sugarcane bagasse and straw are lifted from the temporary storage bin and gravimetric feeder by belt-conveyor to the gasifier feed drum (DR-MIX-3).

Sugarcane bagasse and straw (biomass) is horizontally conveyed into the inject screws to introduce the bagasse (GA-SCR-2) and straw (GA-SCR-1) into the gasifier, near the bottom of the CFB gasifier bed. The mass flow rate of sugarcane bagasse and straw inject-screwed into the atmospheric CFB directly-heated gasifier is controlled by the bagasse screw (GA-SCR-2) and straw screw (GA-SCR-1) in each metering bins (DR-MIX-3 and DR-MIX-4).

The Aspen Plus®v8.4 process model simulation of the drying process-zone consider the bagasse (GA-SEP-2) and straw (GA-SEP-1) instantaneous drying process at 150.0ºC vaporizing the moisture content and volatilizing the extractives content in the inlet dried and sized bagasse and straw, which are sent directly to the oxidizing and gasification reaction (GA-GASEI).

The Aspen Plus®v8.4 process model simulation of the devolatilization process-zone was developed by using a RYield reactor block to represent the atmospheric decomposition at 500ºC of the BAGASSE non-conventional solids (GA-DEV-2) and the STRAW non-conventional solids (GA-DEV-1) into its ‘constituting’ conventional components (‘ELEMENTS’) including carbon (C), hydrogen (H_2), oxygen (O_2), chlorine (Cl_2), nitrogen oxide (NO), sulfur dioxide (SO_2) and hydrogen sulfide (H_2S) using about 16.67%$_{w/w}$ of the sulfur (S) content. Salts, minerals, ashes and soil are specified as inert components in the devolatilization process-zone (bypass).

FORTRAN calculator block CA-GA-CB-2 is used to specify the yield distribution of the bagasse decomposition (GA-DEV-2) in the devolatilization process-zone and the mass flow rate of each constituent component in the outlet stream according to the sugarcane bagasse ultimate analysis (Table 5). FORTRAN calculator block CA-GA-CB-1 is used to specify the yield distribution of the straw decomposition (GA-DEV-1) in the devolatilization process-zone and the mass flow rate of each constituent component in the outlet stream according to the sugarcane straw ultimate analysis (Table 6).

Sep separator block GA-SEP-3 as adjustment model is used to selectively separate specific amounts of char (C) to adjust the carbon conversion efficiency of the atmospheric CFB directly-heated gasifier bypass the carbon around the reaction zones (GA-GASEI) using the design specification DS-GA-FS-1 to control the carbon split fraction to obtain 98.0%$_{w/w}$ of carbon conversion efficiency. The GA-SEP-3 separator block also adjusts and considers a fraction of 10.0%$_{w/w}$ of the salts with potassium and chlorine content as reactive compounds together the integral minerals. The another fraction containing 90.0%$_{w/w}$ of the salts with potassium and chlorine (content in the inlet biomass) is considered as non-reactive compounds and primary bypass the reaction zones (GA-GASEI).

The adjustment model (GA-SEP-3) consider the possibility of the entrained gross-particles (solid fraction) content reactive potassium and chlorine (bed supplementary material linked) captured in the primary gasifier cyclone (GA-CYC-1) return back trough the leg-riser to the gasifier bed (GA-GASEI) as reactive compounds. A small fraction of the fine particles contend the reactive-considered potassium and chlorine leave the primary gasifier cyclone (GA-CYC-1) with gaseous product linked with the bed materials (not included in the Aspen Plus®v8.4 process model simulation) and in form of oxides sulfates or phosphates.

High-purity oxygen (O_2) agent at 98.3%$_{mol}$ of purity is obtained from the double-column cryogenic air separation unit (ASU) with high-purity argon recovery. After the main heat exchanger (AS-2) gaseous high purity O_2 stream (GA-O2-1) is feed in the gasifier buffer/equalizer tank (GA-BUF-1) at 25.0 ºC and atmospheric pressure (ambient conditions). The high-purity oxygen line is composed (model result) on the molar percentage basis by 2.597e^{-10}% of nitrogen (N_2), 98.304% of oxygen (O_2), 1.695% of Argon (Ar), 2.54e^{-23}% of Neon (Ne), 2.546e^{-20}% of Helium (He), 4.629e^{-4}% of Xenon (Xe), 6.053e^{-4} of Krypton (Kr).

The oxidizing agent from the gasifier buffer/equalizer tank (GA-BUF-1) is induced by the advanced blower system (GA-ASP-1) modeled by using a Compr pressure changer block according to isentropic method for compressor considering 85.0% isentropic efficiency and 99.0% mechanical efficiency. The high-purity oxygen is preheated (GA-HEA-1) using the dryer flue-gas and heated (GA-HEA-1) using the HRSG exhaust-gas (HR-HEA-1) to obtain 120.0ºC before being injected in the atmospheric CFB directly-heated gasifier in the primary injection distributor in the bottom of the bed (GA-GASEI) an in the secondary distributor points (close to biomass feed point) in the combustion zone (GA-GASEI).

The quantity of high-purity oxygen agent entering into the atmospheric CFB directly-heated gasifier is controlled by the design specification DS-GA-TG-1 coupled with the design specification DS-AS-FG-2 varying the mass flow rate of the high-purity liquid oxygen extracted from the high-pressure packed-column (AS-COL-2). The high-purity oxygen required is determined by the thermal energy necessary to occurs the gasification reactions and to the crude synthesis gas leave the atmospheric CFB directly-heated gasifier at 850.0ºC, operational temperature selected for the atmospheric CFB directly-heated gasifier model implemented in this research Master's degree.

In the atmospheric CFB directly-heated gasifier the combustion in-bed (GA-GASEI) supply the thermal energy required for the endothermic gasification reactions and to heater the material-compounds, the combustion gas products acts as fluidizing bed agent and gasifying agent. The Aspen Plus®v8.4 process model simulation of oxidizing and gasification process-zones in bed and freeboard was developed by using a RGibbs reactor block (GA-GASEI) to represent the solid and gaseous reaction according to chemical equilibrium by Gibbs free-energy minimization method considering all components as potential products in products sheet, it is a simple approach to represent the oxidizing and gasification reactions to obtain a crude synthesis gas at 850.0ºC.

Chemical equilibrium by Gibbs free-energy minimization method overestimate the Equivalence rate (ER_{AIR}) and the mass flow rate of CO_2 and H_2O (fraction in the crude synthesis gas), mainly because the model does not predict the reverse water gas shift equilibrium effect and the formation of light hydrocarbons and heavy hydrocarbons breaking them into simpler forms. The model predicts the formation of more H_2 and less CO than the real process (experimental data). To break the hydrocarbon compounds is required energy which is supplied by the combustion process (extended) demanding more oxidizing agent and forming consequently more CO_2 and H_2O as a product of combustion.

Steam agent is generated in the synthesis gas heat recovery cooling system (second section) at 2.5 bar and 150.0ºC by the low-temperature vertical CSC (GA-CSC-1), being injected 95.0%$_{w/w}$ of the steam agent at the primary and secondary injection distributor in the bed (GA-GASEI) and 5.0%$_{w/w}$ of the steam agent in the loop-seal (GA-LSE-1) (fluidization agent) in order to fluidize the bed and promote the gasification reactions (GA-GASEI). The ratio of steam agent mass flow rate to dry biomass (bagasse and straw) mass flow rate is calculate by the Equation 7 and controlled by the design specification DS-GA-FG-1 varying the inlet hot water/steam agent mass flow rate to obtain a STBR equal of 0.5 considering the moisture content in the inlet bagasse and straw. The STBR is maintenance in 0.5 due to lack of details for bed fluidization probably this value will be changed in future rigorous models involving fluid dynamic models, raising the steam mass flow rate to fluidizer the bed.

2.0% of the LHV_{db} of the biomass fed is assumed to be lost from the gasifier (GA-GASEI) being controlled by the design specification DS-GA-QL-1 with the aid of parameter calculation blocks (BHV blocks group) implemented.

The gasification of sugarcane bagasse and straw using high-purity oxygen and steam as gasification agents provides a crude synthesis gas content: very-low or insignificant inerter elements present in the surrounding air (N2, Ne, He, Xe, Ar and Kr), water vapor (H_2O), carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), methane (CH_4), hydrogen sulfide (H_2S), hydrogen chlorine (HCl), chlorine (Cl_2), carbonyl sulfide (COS), ammonia (NH_3) nitrogen oxides (NO_x), sulfur oxides (SO_x) and solid particulate matters.

Tar, light hydrocarbons and heavy hydrocarbons is not estimated by the chemical equilibrium applying the Gibbs free-energy minimization method (GA-GASEI), hydrocarbons are converted to simple form as water vapor (H_2O), carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2) and a small fraction of methane (CH_4). Solid particulate matters content bed material, specifics catalytic active materials, unconverted char, coke, ashes content, soil, salts and minerals and others.

The main impurities present in the crude synthesis gas can be ammonia (NH_3), hydrogen sulfide (H_2S), carbonyl sulfide (COS), hydrogen chloride (HCl), chlorine (Cl_2), nitrous oxides (NO_x), sulfur oxides (SO_x) volatile metals, volatile organic compounds, tar and oils (heavy hydrocarbons), fines or submicron particles containing metals and metal salts, unconverted char (C) solid particulates and materials bed particles (not included in the Aspen Plus®v8.4 process model simulation) and others alkali compounds.

Primary gasifier cyclone gas/solid separator (GA-CYC-1) is modeled by using a Cyclone solids separator block as single-cyclone to remove the gross particulate content (ashes, silicates, metal salts, unconverted carbon, bed and additives materials) in the crude synthesis gas according to Muschelknautz calculation method for a maximum pressure drop of 0.012 bar applying spiral inlet cyclone type. The gross-particulate separated from the crude synthesis gas is recycled by the leg-riser back to the gasifier bed (GA-GASEI) to promote second-pass in the reaction zones raising the char conversion (to obtain 98.0%$_{w/w}$ of carbon conversion).

Aspen Plus$^{®}$v8.4 process model simulation consider that 50.0%$_{w/w}$ of the unconverted char (C) is removed in the gasifier bottom particulate materials discharge system (GA-SEP-4) modeled by using a Sep separator block. Another part, can be recycled by the primary gasifier cyclone (GA-CYC-1) and a small fraction of fine particles can be dragged by the crude synthesis gas to the secondary multi-cyclone system (GA-CYC-2) according to the primary gasifier cyclone (GA-CYC-1) efficiency and the size of the solid particles (PSD distribution).

The model consider that 0.2%$_{w/w}$ of the crude synthesis gas conventional phase flowing into the primary gasifier cyclone (GA-CYC-1) return back to the reaction zone (GA-GASEI) by the leg-riser together the particles in the loop-seal (GA-LSE-1).

A secondary multi-cyclone system (GA-CYC-2) designed with five cyclones (battery) and modeled by using a Cyclone solids separator block according to Muschelknautz calculation method for a maximum pressure drop of 0.02 bar applying spiral inlet cyclone type removes part of the residual fines-particulate matters that leaving the top of the primary gasifier cyclone (GA-CYC-1). These particles are belt-conveyed and mixed (GA-SCR-3) with the bottom particulate matters removed from the gasifier (GA-SEP-4) to final disposal. The fine particles not recovered in the secondary multi-cyclone system (GA-CYC-2) is removed from the synthesis gas in the low-temperature synthesis gas wet cleaning system.

Bottom particulate matters (e.g.: sand; ash; slag; specifics catalytic active materials; unconverted materials, metal salts; alkali compounds and others) is discharged from the bottom of the gasifier (GA-GASEI), cooled using directly contact water added to avoid dust (consider the heat loss in the GA-FLA-1) by water-cooled screw conveyor (not simulated). The bottom particulate matters are stored together the fines-particulate matters removed in the multi-cyclone system (GA-CYC-2) in the ashes temporary storage bins to humidified ashes/slag (GA-FLA-1) until offloaded for disposal (field disposal together vinasses).

8.1.5.1 Gasifier bed materials

Spreadsheet calculation model is used to determine the quantity of MgO must be present into the gasifier bed (GA-GASEI) and the make-up mass flow rate of MgO necessary to substantially avoid the formation (sequestering potassium) of low-melting point glass-like bed agglomerations (K_2SiO_4). The bed agglomerations were associated to direct adhesion of the bed particles by partly molten fuel ash derived K–Mg phosphates (ashes content) and K-silicates (ashes and soil content) that should result from the interactions with the biomass potassium content. MgO raise the melting point (ternary eutectic form) sequestering potassium avoiding/reducing it to be carried over in the gasifier cyclones (GA-CYC-1) and deposits in the equipment walls.

MgO supplementary bed material load is estimated to be 2.0 mol mass flow rate per mol of reactive potassium inlet into the gasifier (GA-GASEI). MgO is delivered to thermochemical-biorefinery supplies offloading area by truck to storage, a pneumatic line feed the gasifier loop bed media feed bin, which transfers the supplies to the gasifier by screw-conveyor or pneumatic transporter (not included in the Aspen Plus$^{®}$v8.4 process model simulation).

In the spreadsheet calculation model is considered the olive make-up mass flow rate as being 1.0%$_{w/w}$ of the mass flow rate of dry ash and extractive free (daef) sugarcane bagasse and straw inlet into the gasifier to compensate the olive losses. Olivine recirculate by the primary gasifier cyclone (GA-CYC-1) trough the leg-riser and the major part of the entrained olive is recovered from the crude synthesis gas exiting the gasifier by the secondary multi-cyclone system (GA-CYC-2), only a small part of the olivine as fine particles are dragged and removed in the low-temperature synthesis gas wet cleaning system (losses).

The majority of the bed materials and gross-biomass derived particles are separated in the primary gasifier cyclone (GA-CYC-1) and sent back (recycled) into the leg-riser and gravity-feed back to the gasifier bed (GA-GASEI) using steam fluidized loop-seal (GA-LSE-1). A secondary multi-cyclone system (GA-CYC-2) removes part of the residual fines-particulate matters that leaving the top of the primary gasifier cyclone (GA-CYC-1), this particles are mixed with the bottom particulate material removed from the gasifier (GA-SEP-4) to final disposal (BED MATERIALS AND ASHES).

The mineral-crystal (iron content) olivine catalyst considered as gasifier bed media is a commercial type olivine catalyst α-$(Mg_{0.8}Fe_{0.2})_2SiO_4$ delivered to thermochemical-biorefinery supplies offloading area by truck to storage, a pneumatic line feed the gasifier loop bed media feed bin, which transfers the supplies to the gasifier by screw-conveyor or pneumatic transporter (not included in the Aspen Plus$^{®}$v8.4 process model simulation).

Olivine catalyst is used to reduce by about 60.0%$_{w/w}$ of the tar content in the crude synthesis gas produced in the atmospheric CFB directly-heated gasifier (GA-GASEI). Tar abatement increased up to 92.0%$_{w/w}$ when catalytic CF were combined with the bed, not included in the Aspen Plus$^{®}$v8.4 process model simulation due the limitations of the gasification Gibbs equilibrium model, in future works with rigorous model can be considered.

8.1.6 Double-column cryogenic air separation unit with high-purity argon recovery

A double-column cryogenic air separation unit (ASU) with high-purity argon recovery is simulated integrated at a thermochemical-biorefinery to supply the high-purity oxygen required by the directly-heated gasification technology employed to synthesis gas production aiming its utilization for mixed alcohols production by mixed-alcohol catalytic-synthesis.

The ASU is size-scaled according to the amount of high-purity gaseous oxygen required (considering 5.0%$_{w/w}$ of the high-purity oxygen as reserve in liquid form) for sugarcane bagasse and straw gasification using atmospheric CFB directly-heated gasifier according to Aspen Plus$^{®}$v8.4 process model simulation described in the section 8.1.5 (Gasification of biomass in an atmospheric circulating fluidized bed directly-heated gasifier by using high-purity oxygen and steam agents).

The Aspen Plus$^{®}$v8.4 process model simulation using RGibbs reactor block (GA-GASEI) to represent the solid and gaseous reaction according to chemical equilibrium by Gibbs free-energy minimization method overestimate the equivalence rate (ER$_{O2}$) than the estimated by rigorous kinetic models or realistic process, consequently the ASU is estimated greater than the required for the realistic process.

The Aspen Plus$^{®}$v8.4 process model simulation of the double-column cryogenic ASU with high-purity argon recovery has been modeled using Van Laar model for calculates liquid activity coefficients for the property methods and the Redlich-Kwong equation-of-state calculates vapor phase thermodynamic properties. ASPEN Rate-Sep simulation package is used in the high-pressure tray-column (AS-COL-1), low-pressure multi packed-column (AS-COL-2) and in the argon side arm partitioned packaged-column (AS-COL-3) to non-equilibrium mass transfer rate-based calculations taken in account the mass and heat transfer limitations, liquid and vapor film diffusion and equipment fluid dynamic mechanisms.

As shown in Figure 66, part of the Aspen Plus$^{®}$v8.4 flowsheet of the double-column cryogenic ASU with high-purity argon recovery for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) which is the same model with modified parameters for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) is compost by: aluminum fin-plate multi-zones main heat exchanger (AS-2); aluminum fin-plate three-circuit after-cooler exchanger (AS-1); adsorber vessel (AP-ADS-1) (in adsorption-cycle time); regenerative vessel (AP-REG-1) (in regeneration-cycle time); condenser knock-out drum (AP-SEP-1); inlet multi-way valve 1 (AP-SPL-1); inlet multi-way valve 2 (AS-SPL-3); outlet multi-way valve (AP-SPL-4); vent off-gas multi-way valve and silencer (AP-SPL-2); pre-filter unit (AP-FIL-1); advanced blower system (AP-ASP-1); main air compressor (MAC) integrally-geared centrifugal two stages compressor (AP-COM-1 and AP-COM-2) and one stage expander (AS-EXP-1); MAC water after-cooler (AP-HEA-1); MAC condenser knock-out drum (AP-FLA-1); MAC water inter-cooler exchanger (AP-1); atmospheric condensate buffer/equalizer tank (AP-FLA-2); air splitter (AS-SPL-1); booster air compressor (BAC) integrally-geared centrifugal five stages compressor (AS-COM-2~6); BAC water inter-cooler exchangers (AS-3~6); BAC water after-cooler exchanger (AS-7); BAC condenser knock-out drums (CO-FLA-2~5 and AS-SEP-2); condenser knock-out drum (AS-SEP-1); atmospheric condensate buffer/equalizer tank (AP-FLA-1); high-efficiency turbo booster with expander (AS-EXP-2) and compressor (AS-COM-1); and direct drive permanent magnet motors (not included as block).

Surrounding atmospheric fresh-air (ATMOSPHERIC AIR) is induced by advanced blower system (AP-ASP-1) modeled by using a Compr pressure changer block according to isentropic method for compressor considering 85.0% isentropic efficiency and 99.0% mechanical efficiency with pre-filter unit (AP-FIL-1) modeled by using a FabFl solids separator block according to Piecewise separation efficiency in function of the particle diameter of the solids to protect the blower (AP-ASP-1) and the MAC integrally-geared centrifugal two stages compressor (AP-COM-1 and AP-COM-2) from debris (PARTICLES).

The amount of atmospheric air processed (plant scale) is defined by the gaseous high-purity oxygen demanded by the gasification of biomass in an atmospheric CFB directly-heated gasifier (CA blocks) according to mass balance to avoid surplus oxygen (avoiding overestimated scale).

Atmospheric air flow enters the MAC integrally-geared centrifugal two stages compressor (AP-COM-1 and AP-COM-2) by the inlet guide (AP-COM-1) to distribute the flow providing a uniform condition in the MAC first-stage impeller (AP-COM-1). Atmospheric air is compressed by the MAC high-efficiency first-stage impeller (AP-COM-1) considering 90.0% isentropic efficiency (isentropic compression) modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor.

The air after the first-stage of compression (AP-COM-1) is cooled to 30.0ºC by the MAC water inter-cooler exchanger (AP-1) modeled by using a MHeatX exchanger block generating condensed phase depending on the air moisture (80.0%$_{w/w}$ considered in the model) content water and dissolved gases. The condensed phase is removed in the condenser knock-out drum (AP-FLA-1) modeled by using a Flash2 separator block and send to be after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

The air free of condensate phase enters in the MAC second-stage impeller (AP-COM-2) and is compressed by the MAC high-efficiency second-stage impeller (AP-COM-2) to 5.2 bar and at about 122.0ºC considering 90.0% isentropic efficiency (isentropic compression) modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor. The air after the second-stage of compression (AP-COM-2) is cooled to 30.0ºC by the MAC water after-cooler exchanger (AP-HEA-1) modeled by using a HeatX exchanger block generating condensed phase content water and dissolved gases. The condensed phase is removed in the MAC condenser knock-out drum (AP-SEP-1) modeled by using a Sep separator block and send to be after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-9) to the MAC inter-cooler exchanger (AP-1) and to the MAC after-cooler exchanger (AP-HEA-1). The amount of cooling water required is determined and controlled by design specification DS-CT-FL-10 and design specification DS-CT-FL-11 varying the mass flow rate of cooling water passing through the equipments users. The cooling water is heated at the limit of 43.0ºC and duct-send back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

The Aspen Plus®v8.4 process model simulation of the thermal pressure swing adsorption/desorption (TPSA) system has been developed in steady-state mode using VANL-RK physical property methods in a simplified model applying Flash2 separators blocks to represent the pressurized adsorption of impurities contained in the atmospheric air in the adsorber vessel (AP-ADS-1) and the atmospheric high-temperature desorption/regeneration process in the regenerative vessel (AP-RE-1); based on a physical binding of gas molecules to selective adsorbent material layers.

The compressed cooled air at 5.2 bar and 27.0ºC is supplied to an inlet manifold containing inlet multi-way valve 1 (AS-SPL-1) connected to adsorber vessel (AP-ADS-1) in adsorption-cycle-time and then fed passing the open control inlet multi-way valve 1 (AP-SPL-1) to into adsorber vessel (AP-ADS-1). The compressed air flows through the adsorbing bed material layers using the effect of partial pressure to perform the adsorption cycle (first vessel) in upward direction. Impurities such as H_2O, CO_2, CO, CH_4, and NO_x (e.g.: NO_2, N_2O and NO) are selectively adsorbed on the surface of the adsorbent material. Purified compressed air from the top of the adsorber vessel (AP-ADS-1) flow-out the TPSA system by the outlet multi-way valve (AP-SPL-4).

After adsorption cycle-time the vessel is depressurized to atmospheric pressure and desorption/regeneration cycle beginning carried out at low-pressure (atmospheric discharge) in the regenerative vessel (AP-REG-1) (in regeneration cycle-time), on continuous closed-loop cycle mode.

Synthetic air purged from the low-pressure multi packed-column (AS-COL-2) is pre-heated in the aluminum fin-plate multi-circuits main heat exchanger (AS-2) and heated at 1.05 bar and 150.0ºC in the aluminum fin-plate three-circuit after-cooler exchanger (AS-1). This heated synthetic air is used to regenerate (TSA) the bed materials in the packaged-layers into the regenerative vessel (GU-REG-1) in the regenerative ZnO/CuO-based guard bed adsorber and in the regenerative vessel (AP-RE-1) in the double-column cryogenic ASU with high-purity argon recovery.

Heated low-pressure synthetic air (without impurities) at 1.05 bar and 150.0ºC is part supplied to an inlet manifold containing inlet multi-way valve 2 (AS-SPL-3) connected to regenerative vessel (GU-REG-1) an then feed in the depressurized regenerative vessel (AP-REG-1) passing though the adsorber vessel heating the adsorbing bed material packaged-layers to 150.0ºC. The cycle use the effect of low-pressure and high-temperature to perform the regeneration phase (second vessel), desorbing in an downward direction the impurities adsorbed in the adsorbing bed material surface. Desorbed impurities are being vented to atmosphere by vent off-gas multi-way valve and silencer (AP-SPL-2) together the after-used synthetic air. After the regeneration phase the regenerative vessel (AP-REG-1) is re-pressurized using purified air and placed on-line for adsorption cycle-time.

The amount of heated low-pressure synthetic air destined to regenerative vessel (AP-REG-1) is determined by the amount of synthetic air purged in the low-pressure multi packed-column (AS-COL-2) and dependent on heated low-pressure synthetic air required by the regenerative vessel (GU-REG-1) in the regenerative ZnO/CuO-based guard bed adsorber. The mass flow rate is controlled by design specification DS-GU-FG-1 varying the mass flow rate of the heated low-pressure synthetic air to regenerative vessel (GU-REG-1) coupled with design specification DS-AS-FG-3 varying the mass splitted (AS-SPL-9).

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) the Aspen Plus®v8.4 process model simulation of the low-pressure multi packed-column (AS-COL-2) consider the synthetic air mass flow rate (purge) as $10.0\%_{w/w}$ of the atmospheric air mass flow rate processed by the double-column cryogenic ASU with high-purity argon recovery. The mass flow rate is controlled by design specification DS-AS-FG-1 varying the configuration of the synthetic air-side-product stream mass flow rate in the low-pressure multi packed-column (AS-COL-2).

Spreadsheet calculation model of the adsorber (AP-ADS-1) and regenerative (AP-REG-1) vessels consider the especially adsorbent bed material's compost by about $67.0\%_{w/w}$ of SiO_2/Al_2O_3 catalyst layer and $33.0\%_{w/w}$ of Zeolite's catalyst layers. The order of layers is defined from the bottom of the bed (raw atmospheric air entrance) by first layer content SiO_2/Al_2O_3 catalyst and second layer content Zeolite's catalyst family subdivided in layers content 3A Zeolite catalyst and/or 13X Zeolite catalyst. The Zeolite family layer is considered in the spreadsheet calculation model as single layer containing Zeolite catalyst type.

Zeolite's catalyst layers considered in the adsorber (AP-ADS-1) and regenerative (AP-REG-1) vessels are a commercial type 3A Zeolite catalyst and/or 13X Zeolite catalyst selective for carbonaceous (e.g.: CO, CO_2 and CH_4) and low-selectivity for

NO_x (e.g.: NO_2, N_2O and NO), weight loaded considering the saturation ratio limits of 32.0%$_{w/w}$ to adsorbing H_2O and carbonaceous compounds per adsorption cycle. Zeolite's catalyst lifetime is expected to be about 2 year before the necessity of deactivated catalyst be partial or full discharged and new activity catalyst be loaded, deactivated catalyst is send to be regenerated and/or to final disposal.

SiO_2/Al_2O_3 catalyst layer considered in the adsorber (AP-ADS-1) and regenerative (AP-REG-1) vessels is a commercial type selective for H_2O and carbonaceous (e.g.: CO, CO_2), weight loaded considering the saturation ratio limits of 50.0%$_{w/w}$ to adsorbing H_20 and 5.0%$_{w/w}$ to adsorbing carbonaceous compounds per adsorption cycle. SiO_2/Al_2O_3 catalyst lifetime is expected to be about 1 year before the necessity of deactivated catalyst be partial or full discharged and new activity catalyst be loaded, deactivated catalyst is send to be regenerated and/or to final disposal.

The purified pressurized air from the TPSA adsorption/desorption system is separated in two fractions in the air splitter (AS-SPL-1). In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) a fraction of 53.0%$_{w/w}$ is sent to BAC integrally-geared centrifugal five stages compressor (AS-COM-2~6) and another fraction of 47.0%$_{w/w}$ is sent to turbo booster with expander (AS-EXP-2) and compressor (AS-COM-1) energy save system.

The Aspen Plus®v8.4 process model simulation of the BAC integrally-geared centrifugal five stages compressor (AS-COM-2~6) feature a single-shaft arrangement was developed in steady-state mode using VANL-RK physical property methods for the air-side and IAPWS-95 physical property methods for the water side, compost by BAC integrally-geared centrifugal impeller stages (AS-COM-2~6), BAC water inter-cooler exchangers (AS-3~6), BAC water after-cooler exchanger (AS-7), condenser knock-out drums (AS-FLA-2~5 and AS-SEP-2), direct drive permanent magnet motor (not included in the Aspen Plus®v8.4 process model simulation) and atmospheric condensate buffer/equalizer tank (AS-FLA-1).

Part of the purified pressurized air from the TPSA adsorption/desorption system is compressed to 60.0 bar by the BAC Integrally-geared centrifugal five stages compressor (AS-COM-2~6) considering 83.0% isentropic efficiency (isentropic compression) modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor. The compressed air between the BAC stages is cooled to 30.0ºC by the BAC water inter-cooler exchangers (AS-3~6) and after-cooled to 30.0ºC by the BAC water after-cooler exchanger (AS-7) modeled by using MHeatX exchanger blocks generating condensed phase content water and dissolved gases. The condensed phase is removed in the condenser knock-out drums (AS-FLA-2~5) modeled by using Flash2 separator blocks and by using a Sep separator block (AS-SEP-2) and then to atmospheric condensate buffer/equalizer tank (AS-FLA-1) modeled by using a Flash2 separator block at ambient conditions to be after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

Sep separator block (AS-SEP-2) is used to remove all of the impurities (simulation artifice) in the Aspen Plus®v8.4 process model simulation before the cryogenic processes leaving only the main compounds (e.g.: O_2, N_2, Ne, He, Ar, Kr and Xe).

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM11) to the inter-cooler exchangers (AP-3~7) and to the after-cooler exchanger (AS-7). The amount of cooling water required is determined and controlled by design specification DS-CT-FL-13 varying the mass flow rate of cooling water passing through the equipments users. The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

The single shaft and multiple pinions in the integrally-geared centrifugal five stages compressor (CC-COM blocks) is drive by a synchronous direct drive permanent magnet motor modeled by AS-E-6 work stream and optimized to obtain the same compression ratio in the compression stages by design specification DS-AS-TR-1 and FORTRAN calculation block CA-AS-TR-2 varying the pressure ratio in all of the five compression stages (CO-COM blocks). The electrical potential losses by attrite in the mechanical move parts was considered as 1.0% of the mechanical energy required by the stage (99.0% mechanical efficiency).

Another part of the purified pressurized air from the TPSA adsorption/desorption system is compressed by high-efficiency turbo booster compost by expander (AS-EXP-2) and compressor (AS-COM-1). The turbine side (AS-EXP-2) is modeled by using a Compr pressure changer block in turbine model considering 90.0% isentropic efficiency (isentropic expansion) to represent the expansion from 60.0 bar and 30.0ºC to 5.65 bar and at about -108.0ºC. The compressor side AS-COM-1) is modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 90.0% isentropic efficiency (isentropic compression) to represent the compression from 5.0 bar and 30.0ºC to about 17.0 bar and 172.0ºC.

The air after compressed by the high-efficiency turbo booster is cooled-down to 17.17 bar and 30.0ºC in the aluminum fin-plate three-circuit after-cooler exchanger (AS-1) by cooling water from the water-cooling tower system at 27.0ºC pumped (CT-PUM10) through the water-circuit and by synthetic air at 1.08 bar and 0.0ºC flowing in the gas-circuit. The condensed phase is removed in the condenser knock-out drum (AS-SEP-1) modeled by Sep separator block used to remove all of the impurities (simulation artifice) in the Aspen Plus®v8.4 process model simulation before the cryogenic processes leaving only the main compounds (e.g.: O_2, N_2, Ne, He, Ar, Kr and Xe). The condensate if there is after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

Synthetic air purged from the low-pressure multi packed-column (AS-COL-2) is pre-heated in the aluminum fin-plate multi-zones main heat exchanger (AS-2) and then in the aluminum fin-plate three-circuit after-cooler exchanger (AS-1) is heated from 1.08 bar and 0.0ºC to 1.05 bar and 150.0ºC. Heat is recovered and the synthetic air conditioned to achieve time-optimized regeneration phase in the regenerative vessel (GU-REG-1) in the regenerative ZnO/CuO-based guard bed adsorber and in the regenerative vessel (AP-RE-1) in the double-column cryogenic ASU with high-purity argon recovery.

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM10) to the cooling water circuit in the aluminum fin-plate three-circuit after-cooler exchanger (AS-1). The amount of cooling water required is determined and controlled by design specification DS-CT-FL-12 varying the mass flow rate of cooling water passing through the aluminum fin-plate three-circuit after-cooler exchanger (AS-1). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

The Aspen Plus®v8.4 process model simulation of the aluminum fin-plate multi-zones main heat exchanger (AS-2) was developed using VANL-RK physical property methods and modeled by using a MHeatX exchanger block to represent the cooling down of the compressed air from 17.17 bar and 30.0ºC to about 17.17 bar and -29.0ºC and the cooling down and liquefaction (phase change) of the expanded air from 5.65 bar and -108.0ºC to about 5.62 bar and -178.0ºC. To cool down and liquefy the air are used: gaseous nitrogen product, that is obtained from the 1º theoretically vapor stage (top column stage) in the low-pressure multi-packed column (AS-COL-2) after heat exchange in the aluminum fin-plate sub-cooler exchanger (AS-9) available at about 1.07 bar and -174.2ºC being heated in the aluminum fin-plate multi-zones main heat exchanger (AS-2) to about 1.05 bar and -67.7ºC; synthetic air purged from the 22º theoretically gaseous stage in the low-pressure multi-packed column (AS-COL-2) after heat exchanger in the aluminum fin-plate sub-cooler exchanger (AS-9) available at about 1.12 bar and -173.0ºC being heated in the aluminum fin-plate multi-zones main heat exchanger (AS-2) to about 1.08 bar and 0.0ºC; and liquid oxygen product at about 1.30 bar and -180.6ºC from the 75º theoretically liquid stage (bottom column stage) from the low-pressure multi-packed column (AS-COL-2) being heated and vaporized (phase change) in the aluminum fin-plate multi-zones main heat exchanger (AS-2) to about 1.01325 bar and 25.0ºC (ambient conditions).

The gaseous high-purity nitrogen product at 1.05 bar and -67.7ºC is sent to the optional high-pressure double-Claude cycle nitrogen liquefier (LNG-based nitrogen liquefier) to be liquefied and commercialized another value-added bio-based product in the product-portfolio of the thermochemical-biorefinery. Another option is vent to atmosphere in ambient conditions economizing the electricity required by the LNG-based nitrogen liquefiers with the possibility to export the electricity (equivalent generated) to the electric power grid (market flexible configurations).

High-purity gaseous oxygen (O_2) at 98.3%$_{mol}$ is fed into the gasifier buffer/equalizer tank (GA-BUF-1) at 25.0ºC and atmospheric pressure (ambient conditions) and after-used as gasification agent (oxidizing) in the gasification of biomass in an atmospheric CFB directly-heated gasifier (CA blocks).

Compressed air is expanded before to be fed in the high-pressure tray-column (AS-COL-1) saving energy in the expander stage (AS-EXP-1) modeled by using a Compr pressure changers block in turbine model to represent the expansion side from 17.17 bar and -29.0ºC to 5.8 bar and -90.1ºC integrated in the MAC integrally-geared centrifugal compressor (turbo booster section).

Liquefied air at about 5.62 bar and -178.0ºC is separated in two fraction in the liquid air splitter (AS-SPL-2), being 50.0%$_{w/w}$ fed into the high-pressure tray-column (AS-COL-1) in the 32º theoretically liquid stage and the another 50.0%$_{w/w}$ fed into the low-pressure multi-packed column (AS-COL-2) in the 23º theoretically liquid stage.

As shown in Figure 67, Aspen Plus®v8.4 flowsheet of the cold box section in the double-column cryogenic ASU with high-purity argon recovery for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) which is the same model with modified parameters for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) is compost by: high-pressure tray-column (AS-COL-1); low-pressure multi packaged-column (AS-COL-2); argon side arm partitioned packaged-column (AS-COL-3); aluminum fin-plate sub-cooler exchanger (AS-9); aluminum fin-plate condenser/reboiler exchanger (AS-8); aluminum fin-plate condenser exchanger (AS10); liquid air splitter (AS-SPL-2); cryogenic liquid oxygen pump (AS-PUM-1); cryogenic liquid argon pump (AS-PUM-2); cryogenic liquid nitrogen storage tank (AS-STO-1); cryogenic liquid oxygen storage tank (AS-STO-2) and cryogenic liquid argon storage tank (AS-STO-3); anti-flash security valve 1 (AS-VAL-1); anti-flash security valve 2 (AS-VAL-3); anti-flash security valve 3 (AS-VAL-4); adiabatic expansion valve (AS-VAL-2); and vent valve (AS-FLA-7).

Cryogenic gaseous air at 5.8 bar and at about -90.1ºC is fed in the high-pressure tray-column (AS-COL-1) in the 45º theoretically vapor stage (bottom column stage), an part of the cryogenic liquid air at about 5.62 bar and -178.0ºC is fed in the high-pressure tray-column (AS-COL-1) in the 32º theoretically liquid stage.

Rigorous Aspen Plus®v8.4 process model simulation of the high-pressure tray-column (AS-COL-1) was developed using VANL-RK physical property methods for RadFrac columns block on cryogenic convergence mode without in-bed condenser and reboiler. The model was optimized for estimated 45 theoretical stages considering a Nutter Float Valve (Aspen96) tray section with two-passes per tray with valve type BDH 14 gauge deck thickness and standards panel A and B with weir height of 30.0 mm and tray diameter of 1.00 m. The model use rate-based calculation for Mixed flow model without reactions and film resistance in vapor phase, without reactions and with film resistance in liquid phase, and employing vapor and liquid phase film non-ideality corrections. Default Aspen Plus®v8.4 tray parameters is applied to calculate interfacial area and the mass transfer coefficient by Scheffe and

Weiland (1987) method, and heat transfer coefficient by Chilton–Colburn (Taylor and Krishna, 1993) method.

The gaseous top-product containing mainly high-purity nitrogen at about 5.20 bar and -178.5ºC leave from the 1º theoretically vapor stage (top column stage) in the high-pressure tray-column (AS-COL-1) is cooled and condensate to 5.20 bar and at about -180.5ºC in the aluminum fin-plate condenser/reboiler exchanger (AS-8) condenser-zone. Part ($47.5\%_{w/w}$ by model result) of the high-purity liquid nitrogen return back (as reflux) to the 1º theoretically liquid stage (top column stage) in the high-pressure tray-column (AS-COL-1).

The liquid bottom product containing mainly high-purity liquid oxygen at about 1.30 bar and -180.6ºC from the 75º theoretically liquid stage (bottom column stage) in the low-pressure multi-packed column (AS-COL-2) is used in the aluminum fin-plate condenser/reboiler exchanger (AS-8) vaporizer-zone to cool down and condense the gaseous high-purity nitrogen product at about 5.20 bar and -178.5ºC from the 1º theoretically vapor stage (top column stage) in the high-pressure tray-column (AS-COL-1). The amount of liquid bottom product vaporized and sent-flowing upward back trough the multi-packed column (AS-COL-2) is determined by the exchanger temperature limits (cross-over avoided).

A fraction ($40.5\%_{w/w}$ by model result) of the high-purity liquid nitrogen is sent to the aluminum fin-plate sub-cooler exchanger (AS-9) and after to the low-pressure column (AS-COL-2). Another reminiscent fraction is extracted as high-purity liquid nitrogen product and sent to storage in the cryogenic liquid nitrogen storage tank (AS-STO-1), available as high-purity liquid nitrogen (LIQUID NITROGEN).

Bottom liquid Crude product at about 5.80 bar and -171.4ºC containing about $50.4\%_{w/w}$ of liquid nitrogen and $47.1\%_{w/w}$ of liquid oxygen leaves from the 45º theoretically liquid stage (bottom column stage) in the high-pressure tray-column (AS-COL-1). The high-pressure tray-column (AS-COL-1) does not have reboiler, being the bottom liquid Crude product after-sent directly to the aluminum fin-plate sub-cooler exchanger (AS-9).

The another part of the cryogenic liquid air at about 5.62 bar and -178.0ºC is fed in the low-pressure multi-packed column (AS-COL-2) in the 23º theoretically liquid stage passing before through anti-flash security valve 1 (AS-VAL-1) avoiding flash-explosion effect, adjusting the pressure to tray-pressure requirements. Liquid bottom crude product at about 5.62 bar and -178.0ºC from the aluminum fin-plate condenser exchanger (AS10) is fed in the low-pressure multi-packed column (AS-COL-2) in the in the 24º theoretically liquid stage passing before through anti-flash security valve 2 (AS-VAL-3). Cryogenic liquid nitrogen at about 1.10 bar and -190.4ºC from the aluminum fin-plate sub-cooler exchanger (AS-9) is fed in the low-pressure multi-packed column (AS-COL-2) in the in the 1º theoretically liquid stage (top column stage) passing before through anti-flash security valve 3 (AS-VAL-4). Liquid bottom product at about 1.23 bar and -181.3ºC from the bottom of the argon side arm partitioned packaged-column (AS-COL-3) is fed in the low-pressure multi-packed column (AS-COL-2) in the in the 47º theoretically liquid stage. Vaporized bottom product at 1.30 bar and at about -178.6ºC in the aluminum fin-plate condenser/reboiler exchanger (AS-8) reboiler-zone is fed in the low-pressure multi-packed column (AS-COL-2) in the 75º theoretically gaseous stage.

Rigorous Aspen Plus®v8.4 process model simulation of the low-pressure multi packed-column (AS-COL-2) was developed using VANL-RK physical property methods for RadFrac columns block on cryogenic convergence mode without in-bed condenser and reboiler. The model was optimized for estimated 75 theoretical stages divided in three packaged section considering a MELLAPAK 170Y packing section from 1º to 23º theoretically stages, a MELLAPAK 500Y packing section from 24º to 44º theoretically stages and a MELLAPAK 750Y packing section from 45º to 75º theoretically stages, considering packed height of 0.40 m (HETP) per stages and column diameter of 1.80 m on standards characteristics. The model use rate-based calculation for Mixed flow model without reactions and film resistance in vapor phase, without reactions and with film resistance in liquid phase. Default Aspen Plus®v8.4 packing parameters is applied to calculate pressure drop and liquid holdup by Stichlmair method, to predict the mass transfer coefficient and interfacial area by Onda et al. (1968) correlation, and heat transfer coefficient by Chilton- Colburn (Taylor and Krishna, 1993) method.

Synthetic air is purged at about 1.16 bar and -189.8ºC from the 22º theoretically gaseous stage in the low-pressure multi-packed column (AS-COL-2). The model consider the amount of purged synthetic air as 10.0%$_{w/w}$ of the atmospheric air mass flow rate processed by the double-column cryogenic ASU with high-purity argon recovery and controlled by design specification DS-ASFG-1 varying the configuration of the synthetic air-side-product stream mass flow rate in the low-pressure multi packed-column (AS-COL-2). The purged synthetic air is sent to the aluminum fin-plate sub-cooler exchanger (AS-9).

The gaseous top-product containing mainly gaseous cryogenic nitrogen at about 1.16 bar and -189.8ºC leave from the 1º theoretically vapor stage (top column stage) from the low-pressure multi-packed column (AS-COL-2) is directly sent to the aluminum fin-plate sub-cooler exchanger (AS-9).

Aspen Plus®v8.4 process model simulation of the aluminum fin-plate condenser/reboiler exchanger (AS-8) modeled by using a MHeatX exchanger block to represent the integrated condenser for the high-pressure column (AS-COL-1) and reboiler for the low-pressure column (AS-COL-2).

The liquid bottom product containing mainly purity oxygen at about 1.30 bar and -180.6ºC from the 75º theoretically liquid stage (bottom column stage) in the low-pressure multi-packed column (AS-COL-2) is heated and vaporized to 1.30 bar and at about -178.6ºC in the aluminum fin-plate condenser/reboiler exchanger (AS-8) reboiler-zone. The vaporized bottom product flow upward through the packed-column. A fraction of the liquid bottom product necessary to condense the gaseous top-product from the 1º theoretically vapor stage (top column stage) in the high-pressure tray-column (AS-COL-1) containing mainly high-purity nitrogen at about 5.20 bar and -178.5ºC is determined by the exchanger temperature limits (cross-over avoided).

A fraction of the liquid bottom product containing mainly purity oxygen from the 75º theoretically liquid stage (bottom column stage) is extracted as product and sent to the aluminum fin-plate multi-zones main heat exchanger (AS-2) and after to the atmospheric CFB directly-heated gasifier (CA blocks). The amount of gaseous purity oxygen produced is controlled by design specification DS-AS-FG-2 and determined by the design specification DS-GA-TG-1 varying the mass flow rate of oxygen produced and by the atmospheric air mass flow rate processed by the double-column cryogenic ASU with high-purity argon recovery.

Another remain fraction of the liquid bottom product from the low-pressure multi-packed column (AS-COL-2) is extracted as high-purity liquid oxygen product and pumped by cryogenic liquid oxygen pump (AS-PUM-1) to storage in the cryogenic liquid oxygen storage tank (AS-STO-2) as reserve for brief stops and start-up, available as liquid oxygen (LIQUID OXYGEN). The model of double-column cryogenic ASU with high-purity argon recovery considered a reserve of $5.0\%_{w/w}$ of the gaseous oxygen produced and based on the gaseous oxygen required (bagasse reserve equivalence) by the gasification of biomass in an atmospheric CFB directly-heated gasifier (CA blocks).

Side gaseous cryogenic crude product at about 1.23 bar and -181.3ºC extracted from the 47º theoretically gaseous stage in the low-pressure multi-packed column (AS-COL-2) is fed in the in the 100º theoretically gaseous stage (bottom column stage) in the argon side arm partitioned packaged-column (AS-COL-3). The amount of side gaseous extracted is determined by the composition of the gaseous phase obtained in the 47º theoretically stage by the ASPEN Rate-Sep simulation package methods and dependent on the atmospheric air mass flow rate processed by the double-column cryogenic ASU with high-purity argon recovery and on the desired purity level of the bottom liquid product obtained in the 75º theoretically liquid stage (bottom column stage) in the low-pressure multi-packed column (AS-COL-2).

Rigorous Aspen Plus®v8.4 process model simulation of the argon side arm partitioned packaged-column (AS-COL-3) was developed using VANL-RK physical property methods for RadFrac columns block on cryogenic convergence mode without in-bed condenser and reboiler. The model was optimized for estimated 100 theoretical stages considering a MELLAPAKPL 452Y packing section from 1º to 100º theoretically stages. The simplified model represents the argon recovery column section and the argon purification section grouped into a single column model considering the packed height of 0.38 m (HETP) per stages and column diameter of 0.70 m on standards characteristics. The model use rate-based calculation for Mixed flow model without reactions and film resistance in vapor phase, without reactions and with film resistance in liquid phase, and employing vapor and liquid phase film non-ideality corrections. Default Aspen Plus®v8.4 packing parameters is applied to calculate pressure drop, liquid holdup, mass transfer coefficient and interfacial area by Bravo et al. (1985) correlation, and heat transfer coefficient by Chilton–Colburn (Taylor and Krishna, 1993) method.

The gaseous top-product containing mainly high-purity argon at about 1.22 bar and -184.5ºC leave from the 1º theoretically vapor stage (top column stage) in the argon side arm partitioned packaged-column (AS-COL-3) is cooled and condensate to 1.22 bar and about -184.5ºC in the aluminum fin-plate condenser exchanger (AS10). Part of the high-purity liquid argon is refluxed back to the argon side arm partitioned packaged-column (AS-COL-3) in the 1º theoretically liquid stage (top column stage) in the argon side arm partitioned packaged-column (AS-COL-3).

The liquid bottom product at about 1.23 bar and -181.3ºC from the 100º theoretically liquid stage (bottom column stage) in the argon side arm partitioned packaged-column (AS-COL-3) is fed in the low-pressure multi-packed column (AS-COL-2) in the in the 47º theoretically liquid stage. The amount of liquid bottom product sent-flowing back is determined by ASPEN Rate-Sep simulation package methods and by the amount of high-purity liquid argon refluxed back to the top (argon purity) of the argon side arm partitioned packaged-column (AS-COL-3).

Aspen Plus®v8.4 process model simulation of the aluminum fin-plate sub-cooler exchanger (AS-9) was developed using MHeatX exchanger block considering 4 zones in countercurrent mode. Bottom liquid Crude product at about 5.80 bar and -171.4ºC from the 45º theoretically liquid stage (bottom column stage) in the high-pressure tray-column (AS-COL-1) is sub-cooled to 5.65 bar and at about -183.8ºC and then expanded in the adiabatic expansion valve (AS-VAL-2) to 1.18 bar and -190.1ºC before inlet in the aluminum fin-plate condenser exchanger (AS10). Top high-purity liquid nitrogen product at about 5.20 bar and -180.5ºC from the aluminum fin-plate sub-cooler exchanger (AS-9) is sub-cooled to 5.00 bar and at about -190.5ºC and then expanded in the anti-flash security valve 3 (AS-VAL-4) adjusting the pressure to tray-pressure requirements (1.10 bar and -190.4ºC) before inlet in the low-pressure multi packed-column (AS-COL-2) in the in the 1º theoretically liquid stage (top column stage).

To sub-cooling the bottom liquid Crude and the top high-purity liquid nitrogen products from the high-pressure tray-column (AS-COL-1) is used gaseous high-purity nitrogen product obtained from the 1º theoretically vapor stage (top column stage) in the low-pressure multi-packed column (AS-COL-2) available at about 1.10 bar and -194.7ºC and synthetic air purged from the 22º theoretically gaseous stage in the low-pressure multi-packed column (AS-COL-2) available at about 1.16 bar and -189.8ºC. The gaseous high-purity nitrogen is heated to about 1.07 bar and - 174.2ºC and the synthetic air purged is heated to about 1.12 bar and -173.0ºC.

Aspen Plus®v8.4 process model simulation of the aluminum fin-plate condenser exchanger (AS10) was developed using MHeatX exchanger block considering 2 zones in countercurrent mode. High-purity gaseous argon product at about 1.22 bar and -184.1ºC from the 1º theoretically vapor stage (top column stage) in the argon side arm partitioned packaged-column (AS-COL-3) is condensed at about 1.22 bar and -184.5ºC using depressurized sub-cooled bottom liquid Crude product. The depressurized sub-cooled bottom liquid Crude product available at about 1.18 bar and -190.1ºC after the adiabatic expansion valve (AS-VAL-2) is heated to about 1.17 bar and -188.1ºC.

Part of condensate high-purity liquid argon top product at about 1.22 bar and -184.5ºC from the aluminum fin-plate condenser exchanger (AS10) is refluxed back (98.19%$_{w/w}$ model result) to the argon side arm partitioned packaged-column (AS-COL-3) in the 1º theoretically liquid stage (top column stage) to achieve the high-purity level. Another remain fraction (1.81%$_{w/w}$ model result) is extracted as high-purity liquid argon product and pumped by cryogenic liquid argon pump (AS-PUM-2) to storage in the cryogenic liquid argon storage tank (AS-STO-3), available as high-purity liquid argon (LIQUID ARGON).

As shown in Figure 68, Aspen Plus®v8.4 flowsheet of the high-pressure double-Claude cycle nitrogen liquefier employed in the double-column cryogenic ASU with high-purity argon recovery for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) which is the same model with modified parameters for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) is compost by: water inter-cooler exchanger (AS-HEA-1); water after-cooler exchanger 1 (AS-HEA-2); water after-cooler exchanger 2 (AS-HEA-3); water after-cooler exchanger 3 (AS-HEA-4); high-efficiency centrifugal two stages compressor (AS-COM-7 and AS-COM-8) with first-stage impeller (AS-COM-7) and second-stage impeller (AS-COM-8); splitter 1 (AS-SPL-6); splitter 2 (AS-SPL-7); splitter 3 (AS-SPL-8); mixer 1 (AS-MIX-2); mixer 2 (AS-MIX-3); mixer 3 (AS-MIX-4); first heat exchanger (AS11); second heat exchanger (A12); cold heat exchanger (AS13); warm high-efficiency turbo booster (AS-COM-9 and AS-EXP-3) with centrifugal compressor (AS-COM-9) and expander (AS-EXP-3); cold high-efficiency turbo booster (AS-COM-10 and AS-EXP-4) with centrifugal compressor (AS-COM-10) and expander (AS-EXP-4); recycle mixer (AS-MIX-1); phase separator vessel (AS-FLA-6); and Joule-Thompson valve (AS-VAL-6).

The Aspen Plus®v8.4 process model simulation of the high-pressure double-Claude cycle nitrogen liquefier has been developed in steady-state mode using VANL-RK physical property methods for the high-purity nitrogen side and IAPWS-95 physical property methods for the cooling water side.

Gaseous high-purity nitrogen product at 1.05 bar and at about -67.7ºC (compression energy-save) from the aluminum fin-plate multi-zones main heat exchanger (AS-2) is sent-enter to the high-pressure double-Claude cycle nitrogen liquefier (LNG-based nitrogen liquefier) in the recycle mixer (AS-MIX-1). The gaseous high-purity nitrogen is mixed (AS-MIX-1) with the heated low-pressure high-purity nitrogen at 1.05 bar and at about -28.1ºC recycled back in loop-cycle. The amount of recycled nitrogen according to Aspen Plus®v8.4 process model simulation is than about 3.6 times the amount of liquefied high-purity nitrogen produced by the high-pressure double-Claude cycle nitrogen liquefier, controlled by the mass and energy balances.

Gaseous high-purity nitrogen product after mixed at 1.05 bar and at about 7.0ºC flow enters the high-efficiency centrifugal two stages compressor (AS-COM-7 and AS-COM-8) by the inlet guide (AS-COM-7) to distribute the flow providing a uniform condition in the first-stage impeller (AS-COM-7). Gaseous high-purity nitrogen is compressed to optimized pressure level and at about 190.0ºC by the first-stage impeller (AS-COM-7) modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering about 90.0% isentropic efficiency (isentropic compression) and 99.0% mechanical efficiency.

The compressed gaseous nitrogen after the first-stage of compression (AS-COM-7) ducted-leaving is cooled from about 190.0ºC to 40.0ºC without form condensed phase (free of impurities) in the water inter-cooler exchanger (AS-HEA-1) modeled by using a HeatX exchanger block and then compressed in the second-stage impeller (AS-COM-8) to optimized intermediate-pressure level and at about 190.0ºC considering of about 90.0% of isentropic efficiency (isentropic compression) and 99.0% of mechanical efficiency modeled by Compr pressure changers block according to rigorous ASME method for isentropic compressor. The compressed gaseous high-purity nitrogen after the second-stage of compression (AS-COM-8) ducted-leaving is cooled from about 190.0ºC to 40.0ºC without condensed phase (free of impurities) in the water after-cooler exchanger (AS-HEA-2) modeled by using a HeatX exchanger block.

The pressure levels in the first-stage impeller (AS-COM-7) and second-stage impeller (AS-COM-8) is controlled by design specification DS-AS-PG-1 varying the pressure obtained after the centrifugal compression stages (AS-COM-7 and AS-COM-8) defining the inter-stage pressure for high-efficiency compression (minimizing the electricity consumption). The cycle pressure is defined by the mass and energy balances in the warm high-efficiency turbo booster (AS-COM-9 and AS-EXP-3) and cold high-efficiency turbo booster (AS-COM-10 and AS-EXP-4) to obtain a final pressure of 40.0 bar after the turbo booster compression/expansion steps.

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM12) to the cooling water circuit in the inter-cooler exchanger (AS-HEA-1) and to the cooling water circuit in the after-cooler exchanger (AS-HEA-2). The amount of water used to cool-down the gaseous high-purity nitrogen after compression stages is determined and controlled by design specification DS-AS-FL-14 varying the mass flow rate of cooling water passing through the water inter-cooler exchanger (AS-HEA-1) and design specification DS-AS-FL-15 varying the mass flow rate of cooling water passing through the water after-cooler exchanger (AS-HEA-2), The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

The intermediate-pressurized gaseous nitrogen (at about 18.75 bar by model result) and 40.0ºC is separated in two fraction in the splitter 1 (AS-SPL-6) being considered in the Aspen Plus®v8.4 process model simulation 65.0%$_{w/w}$ destined to the cold high-efficiency turbo booster compressor (AS-COM-10) and the other 35.0%$_{w/w}$ destined to the warm high-efficiency turbo booster compressor (AS-COM-9).

One fraction (65.0%$_{w/w}$) is compressed by the cold booster centrifugal impeller (AS-COM-10) to 40.0 bar and at about 123.0ºC modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 92.0% isentropic efficiency (isentropic compression) and 99.0% mechanical efficiency. Another fraction (35.0%$_{w/w}$) is compressed by the warm booster centrifugal impeller (AS-COM-9) to 40.0 bar and at about 123.0ºC modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 92.0% isentropic efficiency (isentropic compression) and 99.0% mechanical efficiency.

The high-pressure gaseous nitrogen after the high-efficiency cold booster compression steps (AS-COM-10) is cooled in the water after-cooler exchanger 2 (AS-HEA-3) from about 123.0ºC to 30.0ºC without condensed phase (free of impurities) modeled by using a HeatX exchanger block (AS-HEA-1). The high-pressure gaseous nitrogen after the warm booster compression steps (AS-COM-9) is cooled in the water after-cooler exchanger 3 (AS-HEA-4) from about 123.0ºC to 30.0ºC without condensed phase (free of impurities) modeled by using a HeatX exchanger block (AS-HEA-1).

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM12) to the cooling water circuit in the water after-cooler exchanger 2 (AS-HEA-3) and to the cooling water circuit in the water after-cooler exchanger 3 (AS-HEA-4). The amount of cooling water used to cool-down the high-pressure gaseous high-purity nitrogen after the high-efficiency booster compression stages is controlled by design specification DS-AS-FL-17 varying the mass flow rate of cooling water passing through the water after-cooler exchanger 2 (AS-HEA-3) and design specification DS-AS-FL-16 varying the mass flow rate of cooling water passing through the water after-cooler exchanger 3 (AS-HEA-4). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

The two fractions of high-pressure and cooled gaseous high-purity nitrogen are mixed in the mixer 1 (AS-MIX-2) and then is fed in the sequential cryogenic aluminum fin-plate heat exchangers.

In the hot-side of the first heat exchanger (AS11) modeled by using a MHeatX exchanger block the nitrogen at 40.0 bar and 30.0ºC is cooled-down to 40.0 bar and at about -5.0ºC by coolant nitrogen in the cold-side. Coolant nitrogen is heated from 1.05 bar and at about -20.0ºC to 1.05 bar and 28.0ºC leave-recycled back to recycle mixer (AS-MIX-1).

A fraction (about 20.0%$_{w/w}$ by model result) of the cooled high-purity nitrogen is splitted in the splitter 2 (AS-SPL-7) and sent to the warm high-efficiency turbo booster expander (AS-EXP-3) modeled by using a Compr pressure changer block in turbine model considering 92.0% isentropic efficiency and 99.0% mechanical efficiency. Cooled high-purity nitrogen is expanded from 40.0 bar and -5.0ºC to 1.05 bar and -167.2ºC. The expanded gaseous nitrogen is mixed in the mixer 2 (AS-MIX-3) with coolant nitrogen at 1.05 bar and -71.1ºC from the second heat exchanger (A12) and then sent back to the cold-side of the first heat exchanger (AS11).

A fraction (about 80.0%$_{w/w}$ by model result) of the cooled high-purity nitrogen that bypass the warm high-efficiency turbo booster expander (AS-EXP-3) is cooled-down passing through the hot-side of the second heat exchanger (AS12) modeled by using a MHeatX exchanger block. The cooled high-purity nitrogen is sub-cooled from 40.0 bar and at about -5.0ºC to 40.0 bar and at about -70.0ºC by the coolant nitrogen in the cold-side of the second heat exchanger (AS12). Coolant nitrogen is heated from 1.05 bar and at about -95.0ºC to 1.05 bar and -20.0ºC leaving to first heat exchanger (AS11).

A fraction of the sub-cooled high-purity nitrogen is splitted in the splitter 3 (AS-SPL-8) and send to the cold high-efficiency turbo booster expander (AS-EXP-4) modeled by using a Compr pressure changer block in turbine model considering 92.0% isentropic efficiency (isentropic compression) and 99.0% mechanical efficiency. Sub-cooled high-purity nitrogen is expanded from 40.0 bar and -70.0ºC to 1.05 bar and -195.2ºC producing work power for the cold high-efficiency turbo booster compressor (AS-COM-10). The splitted fraction (AS-SPL-8) is controlled by design specification DS-AP-PG-2 varying the mass flow rate of cooled high-purity nitrogen expanded-required to (work power requirements) compress the intermediate-pressure high-purity nitrogen to 40.0 bar and at about 123.0ºC in the cold booster centrifugal high-efficiency compression impeller (AS-COM-10). The expanded gaseous high-purity nitrogen is mixed in the mixer 3 (AS-MIX-4) with coolant nitrogen at 1.05 bar and -195.4ºC from the phase separator vessel (AS-FLA-6) and then sent back to the cold-side of the cold heat exchanger (AS13).

A fraction of sub-cooled high-purity nitrogen that bypass the cold high-efficiency turbo booster expander (AS-EXP-4) is cooled-down passing through the hot-side of the cold heat exchanger (AS13) modeled by sing a MHeatX exchanger block. The sub-cooled high-purity nitrogen is sub-cooled from 40.0 bar and at about -70.0ºC to 40.0 bar and optimized temperature (about -168.2ºC by model result) being liquefied by the gaseous coolant nitrogen in the cold-side of the cold heat exchanger (AS13). Coolant nitrogen is heated from 1.05 bar and at about -195.3ºC to 1.05 bar and at about -71.0ºC leaving to the mixer 2 (AS-MIX-3). The outlet optimized temperature of the high-pressure liquefied nitrogen is determined by design specification DS-AS-VF-

1 varying the hot-side temperature in the cold heat exchanger (AS13) to obtain the vapor fraction of 0.30 after expansion in the Joule-Thompson valve (AS-VAL-6).

Joule-Thompson valve (AS-VAL-6) modeled by Valve pressure changers expand the high-pressure liquefied nitrogen at 40.0 bar and at about -168.2ºC to 1.05 bar and at about -195.4ºC. In the Aspen Plus®v8.4 process model simulation the high-pressure double-Claude cycle is configured to obtain $30\%_{w/w}$ of vapor phase and $70\%_{w/w}$ of liquid phase (vapor fraction of 0.30) according to temperature limits between the first heat exchanger (AS11), second heat exchanger (A12) and cold heat exchanger (AS13) (crossover avoided). Model also considers the relation between the mass flow rate of the cryogenic gaseous nitrogen recycled as coolant fluid and the consumption of electricity (work power) to re-compress this cryogenic gaseous nitrogen recycled (loop-cycle). The vapor fraction form by the expansion in the joule-Thompson valve (AS-VAL-6) is controlled by design specification DS-AS-VF-1 varying the hot-side outlet temperature in the cold heat exchanger (AS13).

The liquid and vapor phases is flash separated in the phase separator vessel (AS-FLA-6) modeled by using a Flash2 separator block without heat loss (adiabatic flash separation) at pressure of 1.05 bar to represent the phase separation process. The vapor phase of high-purity nitrogen is sent-back recycled and mixed in the mixer 3 (AS-MIX-4) with the expanded gaseous high-purity nitrogen at 1.05 bar and at about -195.4ºC (same conditions) from the high-efficiency turbo booster expander (AS-EXP-4). This mixture of nitrogen streams is used to cool-down in countercurrent the main stream of high-pressure nitrogen in the cold-side of the heater exchangers to obtain the liquefied state.

The liquid phase containing mainly nitrogen is drained as final high-purity product from the phase separator vessel (AS-FLA-6) and sent to storage in the cryogenic liquid nitrogen storage tank (AS-STO-1) been mixed together with the fraction of the high-purity liquid nitrogen condensed in the aluminum fin-plate condenser/reboiler exchanger (AS-8) condenser-zone obtained from the 1º theoretically stage (top column stage) in the high-pressure tray-column (AS-COL-1), available as high-purity liquid nitrogen (LIQUID NITROGEN).

8.1.7 Syngas cooling and heat recovery

The synthesis gas at low-pressure require compression process to achieve the required pressure for the high-performance sequential combustion full-flow advanced EvGT, HT and LT catalyst WGS reactors at intermediate-pressure level with energy-saving and steam generation and mixed alcohols catalytic-synthesis. To compress the synthesis gas is necessary reducing the synthesis gas temperature in order to reduce the consumption of electrical energy and fit the maximum temperature allowed by the compressor. Hot synthesis gas has a great potential to thermal energy generation (sensible heat) and recovery this heat can increase the process steam production and reduce the stress on the HRSG system in the Biomass-to-Mixed alcohols route.

As shown in Figure 37, Aspen Plus®v8.4 flowsheet of the syngas cooling and heat recovery for BIG-ICE/CC (SC1) and for BIG-ICE/CC (SC2) which is the same model with modified parameters for Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC) is compost by: high-temperature vertical CSC (GA-CSC-1); low-temperature vertical CSC (GA-CSC-2); water pump 1 (GA-PUM-1); and water pump 2 (GA-PUM-2).

Atmospheric crude hot-synthesis gas that leave the secondary multi-cyclone system (GA-CYC-2) is cooled in two cooling sections generating intermediate-pressure steam by the high-temperature vertical CSC (GA-CSC-1) and low-pressure steam by the low-temperature vertical CSC (GA-CSC-2), without the catalytic high-performance CF.

The high-temperature vertical CSC (GA-CSC-1) modeled by HeatX exchanger block using RKS-BM physical property methods to atmospheric crude hot-synthesis gas side and IAPWS-95 physical property methods to hot water/steam side. The low-temperature vertical CSC (GA-CSC-2) modeled by HeatX exchanger block using RKS-BM physical property methods to atmospheric crude hot-synthesis gas side and IAPWS-95 physical property methods to hot water/steam side.

In the Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC3) the atmospheric crude hot-synthesis gas produced by the atmospheric CFB directly-heated gasifier at 850.0ºC is cooled to about 124.0ºC. In the Biomass-to-Mixed alcohols (SC2) the atmospheric crude hot-synthesis gas produced by the atmospheric CFB directly-heated gasifier at 850.0ºC is cooled to about 111.0ºC.

Deaerated hot process water from first deaerator unit (HR-DEA-1) at 1.4 bar and 105.0ºC is pumped (GA-PUM-2) to 23.0 bar before entering into the high-temperature vertical CSC (GA-CSC-1). The atmospheric crude hot-synthesis gas is cooled in the first-section of (GA-CSC-1) exchange sensible heat to produce intermediate-pressure steam. In the Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC2), intermediate-pressure steam at 23.0 bar and 345.9ºC is produced and expanded in the second-section of the EBPST system (ST blocks) to generate electrical energy. In the Biomass-to-Mixed alcohols (SC3), intermediate-pressure steam at 23.0 bar and 480.0ºC (reheater pipe bank) is produced and expanded in the second-section of the CEST system (ST blocks) to generate electrical energy.

In the Biomass-to-Mixed alcohols (SC2) the atmospheric crude hot-synthesis gas at 411.0ºC after the high-temperature vertical CSC (GA-CSC-1) is cooled in the second section (GA-CSC-2) at about 111.0ºC. In the Biomass-to-Mixed alcohols (SC1) and

Biomass-to-Mixed alcohols (SC3) the atmospheric crude hot-synthesis gas at 416.0ºC after the high-temperature vertical CSC (GA-CSC-1) is cooled in the second section (GA-CSC-2) at about 124.0ºC.

In the Biomass-to-Mixed alcohols (SC2) condensed water after the stripper reboiler (CA-REB-1) at 2.3 bar and 124.0ºC and part of the deaerated hot process water from first deaerator unit (HR-DEA-1) at 1.4 bar and 105.0ºC are sent to equalizer tank (HR-Tan-1) as conditioned hot water and after-pumped (GA-PUM-1) to the syngas cooling and heat recovery (GA blocks) to produce the gasification steam agent at 2.5 bar and 150.0ºC in the low-temperature vertical CSC (GA-CSC-2). In the Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC3) part of the condensed water after the stripper reboiler (CA-REB-1) at 2.3 bar and 123.0ºC is pumped (GA-PUM-1) to the syngas cooling and heat recovery (GA blocks) to produce the gasification steam agent at 2.5 bar and 150.0ºC in the low-temperature vertical CSC (GA-CSC-2).

Cooled crude synthesis gas is fed in the evaporative vertical quencher (spray tower) (SC-SCR-1) in the low-temperature synthesis gas wet cleaning system (wet scrubbing unit).

The mass flow rate of deaerated hot process water to intermediate-pressure steam generation is controlled by the design specification DS-GA-TL-1 varying the inlet mass flow rate of deaerated hot process water in the high-temperature vertical CSC (GA-CSC-1) coupled with the design specification DS-GA-TL-2 which determines the temperature between the high-temperature vertical CSC (GA-CSC-1) and low-temperature vertical CSC (GA-CSC-2) sections.

The mass flow rate of deaerated hot process water to low-pressure steam generation is controlled by design specification DS-GA-FG-1 varying the inlet mass flow rate to produce gasification steam agent at 2.5 bar and 150.0ºC to atmospheric CFB directly-heated gasifier (GA-GASEI and GA-LSE-1). The amount of gasification steam agent is determined by Equation 7 to obtain a STBR of 0.5, considering the moisture present in the biomass-fuel inlet into the gasifier (GA-GASEI).

The catalytic high-performance CF between the high-temperature vertical CSC (GA-CSC-1) and the low-temperature vertical CSC (GA-CSC-2) to reforming the reminiscent tar and heavy hydrocarbons, and remove part of the particle content in the atmospheric crude synthesis gas is not implemented in the Aspen Plus®v8.4 process model simulation of the syngas cooling and heat recovery due the limitations of the gasification Gibbs equilibrium model (GA-GASEI). Considering the presence of olivine catalyst in the gasifier bed (GA-GASEI) only traces of tar and heavy hydrocarbons is expected.

8.1.8 Low-temperature synthesis gas wet cleaning system

After the initial particulate removal accomplished by the multi-cyclones system (GA-CYC-2) and the convective indirect cooling of the crude synthesis gas by the syngas cooling and heat recovery an additional cooling step is carried out by wet scrubbing unit (direct water contact cooling).

The low-temperature synthesis gas wet cleaning system (wet scrubbing unit) is used to remove water-soluble contaminants and particles from the synthesis gas including (NH_3), hydrogen chloride (HCl), sulfur oxides (SO_x), carbonyl sulfide (COS), volatile organic compounds, tar and oils (heavy hydrocarbons), particles containing metals and metal salts, unconverted char (C) solid particulates, materials bed particles (not included in the Aspen Plus®v8.4 process model simulation) and others alkali compounds. Also remove a small part of hydrogen sulfide (H_2S), nitrous oxides (NO_x) and carbon dioxide (CO_2).

As shown in Figure 38, Aspen Plus®v8.4 flowsheet of the low-temperature synthesis gas wet cleaning system for BIG-ICE/CC (SC1) and for BIG-ICE/CC (SC2) which is the same model with modified parameters for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) is compost by: vertical down-flow water spray quencher (SC-SCR-1); vertical water venturi scrubber (SC-SCR-1); decanter to separate the heavy hydrocarbons from the water (not included in the Aspen Plus®v8.4 process model simulation); water recovery and recycle unit (SC-FLA-2); packet-bed condenser/absorber sub-cooler (SC-FLA-1); mist eliminator (demister) drum (SC-FLA-3); wet electrostatic precipitator (WESP) (SC-ESP-1); blower system (SC-BLO-1); after air cooler (SC-FLA-4); condensate knock-out drum (SC-FLA-4); clarifier and decanter units (SC-FLA-2) to separate sludge from the water; sludge setting tank (SC-SEP-2) slurry pump (SC-PUM-2); water pumps (SC-PUM-1); cleaned water recirculation tank (SC-SEP-2); and humidified particles temporary bin (SC-FLA-5).

The Aspen Plus®v8.4 process model simulation of the low-temperature synthesis gas wet cleaning system was developed using Electrolyte NRTL physical property methods for liquid phase and RK equation of state for vapor phase (ELECNRTL physical property methods) for electrolytes calculation using true components approach and aqueous activity coefficient basis for Henry components. The selected components (e.g.: H_2, O_2, N_2, Ne, He, Ar, Kr, Xe, CO, CO_2, Cl_2, SO_2, NH_3, H_2S, CHN, HCL) to employ the Henry's law as supercritical and non-condensable components for represent the behavior of dissolved gases according to the affinity with water and their interaction with other electrolytes presents.

The interaction of the key components potentially presents in the cooled crude synthesis gas in the presence of pure-water is evaluated in the Aspen Plus®v8.4 process model simulation of the low-temperature synthesis gas wet cleaning system.

The model was developed with a chemistry model for specify reactions method applying the Elec Wizard auxiliary tool to generate possible components and reactions for the electrolyte simulation approach. The approach include the salt formation and dissociation reaction in water based on the hydronium ion (H_3O^+) reactions mechanism according to the electrolyte solution chemistry (Chemistry ID: CH-SC-SOU) presented in the section 6.1.7 (Low-temperature synthesis gas wet cleaning system) as described for BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2).

The cooled crude synthesis gas from the low-temperature vertical CSC (GA-CSC-2) is down-flow conducted through the vertical water spray quencher (SC-SCR-1) in direct contact with recycled pure-water (without alkali addition) at 25.0ºC injected by spray nozzles. The injected water is vaporized cooling down (pre-cooling chamber) the synthesis gas to saturation conditions at about 100.0ºC (without water condensation) before entering the vertical venturi scrubber (SC-SCR-1) with water loop tar removal system.

The Aspen Plus®v8.4 process model simulation for the vertical water spray quencher (SC-SCR-1) coupled in the vertical venturi scrubber (SC-SCR-1) uses Calvert's calculation method for spray tower designed for separation efficiency of 0.7 in the vertical venturi scrubber (SC-SCR-1) and the electrolyte solution chemistry (CH-SC-SOU) to estimate the dissolved gases, the electrolytes interactions by salt formation and dissociation reaction in pure water. The solid particles scrubbed (SC-SCR-1) are removed in the VSscrub solids separator block, the scrubbing liquid phase is removed in the Flash2 separator block (SC-FLA-1) together the condensed phase in the packet-bed condenser/absorber sub-cooler (SC-FLA-1).

The electrolyte solution chemistry model Chemistry ID: CH-SC-SOU implemented in the Aspen Plus®v8.4 process model simulation of the low-temperature synthesis gas wet cleaning system was developed with a CHEMISTRY model according to section 6.1.7 (Low-temperature synthesis gas wet cleaning system) as described for BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2).

In the vertical venturi scrubber (SC-SCR-1) is collected the gross-particulate according to the aerodynamic size and removed the condensed residual heavy hydrocarbons (e.g.: tar, oils) in the basin (SC-FLA-2) of the venturi scrubber (liquid drain) by the water loop tar removal system (not included in the Aspen Plus®v8.4 process model simulation). The scrubbed liquid with heavy hydrocarbons mixed with water is collected in the basin (SC-FLA-2) and sent to oil/water separator (not included in the Aspen Plus®v8.4 process model simulation) to remove the hydrocarbons from the water by density differences. The liquid hydrocarbons removed is sent to final disposal or sent-back to the gasifier (GA-GASEI), the water phase is recovered and recycle to the venturi scrubber (SC-SCR-1) at 25.0ºC and injected by spray nozzles in the chamber.

Cleaned water is pumped from the cleaned water recirculation tank (SC-SEP-2) in closed-loop cycle to the packet-bed condenser/absorber sub-cooler (SC-FLA-1).

Cooled synthesis gas is then sub-cooled to 45.0ºC being removed 15.0%$_{w/w}$ of the entrained fine-particles. Is used a large amount of recycled-water from the cleaned water recirculation tank (SC-SEP-2) in the packet-bed condenser/absorber sub-cooler (SC-FLA-1).

The Aspen Plus®v8.4 process model simulation consider 0.5%$_{w/w}$ of entrained water to mist eliminator (SC-FLA-3) which is responsible to remove the excess of water content droplets in the sub-cooled synthesis gas at saturation conditions before entering in the WESP (SC-ESP-1).

The amount of cleaned-water recycled to vertical water spray quencher (SC-SCR-1) and to vertical venturi scrubber (SC-SCR-1) is controlled by design specification DS-SC-TG-1 varying the inlet cleaned-water (SC-SPL-1) in order to achieve the saturation condition (cooling). The amount of cleaned-water recycled to packet-bed condenser/absorber sub-cooler (SC-FLA-1) is controlled by design specification DS-SC-TG-2 varying the inlet cleaned-water (SC-SPL-2) in order to achieve the sub-cooled condition for WESP system (SC-ESP-1) and the synthesis gas temperature required by the low-pressure absorber packed-column (CA-ABS-1) in the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks).

The built-in expression (Equation 2731) for calculating equilibrium constants is used for the reactions from 1 to 17 in CH-SC-SOU electrolyte solution chemistry. The built-in expression (Equation 28) for calculating salt precipitation equilibrium constants is used for the reactions from 18 to 25 in CH-SC-SOU electrolyte solution chemistry.

The ELECNRTL physical property methods is used in the low-temperature synthesis gas wet cleaning system (SC blocks) with the same properties assumption employed in the Aspen Plus®v8.4 process model simulation of the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks) detailed-described in the section 7.2.12 (Co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution) described for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3), and according to section 6.1.7 (Low-temperature synthesis gas wet cleaning system) described for BIG-ICE/CC (SC1) and BIG-ICE/CC (SC2).

The excess of the wastewater recovered from the basin (SC-FLA-2) of the vertical venturi scrubber (SC-SCR-1), from the cooler condenser basin (SC-FLA-2) and from the mist eliminator (SC-FLA-3) is sent to the clarifier and decanter units (SC-SEP-2) and cleaned water recirculation tank (SC-SEP-2) to remove the sludge and to be cooled at ambient conditions. The contend solids and precipitated or dissociated salts is concentrate in the bottom sludge phase and sent to the sludge setting tank (SC-SEP-2) to be removed and sent of-site to final disposal in the sugarcane field. In the Aspen Plus®v8.4 process model simulation is considered 50.0%$_{w/w}$ of water content in the sludge phase, which can be pumped by slurry pump (SC-PUM-2) to storage tank before send-off the site by tank truck transporter (SLURRY TO DISPOSAL).

The cleaned water from the clarifiers (SC-SEP-2) at quality requirements to be recycled to vertical water spray quencher (SC-SCR-1) and to vertical venturi scrubber (SC-SCR-1) is stored in the cleaned water recirculation tank (SC-SEP-2). The excess of water recovered from the synthesis gas is separate (SC-SPL2) and pumped (SC-PUM-1) to wastewater treatment plant (WASTEWATER TO TREATEMNT PLANT) to be used as make-up water for other processes (loss reduction principles).

In the Aspen Plus$^{®}$v8.4 process model simulation of the synthesis gas cleaning wet system is considered the WESP (SC-ESP-1) operating at satured synthesis gas conditions (100% relative humidity) to remove the persistent fine-particles (final particles) as additional particulate polishing step. The WESP (SC-ESP-1) is modeled according to Svarovsky calculation model for vertically mounted collecting plate's model with separation efficiency of 92.0% of the particles present in the sub-cooled synthesis gas stream and based on the migration velocity and the ratio of precipitation area.

The persistent fine-particles collected is removed from the basin (SC-ESP-1) and conveyed to be stored into the humidified particles temporary bin (SC-FLA-5) until offloaded (PARTICLES TO DISPOSAL) for the final disposal (field disposal together vinasses and gasifier bottom particulate materials).

Blower system (SC-BLO-1) with induced draft fan is modeled by using a Compr pressure changer block according to isentropic method for compressor considering 85.0% isentropic efficiency and 99.0% mechanical efficiency. The system is used to produce the desired pressure drop across the venturi scrubber system and to equalize the pressure (drop pressure) inducing the synthesis gas flow through the system at desired mass flow rate. After pressurized (SC-BLO-1) the sub-cooled synthesis gas is cooled in the air cooler (SC-FLA-4) and the condensed phase removed in the knock-out drum (SC-FLA-4) back to the cleaned water recirculation tank (SC-SEP-2).

The sub-cooled synthesis gas for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3) is sent-ducted as partial-cleaned synthesis gas to integrally-geared centrifugal three stages compressor (CO blocks) in the first-section of synthesis gas compression (conditioning). The integrally-geared centrifugal three stages compressor (CO blocks) is used to conditioning the sub-cooled and partial-cleaned synthesis gas to be used in the high-performance sequential combustion full-flow advanced EvGT (GT blocks) and in the HT and LT catalyst WGS reactors (WS blocks) at intermediate-pressure level with energy-saving and steam generation.

8.1.9 First-section of synthesis gas compression (conditioning)

The sub-cooled synthesis gas obtained in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3) is compressed to an intermediate pressure between the gasifier and mixed alcohols catalytic-synthesis pressure by integrally-geared centrifugal three stages compressor (CO blocks).

The Aspen Plus®v8.4 process model simulation of the integrally-geared centrifugal three stages compressor (CO-COM blocks) is based on the Siemens STC-GV integrally-geared centrifugal multi-stages compressor series feature a single-shaft arrangement and configured to allow inter-cooling steps.

As shown in Figure 69, Aspen Plus®v8.4 flowsheet of the first-section of synthesis gas compression (conditioning) in the Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) which is the same model with modified parameters in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) is compost by: integrally-geared centrifugal three stages compressor (CO-COM-1~3); tree-circuits water inter-cooler exchanger (CO-1); water inter-cooler exchanger (CO-2); condenser knock-out drums (CO-FLA-1~3); direct drive permanent magnet motor (not included as block); atmospheric condensate buffer/equalizer tank (CO-FLA-4); and liquid water pump (CO-PUM-1).

The sub-cooled and partial-cleaned synthesis gas from the knock-out drum (SC-FLA-4) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) from the low-temperature synthesis gas wet cleaning system flow enters the compressor by the inlet guide (CO-COM-1) to distribute the flow providing a uniform condition in the first-stage impeller (CO-COM-1). The sub-cooled and partial-cleaned synthesis gas is compressed to an optimized pressure (OP-CO-PG-1) by the first-stage impeller (CO-COM-1) modeled by using a Compr pressure changer block (CO-COM-1) according to rigorous ASME method for isentropic compressor considering 83.0% isentropic efficiency (isentropic compression).

The synthesis gas after the first-stage of compression (CO-COM-1) ducted-leaving is cooled to 30.0ºC by the tree-circuits water inter-cooler exchanger (CO-1) modeled by using a MHeatX exchanger block generating condensed phase content water and dissolved gases. The condensed phase is removed in the condenser knock-out drum (CO-FLA-1) modeled by using a Flash2 separator block and sent to atmospheric condensate buffer/equalizer tank (CO-FLA-4) modeled by using a Flash2 separator block (CO-FLA-4) at ambient conditions.

The synthesis gas free of the condensate phase enters in the second-stage impeller (CO-COM-2) and is compressed to an optimized pressure (OP-CO-PG-1) modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 83.0% isentropic efficiency (isentropic compression).

The synthesis gas after the second-stage of compression (CO-COM-2) ducted-leaving is cooled to 30.0ºC by the water inter-cooler exchanger (CO-2) modeled by using a MHeatX exchanger block generating condensed phase content water and dissolved gases. The condensed phase is removed in the condenser knock-out drum (CO-FLA-2) modeled by using a Flash2 separator block (CO-FLA-2) and sent to atmospheric condensate buffer/equalizer tank (CO-FLA-4) to be after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

The synthesis gas free of the condensate phase enters in the third-stage impeller (CO-COM-3) and is compressed delivering conditioned synthesis gas at required pressure by the downdraft equipment. The high-performance sequential combustion full-flow advanced EvGT (GT blocks) requires a pressure at about 23.0 bar (turbine configuration) in their injection system (GT-SPL-1). The third-stage impeller (CO-COM-3) is modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 83.0% of isentropic efficiency (isentropic compression). The synthesis gas after the third-stage of compression (CO-COM-3) ducted-leaving is not cooled by after-cooler and is ducted to buffer/equalizer tank (CO-FLA-3) or condenser knock-out drum (CO-FLA-3) modeled by using a Flash2 separator block as conditioned synthesis gas to be used as fuel-gas in the high-performance sequential combustion full-flow advanced EvGT (GT blocks) operating in CC mode.

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-4) to the cooling water circuits in the inter-cooler exchangers (CO-1 and CO-2). The amount of water used to cool-down the synthesis gas is determined and controlled by design specification DS-CO-TL-1 varying the mass flow rate of cooling water passing through the cooling water circuit in the three-circuit water inter-cooler exchanger (CO-1) and by design specification DS-CO-TL-2 varying the mass flow rate of cooling water passing through the water inter-cooler exchanger (CO-2). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system. The lubricating oil circuit and the lubricating water-cooling system are suppressed from the Aspen Plus®v8.4 process model simulations in this research Master`s degree.

Part of the deaerator make-up water (WATER FROM TREATMENT PLANT) at atmospheric pressure and 25.0ºC is pumped at 1.42 bar by the liquid water pump (CO-PUM-1) and preheated at 105ºC (deaerator requirements) in the three-circuit water inter-cooler exchanger (CO-1) and then sent-fed in the first deaerator unit (HR-DEA-1), recovering heat and consequently reducing the low-pressure steam required by the first deaerator unit (HR-DEA-1).

The single shaft and pinions with variable speed gears in the integrally-geared centrifugal three stages compressor (CO-COM blocks) is driver by a synchronous direct drive permanent magnet motor modeled by CO-E-3 work stream and optimized to achieve the lowest consumption of electric power energy. The electric power energy consumed is optimize-minimized using optimization model analysis tools OP-CO-PG-1 varying the pressure obtained after the first-stage impeller (CO-COM-1) and after the second-stage impeller (CO-COM-2) in combined mode according with model analysis tools constraint CN-CO-PG-1 ensuring the technical compression fundaments (raise pressure in the next stage). The electrical potential losses by attrite in the mechanical move parts was considered as 1.0% of the mechanical energy required by the stage (99.0% mechanical efficiency).

8.1.10 Synthesis gas destinations (split)

The synthesis gas at intermediate-pressure from the condenser knock-out drum (CO-FLA-3) in the first-section of synthesis gas compression (conditioning) (CO blocks) is separated in the intermediate-pressure synthesis gas splitter (WS-SPL-1). In the Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC3) is separated in two streams and in the Biomass-to-Mixed alcohols (SC2) in three streams.

In the Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC3) a fraction of the intermediate-pressure synthesis gas is destined to HT and LT catalyst WGS reactors (WS blocks) and the another fraction bypass the catalyst WGS reactors and is sent directly to the energy-saving and steam generation section (WS blocks) before fed-enter the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks).

In the Biomass-to-Mixed alcohols (SC2) a fraction of the intermediate-pressure synthesis gas is destined to HT and LT catalyst WGS reactors (WS blocks), another fraction to high-performance sequential combustion full-flow advanced EvGT (GT blocks) and the reminiscent fraction bypass the catalyst WGS reactors and is sent directly to the energy-saving and steam generation section (WS blocks) before fed-enter the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks).

8.1.11 Co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution

PZ/MDEA blend-based aqueous absorbing-solution for the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3) consider the use of PZ/MDEA blend absorbing-solution with 5.0%$_{w/w}$ of piperazine (PZ) and 33.0%$_{w/w}$ of methyl-diethanolamine (MDEA) in aqueous solution.

Aspen Plus®v8.4 process model simulation of the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution at intermediate-pressure with lower emissions of degradation products is considered in order to remove 96.0%$_{w/w}$ of CO_2 (to achieve the requirement for mixed alcohols catalytic-synthesis) content in the synthesis gas. The PZ/MDEA blend-based aqueous absorbing-solution has the potential to co-capture H_2S and fractions of carbonyl sulfide (COS), carbonyl disulfide (CS_2) and mercaptans (is not the main goal) removed a lesser extension from the system. The amount of co-captured compounds depends on the PZ/MDEA-based aqueous absorbing-solution mass flow rate circulating in the system.

In Biomass-to-Methanol scenarios the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution is used only to remove components of the synthesis gas main stream from gasification process (after cleaning and compression processes). In Biomass-to-Mixed-alcohol scenarios the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution is used to remove components in the synthesis gas main stream (intermediate-pressure synthesis gas) from gasification process (after cleaning and compression processes) and components in the intermediate-pressure off-gas (low hydrogen concentration) from the hydrogen recovery by four-bed PSA system.

The rigorous Aspen Plus®v8.4 process model simulation of co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks) consider the complete cycle in closed-loop cycle mode under the steady state operating conditions. The model was developed using Electrolyte NRTL physical property methods for liquid phase and RK equation of state for vapor phase (ELECNRTL physical property methods) for electrolytes calculation using true components approach and aqueous activity coefficient basis for Henry components. The selected components (e.g.: H_2, O_2, N_2, Ne, He, Ar, Kr, Xe, CO, CO_2, Cl_2, NH_3, CHN, HCL, CH4, NO_x, SO_x) to employ the Henry's law as supercritical and non-condensable components for represent the behavior of dissolved gases according to the affinity with water and their interaction with electrolytes.

Figure 87 shows the Aspen Plus®v8.4 flowsheet of the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (5.0%$_{w/w}$ of PZ and 33.0%$_{w/w}$ of MDEA aqueous blend absorbing-solution) for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3).

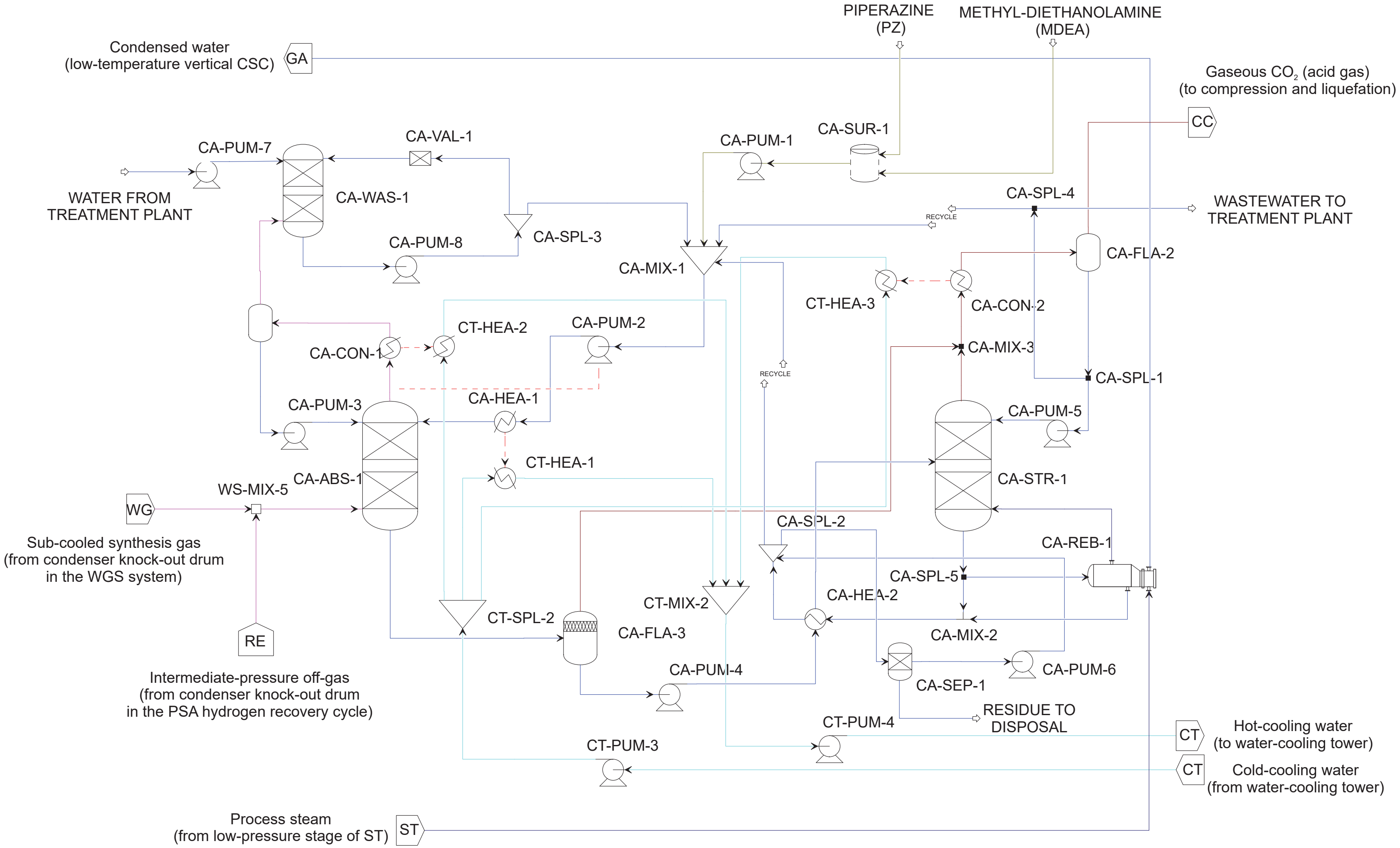


Figure 87 - Aspen Plus® v8.4 flowsheet of the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (5.0%$_{w/w}$ of PZ and 33.0%$_{w/w}$ of MDEA aqueous blend absorbing-solution) for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3)

As shown in Figure 87, Aspen Plus®v8.4 flowsheet of the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3) is compost by: intermediate-pressure absorber tray-column (CA-ABS-1); low-pressure stripper packed-column (CA-STR-1); washer packed-column section (CA-WAS-1); gases mixer (WS-MIX-5); washer water recycle-pump (CA-PUM-8); washer water bleed (CA-SPL-3); rich-amine flash vessel (CA-FLA-3); gaseous mixer (CA-MIX-3); cross-solution heat exchanger (CA-HEA-2); mixture tank (CA-MIX-1); amine surge tank (CA-SUR-1); amine supply pump (CA-PUM-1); lean-amine pump (CA-PUM-2); absorber reflux-pump (CA-PUM-3); desorber reflux pump (CA-PUM-5); absorber condenser (CA-CON-1 and CT-HEA-2); absorber liquid reflux-drum (CA-FLA-1); water purge splitter (CA-SPL-4); striper liquid reflux-drum (CA-FLA-2); stripper condenser (CA-CON-2 and CT-HEA-3); striper water bleed (CA-SPL-1); lean-amine water cooler (CA-HEA-1 and CT-HEA-1); rich-amine pump (CA-PUM-4); carbon-based filter (CA-SEP-1); stripper reboiler (CA-REB-1); lean-amine sump splitter (CA-SPL-5); amine reclaimer (CA-SPL-2); reclaimer recirculation pump (CA-PUM-6); lean-amine regenerated mixer (CA-MIX-2); make-up water pump (CA-PUM-7); and cooling water pumps (CT-PUM-3 and CT-PUM-4)

The model consider the heat integrations to obtain the rigorous energy balance of the system and the mass flow rate of process steam (thermal energy) and cooling water required by the system (reboiler and condensers equipments). The rigorous model is essential and indispensable to determine the influence of this system in the thermal energy balances of the integrated processes in the thermochemical-biorefinery.

ASPEN Rate-Sep simulation package is used in the intermediate-pressure absorber tray-column (CA-ABS-1), low-pressure stripper packed-column (CA-STR-1), washer packed-column section (CA-WAS-1) to non-equilibrium mass transfer rate-based calculations taken in account the mass and heat transfer limitations, liquid and vapor film diffusion, equipment hydrodynamics and chemical reaction mechanisms.

The degradation products generated during the solvent degradation process may produce new pollutants which could be emitted to the atmosphere. Thermal and oxidative degradation, and polymerization reactions has been considered undergoes thermal degradation temperature limits in presence of dissolved CO2 simplified in the Aspen Plus process simulation model of the co-capture of CO_2 and H_2S by using PZ/MDEA bleed-based aqueous absorbing-solution (CA blocks) as mass balance of the system to remove part of the PZ/MDEA blend-based aqueous absorbing-solution to represent the degraded fraction, removed as input parameters in the carbon-based filter (CA-SEP-1).

The electrolyte solution chemistry model Chemistry ID: CH-CA-PZMDE implemented in the Aspen Plus®v8.4 process model simulation of the co-capture of CO_2 and H_2S by using PZ/MDEA bleed-based aqueous absorbing-solution was developed with a CHEMISTRY model and equilibrium constants for the CH-CA-PZMDE according to section 7.2.12 (Co-capture of CO2 and H2S by using PZ/MDEA blend-based aqueous absorbing-solution).

The built-in expression for calculating equilibrium constants is used for the reactions from 1 to 10 in CH-CA-PZMDE electrolyte solution chemistry, according to Equation 31.

The Aspen Plus®v8.4 parameters used to calculate the standard Gibbs free energy of $MDEAH^+$, PZH^+, $PZCOO^-$, $PZ(COO^-)_2$ and HPZCOO and the ELECNRTL physical property methods used in the model of co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution are defined and detailed in the section 7.2.12 (Co-capture of CO2 and H2S by using PZ/MDEA blend-based aqueous absorbing-solution) described for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3).

The reaction model Reaction ID: RE-CA-PZMDE implemented in the Aspen Plus®v8.4 process model simulation of the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution was developed with a REACTIONS model and equilibrium constants for the RE-CA-PZMDE according to section 7.2.12 (Co-capture of CO2 and H2S by using PZ/MDEA blend-based aqueous absorbing-solution) described for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3).

The power law reduced expressions is used for the reactions from 8 to 15 in RE-CA-PZMDE rate-controlled reactions, according to Equation 30 or Equation 32.

The intermediate-pressure synthesis gas (WS-G-16) from the condenser knock-out drum (WS-FLA-1) in the catalyst WGS reactors at intermediate-pressure level with energy-saving and steam generation (WS blocks) at 40.0ºC and 1.1 bar containing CO_2 and H_2S and others pollutants not removed in the low-temperature wet cleaning steps is mixed in the gases mixer (WS-MIX-5) with intermediate-pressure off-gas from the off-gas condenser knock-out drum (RE-FLA-2) in the PSA hydrogen recovery cycle (RE-ADS blocks). After mixed, the mixture (WS-G-17) is then fed-enter into the bottom of the intermediate-pressure absorber tray-column (CA-ABS-1) and flows upwards through the tray stages in contact with the down flow PZ/MDEA blend-based aqueous absorbing-solution (lean-amine solution) to exit as clean outlet gas at the absorber top stage (CA-ABS-1).

Due the recycle of intermediate-pressure off-gas (containing large amounts of CO_2) to adjust-maintenance the ratio of hydrogen to carbon monoxide - H_2/CO ratio – the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution for Biomass-to-Mixed-alcohol scenarios is design-sized to remove much more CO_2 than the system design-sized for Biomass-to-Methanol scenarios raising the thermal and electrical energy required by the system. The differences between the scenario-systems can be showed in the Table 24. This recycle method employed is an alternative to adjust the - H_2/CO ratio –as opposed to the reverse WGS system, which uses large amounts of CO_2 to achieve the reverse equilibrium in the WGS reaction (Chemical equation c.8).

The PZ and MDEA considered to forming the absorbing-solution is a commercial type high concentrate MDEA-based solution and crystal-PZ (hydrated or anhydrous) shipped and delivered to thermochemical-biorefinery supplies offloading area by truck. From the storage tank the high concentrate MDEA-based solution are ducted to the amine surge tank (CA-SUR-1) and pumped by the amine supply pump (CA-PUM-1) to the mixture tank (CA-MIX-1). Crystal-PZ is sent to mixture stirred-tank (not included in the Aspen Plus®v8.4 process model simulation) to be diluted and mixed with water and the MDEA-based solution to be after added to the lean-amine solution in circulation on closed-loop cycle mode.

The make-up of high concentrate MDEA-based solution and crystal-PZ added into the system depend on the losses (thermal, oxidative, reclaimed and entrained-off). The make-up is made from time to time but simulated in the Aspen Plus®v8.4 process model simulation as continues process in steady state mode. The mass flow rate of high concentrate MDEA-based solution is controlled by design specification DS-CA-CL-1 varying the mass flow rate inlet the system to maintenance the lean-amine solution content $33.0\%_{w/w}$ of MDEA in the inlet stream (CA-L-7) in the top of the intermediate-pressure absorber tray-column (CA-ABS-1). The design specification considers all active MDEA ionic forms present in the solution measured by apparent component mass fraction for electrolyte system as property sets. The mass flow rate of crystal-PZ is controlled by design specification DS-CA-CL-2 varying the mass flow rate inlet the system to maintenance the lean-amine solution content $5.0\%_{w/w}$ of PZ in the inlet stream (CA-L-7) in the top of the intermediate-pressure absorber tray-column (CA-ABS-1). The design specification considers all active PZ ionic forms present in the solution measured by apparent component mass fraction for electrolyte system as property sets.

The lean-amine solution formed in the mixture tank (CA-MIX-1) is pumped to 21.8 bar by the lean-amine pump (CA-PUM-2) and cooled by the lean-amine water cooler (CA-HEA-1) by cooling water (CT-HEA-2) modeled by using Heater exchanger blocks to maintenance the inlet conditions at 21.6 bar and 40.0ºC. The lean-amine solution with low fraction of CO_2, H_2S and others pollutants content (e.g.: NH_3, SOx, CHN, COS, hydrocarbons) without degradation products (not included in the Aspen Plus®v8.4 process model simulation) is then feed in the 1º theoretically liquid stage (top column stage) in the intermediate-pressure absorber tray-column (CA-ABS-1).

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-3) to the lean-amine water cooler (CT-HEA-1). The amount of cooling water required is determined and controlled by design specification DS-CA-TL-1 varying the mass flow rate of cooling water passing through the lean-amine water cooler (CT-HEA-1). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

Rigorous Aspen Plus®v8.4 process model simulation of the intermediate-pressure absorber tray-column (CA-ABS-1) was developed using RadFrac columns block on standard convergence mode with reaction model RE-CA-PZMED and electrolyte solution chemistry model CH-CA-PZMDE without in-bed condenser and reboiler. The model was optimized for estimated 20 theoretical stages considering a Glitsch Ballast (Glitsch6) tray section with valve type V-1 12 gauge deck thickness and panel weir height of 40.0 mm with height and diameter optimized for each system requirements (scenarios dependence) on standards characteristics. The model use rate-based calculation for Mixed flow model without reactions and film resistance in vapor phase, without reactions and with film resistance in liquid phase. Default Aspen Plus®v8.4 tray parameters is applied to calculate liquid holdup, interfacial area, and to predict the mass transfer coefficient by Scheffe and Weiland (1987) method, and heat transfer coefficient by Chilton–Colburn (Taylor and Krishna, 1993) method.

The gaseous top-product at about 21.6 bar and 56.3ºC leave from the 1º theoretically vapor stage (top column stage) in the intermediate-pressure absorber tray-column (CA-ABS-1) is cooled to 21.4 bar and 40.0ºC in the absorber condenser (CA-CON-1) by cooling water (CT-HEA-2) modeled by using Heater exchanger blocks condensing a fraction of the entrained water with PZ/MDEA.

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-3) to the absorber condenser (CT-HEA-2). The amount of cooling water required is determined and controlled by design specification DS-CA-TL-2 varying the mass flow rate of cooling water passing through the absorber condenser (CT-HEA-2). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

The condensed phase formed at 21.4 bar and 40.0ºC is flash-separated in the absorber liquid reflux-drum (CA-FLA-1) modeled by using a Flash2 separator block. The condensate top product from the absorber liquid reflux-drum (CA-FLA-1) is pumped at 21.6 bar and 40.0ºC by the absorber reflux-pump (CA-PUM-3) and refluxed back to the 1º theoretically liquid stage (top column stage) in the intermediate-pressure absorber tray-column (CA-ABS-1).

The gaseous phase from the absorber liquid reflux-drum (CA-FLA-1) is ducted-fed into the bottom of the washer packed-column section (CA-WAS-1) at 21.4 bar and 40.0ºC.

The liquid bottom product is obtained at 22.0 bar and about 101.0ºC from the 20º theoretically liquid stage (bottom column stage) in the intermediate-pressure absorber tray-column (CA-ABS-1) as a CO_2 and H_2S rich solution (rich-amine solution) with others pollutants content (e.g.: NH_3, SOx, CHN, COS, hydrocarbons) without degradation products (not included in the Aspen Plus®v8.4 process model simulation) is flashed in the rich-amine flash vessel (CA-FLA-3) modeled by using a Flash2 separator block. In the rich-amine flash vessel (CA-FLA-3) the pressure of the rich-amine solution is reduced from 22.0 bar to 1.72 bar and then after-pumped by the rich-amine pump (CA-PUM-4) to the cross-solution heat exchanger (CA-HEA-2). Rich-amine flash vessel (CA-FLA-3) remove part of the dissolved gases presents in the rich-amine according to vapor-liquid equilibrium calculations for ELECNRTL physical properties.

Make-up water (WATER FROM TREATMENT PLANT) at atmospheric pressure and 25.0ºC from the treatment plant is pumped (CA-PUM-7) at 21.0 bar to the 1º theoretically liquid stage (top column stage) in the washer packed-column section (CA-WAS-1). Reticulating water is pumped by the washer water recycle-pump (CA-PUM-8) to the 1º theoretically liquid stage (top column stage) to enter at 21.0 bar and about 37.0ºC in the washer packed-column section (CA-WAS-1). The water mass flow rate of water circulating in close-loop cycle is defined by the parameters of the washer packed-column section (CA-WAS-1) and the employed temperature limits in the Aspen Plus®v8.4 process model simulation.

The single washer water step as final polishing step reduces the concentration of PZ, MDEA and others water affinity contaminants in the cleaned synthesis gas.

Rigorous Aspen Plus®v8.4 process model simulation of the washer packed-column section (CA-WAS-1) was developed as a top section of the absorber tray-column (CA-ABS-1) using RadFrac columns block on standard convergence mode with reaction model RE-CA-PZMDE and electrolyte solution chemistry model CH-CA-PZMDE without in-bed condenser and reboiler. The model was optimized for estimated 5 theoretical stages considering NORTON IMTP 38.0 mm packing section from 1º to 5º theoretically stages with section packed height and diameter optimized for each system requirements (scenarios dependence) on standards characteristics and according to diameter of the intermediate-pressure absorber tray-column (CA-ABS-1). The model use rate-based calculation for Mixed flow model without reactions and film resistance in vapor phase, without reactions and with film resistance in liquid phase. Default Aspen Plus®v8.4 packing parameters is applied to calculate pressure drop and liquid holdup by Stichlmair method, to predict the mass transfer coefficient and interfacial area by Onda et al. (1968) correlation, and heat transfer coefficient by Chilton- Colburn (Taylor and Krishna, 1993) method.

A fraction of 0.45% of the circulating water is drained in the washer water bleed (CA-SPL-3) to recovery and removes the concentrate washer-recovered PZ/MDEA blend-based aqueous absorbing-solution and dissolved gases (amine contaminated wash water) in the closed-loop water cycle. The drained water is sent back to mixture tank (CA-MIX-1).

The wet cleaned-synthesis gas (gaseous top-product) from washer packed-column section (CA-WAS-1) at about 37.0ºC and 21.0 bar is ducted to the regenerative ZnO/CuO-based guard bed adsorber (GU blocks).

Rich-amine solution from the rich-amine flash vessel (CA-FLA-3) is sent by rich-amine pump (CA-PUM-4) to cross-solution heat exchanger (CA-HEA-2) modeled by using a HeatX exchanger block for exchange heat (thermal energy recovery) with the lean-amine solution from the low-pressure stripper packed-column (CA-STR-1). Lean-amine solution is cooled from about 122.0ºC to about 43.0ºC heating the rich-amine from about 37.0ºC to about 108.0ºC. The heated rich-amine solution is fed into the 6º theoretical stage in the low-pressure stripper packed-column (CA-STR-1) on top of the regenerative section. The cooled lean-amine solution is sent to amine reclaimer (CA-SPL-2) or directly back to mixture tank (CA-MIX-1) closing the PZ/MEA blend-based aqueous absorbing-solution cycle.

Rigorous Aspen Plus®v8.4 process model simulation of the low-pressure stripper packed-column (CA-STR-1) was developed using RadFrac columns block on standard convergence mode with reaction model RE-CA-PZMDE and electrolyte solution chemistry model CH-CA-PZMDE without in-bed condenser and reboiler. The model was optimized for estimated 25 theoretical stages (5 theoretical stages as washer section) considering a NORTON IMTP 38.0 mm packing section from 1º to 25º theoretically stages with height and diameter for regenerative and washer packed sections optimized for each system requirements (scenarios dependence) on standards characteristics. The model use rate-based calculation for Mixed flow model without reactions and film resistance in vapor phase, without reactions and with film resistance in liquid phase. Default Aspen Plus®v8.4 packing parameters is applied to calculate pressure drop and liquid holdup by Stichlmair method, to predict the mass transfer coefficient and interfacial area by Onda et al. (1968) correlation, and heat transfer coefficient by Chilton- Colburn (Taylor and Krishna, 1993) method.

The gaseous top-product containing mainly acid gases (CO_2 and H_2S) at about 1.72 bar and 115.6ºC from the 1º theoretically vapor stage (top column stage) in the low-pressure stripper packed-column (CA-STR-1) is mixed with the fleshed gases from the rich-amine flash vessel (CA-FLA-3) at about 1.72 bar and 36.6ºC and then cooled in the stripper condenser (CA-CON-2) by cooling water (CT-HEA-3) modeled by using Heater exchanger blocks form-condensing 51.0%$_{w/w}$ (model result) of the gaseous top-product (condensate phase) in saturation equilibrium conditions.

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-3) to the stripper condenser (CT-HEA-3). The amount of cooling water required is determined and controlled by design specification DS-CA-TL-3 varying the mass flow rate of cooling water passing through the stripper condenser (CT-HEA-3). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

The condensed phase formed at 1.7 bar and 40.0ºC is flash-separated in the striper liquid reflux-drum (CA-FLA-2) modeled by using a Flash2 separator block. Part of the condensate top product containing mainly water from the striper liquid reflux-drum (CA-FLA-2) is splitted in the striper water bleed (CA-SPL-1) and sent-recycled back to the mixture tank (CA-MIX-1) as recovered water (recycle) in closed-loop-cycle mode. Another part (17.0%$_{w/w}$ by model result) of the condensate top product is pumped at 1.72 bar and about 40.0ºC by the desorber reflux pump (CA-PUM-5) and refluxed back to the 1º theoretically liquid stage (internal washer section) in the low-pressure stripper packed-column (CA-STR-1). If there is water in excess its can be sent to wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for reuse as make-up water (WATER FROM TREATMENT), in the Biomass-to-Mixed alcohols scenarios this is not the case (recycled in the system).

About 49.0%$_{w/w}$ of gaseous top-product (non-condensed) containing mainly CO_2 and H_2S leaving from the striper liquid reflux-drum (CA-FLA-2) at 1.7 bar and 40.0ºC (saturation condition) is directly sent to be compressed and liquefied by the integrally-geared centrifugal six stages compressor (CC blocks).

The liquid bottom product containing mainly regenerated amine solution at 1.78 bar and about 118.3ºC from the 25º theoretically liquid stage (bottom column stage) in the regenerative section in the low-pressure stripper packed-column (CA-ABS-1) as lean-amine solution is splitted in the lean-amine sump splitter (CA-SPL-5) of the stripper reboiler (CA-REB-1). 80.0%$_{w/w}$ of the bottom liquid product in the sump is fed in the stripper reboiler (CA-REB-1) and 20.0%$_{w/w}$ of the bottom liquid product in the sump is drained as product and mixed in the lean-amine regenerated mixer (CA-MIX-2) with heated bottom liquid phase overflow the baffle.

The reboiler circulation baffle model was developed using HeatX exchanger block (CA-REB-1) and FSplit splitter block (CA-SPL-5) to represent the stripper reboiler configured for circulation with baffle.

The bottom liquid product from the lean-amine regenerated mixer (CA-MIX-2) contain regenerated MDEA and PZ, low fraction of CO_2, H_2S and others pollutants content (e.g.: NH_3, SOx, CHN, COS, hydrocarbons) without degradation products (not included in the Aspen Plus®v8.4 process model simulation).

The thermal energy for stripper reboiler (CA-REB-1) determine the PZ/MDEA blend-based aqueous absorbing-solution vaporized in the reboiler and the regeneration extent trough the low-pressure stripper packed-column (CA-STR-1) to obtain the required capture levels (adjust the required fraction of CO_2 captured to 96%$_{w/w}$ of the inlet).

The thermal energy required by the stripper reboiler (CA-REB-1) in the Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC2) is supplied by process steam at 2.5 bar and 130.0ºC part generated in the low-pressure steam-circuit heat exchanger (ET-HEA-2) in the mixed alcohols catalytic-synthesis and part in the low-pressure vaporizer (WS-HEA-2) in the catalyst WGS system. The thermal energy required by the stripper reboiler (CA-REB-1) in the Biomass-to-Mixed alcohols (SC3) is supplied by process steam at 2.5 bar and 130.0ºC part generated in the steam extraction at 2.5 bar (ST-SPL-2) from the CEST system and part in the low-pressure vaporizer (WS-HEA-2) in the catalyst WGS system.

The mass flow rate of process steam at 2.5 bar and 130.0ºC required is determined by thermal requirements and exchanger temperature limits (cross-over avoided) in the cycle-system and controlled by design specification DS-CA-FL-2 varying the mass flow rate of water/steam circulating through the reboiler exchanger cycle.

In the Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC3) part of the condensed water after the stripper reboiler (CA-REB-1) is pumped (GA-PUM-1) as conditioned hot water to syngas cooling and heat recovery (GA blocks) to produce the gasification steam agent in the low-temperature vertical CSC (GA-CSC-2) and the reminiscent part is sent-back (recycle) to the first deaerator unit (HR-DEA-1). In the Biomass-to-Mixed alcohols (SC2) integral condensed water after the stripper reboiler (CA-REB-1) is ducted to hot water reservoir (HR-TAN-1) and after pumped (GA-PUM-1) together the deaerated hot process water from the first deaerator unit (HR-DEA-1) as conditioned hot water to syngas cooling and heat recovery (GA blocks) to produce the gasification steam agent in the low-temperature vertical CSC (GA-CSC-2).

The lean-amine solution regenerated from the lean-amine regenerated mixer (CA-MIX-2) is send to be cooled from about 122.0ºC to about 43.0ºC recovering the heat in the cross-solution heat exchanger (CA-HEA-2). After cooled the lean-amine solution is sent to the amine reclaimer (CA-SPL-2).

Amine reclaimer (CA-SPL-2) split 0.18%$_{w/w}$ of the lean-amine solution circulating back to absorber tray-column (CA-ABS-1) and is modeled by using a FSplit splitter block to adjust the amine make-up and simulate the losses of PZ and MDEA due the thermal and oxidizing degradation according to input fraction of components removed in the carbon-based filter (CA-SEP-1) as simplified mode (model artifice). In the carbon-based filter (CA-SEP-1) modeled by using a Sep separator block is considered a loss of 10.0%$_{w/w}$ of the circulating water in the reclaimer cycle and the downdraft of all dissolved gases and electrolyte entering the filter system (CA-SEP-1).

The reclaimed fraction of lean-amine solution is filtered by carbon-based filter (CA-SEP-1) containing activated charcoal medium put on stream at every 3 to 4 weeks of interval (continues stead-state simulated) to remove sulphur and nitrogen compounds, amine salts, particles and degradation products (not included in the Aspen Plus®v8.4 process model simulation) formed over time in the amine cycle in closed loop-cycle mode.

Part of the amine reclaimed is recovered in the presence of a strong alkali (e.g.: NaOH) solution and with the application of heat (not included in the Aspen Plus®v8.4 process model simulation) and sent-back in the amine-lean solution line (CA-SPL-2) by the recirculation pump (CA-PUM-6) together the 90.0%$_{w/w}$ of the cleaned-water that passes through the carbon-based filter (CA-SEP-1). Another part retained and removed by the carbon-based filter (CA-SEP-1) is sent to wastewater treatment plant and after to final disposal (e.g.: landfill) with carbon filter active medium (activated charcoal) (RESIDUE TO DISPOSAL).

MDEA-based aqueous absorbing-solution and PZ-based aqueous absorbing-solution are a solvent with high resistance to oxidative and thermal degradation in intermediate-pressure systems different from the MEA-based aqueous absorbing-solution which can undergo extensive degradation effect due to the internal temperatures reached in the absorber column (CA-ABS-1). Based systems on PZ/MDEA blend-based aqueous absorbing-solution can be used to compact the CO2 absorption/desorption system reducing the thermal energy required (steam process) by the stripper reboiler (CA-REB-1) in the regeneration process.

8.1.12 Carbon dioxide compression and storage/use

The gaseous CO_2 captured (acid gas) is compressed by the integrally-geared centrifugal six stages compressor (CC blocks) (multiple pinions) based on the Siemens STC-GV integrally-geared centrifugal multi-stages compressor series feature a single-shaft arrangement and configured to allow inter-cooling steps. The compressed gaseous CO_2 is after-cooled been liquefied producing liquid CO_2 at 73.0 bar and 30.0ºC for further uses. High-pressure liquid pump (CC-PUM-1) is used to adjust the pressure to 150.0 bar (or more) to be injected into the geological formations for permanent storage (CCS).

As shown in Figure 71, Aspen Plus®v8.4 flowsheet of the CO_2 compression and storage/use area for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) which is the same model with modified parameters for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) is compost by; integrally-geared centrifugal six stages compressor (CC-COM-1~6); water inter-cooler exchangers (CC-1~5); supercritical liquefactor-cooler (CC-HEA-1); condenser knock-out drum (CC-FLA-5); liquid water pump (CC-PUM-1); high-pressure liquid pump (CC-PUM-1); direct drive permanent magnet motor (mechanical efficiency); degases warm (CC-FLA-6); atmospheric condensate buffer/equalizer tank (CO-FLA-7); high-pressure buffer/equalizer tank (CO-FLA-6); and liquid CO_2 temporary storage tank (CC-SPL-1).

The integrally-geared centrifugal six stages compressor (CC blocks) is modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 83.0% isentropic efficiency (isentropic compression).

The gaseous top-product containing mainly CO_2 and H_2S from the striper liquid reflux-drum (CA-FLA-2) at 1.7 bar and 40.0ºC (saturation condition) is compressed by the six impellers (CC-COM-1~6). The pressurized gases between the compression stages (CC-COM-1~5) is cooled to 30.0ºC by the water inter-cooler exchangers (CC-1~5) modeled by using MHeatX exchanger blocks generating condensed phase content water and dissolved gases. The condensed phase is removed in the condenser knock-out drums (CC-FLA-1~5) modeled by Flash2 separators block and sent to atmospheric condensate buffer/equalizer tank (CC-FLA-7) modeled by using a Flash2 separator block at ambient conditions equalizer.

The cooled high-pressure gaseous CO_2 at about 78.0 bar and 93.0ºC (supercritical pressure) after the six-stage impeller (CO-COM-6) is cooled to 30.0ºC and liquefied by the supercritical liquefactor-cooler (CC-HEA-1) modeled by using HeatX exchanger block. Liquid CO_2 is sent to high-pressure buffer/equalizer tank (CO-FLA-6) to remove any non-condensable gases present in the line to atmosphere (VENT TO ATMOSPHERE) coupled with the liquid CO_2 temporary storage tank (CC-SPL-1) to maintenance the liquid phase at 78.0 bar and 30.0CºC.

The liquid CO_2 produced-captured can be sent to permanent storage (HIGH-PRESSURE CO_2 TO STORAGE) in geological formations (CCS) (e.g.: aquifers, oil and gas fields, unmineable coal beds) at about 150.0 bar using a high-pressure liquid pump (CC-PUM-1) to compress the liquid CO_2. The liquid CO_2 produced-captured can be sent to process use (LIQUID CO_2 TO PROCESS) at adequate conditions required by the downstream process (not included in the model) or by the transportation off-site (e.g.: algae-based liquid biofuels, catalytic methanol). The use of the captured CO_2 is not defined in this research Master`s degree.

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-5) to the water inter-cooler exchangers (CC-1~5) and to the supercritical liquefactor-cooler (CC-HEA-1). The amount of cooling water required is determined and controlled varying the mass flow rate of cooling water passing through the equipment users. The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system. The lubricating oil circuit and the lubricating oil water-cooling system (low make-up and electricity requirements) are suppressed from the Aspen Plus®v8.4 process model simulations in this research Master`s degree.

The ambient equalized condensate (CC-FLA-7) is after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

The single shaft and multiple pinions in the integrally-geared centrifugal six stages compressor (CC-COM blocks) is drive by a synchronous direct drive permanent magnet motor modeled by CC-E-6 work stream. The compression stages (impellers) are optimized to obtain the same compression ratio by design specification DS-CC-

TR-1 and FORTRAN calculation block CA-CC-TR-2 varying the pressure ratio in the six compression stages (CO-COM blocks). The electrical potential losses by attrite in the mechanical move parts was considered as 1.0% of the mechanical energy required by the stage (99.0% mechanical efficiency).

8.1.13 Water-gas-shift reactors

Water-gas-shift (WGS) reaction as described in the section 4.1.16 (Water-gas-shift (WGS) and reverse Water-gas-shift (RWGS) reaction) is carried out as direct-direction reaction mode according to Chemical equation c.8 to increase the H_2 yield (content) in the intermediate-pressure synthesis gas before the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks).

High-temperature (HT) catalyst WGS reactor (WS-HTR-1) followed by a low-temperature (LT) catalyst WGS reactor (WS-LTR-1) with intercooling stage is used in sequential combined arrangement.

in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) the Aspen Plus$^{®}$v8.4 process model simulation of the HT and LT catalyst WGS reactors at intermediate-pressure level with energy-saving and steam generation was developed operating at a minimum level in order to increase the energy density of the fuel-gas required by the high-performance sequential combustion full-flow advanced EvGT, without requiring significant changes in the turbine design.

The Aspen Plus$^{®}$v8.4 process model simulation of the gasification of biomass in an atmospheric CFB directly-heated gasifier by using high-purity oxygen and steam agents according to section 8.1.5 (Gasification of biomass in an atmospheric circulating fluidized bed directly-heated gasifier by using high-purity oxygen and steam agents) applying the chemical equilibrium by Gibbs free-energy minimization approach overestimates the water gas shift equilibrium effect and the formation of light hydrocarbons and heavy hydrocarbons. The gasification model breaking the higher molecular compounds into simpler forms, according to this model is formed more H_2 and less CO than the predicted by rigorous kinetic models. The quantity of H_2 in the synthesis gas (mixed with the recycled light-gas) is more than sufficient to obtain the hydrogen to carbon monoxide ratio – H_2/CO ratio – required by the mixed alcohols catalyst-synthesis, there is no need to use a catalyst WGS system operating in direct direction reaction mode.

Reverse direction WGS reaction can be carried out using the captured CO_2 instead of steam in the stoichiometric molar ratio of 12 times the H_2 content (CO_2/H_2 ratio) to alter the equilibrium of WGS reaction (Chemical equation c.8) reducing the H_2 yield and raising the CO yield in the intermediate-pressure synthesis gas. The CO_2 recycled-back must be re-captured in the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution increasing the thermal and electrical energy requirements and the sizing of the system (infeasible option).

As shown in Figure 72, Aspen Plus®v8.4 flowsheet of the high-temperature and low-temperature catalyst water-gas-shift reactors at intermediate-pressure level with energy-saving and steam generation for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) which is the same model with modified parameters for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) is compost by: HT catalyst WGS reactor (WS-HTR-1); LT catalyst WGS reactor (WS-LTR-1); cross-gaseous heat exchanger (WS-HEA-1); HT after-cooler (WS-1); intermediate-pressure synthesis gas splitter (WS-SPL-1); intermediate-pressure synthesis gas mixer (WS-MIX-1); steam-gases mixer (WS-MIX-2); steam mixer and injection (WS-MIX-3). Also shows the Aspen Plus®v8.4 flowsheet of the energy-saving and steam generation compost by fresh-water pump (WS-PUM-1); condensed water recovery and recycle system (WS-SEP-1); intermediate-pressure water pump (WS-PUM-2); high-temperature cooler (WS-2); low-temperature cooler (WS-3); low-pressure vaporizer (WS-HEA-2); low-pressure process steam mixer (WS-MIX-4); and condenser knock-out drum (WS-FLA-1).

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) the synthesis gas at intermediate-pressure from the condenser knock-out drum (CO-FLA-3) in the first-section of synthesis gas compression (conditioning) (CO blocks) is separated in the intermediate-pressure synthesis gas splitter (WS-SPL-1) being $5.0\%_{w/w}$ (operational minimum mass-fraction) used in the catalyst WGS reactors.

The fraction of the intermediate-pressure synthesis gas is before pre-heated in the cross-gaseous heat exchanger (WS-HEA-1) modeled by using a HeatX exchanger block cooling down the product gas from the LT catalyst WGS reactor (WS-LTR-1), recovering energy. The temperature was optimized to obtain the required inlet temperature and the ratio of steam to carbon monoxide – H_2O/CO ratio – in the HT catalyst WGS reactor (WS-HTR-1) and is controlled by design specification DS-WS-RST-1 varying the temperature of synthesis gas obtained after the cross-gaseous heat exchanger (WS-HEA-1) coupled with the design specification DS-WS-TG-1 and dependent on the design specification DS-WS-TG-2.

After pre-heated the intermediate-pressure synthesis gas is mixed (WS-MIX-2) with superheated steam at same pressure level obtained from the HT after-cooler (WS-1) modeled by using a MHeatX exchanger block. The product gas from the HT catalyst WGS reactor (WS-HTR-1) is cooled down to 22.3 bar and 230.0ºC (catalyst temperature limit) before inlet in the LT catalyst WGS reactor (WS-LTR-1), recovering the energy and economizing intermediate-pressure steam obtained from the high-temperature vertical CSC (GA-CSC-1) and used in the catalyst WGS reactors. The amount of water used to cool down the product gas from the HT catalyst WGS reactor (WS-HTR-1) is determined and controlled by design specification DS-WS-TG-2 varying the mass flow rate of water passing through the HT after-cooler (WS-1) limited to achieve the Synthesis gas inlet temperature in the LT catalyst WGS reactor (WS-LTR-1).

Part of the intermediate-pressure steam produced in the high-temperature vertical CSC (GA-CSC-1) is splitted (GA-SPL-3) and mixed (WS-MIX-3) with the pre-heated intermediate-pressure synthesis gas. In the Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC2) is produced intermediate-pressure steam at 23.0 bar and 345.9ºC. In the Biomass-to-Mixed alcohols (SC3) is produced intermediate-pressure steam at 23.0 bar and 480.0ºC (reheater pipe bank).

The intermediate-pressure steam is used to heat the inlet gases in the HT catalyst WGS reactor (WS-HTR-1) achieving the temperature for reaction in the HT catalyst WGS reactor (WS-HTR-1). Also is used to achieve the stoichiometric molar ratio of steam to carbon monoxide – H_2O/CO ratio – to 4 times the carbon monoxide content in the inlet line (WS-G-7). The amount of intermediate-pressure steam required is determined and controlled by design specification DS-WS-TG-1 varying the intermediate-pressure steam mass flow rate splitted (GA-SPL-3).

The Aspen Plus®v8.4 process model simulation of HT catalyst WGS reactor (WS-HTR-1) was developed by using a REquil reactor block to represent the water-gas-shift reaction (Chemical equation c.8) according to Gibbs free-energy approach to chemical equilibrium and constants restricted by chemical equilibrium temperature approach. In the Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC2) the HT catalyst WGS reactor (WS-HTR-1) operates at 23.0 bar and 315.0ºC and in the Biomass-to-Mixed alcohols (SC3) at 23.0 bar and 350.0ºC, limited by the intermediate-pressure steam generated in the high-temperature vertical CSC (GA-CSC-1).

The Aspen Plus®v8.4 process model simulation of LT catalyst WGS reactor (WS-LTR-1) was developed by using a REquil reactor block to represent the water-gas-shift reaction (Chemical equation c.8) according to Gibbs free-energy approach to chemical equilibrium and constants restricted by chemical equilibrium temperature approach. In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) the LT catalyst WGS reactor (WS-LTR-1) operates at 22.5 bar and 230.0ºC, limited by the Zn-CuO/Al_2O_3 catalyst operational temperature (low-temperature catalyst).

After the LT catalyst WGS reactor (WS-LTR-1) the intermediate-pressure synthesis gas at about 22.5 bar and 249.0ºC in the Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC2 and at about 22.5 bar and 254.0ºC in the Biomass-to-Mixed alcohols (SC3) is cooled in the cross-gaseous heat exchanger (WS-HEA-1) to obtain a optimized inlet temperature and the ratio of steam to carbon monoxide in the HT catalyst WGS reactor (WS-HTR-1) according to design specification DS-WS-

RST-1. The intermediate-pressure synthesis gas is mixed back in the intermediate-pressure synthesis gas mixer (WS-MIX-1) with the synthesis gas bypass fraction from the intermediate-pressure synthesis gas splitter (WS-SPL-1), obtaining synthesis gas at 22.0 bar at about 176.0 ºC.

Spreadsheet calculation models are used to determine the quantity of Zn-CuO/Al_2O_3 catalyst must be loaded into LT catalyst WGS reactor (WS-LTR-1) and the quantity of Fe_2O_3/Cr_2O_3 MgO catalyst must be loaded into HT catalyst WGS reactor (WS-HTR-1). ZnO-based catalyst can be added in the HT catalyst WGS reactor (WS-HTR-1) to protect the low activity Zn-CuO/Al_2O_3 catalyst from poisons such as sulphur and chlorine compounds. On the other hand, Fe_2O_3/Cr_2O_3 MgO catalyst is not particularly sensitive to sulphur poisoning, relatively slow sintering still causes a decrease in activity of the catalyst.

Fe_2O_3/Cr_2O_3 MgO catalyst considered in the HT catalyst WGS reactor (WS-HTR-1) is a commercial type high activity catalyst content 92.0$\%_{w/w}$ of Fe_2O_3, 6.0$\%_{w/w}$ of Cr_2O_3 and 2.0$\%_{w/w}$ of MgO. The Fe_2O_3/Cr_2O_3 MgO catalyst is weight loaded to obtain 20.0 kg of Fe_2O_3/Cr_2O_3 MgO catalyst per kmol of CO flowing through the system. Fe_2O_3/Cr_2O_3 MgO catalyst lifetime is expected to be about 4 years before the necessity of deactivated catalyst be partial or full discharged and new activity catalyst be loaded, deactivated catalyst is send to be regenerated and/or to final disposal.

Zn-CuO/Al_2O_3 catalyst considered in the LT catalyst WGS reactor (WS-LTR-1) is a commercial type low activity catalyst content 20.0$\%_{w/w}$ of Al_2O_3, 47.0$\%_{w/w}$ of ZnO and 33.0$\%_{w/w}$ of CuO. The Zn-CuO/Al_2O_3 catalyst is weight loaded to obtain 20.0 kg of Zn-CuO/Al_2O_3 catalyst per kmol of CO flowing through the system. Zn-CuO/Al_2O_3 catalyst lifetime is expected to be about 2 years before the necessity of deactivated catalyst be partial or full discharged and new activity catalyst be loaded, deactivated catalyst is send to be regenerated and/or to final disposal.

The hot intermediate-pressure synthesis gas enriched with hydrogen enters in the energy-saving and steam generation section to be sub-cooled to 40.0ºC generating steam at low-pressure level. All of the amount of steam generated is used as process steam destined to stripper reboiler (CA-REB-1) in the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks) and hot-liquid water to be used to cooling down the product gas from the HT catalyst WGS reactor (WS-HTR-1) to 22.3 bar and 230.0ºC (catalyst temperature limit) before inlet in the LT catalyst WGS reactor (WS-LTR-1).

In the high-temperature cooler (WS-2) modeled by using a MHeatX exchanger block the pressurized water at about 47.0 ºC and 23.4 bar is heated generating hot-liquid water at about 175.0ºC controlled by design specification DS-WS-FL-2 varying the synthesis gas outlet temperature in the low-pressure vaporizer (WS-HEA-2) closing the energy balance. The design specification aims the maximum recovery efficiency according to temperature limits between the cooling/heating steps.

In the low-pressure vaporizer (WS-HEA-2) modeled by using a HeatX exchanger block (WS-HEA-2) heat is recovered to generate low-pressure steam raising the supply and reducing the stress on the HRSG system (HR blocks). Process steam at 2.5 bar and 130.0ºC is generated and sent to steam-gases mixer (WS-MIX-2). This low-pressure steam generated is mixed with the low-pressure steam generated from the low-pressure steam-circuit heat exchanger (ET-HEA-2) in the mixed alcohols catalytic-synthesis for Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC2) or to be mixed with the low-pressure steam extracted in the steam extraction at 2.5 bar (ST-SPL-2) from the CEST system for the Biomass-to-Mixed alcohols (SC3).

The low-pressure steam generated in the low-pressure vaporizer (WS-HEA-2) is used in the stripper reboiler (CA-REB-1) in the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks) as thermal energy utility. The amount of low-pressure steam at 2.5 bar and 130.0ºC generated depend on the energy balance and is controlled by design specification DS-WS-FL-2 coupled with design specification DS-WS-FL-1 varying the water/steam mass flow rate through the low-pressure vaporizer (WS-HEA-2) according to temperature limits between the exchangers and the heat available to recovery.

The intermediate-pressure synthesis gas is sub-cooled in the low-temperature cooler (WS-3) modeled by using a MHeatX exchanger block reducing the temperature to 22.0 bar and 40.0ºC generating condensed phase content water and dissolved gases. The condensed phase formed is removed in the condenser knock-out drum (WS-FLA-1) modeled by using a Flash2 separator block and sent to the condensed water recovery and recycle system (WS-SEP-1). The sub-cooled synthesis gas is ducted and mixed in the gases mixer (WS-MIX-5) with intermediate-pressure off-gas from the off-gas condenser knock-out drum (RE-FLA-2) in the PSA hydrogen recovery cycle (RE-ADS blocks) and then fed into the bottom of the intermediate-pressure absorber tray-column (CA-ABS-1) in the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution.

Condensed water at 22.0 bar and 40.0ºC is fleshed to 2.8 bar removing part of the dissolved gases in the condensed water recovery and recycle system (WS-SEP-1) and is after-sent to basin water tank (WS-SEP-1). 10.0%$_{w/w}$ of the condensed water is purged together 50.0%$_{w/w}$ of the impurities contained in the condensate as basin blowdown. The purged condensate is sent to wastewater treatment plant when 95.0%$_{w/w}$ of the water is recovered and mixed with make-up raw water at 25.0ºC pumped (CT-PUM-1) from treatment plant (WATER FROM TREATMENT PLANT) to water recirculation tank (WS-SEP-1).

The amount of make-up raw water (WATER FROM TREATMENT PLANT) required by the energy-saving and steam generation section is controlled by design specification DS-WS-FL-3 varying the mass flow rate of water inlet in the system to maintenance the steam generation and replace the blowdown losses.

8.1.14 Regenerative Metallic oxides-based guard bed adsorber

In this research Master's degree is considered removal the sulfur and chlorine reminiscent poisoning content in the synthesis gas with potential to poisoning the Sulfided K-Co-Mo/C catalyst bed by using a combinations of ZnO and CuO catalyst sorbents in a regenerative guard bed absorber before the mixed alcohols catalytic-synthesis.

The Aspen Plus®v8.4 process model simulation of the regenerative ZnO/CuO-based guard bed adsorber for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3) was developed in steady-state mode using RKS-BM physical property methods without adsorbing and regenerative reactions (simplified model).

The adsorber catalyst bed material in the spreadsheet calculation model of the regenerative ZnO/CuO-based guard bed adsorber consider the bed content $70.0\%_{w/w}$ of ZnO and $30.0\%_{w/w}$ of CuO disposed in defined layers with ZnO catalyst in the bottom layer to adsorb in first time sulfur poisoning (e.g.: H_2S and SO_x) with final polishing by the CuO catalyst in the top layer guaranteeing lower sulphur and chlorines poisoning in the synthesis gas. A fraction of the bottom layer act as ZnO-based chloride trap removing part of the chlorines (e.g.: HCl and Cl_2) reminiscent in the cleaned and sub-cooled synthesis gas.

The main reactions considered in the interaction between the synthesis gas and the ZnO catalyst layer and CuO catalyst layer are defined and detailed in the section 4.1.17 (Regenerative guard bed adsorbers) represent by the Chemical equations c.9, c.10, c.11 and c.12, and the competitive side-reaction by the Chemical equation c.13.

The Aspen Plus®v8.4 process model simulation in steady-state mode of the adsorbing and regenerative reactions in the ZnO catalyst layer and CuO catalyst layer consider only the atomic balance in the system based on the spreadsheet calculation model to determine the amount of ZnO and CuO catalysts must be loaded into the two vessels.

As shown in Figure 73, Aspen Plus®v8.4 flowsheet of the regenerative Metallic oxides-based guard bed adsorber for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) which is the same model with modified parameters for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) is compost by: adsorber vessel (GU-ADS-1) (in adsorption cycle-time); regenerative vessel (GU-RE-1) (in regeneration cycle-time); condenser knock-out drum (GU-SEP-1); high-pressure blower system (GU-BLW-1); atmospheric air after-cooler (GU-HEA-1); inlet multi-way valve 1 (GU-SPL-1); inlet multi-way valve 2 (GU-SPL-2); outlet multi-way valve (GU-MIX-2); and vent off-gas multi-way valve (GU-MIX-1).

Cleaned and sub-cooled synthesis gas from the top of the washer packed-column section (CA-WAS-1) in the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks) is supplied into condenser knock-out drum (GU-SEP-1) modeled by using a Sep separator block. The model considers removal 80.0%$_{w/w}$ of the water content in the sub-cooled synthesis gas on liquid form as condensate. This block also is used as simulation artifice for remove together the condensate all of the PZ and MDEA entrained from the washer packed-column section (CA-WAS-1). The ambient equalized condensate (GU-SEP-1) is after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

From the condenser knock-out drums (GU-SEP-1) the cleaned and sub-cooled synthesis gas is fed by inlet multi-way valve 1 (GU-SPL-1) into the adsorber vessel (GU-ADS-1) modeled by using a Flash2 separator block to obtain the mass balance without bed material reactions. The adsorber vessel (GU-ADS-1) model consider the intermediate-pressure synthesis gas at 21.0 bar and about 37.0ºC (can be heated to increase the catalyst activity) flowing through the ZnO catalyst layer and CuO catalyst layer.

Cleaned synthesis gas flow-off the absorber vessel (GU-ADS-1) in the regenerative ZnO/CuO-based guard bed adsorber system by outlet multi-way valve (GU-MIX-2). Cleaned synthesis gas is after-sent directly to the second-section of synthesis gas compression (conditioning) by integrally-geared centrifugal two stages compressor (CO blocks).

The Aspen Plus®v8.4 process model simulation and the spreadsheet calculation model of the regenerative ZnO/CuO-based guard bed adsorber consider that 3.0%$_{w/w}$ of the CO_2, 2.0%$_{w/w}$ of the NO_x and 10.0%$_{w/w}$ of the NH_3 flowing through the adsorbed are removed from the system in the regeneration cycle together 99.0% of the sulfur content (e.g.: H_2S and SO_x), 80.0%$_{w/w}$ of the chlorine content (e.g.: HCl, and HClO) and 95.0%$_{w/w}$ of the Cl_2.

In the Aspen Plus®v8.4 process model simulation of the oxygen-regeneration cycles is considered the use of the synthetic air (similar to atmospheric air) purged from the low-pressure multi packed-column (AS-COL-2) in the double-column cryogenic ASU. Synthetic air has similar composition to the surrounding atmospheric air however without the presence of pollutants (e.g.: CO_2 CH_4 and NO_x) normally presents in the surrounding atmospheric air (ATMOSPHERIC AIR) aiming maintain activity through many regeneration cycles considered to improve the sulfur and chlorine poisoning adsorption.

The synthetic air is pre-heated in the aluminum fin-plate multi-zones main heat exchanger (AS-2) and heated in the aluminum fin-plate three-circuit after-cooler exchanger (AS-1) to 1.05 bar and 150.0ºC. Part of this synthetic air is splitted (AS-SPL-9) and used to achieve time-optimized regeneration phase in the regenerative vessel (GU-REG-1) of the regenerative ZnO/CuO-based guard bed adsorber. The conditioned synthetic air is induced and compressed to 5.0 bar and about 409.2ºC by the blower system (GU-BLW-1) modeled by using a Compr pressure changer block according to isentropic method for compressor considering 85.0% isentropic efficiency and 99.0% mechanical efficiency.

The spreadsheet calculation model determines the amount of regenerative conditioned synthetic air mass flow rate is required in the regeneration-cycle. The model consider the limits per pass of 0.01 g of sulfur content per g of ZnO catalyst, 0.05 g of CO_2 per g of ZnO catalyst and 0.02 g of HCl per g of CuO catalyst, and the saturation limits (very low activity catalyst) of 0.15 g of sulfur content per g of ZnO catalyst, 0.30 g of CO_2 per g of ZnO catalyst and 0.1 g of HCl per g of CuO catalyst.

The mass flow rate of the synthetic air required to regenerate the ZnO/CuO-based guard bed is controlled by design specification DS-GU-FG-1 varying the mass flow rate of the synthetic gas passing thought the regenerative vessel (GU-REG-1) coupled with design specification DS-AS-FG-3 varying the heated synthetic air mass fraction splitted (AS-SPL-9).

The blower system (GU-BLW-1) force the synthetic air through the atmospheric air after-cooler (GU-HEA-1) to be cooled to 5.0 bar and 350.0ºC by atmospheric air. The conditioned synthetic air is then fed by inlet multi-way valve 2 (GU-SPL-2) in the regenerative vessel (GU-REG-1) (in regeneration cycle-time) modeled by using a Flash2 separator block to obtain the mass balance without bed material reactions. Sorbent bed material ZnO catalyst layer and CuO catalyst layer is regenerated to maintain activity through regenerative-cycles removing the adsorbed contaminants from the catalyst.

Metal sulfides formed in the ZnO catalyst layer and CuO catalyst layer are regenerated to oxides and byproducts contain gaseous sulfur and chlorine, according to Chemical equations c.15, c.16 and c.17 by partial oxidation, to Chemical equations c.18 and c.19 by total oxidation (in presence of oxygen), and by catalytic reaction in presence of water according to Chemical equations c.20 and c.21. Side-reactions forming sulfates occurs in lower extension according to Chemical equations c.22 and c.23. The sulfate forms are non-reactive with respect to the desulphurization reactions in the conditions employed during the regenerative-cycle, and thus there is a loss of active material. Reactions are defined and detailed in the section 4.1.17 (Regenerative guard bed adsorbers).

Sulfur content (H_2S and COS) is reduced to an acceptable level which is measured in the inlet line for the isothermal water-cooled fixed bed catalytic-synthesis reactor (ET-REA-1). According to Dutta and Philips (2009) for this type of catalyst selected for mixed alcohols catalytic-synthesis by mixed alcohols catalytic-synthesis the required level should remain below 100.0 ppm (theoretical limit) in molar basis. Chlorines and nitrous oxides are reduced to traces level (not significant content) in the model (at ppb level).

ZnO catalyst is weight loaded to obtain 0.01 g of sulfur adsorber per g of ZnO catalyst (0.15 g of sulfur saturation limit) and CuO catalyst is weight loaded to obtain 0.03 g of chlorine adsorber per g of ZnO and CuO catalyst (0.05 g of chlorine saturation limit).

The lifetime depends on the regeneration cycle and due the significant presence of sulfur and chlorine compounds in the biomass processed by the thermochemical-biorefinery. ZnO catalyst and CuO catalyst considered in the regenerative ZnO/CuO-based guard bed adsorber are a commercial type catalyst considering a catalyst lifetime expected to be about 1 year before the necessity of deactivated catalyst be partial or full discharged and new activity catalyst be loaded, deactivated catalyst is send to be regenerated and/or to final disposal.

Unconverted light-gas recycled back to main stream (synthesis gas) with low hydrogen content after the hydrogen recovery by four-bed PSA system is added to intermediate-pressure synthesis gas before the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution. The CO_2 present in the intermediate-pressure synthesis gas and in the recycled unconverted light-gas (off-gas fraction) is removed by the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks) and regenerative ZnO/CuO-based guard bed adsorber to acceptable levels measured in the inlet line for the isothermal water-cooled fixed bed catalytic-synthesis reactor (ET-REA-1).

The hot synthetic gas with the potential pollutants (poisoning) removed from the vessel in the regeneration-cycle is emitted to atmosphere (VENT TO ATMOSPHERE) by the vent off-gas multi-way valve (GU-MIX-1).

8.1.15 Second-section of synthesis gas compression (conditioning)

The synthesis gas at intermediate-pressure destined to mixed alcohols production in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) is compressed by integrally-geared centrifugal two stages compressor (CO blocks). High-efficiency turbo booster centrifugal compressor (CO-COM-6) is used as energy-save third stage for the final compression step to achieve the pressure requirements by the mixed alcohols catalytic-synthesis.

The Aspen Plus®v8.4 process model simulation of the integrally-geared centrifugal two stages compressor (CO-COM blocks) is based in the Siemens STC-GV integrally-geared centrifugal multi-stages compressor series feature a single-shaft arrangement configured to allow inter-cooling step.

Figure 88 shows the Aspen Plus®v8.4 flowsheet of the second-section of synthesis gas compression (conditioning) for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3).

After the regenerative ZnO/CuO-based guard bed adsorber system the intermediate-pressure synthesis gas mixed with the recycled unconverted light-gas (CO-MIX-1) flow enters the compressor by the inlet guide (CO-COM-4) to distribute the flow providing a uniform condition in the first-stage impeller (CO-COM-4). The synthesis gas is compressed to an optimized pressure ratio (CA-CO-TR-1) by the first-stage impeller (CO-COM-4) modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 83.0% isentropic efficiency (isentropic compression).

The synthesis gas after the first-stage of compression (CO-COM-4) ducted-leaving is cooled to 30.0ºC by the water inter-cooler exchanger (CO-3) modeled by using a MHeatX exchanger block. Condensed phase content water and dissolved gases if formed is removed in the condenser knock-out drum (CO-FLA-5) modeled by using a Flash2 separator block and sent to atmospheric condensate buffer/equalizer tank (CO-FLA-7) modeled by using a Flash2 separator block at ambient conditions.

The synthesis gas free of the condensate phase enters in the second-stage impeller (CO-COM-5) and is compressed to an optimized pressure ratio (CA-CO-TR-1) modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 83.0% isentropic efficiency (isentropic compression). The synthesis gas after the second-stage of compression (CO-COM-5) ducted-leaving is not cooled by after-cooler being directly ducted to the high-efficiency turbo booster (CO-COM-6 and LG-EXP-3) when is compressed to obtain the final required pressure by the mixed alcohols catalyst-synthesis.

Not cooled synthesis gas is compressed by the high-efficiency turbo booster compressor (CO-COM-6) resulting in outlet synthesis gas at high-temperature (within the range allowed) after compression. The heat exchanged between the crude high-temperature gaseous product formed and the synthesis gas is reduced increasing the amount of heat available to generate process steam (thermal energy supply) at the expense of increased consumption of electric power energy in the high-efficiency turbo booster (CO-COM-6 and LG-EXP-3). The energy required is supplied without additional cost by the expansion of the high-pressure unconverted light-gas from 82.0 bar to 25.0 bar (intermediate-pressure) in the high-efficiency turbo booster expander (LG-EXP-3).

After the high-efficiency turbo booster compressor (CO-COM-6) the conditioned synthesis gas at 87.0 bar is directly feed without cooling-step to buffer/equalizer tank (CO-FLA-6) modeled by using a Flash2 separator block.

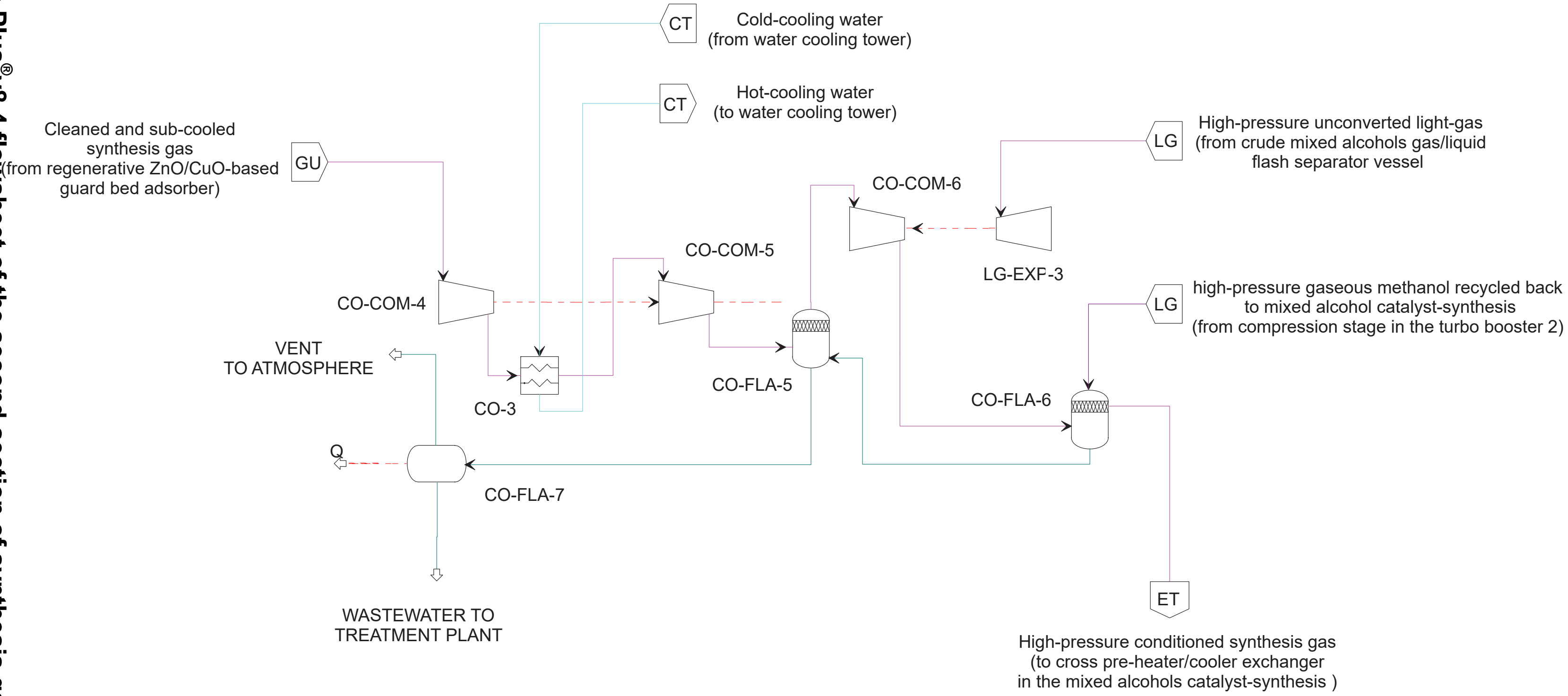


Figure 88 - Aspen Plus® v8.4 flowsheet of the second-section of synthesis gas compression (conditioning) by integrally-geared centrifugal two stages compressor coupled at a high-efficiency turbo booster for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3)

As shown in Figure 88, Aspen Plus®v8.4 flowsheet of the second-section of synthesis gas compression (conditioning) for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) is compost by: integrally-geared centrifugal two stages compressor (CO-COM-4 and CO-COM-5); high-efficiency turbo booster (CO-COM-6 and LG-EXP-3) with centrifugal compressor (CO-COM-6) and expander (LG-EXP-3); water inter-cooler exchanger (CO-3); condenser knock-out drum (CO-FLA-5); buffer/equalizer tank (CO-FLA-6); direct drive permanent magnet motor (not included as block); hydrogen mixer (CO-MIX-1); and atmospheric condensate buffer/equalizer tank (CO-FLA-7).

The high-pressure gaseous methanol recycled back to mixed alcohols catalyst-synthesis enters in the buffer/equalizer tank (CO-FLA-6) and is mixed with the high-pressure synthesis gas at required pressure by the downdraft equipment. The mixed alcohols catalyst-synthesis require, in this case, pressure at about 86.0 bar as inlet pressure in the isothermal water-cooled fixed bed catalytic-synthesis reactor (ET-REA-1).

The compression stage of the high-efficiency turbo booster (CO-COM-6) is modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 90.0% isentropic efficiency. The high-efficiency turbo booster (CO-COM-6 and LG-EXP-3) is detailed in the section 8.1.18 (Energy-saving integrated turbo compressor & expander (turbo booster)).

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-6) to the inter-cooler exchanger (CO-3). The amount of cooling water required is determined and controlled by design specification DS-CO-TL-3 varying the cooling water mass flow rate through the water inter-cooler exchanger (CO-1). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system. The lubricating oil circuit and the lubricating water-cooling system are suppressed from the Aspen Plus®v8.4 process model simulations in this research Master`s degree.

The ambient equalized condensate (CO-FLA-7) if formed is after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

The compression process is optimized by FORTRAN calculator block CA-CO-TR-1 varying the pressure ratio of the compression stages (CO-COM blocks) coupled with the maximum of energy recovered by the high-efficiency turbo booster expander (LG-EXP-3). The integrally-geared centrifugal two stages compressor (CO-COM blocks) is driver by a synchronous direct drive permanent magnet motor modeled by CO-E-7 work stream. The electric power energy consumed by the integrally-geared centrifugal two stages compressor (CO-COM blocks) is optimize-minimized by FORTRAN calculator block CA-CO-TR-1 varying the pressure ratio of the compression stages coupled with the maximum of expansion work-energy recovered by the high-efficiency turbo booster expander (LG-EXP-3). The electrical potential losses by attrite in the mechanical move parts was considered as 1.0% of the mechanical energy required by the stage (99.0% mechanical efficiency).

8.1.16 Hydrogen separation by four-bed pressure swing adsorption (PSA) system

The Aspen Plus®v8.4 process model simulation of the four-bed PSA system (RE blocks) consider a short-cycles system based on a physical binding of gas molecules to selective adsorbent material layers, working at constant temperature (ambient temperature). The system use the effect of alternating pressure and partial pressure to perform the adsorption and desorption cycle-times (phases), carried out at intermediate-pressure and four basic process steps (adsorption, depressurization, regeneration and re-pressurization) in continuous closed-loop cycle phases (8 time-cycle steps).

The Aspen Plus®v8.4 process model simulation of the hydrogen separation by four-bed PSA system was developed in steady-state mode using RKS-BM physical property methods in a simplified model applying Sep separator blocks to represent the pressure swing adsorption cycle and obtain the mass balance estimation for the high-purity hydrogen recovery system without the influence of the cycle-time, normally a short cycle-time lasts about 650 seconds.

As shown in Figure 75, Aspen Plus®v8.4 flowsheet of the hydrogen recovery by four-bed PSA system for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2), and Biomass-to-Methanol (SC3) which is the similar model with modified parameters for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) is compost by: adsorber vessel 1 (RE-ADS-1); adsorber vessel 2 (RE-ADS-2); adsorber vessel 3 (RE-ADS-3); adsorber vessel 4 (RE-ADS-4); inlet multi-way valve skids (RE-V-1; RE-V-2 and RE-V-3); outlet multi-way valve skids (RE-V-4; RE-V-5; RE-V-6; RE-V-7; RE-V-8; and RE-V-9); light-gas condenser knock-out drum (RE-FLA-1); buffer/equalizer hydrogen tank (RE-BUF-1); off-gas condenser knock-out drum (RE-FLA-2); condensate mixer (RE-MIX-1); and condensate recycle pump (RE-PUM-1).

Intermediate-pressure light-gas from the gases mixer (LG-MIX-1) in the energy-saving integrated turbo compressor & expander (turbo booster) enter in the light-gas condenser knock-out drum (RE-FLA-1) modeled by using a Flash2 separator block. The condensed phase formed content alcohols; water and dissolved gases is removed and sent to condensate mixer (RE-MIX-1) to be after-pumped back to the crude mixed alcohols gas/liquid flash separator vessel (LG-FLA-2) for recovery the alcohols content.

Hydrogen is removed only from part of the intermediate-pressure light-gas, which obvious is destined to recycle (RE-FLA-1). This part of intermediate-pressure light-gas is fed guided by inlet multi-way valve skids (RE-V-1, RE-V-2 and RE-V-3) in the pressure swing adsorption cycle compost by four basic process steps: adsorption; depressurization; regeneration; re-pressurization. The another part of the intermediate-pressure light-gas that is not recycled back to synthesis gas main stream, bypass (considered in the Spreadsheet calculation) the four-bed PSA system (RE blocks) being directly sent to the high-performance sequential combustion full-flow advanced EvGT (GT blocks) as fuel-gas.

A fraction around of 45.0%$_{w/w}$ (model result) of the intermediate-pressure light-gas is recycled and flows through the adsorber vessels (first vessel) in an upward direction. Impurities such as H_2O, heavy hydrocarbons, light hydrocarbons, aromatic compounds, and nitrogen compounds, CO2, CO, CH_4 and H_2S are selectively adsorbed on the surface of the adsorbent. After the adsorption cycle-time this vessel (first vessel) stops and the new adsorption cycle-time is initiated in other conditioned vessel (second vessel) in closed-loop cycle.

The regeneration phase starts after the adsorption cycle-time depressurizing the vessel (first vessel) in counter-current. On depressurizing cycle-time the gas content in the vessel is transferred and used to pressurize other vessel (fourth vessel) after regenerated, closing the cycle. The desorbed impurities leave at the bottom of the vessel (third vessel) flowing guided by outlet multi-way valve skids (RE-V-4, RE-V-5 and RE-V-6) to the off-gas system (RE-FLA-2).

Spreadsheet calculation model is used to determine the amount of specific Zeolite’s catalyst, activated charcoal catalyst and SiO_2/Al_2O_3 catalyst must be loaded into adsorber vessels (RE-ADS-1~4) to adsorb the impurities according to characteristically adsorption-saturation limits of the individually selected adsorbent materials.

High-purity hydrogen exits at the top of the adsorber vessel 1 (RE-ADS-1) guided by outlet multi-way valve skids (RE-V-7, RE-V-8, and RE-V-9) to the buffer/equalizer hydrogen tank (RE-BUF-1). Part of this hydrogen is used in the PSA internal-cycle and another part is supplied to the gases mixer (GT-MIX-1) in the high-performance sequential combustion full-flow advanced EvGT (GT blocks) raising the energetic density of the fuel-gas.

Intermediate-pressure off-gas from the PSA hydrogen recovery cycle (RE-ADS blocks) enter in off-gas condenser knock-out drum (RE-FLA-2) modeled by using a Flash2 separator block. The condensed phase formed content alcohols, water and dissolved gases is removed and sent to condensate mixer (RE-MIX-1) to be after-pumped back to the crude mixed alcohols gas/liquid flash separator vessel (LG-FLA-2) for recovery the alcohols content.

Off-gas or light-gas after the off-gas condenser knock-out drum (RE-FLA-2) is sent to the gases mixer (GT-MIX-1) to be used as fuel-gas in the high-performance sequential combustion full-flow advanced EvGT (GT blocks). The light-gas streamline is mixed (RE-MIX-1) together with the fraction of intermediate-pressure light-gas that by-passed the four-bed PSA system (RE blocks).

Spreadsheet calculation model of the adsorber vessel's bed consider the adsorbent bed material's compost by $60.0\%_{w/w}$ of Zeolite's catalyst layers, $35.0\%_{w/w}$ of activated charcoal catalyst layer and $5.0\%_{w/w}$ of SiO_2/Al_2O_3 catalyst layer. The order of layers is defined from the bottom of the bed (raw light-gas entrance) by first layer content SiO_2/Al_2O_3 catalyst, second layer content activated charcoal catalyst and a third layer content the Zeolite's catalyst family subdivided in layers content 5A Zeolite catalyst, CaX Zeolite catalyst, VSA6 Zeolite catalyst and 13X Zeolite catalyst. The Zeolite family layer is considered in the spreadsheet calculation model as single layer containing Zeolite catalyst type.

Zeolite's catalyst layers in the adsorber vessels (RE-ADS-1~4) are considered as commercial type 5A Zeolite catalyst and CaX Zeolite catalyst selective for N_2 and NO_x (e.g.: NO_2, N_2O and NO), VSA6 Zeolite catalyst selective for carbonaceous (e.g.: CO, CO_2 and CH_4) and 13X Zeolite catalyst selective for CO_2, H_2S and aromatic compounds. Zeolite's catalyst, weight loaded considering the capacity limits of $20.0\%_{w/w}$ to adsorbing H_2O, $80.0\%_{w/w}$ to adsorbing H_2S and $60.0\%_{w/w}$ to adsorbing carbonaceous compounds content in the light-gas. Zeolite's catalyst lifetime is expected to be about 2 years before the necessity of deactivated catalyst being partial or full discharged and new activity catalyst loaded, deactivated catalyst is sent to be regenerated and/or to final disposal.

SiO_2/Al_2O_3 catalyst layer in the adsorber vessels (RE-ADS-1~4) is considered as commercial type selective for H_2O and carbonaceous (e.g.: CO, CO_2). SiO_2/Al_2O_3 catalyst, weight loaded considering the capacity limits of $50.0\%_{w/w}$ to adsorbing H_20 and $5.0\%_{w/w}$ to adsorbing carbonaceous compounds content in the light-gas. Catalyst lifetime is expected to be about 1 year before the necessity of deactivated catalyst being partial or full discharged and new activity catalyst loaded, deactivated catalyst is sent to be regenerated and/or to final disposal.

Activated charcoal catalyst layer in the adsorber vessels (RE-ADS-1~4) is considered as commercial type selective for H_2O and carbonaceous (e.g.: CO, CO_2, CH_4 and light hydrocarbons) weight loaded considering the capacity limits of $30.0\%_{w/w}$ to adsorbing H_20 $20.0\%_{w/w}$ to adsorbing H_2S, and $35.0\%_{w/w}$ to adsorbing carbonaceous compounds content in the light-gas. Catalyst lifetime is expected to be about 1 year before the necessity of deactivated catalyst being partial or full discharged and new activity catalyst loaded, deactivated catalyst is sent to be regenerated and/or to final disposal.

8.1.17 Mixed alcohols catalyst-synthesis

The Aspen Plus®v8.4 process model simulation of the mixed alcohols catalytic-synthesis is based on the synthesis process described by Dutta and Phillips (2009) applying $KCoMoS_2/C$ catalysts (Sulfided Co-K-Mo/C) for mixed alcohols catalyst-synthesis (advanced catalyst).

In this process concept the synthesis gas is converted under near-isothermal conditions, while the heat of reaction is utilized for the production of satured steam, aiming the production of methanol, ethanol, propanol, butanol, and more higher-molecular alcohols, and improving the ethanol yield by methanol homologation reactions. Another side reactions are considered according to described in the section 4.1.20 (Mixed alcohols catalytic-synthesis: Ethanol).

The Aspen Plus®v8.4 process model simulation of the mixed alcohols catalytic-synthesis for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3) is based on the Chemical equation c.29 for alcohol formation, Chemical equation c.30 for hydrocarbon formation and Chemical equation c.8 for WGS reaction, according to section 4.1.20 (Mixed alcohols catalytic-synthesis: Ethanol.

To simulate the mixed alcohols catalytic-synthesis reactor in steady state operation mode was considered the stoichiometric type-reactor (RStoic) models in the Aspen Plus®v8.4 process model simulation applying the set of representative stoichiometric reactions to represent the mixed alcohols catalyst-synthesis based on the set of stoichiometric reactions proposal by Dutta and Phillips (2009) according to section 4.1.20 (Mixed alcohols catalytic-synthesis: Ethanol.

The Aspen Plus®v8.4 process model simulation of the mixed alcohols catalytic-synthesis was developed using RKS-BM physical property methods for the gas side-streams and IAPWS-95 physical property methods for the steam/water side-streams (exchangers).

Figure 89 shows the Aspen Plus®v8.4 flowsheet of the mixed alcohols catalytic-synthesis for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Figure 90 shows the Aspen Plus®v8.4 flowsheet of the mixed alcohols catalytic-synthesis for Biomass-to-Mixed alcohols (SC3).

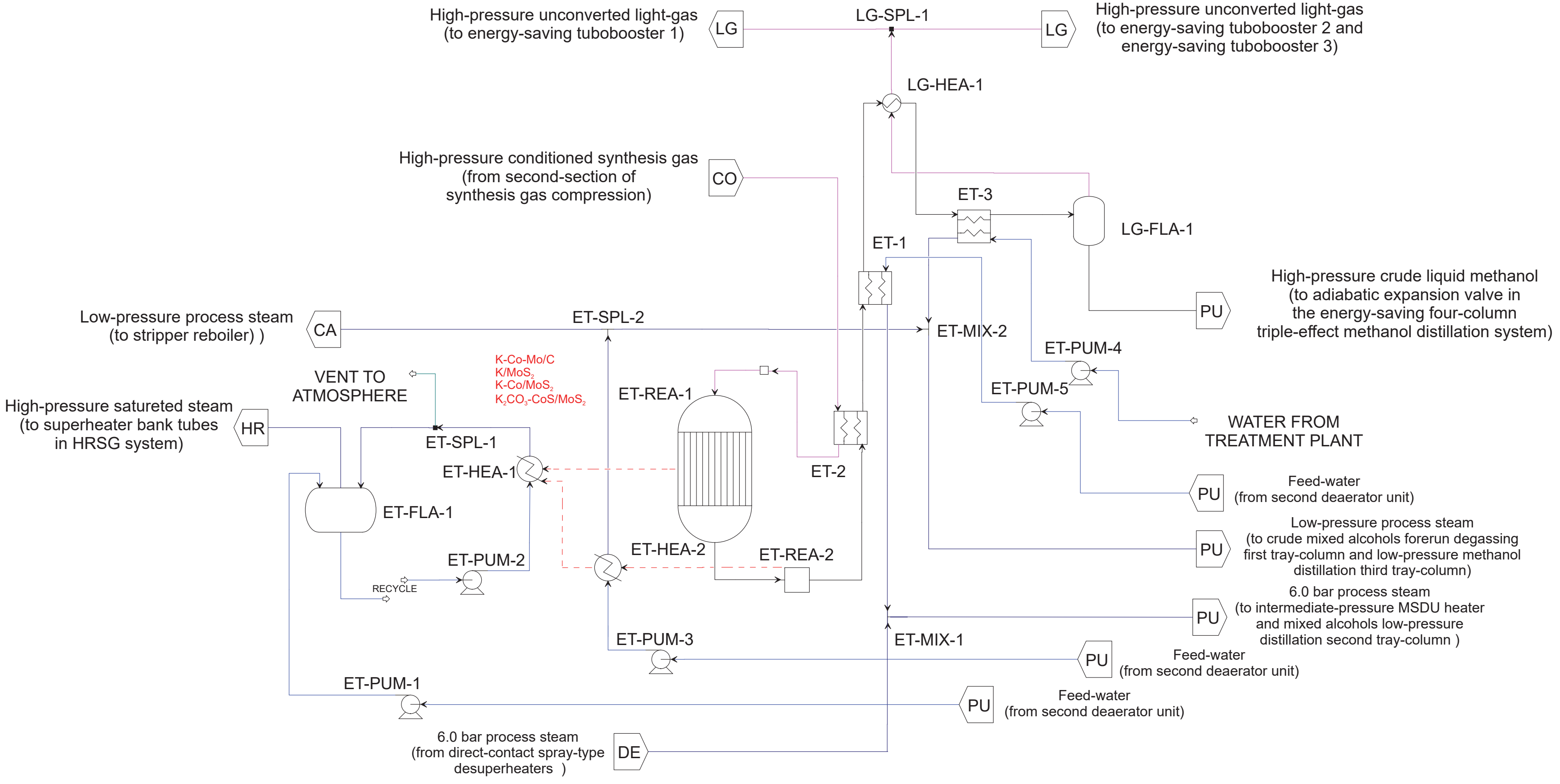


Figure 89 - Aspen Plus® v8.4 flowsheet of the mixed alcohols catalytic-synthesis by isothermal water-cooled fixed bed fixed bed catalytic-synthesis reactor (Sulfided Co-K-Mo/C catalyst) for Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC2)

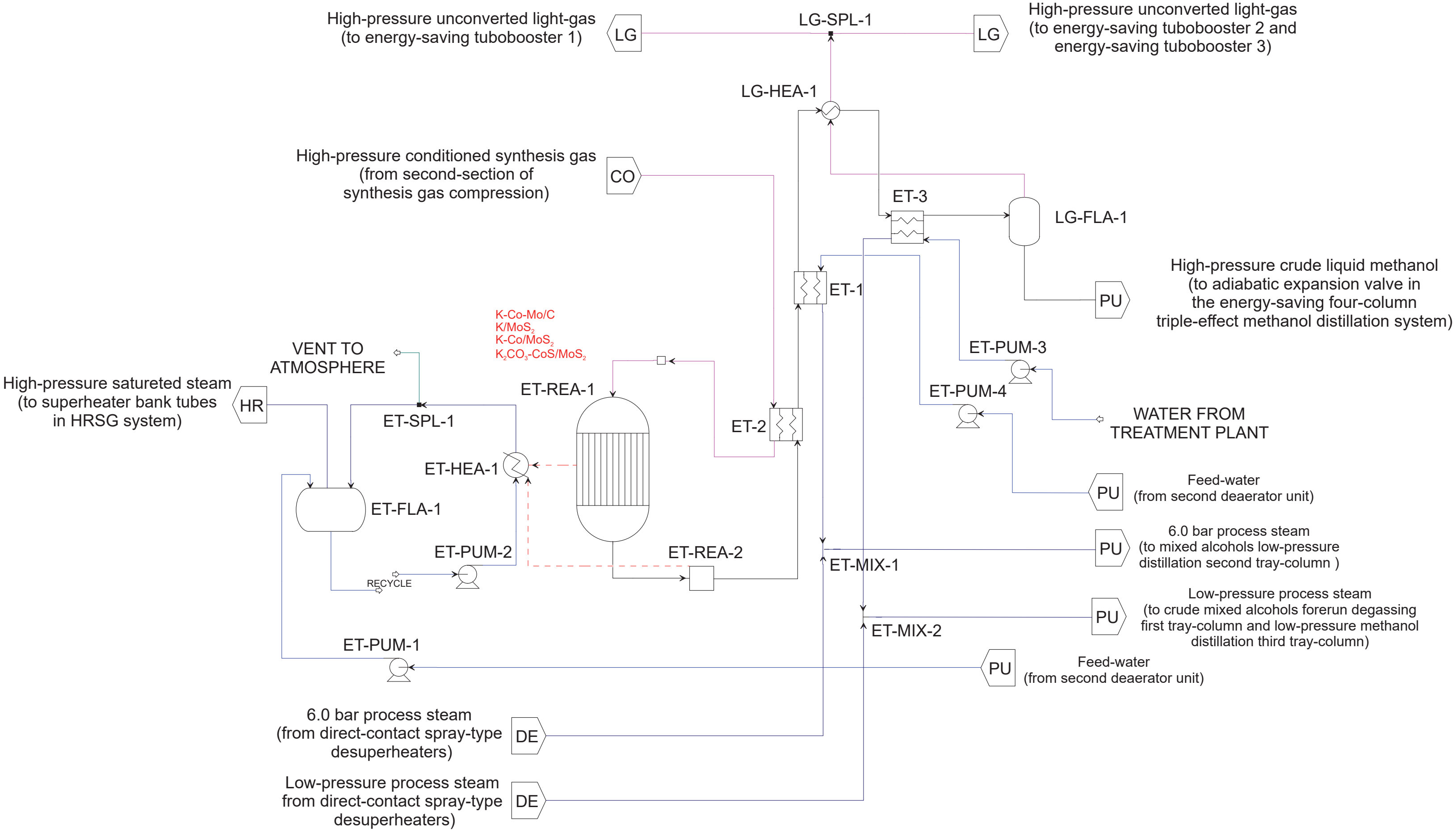


Figure 90 - Aspen Plus® v8.4 flowsheet of the mixed alcohols catalytic-synthesis by isothermal water-cooled fixed bed catalytic-synthesis reactor (Sulfided Co-K-Mo/C catalyst) for Biomass-to-Mixed alcohols (SC3)

As shown in Figure 89, Aspen Plus®v8.4 flowsheet of the mixed alcohols catalytic-synthesis for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) compost by: isothermal water-cooled fixed bed catalytic-synthesis reactor (ET-REA-1); high-pressure steam drum (ET-FLA-1); steam drum vent valve (ET-SPL-1); steam drum water circulation pump (ET-PUM-2); high-pressure water cooler internal exchanger pipe bank (ET-HEA-1); low-pressure steam-circuit heat exchanger (ET-HEA-2); steam splitter (ET-SPL-2); cross pre-heater/cooler exchanger (ET-2); cross heater/cooler exchanger (LG-HEA-1); low-temperature water cooler (ET-3); synthesis-products water cooler (ET-1); water high-pressure pump (ET-PUM-1); water pump 1 (ET-PUM-3); water pump 2 (ET-PUM-4); water circulation pump (ET-PUM-5); high-pressure gas/liquid flash phase separator vessel (LG-FLA-1); crude mixed alcohols gas/liquid flash separator vessel (LG-FLA-1); recycle splitter (LG-SPL-1); and steam mixer 1 (ET-MIX-1).

As shown in Figure 90, Aspen Plus®v8.4 flowsheet of the mixed alcohols catalytic-synthesis for Biomass-to-Mixed alcohols (SC3) compost by: isothermal water-cooled fixed bed synthesis catalytic-synthesis reactor (ET-REA-1); high-pressure steam drum (ET-FLA-1); steam drum vent valve (ET-SPL-1); steam drum water circulation pump (ET-PUM-2); high-pressure water cooler internal exchanger pipe bank (ET-HEA-1); cross pre-heater/cooler exchanger (ET-2); cross heater/cooler exchanger (LG-HEA-1); low-temperature water cooler (ET-3); synthesis-products water cooler (ET-1); water high-pressure pump (ET-PUM-1); water pump 1 (ET-PUM-3); water pump 2 (ET-PUM-4); water pump 3 (ET-PUM-5); water circulation pump (ET-PUM-4); high-pressure gas/liquid flash phase separator vessel (LG-FLA-1); crude mixed alcohols gas/liquid flash separator vessel (LG-FLA-2); recycle splitter (LG-SPL-1); steam mixer 1 (ET-MIX-1); and steam mixer 2 (ET-MIX-2).

The Aspen Plus®v8.4 process model simulation of the mixed alcohols catalytic-synthesis for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3) consider the H_2/CO ratio (S_2) of the synthesis gas inlet the gas-cooled fixed bed catalytic-synthesis reactor (ME-REA-1) equal to 1.3 (Equation 20) as described in the section 3.9.16 (Hydrogen to carbon ratios) according to 4.1.20 (Mixed alcohols catalytic-synthesis: Ethanol)

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3), the high-pressure unconverted synthesis gas (light-gas) is sent to the energy-saving integrated turbo compressor & expander (turbo booster) to recovery energy by expansion process. After, part of the high-pressure unconverted synthesis gas is sent to four-bed PSA system (RE blocks) to remove hydrogen for adjust-maintenance the ratio of hydrogen to carbon monoxide - (H_2/CO) ratio - before recycle as light-gas poor in hydrogen (necessary remove hydrogen to reduce the H_2 content).

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3), high-purity hydrogen from the buffer/equalizer hydrogen tank (RE-BUF-1) is sent to the high-performance sequential combustion full-flow advanced EvGT (GT blocks) and the unconverted synthesis gas (light-gas) poor in hydrogen recycled back and mixed with the intermediate-pressure synthesis gas in the gases mixer (WS-MIX-5) before the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks), because the high-content of CO_2 that is generated in the mixed alcohols catalytic-synthesis due the catalyst activity for WGS reaction.

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3), the gaseous methanol at 1.8 bar and about 145.0ºC from the third vessel in methanol back-flushing regeneration cycle (DH-FLU-1) is compressed to 87.0 bar and at about 480.0ºC (single compression stage) by energy-saving integrated turbo compressor (DH-COM-1) and recycled back to mixed alcohols catalyst-synthesis augment the ethanol obtained by the thermochemical-biorefinery (homologation reactions).

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3), the high-pressure gaseous methanol from the turbo compressor (DH-COM-1) enters in the buffer/equalizer tank (CO-FLA-6) and is mixed with the high-pressure synthesis gas at 87.0 bar at about 167.0ºC.

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3), conditioned synthesis gas at 87.0 bar at about 167.0ºC is heated in the cross pre-heater/cooler exchanger (ET-2) to 300.0ºC before enters the isothermal water-cooled fixed bed catalytic-synthesis reactor (ET-REA-1) by the high-temperature and high-pressure crude gas product from the isothermal water-cooled fixed bed catalytic-synthesis reactor (ET-REA-1). In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3), high-temperature and high-pressure crude gas product at 350.0ºC and about 85.0 bar is cooled by the conditioned synthesis gas in the cross pre-heater/cooler exchanger (ET-2) to intermediate-temperature.

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3), conditioned synthesis gas at 86.0 bar and 300.0ºC enters the isothermal water-cooled fixed bed synthesis catalytic-synthesis reactor (ET-REA-1), a major fraction of the gases reacts in the high-activity Sulfided Co-K-Mo/C catalyst-bed to form according to Chemical equation c.29 linear-chain alcohols (e.g.: methanol, ethanol, propanol, butanol, and other higher-molecular alcohols) and according to Chemical equation c.30 higher hydrocarbon gases (e.g.: ethane/ethene, propane/propene, butane/butene and methane), as described in the section 4.1.20 (Mixed alcohols catalytic-synthesis: Ethanol).

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3), the heat of the mixed alcohols synthesis reactions (exothermic reactions) in the isothermal water-cooled fixed bed synthesis catalytic-synthesis reactor (ET-REA-1) is removed by high-pressure satured water from the high-pressure steam drum (ET-FLA-1) controlling the temperature of the isothermal water-cooled fixed bed synthesis catalytic-synthesis reactor (ET-REA-1) at 350.0ºC. The high-pressure saturated water is pumped from the high-pressure steam drum (ET-FLA-1) by the steam drum water circulation pump (ET-PUM-2) at 87.0 bar and about 300.0ºC passing through the tube side of the isothermal water-cooled fixed bed synthesis catalytic-synthesis reactor (ET-REA-1) removing the heat released by the mixed alcohols synthesis reactions (exothermic reactions) generating high-pressure satured steam at about same conditions 86.0 bar and 300.0ºC.

The amount of satured water at 87.0 bar and about 300.0ºC circulating in the tube side of the isothermal water-cooled fixed bed synthesis catalytic-synthesis reactor (ET-REA-1) is determined and controlled by design specification DS-ET-TG-1 varying the mass flow rate of water passing through the isothermal water-cooled fixed bed synthesis catalytic-synthesis reactor (ET-REA-1) that is necessary to maintain the temperature of the reactor (removal heat).

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3), the high-pressure satured steam is send back to the high-pressure steam drum (ET-FLA-1) maintaining the temperature and pressure of the drum (ET-FLA-1), a fraction of 2.0% of the steam generated is considered as losses, being vented to atmosphere (TO ATMOSPHERE) by the steam drum vent valve (ET-SPL-1).

In the Biomass-to-Mixed alcohols (SC3), a part of heat of the mixed alcohols synthesis reactions (exothermic reactions) in the isothermal water-cooled fixed bed synthesis catalytic-synthesis reactor (ET-REA-1) is used to generate low-pressure process steam at 2.5 bar and 130.0ºC to supply part of the thermal energy required by the three-column double-effect alcohols distillation system (ethanol purification) and part of the thermal energy required by the stripper reboiler (CA-REB-1) of the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution system (CA blocks).

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3), the high-pressure satured steam at 85.0 bar and about 299.0ºC generated in the high-pressure steam drum (ET-FLA-1) is sent to the horizontal gas-flow drum type HRSG system (HR blocks) to be mixed in the high-pressure steam mixer (HR-MIX-1 or HR-MIX-2) with the steam vaporized by the HP vaporizer bank tubes (HR-HPV-1). After, high-pressure saturated steam at about 85.0 bar and 257.0ºC is superheated to 530.0ºC in the HP superheater bank tubes (HR-HPS-1) and sent to the ST to generate electricity in the high-pressure expansion stage (ST blocks).

Make-up water for the high-pressure steam drum (ET-FLA-1) is made by using deaerated water at 105.0ºC and 1.4 bar from the second deaerator unit (PU-DEA-1), the deaerator water is pumped by the water high-pressure pump (ET-PUM-1) inlet the high-pressure steam drum (ET-FLA-1) at 87.0 bar and 117.0ºC. The amount of deaerated water used/circulating as make-up for the high-pressure steam drum (ET-

FLA-1) is determined and controlled by design specification DS-ET-FL-1 varying the mass flow rate inlet the high-pressure steam drum (ET-FLA-1) depending on the mass flow rate of steam generated.

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3), the high-pressure crude gas product at intermediate-temperature after the cross pre-heater/cooler exchanger (ET-2) is cooled to 166.0ºC at 83.0 bar in the synthesis-products water cooler (ET-1) by low-temperature low-pressure water-circuit. In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3), the heat recovered from the synthesis-products water cooler (ET-1) is used to generate low-pressure process steam at 6.0 bar and 160.0ºC to supply all of the thermal energy required by the Zeolite-based MSDU system am part of the thermal energy required to vaporize the bottom liquid products in the distillation second-column reboiler (DS-REB-1).

Deaerated water at 105.0ºC and 1.4 bar from the second deaerator unit (PU-DEA-1) is pumped to 2.5 bar by the water pump 2 (ET-PUM-4) passing thought the synthesis-products water cooler (ET-1) to generate low-pressure process steam at 6.0 bar and 160.0ºC. The amount of deaerated water used/circulating to cool down the crude gas product to 166.0ºC at 83.0 bar in the synthesis-products water cooler (ET-1) is determined and controlled by design specification DS-ET-TG-2 varying the mass flow rate of deaerated water passing through the synthesis-products water cooler (ET-1) limited by the temperature limits of the enchanter (ET-1).

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3), the high-pressure crude gas product at 166.0ºC and 83.0 bar change heat in the cross heater/cooler exchanger (LG-HEA-1) with the high-pressure unconverted light-gas at 82.0 bar and 50.0ºC from the high-pressure gas/liquid flash phase separator vessel (LG-FLA-1). High-pressure crude gas product is cooled to 131.0ºC at 83 bar and high-pressure unconverted light-gas is heated to 125.0ºC at 82.0 bar.

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3), the high-pressure crude gas product at 166.0ºC and 83.0 bar is cooled in the low-temperature water cooler (ET-3) to 50.0ºC at 82 bar by low-temperature low-pressure water-circuit. In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3), the heat recovered from the low-temperature water cooler (ET-3) is used to generate low-pressure process steam at 2.5 bar and 130.0ºC to supply part of the thermal energy required by the three-column double-effect alcohols distillation system (ethanol purification).

Water as make-up water (WATER FROM TREATMENT PLANT) is pumped to 2.5 bar by the water pump 1 (ET-PUM-3) passing thought the low-temperature water cooler (ET-3) to generate low-pressure process steam at 2.5 bar and 130.0ºC. The amount of make-up water used to cool down the crude gas product to 50.0ºC at 82 bar in the low-temperature water cooler (ET-3) is determined and controlled by design specification DS-ET-TG-3 varying the mass flow rate of water passing through the low-temperature water cooler (ET-3) limited by the temperature limits of the exchanger (ET-3).

The low-temperature and high-pressure crude gas product at 82.0 bar and 50.0ºC forming two phases, the liquid phase and gaseous phases is separated in the high-pressure gas/liquid flash phase separator vessel (LG-FLA-1).

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3), the gaseous phase, high-pressure unconverted light-gas (unconverted synthesis gas) at about 82.0 bar and 50.0ºC from the high-pressure gas/liquid flash phase separator vessel (LG-FLA-1) pass thought the cross heater/cooler exchanger (LG-HEA-1) being pre-heated to 125.0ºC at 82.0 bar before sent to be expanded in the energy-saving integrated turbo compressor & expander (turbo booster) to recovery the expansion energy potential of the high-pressure unconverted light-gas. After the heater (LG-HEA-1), the high-pressure unconverted light-gas is splitted in the recycle splitter (LG-SPL-1) being one fraction destined to the expander (LG-EXP-3) of the high-efficiency turbo booster 1 (CO-COM-6 and LG-EXP-3), another part to expander (LG-EXP-1) of the high-efficiency turbo booster 2 (LG-COM-1 and LG-EXP-1), and another part to expander (LG-EXP-2) of the high-efficiency turbo booster 3 (DH-COM-1 and LG-EXP-2).

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3), the liquid phase, high-pressure crude liquid mixed alcohols at about 82.0 bar and 50.0ºC from the high-pressure gas/liquid flash phase separator vessel (LG-FLA-1) is sent to the crude mixed alcohols gas/liquid flash separator vessel (LG-FLA-2) in the energy-saving integrated turbo compressor & expander (turbo booster) to remove dissolved gases at intermediate-pressure before enters in crude mixed alcohols forerun degassing first tray-column (PU-COL-1).

Spreadsheet calculation models are used to determine the quantity of $KCoMoS_2/C$ catalysts (Sulfided Co-K-Mo/C) must be loaded into isothermal water-cooled fixed bed catalytic-synthesis reactor (ET-REA-1).

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3), the Sulfided Co-K-Mo/C catalyst considered in the isothermal water-cooled fixed bed catalytic-synthesis reactor (ET-REA-1) is sulfur tolerant catalyst compost by $19.0\%_{w/w}$ of Mo, $4.0\%_{w/w}$ of Co, $10\%_{w/w}$ of K and $75.0\%_{w/w}$ of C (generic). The $CuO/ZnO/Al_2O_3$ catalyst is weight loaded considering the productivity of 350 g of crude mixed alcohols per kg of catalyst per hour (STY). Sulfided Co-K-Mo/C catalyst lifetime is expected to be about 4 years before the necessity of deactivated catalyst be partial or full discharged and new activity catalyst be loaded, deactivated catalyst is send to be regenerated and/or to final disposal.

8.1.18 Energy-saving integrated turbo compressor & expander (turbo booster)

Unconverted light-gas leaving on the top of the high-pressure gas/liquid flash phase separator vessel (LG-FLA-1) at about 82.0 bar and 50.0ºC can be expanded to intermediate pressure level providing useful work-energy before being sent to hydrogen recovery by four-bed PSA system (RE blocks) or to high-performance sequential combustion full-flow advanced EvGT (GT blocks).

The expansion work-energy is used to compress the synthesis gas after the second stage of compression by the integrally-geared centrifugal two stages compressor (CO-COM blocks) as a third stage of compression using the high-efficiency turbo booster 1 centrifugal compressor (CO-COM-6). The expansion work-energy is used to compress tail-gas from the crude mixed alcohols forerun degassing first tray-column (PU-COL-1) using the high-efficiency turbo booster 2 centrifugal compressor (LG-COM-1). The expansion work-energy is used to compress the gaseous methanol obtained from the low-pressure methanol distillation third tray-column (DS-COL-2) using the high-efficiency turbo booster 3 centrifugal compressor (DH-COM-1), which is recycled back to the mixed alcohols catalyst-synthesis.

Aspen Plus®v8.4 process model simulation of the energy-saving integrated turbo compressor & expander (turbo booster) has been developed using RKS-BM physical property methods for almost all of the blocks involved in the system, only the crude mixed alcohols gas/liquid flash separator vessel 2 (LG-FLA-2) was developed using NRTL-RK physical property methods (change point).

Figure 91 shows the Aspen Plus®v8.4 flowsheet of the energy-saving integrated turbo compressor & expander (turbo booster) for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3).

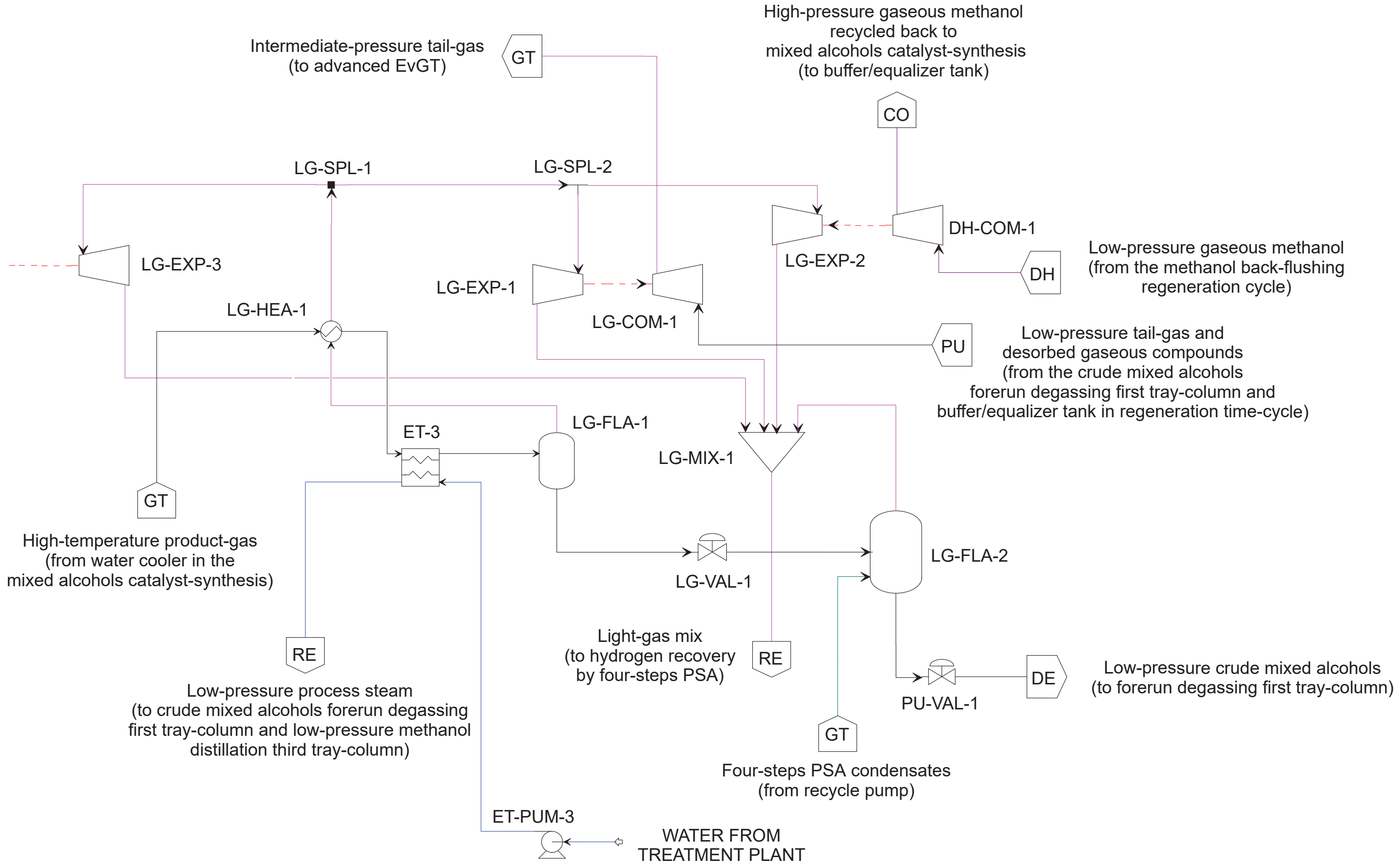


Figure 91 - Aspen Plus® v8.4 flowsheet of the energy-saving integrated turbo compressor & expander (turbo booster) for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3)

As shown in Figure 91, Aspen Plus®v8.4 flowsheet of the of the energy-saving integrated turbo compressor & expander (turbo booster) for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) is compost by: high-pressure gas/liquid flash phase separator vessel (LG-FLA-1); crude mixed alcohols gas/liquid flash separator vessel (LG-FLA-2); cross heater/cooler exchanger (LG-HEA-1); gases splitter 1 (LG-SPL-1); gases splitter 2 (LG-SPL-2); gases mixer (LG-MIX-1); buffer/equalizer tank (LG-FLA-3); high-efficiency turbo booster 1 (CO-COM-6 and LG-EXP-3) with centrifugal compressor (CO-COM-6) and expander (LG-EXP-3); high-efficiency turbo booster 2 (LG-COM-1 and LG-EXP-1) with centrifugal compressor (LG-COM-1) and expander (LG-EXP-1); high-efficiency turbo booster 3 (DH-COM-1 and LG-EXP-2) with centrifugal compressor (DH-COM-1) and expander (LG-EXP-2); adiabatic expansion valve 1 (LG-VAL-1); and adiabatic expansion valve 2 (PU-VAL-1).

The high-pressure unconverted light-gas at 82.0 bar and 50.0ºC obtained after separation of phases in the high-pressure gas/liquid flash phase separator vessel (LG-FLA-1) modeled by using a Flash2 separator block is heated to 82.0 bar and 125.0ºC (drop pressure not evaluated) in the cross heater/cooler exchanger (LG-HEA-1) modeled by using a HeaterX exchanger block. High-pressure crude gaseous product at 83.0 bar and 166.5ºC obtained by mixed alcohols catalyst-synthesis is cooled down to 82.5 bar and 131.1ºC in the cross heater/cooler exchanger (LG-HEA-1) as energy-save heat exchanger step. The high-pressure unconverted light-gas is heated aiming positive temperatures after the expansion processes,

Part of the heated high-pressure unconverted light-gas is splitted in the gases splitter 1 (LG-SPL-1) modeled by using a FSplit splitter block being destined to compress the tail-gas from the crude mixed alcohols forerun degassing first tray-column (PU-COL-1) in the high-efficiency turbo booster 2 centrifugal compressor (LG-COM-1) and to compress the gaseous methanol from the third vessel in methanol back-flushing regeneration cycle (DH-FLU-1) in the high-efficiency turbo booster 3 centrifugal compressor (DH-COM-1). Another part of the heated high-pressure unconverted light-gas is expanded achieving the work-energy needed to compress and suit the synthesis gas main stream at required pressure level in the high-efficiency turbo booster 1 centrifugal compressor (CO-COM-6).

An optimized part of the heated high-pressure unconverted light-gas at 82.0 bar and 125.0ºC is splitted in the gases splitter 2 (LG-SPL-2) modeled by using a FSplit splitter block and expanded to 25.0 bar and about 28.1ºC by the high-efficiency turbo booster 2 centrifugal expander (LG-EXP-1) modeled by using a Compr pressure changer block in turbine model considering 90.0% isentropic efficiency (isentropic expansion). The tail-gas at 3.6 bar and about 150.0ºC from the buffer/equalizer tank (LG-FLA-3) is compressed to 23.5 bar and about 360.0ºC by the high-efficiency turbo booster 2 centrifugal compressor (LG-COM-1) modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 90.0% isentropic efficiency (isentropic compression), allowing its use as fuel-gas in the high-performance sequential combustion full-flow advanced EvGT (GT blocks).

The mass flow rate of heated high-pressure unconverted light-gas destined to the high-efficiency turbo booster 2 centrifugal expander (LG-EXP-1) is determined by the work-energy generated by the expansion of the heated high-pressure unconverted light-gas and the work-energy required to compress the tail-gas. The work-energy required/generated is controlled by design specification DS-LG-PG-1 varying the mass flow rate of the high-pressure unconverted light-gas passing through the centrifugal expander (LG-EXP-1).

Another optimized part of the heated high-pressure unconverted light-gas splitted in the gases splitter 2 (LG-SPL-2) is expanded from 82.0 bar and 125.0ºC to 25.0 bar and about 28.1ºC by the high-efficiency turbo booster 3 centrifugal expander (LG-EXP-2) modeled by using a Compr pressure changer block in turbine model considering 90.0% isentropic efficiency (isentropic expansion). The gaseous methanol at 1.8 bar and about 145.0ºC from the third vessel in methanol back-flushing regeneration cycle (DH-FLU-1) is compressed to 87.0 bar and at about 480.2ºC (single compression stage) by centrifugal compressor (DH-COM-1) modeled by using a Compr pressure changer block according to rigorous ASME method for isentropic compressor considering 90.0% isentropic efficiency (isentropic compression), allowing its recycle to mixed alcohols catalyst-synthesis augment the ethanol obtained by the thermochemical-biorefinery.

The mass flow rate of heated high-pressure unconverted light-gas destined to the high-efficiency turbo booster 3 centrifugal expander (HD-EXP-1) is determined by the work-energy generated by expansion of the heated high-pressure unconverted light-gas and work-energy required to compress the gaseous methanol, and is controlled by design specification DS-LG-PG-2 varying the mass flow rate of the high-pressure unconverted light-gas passing through centrifugal expander (LG-EXP-2).

An large reminiscent fraction of the heated high-pressure unconverted light-gas at 82.0 bar and 125.0ºC is splitted in the gases splitter 1 (LG-SPL-1) being use-expanded to 25.0 bar and at about 28.1ºC by the high-efficiency turbo booster 1 centrifugal expander (LG-EXP-3) as save-energy step modeled by using a Compr pressure changer block in turbine model considering 90.0% isentropic efficiency (isentropic expansion). Synthesis gas (main stream) at optimized conditions is compressed to about 87.0 bar and 160.0ºC by centrifugal compressor (CO-COM-6) modeled by using a Compr pressure changer block as the third stage of synthesis gas compression according to rigorous ASME method for isentropic compressor considering 90.0% isentropic efficiency (isentropic compression).

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) the fraction of unconverted light-gas recycled back to the mixed alcohols catalyst-synthesis is determined in the hydrogen recovery by four-bed PSA system (RE blocks) as intermediate-pressure off-gas (containing large amounts of CO_2) according to the ratio of hydrogen to carbon monoxide – H_2/CO ratio – being fed before the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution.

High-pressure crude liquid mixed-alcohol from the high-pressure gas/liquid flash phase separator vessel (LG-FLA-1) is expanded in the adiabatic expansion valve 1 (LG-VAL-1) modeled using a Valve pressure changer block to intermediate-pressure level. The small fraction of gaseous phase formed in the expansion process is separated in the crude mixed alcohols gas/liquid flash separator vessel (PU-FLA-1).

After expanded to intermediate-pressure level in the adiabatic expansion valve 1 (LG-VAL-1) the unconverted light-gas from the crude mixed alcohols gas/liquid flash separator vessel (LG-FLA-2) is mixed in the gases mixer (LG-MIX-1) with the intermediate-pressure level unconverted light-gas obtained after expansion in the high-efficiency turbo booster centrifugal expander 1 (LG-EXP-3), high-efficiency turbo booster centrifugal expander 2 (LG-EXP-1) and high-efficiency turbo booster centrifugal expander 3 (LG-EXP-2). The resultant mix-stream is sent to hydrogen recovery by four-bed PSA system (RE blocks).

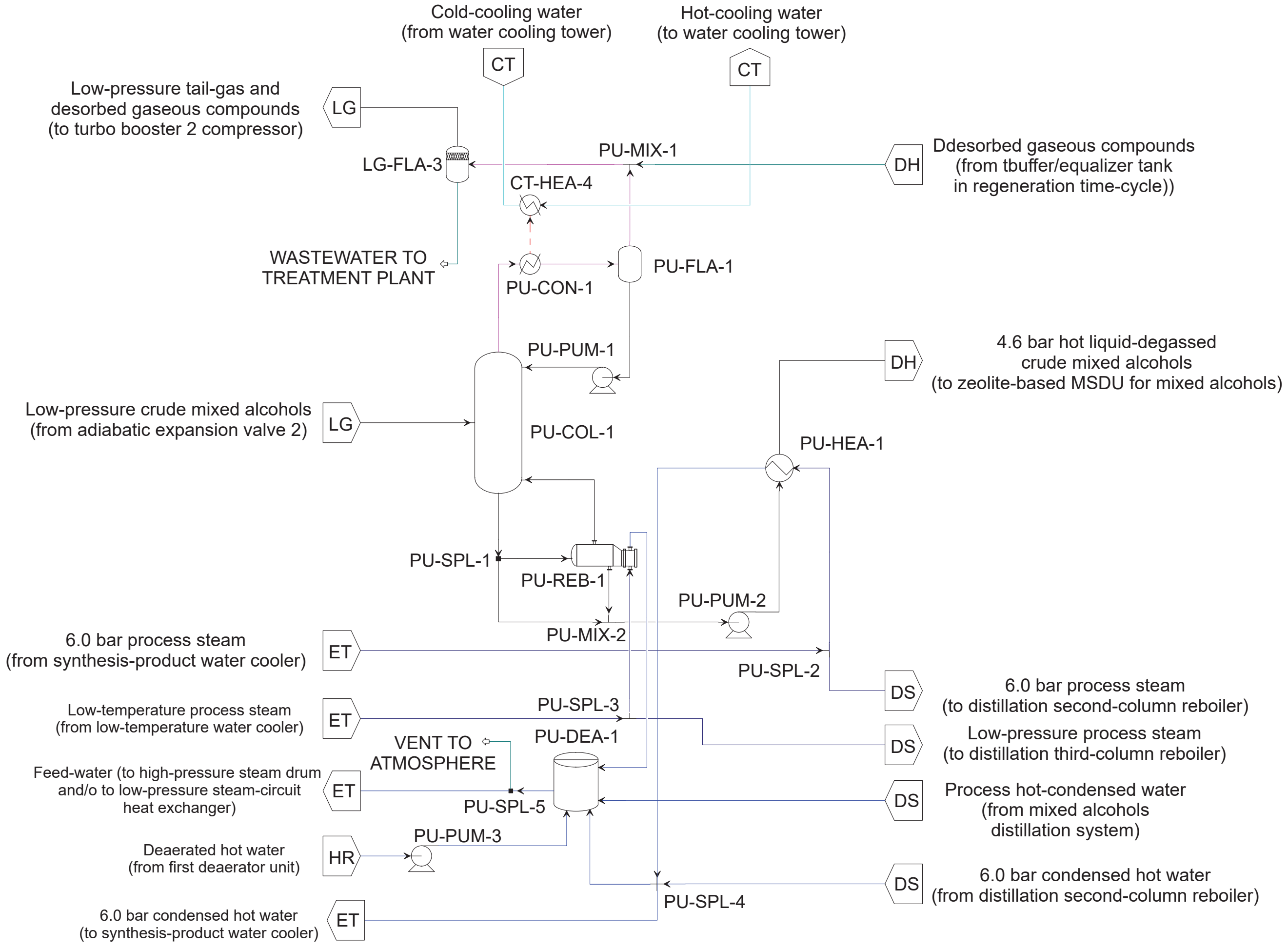
Intermediate-pressure crude mixed alcohols from the crude mixed alcohols gas/liquid flash separator vessel (LG-FLA-2) is expanded in the adiabatic expansion valve 2 (PU-VAL-1) modeled by using a Valve pressure changer block to low-pressure level. The low-pressure crude mixed alcohols is then fed in the crude mixed alcohols forerun degassing first tray-column (PU-COL-1).

8.1.19 Three-column double-effect alcohols distillation system (ethanol purification)

The crude mixed alcohols obtained from the mixed alcohols catalytic-synthesis is distillated in the three-column train in sequential multi-effect arrangement to obtain anhydrous ethanol with about $99.5\%_{w/w}$ of purity intended for use as bio-based liquid fuel. The wet crude mixed alcohols is dehydrated using Zeolite-based MSDU for mixed alcohols according to section 8.1.20 (Zeolite-based molecular sieve dehydration unit for mixed alcohols).

Figure 92 shows the Aspen Plus$^{®}$v8.4 flowsheet of the crude mixed alcohols forerun degassing first tray-column for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3). Figure 93 shows the Aspen Plus$^{®}$v8.4 flowsheet of the mixed alcohols low-pressure distillation second tray-column and the low-pressure methanol distillation third tray-column for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3).

Figure 92 - Aspen Plus® v8.4 flowsheet of the crude mixed alcohols forerun degassing first tray-column for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3)



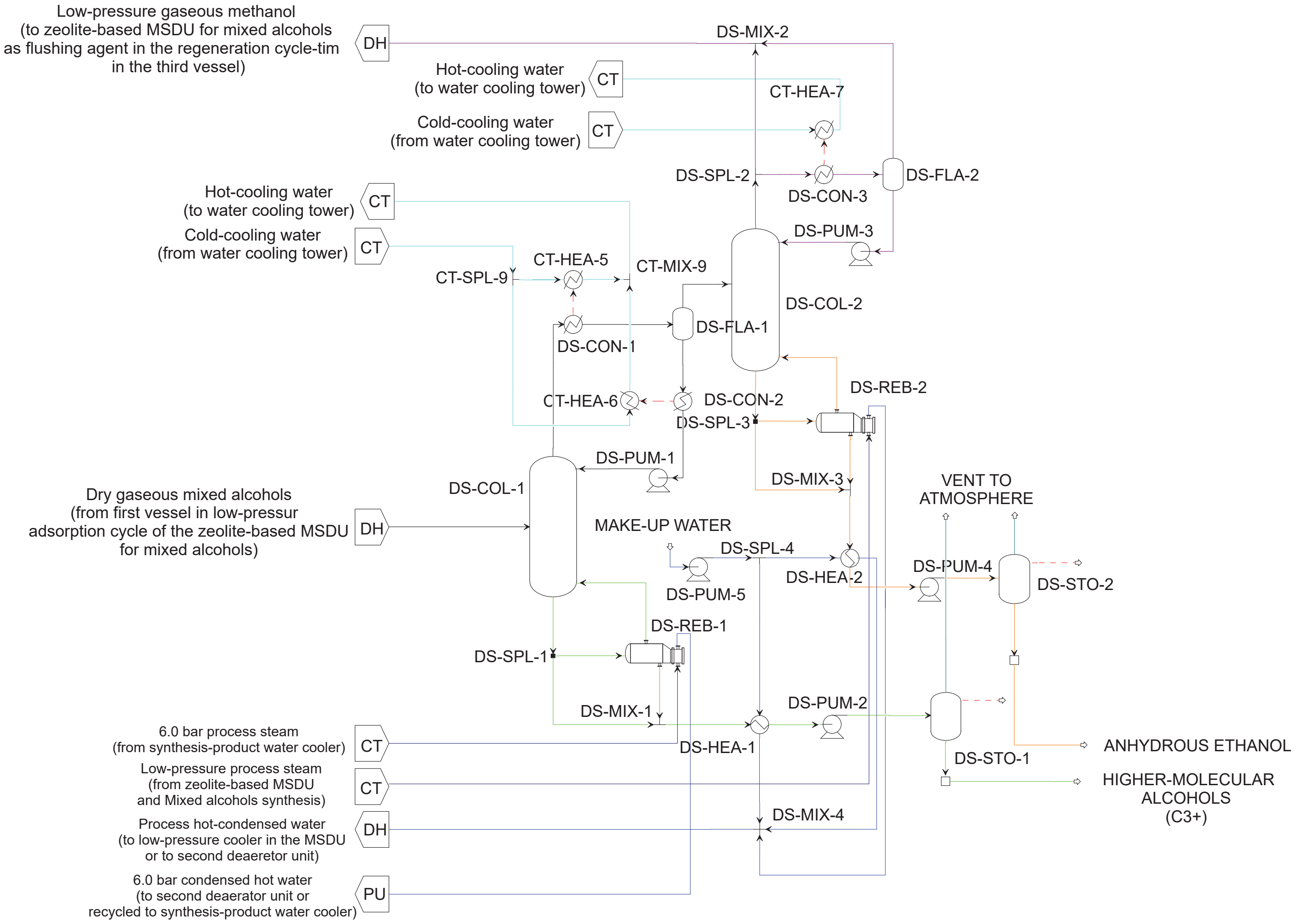


Figure 93 - Aspen Plus$^{®}$v8.4 flowsheet of the mixed alcohols low-pressure distillation second tray-column and the low-pressure methanol distillation third tray-column for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3)

As shown in Figure 92, Aspen Plus®v8.4 flowsheet of the three-column double-effect alcohols distillation system (ethanol purification) for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) is compost by: crude mixed alcohols forerun degassing first tray-column (PU-COL-1); first-column reflux pump 1 (PU-PUM-1); crude mixed alcohols pump (PU-PUM-2); first-column partial condenser (PU-CON-1 and CT-HEA-4); first-column liquid reflux-drum (PU-FLA-1); tail-gas mixer (PU-MIX-1); distillation first-column reboiler (PU-REB-1); crude mixed alcohols sump splitter (PU-SPL-1); crude mixed alcohols mixer (PU-MIX-2); intermediate-pressure heater (PU-HEA-1); second deaerator unit (PU-DEA-1); steam splitter 1 (PU-SPL-2); steam splitter 2 (PU-SPL-3); deaerated hot process water splitter (PU-SPL-5); and deaerated hot process water pump (PU-PUM-3).

The Aspen Plus®v8.4 process model simulation of the three-column double-effect alcohols distillation system (ethanol purification) was developed in steady-state mode using NRTL-RK physical property methods for the main processes (alcohols content) and IAPWS-95 physical property methods for the steam/water side in the heater exchangers.

Intermediate-pressure crude liquid mixed alcohols from the crude mixed alcohols gas/liquid flash separator vessel (LG-FLA-2) is expanded in the adiabatic expansion valve 2 (PU-VAL-1) modeled by using a Valve pressure changer block to 3.947 bar (tray-pressure) and at about 48.7ºC and then fed in the 8º theoretically stage of the crude mixed alcohols forerun degassing first tray-column (PU-COL-1).

Crude mixed alcohols forerun degassing first tray-column (PU-COL-1) remove the non-condensable gases (e.g.: H_2, O_2, N_2, Ar, Xe, Kr, CO, CO_2, CH_4, light hydrocarbons, heavy hydrocarbons and the reminiscent impurities as COS, SO_X, NO_x, NH_3, H_2S, CHN and others) content in the crude liquid mixed alcohols.

Rigorous Aspen Plus®v8.4 process model simulation of the crude mixed alcohols forerun degassing first tray-column (PU-COL-1) was developed by using RadFrac column block on standard convergence mode without in-bed condenser and reboiler. The model was optimized for estimated 20 theoretical stages considering Bubble cap (Aspen90) tray section with one-pass per tray with cap diameter of 76.2 mm and standards panel A with weir height of 30.0 mm and tray diameter of 1.00 m. The model use rate-based calculation for mixed flow model without reactions and film resistance in vapor phase, without reactions and with film resistance in liquid phase, and employing vapor and liquid phase film non-ideality corrections. Default Aspen Plus®v8.4 tray parameters is applied to calculate interfacial area by AIChE (1958) method, to predict the mass transfer coefficient by Scheffe and Weiland (1987) method, and heat transfer coefficient by Chilton–Colburn (Taylor and Krishna, 1993) method.

The gaseous top-product at about 3.7 bar and 78.5ºC leave from the 1º theoretically vapor stage (top column stage) in the crude mixed alcohols forerun degassing first tray-column (PU-COL-1) is cooled in the first-column partial condenser (PU-CON-1) by cooling water (PU-HEA-4) modeled by using Heater exchanger blocks. The condensed phase formed at 3.6 bar and 35.0ºC is flash-separated in the first-column liquid reflux-drum (PU-FLA-1) modeled by using a Flash2 separator block form-condensing about 30.0%$_{w/w}$ (model result) of the gaseous top-product (condensate phase) in saturation equilibrium conditions.

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-7) to the first-column partial condenser (CT-HEA-4). The amount of cooling water required is determined and controlled by design specification DS-PU-TL-1 varying the mass flow rate of cooling water passing through the first-column partial condenser (CT-HEA-4). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

The condensed phase formed at 3.6 bar and 35.0ºC containing mainly ethanol and methanol (methanol recovery) from the first-column liquid reflux-drum (PU-FLA-1) modeled by using a Flash2 separator block is pumped at 3.7 bar and about 35.0ºC by the first-column reflux pump 1 (PU-PUM-1) and refluxed back to the 1º theoretically liquid stage in the crude mixed alcohols forerun degassing first tray-column (PU-COL-1).

About 70.0%$_{w/w}$ of gaseous top-product (non-condensed) containing mainly CO_2 (less than 10.0%$_{w/w}$ is combustible) leaving from the first-column liquid reflux-drum (PU-FLA-1) at 3.6 bar and 35.0ºC as tail-gas is send to be compressed in the high-efficiency turbo booster 2 centrifugal compressor (LG-COM-1) and after-fed as fuel-gas in the high-performance sequential combustion full-flow advanced EvGT (GT blocks).

The liquid bottom product containing degassed crude mixed alcohols at 4.1 bar and about 118.9ºC from the 20º theoretically liquid stage (bottom column stage) in the crude mixed alcohols forerun degassing first tray-column (PU-COL-1) is splitted in the crude mixed alcohols sump splitter (PU-SPL-1) of the distillation first-column reboiler (PU-REB-1).

The reboiler circulation baffle model was developed using HeatX exchanger block to generate liquid and vapor products in the cold side and FSplit splitters block (PU-SPL-1) to drained part of the liquid bottom product (without heat). 90.0%$_{w/w}$ of the liquid phase in the crude mixed alcohols sump splitter (PU-SPL-1) is feed in the reboiler feed section and 10.0%$_{w/w}$ of the liquid phase in the crude mixed alcohols sump splitter (PU-SPL-1) is drained as overflow bottom liquid degassed crude product.

In the distillation first-column reboiler (PU-REB-1) section the bottom product from the sump is heated and vaporized considering 35.0%$_{w/w}$ of the liquid phase vaporized at 4.1 bar and 119.5ºC flowing upward back trough the tray-column (PU-COL-1).

Another 65.0%$_{w/w}$ overflowing the baffle as heated bottom liquid degassed crude product. The amount of bottom product vaporized in the distillation first-column reboiler (PU-REB-1) is determined according the gaseous content in the bottom liquid degassed crude product and the entrained liquid phase (alcohols) formed in the first-column liquid reflux-drum (PU-FLA-1).

The thermal energy required to heat and vaporize the bottom liquid product in the distillation first-column reboiler (PU-REB-1) is supplied by the low-pressure process steam at 2.5 bar and 130.0ºC generated in the Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC2) by the low-temperature water cooler (ET-3) of the mixed alcohols catalyst-synthesis (ET blocks) or in the Biomass-to-Mixed alcohols (SC3) part in the direct-contact multi-nozzles axial spray-type water injection desuperheater (DE-MIX-2) and another part in the low-temperature water cooler (ET-3).

The mass flow rate of low-pressure process steam at 2.5 bar and 130.0ºC required is determined by thermal requirements and exchanger temperature limits (cross-over avoided) in the cycle-system and controlled by design specification DS-PU-FL-1 varying the mass flow rate of water/steam circulating through the reboiler exchanger cycle (heat and cool down cycle) in closed-cycle mode.

The design specification DS-PU-FL-1 is coupled with design specification DS-PU-FL-2 determining the amount of low-pressure steam at 2.5 bar and 130.0ºC is required by the mixed alcohols purification system considering the condensate after the user equipments sent to second deaerator unit (PU-DEA-1) at about 2.3 bar.

For Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC2) these design specifications are coupled with design specification DS-ET-TG-2 and design specification DS-ET-FL-3 or for Biomass-to-Mixed alcohols (SC3) with design specification DS-ET-TG-3 and DS-ET-FL-3. The design specifications determine and adjust the necessary amounts of low-pressure steam at 2.5 bar and 130.0ºC is generated in the mixed alcohols catalyst-synthesis and extracted from the steam turbine applied in combined-cycles.

Bottom liquid degassed crude product from the crude mixed alcohols mixer (PU-MIX-2) is pumped by the crude mixed alcohols pump (PU-PUM-2) at 4.6 bar and of about 119.4ºC to the intermediate-pressure heater (PU-HEA-1) in the Zeolite-based MSDU for mixed alcohols.

The Zeolite-based MSDU for mixed alcohols is detailed in the section 8.1.20 (Zeolite-based molecular sieve dehydration unit for mixed alcohols).

As shown in Figure 93; Aspen Plus®v8.4 flowsheet of the mixed alcohols low-pressure distillation second tray-column and the low-pressure methanol distillation third tray-column for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) is compost by: mixed alcohols low-pressure distillation second tray-column (DS-COL-1); low-pressure methanol distillation third tray-column (DS-COL-2); second-column reflux pump 2 (DS-PUM-1); third-column reflux pump 3 (DS-PUM-3); second-column partial condenser (DS-CON-1 and CT-HEA-5); second-column sub-cooler (DS-CON-2 and CT-HEA-6); third-column partial condenser (DS-CON-3 and CT-HEA-7); second-column liquid reflux drum (DS-FLA-1); third-column liquid reflux-drum (DS-FLA-2); tail-gas mixer (PU-MIX-1); distillation second-column reboiler (DS-REB-1); distillation third-column reboiler (DS-REB-2); gaseous methanol splitter (DS-SPL-2); gaseous methanol mixer (DS-MIX-2); higher-molecular alcohols sump splitter (DS-SPL-1); higher-molecular alcohols mixer (DS-MIX-1); ethanol sump splitter (DS-SPL-3); ethanol mixer (DS-MIX-3); higher-molecular alcohols pump (DS-PUM-2); ethanol pump (DS-PUM-4); higher-molecular alcohols sub-cooler exchanger (DS-HEA-1); ethanol sub-cooler exchanger (DS-HEA-2); higher-molecular alcohols storage tank (DS-STO-1); anhydrous ethanol storage tank (DS-STO-2); make-up water pump (DS-PUM-5); water splitter (DS-SPL-4); hot water splitter (DS-SPL-5); hot water mixer (DS-MIX-4); and steam mixer (DS-MIX-5).

Dry gaseous mixed alcohols cooled at saturation conditions by the low-pressure cooler (DH-HEA-2) is fed in the mixed alcohols low-pressure distillation second tray-column (DS-COL-1) passing by the adiabatic expansion valve 1 (DH-VAL-1) to adjust the pressure level to 2.737 bar (stage pressure) at 118.3ºC (saturation liquid temperature). The conditioned gaseous mixed alcohols are fed in the 25º theoretically on-stage of the mixed alcohols low-pressure distillation second tray-column (DS-COL-1).

In the mixed alcohols low-pressure distillation second tray-column (DS-COL-1) is separates mainly methanol and ethanol in the top (gaseous product) of the second tray-column from the mixed higher-molecular alcohols (propanol, butanol, and pentanol) in the bottom of the second tray-column (liquid product). The fraction of pentanol is the representative fraction of the alcohols containing more than four carbon atoms in its molecular structure, propanol and butanol can be recovered and purified by adding two more tray-columns in the scenarios.

Simplified Aspen Plus®v8.4 process model simulation of the mixed alcohols low-pressure distillation second tray-column (DS-COL-1) was developed using RadFrac columns block on standard convergence mode without in-bed condenser and reboiler. The model was optimized for estimated 60 theoretical stages considering equilibrium calculation type and default Aspen Plus®v8.4 parameters and methods.

The gaseous top-product at about 2.6 bar and 103.6ºC from the 1º theoretically vapor stage (top column stage) in the mixed alcohols low-pressure distillation second tray-column (DS-COL-1) is cooled in the second-column partial condenser (DS-CON-1) by cooling water (PU-HEA-5) modeled by using Heater exchanger blocks form-condensing 39.0%$_{w/w}$ of the gaseous top-product (condensate phase) in saturation equilibrium conditions.

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-7) to the second-column partial condenser (DS-CON-1) and to second-column sub-cooler (CT-HEA-6). The amount of cooling water required is determined and controlled by design specification DS-DS-TL-1 varying the mass flow rate of cooling water passing through the first-column partial condenser (PU-CON-1) and by design specification DS-DS-TL-2 varying the mass flow rate of cooling water passing through the second-column sub-cooler (DS-CON-2). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

The condensate phase formed at 2.5 bar and 102.2ºC is flash-separated from the gaseous phase in the second-column liquid reflux drum (DS-FLA-1) modeled by using Flash2 separator block and then sub-cooled to 2.4 bar and 50.0ºC in the second-column sub-cooler (DS-CON-2) by cooling water (CT-HEA-6) modeled by using Heater exchanger blocks. The condensate fraction sub-cooled is pumped at 2.6 bar and of about 50.0ºC by the second-column reflux pump 2 (DS-PUM-1) and refluxed back to the mixed alcohols low-pressure distillation second tray-column (DS-COL-1) in the 1º theoretically liquid stage (top column stage).

61.0%$_{w/w}$ of gaseous top-product (non-condensed) containing mainly ethanol and methanol leaving the second-column liquid reflux drum (DS-FLA-1) at 2.5 bar and 102.2ºC (saturation condition) is directly fed in the 28º theoretically vapor-stage of the low-pressure methanol distillation third tray-column (DS-COL-2).

Liquid bottom product containing mainly mixed higher-molecular alcohols at about 2.9 bar and 129.6ºC, from the 60º theoretically liquid stage (bottom column stage) in the mixed alcohols low-pressure distillation second tray-column (DS-COL-1), is splitted purging 0.1%$_{w/w}$ of the bottom liquid product in the higher-molecular alcohols sump splitter (DS-SPL-1) of the distillation second-column reboiler (DS-REB-1).

The reboiler circulation baffle model was developed using HeatX exchanger block (DS-REB-1) and FSplit splitters block (DS-SPL-1) to represent the distillation second-column reboiler configured for circulation without baffle. The bottom liquid product is heated being 94.3%$_{w/w}$ vaporized at 2.9 bar and about 130.4ºC flowing upward back trough the tray-column (DS-COL-1). Bottom liquid product from the higher-molecular alcohols mixer (DS-MIX-1) contain mixed higher-molecular alcohols (propanol, butanol, and pentanol) and a small fraction or just traces of impurities (e.g.: H_2O, methanol, ethanol, and dissolved gases).

The thermal energy required to heat and vaporize the bottom liquid product in the distillation second-column reboiler (DS-REB-1) is supplied by the process steam at 6.0 bar and 160.0ºC generated in the direct-contact multi-nozzles axial spray-type water injection desuperheater (DE-MIX-1) and in the synthesis-products water cooler (ET-1) in the mixed alcohols catalyst-synthesis (ET blocks).

The required mass flow rate of process steam at 6.0 bar and 160.0ºC is determined by thermal requirements and exchanger temperature limits (cross-over avoided) in the cycle-system and controlled by design specification DS-DS-FL-1 varying the mass flow rate of water/steam circulating through the reboiler exchanger cycle (heat and cool down cycle) in closed-cycle mode. The condensate after the user equipments is sent to second deaerator unit (PU-DEA-1) at about 5.7 bar and 140.0ºC to be used as degassing agent.

Design specification DS-DS-FL-1 is coupled with design specification DS-PU-TG-1 determining the required amount of steam at 6.0 bar and 160.0ºC for the mixed alcohols purification system considering the condensate after the user equipments sent to second deaerator unit (PU-DEA-1) at about 5.7 bar and 140.0ºC (used as degassing agent). For Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC2) these design specifications are coupled with design specification DS-ET-TG-1, design specification DS-ET-FL-2 and design specification DS-PU-FL-3, or for Biomass-to-Mixed alcohols (SC3) with design specification DS-ET-TG-2, design specification DS-PU-FL-3, design specification DS-ST-FL-3 and design specification DS-ET-FL-2. The design specifications determine and adjust the necessary amounts of process steam at 6.0 bar and 160.0ºC are generated by the mixed alcohols catalyst-synthesis and extracted from the steam turbine applied in combined-cycles.

The mixed higher-molecular alcohols line is sub-cooled from 2.9 bar and 130.4ºC to 2.5 bar and 35.0ºC using make-up water (WATER FROM TREATMENT PLANT) at atmospheric pressure and 25.0ºC by the higher-molecular alcohols sub-cooler exchanger (DS-HEA-1). The sub-cooled mixed higher-molecular alcohols are then pumped by the higher-molecular alcohols pump (DS-PUM-2) to the higher-molecular alcohols storage tank (DS-STO-1) as final product, available as liquid higher-molecular mixed alcohols at ambient conditions (MIXED HIGH MOLECULAR ALCOHOLS).

The mass flow rate of make-up water (WATER FROM TREATMENT PLANT) from the treatment plant required to cool-down the mixed higher-molecular alcohols is determined by thermal requirements and exchanger temperature limits (cross-over avoided) in the cycle-system and controlled by design specification DS-DS-FL-3 varying the mass flow rate of water pumped by the make-up water pump (DS-PUM-5) through the higher-molecular alcohols sub-cooler exchanger (DS-HEA-1). The hot water after-obtained is sent to second deaerator unit (PU-DEA-1) at about 2.3 bar and 110.0ºC supplying part of the make-up water requirements.

In the low-pressure methanol distillation third tray-column (DS-COL-2) are separates methanol in the top (gaseous product) of the low-pressure methanol distillation third tray-column (DS-COL-2) from ethanol in bottom (liquid product) of the low-pressure methanol distillation third tray-column (DS-COL-2).

Simplified Aspen Plus®v8.4 process model simulation of the low-pressure methanol distillation third tray-column (DS-COL-2) was developed using RadFrac columns block on standard convergence mode without in-bed condenser and reboiler. The model was optimized for estimated 70 theoretical stages considering equilibrium calculation type and default Aspen Plus®v8.4 parameters and methods.

The gaseous top-product at about 2.38 bar and 87.8ºC from the 1º theoretically vapor stage (top column stage) in the low-pressure methanol distillation third tray-column (DS-COL-2) is cooled in the third-column partial condenser (DS-CON-3) by cooling water (PU-HEA-7) modeled by using a Heater exchanger blocks form-condensing 97.52%$_{w/w}$ of the gaseous top-product (condensate phase). 2.0%$_{w/w}$ of the gaseous top-product bypass the third-column partial condenser (DS-CON-3) and is mixed in the gaseous methanol mixer (DS-MIX-2) with 5.0%$_{w/w}$ of the gaseous top-product non-condensed in the third-column partial condenser (DS-CON-3) and separated as vapor phase in the third-column liquid reflux-drum (DS-FLA-2).

Cooling water from the multi-cells water-cooling tower (CT blocks) at 27.0ºC is pumped (CT-PUM-7) to the third-column partial condenser (CT-HEA-7). The amount of cooling water required is determined and controlled by design specification DS-DS-TL-3 varying the mass flow rate of cooling water passing through the third-column partial condenser (CT-HEA-7). The cooling water is heated at the limit of 43.0ºC and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

The condensate phase formed at 2.3 bar and 86.8ºC is flash-separated from the gaseous phase in the third-column liquid reflux-drum (DS-FLA-2) modeled by using a Flash2 separator block. The condensate top product is pumped at 2.38 bar and about 86.8ºC by the third-column reflux pump 3 (DS-PUM-3) and refluxed back to the 1º theoretically liquid stage in the low-pressure methanol distillation third tray-column (DS-COL-2).

About 2.48%$_{w/w}$ of gaseous top-product (non-condensed) containing mainly methanol with less than 0.1%$_{w/w}$ of water leaving from the second-column liquid reflux drum (DS-FLA-1) at 2.5 bar and 102.2ºC (saturation condition) is sent to the Zeolite-based MSDU for mixed alcohols to be used as flushing agent in the regeneration cycle-time to remove the persistent water and another gases from the Zeolite bed material in the third vessel in methanol back-flushing regeneration cycle (DH-FLU-1).

The liquid bottom product containing mainly ethanol at about 2.58 bar and 104.1ºC from the 70º theoretically liquid stage (bottom column stage) in the low-pressure methanol distillation third tray-column (DS-COL-2) is splitted purging 0.1%$_{w/w}$ of the bottom liquid product in the ethanol sump splitter (DS-SPL-3) of the distillation third-column reboiler (DS-REB-2).

The reboiler circulation baffle model was developed using HeatX exchanger block (DS-REB-2) and FSplit splitter block (DS-SPL-3) to represent the distillation third-column reboiler configured for circulation without baffle. The bottom liquid product is heated being 71.25%$_{w/w}$ vaporized at 2.58 bar and at about 104.1ºC flowing upward back trough the tray-column (DS-COL-2). The bottom liquid product from the ethanol mixer (DS-MIX-3) contain anhydrous ethanol and a small fraction or just traces of impurities (e.g.: H_2O, methanol, ethanol, and dissolved gases).

The thermal energy required to heat and vaporize the bottom liquid product in the distillation third-column reboiler (DS-REB-2) is supplied by the low-pressure process steam at 2.5 bar and 130.0ºC. The low-pressure process steam in the Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC2) is generated in the low-temperature water cooler (ET-3) of the mixed alcohols catalyst-synthesis (ET blocks). The low-pressure process steam in the Biomass-to-Mixed alcohols (SC3) is part generated in the direct-contact multi-nozzles axial spray-type water injection desuperheater (DE-MIX-2) and another part generated in the low-temperature water cooler (ET-3).

The mass flow rate of low-pressure process steam at 2.5 bar and 130.0ºC required is determined by thermal requirements and exchanger temperature limits (cross-over avoided) in the cycle-system and controlled by design specification DS-DS-FL-2 varying the mass flow rate of water/steam circulating through the reboiler exchanger cycle (heat and cool down cycle) in closed-cycle mode. The condensate after the user equipments is sent to second deaerator unit (PU-DEA-1) at about 2.3 bar and 110.0ºC closing the loop-cycle.

The anhydrous ethanol line is sub-cooled from 2.58 bar and 104.1ºC to 2.3 bar and 35.0ºC using make-up water (WATER FROM TREATMENT PLANT) at atmospheric pressure and 25.0ºC by the ethanol sub-cooler exchanger (DS-HEA-2). The sub-cooled anhydrous ethanol is then pumped by the ethanol pump (DS-PUM-4) to the anhydrous ethanol storage tank (DS-STO-2) as final product, available as liquid anhydrous ethanol at ambient conditions (ANHYDROUS ETHANOL).

The mass flow rate of make-up water (WATER FROM TREATMENT PLANT) at ambient conditions from the treatment plant required to cool-down the anhydrous ethanol is determined by thermal requirements and exchanger temperature limits (cross-over avoided) in the cycle-system and controlled by design specification DS-DS-FL-4 varying the mass flow rate of water pumped by the make-up water pump (DS-PUM-5) through the ethanol sub-cooler exchanger (DS-HEA-2). The hot water after-obtained is sent to second deaerator unit (PU-DEA-1) at about 2.3 bar and 100.0ºC supplying part of the make-up water requirements.

8.1.20 Zeolite-based molecular sieve dehydration unit for mixed alcohols

In the Biomass-to-Mixed alcohols scenarios of this research Master's degree is employed the vapor-phase molecular sieve dehydration unit (MSDU) energy savings based on a physical binding of gas molecules. This unit is employed in place of the traditional dehydration of alcohols by extractive distillation (extractive and rectification columns) using ethylene glycol or others chemicals as extractive agent (solvent).

The Aspen Plus®v8.4 process model simulation of Zeolite-based MSDU considering a typical continuous dehydration operation under the steady state operating conditions to represent the complete adsorption, desorption and regenerating cycles has been modeled using NRTL-RK physical property methods.

Figure 94 shows the Aspen Plus®v8.4 flowsheet of the Zeolite-based molecular sieve dehydration unit for mixed alcohols for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3).

Degassed liquid Crude mixed alcohols at 4.1 bar and about 119.4ºC from the crude mixed alcohols mixer (PU-MIX-2) in the crude mixed alcohols forerun degassing first tray-column (PU-COL-1) is pumped by the crude mixed alcohols pump (PU-PUM-2) to the intermediate-pressure heater (PU-HEA-1) modeled by using a HeatX exchanger block used to vaporize and superheater the crude mixed alcohols from about 119.4ºC to about 145.0ºC.

The thermal energy required to vaporize the degassed liquid Crude mixed alcohols is supplied by the process steam at 6.0 bar and 160.0ºC generated in the direct-contact multi-nozzles axial spray-type water injection desuperheater (DE-MIX-1) and in the synthesis-products water cooler (ET-1) in the mixed alcohols catalyst-synthesis (ET blocks).

The mass flow rate of process steam at 6.0 bar and about 160.0ºC required is controlled by design specification DS-PU-TG-1 varying the steam mass flow rate inlet in the intermediate-pressure heater (PU-HEA-1) to obtain vaporized crude mixed alcohols at 145.0ºC.

The design specification DS-PU-TG-1 is coupled with design specification DS-DS-FL-1 determining the amount of steam at 6.0 bar and 160.0ºC is required by the mixed alcohols purification system considering the condensate after the user equipments sent to second deaerator unit (PU-DEA-1) at about 5.7 bar and 140.0ºC (used as degassing agent).

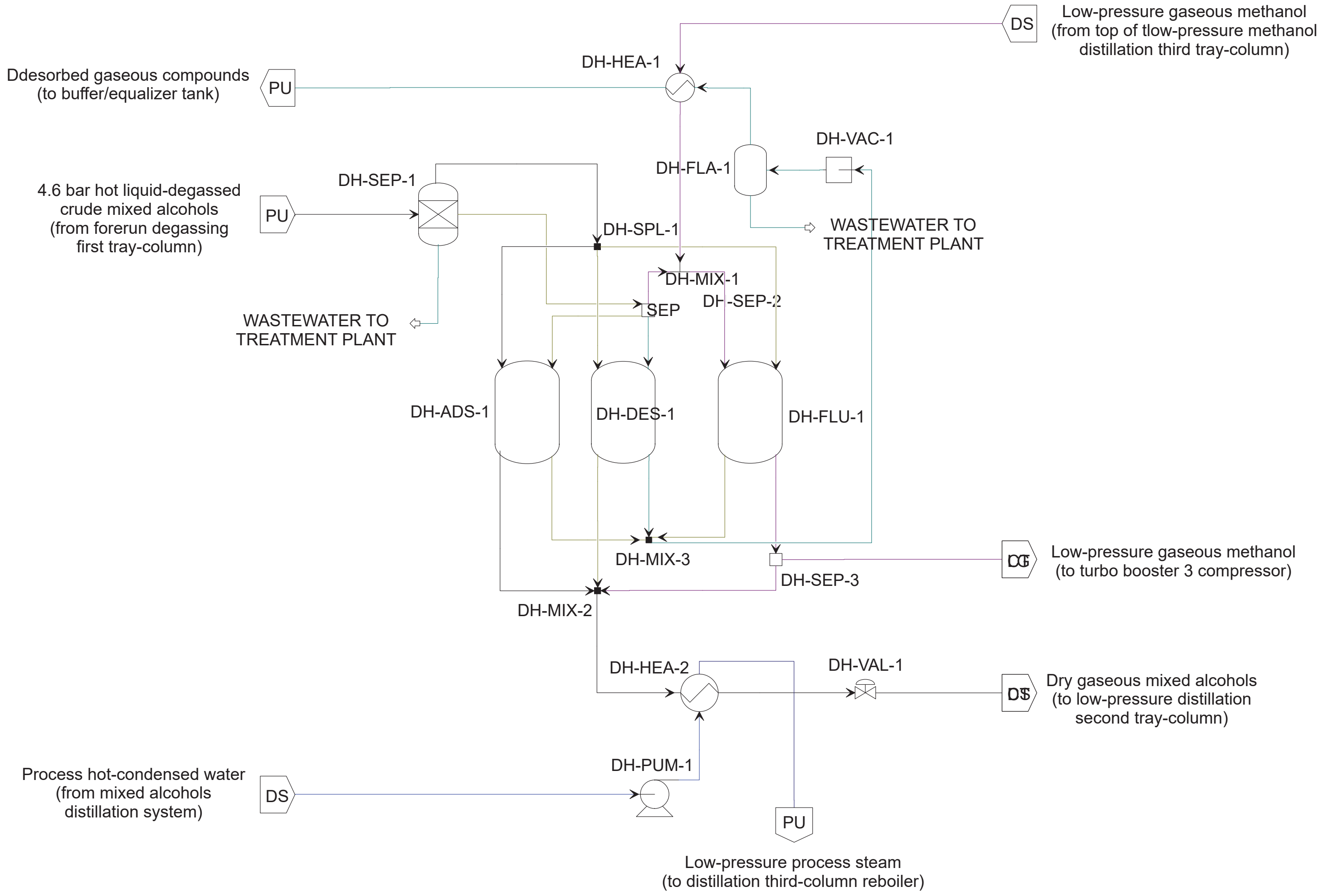


Figure 94 - Aspen Plus® v8.4 flowsheet of the Zeolite-based molecular sieve dehydration unit for mixed alcohols for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3)

As shown in Figure 94, Aspen Plus®v8.4 flowsheet of the of the Zeolite-based MSDU for mixed alcohols under the steady state operating conditions for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) is compost by: intermediate-pressure heater (PU-HEA-1); buffer tank (DH-SEP-1); first vessel in low-pressure adsorption cycle (DH-ADS-1); second vessel in vacuum desorption cycle (DH-DES-1); third vessel in methanol back-flushing regeneration cycle (DH-FLU-1); vacuum pump (DH-VAC-1); buffer/equalizer tank (DH-FLA-1); cross heater/cooler exchanger (DH-HEA-1); inlet multi-way valve skids (DH-SPL-1 and DH-MIX-1); outlet multi-way valve skids (DH-MIX-2 and DH-MIX-3); water pump (DH-PUM-1); low-pressure cooler (DH-HEA-2); adiabatic expansion valve 1 (DH-VAL-1); and adjustment blocks representing internal bed material conditions (DH-SEP-2 and DH-SEP-3).

In the Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC2) these design specifications are coupled with design specification DS-ET-TG-1, design specification DS-ET-FL-2 and design specification DS-PU-FL-3 or in the Biomass-to-Mixed alcohols (SC3) with design specification DS-ET-TG-2, design specification DS-PU-FL-3, design specification DS-ST-FL-3 and design specification DS-ET-FL-2. The design specifications determine and adjust the necessary amounts of process steam at 6.0 bar and 160.0ºC are generated in the mixed alcohols catalyst-synthesis and extracted from the steam turbine applied in combined-cycles.

Aspen Plus®v8.4 process model simulation considers a time-frame of the Zeolite-based MSDU with the vessels operating in different time-cycles. The first vessel operate in low-pressure adsorption cycle (DH-ADS-1) adsorber the moisture out of the wet crude mixed alcohols vapor applying low-pressure swing adsorption/desorption (PSA) principles. The second vessel operate in vacuum desorption cycle (DH-DES-1) regenerate the Zeolite molecular sieve packed-bed applying vacuum swing adsorption/desorption (VSA) principles. The third vessel operate in methanol back-flushing regeneration cycle (DH-FLU-1) regenerate the Zeolite bed material applying thermal swing adsorption/desorption (TSA) principles.

Vaporized and superheated wet crude mixed alcohols in supply line after the intermediate-pressure heater (PU-HEA-1) is fed at about 4.4 bar and 145.0ºC in the buffer tank (DH-SEP-1). The control valve arrangement is designated to head the wet crude mixed alcohols to the vessel in low-pressure adsorption cycle (DH-ADS-1).

Aspen Plus®v8.4 process simulation simplified model of the first vessel in low-pressure adsorption cycle (DH-ADS-1) was developed using Flash2 separator blocks to represent the operation in low-pressure PSA cycle-time. The low-pressure adsorption cycle (DH-ADS-1) has the capacity to adsorbs water (H_2O) reducing the water molar fraction to $1.0\%_{mol}$ (target). The model consider the additional adsorption in less extension of $5.0\%_{w/w}$ of the carbon dioxide (CO_2), $2.0\%_{w/w}$ of the methane (CH_4), $2.0\%_{w/w}$ of the methanol (CH_3OH), $1.0\%_{w/w}$ of the ethanol (C_2H_5OH), $0.5\%_{w/w}$ of the propanol (C_3H_7OH) and $0.5\%_{w/w}$ of the butanol (C_4H_9OH).

The quantity of water removed by the Zeolite-based MSDU for mixed alcohols is controlled by design specification DS-DH-FM-1 varying the mass flow rate of water content in the main stream (wet crude mixed alcohols) passing the first vessel to after-obtain the water molar fraction of 1.0%$_{mol}$.

Superheated wet crude mixed alcohols pass through the Zeolite molecular sieve packed-bed (upwardly or downwardly) to after-obtain superheated dry mixed alcohols at about of 3.5 bar and 144.2ºC (adiabatic flash). The superheated dry mixed alcohols exit from the first vessel in low-pressure adsorption cycle (DH-ADS-1) by mixed alcohols vapor output line. The control valve arrangement is designated to head the superheated dry mixed alcohols to the low-pressure cooler (DH-HEA-2) to be cooled at vapor saturation condition.

Dry mixed alcohols at about of 3.5 bar and 144.2ºC is cooled to about 3.2 bar and 119.0ºC (vapor saturation condition) by the low-pressure cooler (DH-HEA-2), recovering the heat using process hot-condensed water at 110.0ºC to produce process steam at 2.5 bar and 130.0ºC. The amount of process hot water required to cool-down the dry gaseous mixed alcohols is controlled by design specification DS-DH-TG-1 varying the mass flow rate of the process hot-condensed water pumped by the water pump (DH-PUM-1) passing through the exchanger (DH-HEA-2) to obtain low-pressure process steam.

The dry gaseous mixed alcohols is fed in the mixed alcohols low-pressure distillation second tray-column (DS-COL-1) to separate the alcohols according to section 8.1.19 (Three-column double-effect alcohols distillation system (ethanol purification)).

The first stage of the regeneration cycle occurs in the second vessel in vacuum desorption cycle (DH-DES-1) using a vacuum pump (DH-VAC-1) modeled by using a Compr pressure changer block according to rigorous ASME method for polytropic compressor considering 80.0% polytropic efficiency (polytropic compression). The vacuum pump (DH-VAC-1) reduces the pressure in the vessel from about 3.5 bar and 145.0ºC to about 0.4 bar and 74.0ºC draining and forcing the desorption of the adsorbed and adhered molecules in the 3A Zeolite molecular sieve.

Aspen Plus®v8.4 process simulation simplified model of the second vessel in vacuum desorption cycle (DH-DES-1) was developed using Flash2 separator blocks to represent the operation in vacuum-pressure VSA cycle-time. The vacuum desorption cycle (DH-DES-1) has the capacity to desorbs from the Zeolite bed material (adsorbed fraction) 99.0%$_{w/w}$ of the water (H_2O), 100.0%$_{w/w}$ of the carbon dioxide (CO_2), 100.0%$_{w/w}$ of the methane (CH_4), 95.0%$_{w/w}$ of the methanol (CH_3OH), 99.0%$_{w/w}$ of the ethanol (C_2H_5OH), 99.0%$_{w/w}$ of the propanol (C_3H_7OH), 99.5%$_{w/w}$ of the butanol (C_4H_9OH) and 99.9%$_{w/w}$ of the pentanol ($C_5H_{10}OH$).

The desorbed water and others gaseous compounds are removed through the vacuum pump (DH-VAC-1) and fed into the buffer/equalizer tank (DH-FLA-1) and then after-cooled in the cross heater/cooler exchanger (DH-HEA-1). If there condensed phase formed it is removed and sent to wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse.

The desorbed gaseous compounds are mixed with the tail-gas at about of 3.6 bar obtained from the crude mixed alcohols forerun degassing first tray-column (PU-COL-1) and sent along to this to be compressed to 23.5 bar by the high-efficiency turbo booster 2 centrifugal compressor (LG-COM-1) according to section 8.1.18 (Energy-saving integrated turbo compressor & expander (turbo booster)). The compressed tail-gas is sent-back (recycled) as fuel-gas to the high-performance sequential combustion full-flow advanced EvGT (GT blocks).

After the vacuum desorption cycle (DH-DES-1) the vessel is pressurized (atmospheric level) using the hot-methanol flushing agent being initiated the thermal swing desorption cycle-time (second stage of the regeneration).

The second stage of the regeneration cycle (reactivated) occurs in the third vessel in methanol back-flushing regeneration cycle (DH-FLU-1) passing hot-methanol through the Zeolite molecular sieve packed-bed in counter-flow on the first vessel flow-direction (upwardly or downwardly). Hot-methanol is used to restore the water adsorbing capacity force-desorbing the maximum amount of water.

Methanol containing not more than 0.1%$_{w/w}$ (model result) of water obtained as top gaseous product from the low-pressure methanol distillation third tray-column (DS-COL-2) is brought into contact with the 3A Zeolite molecular sieve packed-bed.

Aspen Plus$^{®}$v8.4 process simulation simplified model of the third vessel in methanol back-flushing regeneration cycle (DH-FLU-1) was developed using Flash2 separator block to represent the operation in low-pressure TSA cycle-time. The methanol back-flushing regeneration cycle (DH-FLU-1) has the capacity to desorber the maximum amount of the reminiscent Adsorbed compounds in the Zeolite molecular sieve packed-bed (adsorbed fraction). The model considers the desorption of 99.0%$_{w/w}$ of the water (H_2O), 99.0%$_{w/w}$ of the methanol (CH_3OH), 99.9%$_{w/w}$ of the ethanol (C_2H_5OH), 99.9%$_{w/w}$ of the propanol (C_3H_7OH), 100.0%$_{w/w}$ of the butanol (C_4H_9OH) and 100.0%$_{w/w}$ of the pentanol ($C_5H_{10}OH$).

The gaseous methanol at 2.3 bar and 87.5ºC is heated to 2.2 bar and 180.0ºC in the cross heater/cooler exchanger (DH-HEA-1). Hot gaseous methanol is continues fed by the inlet multi-way valve skids (DH-SPL-1 and DH-MIX-1) into the vessel in methanol back-flushing regeneration cycle (DH-FLU-1).

The persistent water and another gases is desorbed from the Zeolite bed material during the methanol back-flushing regeneration cycle (DH-FLU-1) and then exits either by flushing vapor output line. Outlet multi-way valve skids (DH-MIX-2 and DH-MIX-3) as control valve arrangement is designated to head the gaseous methanol to be compressed by the high-efficiency turbo booster 3 centrifugal compressor (DH-COM-1) in the energy-saving integrated turbo compressor & expander (turbo booster).

After the thermal regeneration cycle (DH-FLU-1) using hot gaseous methanol the methanol remaining in the vessel is drained therefore. The third vessel in methanol back-flushing regeneration cycle (DH-FLU-1) is pressurized at 4.2 bar and 145.0ºC (adsorption operational) using the superheated wet crude mixed alcohols closing the cycle-time being again ready to be used as first vessel in low-pressure adsorption cycle (DH-ADS-1).

Gaseous methanol content the desorbed gaseous compounds at about of 1.8 bar and 145.0ºC from the methanol back-flushing regeneration cycle (DH-FLU-1) is compressed to 87.0 bar and 480.2ºC (without aftercooler) by the high-efficiency turbo booster 3 centrifugal compressor (DH-COM-1) according to section 8.1.18 (Energy-saving integrated turbo compressor & expander (turbo booster)). The compressed gaseous methanol is sent-back (recycled) to the mixed alcohols catalyst-synthesis process (ET blocks) raising the production of ethanol (by homologation).

The regeneration efficiency is a function of the mass flow rate, temperature, pressure, time in regeneration cycle and compositions of the methanol used as flushing agent and cannot be accurately estimated.

The molecular sieve packed-bed is compound by crystalline Zeolite having a basic empirical formula $M_{2/n}O.Al_2O_3.xSiO_2.yH_2O$ where M is the exchangeable cation, n is its valence, x is equal or greater than 2 and y is the hydrations number.

In the Aspen Plus®v8.4 process simulation and spreadsheet calculation models is considered the adsorbent bed material compost only by a commercial type 3A Zeolite molecular sieve (not specified) with effective microporous opening about 3.0 angstroms (0.3 nm) selective for water (H_2O) and for others lower-diameter molecules (e.g.: H_2, CO, CO_2 and CH_4), molecules larger than 3.0 angstroms will not be able to be adsorbed.

Spreadsheet calculation model consider the commercial type 3A Zeolite molecular sieve weight loaded in the three vessels according to the saturation ratio limits of $20.0\%_{w/w}$ to adsorbing H_2O and carbonaceous compounds per adsorption/desorption cycles. Zeolite's molecular sieve lifetime is expected to be about 2 year before the necessity of partial or full discharged and new material be loaded (conservative estimate), molecular sieve material with lower-capacity of water adsorption is send to be regenerated and/or to final disposal.

8.1.21 High-performance sequential combustion full-flow evaporative-class gas turbine (EvGT) operating in combined-cycle mode

The Aspen Plus®v8.4 process model simulation of topping Brayton-cycle by the high-performance sequential combustion full-flow advanced EvGT is based on the

ALSTOM advanced-class GT24 gas turbine and GE H-class 7HA gas turbines parameters. The model employed assumes that there are not significant design changes when using the conditioned synthesis gas obtained from gasification of sugarcane bagasse and straw by atmospheric CFB directly-heated gasifier.

EvGT or HAT cycle with injection of water by a humidification tower was developed using RKS-BM physical property methods (i.e. density, humidity, enthalpy and entropy) for the air–water mixtures side and for the synthesis gas side, and using IAPWS-95 physical property methods for the cooling water side (exchangers).

As shown in Figure 54, Aspen Plus®v8.4 flowsheet of the high-performance sequential combustion full-flow advanced EvGT for BIG-GT/CC (SC1), BIG-GT/CC (SC2), BIG-GT/CC (SC3), BIG-GT/CC (SC4) and BIG-GT/CC (SC5) which is the same model with modified parameters for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) is compost by: low-pressure compressor (GT-COM-1); high-pressure compressor (GT-COM-2); 4-stage low-pressure turbine (GT-LPT-1); high-pressure turbine (GT-HPT-1); three-circuit water inter-cooler exchanger (GT-1); low-pressure bleed air (GT-SPL-2); high-pressure bleed air (GT-SPL-3); EnVironmental (EV) burner (GT-BUR-1); sequential EnVironmental (SEV) burner (GT-BUR-2); first annular combustion chamber (GT-BUR-1); second annular combustion chamber (GT-BUR-2); first-stage fuel nozzle (GT-BUR-1); second-stage fuel nozzle (GT-BUR-2); high-pressure counter-current double-stage humidification packaged-tower (GT-SAT-1); recuperator heat cross-exchanger (GT-2); vortex generators (not included as block); direct drive permanent magnet motor (not included as block); make-up water pump (GT-PUM-1); water mixer (GT-MIX-2); water splitter (GT-SPL-4); gases mixer (GT-MIX-1); buffer/equalizer inlet tank (GT-BUF-1); inlet air pre-filter and fine-filter self-cleaned unit (GT-FIL-1); water inter-cooler exchanger (GT-1); heat recovery after-cooling (GT-HEA-1); high-pressure condensate basin tank (GT-SAT-1); high-pressure recirculation pump (GT-PUM-2); and condenser knock-out drum (GT-FLA-1).

Surrounding atmospheric air (ATMOSPHERIC AIR) at ambient conditions of 1.01325 bar and 25.0ºC are induced to an air duct and then to the pre-filter and fine-filter self-cleaned unit (GT-FIL-1) modeled by using a Fabric filter solids separator block to remove/reduce contaminants and particulate matter (considered 100.0% of efficiency) avoiding damages by debris (erosion) in the gas turbine internal parts (e.g.: blades, chambers, nozzles, ducts).

Filtered air enter the low-pressure compressor (GT-COM-1) modeled by using a Compr pressure changer block according to rigorous ASME method for polytropic compressor considering 91.0% polytropic efficiency (polytropic compression) to first-section of compression leaving the low-pressure compressor (GT-COM-1) at 4.8 bar and about 215.0ºC. A fraction of this pressurized hot-air is bleed as low-pressure bleed air (GT-SPL-2) for cooling the second-stage fuel nozzle (GT-LPT-1) and blades in the 4-stage low-pressure turbine (GT-LPT-1).

Pressurized hot-air flowing through the third circuit (hot side) of the three-circuit water inter-cooler exchanger (GT-1) in counter-current flow direction being sub-cooled to about 4.8 bar and 27.0ºC (optimized according to SEV-burner combustion chamber requirements) generating a condensed phase content water and dissolved gases. The condensed phase formed is removed in the condenser knock-out drum (GT-FLA-1) modeled by using a Flash2 separator block and is after-pumped to the wastewater treatment plant (WASTEWATER TO TREATMENT PLANT) for recycle and reuse as make-up water (WATER FROM TREATMENT PLANT).

Fresh-water at ambient conditions from treatment plant (WATER FROM TREATMENT PLANT) is pumped to 24.0 bar and about 25.0ºC by make-up water pump (GT-PUM-1) passing-trough the first-circuit of the three-circuit water inter-cooler exchanger (GT-1) modeled by using a MHeatX exchanger block considering a first-circuit (cold side) in counter-current flow direction to achieve sub-cooled conditions in the low-pressure air-side. The pressurized hot water is heated at 23.8 bar and about 61.0ºC, same conditions of the recirculating water.

Recirculating water at about 61.0ºC and 23.8 bar obtained from the high-pressure condensate basin tank (GT-SAT-1) in the high-pressure counter-current double-stage humidification packaged-tower (GT-SAT-1) mixed with the pressurized hot water after the first-circuit (same conditions) is pumped to 23.8 bar and about 61.0ºC by recirculating water pumped (GT-PUM-2) passing-trough the second-circuit (cold side) of the three-circuit water inter-cooler exchanger (GT-1). The pressurized hot water is heated at 23.1 bar and about 210.0ºC and then fed in the top liquid stage of the high-pressure counter-current double-stage humidification packaged-tower bottom section (GT-SAT-1).

The mass flow rate of make-up water from treatment plant (WATER FROM TREATMENT PLANT) depend on the mass flow rate of water evaporated and entrained with the humidified air leaving on top gaseous stage of the double-stage humidification packaged-tower top section (GT-SAT-1). The mass flow rate of make-up water is controlled by design specification DS-GT-FL-1 varying the inlet water mass flow rate to achieve the temperature required by the double-stage humidification packaged-tower bottom section (GT-SAT-1) and to maintenance the cooling water in closed-loop cycle.

Cooled low-pressure air enter the high-pressure compressor (GT-COM-2) modeled by using a Compr pressure changer block according to rigorous ASME method for polytropic compressor considering 91.0% polytropic efficiency (polytropic compression) to second-section of compression leaving the high-pressure compressor (GT-COM-2) at 23.6 bar and 219.0ºC. A fraction of this pressurized hot-air is bleed off as high-pressure air bleed (GT-SPL-3) for cooling the first-stage fuel nozzle (GT-HPT-1) and blades in the high-pressure turbine (GT-HPT-1).

The mass flow rate of combustion air agent is determined and controlled by the design specification DS-GT-FG-1 varying the intake-air mass flow rate strongly coupled with design DS-GT-TG-1, design specification DS-GT-PB-1, design specification DS-GT-FG-2, design specification DS-GT-FG-3, FORTRAN calculation block CA-GT-QL-1 and optimization model analysis tools OT-GT-PG-1.

Aspen Plus®v8.4 process simulation simplified model of fuel nozzle and turbine blades cooling systems was developed using FSplit splitter block to represent the high-pressure bleed air (GT-SPL-3) for advanced open loop air-cooled first-stage fuel nozzle (GT-HPT-1) and for blades effusion cooling in the high-pressure turbine (GT-HPT-1), and to represent the low-pressure bleed air (GT-SPL-2) for advanced open loop air-cooled second-stage fuel nozzle (GT-LPT-1) and for blades effusion cooling in the 4-stage low-pressure turbine (GT-LPT-1).

The coolant air mass flow rate bleed of is determined in function of the turbine inlet temperature and pressure ratio admitted in the low and high turbine sections of the high-performance sequential combustion full-flow advanced EvGT (GT blocks). In the Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC3) with inlet pressure at 23.0 bar and TIT of 1500.0ºC consider the low-pressure air bleed off as $4.0\%_{w/w}$ of the exhausted gases per expander sections, cooling air consumption of 0.04 kg of air per kg of exhaust-gas. The mass flow rate of the air bleed off is controlled by design specification DS-GT-FG-2 varying the mass flow rate destined to low-pressure bleed air (GT-SPL-2) and by design specification DS-TG-FG-3 varying the mass flow rate destined to high-pressure bleed air (GT-SPL-3). In the Biomass-to-Mixed alcohols (SC2) with inlet pressure at 23.0 bar and TIT of 1300.0ºC is considered the low-pressure air bleed off as $2.0\%_{w/w}$ of the exhausted gases per expander sections, cooling air consumption of 0.020 kg of air per kg of exhaust-gas. The mass flow rate of the air bleed off is controlled by design specification DS-GT-FG-2 varying the mass flow rate destined to low-pressure bleed air (GT-SPL-2) and by design specification DS-TG-FG-3 varying the mass flow rate destined to high-pressure bleed air (GT-SPL-3).

The coolant air (bleed air) is guided through the advanced open loop air-cooling internal circuit according to blades effusion cooling method (single-pass or multiple pass circuits) flowing-out together the exhaust-gas (high combustion oxygen content in excess).

High-pressure combustion air destined as oxidant for combustion processes is cooled to 80.0ºC at 23.6 bar by recirculating water at about 61.0ºC and 23.8 bar in the heat recovery after-cooling (GT-HEA-1) modeled by Heater exchanger block using RKS-BM physical property methods to air-water mixture side and IAPWS-95 physical property methods to water side. The cooled high-pressure combustion air is then injected in bottom of the high-pressure counter-current double-stage humidification packaged-tower (GT-SAT-1).

The water coolant heat recovery fluid (recirculating water) is heated in the heat recovery after-cooling (GT-HEA-1) to 23.1 bar and 210.0ºC and then fed in the top stage of the double-stage humidification packaged-tower top section (GT-SAT-1).

The water mass flow rate passing-through the heat recovery after-cooling (GT-HEA-1) is controlled by design specification DS-GT-FL-2 coupled whit the design specification DS-GT-FL-3 varying the amount of water splitted in the water splitter (GT-SPL-4) pumped by the high-pressure recirculation pump (GT-PUM-2) passing-trough the heat recovery after-cooling (GT-HEA-1).

Rigorous Aspen Plus®v8.4 process model simulation of the high-pressure counter-current double-stage humidification packaged-tower (GT-SAT-1) was developed using RadFrac columns block on standard convergence mode without in-bed condenser and reboiler. The model was optimized for estimated 5 theoretical stages considering NORTON INTX packing sections with dimension of 6.0 mm and standards characteristics with height and diameter optimized for each system requirements (scenarios dependence). The model use rate-based calculation for Countercurrent flow model without reactions and film resistance in vapor phase and liquid phases. Default Aspen Plus®v8.4 packing parameters is applied to predict the mass transfer coefficient and interfacial area by Onda et al. (1968) correlation, and heat transfer coefficient by Chilton–Colburn (Taylor and Krishna, 1993) method.

Humidified combustion air at 23.1 bar and 195.0ºC leaving from the 1º theoretically vapor stage (top column stage) in the double-stage humidification packaged-tower top section (GT-SAT-1) is heated by the exhaust-gas from the 4-stage low-pressure turbine (GT-LPT-1) in the recuperator heat cross-exchanger (GT-2).

In the Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC3) the exhaust-gas is cooled down to 1.01 bar and 600.0ºC. In the Biomass-to-Mixed alcohols (SC2) the exhaust-gas is cooled down to 1.01 bar and 750.0ºC. The temperature of the humidified combustion air after the recuperator heat cross-exchanger (GT-2) is determined and controlled by the energy balance (free-degree).

Intermediate-pressure light-gas (bypass) and off-gas from the light-gas condenser knock-out drum (RE-FLA-1) non-recycled after the hydrogen recovery by four-bed PSA system and tail-gas from crude mixed alcohols forerun degassing first tray-column (PU-COL-1) mixed with the desorber gases from the second vessel in vacuum desorption cycle (DH-DES-1) in the Zeolite-based MSDU are mixed in the gases mixer (GT-MIX-1). Only for the Biomass-to-Mixed alcohols (SC2) a part of the intermediate-pressure cleaned synthesis gas from the intermediate-pressure synthesis gas splitter (WS-SPL-1) is mixed in the gases mixer (GT-MIX-1) and used as complementary fuel-gas (EvGT), necessary to achieve and supply the thermal and electrical energy demand by the thermochemical-biorefinery (SC2).

The mixture of gases is feed in the buffer/equalizer inlet tank (GT-BUF-1) as available fuel-gas to be injected in the combustion chambers at about 160.0ºC to 170.0ºC (scenario conditions dependence) and 23.0 bar. Part of the conditioned synthesis gas is injected in the first annular EV-burner combustion chamber (GT-BUR-1) and another part is injected in the second annular SEV-burner combustion chamber (GT-BUR-2) according to limits in the TIT admitted by the high-performance sequential combustion full-flow advanced EvGT.

Aspen Plus®v8.4 process model simulation of the injection system coupled with the turbine inlet temperature control for the first annular EV-burner combustion chamber (GT-BUR-1) and for the second annular SEV-burner combustion chamber (GT-BUR-2) consider the optimized combustion air mass flow rate, the optimized discharge pressure (DS-GT-PB-1) of the high-pressure turbine (GT-HPT-1), the heat loss from the systems (CA-GT-QL-1) and the fraction of fuel-gas (GT-SPL-1) injected in the first (GT-BUR-1) or second (GT-BUR-2) combustion chamber.

Aspen Plus®v8.4 process model simulation of the first annular combustion chamber (GT-BUR-1) and EV-burner (GT-BUR-1) is represented together the first-stage fuel nozzle (GT-BUR-1) as simple-aggregated model by RGibbs reactors block (GT-BUR-1) to represent the oxidizing gaseous and formation reactions according to chemical equilibrium by Gibbs free-energy minimization method. In the model was considered all gaseous components expected as potential products in products sheet.

Aspen Plus®v8.4 process model simulation of the second annular combustion chamber (GT-BUR-2) and SEV-burner (GT-BUR-2) is represented together the second-stage fuel nozzle (GT-BUR-2) as simple-aggregated model by using a RGibbs reactor block (GT-BUR-2) to represent the gaseous oxidation and formation reactions according to chemical equilibrium by Gibbs free-energy minimization method. In the model was considered all gaseous components expected as potential products in products sheet.

Chemical equilibrium by Gibbs free-energy minimization method estimates the maximum of NO_x (e.g.: NO, NO_2, N_2O) and SO_x (SO_2, SO_3, CO_S) and NH_3 from the precursors contained in the synthesis gas and combust-generated in the first annular EV-burner combustion chamber (GT-BUR-1) and in the second annular SEV-burner combustion chamber (GT-BUR-2). The method only consider the effect of temperature and the amount of humidified air injected in the chamber, others effect is not considered in the Aspen Plus®v8.4 process model simulation.

The total heat loss from the first annular EV-burner combustion chamber (GT-BUR-1) and from the second SEV-burner annular combustion chamber (GT-BUR-2) was considered to be 0.5% of the LHV_{db} of the fuel-gas fed into the high-performance sequential combustion full-flow advanced EvGT (GT blocks). The heat flow-out is controlled by FORTRAN calculator block CA-GT-QL-1 with aid of parameter calculation blocks (EHV blocks group).

The mass flow rate of fuel-gas injected in the first annular EV-burner combustion chamber (GT-BUR-1) and consequently the mass flow rate of fuel-gas injected in the second annular SEV-burner combustion chamber (GT-BUR-2) is determined and controlled by DS-GT-TG-1 varying the split fraction (GT-SPL-1) of fuel-gas to obtain TIT of 1300.0ºC in the Biomass-to-Mixed alcohols (SC2) and to obtain TIT of

1500.0ºC in the Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC3).

The oxygen consumed in the second annular SEV-burner combustion chamber (GT-BUR-2) pass through the first annular EV-burner combustion chamber (GT-BUR-1) as excess of air. The excess of oxygen mixed with the gaseous combustion products heated in the first chamber (GT-BUR-1) is after-expanded in the high-pressure turbine (GT-HPT-1) modeled by using a Compr pressure changer block in turbine mode considering 94.0% isentropic efficiency model. Gaseous combustion products are expanded to optimized pressure (OP-GT-PG-1) before the second annular SEV-burner combustion chamber (GT-BUR-2).

Part of the fuel-gas is injected through second-stage fuel nozzle (GT-BUR-2) at the cone tip and then into the second annular SEV-burner combustion chamber (GT-BUR-2) being mixed with the expanded gaseous combustion products containing the necessary oxygen to burn-ignite the fuel-gas injected.

The TIT of the second annular SEV-burner combustion chamber (GT-BUR-2) is adjusted by design specification DS-GT-FG-1 varying the mass flow rate of intake-air flowing through the system in excess, according to limits admitted by the high-performance sequential combustion full-flow advanced EvGT. The TIT of the 4-stage low-pressure turbine (GT-LPT-1) is adjusted to be equal to the TIT of the high-pressure turbine (GT-HPT-1).

Gaseous combustion products from the second annular SEV-burner combustion chamber (GT-BUR-2) are expanded to atmospheric level in the 4-stages low-pressure turbine (GT-LPT-1) modeled by using a Compr pressure changer block in turbine model considering 94.0% isentropic efficiency. The low-pressure gaseous combustion products are cooled in the recuperator heat cross-exchanger (GT-2) heating the humidified air leaving from the top of the double-stage humidification packaged-tower top section (GT-SAT-1). In the Biomass-to-Mixed alcohols (SC2) the cooled low-pressure gaseous are exhausted at 1.01 bar and 750.0ºC being directly fed into the HRSG system. In the Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC3) the cooled low-pressure gaseous are exhausted at 1.01 bar and 600.0ºC being directly fed into the HRSG system.

The single shaft air/hydrogen cooled generator is modeled by GT-E-4 work stream and optimized to produce and export the maximum of electricity to the electric power grid. The electricity generation (GT-E-4 work stream) is optimized by optimization model analysis tools OP-GT-PG-1 varying the pressure obtained after the expansion of the high-pressure combustion product gases in the high-pressure turbine (GT-HPT-1) with model analysis tools constraint CN-GT-TI-1 ensuring the technical temperature and expansion limits.

The sequential combustion process (dual-chamber) offers high gas turbine exhaust conditions allowing achieve the necessary steam generation optimally-adjusting the recuperator heat cross-exchanger (GT-2) output conditions (flexible conditions), closing the thermal energy cycle and energy global-system balances. Changes in the recuperator heat cross-exchanger (GT-2) affect significantly the net-electricity efficiency of the high-performance sequential combustion full-flow advanced EvGT.

8.1.22 Heat recovery steam generator (HRSG)

The heat recovery steam generators for the combined-cycles and co-generation was simulated based on the horizontal gas-flow drum type aiming primary supply the thermal energy required by the biorefinery-technologies and secondarily generate steam to be expanded in steam turbines system for power generation.

Aspen Plus®v8.4 process model simulation of the staggered exchanger tube banks was developed using RKS-BM physical property methods for the hot exhaust-gas side and IAPWS-95 physical property methods for the water and steam side. The exchanger tube banks are modeled by using HeatX exchanger blocks considering the temperature limits (crossover avoided) between the exchanger tube banks and their influence on the water/steam mass flow rate for each circuit-level.

The arrangement of the exchanger tube banks in the Aspen Plus®v8.4 process model simulation consider the pressure-levels coupled with the temperature approach required per each circuit-level. The quantity of heat recovered is dependent on the heat requirements of the biomass multi-step dryer and control particulate emissions.

Figure 95 shows the Aspen Plus®v8.4 flowsheet of the triple pressure circuit-levels HRSG system for Biomass-to-Mixed alcohols (SC1). Figure 96 shows the Aspen Plus®v8.4 flowsheet of the triple pressure circuit-levels HRSG system for Biomass-to-Mixed alcohols (SC2). Figure 97 shows the Aspen Plus®v8.4 flowsheet of the triple pressure circuit-levels reheated HRSG system for Biomass-to-Mixed alcohols (SC3).

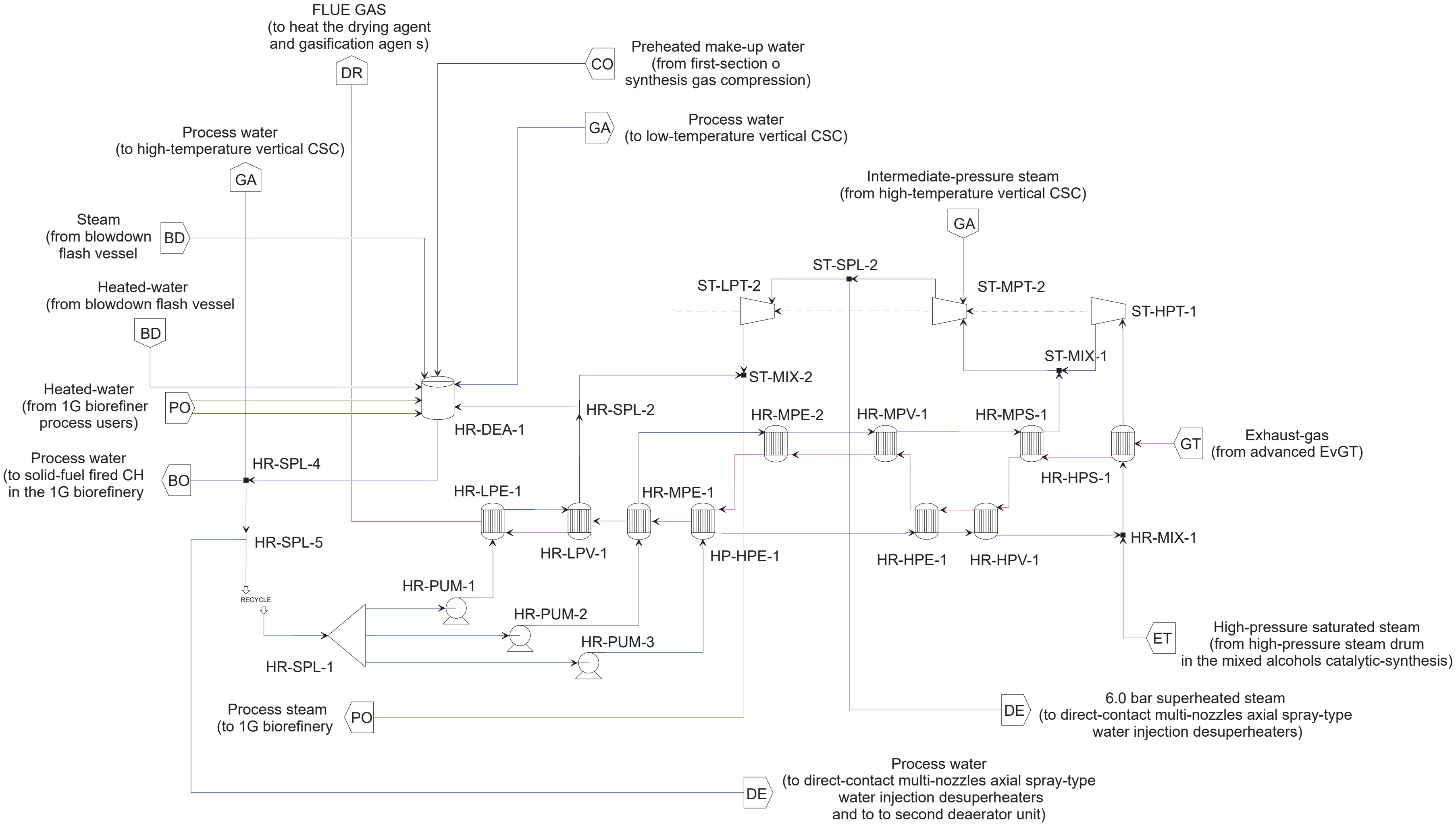


Figure 95 - Aspen Plus® v8.4 flowsheet of the triple pressure circuit-levels Heat recovery steam generator (HRSG) and extraction back-pressure steam turbine for Biomass-to-Mixed alcohols (SC1)

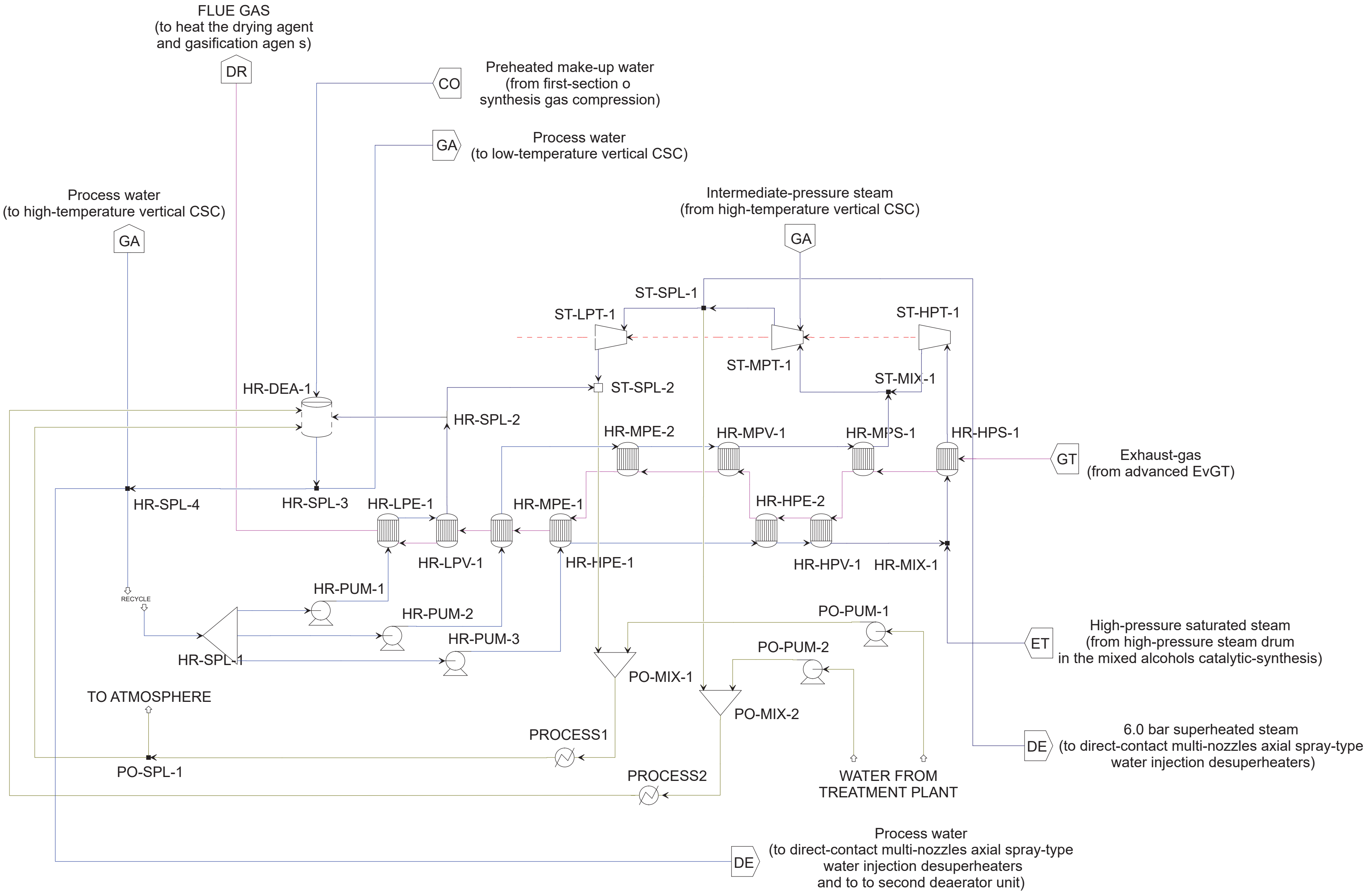


Figure 96 - Aspen Plus® v8.4 flowsheet of the triple pressure circuit-levels Heat recovery steam generator (HRSG) and extraction back-pressure steam turbine for Biomass-to-Mixed alcohols (SC2)

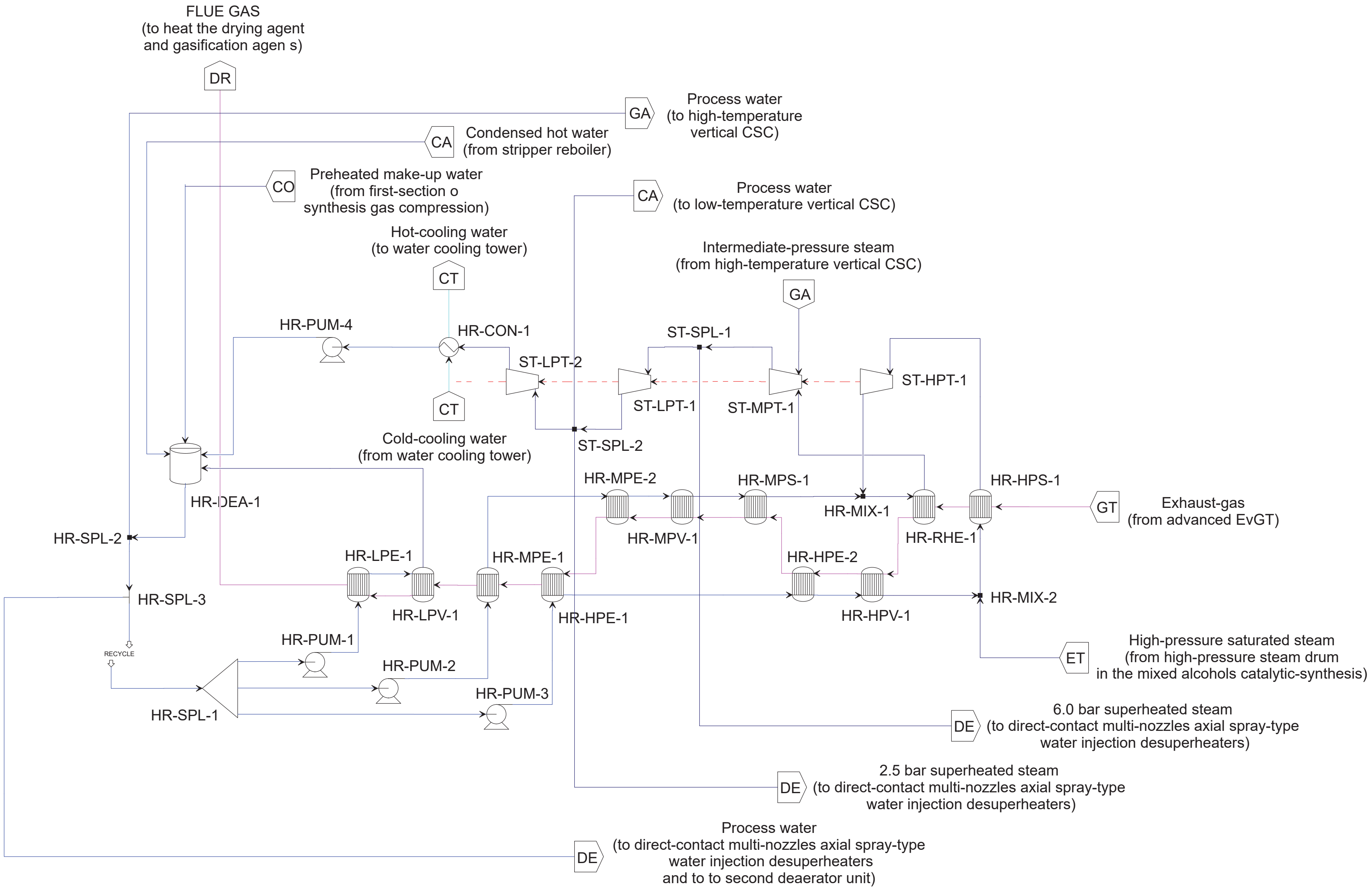


Figure 97 - Aspen Plus® v8.4 flowsheet of the triple pressure circuit-levels reheated Heat recovery steam generator (HRSG) and condensed-extraction steam turbine system for Biomass-to-Mixed alcohols (SC3)

As shown in Figure 95, Aspen Plus®v8.4 flowsheet of the triple pressure circuit-levels HRSG system in the Biomass-to-Mixed alcohols (SC1) is compost by: LP circuit-level water pump (HR-PUM-1); IP circuit-level water pump (HR-PUM-2); HP circuit-level water pump (HR-PUM-3); LP economizer bank tubes (HR-LPE-1); LP vaporizer bank tubes (HR-LPV-1); IP economizer bank tubes 1 (HR-MPE-1); IP economizer bank tubes 2 (HR-MPE-2); IP vaporizer bank tubes (HR-MPV-1); IP superheater bank tubes (HR-MPS-1); HP economizer bank tubes 1 (HR-HPE-1); HP economizer bank tubes 2 (HR-HPE-2); HP vaporizer bank tubes (HR-MPV-1); HP superheater bank tubes (HR-HPS-1); steam splitter (HR-SPL-2); high-pressure steam mixer (HR-MIX-1); first deaerator unit (HR-DEA-1); and deaerated hot process water splitter (HR-SPL-1).

The conventional triple pressure circuit-levels HRSG system (HR blocks) receive exhaust-gas at 1.01 bar and 600.0ºC generated after the recuperator heat cross-exchanger (GT-2) of the high-performance sequential combustion full-flow advanced EvGT. In the Biomass-to-Mixed alcohols (SC1), the high-pressure and intermediate-pressure steam generated by the triple pressure circuit-levels HRSG system (HR blocks) is supplied to EBPST system (ST blocks) (BC).

The Aspen Plus®v8.4 process model simulation of the horizontal gas-flow drum type HRSG system under consideration in the Biomass-to-Mixed alcohols (SC1) was designed with customized low-pressure (LP) circuit-level to produce steam at 2.5 bar and 130.0ºC, intermediate-pressure (IP) circuit-level to produce steam at 23.0 bar and 346.0ºC, and high-pressure (HP) circuit-level to produce steam at 85.0 bar and 520.0ºC.

In the Aspen Plus®v8.4 process model simulation, the deaerator exchanger bank tubes is considered coupled with the LP circuit-level (HR-LPE-1 and HR-LPV-1) producing steam to first deaerator unit (HR-DEA-1) and process steam to supply part of the thermal energy required by the thermochemical-biorefinery (SC1).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from first deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 2.5 bar (drum pressure) by the LP circuit-level water pump (HR-PUM-1). The pressure-adequate water is heated to about 127.0ºC (saturated liquid) circulate flowing through the LP economizer bank tubes (HR-LPE-1) and vaporized producing process steam at 2.5 bar and 130.0ºC in the LP vaporizer bank tubes (HR-LPV-1).

Part of the low-pressure steam at 2.5 bar and 130.0ºC is splitted in the steam splitter (HR-SPL-2) and destined to the first deaerator unit (HR-DEA-1) as degassing agent. Low-pressure steam mainly remove dissolved gasses (e.g.: O_2 and CO_2) by raises the water temperature (make-up water and condensed process water) to produce hot water at 1.4 bar and 105.0ºC in the first deaerator unit (HR-DEA-1). Another part of the low-pressure steam at 2.5 bar and 130.0ºC splitted in the steam splitter (HR-SPL-

2) is destined to supply part of the thermal energy required by the thermochemical-biorefinery (SC1).

The amount of steam at 2.5 bar from the LP vaporizer bank tubes (HR-LPV-1) supplied to first deaerator unit (HR-DEA-1) and supplied as process steam to thermochemical-biorefinery (SC1) is controlled by design specification DS-HR-TL-1 varying the water/steam mass flow rate need to close the thermal energy balance of the thermochemical-biorefinery (SC1).

Part of conditioned feed water at 1.4 bar and 105.0ºC from the first deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 23.0 bar (drum pressure) by the IP circuit-level water pump (HR-PUM-2). Circulate-flowing pressurized water is heated to about 170.0ºC (hot liquid) in the IP economizer bank tubes 1 (HR-MPE-1), and heated to about 220.0ºC (hot liquid) in the IP economizer bank tubes 2 (HR-MPE-2). Hence it is vaporized to about 220.0ºC (saturated vapor) in the IP vaporizer bank tubes (HR-MPV-1) passing from liquid to vapor phase, generating saturated steam at 23.0 bar. The saturated steam is superheated to 346.0ºC in the IP superheater bank tubes (HR-MPS-1).

The amount of subcritical superheated steam at 23.0 bar and 346.0ºC generated is determined by heat exchanger surface area required by the IP exchanger tube banks, the temperature limitations (approaches and cross-over) between the tube banks (heating zones) and the technical parameters of the steam turbine under consideration.

Conditioned feed water and steam mass flow rate passing through the IP staggered exchanger tube banks (HR-MP blocks) is controlled by design specification DS-HR-TG-2 varying the mass flow rate of the deaerated feed water circulating in the exchanger tube banks in order to promote efficient heat exchange.

The temperature of the intermediate-pressure steam obtained after the IP superheater bank tubes (HR-MPS-1) is determined by the conditions (temperature and pressure) of the expanded steam obtained after the high-pressure expansion stage (ST-HPT-1) of the EBPST system and controlled by design specification DS-HR-TG-1 to obtain the same conditions in the IP steam mixer (ST-MIX-1).

The subcritical steam at 23.0 bar and 346.0ºC is expanded in the intermediate-pressure expansion stage (ST-MPT-2) of the EBPST system in the Biomass-to-Mixed alcohols (SC1), producing electrical power energy according to described in the section 8.1.23 (Steam turbine applied in combined-cycles).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from first deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 85.0 bar (drum pressure) by the HP circuit-level water pump (HR-PUM-3). Circulate-flowing pressurized water is heated to about 200.0ºC (hot liquid) in the HP economizer bank tubes 1 (HR-HPE-1) and heated to about 299.0ºC (hot liquid) in the HP economizer bank tubes 2 (HR-HPE-2). Hence it is vaporized to

about 299.0ºC (saturated vapor) in the HP vaporizer bank tubes (HR-HPV-1) passing from liquid to vapor phase, generating saturated steam at 85.0 bar.

High-pressure saturated steam at 85.0 bar and about 299.0ºC (satured condition) generated in the high-pressure steam drum (ET-FLA-1) in the mixed alcohols catalytic-synthesis (ET blocks) is mixed in the high-pressure steam mixer (HR-MIX-1) with the steam vaporized by the HP vaporizer bank tubes (HR-HPV-1). After the mixer, high-pressure saturated steam is superheated to 520.0ºC in the HP superheater bank tubes (HR-HPS-1).

The amount of subcritical superheated steam at 85.0 bar and 520.0ºC generated depends on the amount of steam generated in the high-pressure steam drum (ET-FLA-1), on the temperature limitations (approach) between the exchanger tube banks (heating zones), and on technical parameters of the steam turbine under consideration.

Conditioned feed water and steam mass flow rate passing through the HP staggered exchanger tube banks (HR-MP blocks) is controlled by the deaerated hot process water splitter (HR-SPL-1) varying the mass flow rate of the deaerated feed water circulating in the exchanger tube banks in order to promote efficient heat exchange.

The subcritical steam at 85.0 bar and 520.0ºC is expanded in the high-pressure expansion stage (ST-HPT-1) of the EBPST system in the Biomass-to-Mixed alcohols (SC1), producing electrical power energy according to described in the section 8.1.23 (Steam turbine applied in combined-cycles).

In the Biomass-to-Mixed alcohols (SC1), gases exhausted at 1.01 bar and 600.0ºC from the recuperator heat cross-exchanger (GT-2) of the high-performance sequential combustion full-flow advanced EvGT enters the conventional triple pressure circuit-levels HRSG system (HR blocks) transfer the sensible heat to the water/steam and exits at atmospheric pressure and 128.0ºC (liquid-gas exchange process zone).

The flue-gas at about 128.0ºC after the HRSG system is mixed in the gases mixer (HR-MIX-2) with the flue-gas at 160.0ºC from the traditional 1G-CHP/EBPST system (SC1). The mixed flue-gas at about 138.0ºC is then routed to additional exchanger tube banks (gas-gas exchange process zone) to heat the drying air agent (ATMOSPHERIC AIR) to 120.0ºC. The hot drying air agent supply the thermal energy required and promote the drying process of the biomass in the bagasse flash dryers (DR-DRY-1) and the straw flash dryers (DR-DRY-2).

In the Biomass-to-Mixed alcohols (SC1), high-purity oxygen (O_2) gasification agent from gasifier buffer/equalizer tank (GA-BUF-1) at ambient conditions is heated to 120.0ºC (GA-HEA-1) by using the HRSG hot exhaust-gas (HR-HEA-1) before being injected into the atmospheric CFB directly-heated gasifier (GA blocks).

As shown in Figure 96, Aspen Plus®v8.4 flowsheet of the triple pressure circuit-levels HRSG system in the Biomass-to-Mixed alcohols (SC2) is compost by: LP circuit-level water pump (HR-PUM-1); IP circuit-level water pump (HR-PUM-2); HP circuit-level water pump (HR-PUM-3); LP economizer bank tubes (HR-LPE-1); LP vaporizer bank tubes (HR-LPV-1); IP economizer bank tubes 1 (HR-MPE-1); IP economizer bank tubes 2 (HR-MPE-2); IP vaporizer bank tubes (HR-MPV-1); IP superheater bank tubes (HR-MPS-1); HP economizer bank tubes 1 (HR-HPE-1); HP economizer bank tubes 2 (HR-HPE-2); HP vaporizer bank tubes (HR-MPV-1); HP superheater bank tubes (HR-HPS-1); steam splitter (HR-SPL-2); high-pressure steam mixer (HR-MIX-1); first deaerator unit (HR-DEA-1); and deaerated hot process water splitter (HR-SPL-1).

The conventional triple pressure circuit-levels HRSG system (HR blocks) receive exhaust-gas at 1.01 bar and 750.0ºC generated after the recuperator heat cross-exchanger (GT-2) of the high-performance sequential combustion full-flow advanced EvGT. In the Biomass-to-Mixed alcohols (SC2), the high-pressure and intermediate-pressure steam generated by the triple pressure circuit-levels HRSG system (HR blocks) is supplied to EBPST system (ST blocks) (BC).

The Aspen Plus®v8.4 process model simulation of the horizontal gas-flow drum type HRSG system under consideration in the Biomass-to-Mixed alcohols (SC2) was designed with customized low-pressure (LP) circuit-level to produce steam at 2.5 bar and 130.0ºC, intermediate-pressure (IP) circuit-level to produce steam at 23.0 bar and 346.0ºC, and high-pressure (HP) circuit-level to produce steam at 85.0 bar and 520.0ºC.

In the Aspen Plus®v8.4 process model simulation, the deaerator exchanger bank tubes is considered coupled with the LP circuit-level (HR-LPE-1 and HR-LPV-1) producing steam to first deaerator unit (HR-DEA-1) and process steam to supply part of the thermal energy required by the thermochemical-biorefinery (SC2).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from first deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 2.5 bar (drum pressure) by the LP circuit-level water pump (HR-PUM-1). The pressure-adequate water is heated to about 127.0ºC (saturated liquid) circulate flowing through the LP economizer bank tubes (HR-LPE-1) and vaporized producing process steam at 2.5 bar and 130.0ºC in the LP vaporizer bank tubes (HR-LPV-1).

Part of the low-pressure steam at 2.5 bar and 130.0ºC is splitted in the steam splitter (HR-SPL-2) and destined to the first deaerator unit (HR-DEA-1) as degassing agent. Low-pressure steam mainly remove dissolved gasses (e.g.: O_2 and CO_2) by raises the water temperature (make-up water and condensed process water) to produce hot water at 1.4 bar and 105.0ºC in the first deaerator unit (HR-DEA-1). Another part of the low-pressure steam at 2.5 bar and 130.0ºC splitted in the steam splitter (HR-SPL-

3) is destined to supply part of the thermal energy required by the thermochemical-biorefinery (SC2).

The amount of steam at 2.5 bar from the LP vaporizer bank tubes (HR-LPV-1) supplied to first deaerator unit (HR-DEA-1) and supplied as process steam to thermochemical-biorefinery (SC1) is controlled by design specification DS-HR-TL-1 varying the water/steam mass flow rate need to close the thermal energy balance of the thermochemical-biorefinery (SC2).

Part of conditioned feed water at 1.4 bar and 105.0ºC from first deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 23.0 bar (drum pressure) by the IP circuit-level water pump (HR-PUM-2). Circulate-flowing pressurized water is heated to about 175.0ºC (hot liquid) in the IP economizer bank tubes 1 (HR-MPE-1), and heated to about 220.0ºC (hot liquid) in the IP economizer bank tubes 2 (HR-MPE-2). Hence it is vaporized to about 220.0ºC (saturated vapor) in the IP vaporizer bank tubes (HR-MPV-1) passing from liquid to vapor phase, generating saturated steam at 23.0 bar. The saturated steam is superheated to 346.0ºC in the IP superheater bank tubes (HR-MPS-1).

The amount of subcritical superheated steam at 23.0 bar and 346.0ºC generated is determined by heat exchanger surface area required by the IP exchanger tube banks, the temperature limitations (approaches and cross-over) between the tube banks (heating zones) and the technical parameters of the steam turbine under consideration.

Conditioned feed water and steam mass flow rate passing through the IP staggered exchanger tube banks (HR-MP blocks) is controlled by design specification DS-HR-TG-2 varying the mass flow rate of the deaerated feed water circulating in the exchanger tube banks in order to promote efficient heat exchange.

The temperature of the intermediate-pressure steam obtained after the IP superheater bank tubes (HR-MPS-1) is determined by the conditions (temperature and pressure) of the expanded steam obtained after the high-pressure expansion stage (ST-HPT-1) of the EBPST system and controlled by design specification DS-HR-TG-1 to obtain the same conditions in the IP steam mixer (ST-MIX-1).

The subcritical steam at 23.0 bar and 346.0ºC is expanded in the intermediate-pressure expansion stage (ST-MPT-2) of the EBPST system in the Biomass-to-Mixed alcohols (SC2), producing electrical power energy according to described in the section 8.1.23 (Steam turbine applied in combined-cycles).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from first deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 85.0 bar (drum pressure) by the HP circuit-level water pump (HR-PUM-3). Circulate-flowing pressurized water is heated to about 200.0ºC (hot liquid) in the HP economizer bank tubes 1 (HR-HPE-1) and heated to about 299.0ºC (hot liquid) in the HP economizer bank tubes 2 (HR-HPE-2). Hence it is vaporized to

about 299.0ºC (saturated vapor) in the HP vaporizer bank tubes (HR-HPV-1) passing from liquid to vapor phase, generating saturated steam at 85.0 bar.

High-pressure saturated steam at 85.0 bar and about 299.0ºC (satured condition) generated in the high-pressure steam drum (ET-FLA-1) in the mixed alcohols catalytic-synthesis (ET blocks) is mixed in the high-pressure steam mixer (HR-MIX-1) with the steam vaporized by the HP vaporizer bank tubes (HR-HPV-1). After the mixer, high-pressure saturated steam is superheated to 520.0ºC in the HP superheater bank tubes (HR-HPS-1).

The amount of subcritical superheated steam at 85.0 bar and 520.0ºC generated depends on the amount of steam generated in the high-pressure steam drum (ET-FLA-1), on the temperature limitations (approach) between the exchanger tube banks (heating zones), and on technical parameters of the steam turbine under consideration.

Conditioned feed water and steam mass flow rate passing through the HP staggered exchanger tube banks (HR-MP blocks) is controlled by the deaerated hot process water splitter (HR-SPL-1) varying the mass flow rate of the deaerated feed water circulating in the exchanger tube banks in order to promote efficient heat exchange.

The subcritical steam at 85.0 bar and 520.0ºC is expanded in the high-pressure expansion stage (ST-HPT-1) of the EBPST system in the Biomass-to-Mixed alcohols (SC2), producing electrical power energy according to described in the section 8.1.23 (Steam turbine applied in combined-cycles).

In the Biomass-to-Mixed alcohols (SC2), gases exhausted at 1.01 bar and 750.0ºC from the recuperator heat cross-exchanger (GT-2) of the high-performance sequential combustion full-flow advanced EvGT enters the conventional triple pressure circuit-levels HRSG system (HR blocks) transfer the sensible heat to the water/steam and exits at atmospheric pressure and 121.0ºC (liquid-gas exchange process zone).

The flue-gas at about 121.0ºC after the HRSG system is routed to additional exchanger tube banks (gas-gas exchange process zone) to heat the drying air agent (ATMOSPHERIC AIR) to 120.0ºC. The hot drying air agent supply the thermal energy required and promote the drying process of the biomass in the bagasse flash dryers (DR-DRY-1) and the straw flash dryers (DR-DRY-2).

In the Biomass-to-Mixed alcohols (SC2), high-purity oxygen (O_2) gasification agent from gasifier buffer/equalizer tank (GA-BUF-1) at ambient conditions is heated to 120.0ºC (GA-HEA-1) by using the HRSG hot exhaust-gas (HR-HEA-1) before being injected into the atmospheric CFB directly-heated gasifier (GA blocks).

As shown in Figure 97, Aspen Plus®v8.4 flowsheet of the triple pressure circuit-levels reheated HRSG system in the Biomass-to-Mixed alcohols (SC3) is compost by: LP circuit-level water pump (HR-PUM-1); IP circuit-level water pump (HR-PUM-2); HP circuit-level water pump (HR-PUM-3); LP economizer bank tubes (HR-LPE-1); LP vaporizer bank tubes (HR-LPV-1); IP economizer bank tubes 1 (HR-MPE-1); IP economizer bank tubes 2 (HR-MPE-2); IP vaporizer bank tubes (HR-MPV-1); IP superheater bank tubes (HR-MPS-1); IP reheater pipe banks (HR-RHE-1); HP economizer bank tubes 1 (HR-HPE-1); HP economizer bank tubes 2 (HR-HPE-2); HP vaporizer bank tubes (HR-MPV-1); HP superheater bank tubes (HR-HPS-1); IP steam mixer (HR-MIX-1); high-pressure steam mixer (HR-MIX-2); first deaerator unit (HR-DEA-1); and deaerated hot process water splitter (HR-SPL-1).

The conventional triple pressure circuit-levels HRSG system (HR blocks) receive exhaust-gas at 1.01 bar and 600.0ºC generated after the recuperator heat cross-exchanger (GT-2) of the high-performance sequential combustion full-flow advanced EvGT. In the Biomass-to-Mixed alcohols (SC3), the high-pressure and intermediate-pressure steam generated by the triple pressure circuit-levels reheated HRSG system (HR blocks) is supplied to CEST system (ST blocks) (BC).

The Aspen Plus®v8.4 process model simulation of the horizontal gas-flow drum type HRSG system under consideration in the Biomass-to-Mixed alcohols (SC3) was designed with customized low-pressure (LP) circuit-level to produce steam at 2.5 bar and 130.0ºC, intermediate-pressure (IP) circuit-level to produce steam at 23.0 bar and 343.0ºC, intermediate-pressure (IP) reheater bank tubes (HR-RHE-1) to produce steam at 23.0 bar and 480.0ºC, and high-pressure (HP) circuit-level to produce steam at 85.0 bar and 520.0ºC.

In the Aspen Plus®v8.4 process model simulation, the deaerator exchanger bank tubes is considered as the LP circuit-level (HR-LPE-1 and HR-LPV-1) producing steam at 2.5 bar and 130.0ºC (degassing agent) to be used only in the first deaerator unit (HR-DEA-1).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from first deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 2.5 bar (drum pressure) by the LP circuit-level water pump (HR-PUM-1). The pressure-adequate water is heated to about 127.0ºC (saturated liquid) circulate flowing through the LP economizer bank tubes (HR-LPE-1) and vaporized producing process steam at 2.5 bar and 130.0ºC in the LP vaporizer bank tubes (HR-LPV-1).

Low-pressure steam at 2.5 bar and 130.0ºC is destined to the first deaerator unit (HR-DEA-1) as degassing agent. Low-pressure steam mainly remove dissolved gasses (e.g.: O_2 and CO_2) by raises the water temperature (make-up water and condensed process water) to produce hot water at 1.4 bar and 105.0ºC in the first deaerator unit (HR-DEA-1). The amount of steam at 2.5 bar from the deaerator vaporizer bank tubes (HR-LPV-1) is controlled by design specification DS-HR-TL-1 adjusting the amount of steam fed into the first deaerator unit (HR-DEA-1) varying the water/steam mass flow rate estimate-used into the first deaerator unit (HR-DEA-1) according to described in the section 8.1.27 (Water cycles).

Part of conditioned feed water at 1.4 bar and 105.0ºC from the first deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 23.0 bar (drum pressure) by the IP circuit-level water pump (HR-PUM-2). Circulate-flowing pressurized water is heated to about 185.0ºC (hot liquid) in the IP economizer bank tubes 1 (HR-MPE-1), and heated to about 220.0ºC (hot liquid) in the IP economizer bank tubes 2 (HR-MPE-2). Hence it is vaporized to about 220.0ºC (saturated vapor) in the IP vaporizer bank tubes (HR-MPV-1) passing from liquid to vapor phase, generating saturated steam at 23.0 bar. The saturated steam is superheated to 343.0ºC in the IP superheater bank tubes (HR-MPS-1).

The amount of subcritical superheated steam at 23.0 bar and 343.0ºC generated is determined by heat exchanger surface area required by the IP exchanger tube banks, the temperature limitations (approaches and cross-over) between the tube banks (heating zones) and the technical parameters of the steam turbine under consideration.

Conditioned feed water and steam mass flow rate passing through the IP staggered exchanger tube banks (HR-MP blocks) is controlled by design specification DS-HR-TG-1 varying the mass flow rate of the deaerated feed water circulating in the exchanger tube banks in order to promote efficient heat exchange.

The superheated steam obtained in IP superheater bank tubes (HR-MPS-1) is mixed in the IP steam mixer (HR-MIX-1) with the expanded steam at 23.0 bar and 343.0ºC (intermediate-pressure level), obtained after the expansion of high-pressure steam at 85.0 bar and 520.0ºC by high-pressure expansion stage (ST-HPT-1) of the CEST system for Biomass-to-Mixed alcohols (SC3). The resultant intermediate-pressure steam is superheated in the IP reheater bank tubes (HR-RHE-1) to obtain steam at 23.0 bar and 480.0ºC.

The temperature of the intermediate-pressure steam obtained after the IP superheater bank tubes (HR-MPS-1) is determined by the conditions (temperature and pressure) of the expanded steam obtained after the high-pressure expansion stage (ST-HPT-1) of the CEST system and controlled by design specification DS-HR-TG-2 to obtain the same conditions in the IP steam mixer (HR-MIX-1).

The subcritical steam at 23.0 bar and 480.0ºC is expanded in the intermediate-pressure expansion stage (ST-MPT-2) of the CEST system in the Biomass-to-Mixed alcohols (SC3), producing electrical power energy according to described in the section 8.1.23 (Steam turbine applied in combined-cycles).

Part of condition-deaerated feed water at 1.4 bar and 105.0ºC from first deaerator unit (HR-DEA-1) is splitted in the deaerated hot process water splitter (HR-SPL-1) and pumped to 85.0 bar (drum pressure) by the HP circuit-level water pump (HR-PUM-3). Circulate-flowing pressurized water is heated to about 200.0ºC (hot liquid) in the HP economizer bank tubes 1 (HR-HPE-1) and heated to about 299.0ºC (hot liquid) in the HP economizer bank tubes 2 (HR-HPE-2). Hence it is vaporized to

about 299.0ºC (saturated vapor) in the HP vaporizer bank tubes (HR-HPV-1) passing from liquid to vapor phase, generating saturated steam at 85.0 bar.

High-pressure saturated steam at 85.0 bar and about 299.0ºC (satured condition) generated in the high-pressure steam drum (ME-FLA-1) in the low-pressure methanol catalytic-synthesis (ME blocks) is mixed in the high-pressure steam mixer (HR-MIX-2) with the steam vaporized by the HP vaporizer bank tubes (HR-HPV-1). After the mixer, high-pressure saturated steam is superheated to 520.0ºC in the HP superheater bank tubes (HR-HPS-1).

The amount of subcritical superheated steam at 85.0 bar and 520.0ºC generated depends on the amount of steam generated in the high-pressure steam drum (ET-FLA-1), on the temperature limitations (approach) between the exchanger tube banks (heating zones), and on technical parameters of the steam turbine under consideration.

Conditioned feed water and steam mass flow rate passing through the HP staggered exchanger tube banks (HR-MP blocks) is controlled by the deaerated hot process water splitter (HR-SPL-1) varying the mass flow rate of the deaerated feed water circulating in the exchanger tube banks in order to promote efficient heat exchange.

The subcritical steam at 85.0 bar and 520.0ºC is expanded in the high-pressure expansion stage (ST-HPT-1) of the CEST system in the Biomass-to-Mixed alcohols (SC3), producing electrical power energy according to described in the section 8.1.23 (Steam turbine applied in combined-cycles).

In the Biomass-to-Mixed alcohols (SC3), gases exhausted at 1.01 bar and 600.0ºC from the recuperator heat cross-exchanger (GT-2) of the high-performance sequential combustion full-flow advanced EvGT enters the conventional triple pressure circuit-levels HRSG system (HR blocks) transfer the sensible heat to the water/steam and exits at atmospheric pressure and 161.0ºC (liquid-gas exchange process zone).

The flue-gas at about 161.0ºC after the HRSG system is routed to additional exchanger tube banks (gas-gas exchange process zone) to heat the drying air agent (ATMOSPHERIC AIR) to 120.0ºC. The hot drying air agent supply the thermal energy required and promote the drying process of the biomass in the bagasse flash dryers (DR-DRY-1) and the straw flash dryers (DR-DRY-2).

In the Biomass-to-Mixed alcohols (SC3), high-purity oxygen (O_2) gasification agent from gasifier buffer/equalizer tank (GA-BUF-1) at ambient conditions is heated to 120.0ºC (GA-HEA-1) by using the HRSG hot exhaust-gas (HR-HEA-1) before being injected into the atmospheric CFB directly-heated gasifier (GA blocks).

8.1.23 Steam turbine applied in combined-cycles

The Aspen Plus®v8.4 process model simulation of the steam turbine applied in combined-cycles considers conventional subcritical steam turbines operating in Rankine-cycle mode.

As shown in Figure 95, Aspen Plus®v8.4 flowsheet of the EBPST system for Biomass-to-Mixed alcohols (SC1) is compost by: high-pressure expansion stage (ST-HPT-1); intermediate-pressure expansion stage (ST-MPT-2); low-pressure expansion stage (ST-LPT-2); steam extraction at 6.0 bar (ST-SPL-2); steam mixer (ST-MIX-1); and steam splitter (ST-SPL-2).

The Aspen Plus®v8.4 process model simulation of the EBPST (ST blocks) in the Biomass-to-Mixed alcohols (SC1) was developed using IAPWS-95 physical property methods considering about 82.26% isentropic efficiency (isentropic expansion). The model considers exhaust-steam at 2.5 bar and 130.0ºC in the low-pressure section (ST-LPT-2).

The high-pressure steam at 85.0 bar and 520.0ºC generated in the HP circuit-level (HR-HPS-1) is expanded to 23.0 bar and about 345.9ºC (intermediate-pressure level) by the first-section of the EBPST (ST-HPT-1) modeled by using a Compr pressure changer block in turbine model. After expanded the steam is mixed (ST-MIX-1) with intermediate-pressure steam at 23.0 bar and about 345.9ºC generated in the IP circuit-level (HR-MPS-1) of the HRSG system and with the intermediate-pressure steam at 23.0 bar and about 345.9ºC generated in the high-temperature vertical CSC (GA-CSC-1).

The intermediate-pressure steam is expanded to 6.0 bar and about 205.0ºC by the second-section of the EBPST (ST-MPT-2) modeled by using a Compr pressure changer block in turbine model. Part of expanded steam is extracted (ST-SPL-2) as process steam to supply part of the thermal energy required by the intermediate-pressure heater (PU-HEA-1) in the Zeolite-based MSDU for mixed alcohols (DH blocks) and by the distillation second-column reboiler (DS-REB-1) in the mixed alcohols distillation second tray-column (DS-COL-1).

Surplus steam at 6.0 bar and 205.0ºC from the second-section of the EBPST (ST-MPT-2) is expanded to 2.5 bar and 130.0ºC (exhaust) by the third section of the EBPST (ST-LPT-2) modeled by using a Compr pressure changer block in turbine model. The exhaust-steam is used as process steam (ST-SPL-2) to supply part of the thermal energy required by 1G-thecnologies (integrated scenario).

As shown in Figure 96, Aspen Plus®v8.4 flowsheet of the EBPST system for Biomass-to-Mixed alcohols (SC2) is compost by: high-pressure expansion stage (ST-HPT-1); intermediate-pressure expansion stage (ST-MPT-1); low-pressure expansion stage (ST-LPT-1); steam extraction at 6.0 bar (ST-SPL-1); steam mixer (ST-MIX-1); and steam splitter (ST-SPL-2).

Aspen Plus®v8.4 process model simulation of the EBPST (ST blocks) in the Biomass-to-Mixed alcohols (SC2) was developed using IAPWS-95 physical property methods considering about 82.26% isentropic efficiency (isentropic expansion). The model considers exhaust-steam at 2.5 bar and 130.0ºC in the low-pressure section (ST-LPT-1).

The high-pressure steam at 85.0 bar and 520.0ºC generated in the HP circuit-level (HR-HPS-1) is expanded to 23.0 bar and about 345.9ºC (intermediate-pressure level) by the first-section of the EBPST (ST-HPT-1) modeled by using a Compr pressure changer block in turbine model. After expanded the steam is mixed (ST-MIX-1) with intermediate-pressure steam at 23.0 bar and about 345.9ºC generated in the IP circuit-level (HR-MPS-1) of the HRSG system and with the intermediate-pressure steam at 23.0 bar and about 345.9ºC generated in the high-temperature vertical CSC (GA-CSC-1).

The intermediate-pressure steam is expanded to 6.0 bar and about 205.0ºC by the second-section of the EBPST (ST-MPT-1) modeled by using a Compr pressure changer block in turbine model. Part of this steam is extracted (ST-SPL-1) as process steam to supply the thermal energy for dehydration molecular sieve in the 1G sugarcane biorefinery (integrated scenario), part of the thermal energy required by intermediate-pressure heater (PU-HEA-1) in the Zeolite-based MSDU for mixed alcohols (DH blocks) and by distillation second-column reboiler (DS-REB-1) in the mixed alcohols distillation second tray-column (DS-COL-1).

Surplus steam at 6.0 bar and 205.0ºC from the second-section of the EBPST (ST-MPT-1) is expanded to 2.5 bar and 130.0ºC (exhaust) by the third section of the EBPST (ST-LPT-1) modeled by Compr pressure changers block in turbine model. The exhaust-steam together the steam at 2.5 bar and 130.0ºC from the LP circuit-level (HR-LPV-1) in the HRSG system is used as process steam (ST-SPL-2) to supply the entire thermal energy required by 1G-thecnologies (integrated scenario).

As shown in Figure 97, Aspen Plus®v8.4 flowsheet of the CEST system in the Biomass-to-Mixed alcohols (SC3) is compost by: high-pressure expansion stage (ST-HPT-1); intermediate-pressure expansion stage (ST-MPT-1); low-pressure expansion stage (ST-LPT-1); condensing expansion stage (ST-LPT-2); steam extraction at 6.0 bar (ST-SPL-1); steam extraction at 2.5 bar (ST-SPL-2); water-cooled surface condenser (HR-CON-1); and condensed water pump (HR-PUM-4).

The Aspen Plus®v8.4 process model simulation of the CEST (ST blocks) in the Biomass-to-Mixed alcohols (SC3) was developed using IAPWS-95 physical property methods considering about 83.98% isentropic efficiency (isentropic expansion).

The high-pressure steam at 85.0 bar and 520.0ºC generated in the HP circuit-level (HR-HPS-1) is expanded to 23.0 bar and about 345.9ºC (intermediate-pressure level) by the first-section of the CEST (ST-HPT-1) modeled by using a Compr pressure changer block in turbine model. After expanded the steam is mixed with intermediate-pressure steam at 23.0 bar and about 345.9ºC generated in the IP circuit-level (HR-MPS-1) of the HRSG system and then reheated to 23.0 bar and 480.0ºC in the reheated exchanger pipe banks (HR-RHE-1) in the HRGS intermediate-pressure circuit-level.

The intermediate-pressure steam at 23.0 bar and 480.0ºC generated in the high-temperature vertical CSC (GA-CSC-1) and the intermediate-pressure reheated steam are expanded to 6.0 bar and at about 312.6ºC in the second-section of the CEST (ST-MPT-1) modeled by using a Compr pressure changer block in turbine model. Part of this steam is extracted (ST-SPL-1) as process steam to supply part of the thermal energy required by the intermediate-pressure heater (PU-HEA-1) in the Zeolite-based MSDU for mixed alcohols (DH blocks) and by the distillation second-column reboiler (DS-REB-1) in the mixed alcohols distillation second tray-column (DS-COL-1).

Surplus steam at 6.0 bar and at about 312.6ºC from the second-section of the CEST is expanded to 2.5 bar and 220.9ºC in third section of the CEST (ST-LPT-1) modeled by using a Compr pressure changer block in turbine model. Part of this steam is extracted (ST-SPL-2) as process steam to supply part of the thermal energy required by the thermochemical technologies (standalone scenario).

Surplus steam at 2.5 bar and 220.9ºC from the third section of the CEST (ST-LPT-1) is expanded to 0.11 bar and 48.0ºC by the four section of the CEST (ST-LPT-2) modeled by using a Compr pressure changer block in turbine model, ensuring that the quality of the steam-exiting a CEST condensing-stage (ST-LPT-2) is greater than 90.0% (technical limit). CEST condensing-stage (ST-LPT-2) is directly connected to water-cooled surface condenser (HR-CON-1) modeled by using a Heater exchanger block. The vacuum-pressure steam exhausted is condensed generating a water condensate (liquid phase) available to be after pumped (HR-PUM-4) back to first deaerator unit (HR-DEA-1) in closed-loop cycle.

The electrical potential losses (turbine-mechanical generator) by attrite in the mechanical move parts was considered as 1.0% of the mechanical potential energy produced by the STs (99.0% mechanical efficiency).

8.1.24 Direct-contact multi-nozzles axial spray-type water injection desuperheater

The processes of mixed alcohols separation and purification in the Biomass-to-Mixed alcohols scenarios designed and assessed in this research Master’s degree requires a significant quantity of thermal energy. Supply its demand require more than the available low-quality thermal energy (low-pressure steam) generated in the efficient energy-save stages employed to cooling down the high-pressure crude gaseous product from the mixed alcohols catalyst-synthesis being necessary allocate more process steam to supply the thermal energy required.

Figure 98 shows the Aspen Plus®v8.4 flowsheet of the direct-contact multi-nozzles axial spray-type water injection desuperheaters for: a) Biomass-to-Mixed alcohols (SC1), and Biomass-to-Mixed alcohols (SC2); and b) Biomass-to-Mixed alcohols (SC3)

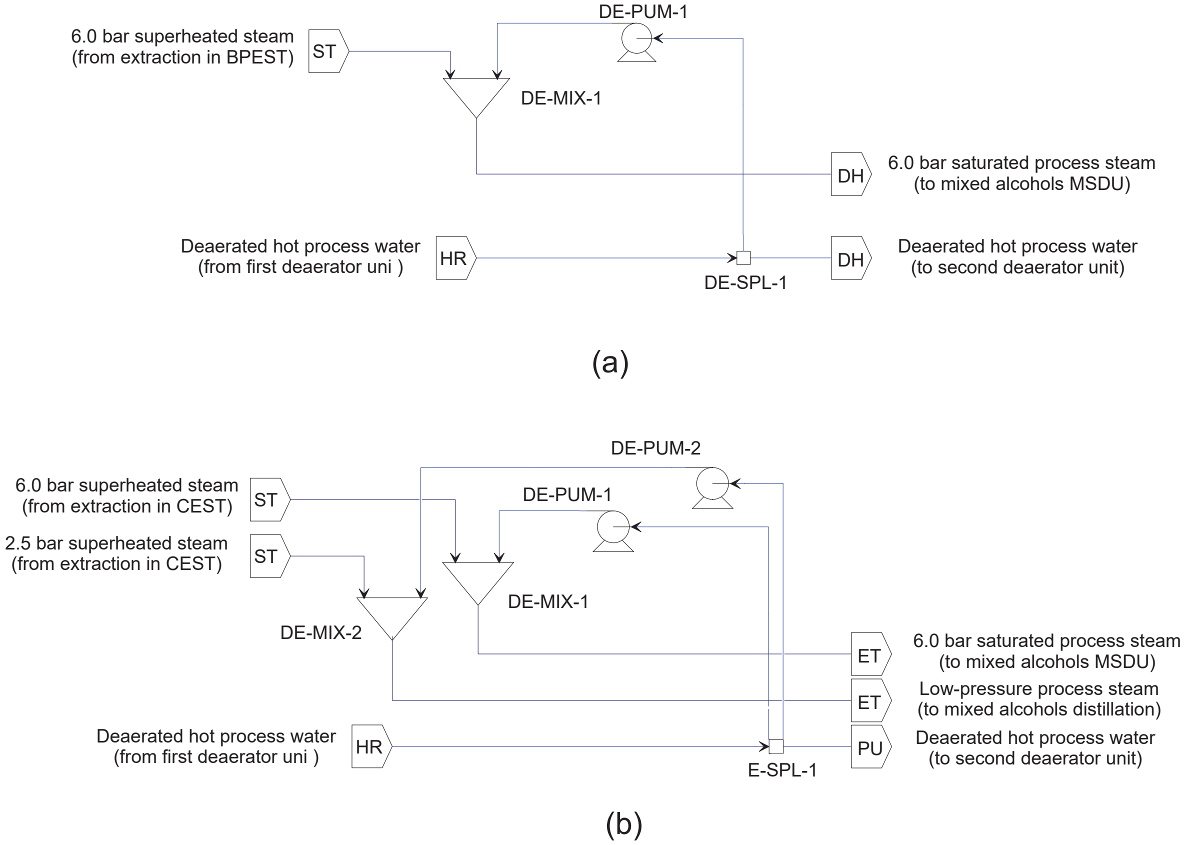


Figure 98 - Aspen Plus®v8.4 flowsheet of the desuperheater units for: a) Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC2); and b) Biomass-to-Mixed alcohols (SC3)

As shown in Figure 98 (a), Aspen Plus®v8.4 flowsheet of the of the direct-contact multi-nozzles axial spray-type water injection desuperheaters for Biomass-to-Mixed alcohols (SC1), and Biomass-to-Mixed alcohols (SC2) is compost by: desuperheater axial co-current injectors 1 (DE-MIX-1); variable water spray multi-nozzles 1 (DE-MIX-1); deaerated water pump 1 (DE-PUM-1); and water splitter 1 (DE-SPL-1). As shown in Figure 98 (b), Aspen Plus®v8.4 flowsheet of the direct-contact multi-nozzles axial spray-type water injection desuperheaters for Biomass-to-Mixed alcohols (SC3) is compost by: desuperheater axial co-current injectors 1 (DE-MIX-1); variable water spray multi-nozzles 1 (DE-MIX-1); desuperheater axial co-current injectors 2 (DE-

MIX-2); variable water spray multi-nozzles 2 (DE-MIX-2); deaerated water pump 1 (DE-PUM-1); deaerated water pump 2 (DE-PUM-2); water circulation pump (HR-PUM-5); water splitter 1 (DE-SPL-1); and water splitter 2 (DE-SPL-1).

The Aspen Plus®v8.4 process model simulation of the direct-contact multi-nozzles axial spray-type water injection desuperheaters was developed using IAPWS-95 physical property methods. The model considers the differential pressure between the deaerated hot process water and the superheated steam at about 6.0 bar to achieve the effect of atomization in the water spray jet.

Superheated steam is made available through extractions in the steam turbine on the desired pressure in the Biomass-to-Mixed alcohols scenarios to complement the thermal energy supply. Steam for use in process applications is typically saturated steam being necessary adjusts the temperature to the limits of each equipment users.

In the Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC2), steam on superheated conditions at 6.0 bar and 205.0ºC is extracted from the EBPST (ST blocks) and in the Biomass-to-Mixed alcohols (SC3) steam on superheated conditions at 6.0 bar and 312.6ºC is extracted from the CEST (ST blocks). The superheated steam is cooled down by the adiabatic steam temperature reduction process to about near saturation conditions (6.0 bar and 160.0ºC) in the direct-contact multi-nozzles axial spray-type water injection desuperheater (DE-MIX-1) modeled by using a Mixer block. After cooled the steam is mixed (ET-MIX-1) with the steam generated at 6.0 bar and 160.0ºC in the synthesis-products water cooler (ET-1) in the mixed alcohols catalyst-synthesis (ET blocks). Steam at 6.0 bar and 160.0ºC supply the thermal energy demanded by the intermediate-pressure heater (PU-HEA-1) in the Zeolite-based MSDU for mixed alcohols (DH blocks) and by the distillation second-column reboiler (DS-REB-1) in the mixed alcohols distillation second tray-column (DS-COL-1).

In the Biomass-to-Mixed alcohols (SC3) steam on superheated conditions at 2.5 bar and 221.0ºC is extracted from the CEST (ST blocks) and cooled down adiabatic steam temperature reduction process to near saturation conditions (2.5 bar and 130.0ºC) in the direct-contact multi-nozzles axial spray-type water injection desuperheater (DE-MIX-2) modeled by using a Mixer block. After cooled the steam is mixed (ET-MIX-2) with the steam generated at 2.5 bar and 130.0ºC in the low-temperature water cooler (ET-3) in the mixed alcohols catalyst-synthesis (ET blocks). Steam at 2.5 bar and 130.0ºC supply the thermal energy demanded by the distillation first-column reboiler (PU-REB-1) in the crude mixed alcohols forerun degassing first tray-column (PU-COL-1) an by the distillation third-column reboiler (DS-REB-2) in the low-pressure methanol distillation third tray-column (DS-COL-2).

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3), part of the deaerated hot process water from the first deaerator unit (HR-DEA-1) at 1.4 bar and 105.0ºC is splitted (DE-SPL-1) and pumped by the deaerated water pump 1 (DE-PUM-1) at about 12.0 bar (atomizing effect) and then fed in the desuperheater axial co-current injectors 1 (DE-MIX-1) being injected through the variable water spray multi-nozzles 1 (DE-MIX-1) into the 6.0 bar steam pipe line. Atomized water from the variable water spray multi-nozzles 1 (DE-MIX-1) coming into contact with superheated steam in the 6.0 bar steam pipe line causing a complete evaporation of the water injected (DE-MIX-1) reducing the temperature of the superheated steam to saturation conditions at about 6.0 bar and 160.0ºC.

In the Biomass-to-Mixed alcohols (SC3), part of the deaerated hot process water from the first deaerator unit (HR-DEA-1) at 1.4 bar and 105.0ºC is splitted (DE-SPL-2) and pumped by the deaerated water pump 2 (DE-PUM-2) at about 8.5 bar (atomizing effect) and then fed in the desuperheater axial co-current injectors 2 (DE-MIX-2) being injected through the variable water spray multi-nozzles 2 (DE-MIX-2) into the 2.5 bar steam pipe line. Atomized water from the variable water spray multi-nozzles 2 (DE-MIX-2) coming into contact with superheated steam in the 2.5 bar steam pipe line causing a complete evaporation of the water injected (DE-MIX-1) reducing the temperature of the superheated steam to saturation conditions at about 2.5 bar and 130.0ºC.

The temperature control and the amount of injection water in the 6.0 bar steam pipe line is controlled by design specification DS-DE-TG-1 for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) and in the 2.5 bar steam pipe line is controlled by design specification DS-DE-TG-2 for Biomass-to-Mixed alcohols (SC3), also employed to represent the number of injection nozzles in operation. The adjust and control is made varying the deaerated hot process water mass flow rate injected in the steam pipe line to obtain the desired conditions by the variable water spray multi-nozzles (DE-MIX-1).

8.1.25 Traditional *c*ombined heat and power generation system applying extraction back-pressure steam turbine

In the thermochemical-biorefinery scenario 1 (SC1) and thermochemical-biorefinery scenario 3 (SC3) is considered the optimized 1G sugarcane biorefinery (1G sugarcane biorefinery) with annexed ethanol distillery using a typical solid-fuel fired boiler bottoming-cycle system (grate type) and non-condensing type extraction back-pressure steam turbine (EBPST) operating at 22.0 bar and 320.0ºC (SC1) in Rankine-cycle mode for thermal and electrical energy generation (CHP). Part of the sugarcane bagasse (SUGARCANE BAGASSE) from mills (without use of straw) as fuel is consumed in the solid-fuel fired boiler bottoming-cycle system, the surplus bagasse (SUGARCANE BAGASSE) and the straw (SUGARCANE STRAW) available is used as feedstock in the self-sufficient in energy terms Biomass-to-Mixed alcohols route.

In the thermochemical-biorefinery scenario 1 (SC1) the traditional 1G-CHP/EBPST (SC1) system supply part of the thermal and electrical energy required by the 1G-thecnologies, another part is supplied by the Biomass-to-Mixed alcohols (SC1) operating in integrated mode. In the thermochemical-biorefinery scenario 3 (SC3) the traditional 1G-CHP/EBPST (SC1) system supply the entire thermal and electrical energy required by the 1G sugarcane biorefinery, Biomass-to-Mixed alcohols (SC3) operating in standalone mode.

Traditional 1G-CHP/EBPST system (SC1) with surplus biomass is simulated and detailed according to Aspen Plus®v8.4 process model simulation described in the section 5.2.3 (Solid-fuel fired boiler).

As shown in Figure 45, Aspen Plus®v8.4 flowsheet of the 1G-CHP/EBPST (SC1) system for BIG-ICE/CC (SC1) which is the same model with modified parameters for Biomass-to-Mixed alcohols (SC1) is compost by: feed tray (PR-MIX-5); conveyor boiler fuel feeders (PR-SCR-8); breakdown RYield reactor block (BO-DEV-1); burner chamber (BO-COMBU); adjust Sep separator block (BO-SEP-1); heat loss adjust Heater exchanger block (BO-HEA-1); wet ashes removal grate system (BO-SEP-2); ashes bins (BO-RES-1); air pre-filter unit (BO-FIL-1); air preheated (BO-PRE-1); advanced blower system (BO-ASP-1); feed-water pump (BO-PUM-1); low-temperature economizers and high-temperature economizers (BO-ECO-1); radiant heat adjust Heater exchanger blocks (BO-HEA-2 and BO-HEA-3); evaporator (BO-EVA-1); superheater (BO-SUP-1); saturated water purge (BO-SPL-3); blowdown flash vessel (BD-FLASH-1); multi-cyclone unit (BO-CYC-1); electrostatic precipitator unit (BO-ESP-1); ashes temporary storage bins (BO-RES-2); intermediate-pressure EBPST stage (ST-HPS-1); low-pressure EBPST stage (ST-LPS-1); steam extraction at 6.0 bar (ST-SPL-1); make-up water pump (BO-PUM-2); and blowdown heat recovery exchanger (BD-1).

A fraction of the bagasse from the mills (SUGARCANE BAGASSE) can be directly belt-conveyed to boiler fuel feeders (PR-SCR-8) or carried by tractors (actual system) from the bagasse pile to the conveyor feed tray (PR-MIX-5) to be fed by drum and hydraulic/pneumatic fuel feeders (PR-SCR-8) into the combustion chamber (BO-COMBU).

The Aspen Plus®v8.4 process model simulation of the typical solid-fuel fired boiler use a breakdown RYield reactors type (BO-BEV-1) as a theoretical artifice to simulate the decomposition of the non-conventional solids BAGASSE (BO-DEV-1) into its ‘constituting’ conventional components (‘ELEMENTS’) including carbon (C), hydrogen (H_2), oxygen (O_2), chlorine (Cl_2), nitrogen oxide (NO), sulfur dioxide (SO_2) and hydrogen sulfide (H_2S) using about 16.67%$_{w/w}$ of the sulfur (S) content. Salts, minerals, ashes and soil are specified as inert components in the devolatilization process-zone (bypass).

FORTRAN calculator block CA-BO-CS-1 is used to specify the yield distributions and the mass flow rate of each constituent component in the outlet stream according to the bagasse ultimate analysis (Table 5). The blocks BO-SPL-1 and BO-SPL-2 split the volatile material from the biomass and sent directly to the combustor chamber (BO-COMBU).

Sep separator block BO-SEP-1 as adjustment model is used to adjust the biomass conversion, the carbon conversion (CA-BO-XS-1) and the ashes content (solids formation) as bottom ashes (ASHES) or fly-ashes (FLY-ASHES). The amount of bottom ashes (ASHES) and fly-ashes (FLY-ASHES) and hers composition are controlled by BO-SEP-2 block which simulate the grate system and the automatically wet ashes removal system (BO-SEP-2), without considering the water use in the simulation (cleaning grate system). The ashes temporary storage bins (BO-RES-1) consider the heat loss (heat transported with ashes) by natural heat changes with the ambient conditions.

The solid-fuel fired boiler models consider a heat loss (BO-HEA-1) due the surface radiation and convection with to surrounding ambient. The heat loss (BO-HEA-1) is calculated by FORTRAN calculator block CA-BO-QL-1 based on the fraction of the LHV_{db} of the biomass inlet in the boiler, according to Equation 16 detailed in the section 3.9.13 (Heat losses to surrounding ambient).

The Aspen Plus®v8.4 process model simulation of the burner chamber (BO-COMBU) was developed using RGibbs reactor type which uses the Gibbs free energy minimization method, considering all the possible solids emissions (soil and atmosphere) and gaseous emissions (atmosphere). The Gibbs free energy minimization method determines the equilibrium composition of the products resulting from the many reactions that can occur. The burner chamber (BO-COMBU) model can determine in the gaseous phase the formation of NO_2, N_2O, NO, SO_2, SO_3, NH_3, H_2S, HCL, Cl_2, COS, CHN, volatile organic compounds and particulate matter formation (salt and solid compounds), and in the solid phase (ashes and fly-ashes) the formation of unconverted biomass (BAGASSE and STRAW) and carbon (C), SiO_2 (biomass constitutional ash content), soil, MgO, CaO, KCl, K_2O, K_3PO_4, salts and mineral (biomass constitutional content). The Gibbs free energy minimization method cannot estimate the formation of CaS, MgS and S, sulfur content being emitted on gaseous forms in Gibbs combustion models (oxidized metals are more stable form).

Combustion air (ATMOSPHERIC AIR) is preheated (BO-PRE-1) and forced-injected in the burner chamber (BO-COMBU) by advanced blower system (BO-ASP-1) with pre-filter unit (BO-FIL-1) to protect the blower and burner from debris (PARTICLES). The amount of air employed is controlled by design specification DS-BO-FG-1 varying the mass flow rate of atmospheric air (ATMOSPHERCI AIR) inlet into the burner chamber (BO-COMBU). The model consider $8.0\%_{w/w}$ as the ratio of the oxygen mass flow rate out off the burner chamber (BO-COMBU) to the oxygen mass flow rate inlet into the burner chamber (BO-COMBU).

The liquid non-saturated feed-water from first deaerator unit (HR-DEA-1) at 1.4 bar and 105.0ºC is pumped-compressed to 22.0 bar by the feed-water pump (BO-PUM-1) and then fed into the solid-fuel fired boiler pipes banks. Non-saturated feed-water is heated at saturation conditions in the low-temperature and high-temperature economizers (BO-ECO-1) by radiant (BO-HEA-2 and BO-HEA-3) and convective heat (BO-ECO-1), is evaporate to saturated steam in the evaporator (BO-EVA-1) and superheated in the superheater (BO-SUP-1) leaving the boiler at 22.0 bar and 320ºC to be expanded in the EBPST system (ST blocks).

The temperature of the flue-gas after the air pre-heater exchanger (BO-PRE-1) is controlled by design specification DS-BO-FL-1 to be 160.0ºC varying the mass flow rate of the boiler feed-water flowing through the water-side pipe bank coupled with the design specification DS-BO-FG-1 varying the mass flow rate of the atmospheric air inlet into the burner chamber (BO-COMBU) to control the excess air ratio.

4.0%$_{w/w}$ of the saturated water mass flow rate is purged (BO-SPL-3) from the boiler as continue water blowdown and fleshed to 1.4 bar (deaerator pressure) in the blowdown flash vessel (BD-FLASH-1). The vaporized phase is sent to the first deaerator unit (HR-DEA-1) to heat recovery (reducing the amount of steam 2.5 bar used in the deaerator). The liquid phase is cooled to 30.0ºC by the blowdown heat recovery exchanger (BD-1) heating the make-up raw water (WATER FROM TREATMENT PLANT) which is pumped to 1.4 bar by the make-up water pump (BO-PUM-2) to the first deaerator unit (HR-DEA-1). Water blowdown removal impurities from boiler as dissolved impurities, in the Aspen Plus$^{®}$v8.4 process model simulation is not considered the presence of impurities. The amount of impurities depends on the fresh-water quality, on make-up water treatment process and maintenance treatment of process water cycle.

In the spreadsheet calculation model of the treatment processes was considered the recovery of 87.0%$_{w/w}$ of the water blowdown according to Equation 24.

Particulate material content in the flue-gas (FLY-ASHES) are reduced by control particulate emissions system applying a multi-cyclone unit (BO-CYC-1) modeled by using a Cyclone solids separator block. The multi-cyclone unit (BO-CYC-1) was designed optimized with 5 cyclones (battery) to remove the gross particulate content in the exhaust-gas according to Muschelknautz calculation method for a maximum pressure drop of 0.01 bar applying spiral inlet cyclones type.

Part of the persistent fine particulate matters after the multi-cyclone unit (BO-CYC-1) is removed by the electrostatic precipitator (DR-ESP-1) modeled by using a ESP solids separator block according to Svarovsky calculation model for vertically mounted collecting plates model with separation efficiency of 92.0% based on the migration velocity and the ratio of precipitation area. The fly-ashes (FLY AHSES) are stored in the ashes temporary storage bins (BO-RES-2) and mixed with the ASHES to be after-sent to application in the sugarcane crops.

The flue-gas from the boiler system content steam (H_2O), NO_2, N_2O, NO, SO_2, SO_3, NH_3, H_2S, HCL, Cl_2, COS, CHN, volatile organic compounds, and particulate matter (MgO, CaO, KCl, K_2O, K_3PO_4, BIOMASS, C, salts and mineral) is mixed with the flue-gas from the HRSG system and sent to heat the drying agent and gasification agent (heat recovery).

The Aspen Plus®v8.4 process model simulation of the EBPST (ST blocks) of the 1G-CHP/EBPST (SC1) system in the Biomass-to-Mixed alcohols (SC1) was developed using IAPWS-95 physical property methods considering about 74.55% isentropic efficiency (isentropic expansion). The model considers exhaust-steam at 2.5 bar and 130.0ºC in the low-pressure section (ST-LPS-1).

The intermediate-pressure steam at 22.0 bar and 320.0ºC generated in the solid-fuel fired boiler pipes banks is expanded to 6.0 bar and about 198.3ºC by the first-section of the EBPST (ST-HPT-1) modeled by using a Compr pressure changer block in turbine model. After expanded a part of the steam is extracted (ST-SPL-1) to supply part of the thermal energy required by the dehydration ethanol process (1G-thecnologie).

Another part of the steam at 6.0 bar and about 198.3ºC is expanded to 2.5 bar and 130.0ºC in the second-section of the EBPST (ST-MPS-1) modeled by using a Compr pressure changer block in turbine model. The exhaust-steam at 2.5 bar and 130.0ºC is used to supply part of the 1G-thecnologies thermal energy requirements.

The electricity generated by the EBPST (ST blocks) of the 1G-CHP/EBPST (SC1) system in the Biomass-to-Mixed alcohols (SC1) is used to supply part of electricity required by the 1G sugarcane biorefinery. Another part is supplied by the Biomass-to-Mixed alcohols route. The electrical potential losses (turbine-mechanical generator) by attrite in the mechanical move parts was considered as 1.0% of the mechanical energy produced by the turbine (99.0% mechanical efficiency).

Spreadsheet calculation considering the wastewater treatment process (WASTEWATER TO TREATMENT PLANT) with a maximum of 85.0%$_{w/w}$ recovery efficiency is used to determine the amount of water (TO WASTEWATER TREATMENT PLANT) is recovered and recycled to the first deaerator unit (HR-DEA-1) after treatment as make-up water and the requirements of supplementary fresh-make-up water to close the water balance.

8.1.26 Multi-cells water-cooling tower

The Aspen Plus®v8.4 process model simulation consider modules of draft-packaged water-cooling induced-tower 43.0ºC/30.0ºC/27.0ºC type with capacity for 700.0 m³/hr of water mass flow rate. The model was developed using IAPWS-95 physical property methods for the water-side streams and RKS cubic equation of state with BM alpha function property method to simulate the air-side streams and the heat transfer between the atmospheric air-side and the water-side in the water tower module (CT-TOW blocks). The heat transfer in the gas-side or liquid-side streams in the cooling water equipment users depends on the physical property methods employed in the area in which they are allocated.

The multi-cells water-cooling tower (CT-blocks) provides cooling water to remove heat and adjust the process temperature to appropriate levels. The cooling water is distributed to the cooling water equipment users in the Biomass-to-Mixed alcohols scenarios to:

a) condense and cool-down the top gas product from the absorber (CT-HEA-2) an stripper (CT-HEA-3) columns in the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3);
b) cool down the absorber inlet lean amine aqueous solution (CT-HEA-1) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3);
c) cool-down the sub-cooled and partial-cleaned synthesis gas in the inter-stages (CO-1 and CO-2) of the first-section of compression (intercooler) by integrally-geared three stages centrifugal compressor in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3);
d) cool-down the cleaned synthesis gas in the inter-stage (CO-3) of the second-section of compression (intercooler) by integrally-geared two stages centrifugal compressor in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3);
e) cool-down the CO_2 gas in the inter-stages (CO-1~5) of compression in the integrally-geared six stage centrifugal compressor (inter-cooler and after-cooler) and liquefier the captured CO_2 (CC-HEA-1) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3);
f) condense and cool-down the top gaseous product from the first tray-column (degases) in the three-column double-effect alcohols distillation system (CT-HEA-4) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3);
g) condense the top gaseous product from the second tray-column in the three-column double-effect alcohols distillation system (CT-HEA-5) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3);
h) cool down the refluxed top product (liquid phase) from the second tray-column in the three-column double-effect alcohols distillation system (CT-HEA-6) in

the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3);

i) condense the top gaseous product from the third tray-column in the three-column double-effect alcohols distillation system (CT-HEA-7) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3);
j) cool-down the atmospheric air in the inter-stage (AP-1) and after-stage (AP-HEA-1) (intercooler and after-cooler) of the integrally-geared two stages centrifugal compressor (MAC) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3);
k) cool-down the atmospheric air in the inter-stages (AS-3~6) and after-stage (AS-7) of (intercooler and after-cooler) of the integrally-geared six stages centrifugal compressor (BAC) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3);
l) cool-down the atmospheric air in the after-stage (AS-1) (after-cooler) of the high-efficiency turbo booster in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3);
m) cool-down the high-purity gaseous nitrogen (N_2) in the inter-stages (AS-HEA-1~4) of the gaseous compression side (intercooler) in the high-pressure double-Claude cycle nitrogen liquefier in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2), and Biomass-to-Mixed alcohols (SC3);
n) condense the low-pressure exhausted steam from the condensing section turbine (CEST) employed in the Biomass-to-Mixed alcohols (SC3).

The Aspen Plus®v8.4 process model simulation of water-cooling tower system operating in water recirculation mode determine the requirements of cooling water heat exchanger, make-up of recycled and fresh water, water blowdown, and electric motor drives (fan drivers and pumps). In the model are used the standards design equations as defined in the section 3.9.17 (Water-cooling tower) for the modular single fan-cells arrangement operates as staged mode by sections each with variable-frequency drivers.

As shown in Figure 82, Aspen Plus®v8.4 flowsheet of the simplified first-section of the multi-cells water-cooling tower for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3) which is the same model with modified parameters for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) is composts by: pumps (CT-PUM blocks); fans (CT-EFT streams); water-cooling tower modules (CT-TOW blocks); water-cooling tower basin (CT-SEP blocks); adjust losses (evaporation and drift) and blowdown system (CT-SPL blocks); and spreadsheet calculation of blowdown cycles of concentration (C.O.C) system.

As shown in Figure 83 (a), Aspen Plus®v8.4 flowsheet of the simplified second-section of the multi-cells water-cooling tower, and as shown in Figure 83 (b), Aspen Plus®v8.4 flowsheet of the simplified third section of the multi-cells water-cooling tower for Biomass-to-Methanol (SC1), Biomass-to-Methanol (SC2) and Biomass-to-Methanol (SC3) which is the same model with modified parameters for Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) are composts by: pumps (CT-PUM blocks); fans (CT-EFT streams); water-cooling tower modules (CT-TOW blocks); water-cooling tower basin (CT-SEP blocks); adjust losses (evaporation and drift) and blowdown system (CT-SPL blocks); and spreadsheet calculation of blowdown cycles of concentration (C.O.C) system.

The induced surrounding air exchange convective heat with the hot water in the water-cooling tower (CT-TOW blocks) represented as a simple HeateX exchange block (CT-TOW blocks). The surrounding air is induced upward through the fill (CT-TOW blocks) being heated from 25.0ºC to 40.0ºC. The hot cooling water flow downward through the fill (CT-TOW blocks) been cooled down from 43.0ºC to 30.0ºC.

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) the amount of surrounding air flowing through the fill (CT-TOW blocks) of the first-section of the multi-cells water-cooling tower is determined and controlled by design specification DS-CT-FG-1, design specification DS-CT-FG-2, FORTRAN calculator block CA-CT-FG-4 and FORTRAN calculator block CA-CT-FG-5 varying the mass flow rate (CT-AIR streams) of the surrounding air passing through the fill (CT-TOW blocks) to cooling down the hot water.

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) the amount of surrounding air flowing through the fill (CT-TOW blocks) of the second-section of the multi-cells water-cooling tower is determined and controlled by design specification DS-CT-FG-3 and FORTRAN calculator block CA-CT-FG-6 varying the mass flow rate (CT-AIR streams) of the surrounding air passing through the fill (CT-TOW blocks) to cooling down the hot water.

In the Biomass-to-Mixed alcohols (SC3) the amount of surrounding air flowing through the fill (CT-TOW blocks) of the third section of the multi-cells water-cooling tower is determined and controlled by design specification DS-CT-FG-7 varying the mass flow rate (CT-AIR streams) of the surrounding air passing through the fill (CT-TOW blocks) to cooling down the hot water.

Treated fresh and recycled water as make-up water (WATER FROM TREATMENT PLANT) at atmospheric pressure and 25.0ºC is pumped (simplified by one pump) by make-up pump (CT-PUM-1) to the first-section of the multi-cells water-cooling tower and mixed with the down flow cooled-water at 30.0ºC in the water-cooling tower basin (CT-SEP-1). For the second-section of the multi-cells water-cooling tower make-up water (WATER FROM TREATMENT PLANT) is pumped by make-up pump

(CT-PUM-8) and mixed with the down flow cooled-water at 30.0ºC in the water-cooling tower basin (CT-SEP-2).

For the third section of the multi-cells water-cooling tower in the Biomass-to-Mixed alcohols (SC3) make-up water (WATER FROM TREATMENT PLANT) is pumped by make-up pump (CT-PUM13) and mixed with the down flow cooled-water at 30.0ºC in the water-cooling tower basin (CT-MIX-24).

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) the cooling water available at 27.0ºC (heat sink) for the first-section of the multi-cells water-cooling tower is pumped (CT-PUM-2) to first-section of synthesis gas compression (conditioning), pumped (CT-PUM-3) to co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution, pumped (CT-PUM-5) to CO_2 gas integrally-geared multi-stage centrifugal compressor, pumped (CT-PUM-6) to second-section of synthesis gas compression (conditioning) and pumped (CT-PUM-7) to three-column double-effect alcohols distillation system (ethanol purification).

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) the cooling water available at 27.0ºC (heat sink) for the second-section of the multi-cells water-cooling tower is pumped (CT-PUM-9) to integrally-geared two stages centrifugal compressor (MAC), pumped to (CT-PUM-10) high-efficiency turbo booster, pumped (CT-PUM-11) to integrally-geared centrifugal five stages compressor (BAC), pumped (CT-PUM-12) to high-pressure double-Claude cycle nitrogen liquefier.

In the Biomass-to-Mixed alcohols (SC3) the cooling water available at 27.0ºC (heat sink) for the third section of the multi-cells water-cooling tower is pumped (CT-PUM-14) to CEST condenser.

The cooling water at 27.0ºC is heated by passing through the user equipments to 43.0ºC (tower design limit), the hot water is duct-sent back to the multi-cells water-cooling tower (CT blocks) and discharged inlet into the cooling tower cells (CT-TOW blocks) at 43.0ºC to be cooled in a water closed-loop cycle system. The amount of water necessary for cooling down the equipments at required levels is determined and controlled by a set of design specification (e.g.: DS-CA-TL-1, DS-CA-TL-2, DS-CA-TL-3, DS-CO-TL-1, DS-CO-TL-2, DS-CO-TL-3, DS-PU-TL-1, DS-DS-TL-1, DS-DS-TL-2, DS-DS-TL-3, DS-CT-FL-10, DS-CT-FL-11, DS-CT-FL-12, DS-CT-FL-13, DS-CT-FL-14, DS-CT-FL-15, DS-CT-FL-16, DS-CT-FL-17, DS-CT-FL-19) varying the mass flow rate of cooling water flows through the equipment users. The cooling water is heated at the limit of 43.0ºC (water-cooling tower design) and duct-sent back to the multi-cells water-cooling tower (CT blocks) to be cooled in a water closed-loop cycle system.

Hot water at 43.0ºC is fed in the first, second and third sections of multi-cells water-cooling tower (CT-TOW blocks) to be cooled down to 30.0ºC by direct contact in counter-flow with vertically upward induced (mechanical axial propeller fans) surrounding air through the fill (CT-TOW blocks) at atmospheric pressure and 25.0ºC. The model consider relative humidity of 80.0% and web bulb temperature at about 21.3ºC, which results in a range of 13.0ºC and an approach of 8.7ºC.

Aspen Plus®v8.4 process model simulation of water-cooling tower system considers the water evaporation rate obtained by the Equation 21 and the drift loss rate obtained by the Equation 22. In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3), the equations is employed in the CT-SPL-14 for the first-section of the multi-cells water-cooling tower to determine the CT-EVA-1 and CT-DRI-1 streams by using FORTRAN calculator block CA-CT-LL-1 and in the CT-SPL-23 for the second-section of the multi-cells water-cooling tower to determine the CT-EVA-2 and CT-DRI-2 streams by using FORTRAN calculator block CA-CT-LL-2. In the Biomass-to-Mixed alcohols (SC3) the equations is employed in the CT-SPL-24 for the third section of the multi-cells water-cooling tower to determine the CT-EVA-3 and CT-DRI-3 streams by using FORTRAN calculator block CA-CT-LL-3.

A tower basin blowdown (CT-BLO streams) to remove or reduce the concentration of the impurities developed in the Aspen Plus®v8.4 process model simulation according to Equation 25 as continuous blowdown system. In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) the first-section of the multi-cells water-cooling tower (CT-SPL-14) consider the tower basin blowdown (CT-BLO-1) and blowdown cycles of concentration (C.O.C) determined by using FORTRAN calculator block CA-CT-LL-1 to remove the solids formed (not included in the Aspen Plus®v8.4 process model simulation). In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) the second-section of the multi-cells water-cooling tower (CT-SPL-23) consider the tower basin blowdown (CT-BLO-2) and blowdown cycles of concentration (C.O.C) determined by using FORTRAN calculator block CA-CT-LL-2 to remove the solids formed (not included in the Aspen Plus®v8.4 process model simulation). In the Biomass-to-Mixed alcohols (SC3) the third section of the multi-cells water-cooling tower (CT-SPL-24) consider the tower basin blowdown (CT-BLO-3) and blowdown cycles of concentration (C.O.C) determined by using FORTRAN calculator block CA-CT-LL-3 to remove the solids formed (not included in the Aspen Plus®v8.4 process model simulation).

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) the make-up water (WATER FROM TREATMENT PLANT) is pumped by make-up pump (CT-PUM-1) to the first-section of the multi-cells water-cooling tower basin (CT-SEP-1) and is pumped by make-up pump (CT-PUM-8) to the second-section of the multi-cells water-cooling tower basin (CT-SEP-2). In the Biomass-to-Mixed alcohols (SC3) is pumped by make-up pump (CT-PUM-13) to the third section of the multi-cells water-cooling tower basin (CT-MIX-24).

The make-up water for the multi-cells water-cooling tower is determined based on the water losses by evaporation (CT-EVA streams), drift (CT-DRI streams), and tower basin blowdown (CT-BLO streams), according to Equation 23.

In this research Master's degree, is considered a recovery of 87.0%$_{w/w}$ of the water blowdown after the treatment as available cooling water to reuse/recycle at 27.0ºC. The amount of water recovered is determined by spreadsheet calculation model of the cooling water treatment process according to Equation 24. The discarded water fraction contains a high concentration of impurities (e.g.: minerals and salts), not included in the Aspen Plus$^{®}$v8.4 process model simulation.

The electricity required by the large mechanically driven axial fans (CT-EFT work streams) to induce the surrounding air upward through the fill in the cell-tower module (CT-TOW blocks) are estimated of 63.0 kWh per fan driver (module). The total of electricity required by the fan drivers is based on the number of cells (CT-TOW blocks) that compose the multi-cells water-cooling tower. The electricity consumed by the mechanical drivers in the axial fans (CT-EFT work streams) is estimated based on the Equation 26.

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) the electricity required (CT-EFT-1 work stream) in the first-section of the multi-cells water-cooling tower by the large mechanically driven axial fans (CT-EFT-1 work stream) to induce the surrounding air upward through the fill in the cell-tower module (CT-TOW blocks) is determined and controlled by FORTRAN calculator block CA-CT-EF-1 varying the input value of the CT-EFT-1 work stream according to the number of necessary fans (63.0 kWh per fan driver).

n the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) the electricity required (CT-EFT-2 work stream) in the second-section of the multi-cells water-cooling tower by the large mechanically driven axial fans (CT-EFT-2 work stream) to induce the surrounding air upward through the fill in the cell-tower module (CT-TOW blocks) is determined and controlled by FORTRAN calculator block CA-CT-EF-2 varying the input value of the CT-EFT-2 work stream according to the number of necessary fans (63.0 kWh per fan driver).

In the Biomass-to-Mixed alcohols (SC3) the electricity required (CT-EFT-3 work stream) in the third section of the multi-cells water-cooling tower by the large mechanically driven axial fans (CT-EFT-3 work stream) to induce the surrounding air upward through the fill in the cell-tower module (CT-TOW blocks) is determined and controlled by FORTRAN calculator block CA-CT-EF-3 varying the input value of the CT-EFT-3 work stream according to the number of necessary fans (63.0 kWh per fan driver).

8.1.27 Water cycles

The water cycle balance consider receive water: from treatment plant (BO-L-6) to process make-up water to deaerator unit (HR-DEA-1) in the Biomass-to-Mixed alcohols (SC1); from treatment plant (CO-L-4) to process make-up water to deaerator unit (HR-DEA-1) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); from treatment plant (CA-L-34) to washer packed-column section (CA-WAS-1) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); from treatment plant (WS-L-2) to energy-saving and steam generation system in the HT and LT catalyst WGS reactors at intermediate-pressure level considered in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); from treatment plant (PO-L-1 and PO-L-3) to desuperheater units (PO-MIX-1 and PO-MIX-2) in the Biomass-to-Mixed alcohols (SC1) and Biomass-to-Mixed alcohols (SC2); from treatment plant (GT-L-1) to three-circuit water inter-cooler exchanger (GT-1) in the high-performance sequential combustion full-flow advanced EvGT in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols SC2) and Biomass-to-Mixed alcohols (SC3); from treatment plant (ET-L-6) to low-temperature cooler in the mixed alcohols catalyst-synthesis (ET-3) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); from treatment plant (DS-L-22) to process make-up water to second deaerator unit (PU-DEA-1) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); from treatment plant to first-section of (CT-L-1) and to second section (CT-L-84) of water-cooling tower system in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); and from treatment plant to third section (CT-L-141) of water-cooling tower system in the Biomass-to-Mixed alcohols (SC3).

Also, sends wastewater: to treatment plant (BD-BLO-1) from boiler liquid-phase water blowdown (BD-FLA-1) in the Biomass-to-Mixed alcohols (SC1); to treatment plant (SC-L-12) from the excess of the wastewater recovered in the low-temperature synthesis gas wet cleaning system (SC-SPL-2) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); to disposal (SC-SLUR) from the sludge phase ($50\%_{w/w}$ of water content) removed in the low-temperature synthesis gas wet cleaning system (SC-SPL-2) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); to disposal (CA-L-28) from the reclaimer carbon-based filter (CA-SEP-1) in the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); to treatment plant (CO-BLO-1) from the condenser knock-out drum in the first-section of the synthesis gas compression in the integrally-geared centrifugal three stages compressor (CO-FLA-4) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); to treatment plant (CO-BLO-2) from the condenser knock-out drum in the second-section of the synthesis gas compression in the integrally-geared centrifugal three stages compressor (CO-FLA-7) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); to treatment plant (WS-BLO-3) from condensed water recovery and recycle system in the energy-saving and steam generation system in the HT and LT catalyst WGS reactors at intermediate-pressure level (WS-SEP-1) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); to treatment plant (GT-BLO-2) from the condenser knock-out drum (GT-FLA-1) in the high-performance sequential combustion full-flow advanced EvGT in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); to treatment plant (GT-BLO-1) from the buffer/equalizer inlet tank (GT-BUF-1) in the high-performance sequential combustion full-flow advanced EvGT in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); to treatment plant (CC-BLO-1) from the condenser knock-out drum in the CO_2 gas integrally-geared centrifugal six stages compressor (CC-FLA-7) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); to treatment plant (CT-BLO-1) from water-cooling tower blowdown (CT-SPL blocks) in the first-section of the multi-cells water-cooling tower in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); to treatment plant (CT-BLO-2) from water-cooling tower blowdown (CT-SPL blocks) in the second-section of the multi-cells water-cooling tower in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); to treatment plant (CT-BLO-3) from water-cooling tower blowdown (CT-SPL blocks) in the third section of the multi-cells water-cooling tower in the Biomass-to-Mixed alcohols (SC3); to treatment plant (GU-BLO-1) from condenser knock-out drum in the regenerative ZnO/CuO-based guard bed adsorber (GU-SEP-1) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); to treatment plant (AP-BLO-1) from condenser knock-out drum in the integrally-geared two stages centrifugal compressor (MAC) (AP-FLA-1) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); to treatment plant (AP-BLO-2) from condenser knock-out drum in the integrally-geared two stages centrifugal compressor (MAC) (AP-FLA-2) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); to treatment plant (AS-BLO-2) from condenser knock-out drum in the integrally-geared six stages centrifugal compressor (BAC) (AS-FLA-1) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); and to treatment plant (AS-BLO-1) from condenser knock-out drum after the high-efficiency turbo booster compressor (AS-COM-1) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3).

Process steam/water losses occur due: water evaporation or condensation (PO-BLO-1) in equipments and pipe lines (PO-SPL-1) discharge 5.0%$_{w/w}$ of the process steam at 2.5 bar (PO-BLO-1) in the Biomass-to-Mixed alcohols (SC1); water evaporation or condensation (PU-SPL-5) in equipments and pipe lines (PU-SPL-5) discharge 5.0%$_{w/w}$ of the process steam at 2.5 bar (ET-VEN-2) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); water evaporation (ET-VEN-1) in equipments and pipe lines (ET-SPL-1) discharge 2.0%$_{w/w}$ of the high-pressure steam (ET-SPL-1) generated in the high-pressure steam drum (ET-FLA-1) of the isothermal water-cooled fixed bed catalytic-synthesis reactor (ET-REA-1) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); treatment of boiler water blowdown discharge 15.0%$_{w/w}$ of the purged water (BD-BLO-1) (recovery and recycle 85.0%$_{w/w}$ of the water blowdown) in the Biomass-to-Mixed alcohols (SC1); sludge disposal discharge 100.0%$_{w/w}$ of the water content in the sludge phase (SC-SLUR) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); treatment of the excess of recovered water in the low-temperature synthesis gas wet cleaning system discharge 5.0%$_{w/w}$ of the water (SC-L-12) (recovery and recycle 95.0%$_{w/w}$ of the recovered water) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); filtered amine residue disposal discharge 100.0%$_{w/w}$ of the water content in the residue fraction (CA-L-29) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); treatment of the water from the condenser knock-out drums discharge 5.0%$_{w/w}$ of the water (CO-BLO-1, CO-BLO-2, WS-BLO-1, WS-BLO-2, WS-BLO-3, GU-BLO-1, CC-BLO-1, GT-BLO-1, GT-BLO-2, LG-BLO-1, DH-BLO-1, AP-BLO-1, AP-BLO-2, AS-BLO-1, and AS-BLO-2 streams) (recovery and recycle of 95.0%$_{w/w}$ of the condensed water) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); water evaporation (CT-EVA-1) and drift (CT-DRI-1) in the first-section of the water-cooling tower discharge 100.0%$_{w/w}$ of the water-stream in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); water evaporation (CT-EVA-2) and drift (CT-DRI-2) in the second-section of the water-cooling tower discharge 100.0%$_{w/w}$ of the water-stream in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); water evaporation (CT-EVA-3) and drift (CT-DRI-3) in the third-section of the water-cooling tower discharge 100.0%$_{w/w}$ of the water-stream in the Biomass-to-Mixed alcohols (SC3); treatment of the first-section of the water-cooling tower blowdown discharge 13.0%$_{w/w}$ of the purged water (CT-BLO-1) (recovery and recycle of 87.0%$_{w/w}$ of the water blowdown) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); treatment of the second-section of the water-cooling tower blowdown discharge 13.0%$_{w/w}$ of the purged water (CT-BLO-2) (recovery and recycle of 87.0%$_{w/w}$ of the water blowdown) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3); treatment of the third-section of the water-cooling tower blowdown discharge

13.0%$_{w/w}$ of the purged water (CT-BLO-3) (recovery and recycle of 87.0%$_{w/w}$ of the water blowdown) in the Biomass-to-Mixed alcohols (SC3).

As shown in Figure 95, the first deaerator unit (HR-DEA-1) in the Biomass-to-Mixed alcohols (SC1) receive steam from the flash vessel (BD-FLA-1) at 1.4 bar (deaerator pressure) and 109.0ºC (BD-G-1), steam at 2.5 bar and 130.0ºC (HR-G-15) from the HRSG LP circuit-level, water at 2.2 bar and 123.0ºC from the stripper reboiler (CA-REB-1) in the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution (CA blocks), pre-heated fresh-water at 1.4 bar and 43.0ºC (BO-L-8) as part of the make-up water (WATER FROM TREATEMENT PLANT) required in the first deaerator unit (HR-DEA-1), water from the 1G sugarcane biorefinery processes at 2.5 bar and 90.0ºC (PO-L-7 and PO-L-8), heated make-up raw water (WATER FROM TREATEMENT PLANT) at 1.4 bar and 105.0ºC (HR-L-13) closing the process water loop-cycle. Also as shown in Figure 95 the first deaerator unit (HR-DEA-1) in the Biomass-to-Mixed alcohols (SC1) send degassed and conditioned water at 1.4 bar and 105.0ºC to solid-fuel fired boiler (1G-thecnology) (HR-L-19), to HRSG system (HR-L-16), to high-temperature vertical CSC (HR-L-18), to direct-contact desuperheater units (HR-L-17) and to second deaerator unit (HR-L-17).

As shown in Figure 96, the first deaerator unit (HR-DEA-1) in the Biomass-to-Mixed alcohols (SC2) receive steam at 2.5 bar and 130.0ºC (HR-G-13) from the HRSG LP circuit-level, condensed water from the 1G sugarcane biorefinery processes at 2.5 bar and 90.0ºC (PO-L-6 and PO-L-7) and heated make-up raw water (WATER FROM TREATEMENT PLANT) at 1.4 bar and 105.0ºC (HR-L-13) closing the process water loop-cycle. Also as shown in Figure 96 the first deaerator unit (HR-DEA-1) in the Biomass-to-Mixed alcohols (SC2) sends degassed and conditioned water at 1.4 bar and 105.0ºC to HRSG system (HR-L-17), to high-temperature vertical CSC (HR-L-19), to low-temperature vertical CSC (HR-L-15) and to direct-contact desuperheater units (HR-L-18).

As shown in Figure 97, the first deaerator unit (HR-DEA-1) in the Biomass-to-Mixed alcohols (SC3) receive steam at 2.5 bar and 130.0ºC (HR-G-13) from the HRSG LP circuit-level, heated make-up raw water (WATER FROM TREATEMENT PLANT) at 1.4 bar and 105.0ºC (HR-L-15) and condensed exhaust-steam at 1.4 bar and at about 48.0ºC (HR-L-14) from the CEST condenser closing the process water loop-cycle. Also as shown in Figure 97 the first deaerator unit (HR-DEA-1) in the Biomass-to-Methanol (SC3) sends degassed and conditioned water at 1.4 bar and 105.0ºC to HRSG system (HR-L-17), to high-temperature vertical CSC (HR-L-18) and to low-temperature vertical CSC (HR-L-19).

As shown in Figure 92, the second deaerator unit (PU-DEA-1) in the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) receive water at 2.3 bar and 123.0ºC (PU-L-10) from the distillation first-column reboiler (PU-REB-1) in the crude mixed alcohols forerun degassing first tray-column (PU-COL-1), water at 5.7 bar and 140.0ºC (PU-L-11) (generate steam at 2.3 bar) from the intermediate-pressure heater (PU-HEA-1) and from the distillation third-column reboiler (DS-REB-2) in the mixed alcohols low-pressure distillation second tray-column (DS-COL-1), water at 2.3 bar and 105.7ºC (DS-L-30) from the distillation third-column reboiler (DS-REB-2), heated make-up raw water (WATER FROM TREATEMENT PLANT) at 2.3 bar and 105.7ºC (DS-L-30) from the higher-molecular alcohols sub-cooler exchanger (DS-HEA-1), heated make-up raw water (WATER FROM TREATEMENT PLANT) at 2.3 bar and 105.7ºC (DS-L-30) from the ethanol sub-cooler exchanger (DS-HEA-2), water at 2.0 bar and 105.0ºC (PU-L-14) from the first deaerator unit (HR-DEA-1) as reticulating water closing the process water loop-cycle.

The amount of low-pressure steam at 2.5 bar and 130.0ºC from the HRSG LP circuit-level destined to first deaerator unit (HR-DEA-1) is determined and controlled by design specification DS-HR-TL-1 varying the water/steam mass flow rate in the HRSG LP circuit-level and estimate-used into the first deaerator unit (HR-DEA-1) as degassing agent. Low-pressure steam at 2.5 bar and 130.0ºC is used mainly to remove dissolved O_2 and CO_2 content in the process water cycle by raises the deaerator water temperature (make-up water and process water condenser return) to 1.4 bar and 105.0ºC in the first deaerator unit (HR-DEA-1).

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) the make-up water supply to the first deaerator unit (HR-DEA-1) from the water treatment plant is based on the mass balance of the process steam/water losses and recycled water cycle. The amount of water required in the Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) is determined and controlled by design specification DS-CO-FL-1 and design specification DS-HR-FL-1 varying the mass flow rate of water (WATER FROM TREATMENT PLANT) fed into the first deaerator unit (HR-DEA-1). The amount of water required in the Biomass-to-Mixed alcohols (SC1) is determined and controlled by design specification DS-CO-FL-1, design specification DS-HR-FL-1 and controlled by design specification DS-AE-FL-1 varying the mass flow rate of water (WATER FROM TREATMENT PLANT) fed into the first deaerator unit (HR-DEA-1).

In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) the make-up water supply to the second deaerator unit (PU-DEA-1) from the water treatment plant is based on the heat exchanger requirements to cool down the product lines at about 35.0ºC before storage tanks by the ethanol sub-cooler exchanger (DS-HEA-2) and higher-molecular alcohols sub-cooler exchanger (DS-HEA-1). The amount of cooling water (WATER FROM TREATMENT PLANT) flowing through the ethanol sub-cooler exchanger (DS-HEA-2) is controlled by design specification DS-DS-FL-4 being heated to 100.0ºC. The amount of cooling water (WATER FROM TREATMENT PLANT) flowing through the higher-molecular alcohols sub-cooler exchanger (DS-HEA-1) is controlled by design specification DS-DS-FL-3 being heated to 110.0ºC.

Make-up water supply to the water-cooling tower system from the water treatment plant is based on the mass balance of the water-cooling tower system considering losses associated with evaporation, drift and blowdown. In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) the make-up water fed (CT-L-1) into the first-section of the water-cooling tower system is controlled by design specification DS-CT-FL-1 varying the mass flow rate of water (WATER FROM TREATMENT PLANT). In the Biomass-to-Mixed alcohols (SC1), Biomass-to-Mixed alcohols (SC2) and Biomass-to-Mixed alcohols (SC3) the make-up water fed (CT-L-84) into the second-section of the water-cooling tower system is controlled by design specification DS-CT-FL-6 varying the mass flow rate of water (WATER FROM TREATMENT PLANT). In the Biomass-to-Mixed alcohols (SC3) the make-up water fed (CT-L-141) into the third section of the water-cooling tower system is controlled by design specification DS-CT-FL-18 varying the mass flow rate of water (WATER FROM TREATMENT PLANT)

8.1.28 Make-up water and water treatments

The mass flow rate of make-up water to treatment plant (fresh water) is determined using spreadsheet calculation model by a global mass balance of the complete water cycle considering the treatment of the wastewater in the wastewater treatment plant (not simulated) estimated according the spreadsheet calculation model of the water cycle (losses, recycles an reuse model).

Four distinct water use types are required for the Biomass-to-Mixed alcohols scenarios, classified as:

a) make-up water for water-cooling tower system: The fresh-water required by the cooling water cycle is defined by the mass flow rate of the evaporation, drift, and tower basin blowdown losses (not recovered);
b) make-up water for process water cycle: The fresh-water required by the process water cycle is defined by the mass flow rate of the evaporative process and condensation losses in pipeline and equipments, by vent streams, blowdown losses and condensate knock-outs (not recovered);
c) make-up water for high-performance sequential combustion full-flow advanced EvGT water cycle: The fresh-water required by the EvGT cooling water circuits and humidifier tower can be defined by the mass flow rate of the evaporative process and entrained vapor in the humidified air in the dual-chamber system;
d) make-up water for high-pressure steam generation drum: The fresh-water required by the isothermal water-cooled fixed bed catalytic-synthesis reactor cooling water circuit can be defined by the mass flow rate of the high-pressure steam generated off-drum at saturation conditions and the steam vent-losses in the high-pressure steam generation drum.

The recovered water fraction after the wastewater treatment to recycle/reuse is considered as “fresh” water (subtracting in the quantity of fresh-water intake) and the water fraction discharged (not recovered) with the impurities removed in the wastewater treatment process a water losses. The water treatment is simplified by the follow categories:

a) make-up raw water treatment: considers only the make-up of fresh-water obtained from the global mass balance of the complete water cycle, taking into account the recycle and reuse of available water;
b) cooling water treatment (maintenance): considers the make-up raw water obtained from the mass balance of the water tower cycle and the water circulating in the water tower cycle in closed loop-cycle (water maintenance), taking into account the recycle and reuse of available water;
c) process water treatment (maintenance): considers the make-up raw water obtained from the mass balance of the water process cycle and the water circulating in the water process cycle in closed loop-cycle (water maintenance), taking into account the recycle and reuse of available water;
d) cooling water treatment for water injection in the EvGT sequential burning chambers: considers the make-up raw water obtained from the mass balance of the cooling water circuits and the water injected by the humidified air in the EvGT sequential burning chambers.

The chemicals compounds and their consumption for treating water are determined by spreadsheet calculation model according to the type of water treatment required (make-up water, process water, cooling water and water special treatment. The water treatment is based on the water treatment processes available in the Ecoinvent 3 library (unit) in SimaPro$^{®}$v.7.3.3 software and in the water treatment process defined by division of AIB of the CTBE/CNPEM for the 1G sugarcane biorefinery.

Table 24 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Mixed alcohols routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Mixed alcohols route scenarios		
	SC1	SC2	SC3
Thermochemical-biorefinery			
Cane stalks (tonnes/hr) 4.0 Mtc (basis)	503.018	503.018	503.018
Sugar production (tonnes/hr)	25.559	25.559	25.559
Anhydrous ethanol production - 1G sugarcane biorefinery (tonnes/hr)	21.013	21.013	21.013
Anhydrous ethanol production - Thermochemical route(tonnes/hr)	13.894	12.946	16.799
Mixed higher-molecular alcohols production (tonnes/hr)	2.118	1.975	2.564
High-purity liquid argon production (tonnes/hr)	0.804	0.788	0.788
High-purity liquid nitrogen production (tonnes/hr)	108.643	130.915	130.915
Electricity exported to the electric power grid (MWh)	none	none	19.984
Installed power generation capacity (MW)	102.747	117.962	125.975
Electricity consumed by the thermochemical-biorefinery (MWh) [m]	102.747	117.962	105.991
Available raw biomass [a]			
Sugarcane bagasse available for use (tonnes/hr)	133.150	133.150	133.150
Sugarcane straw available for use (tonnes/hr)	42.279	42.279	42.279
Sugarcane bagasse imported (tonnes/hr)	none	none	87.396
Sugarcane bagasse reserve (tonnes/hr)	6.658	6.658	13.316
Sugarcane bagasse moisture content (%)	50.0	50.0	50.0
Sugarcane straw moisture content (%)	15.0	15.0	15.0
Consumption of sugarcane bagasse in the Biomass-to-Mixed alcohols route (tonnes/hr)	92.340	126.492	126.492
Consumption of sugarcane straw in the Biomass-to-Mixed alcohols route (tonnes/hr)	42.279	42.279	42.279
Consumption of sugarcane bagasse in the 1G-CHP/EBPST system (tonnes/hr)	34.153	none	81.376
Consumption of sugarcane straw in the 1G-CHP/EBPST system (tonnes/hr)	none	none	none
Dry biomass consumed in the Biomass-to-Mixed alcohols route (tonnes/hr) [a]	81.676	98.764	98.764
Surplus biomass (tonnes/hr) [a]	none	none	none
LHV_{AR} of bagasse (MJ/kg)	7.45	7.45	7.45
LHV_{AR} of straw (MJ/kg)	17.57	17.57	17.51
1G sugarcane biorefinery with annexed ethanol distillery (int)			
CHP/ST system	CHP/EBPST (SC1)	none	CHP/EBPST (SC1)
Integration mode	Integrated	Integrated	Standalone

Table 24 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Mixed alcohols routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Mixed alcohols route scenarios		
	SC1	**SC2**	**SC3**
1G sugarcane biorefinery with annexed ethanol distillery [(int)]			
Electricity required by the 1G sugarcane biorefinery (MWh)	15.0	15.0	15.0
Steam demand at 6.0 bar (dehydration) (tonnes/hr)	14.175	14.175	14.175
Steam demand at 2.5 bar (process) (tonnes/hr)	184.945	184.945	184.945
Biomass handling and sizing for gasification process			
Electricity required for sugarcane bagasse handling and milling (MWh)	2.031	2.783	2.783
Electricity required for sugarcane straw handling and milling (MWh)	0.334	0.344	0.344
Biomass multi-step drying process and control particulate emissions [a]			
Thermal energy required by the biomass dryers (GJ/hr) [a]	614.2	820.5	820.5
HHV_{AR} of biomass mix (MJ/kg) [a]	17.02	17.02	17.02
LHV_{AR} of biomass mix (MJ/kg) [a]	15.52	15.51	15.51
LHV_{db} of biomass mix (MJ/kg) [a]	17.53	17.53	17.53
Biomass mix moisture (%) [a]	10.0	10.0	10.0
Gasification of biomass in an atmospheric CFB directly-heated gasifier [a]			
Gasification agents	Air / Oxygen	Air / Oxygen	Air / Oxygen
High-purity oxygen to gasifier (tonnes/hr)	32.185	38.883	38.884
Steam at 2.5 bar flow into the gasifier (tonnes/hr)	35.301	42.661	42.661
Raw synthesis gas temperature (ºC)	850.0	850.0	850.0
Oxygen agent inlet temperature (ºC)	120.0	120.0	120.0
Steam agent inlet temperature (ºC)	150.0	150.0	150.0
Equivalence ratio (ER_{AIR})	0.297	0.297	0.297
Steam-to-biomass ratio (STBR)	0.50	0.50	0.50
Carbon conversion (%)	98.0	98.0	98.0
Hydrogen mol flow rate (mol/hr)	2,645.1	3,196.6	3,196.6
Monoxide carbon mol flow rate (mol/hr)	1,815.1	2,193,7	2,193.4
H_2/CO ratio	1.457	1.457	1.457
Gasifier cold-gas efficiency (%) [b]	76.31	76.32	76.32
Gasifier hot-gas efficiency (%) [b]	91.74	91.76	91.76

Table 24 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Mixed alcohols routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Mixed alcohols route scenarios		
	SC1	SC2	SC3
Gasification of biomass in an atmospheric CFB directly-heated gasifier [a]			
Synthesis gas flow mass rate (tonnes/hr)	154.902	187.303	187.303
HHV_{db} of synthesis gas (MJ/kg)	11.14	11.14	11.14
LHV_{db} of synthesis gas (MJ/kg)	10.06	10.06	10.06
Generation of bottom particulate material (tonnes/hr) [f]	4.305	5.040	5.040
Olivine mass flow rate - make-up (kg/hr)	860.910	956.649	956.649
MgO mass flow rate - make-up (kg/hr)	225.218	250.2641	250.2641
Fines-particulate matters removed by multi-cyclone system (kg/hr)	116.494	144,529	144,546
Syngas cooling and heat recovery			
Intermediate-pressure steam at 23 bar generated by the HT-CSC (tonnes/hr)	48.055	58.745	52.546
Intermediate-pressure steam temperature (ºC)	351.4	351.4	480.0
Low-pressure steam at 2.5 bar generated by the LT-CSC (tonnes/hr)	35.301	42.661	42.661
Low-pressure steam temperature (ºC)	150.0	150.0	150.0
Synthesis gas temperature after the HT-CSC (ºC)	415.5	411.0	415.5
Synthesis gas temperature after the LT-CSC (ºC)	124.0	111.0	124.0
Low-temperature synthesis gas wet cleaning system			
Recirculation of water in spray scrubber (tonnes/h)	2.463	1.341	2.978
Recirculation of water in condenser cooler (tonnes/h)	1024.128	1190.6063	1238.738
Electricity required by the blower (MWh)	1.039	1.257	1.257
Particulate removal by spray scrubber, condenser cooler and venturi system (kg/hr)	46.0	63.0	63.0
Persistent fine particles removal by WESP (kg/hr)	16.0	21.0	21.0
Generation of slurry (kg/hr)	594.252	710.205	733.498
Excess of water sent off-site to wastewater treatment plant (tonnes/hr)	27.573	33.337	33.256
Synthesis gas temperature after the wet cleaning system (ºC)	50.0	50.0	50.0
Synthesis gas compression (conditioning)			
Number of compression sections (sec)	2	2	2
Number of compression stages - sec 1	3	3	3
Number of compression stages - sec 2 (2 by compressor and 1 by turbo-compressor)	2+1	2+1	2+1
Pressure of the cooled synthesis gas to HT-WGS / LT-WGS and EvGT (bar)	24.0	24.0	24.0

Table 24 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Mixed alcohols routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Mixed alcohols route scenarios		
	SC1	**SC2**	**SC3**
Synthesis gas compression (conditioning)			
Pressure of the conditioned synthesis gas to mixed alcohols catalytic-synthesis (bar)	87.0	87.0	87.0
Synthesis gas mass flow rate to compress - sec 1 (tonnes/hr)	126.711	153.205	153.193
Synthesis gas mass flow rate to compress - sec 2 (tonnes/hr)	70.542	66.152	85.258
Condensed water knock-out to wastewater treatment plant - sec 1 (tonnes/hr)	11.729	14.180	14.180
Condensed water knock-out to wastewater treatment plant - sec 2 (tonnes/hr)	none	none	none
Electricity required to cooled-synthesis gas compression - sec 1 (MWh)	18.396	22.241	22.240
Destination of the intermediate-pressure synthesis gas produced [i]			
Electricity required to synthesis gas final compression - sec 2 (MWh)	5.004	4.680	6.049
Electricity recovered by first-turbo booster expand light-gas - sec 2 (MWh)	2.157	2.013	2.593
Fraction destined to catalyst WGS system for adjust the hydrogen carbon ratio for mixed alcohols catalyst-synthesis (%) [n]	5.0	5.0	5.0
Fraction destined directly to EvGT to thermal and electrical energy supply (%) [g]	none	23.80	none
Fraction destined directly to CO_2 and H_2S co-capture system (%) [h]	95.0	71.20	95.0
HT and LT catalyst WGS reactors at intermediate-pressure level [n]			
Catalyst type for HT catalyst WGS reactor	Fe_2O3/Cr_2O_3 MgO	Fe_2O_3/Cr_2O_3 MgO	Fe_2O_3/Cr_2O_3 MgO
Catalyst type for LT catalyst WGS reactor	Zn-CuO/Al_2O_3	Zn-CuO/Al_2O_3	Zn-CuO/Al_2O_3
Mass of Fe_2O_3/Cr_2O_3 MgO catalyst load (tonnes)	1.551	1.875	1.803
Mass of Zn-CuO/Al_2O_3 catalyst load (tonnes)	0.233	0.564	0.701
Fe_2O_3/Cr_2O_3 MgO catalyst lifetime (low activity) (years)	4	4	4
Zn-CuO/Al_2O_3 catalyst lifetime (low activity) (years)	2	2	2
HT-WGS reactor nominal temperature (ºC)	300.0	300.0	350.0
HT-WGS reactor nominal temperature (ºC)	230.0	230.0	230.0
Synthesis gas pressure inlet into the WGS system (bar)	23.0	23.0	23.0
Steam to carbon monoxide molar ratio	4	4	4
Consumption of intermediate-pressure steam (tonnes/hr)	4.575	5.519	5.194
Intermediate-pressure steam temperature (ºC)	351.4	351.4	480.0

Table 24 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Mixed alcohols routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Mixed alcohols route scenarios		
	SC1	SC2	SC3
WGS energy-saving and steam generation [n]			
Mass flow rate of recovered water by cooling/condensing vapor content in the main gas stream (tonnes/hr)	5.091	6.101	6.159
Make-up raw water to cooling and recovery heat system (tonnes/hr)	18.018	13.018	17.792
Water blowdown to wastewater treatment plant (tonnes/hr)	1.913	1.913	3.093
Steam generation in low-pressure circuit (tonnes/hr)	14.850	14.850	21.805
Temperature of low-pressure steam generated (bar)	130.0	130.0	130.0
Pressure of the low-pressure steam generated - for use as process steam (bar)	2.5	2.5	2.5
Steam generation in intermediate-pressure circuit - to WGS system (tonnes/hr)	2.356	2.356	6.012
Temperature of the intermediate-pressure steam generated - to WGS system (bar)	435.0	435.0	420.0
Pressure of the intermediate-pressure steam generated - to WGS system (bar)	23.0	23.0	23.0
Synthesis gas temperature inlet the system	174.0	176.0	177.0
Synthesis gas temperature outlet the system	40.0	40.0	40.0
Co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution			
Synthesis gas pressure inlet in the absorber (bar)	22.0	22.0	22.0
Pressure of acid gas flow-out the desorber (bar)	1.7	1.7	1.7
Acid gas removal (captured) (tonnes/hr)	68.662	65.480	82.972
CO_2 removal efficiency (%)	96.0	96.0	96.0
H_2S content in the acid gas stream ($\%_{mol}$)	120 PPM	115 PPM	119 PPM
MDEA concentration ($\%_{w/w}$)	33.0	33.0	33.0
PZ concentration ($\%_{w/w}$)	5.0	5.0	5.0
Consumption of MDEA (kg/hr)	282.615	269.399	341.790
Consumption of PZ (kg/hr)	42.926	41.277	56.358
Lean MDEA/PZ aqueous solution mass flow rate (tonnes/hr) [d]	476.629	453.982	574.999
Consumption of thermal energy by the stripper reboiler (GJ/hr)	87.308	83.555	104.356
Fresh cool-make-up water to synthesis gas washer (kg/hr)	1350.0	1279.0	1617.0
Excess of water sent to wastewater treatment plant (tonnes/hr)	none	none	none
Filtered residues sent to waste treatment plant and final disposal (kg/hr)	421.665	401.959	509.745
Cooling water required by the system (tonnes/hr)	1259.762	1205.687	1504.228

Table 24 – Aspen Plus® v8.4 simulation parameters (input and output) of Biomass-to-Mixed alcohols routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Mixed alcohols route scenarios		
	SC1	SC2	SC3
CO_2 compression and storage/use (geological storage)			
Pressure required to liquefier CO_2 and to injection (bar)	75.0 / 150.0	78.0 / 150.	75.0 / 150.
Final generation of Liquid CO_2 to injection (reservoir)	67.414	64.290	81.464
Number of compression stages (+1 liquid pump stage)	6+1	6+1	6+1
Condensed water knock-out to wastewater treatment plant (tonnes/hr)	1.247	1.190	1.507
Consumption of electricity to CO2 compression/liquefaction and injection (MWh)	5.745	5.478	6.942
Regenerative ZnO/CuO-based guard bed adsorber system			
Adsorbed compounds (reduction)	H_2S; COS;SO_x; NO_x;HCl;Cl_2;CO_2	H_2S; COS;SO_x; NO_x;HCl;Cl_2;CO_2	H_2S; COS;SO_x; NO_x;HCl;Cl_2;CO_2
Catalyst bed fraction for selective removal of sulfur compounds	70% of ZnO	70% of ZnO	70% of ZnO
Catalyst bed fraction for selective removal of chlorine compounds	30% of CuO	30% of CuO	30% of CuO
ZnO/CuO catalyst lifetime (low activity) (years)	1 / 1	1 / 1	1 / 1
Mass of ZnO catalyst load (tonnes)	9.566	8.916	8.916
Mass of CuO catalyst load (tonnes)	4.099	3.821	3.821
Adsorption temperature (adsorber) (ºC)	38.0	38.0	38.0
Desorption temperature (desorber) (ºC)	350.0	350.0	350.0
Adsorption pressure (adsorber) (ºC)	22.0	22.0	22.0
Desorption pressure (desorber) (ºC)	5.0	5.0	5.0
Mass flow rate of synthetic air from ASU to partial catalyst bed regeneration (kg/hr) [j]	621.293	576.86	755.355
Desorber flue-gas mass flow rate (kg/hr)	779.204	725.258	946.390
Condensed water mass flow rate knock-out to wastewater treatment plant (kg/hr)	242.071	226.559	292.635
Capture efficiency of sulfur compounds (%)	99.0	99.0	99.0
Capture efficiency of chlorine compounds (%)	80.0 / 95.0	80.0 / 95.0	80.0 / 95.0
Capture efficiency of nitrogen compounds (%)	2.0	2.0	2.0
CO_2 removal efficiency (%)	3.0	3.0	3.0
Hydrogen recovery by four-bed PSA system			
Operational mode	Differential loading pressure	Differential loading pressure	Differential loading pressure
Number of process steps	four-bed process	four-bed process	four-bed process
Adsorbed compounds [k]	Low polarity	Low polarity	Low polarity

Table 24 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Mixed alcohols routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Mixed alcohols route scenarios		
	SC1	SC2	SC3
Hydrogen recovery by four-bed PSA system			
Zeolite catalyst bed fraction (%)	60.0	60.0	60.0
Alumina catalyst bed fraction (%)	5.0	5.0	5.0
Charcoal catalyst bed fraction (%)	35.0	35.0	35.0
Catalyst bed materials lifetime (low activity) (years)	2 / 1 / 1	2 / 1 / 1	2 / 1 / 1
Mass of Zeolite catalyst load (tonnes)	22.213	24.320	28.885
Mass of alumina catalyst load (tonnes)	1.866	2.043	2.426
Mass of charcoal catalyst load (tonnes)	12.951	14.180	16.841
Adsorption pressure (bar)	22.0	22.0	22.0
Desorption and regeneration pressure (bar)	5.0	5.0	5.0
Hydrogen recovery efficiency (%)	98.0	98.0	98.0
Pressurized light-gas inlet mass flow rate (tonnes/hr)	23.398	24.720	28.468
Mass flow rate of hydrogen to EvGT (tonnes/hr)	1.198	1.312	1.562
Mass flow rate of light-gas with low hydrogen content (tonnes/hr)	22.220	23.409	26.780
Condensed water mass flow rate knock-out to wastewater treatment plant (kg/hr)	232.981	217.081	280.358
mixed alcohols catalytic-synthesis			
Catalytic-synthesis type	one-step	one-step	one-step
Catalytic-reactor type	Fixed-bed reactor	Fixed-bed reactor	Fixed-bed reactor
Reactor cooling mode	Water-cooled	Water-cooled	Water-cooled
Commercial catalyst type	Mo based catalyst	Mo based catalyst	Mo based catalyst
Catalyst series	Sulfided K-Co-Mo/C	Sulfided K-Co-Mo/C	Sulfided K-Co-Mo/C
Sulfided Co-K-Mo/C catalyst lifetime (years)	4	4	4
Mass of Sulfided Co-K-Mo/C catalyst load (tonnes)	52.060	133.292	196.660
Crude mixed alcohols productivity (g/kg_{cat} /hr)	350.000	350.000	350.000
Synthesis gas inlet temperature in the water-cooled reactor (ºC)	300.0	300.0	300.0
Synthesis gas inlet pressure in the water-cooled reactor (ºC)	86.0	86.0	86.0
Temperature of the raw gas products after the water-cooled reactor (ºC)	350.0	350.0	350.0
Hydrogen to carbon monoxide ratio (SN_R) / H_2/CO ratio	1.30	1.30	1.30
Multi-pass CO conversion (%)	59.39	59.43	59.41

Table 24 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Mixed alcohols routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Mixed alcohols route scenarios		
	SC1	SC2	SC3
mixed alcohols catalytic-synthesis			
Multi-pass H_2 conversion (%)	47.19	47.23	47.19
Inlet mass flow rate of conditioned synthesis gas in the water-cooled reactor (tonnes/hr)	71.475	67.036	86.405
Mass flow rate of crude mixed alcohols produced at 82.0 bar (tonnes/hr)	19.325	18.019	23.383
Raw gas products condense pressure (bar)	82.0	82.0	82.0
Raw gas products condense temperature (ºC)	50.0	50.0	50.0
Fraction of unconverted syngas after gas/liquid separation phases (light-gas) (%)	86.94	86.99	86.93
Unconverted gas mass flow rate (tonnes/hr)	49.017	10.477	16.800
Fraction of the unconverted gas recycled back to conditioning for new pass in the mixed alcohols catalyst-synthesis (%)	45.08	50.72	45.16
Electricity recovered by first-turbo booster expand light-gas (MWh)	2.157	2.013	2.593
Electricity recovered by second-turbo booster expand light-gas (MWh)	0.199	0.194	0.251
Electricity recovered by third-turbo booster expand light-gas (MWh)	0.161	0.152	0.197
Saturated water and steam drum pressure (bar)	85.2	85.2	85.2
Temperature of the high-pressure saturated steam generated (ºC)	299.4	299.4	299.4
High-pressure saturated steam mass flow rate (tonnes/hr)	24.674	23.153	64.007
Pressure of the intermediate-pressure steam generated (bar)	6.0	6.0	6.0
Pressure of the intermediate-pressure steam generated (bar)	6.0	6.0	6.0
Temperature of the intermediate-pressure steam generated (ºC)	160.0	160.0	160.0
Intermediate-pressure steam mass flow rate - synthesis-products water cooler (tonnes/hr)	9.062	8.448	10.949
Pressure of low-pressure steam generated (bar)	2.5	2.5	2.5
Temperature of low-pressure steam generated (ºC)	130.0	130.0	130.0
Mass flow rate of low-pressure steam - reactor heat exchange (tonnes/hr)	30.931	28.559	none
Mass flow rate of low-pressure steam - product gas heat exchange (tonnes/hr)	9.062	8.450	10.949
Three-column double-effect alcohols distillation system (ethanol purification)			
Distillation columns layout	Three-column / molecular sieve	Three-column / molecular sieve	Three-column / molecular sieve
Ethanol quality	Anhydrous	Anhydrous	Anhydrous
Ethanol purity ($\%_{mol}$)	99.50	99.50	99.50
First- column	Stabilizer degassing	Stabilizer degassing	Stabilizer degassing

Table 24 – Aspen Plus$^{®}$v8.4 simulation parameters (input and output) of Biomass-to-Mixed alcohols routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Mixed alcohols route scenarios		
	SC1	SC2	SC3
Three-column double-effect alcohols distillation system (ethanol purification)			
Second-column	Crude-alcohol	Crude-alcohol	Crude-alcohol
Third column	Methanol	Methanol	Methanol
Number of stages of the degassing column	20	20	20
Number of stages of the crude alcohol distillation column	60	55	55
Number of stages of the methanol distillation column	70	70	70
Pressure in the top of the degassing column (bar)	3.70	3.70	3.70
Pressure in the top of the crude alcohol column (bar)	2.60	2.60	2.60
Pressure in the top of the methanol column (bar)	2.38	2.38	2.38
Temperature of the top-product in the second-column (ºC)	102.2	102.2	102.2
Temperature of the top-product in the third-column (ºC)	87.8	87.8	87.8
Crude mixed alcohols mass flow rate (tonnes/hr)	19.362	18.221	23.645
Mass flow rate of light-end gases (tail-gas) from degassing column (tonnes/hr)	1.577	1.629	2.116
Mass flow rate of top-methanol recycled back (tonnes/hr)	0.933	0.883	1.146
Anhydrous ethanol mass flow rate (tonnes/hr)	13.894	12.946	16.799
Mixed higher-molecular alcohols mass flow rate (tonnes/hr)	2.118	1.975	2.564
First-column reboiler duty (GJ/hr)	6.45	6.02	7.81
Second-column reboiler duty (GJ/hr)	21.57	20.13	26.11
Third-column reboiler duty (GJ/hr)	27.26	25.97	33.71
Consumption of low-pressure steam by the first-column reboiler (tonnes/hr)	2.924	2.729	3.541
Consumption of low-pressure steam by the third-column reboiler (tonnes/hr)	12.061	11.176	14.910
Consumption of intermediate-pressure steam by the second-column reboiler (tonnes/hr)	9.941	9.274	12.035
Generation of hot-water by alcohol cooling final-exchanger - make-up to deaerator (tonnes/hr)	12.257	11.416	14.816
Cooling water consumption (tonnes/hr)	931.792	876.456	1137.485
Zeolite-based MSDU for mixed alcohols			
Molecular sieve dehydration unit-type	Vapor phase	Vapor phase	Vapor phase
Cycle mode	PSA / VSA	PSA / VSA	PSA / VSA
Number of stages	3	3	3
First stage	Adsorption	Adsorption	Adsorption
Second stage	Vacuum desorption	Vacuum desorption	Vacuum desorption

Table 24 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Mixed alcohols routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Mixed alcohols route scenarios		
	SC1	SC2	SC3
Zeolite-based MSDU for mixed alcohols			
Third stage	Methanol Back-flushing	Methanol Back-flushing	Methanol Back-flushing
Mass flow rate of wet mixed alcohols inlet into dehydration unit (tonnes/hr)	17.786	16.592	21.529
Consumption of intermediate-pressure steam to vaporize the degassed crude wet mixed alcohols line and inject into the molecular sieve vessel (tonnes/hr)	6.657	6.213	8.060
Methanol mass flow rate recycled as flushing agent (tonnes/hr)	0.933	0.883	1.146
Mass of Zeolite load (tonnes)	20.477	19.161	24.797
Bed material lifetime (years)	2	2	2
Water content in the mixed alcohols line after dehydration (dried) ($\%_{mol}$)	1.0	1.0	1.0
Water content removal efficiency (%)	91.27	91.82	91.82
Pressure of the adsorption cycle-time (bar)	3.50	3.50	3.50
Pressure of the vacuum desorption cycle-time (bar)	0.40	0.40	0.40
Pressure of the flush cycle-time (bar)	1.80	1.80	1.80
Temperature of the adsorption cycle-time (ºC)	145.0	145.0	145.0
Temperature of the vacuum desorption cycle-time (ºC)	74.0	74.0	74.0
Temperature of the pre-heated back-flush methanol (ºC)	180.0	180.0	180.0
Consumption of electricity by the vacuum pump (kWh)	0.126	0.118	0.152
Mass flow rate of purge gas from desorption cycle-time (treated as tail-gas) (tonnes/hr)	0.841	0.788	1.020
Mass flow rate of back-flushing gas-products as mixed alcohols catalytic-synthesis recycle (tonnes/hr)	0.933	0.833	1.146
Methanol content in the back-flushing gas line ($\%_{mol}$)	98.30	98.30	98.30
Full-flow evaporative advanced class gas turbine (EvGT)			
Gas turbine cycle-type	Evaporative	Evaporative	Evaporative
Operational mode	Combined-cycle	Combined-cycle	Combined-cycle
Humidification-cycle type	Full-flow	Full-flow	Full-flow
Combustor type	Annular	Annular	Annular
Turbine blades cooling system	Bled air points	Bled air points	Bled air points
Ambient temperature (ºC)	25.0	25.0	25.0
Ambient pressure (bar)	1.01325	1.01325	1.01325

Table 24 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Mixed alcohols routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Mixed alcohols route scenarios		
	SC1	SC2	SC3
Full-flow evaporative advanced class gas turbine (EvGT)			
Relative humidity in atmospheric air (%)	80.0	80.0	80.0
HHV_{AR} of fuel-gas (MJ/kg)	10.75	15.60	19.98
LHV_{AR} of fuel-gas (MJ/kg)	11.14	13.81	17.56
Turbine inlet temperature (ºC)	1500.0	1300.0	1500.0
Turbine inlet pressure (bar)	23.0	23.0	23.0
Reheat combustion chamber pressure (bar)	4.75	4.04	4.75
Excess of oxygen (%) [c]	35.44	33.67	35.44
Conditioned fuel-gas mass flow rate (tonnes/hr)	31.950	60.911	38.663
Fraction of fuel-gas to reheat combustion (%)	45.32	40.22	45.30
Fresh-air mass flow rate (tonnes/hr)	258.715	363.917	312.749
Bleed-air coolant mass flow rate (kg of air /kg of inlet gas mass flow rate)	0.040	0.020	0.040
Installed power generation capacity (MW)	81.474	102.212	98.502
Grid frequency (Hz)	60.0	60.0	60.0
Net-electrical efficiency (%) [b]	45.73	38.37	40.13
Gross heat rate (kJ/kWh)	6890.3	8228.7	6891.5
Cooling system type	Closed loop	Closed loop	Closed loop
Air temperature after the intercooler heat exchanger (ºC)	27.0	27.0	27.0
Compressed-air temperature inlet the humidifier tower system (ºC)	80.0	80.0	80.0
Compressed-air temperature outlet the humidifier tower system (ºC)	195.0	195.0	195.0
Exhaust-gas mass flow rate (tonnes/hr)	308.978	451.253	373.561
Turbine exhaust-gas temperature (ºC)	1002.0	908.0	1002.0
Exhaust-gas temperature after the air regenerator heat exchanger (ºC)	600.0	750.0	600.0
Mass flow rate of injected water into EvGT by saturated-air flow (tonnes/hr)	21.235	30.632	25.683
Hot-water temperature inlet the humidifier tower system (ºC)	210.0	210.0	210.0
Temperature of cold-water returning into loop-cycle (ºC)	61.0	61.0	61.0
Heat recovery steam generator (HRSG)			
HRSG type	Triple-pressure	Triple-pressure	Triple-pressure reheated
High-pressure steam (bar)	85.0	85.0	85.0
Intermediate-pressure steam (bar)	23.0	23.0	23.0

Table 24 – Aspen Plus® v8.4 simulation parameters (input and output) of Biomass-to-Mixed alcohols routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Mixed alcohols route scenarios		
	SC1	SC2	SC3
Heat recovery steam generator (HRSG)			
Low-pressure steam (bar)	2.5	2.5	2.5
Steam temperature of the high-pressure circuit (ºC)	520.0	520.0	520.0
Steam temperature of the intermediate-pressure circuit (ºC)	345.9	345.9	480.0
Steam temperature of the low-pressure circuit (ºC)	130.0	130.0	130.0
Steam generation by high-pressure circuit (tonnes/hr)	14.90	19.20	17.380
Steam generation by intermediate-pressure circuit (tonnes/hr)	14.818	22.625	19.697
Steam generation by low-pressure circuit (tonnes/hr)	34.575	97.488	10.523
Steam at 2.5 bar sent to deaerator (tonnes/hr)	5.773	5.258	10.523
Deaerator temperature (ºC)	105.0	105.0	105.0
Deaerator pressure (bar)	1.4	1.4	1.4
EvGT exhaust-gas temperature (ºC)	600.0	600.0	600.0
HRSG flue-gas temperature (ºC)	128.0	121.0	160.6
Steam turbine applied in combined-cycles (ST)			
Steam turbine type	EBPST	EBPST	CEST
High-pressure steam inlet-level (bar)	85.0	85.0	85.0
Intermediate-pressure steam inlet-level (bar)	23.0	23.0	23.0
Exhaust steam pressure (bar)	2.5	2.5	0.11
High-temperature of the steam inlet (ºC)	520.0	520.0	520.0
Exhaust steam at 2.5 bar to thermochemical-biorefinery (tonnes/hr)	83.828	92.344	none
Exhaust steam at 0.11 bar to condenser (tonnes/hr)	none	none	99.709
Extraction steam at 2.5 bar to thermochemical-biorefinery (tonnes/hr)	none	none	33.928
Steam extraction at 6.0 bar sent to 1G-dehydration system (tonnes/hr)	none	13.662	none
Steam extraction at 6.0 bar to thermochemical-dehydration system (tonnes/hr)	13.363	12.452	14.799
Isentropic turbine efficiency (%)	82.26	82.26	83.98
Electrical energy generator efficiency (%)	99.0	99.0	99.0
Installed power generation capacity (MW)	13.622	15.761	39.514
Traditional CHP/EBPST system			
Sugarcane bagasse consumption (tonnes/hr)	34.153	none	81.376
Exhaust steam at 2.5 bar sent to 1G biorefinery (tonnes/hr)	none	none	none

Table 24 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Mixed alcohols routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	**Biomass-to-Mixed alcohols route scenarios**		
	SC1	**SC2**	**SC3**
Traditional CHP/EBPST system			
Oxygen excess ratio ($\%_{w/w}$) [c]	0.08	none	0.12
Steam pressure (bar)	22.0	none	22.0
Steam temperature (ºC)	320.0	none	320.0
Boiler carbon conversion ($\%_{w/w}$)	99.0	none	99.0
Exhaust-gas temperature (Flue-gas) (ºC)	160.0	none	160.0
Boiler water blowdown (to treatment) (tonnes/hr)	3.532	none	8.459
Fly-ashes removal by emission control filters (fine matter) (tonnes/hr)	0.201	none	0.420
Generation of bottom ashes (tonnes/hr)	0.629	none	1.366
Boiler thermal efficiency 1 (%) [b]	86.30	none	86.81
Boiler thermal efficiency 2 (%) [b]	82.85	none	83.16
Steam turbine type	EBPST	none	EBPST
Exhaust steam at 2.5 bar sent to 1G biorefinery (tonnes/hr)	70.994	none	184.945
Steam extraction at 6.0 bar sent to 1G-dehydration system (tonnes/hr)	13.707	none	13.707
Isentropic turbine efficiency (%)	74.55	none	74.55
Electrical energy generator efficiency (%)	99.0	none	99.0
Installed power generation capacity (MW)	7.52	none	18.36
Double-column cryogenic ASU with high-purity argon recovery			
Air separation unit principle	Cryogenic liquefaction	Cryogenic liquefaction	Cryogenic liquefaction
Number of stages of the high-pressure column	45	45	45
Number of stages of the low-pressure column	75	75	75
Number of stages in the argon side arm double-column (by-partitioned)	100	100	100
High-pressure column design	Trays/float valve	Trays–float valve	Trays–float valve
Low-pressure column design	3-Pack/Mellapak	3-Pack/Mellapak	3-Pack/Mellapak
Argon side arm partitioned-column design	Pack/MellapakPl	Pack/MellapakPl	Pack/MellapakPl
High-purity argon production mode	Rectification	Rectification	Rectification
Adsorption/desorption system design	TPSA 2 vessels	TPSA 2 vessels	TPSA 2 vessels
Adsorption pressure (bar) and temperature (ºC)	5.0 / 30.0	5.0 / 30.0	5.0 / 30.0
Desorption pressure (bar) and temperature (ºC)	1.01 / 150.0	1.01 / 150.0	1.01 / 150.0
Mass of Zeolite catalyst load (tonnes)	7.304	8.825	8.822

Table 24 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Mixed alcohols routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(continues)

Parameter	Biomass-to-Mixed alcohols route scenarios		
	SC1	**SC2**	**SC3**
Double-column cryogenic ASU with high-purity argon recovery			
Mass of alumina catalyst load (tonnes)	14.891	17.991	17.987
Zeolite/Al_2O_3 catalyst bed materials lifetime (low activity) (years)	2 / 1	2 / 1	2 / 1
Pressure in the top of the high-pressure column (bar)	5.20	5.20	5.20
Pressure in the top of the low-pressure column (bar)	1.22	1.22	1.22
Temperature in the top of the high-pressure column (ºC)	-178.5	-178.5	-178.5
Temperature in the top of the low-pressure column (ºC)	-194.7	-194.7	-194.7
Number of zones in the plate main heat exchanger	6	6	6
Number of zones in the plate sub-cooler exchanger	4	4	4
Plate condenser/reboiler mode	Energy-saving	Energy-saving	Energy-saving
Nitrogen liquefier type	High-pressure	High-pressure	High-pressure
Nitrogen liquefaction cycle	Double-Claude	Double-Claude	Double-Claude
Nominal pressure of the nitrogen liquefier (bar)	40.0	40.0	40.0
Number of stages of the main air compressor (MAC)	1	1	1
Number of stages of the booster air compressor (BAC)	5	5	5
Atmospheric air mass flow rate (tonnes/hr) [l]	163.960	198.10	198.10
High-purity liquid argon production (tonnes/hr)	0.804	0.788	0.788
High-purity liquid nitrogen production (tonnes/hr)	108.643	130.915	130.915
Mass flow rate of liquid oxygen as reserve (tonnes/hr)	1.607	1.944	1.943
Mass flow rate of gaseous oxygen sent to gasifier (tonnes/hr)	32.174	38.883	38.883
Purity of liquid argon obtained at plant ($\%_{mol}$)	99.7	99.7	99.7
Purity of liquid nitrogen obtained at plant ($\%_{mol}$)	99.2	99.2	99.2
Purity of oxygen obtained at plant ($\%_{mol}$)	98.3	98.3	98.3
Mass flow rate of synthetic air gas vent stream from low-pressure column (tonnes/hr)	16.396	19.810	19.810
Mass flow rate of purge gas from desorption column (tonnes/hr)	17.405	21.203	21.025
Consumption of electricity by inlet-air blower (MWh)	0.532	0.584	0.643
First energy-saving turbo booster (MWh)	1.229	1.485	1.485
Second energy-saving turbo booster (MWh)	3.054	3.690	3.690
Consumption of electricity by integrated main air compressor (MWh)	4.301	5.197	5.197
Consumption of electricity by booster air compressor (MWh)	3.705	4.476	4.476
Consumption of electricity by high-pressure nitrogen liquefier (MWh) [m]	43.866	52.790	52.871

Table 24 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Mixed alcohols routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(conclusion)

Parameter	Biomass-to-Mixed alcohols route scenarios		
	SC1	SC2	SC3
Double-column cryogenic ASU with high-purity argon recovery			
Consumption of electricity by high-pressure nitrogen liquefier (MWh) [m]	43.866	52.790	52.871
Total of electricity required by ASU plant (MWh)	52.786	63.493	63.633
Cooling water consumption by MAC (tonnes/hr)	353.942	424.235	427.421
Cooling water consumption by BAC (tonnes/hr)	211.276	255.159	255.159
Cooling water consumption by high-pressure nitrogen liquefier (tonnes/hr)	2811.352	3385.134	3389.288
Condensed water mass flow rate knock-out to wastewater treatment plant (kg/hr)	407.074	491.835	491.835
Multi-cells water-cooling tower [e]			
Number of sections (sec)	2	2	3
Tower cells required - sec 1	6 cells	6 cells	7 cells
Tower cells required - sec 2	6 cells	7 cells	7 cells
Tower cells required - sec 3	none	none	5 cells
Make-up water (with recycle) - sec 1 (tonnes/hr)	95.332	94.815	113.983
Make-up water (with recycle) - sec 2 (tonnes/hr)	84.4796	101.707	101.884
Make-up water (with recycle) - sec 3 (tonnes/hr)	none	none	81.674
Water evaporation - sec 1 (tonnes/hr)	78.679	78.252	94.071
Water evaporation - sec 2 (tonnes/hr)	69.721	83.940	84.086
Water evaporation - sec 3 (tonnes/hr)	none	none	67.406
Water drift - sec 1 (tonnes/hr)	7.911	7.868	9.459
Water drift - sec 2 (tonnes/hr)	7.011	8.440	8.455
Water drift - sec 3 (tonnes/hr)	none	none	6.778
Tower basin blowdown (to treatment) - sec 1 (tonnes/hr)	8.742	8.695	10.452
Tower basin blowdown (to treatment) - sec 2 (tonnes/hr)	7.747	9.327	9.343
Tower basin blowdown (to treatment) - sec 3 (tonnes/hr)	none	none	7.490
Electricity required by fan drivers - sec 1 (kWh)	378.0	378.0	441.0
Electricity required by driver fans- sec 2 (kWh)	378.0	441.0	441.0
Electricity required by driver fans- sec 3 (kWh)	none	none	315.0
Water cycles			
Process water/steam maintenance (tonnes/hr)	77.0358 *	91.071 *	120.684
Cooling water maintenance (tonnes/hr)	210.078	234.380	332.667

Table 24 – Aspen Plus®v8.4 simulation parameters (input and output) of Biomass-to-Mixed alcohols routes integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery

(conclusion)

Parameter	Biomass-to-Mixed alcohols route scenarios		
	SC1	SC2	SC3
Water cycles			
Make-up raw water (tonnes/hr)	225.999 *	256.560 *	282.877
Pre-heated fresh-water as deaerator make-up (tonnes/hr)	31.483 *	36.835 *	25.016
Generation of deaerated hot water (tonnes/hr)	279.190 *	271.123 *	192.457

(int) reference scenario for surplus biomass and integration with thermochemical routes

[a] biomass refers to sugarcane bagasse and sugarcane straw

[b] efficiency based on LHV_{AR} of fuel at 25ºC and 1 atm

[c] excess based on inlet oxygen and not in the stoichiometric oxygen for combustion

[d] lean MDEA/PZ aqueous absorbing-solution mass flow rate inlet in the top of the absorber

[e] section 1 (sec1) to cooling compressors systems, CO_2 and H_2S co-capture system, distillation columns; section 2 (sec2) to cooling ASU compressors systems, and section 3 (sec 3) to condensing CEST exhaust-steam

[f] considers all solid matters removed, including bed media and catalytic active materials

[g] synthesis gas without passing through the CO_2 and H_2S co-capture system

[h] sent together with the synthesis gas resultant from the catalyst WGS reactors

[I] synthesis gas after the compression-section 1

[j] synthetic air without impurities from ASU vent stream (similar to air composition) used in the catalyst regeneration processes, represented as continuous mass flow rate (simplified form) considering the adsorption/desorption cycle-time

[k] non-adsorbable molecules as N_2, CO, CO_2, hydrocarbons and water vapor

[l] considers all air fractions (e.g.: N_2, O2, Ne, He, Ar, Xe, Kr)

[m] considers the consumption of electricity by the liquefaction process of nitrogen. If the nitrogen is emitted to atmosphere, will be electricity surplus to electric power grid

[n] the synthesis gas have more than 1.4 of hydrogen to carbon ratio, is not necessary a WGS system. But, can be used to increase the energy density of the fuel-gas inlet in the EvGT increasing the efficiency and better tailor the fuel-gas to the already-existing gas turbine technology.

* account for water cycle the 1G-CHP/ST system and the steam (heat) to equipment users in the 1G sugarcane biorefinery.

9 Environmental assessment

This LCA is focused on identify and quantify potential environmental impacts for: electricity during their life cycle from cradle-to-gate: biomass-derived methanol during their life cycle from cradle-to-gate: anhydrous ethanol during their life cycle from cradle-to-grave (system boundary excluding distribution logistic and commercialization steps).

The LCIA was performed using the World midpoint ReCiPe 2008 hierarchism (H) model supported by SimaPro®7.3.3 software to compiling and assess the impact categories evaluating the LCI to obtain the potential environmental impacts for the biomass-based products under assessment, All of the impact categories are determined and presented in the bar charts according to section 2.3.9 (Environmental impact indicators).

climate change (CC); ozone depletion (OD); terrestrial acidification (TA); freshwater eutrophication (FE); marine eutrophication (ME); human toxicity (HT); photochemical oxidant formation (POF); particulate matter formation (PMF); terrestrial ecotoxicity (TET); freshwater ecotoxicity (FET); marine ecotoxicity (MECT); ionizing radiation (IR); agricultural land occupation (ALO); urban land occupation (ULO); natural land transformation (NLT); water depletion (WD); mineral resource depletion (MRD) or metal depletion (MD) and fossil fuel depletion (FD).

LCIA results can provide information to identify critical processes in the assessed scenarios and enable environmental comparisons between technologies and equivalent products derived from fossil resources and/or renewable resources.

For more details about the environmental assessment applied for sugarcane biorefineries by using the VSB tool is recommended read the publication named – *The Virtual Sugarcane Biorefinery (VSB)*: 2011 Report (BRAZILIAN BIOETHANOL SCIENCE AND TECHNOLOGY LABORATORY, 2012) – and the publication named – Virtual Biorefinery: An Optimization Strategy for Renewable Carbon Valorization (BONOMI et al., 2016).

9.1 Comparative analysis of potential environmental impacts

The potential environmental impacts of the main value-added biomass-based products obtained from the integral use of biomass available (sugarcane bagasse and sugarcane straw) are compared with equivalent options obtained from fossil resources (database) or biochemical routes (VSB results) in order to verify advantages or disadvantage in terms of environmental impact indicators.

In this research Master's degree only a few comparisons were made, a more detailed analysis of the results from the industrial phase inventories obtained by the mass and energy balances using the Aspen Plus®v8.4 process simulation platform will be made in future works (complete assessment).

The preliminary comparative assessments proposed consider the main products obtained by the technological routes evaluated, and can be understood as follows:

a) **Comparative analysis of potential environmental impacts for electricity (kWh)**: by first generation sugarcane biorefinery applying different CHP/CEST system configurations;
b) **Comparative analysis of potential environmental impacts for electricity (kWh)**: by first generation sugarcane biorefinery applying different CHP/EBPST system configurations;
c) **Comparative analysis of potential environmental impacts for electricity (kWh)**: by first generation sugarcane biorefinery integrate BIG-ICE/CC route (SC1); and by first generation sugarcane biorefinery integrate BIG-GT/CC routes (SC1, SC2, and SC3);
d) **Comparative analysis of potential environmental impacts for electricity (kWh)**: by first generation sugarcane biorefinery (SC5); by first generation sugarcane biorefinery integrate BIG-ICE/CC route (SC1); by first generation sugarcane biorefinery integrate BIG-GT/CC route (SC3); and based on the Brazil's total electricity final consumption (Matrix);
e) **Comparative potential environmental impacts for methanol (kg)**: by sugarcane biorefinery integrate Biomass-to-Methanol routes (SC1 and SC2) - (renewable resource); and by Steam methane reforming (SMR) of natural gas - (fossil resource);
f) **Comparative potential environmental impacts for anhydrous ethanol (**kg): by first generation sugarcane biorefinery (SC5); by sugarcane biorefinery integrate Biomass-to-Mixed alcohols routes (SC1 and SC2) - (renewable resource); and gasoline by Brazil's petroleum refineries - (fossil resource).

9.2 Group definitions

Smaller or environmentally non-interacting process areas (relative) that do not indicate a significant contribution to main environmental impact indicators are grouped (condensed), and their associated potential environmental impacts come to represent macro-areas of the biorefinery (e.g.: agricultural phase, industrial phase, or end-use phase), or a specific category (e.g. chemicals, water usage, or infrastructure), or a function (e.g. transportation, heat, or cooling) in the boundary system that indicate environmental importance on the environmental impact indicators.

9.2.1 Sugarcane group (agricultural phase)

Represent the entire sugarcane cultivation phase (agricultural phase) until the delivery steps of sugarcane and straw at the inlet-gate of biorefinery (industrial phase). In this research Master’s degree analyze the agricultural phase is not part of the objectives, since there is no significant change in the agricultural phase (comparatively). However, detailed characterized impact indicators for sugarcane production (kg) are added as supplementary material (Figure B7) in the APPENDIX B.

The model consider the emissions to soil, water and atmosphere, and emission factors for industrial waste (vinasse, filter cake, bottom and fly-ashes and slurry) applications, fertilizers uses, agro-chemicals and pesticides use, machinery for agricultural preparations and harvest, sugarcane and straw transports to industrial phase, supplies/inputs transports, vinasse transport from industrial plant to agricultural area, diesel burning in machinery and emissions, among others (BRAZILIAN BIOETHANOL SCIENCE AND TECHNOLOGY LABORATORY, 2012; BONOMI et al., 2016).

9.2.2 Flue-gas (stack)

Represent the emission impact resultants from solid or gaseous burning processes (FLUE-GAS FROM STACK), mainly to generate thermal and electrical energy for the biorefinery. May represents, depending on the scenario, the emissions from: biomass (sugarcane bagasse and straw) burning in CHP system (CHP scenarios); sugarcane bagasse burning in CHP system and synthesis gas burning in SG-ICEs (partial-integrated type); synthesis gas burning in advanced EvGT (fully-integrated type); synthesis gas and light-gas and tail-gas burning advanced EvGT (fully-integrated type); and sugarcane bagasse burning in CHP system and synthesis gas and light-gas and tail-gas burning in advanced EvGT (partial-integrated type).

9.2.3 Infrastructure (1G)

Represent the estimated use of building materials (e.g.: steal, concrete, special metal alloys) necessary for construction of the 1G biorefinery plant held by implementing economic models based on capital invested (CAPEX) (BRAZILIAN BIOETHANOL SCIENCE AND TECHNOLOGY LABORATORY, 2012; BONOMI et al., 2016).

In this research Master's degree is not estimated the infrastructures of the thermochemical routes (recommendations and future works) and their potential environmental impacts, because it is not easy obtain these values (it is known that the thermochemical-infrastructure has a significant impact over the indicators).

9.2.4 Process water (1G) group

Represent the water cycles (i.e.: uses, recycles, losses and treatment needs) only for the optimized 1G sugarcane biorefinery (1G area) considering the consumption of chemicals, emissions (i.e.: soil, water, and atmosphere) and residue disposal methods, that are average estimated in the VSB tool by the division of AIB of the CTBE/CNPEM) (BONOMI et al., 2016).

9.2.5 Process water (thermochemical) group

Represent the complete water cycles (i.e.: uses, reuse/recycles, losses and treatment needs) only for the thermochemical conversion routes of biomass part (thermochemical route area) considering the consumption of chemicals (i.e.: make-up water, process water, cooling water, and special treatment types), emissions (i.e.: soil, water, and atmosphere) and residue disposal methods (sludge). In this group are considered: make-up water for water-cooling tower system (i.e.: evaporation, drift, and tower basin blowdown losses); make-up water for process water cycle (i.e.: evaporative process and condensation losses in pipeline and equipments, vent streams, blowdown losses, and condensate knock-outs); make-up water for advanced EvGT water cycle (i.e.: cooling water circuits, and vapor injection by humidifier tower); make-up water for steam generation drum (i.e.: reactor cooling water circuits, steam vent-drum losses, deaerator unit losses); make-up raw water treatment (i.e.: treatment for water taken from natural fonts); cooling water treatment (i.e.: maintenance of circulating water); process water treatment (i.e.: maintenance of circulating water); special water treatment (i.e.: advanced EvGT, and SG-ICEs).

The specific-type of water treatments are based on the water treatment processes available in the Ecoinvent 3 library (unit) of SimaPro$^{®}$v.7.3.3 software and in the water treatment process average estimated in the VSB tool by the division of AIB of the CTBE/CNPEM).

9.2.6 Catalysts and bed materials group

Represent the potential environmental impacts of the catalysts and absorbent materials consumed in the thermochemical conversion routes of biomass (not includes 1G biorefinery), the following materials (when required) are considered grouped in this category according to their referred areas of the thermochemical routes: commercial-type olivine α-$(Mg_{0.8}Fe_{0.2})_2SiO_4$ (atmospheric CFB directly-heated gasifier – bed material); commercial-type MgO (atmospheric CFB directly-heated gasifier – supplementary bed material); CuO/ZnO (guard bed absorber – bed layers); Cu-ZnO/Al_2O_3 (LT-WGS reactor - catalyst); Fe_2O_3/Cr_2O_3 MgO (HT-WGS reactor - catalyst); Cu-ZnO/Al_2O_3 (L-P methanol catalytic-synthesis reactor - catalyst); Sulfided Co-K-Mo/C (mixed alcohols catalytic-synthesis reactor – catalyst); Zeolite/Alumina/Activated carbon (four-bed PSA system hydrogen recovery vessels – bed layers); Zeolite/Alumina (ASU TPSA absorber/desorber vessels – bed layers); Zeolite (Zeolite-based MSDU absorber/desorber vessels for mixed-alcohols – bed layers).

9.2.7 MEA or PZ/MDEA group

Represent the amine-based co-capture system (i.e.: adsorption and desorption columns) for acid gas removal that can contain carbon dioxide (CO_2), hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbonyl disulfide (CS_2) (if formation) and mercaptans. A fraction of the lean-amine is reclaimed and filtered (i.e.: active carbon filters) to remove sulphur and nitrogen compounds, amine salts, particles and degradation products.

MEA represent a part of the impacts associated with the co-capture of CO_2 and H_2S by using MEA-based aqueous absorbing-solution considering the impacts due: their application (e.g.: production chain, transportation logistics, final disposal) in the form of MEA-based solution; the emissions (i.e.: soil, water, and atmosphere) and its final disposal (e.g.: soil together activated coal filter residue).

PZ/MDEA represent a part of the impacts associated with the co-capture of CO_2 and H_2S by using PZ/MDEA blend-based aqueous absorbing-solution considering the impacts due: their application (i.e.: production, transportation logistics, final disposal) in the form of MDEA-based solution and crystal-PZ rate promoter (mix market); the emissions (i.e.: soil, water, and atmosphere) and its final disposal (i.e.: residual compounds and activated coal filter residue).

9.2.8 Local emissions group

Represent the emission impacts (i.e.: soil, water, and atmosphere) that are not allocated to a specific group/area of processes.

9.2.9 Chemicals group

Represents the chemicals used in the 1G biorefinery processes (e.g.: juice treatment, yeast treatment, fermentation) (BRAZILIAN BIOETHANOL SCIENCE AND TECHNOLOGY LABORATORY, 2012; BONOMI et al., 2016).

Chemicals group does not consider the chemicals used in the thermochemical conversion routes of biomass. The main chemicals used in the scenarios of thermochemical routes are the amine-based absorbing-solution (grouped in the section 9.2.7 - MEA or PZ/MDEA group) and the chemicals for water treatments (grouped in the section 9.2.5 - Process water (thermochemical) group), and the other chemicals (e.g.: lubricant oil, basic water pH correctives, and others) have no significant contribution to main environmental impact indicators being grouped in section 9.2.10 (Others).

9.2.10 Others

Represent the sum of various emission impacts (i.e.: soil, water, and atmosphere) related to inputs/outputs that do not indicate a significant contribution to main environmental impact indicators and has not been grouped in one specific area (e.g.: condensate containing dissolved gasses, vent streams, filter-fine particulate materials, volatile compounds).

9.3 Bar charts

Bar charts are typically used in LCA to present the tabular data’s (results) allowing compare and analyze the potential environmental impacts of the value-added biomass-derived products (i.e.: electricity, methanol, and anhydrous ethanol). Presented for the characterization models based on the ReCiPe 2008 midpoint-oriented (H) methodology performed by use the characterization factors presented in the Table 1 (GOEDKOOP et al., 2009).

9.3.1 Bar charts of characterized impact indicators:

The bar charts of characterized impact indicators show how each process contributes to a specific single impact category indicator.

The left-vertical axis indicates the environmental impact categories (midpoint approach) coded according to Recipe 2008 method as shown in Table 1 and described in the section 2.3.9.1 (ReCiPe impact indicators). The right-vertical axis indicates the magnitude (scores) for each correspondent environmental impact categories (indicated on the left-vertical axis) characterized (characterization factor) into a common equivalence units (specific for each category) as shown in Table 1, providing an overall impact category indicator (midpoint indicators).

The lower-horizontal axis indicates the relative percentage that a determined process/group (legend) contributes/impact (composition) in the overall magnitude (indicated on the right-vertical axis) of one specific impact category indicator (indicated on the left-vertical axis).

The different color segments of the bar represent the partial contribution of process/group (areas) that compound the overall impact category indicator, the sum of the segments represent 100% (score).

9.3.2 Bar charts of comparative potential environmental impacts:

The bar charts of comparative potential environmental impacts show comparatively the relative contribution confronting the scores front a normalized (largest score) specific single impact category indicator.

The left-vertical axis indicates the environmental impact categories (midpoint approach) coded according to Recipe 2008 method as shown in Table 1 and described in the section 2.3.9.1 (ReCiPe impact indicators). The right-vertical axis indicates comparatively the largest magnitude (scores) for each correspondent environmental impact categories (indicated on the left-vertical axis) characterized (characterization factor) into a common equivalence units (specific for each category) as shown in Table 1.

The lower-horizontal axis indicates comparatively the percentage (fraction) of determined process/group (legend) represents when compared front the largest impact indicator in magnitude (100%), indicating the comparative percentage that determined process/group (legend) correspond.

9.4 Comparative analysis of potential environmental impacts for electricity (kWh): by first generation sugarcane biorefinery applying different CHP/CEST system configurations

The purpose of installing advanced CHP applying CEST systems at sugarcane biorefineries is the surplus electricity that is generated while supply the thermal and electrical energy needs (self-sufficient), thus advantages or disadvantages of generate electricity through burning the available biomass (bagasse and straw) depend on the comparative base and considerations (e.g..: cost/price of biomass). Advanced and more efficient cogeneration technologies will replace most of the currently thermal and electrical energy generation, actually by low-efficiency CHP system, in short time.

Aspen Plus®v8.4 process model simulation results show an increase of about 68.0% in the net-electricity production when comparing CHP/CEST (SC5) with CHP/CEST (SC1), with potential to provide improvements in the energy-sector security and reduce the dependence on centralized hydropower plants, mainly during prolonged periods of low rainfall. As regard to atmospheric emissions, significant reductions on the emissions of nitrogen and sulfur content compounds (i.e.: mainly NO_x, SOx) and of fine particulate matter (PMF) when compared with the current low-efficiency situation (CHP/CEST SC1).

CHP/CEST system in sugar-energy sector as fully part of sustainable energy policy play a crucial role in the Brazilian energy sector, contributing according Figure 18 to 7.6% of the Brazil's total electricity final consumption. More advanced high-efficiency boilers there are being installed/connected on grid as a result of promoted governmental incentives and programmes stimulating the production of energy from biomass.

Figure 99 presents the bar chart of comparative potential environmental impacts performed for electricity generation by the optimized 1G sugarcane biorefinery scenarios apply different configuration of CHP/CEST systems. Using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach), in kWh comparative base unit. Highlighted in the Figure 99, CC potential environmental impacts shown the relative differences for commercial CHP technologies applying different CEST systems (Rankine-cycle).

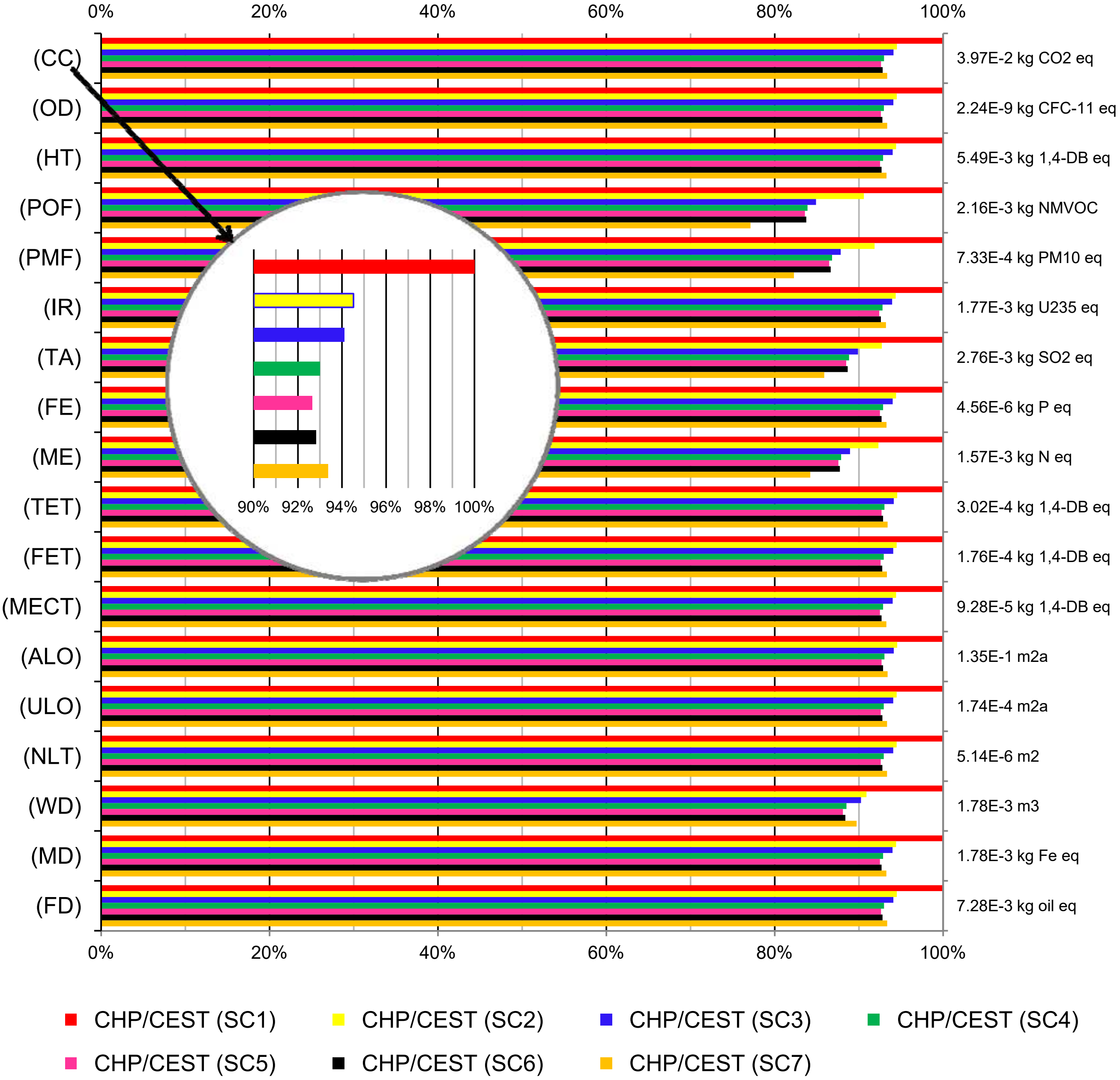


Figure 99 - Comparative potential environmental impacts for electricity generation (kWh) by optimized 1G sugarcane biorefinery applying different configurations of CHP/CEST (SC1, SC2, SC3, SC4, SC5, SC6 and SC7). Method: World ReCiPe (H) midpoint.

Figure 99 shows that for the most environmental impact indicators there is a tendency to decrease the scores with increasing energy efficiency of the CHP/CEST systems.

The scenario with the lower potential environmental impacts is the CHP/CEST (SC5), this scenario proved to be the most energy-efficient according to the results Aspen

Plus$^{®}$v8.4 process simulation platform. CHP/CEST (SC5) has a reduction by about 7.4% on GWP that is equivalent to a reduction of about 2.93E-3 kg CO_2 equivalent per KWh of electricity generated when compared to CHP/CEST (SC1) (lower energy-efficient), which correspond to 3.97E-2 kg CO_2 equivalent per KWh of electricity generated.

For the CHP/CEST (SC6) and CHP/CEST (SC7) is observed an small increase in environmental impact indicators front the CHP/CEST (SC6), this result is very interesting and significant from the technical point of view. This effect is due to the fact that the systems operate at the temperature limit, increasing the pressure of the steam (boiler water-side) more electricity is need by the pumps system and the efficiency of the steam turbine decrease (limited by the process steam required at 2.5 bar and 130.0ºC). The net-electric efficiency is little sensitive to changes in pressure, normally significant gains in efficiency are due to the fact that the temperature increases together.

This assessment results does not consider a detailed evaluation of the impacts related to infrastructure of the cogeneration system (variations), the impacts related to infrastructure are given by VSB data results for a biorefinery considering CHP/CEST at 90.0 bar and 530.0ºC, likely the CHP/CEST (SC5).

The amount of water circulating in the higher energy-efficiency systems is also lower; therefore the water consumption is also relatively smaller than the other system configurations, resulting on a reduction in the water consumption (WDP). For the optimized 1G sugarcane biorefinery (CHP/CEST SC1) the WD indicator corresponds to 1.78E-3 m^3 of water per KWh of electricity generated, while for the optimized 1G sugarcane biorefinery (CHP/CEST SC5) correspond to 1.57E-3 m^3 of water per KWh of electricity generated, a reduction of 12% on WDP.

FDP is directly dependent on the net-electrical efficiency. For the optimized 1G sugarcane biorefinery (CHP/CEST SC1) the FDP corresponds to 7.28E-3 kg of oil equivalent per KWh of electricity generated, while for the optimized 1G sugarcane biorefinery (SC5) correspond to 6.74E-3 kg of oil equivalent per KWh of electricity generated, a reduction of 7.4% on FDP.

Equal to FDP, the ALOP is directly dependent on the biorefinery productivity (net-electrical efficiency in this case), higher electrical efficiency results in lower amount of raw biomass to produce 1 kWh, and therefore, the potential impacts on ALO indicator are lower. ALOP for the optimized 1G sugarcane biorefinery (CHP/CEST SC1) correspond to 1.35E-1 m^2 of area per KWh of electricity generated, and for the optimized 1G sugarcane biorefinery (SC5) correspond to 1.25E-1 m^2 of area per KWh of electricity generated, a reduction of 7% on ALOP.

PMFP, TAP, MEP and POFP depend directly on the technology and operational settings of boilers, being dependents on the combustion chamber conditions and parameters. Reduce the flue-gas temperature and the oxygen excess in the chamber

(chamber temperature and mass flow rate) can reduce the NO_x, SO_x, NH_3, phosphates, VOCs, and particulate matter formation (PMF).

The analysis of processes with greatest impact (contribution) on each indicator allows us to understand more deeply the product system. The main process areas in a optimized 1G sugarcane biorefinery were evaluated and their contributions potential environmental impacts allow us to analyze what process unit or system is more critical for electricity generation in a optimized 1G sugarcane biorefinery.

Figure 100 presents the bar chart of characterized impact indicators performed for electricity generation by optimized 1G sugarcane biorefinery applying CHP/CEST operating at 90 bar and 530ºC (SC5). Using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach), in kWh comparative base unit.

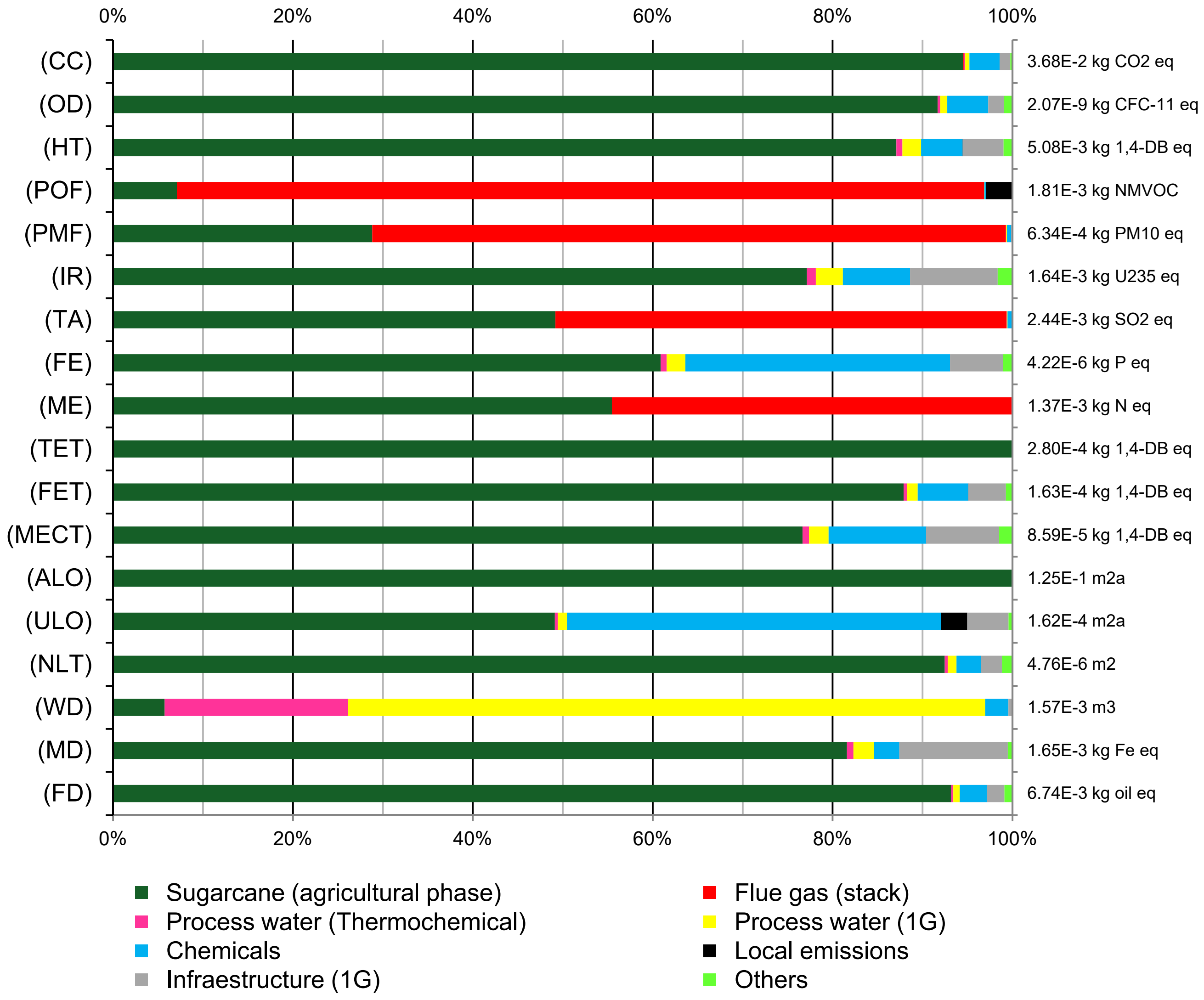


Figure 100 - Characterized impact indicators for electricity generation (kWh) by optimized 1G sugarcane biorefinery with CHP/CEST (SC5) system. Method: World ReCiPe (H) midpoint.

As shown in Figure 100, sugarcane agricultural production phase has the largest contribution in the environmental impact indicators.

The main contribution on GWP came from the agricultural phase, because burning biomass in the boilers considers emission of biogenic CO_2 (carbon dioxide absorbed by sugarcane to growth) in the VSB tool. In agricultural phase contributing for 3.48E-2 kg of CO_2 equivalent per kWh of electricity generated (about 94.5% of the total score), emissions related to fertilizers use and emissions, and transportation burning fossil-diesel are the main responsible on GWP.

All other scenarios have the same profile of this characterized impact indicators for the optimized 1G sugarcane biorefinery applying CHP/CEST (SC5). The results for electricity generation (kWh) applying others CHP/CEST scenarios (configurations) are presented in the APPENDIX B as supplementary materials.

The CHP/CEST system has a significant contribution on WDP, due to the need of a cooling tower system (evaporative and drift losses) to cooling and condensing the steam after the condensing turbine stage. For the optimized 1G sugarcane biorefinery (CHP/CEST SC5) the thermochemical process water group (cooling tower) contributes on the WD indicator for 3.19E-4 m^3 of water (about 20% of the total score) per kWh of electricity generated and the 1G-process water group (other processes) contributes on the WD indicator for 1.11E-3 m^3 of water (about 70% of the total score) per kWh of electricity generated (and chemicals group to 10%).

The formation of NO_x, SO_x and VOCs present in the flue-gas are the major contributors on POFP. The flue-gas emissions contribute to the POF indicator for 1.62E-3 kg of NMVOC per kWh of electricity generated (about 89.7% of the total score).

The flue-gas emission (NO_x, SO_x and NH_3) is also responsible for most of the impacts on TA indicator. The flue-gas emissions contribute to the TA indicator for 1.23E-3 kg of SO_2 equivalent per kWh of electricity generated (about 50.2% of the total score).

The nutrient enrichment of the marine water (MEP) is due to the emission of NOx, SOx, NH_3 and nitrates present in flue-gas, agricultural phase emissions, and smaller emissions of volatile chemicals formed en vent streams, which are mainly phosphoric acid, phosphates, and nitrates. The flue-gas emissions contribute to MEP for 6.11E-3 kg of N equivalent per kWh of electricity generated (about 44.4% of the total score).

PMFP depends on the combustion chamber conditions and their emissions of NOx, SOx, NH3, and particulate matter (as fly-ashes). The flue-gas emissions contribute to PMFP for 4.47E-4 kg of PM10 equivalent per kWh of electricity generated (about 70.5% of the total score).

The impact of the use of chemicals in biorefineries on ULOP is due to the use of roads and buildings related to regional distribution of the chemicals and mineral extraction occupation. In the agricultural phase, the main contribution results from materials transportation (logistics and distribution).

The impacts on FE indicator is due to the use of sulfuric acid in the juice treatment and emissions of phosphates and phosphorus content composts in the agricultural phase (pesticides and fertilization use, vinasse application in the crops and machineries use).

9.5 Comparative analysis of potential environmental impacts for electricity (kWh): by first generation sugarcane biorefinery applying different CHP/EBPST system configurations

Considering the sale of surplus biomass generated in CHP/EBPST systems, environmental impacts were allocated to the surplus bagasse and straw. Currently, there is no a defined and consolidated market for this type of biomass, although it can be considered as a value-added co-product in biorefineries with surplus biomass in future works (market and local factor dependences).

For the scenario CHP/EBPST (SC1) was not considered electricity exportation to grid and their allocation of potential environmental impacts for 3.36 MWh of potential electricity surplus, estimation obtained from the Aspen Plus®v8.4 process model simulation using manufactures technical operational parameters (in practice there is no electricity generation and the exhaust-gas temperature is higher). This amount is not accounted as a potential marketable product, so is not reported in Figure 101 as potential impacts.

Scenario CHP/EBPST (SC1) can be assessed for surplus biomass with interesting results for biomass commercialization area and as raw feedstock for chemical, biochemical, and thermochemical routes as decentralized or standalone plants. The environmental impacts data can be used to represent the intrinsic impacts resulting from the use of surplus biomass as feedstock in other processes.

CHP/EBPST scenarios are intended to meet the thermal and electrical energy needs by the biorefinery, as much as possible, surplus biomass (sugarcane bagasse and straw). EBPST turbine-type is the simplest configuration employed in order to provide thermal (process steam) and electrical energy supply. Applying high-efficiency CHP/EBPST systems, a significant amount of surplus biomass (raw value-added feedstock) can be generated, and consequently will be available for use in other processes, more efficiently.

Like the previous potential environment assessment (Figure 99), Figure 101 presents the bar chart of comparative potential environmental impacts performed for electricity generation by the optimized 1G sugarcane biorefinery scenarios apply different configuration of CHP/EBPST systems. Using the World midpoint ReCiPe 2008 model in SimaPro$^{®}$7.3.3 software (economic allocation approach), in kWh comparative base unit. Highlighted in the Figure 101, CC potential environmental impacts shown the relative differences for commercial CHP technologies applying different EBPST systems (Rankine-cycle).

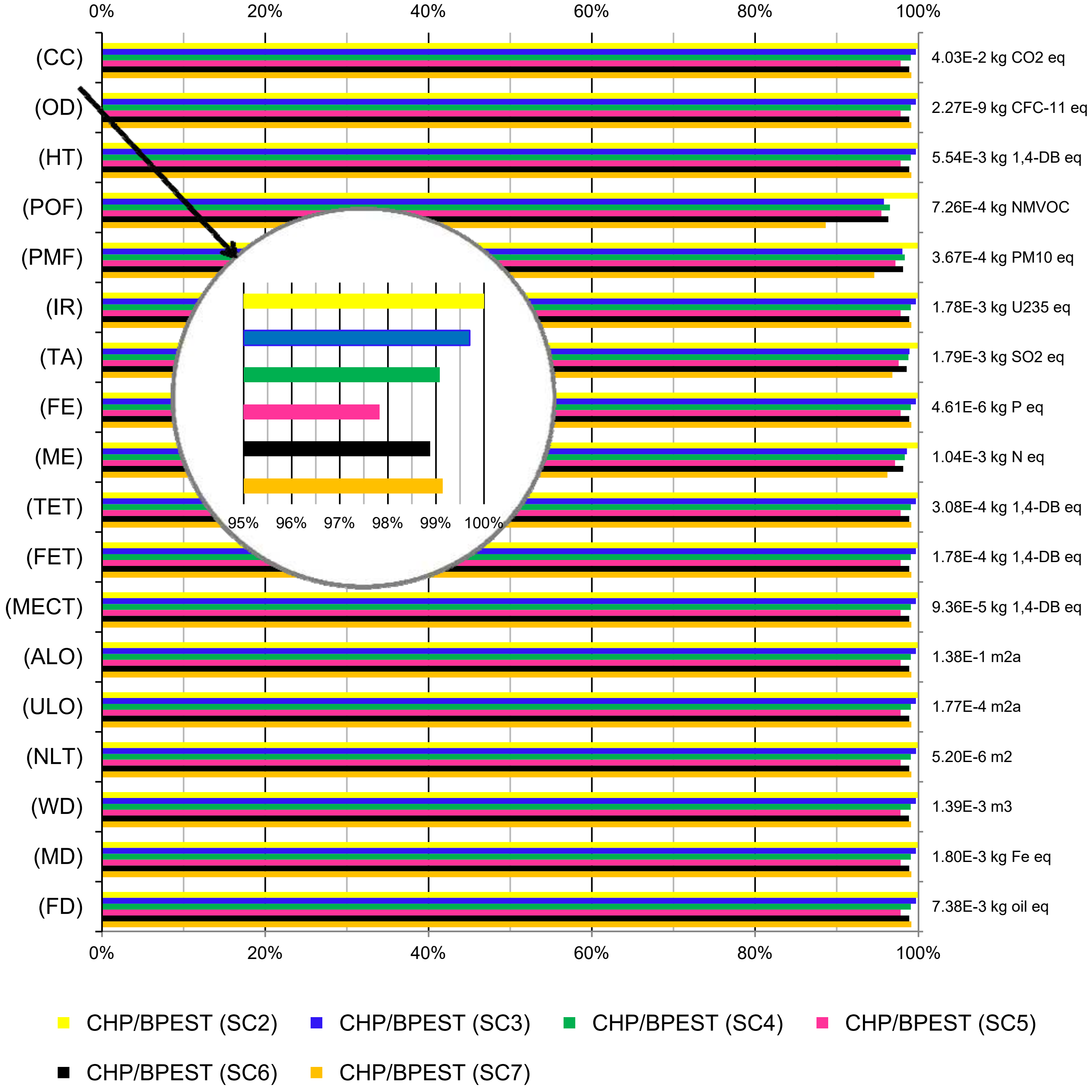


Figure 101 - Comparative potential environmental impacts for electricity generation (kWh) by optimized 1G sugarcane biorefinery applying different configurations of CHP/EBPST (SC2, SC3, SC4, SC5, SC6 and SC7). Method: World ReCiPe (H) midpoint.

As shown in Figure 101, most of the environmental impact indicators there a tendency to decrease by increasing energy efficiency of the CHP/EBPST system, like for the potentials environmental impacts for biorefineries applying differentness CHP/CEST systems. This graph also shows that for all scenarios assessed the relative differences are small, just as for the results of the CHP/CEST scenarios (except when compared to SC1). The total scores of most environmental impact indicators have a small increase when compared with the scores for CHP/CEST scenarios.

The scenario with the lower potential environmental impacts is the CHP/EBPST (SC5), which has a reduction by about 2.1% on GWP that is equivalent to a reduction of about 8.76E-4 kg CO_2 equivalent per KWh of electricity generated when compared to CHP/EBPST (SC2) (lower energy-efficient), which correspond to 4.03E-2 kg CO_2 equivalent per KWh of electricity generated. This relative difference is almost the same as that obtained for CHP/CEST scenarios, the score of the CC indicator has increased by about 1.5% in comparison with the CHP/CEST scenarios.

The amount of water circulating in the CHP/EBPST systems is practically the same for all scenarios assessed (steam supply limited by demand), the goals of the evaluated scenarios is only supply the biorefinery thermal energy demand ensuring the minimum demand of electricity (15 MWh). For the optimized 1G sugarcane biorefinery (CHP/EBPST SC5) the WD indicator corresponds to 1.36E-3 m^3 of water per KWh of electricity generated and 1.39E-3 m^3 of water per KWh of electricity generated for the optimized 1G sugarcane biorefinery (CHP/EBPST SC2), is practically the same consumption (difference of 2.2%).

For the optimized 1G sugarcane biorefinery (CHP/CEST SC2) the FDP corresponds to 7.38E-3 kg of oil equivalent per KWh of electricity generated, while for the optimized 1G sugarcane biorefinery (CHP/CEST SC5) correspond to 7.21E-3 kg of oil equivalent per KWh of electricity generated, a reduction of 2.5% on FDP.

As before, for the CEST systems, ALOP is directly dependent on the biomass surplus and on the net-electrical efficiency, higher electrical efficiency results in lower amount of raw biomass to produce 1 kWh, and therefore, the potential impacts on ALO indicator are lower. ALOP for the optimized 1G sugarcane biorefinery (CHP/EBPST SC5) correspond to 1.34E-1 m^2 of area per KWh of electricity generated.

PMFP, TAP, MEP and POFP has the same behavior as the CEST system, depending directly on quantity of biomass burned, in the technology and operational settings of boilers, being dependents on the combustion chamber conditions and parameters. Reduce the flue-gas temperature and the oxygen excess in the flue-gas (chamber temperature and mass flow rate) can reduce the NO_x, SO_x, ammonia, phosphates, volatile organic compounds, and particulates formation.

Figure 102 presents the bar chart of characterized impact indicators performed for electricity generation by optimized 1G sugarcane biorefinery applying CHP/EBPST operating at 90 bar and 530ºC (SC5). Using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach), in kWh comparative base unit.

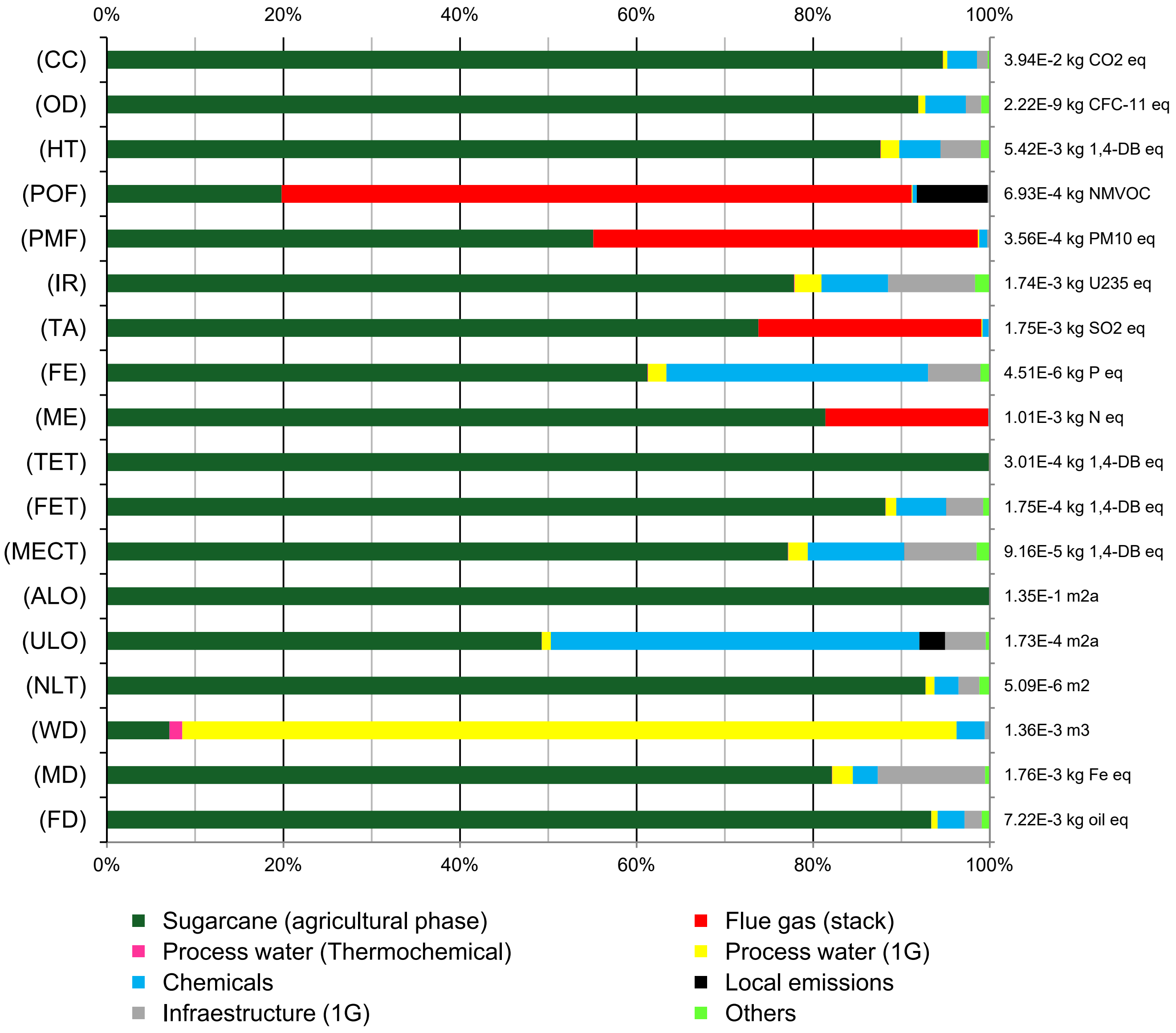


Figure 102 - Characterized impact indicators for electricity generation (kWh) by optimized 1G sugarcane biorefinery with CHP/EBPST (SC5) system. Method: World ReCiPe (H) midpoint.

As shown in Figure 102, the sugarcane agricultural production phase has the largest contribution in the environmental impacts indicators. The characterized impact indicators for the agricultural phase for optimized 1G sugarcane biorefinery applying CHP/EBPST system is more distinguished than for optimized 1G sugarcane biorefinery applying CHP/CEST. This results obtained for the optimized 1G sugarcane biorefinery applying CHP/EBPST are due to the fact that only part of the biomass is used to generate electricity and the economic allocation effect (less electricity generation for the same quantity of processed cane stalks).

All other scenarios have the same profile of this characterized impact indicators for the optimized 1G sugarcane biorefinery applying CHP/EBPST (SC5). The results for electricity generation (kWh) applying other CHP/EBPST scenarios (configurations) are presented in the APPENDIX B as supplementary materials.

The agricultural phase contributes on GWP for 3.73E-2 kg of CO_2 equivalent per kWh of electricity generated (about 94.7% of the total score). Practically the same share contribution obtained for the CHP/CEST (SC5).

Lower impact from thermochemical process water group on WDP is due to non-existence of a condensing turbine stage and to non-necessity of cooling tower system. For the optimized 1G sugarcane biorefinery (CHP/EBPST SC5) the water consumption by the CHP/EBPST (SC5), without condensing-steam turbine stage (water cooling tower is not needed) contribute to WDP for only 1.98E-5 m^3 of water per kWh of electricity generated (only about 1.45% of the total score) and the 1G-process water group (other processes) contributes to the WD indicator for 1.19E-3 m^3 of water per kWh of electricity generated (about 87.7% of the total score).

The flue-gas emitted by the CHP/EBPST scenarios have a lesser impact than the flue-gas emitted from CHP/CEST scenarios, because it burns only a part of the biomass available, which results in fewer potential pollutants emitted.

The formation of NO_x, SO_x and VOCs present in the flue-gas contribute to POFP for 4.95E-4 kg of NMVOC per kWh of electricity generated (about 71.4% of the total score). The flue-gas emission (NO_x, SO_x and NH_3) is also responsible on TAP to 4.42E-4 kg of SO_2 equivalent per kWh of electricity generated (about 25.2% of the total score).

The nutrient enrichment of the marine water (MEP) is due to the emission of NOx, SOx, NH_3 and nitrates present in flue-gas, agricultural phase emissions, and smaller emissions of volatile chemicals formed en vent streams, which are mainly phosphoric acid, phosphates, and nitrates. The flue-gas emissions contribute to MEP for 1.86E-4 kg of N equivalent per kWh of electricity generated (about 18.5% of the total score).

PMFP depends on the combustion chamber conditions and their emissions of NOx, SOx, NH3, and particulate matter (as fly-ashes). As only part of the biomass is burned, the PMFP is smaller than for the CEST systems (without surplus biomass).

As before, for the CEST systems, the impact of the use of chemicals in biorefineries on ULOP is due to the use of roads and buildings related to regional distribution of the chemicals and mineral extraction occupation. In the agricultural phase, the main contribution results from materials transportation (logistics and distribution).

As before, for the CEST systems, the impacts on FE indicator is due to the use of sulfuric acid in the juice treatment and emissions of phosphates and phosphorus content composts in the agricultural phase (pesticides and fertilization use, vinasse application in the crops and machineries use).

For the CHP/CEST (SC6 and SC7) and CHP/EBPST (SC6, SC7) the impacts related to infrastructure maybe can compensate the negative effect obtained analyzing only the operational point of view.

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9.6 Comparative analysis of potential environmental impacts for electricity (kWh): by first generation sugarcane biorefinery integrate BIG-ICE/CC route (SC1); and by first generation sugarcane biorefinery integrate BIG-GT/CC routes (SC1, SC2, and SC3)

The most significant disadvantage of the BIG-ICE/CC route in partial or fully integrated mode scenarios (mass and energy integration) at sugarcane biorefineries is the lower thermal efficiency of the CC (lower steam production) and therefore the necessity for a complementary system to supply thermal energy (process steam) required by the thermochemical-biorefinery. BIG-ICE/CC route operating in standalone mode is efficiently and can be comparable to BIG-GT/CC route.

The need to provide a large amount of process steam to supply the optimized 1G sugarcane biorefinery with annexed ethanol distillery through an auxiliary system such as CHP/EBPST (SC1) reduces dramatically the scale of the thermochemical route and the net-electricity potential and efficiency of the thermochemical biorefinery, reflecting directly on the environmental impact indicators due this lower net-electricity efficiency and higher emissions from the auxiliary CHP/EBPST system (burning part of the available biomass).

BIG-GT/CC route considers a unique high-performance sequential combustion full-flow EvGT operating in CC mode with Rankine-cycle cogeneration system with HRSG system (thermal energy recovery) and subcritical STs (electricity generation).

BIG-ICE/CC route considers parallel units (8 ICE in the scenario SC1) of a single-fueled spark-ignited (lean-burn four-stroke Otto-cycle) internal combustion engine (ICE) with turbo charging system operating in CC mode with Rankine-cycle cogeneration system with HRSG system (thermal energy recovery) and subcritical STs (electricity generation).

In the BIG-ICE/CC (SC1) to generate and supply the thermal energy (process steam) demanded by the thermochemical-biorefinery is necessary burn part of the sugarcane bagasse in the CHP system, which is less efficient than the advanced thermochemical routes (BIG-ICE/CC). The environmental potential impacts are directly dependent on the efficiency (performance) of the boundary-system.

Figure 103 presents the bar chart of comparative potential environmental impacts performed for electricity generation by 1G sugarcane biorefinery integrate BIG-

GT/CC routes and by sugarcane biorefinery integrate BIG-ICE/CC route. Using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach), in kWh comparative base unit.

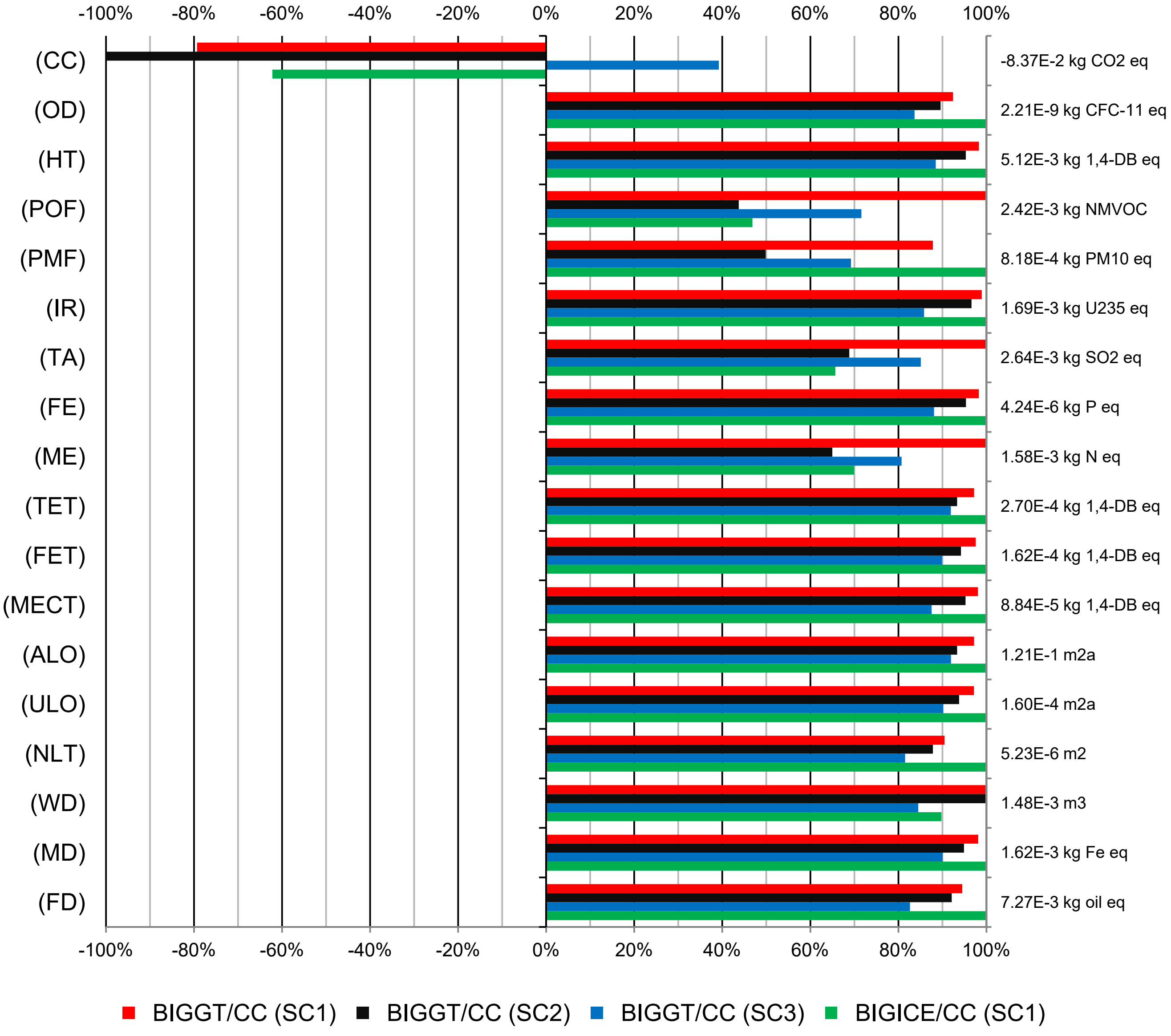

Figure 103 - Comparative potential environmental impacts for electricity generation (kWh) by optimized 1G sugarcane biorefinery integrate BIG-GT/CC (SC1, SC2 and SC3) routes and optimized 1G sugarcane biorefinery integrate BIG-ICE/CC (SC1) route. Method: World ReCiPe (H) midpoint.

Comparative potential environmental impacts (comparative bar chart) for electricity generation (kWh) by 1G sugarcane biorefinery integrate BIG-GT/CC (SC1, SC2 and SC3) routes are presented in the APPENDIX B as supplementary materials.

As shown in Figure 103, almost of the indicators for the thermochemical-biorefinery (BIG-ICE/CC SC1) has greatest impact on environmental indicators and comparatively environmental disadvantages, mainly due to lower electricity generation and the necessity of a complementary system (CHP/EBPST), in relation to other scenarios. Also, shows that for most indicators of environmental impacts for thermochemical- biorefinery (BIG-GT/CC) there is a tendency to decrease with increasing net-electricity efficiency of the system, showing a direct proportionality of electricity generation with the allocated environmental impacts.

Thermochemical-biorefinery (BIG-GT/CC SC3) does not have co-capture of CO_2 and H_2S system and storage, the CO_2 generated in the gasification process and in the EvGT is considered biogenic CO_2 emission. Others scenarios consider the CO_2 geological storage or injected into oil reservoirs (account as negative emissions).

GWP depend of bagasse fraction that is gasified in the thermochemical route and in the fraction that is burned in the traditional CHP/PEST system (auxiliary). In the scenario BIG-ICE/CC (SC1) 54.5% of bagasse is sent to gasifier, in the BIG-GT/CC (SC1) 74.0% is sent to gasifier and in the BIG-GT/CC (SC2 and SC3) scenarios 100% is sent to gasifier. In the BIG-GT/CC (SC3) CO_2 generate by the combustion/gasification reactions is not captured, is sent to EvGT and after is emitted to atmosphere (positive score).

The Thermochemical-biorefinery (BIG-ICE/CC SC1) contributes to GWP in -5.21E-2 kg of CO_2 equivalent per kWh of electricity generated (carbon sequestration) (about -62.2% of the total score). Thermochemical-biorefinery (BIG-GT/CC SC3) contributes to GWP for 3.28E-2 kg of CO_2 equivalent per kWh of electricity generated (about 39.2% of the total score), thermochemical-biorefinery (BIG-GT/CC SC1) contributes to GWP for -6.64E-2 kg of CO_2 equivalent per kWh of electricity generated (about -79.3% of the total score) and thermochemical-biorefinery (BIG-GT/CC SC2) contributes to GWP for -8,37E-2 kg of CO_2 equivalent per kWh of electricity generated (maximum reduction/sequestration).

HTP, water (fresh and marine) and TETP there a tendency to decrease with increasing of the net-electricity efficiency, based on the economic allocation effect (relating to production). The major contributions are due the agricultural phase and the flue-gas emissions.

Also, in Figure 103, is comparatively observed a decreasing tendency in the FDP. Thermochemical-biorefinery (BIG-ICE/CC SC1) contributes to FDP to 7.27E-3 kg of oil equivalent per KWh of electricity generated, while for the thermochemical-biorefinery (BIG-GT/CC SC3) correspond on FDP to 6.01E-3 kg of oil equivalent per KWh of electricity generated, a difference of 17.4% less.

Thermochemical-biorefinery (BIG-GT/CC SC1 and SC2) have a similar WDP due to a similar total water use (similar scenarios) the thermochemical-biorefinery (BIG-GT/CC SC3) has a lower consumption because there is not a system of co-capture of CO_2 and H_2S and its subsequent compression which reduces the cooling water consumption and process water requirements (thermal energy for reboiler).

Marine, terrestrial and fresh-water eutrophication (ME, TE and FE), PMFP and TAP in the comparative analysis depends on the quantity of flue-gas is emitted and in the pollutants content (e.g.: NOx, SOx, NH3, nitrates). The flue-gas emissions from traditional boiler emit more pollutants to atmosphere than the advanced ICE and GT system. The impacts depend on the fraction of bagasse is gasified or burned in the boiler system. Other important factors are the conditions (pressure, temperature) of combustion and the air fuel ratio.

9.7 Comparative analysis of potential environmental impacts for electricity (kWh): by first generation sugarcane biorefinery (SC5); by first generation sugarcane biorefinery integrate BIG-ICE/CC route (SC1); by first generation sugarcane biorefinery integrate BIG-GT/CC route (SC3); and based on the Brazil’s total electricity final consumption (Matrix)

This comparison shows how a technological evolution can change the Brazilian electric sector from an environmental point of view, reflecting the impacts of need to use fossil-based electricity today (natural gas thermo power plants) and the environmental advantages and disadvantages to develop the biomass renewable electricity systems of tomorrow.

The 1G sugarcane biorefinery scenario and thermochemical-biorefineries scenarios that had higher electricity generation to electric power grid were compared with regard to their potential environmental impacts and faced with the potential impacts generated by the Brazilian electric sector (final consumption) in the 2013 situation. The scenarios compared are the optimized 1G sugarcane biorefinery with annexed ethanol distillery applying CHP/CEST (SC5), BIG-ICE/CC (SC1) integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery, and BIG-GT/CC (SC3) integrated at an optimized 1G sugarcane biorefinery with annexed ethanol distillery.

According to Aspen Plus$^{®}$v8.4 obtained results for electricity generation scenarios by advanced technologies has greater net-electrical efficiency for thermochemical-biorefinery (BIG-GT/CC SC3) than thermochemical-biorefinery (BIG-ICE/CC SC1) who is in turn greater than biorefinery applying CHP/CEST systems (decrease order of potentials).

Brazilian electricity mix is represented according to a survey of energy sector conducted by EPE (2014) for the 2013 base-year available at the Brazilian energy balance end report published in 2014, according to section 2.1.5.2 (Renewable electricity). The representation of the survey and some information about of the Brazil total electricity final consumption (2013) and a graphical representation showing the share of renewable and no-renewable resources that compose the Brazil total electricity final consumption (Brazilian electricity mix) can be showed in the Figure 18. Characterized impact indicators for electricity generated based on Brazilian electricity mix are showed in the APPENDIX B as supplementary materials.

Figure 104 presents the bar chart of comparative potential environmental impacts performed for electricity generation by the best scenarios for electricity generation integrated at a 1G sugarcane biorefinery and by the Brazilian electricity mix (electricity supply-sector data for 2013). Using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach), in kWh comparative base unit.

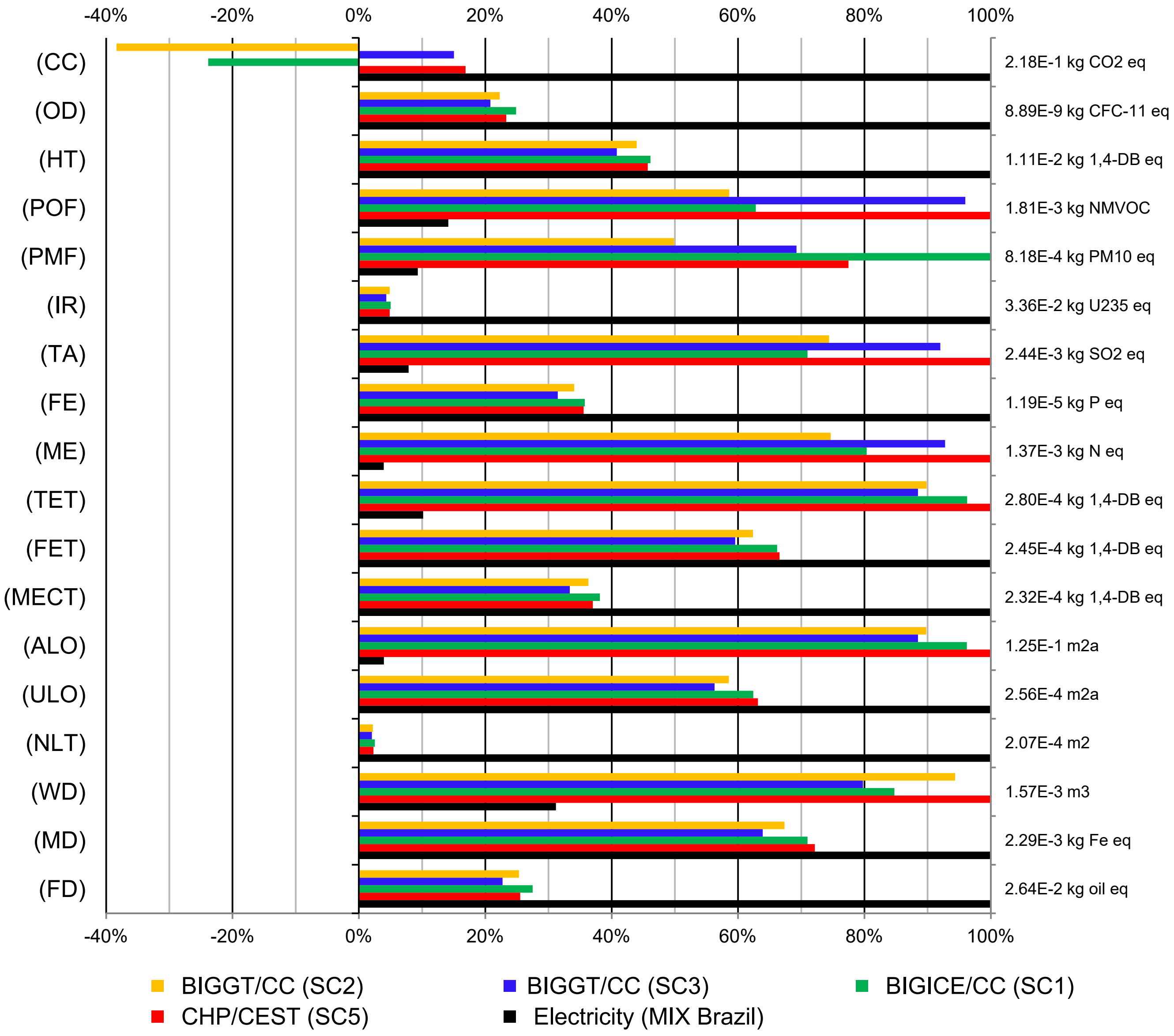

Figure 104 - Comparative potential environmental impacts for electricity generation (kWh) by optimized 1G sugarcane biorefinery integrate BIG-GT/CC (SC3) route; optimized 1G sugarcane biorefinery integrate BIG-ICE/CC (SC1) route; optimized 1G sugarcane biorefinery with CHP/CEST (SC5) route; and Brazilian electricity mix. Method: World ReCiPe (H) midpoint.

As shown in Figure 104 almost of the indicators to advanced technologies assessed for electricity generation by using renewable resources (biomass) has greatest reduction on potential environmental impacts when compared to the. Also, shows that for all most potential environmental impacts (scores) there is a tendency to decrease with increasing net-electricity efficiency of the technologies/routes, showing a direct proportionality with the environmental impact allocations.

Potentials environmental impacts for the Brazilian electricity mix are caused mainly by fossil-fuel burning in the thermo-power plant and by the local ecosystem transformation by the hydropower plant. The electricity final consumption in Brazil (2013) comes basically from hydropower plants (70.6%) and thermo power plants fueled with natural gas (11.3%), coal (2.6%) or oil (4.4%), these characteristics of the scenario is evident in the impact indicators (Figure 104).

Electricity from the Brazilian electricity mix contributes to GWP for 2.50E-1 kg of CO_2 equivalent per kWh of electricity generated while the thermochemical-biorefinery (BIG-GT/CC SC3) contributes to GWP for 3.28E-2 kg of CO_2 equivalent per kWh of electricity generated, a difference of 86.9% on GWP (without CCS sequestration technology). The optimized 1G sugarcane biorefinery applying CHP/CEST (SC5) contributes for 3.68E-2 kg of CO_2 equivalent per kWh of electricity generated, that is 12.2% more than the thermochemical-biorefinery (BIG-GT/CC SC3). The thermochemical-biorefinery (BIG-GT/CC SC2) contributes on GWP for -8.37E-2 kg of CO_2 equivalent per kWh of electricity generated corresponding to a negative impact on CC indicator of 38.4% of the total score (sequestration), that is the Brazilian electricity mix.

Process biomass trough different transformation stages (e.g.: handling, transport, drying, milling/crushing and burning) contribute for PMFP due generate large amounts of fines particulates, burning biomass emits NOx, SOx, NH3, and particulate matter (fly-ashes), that also contribute to PMFP. The impact of process sugarcane bagasse depends on the fractions of the available biomass is processed by the thermochemical route and the fraction of biomass is processed by the CHP/EBPST, milling and drying processes emits fine-matter particles PM_{10} less than the burning process in solid-fuel fired boilers (considering the two systems with control of particulate emissions).

1G sugarcane biorefinery applying CHP/CEST (SC5) contributes to PMFP for 6.34E-4 kg of PM_{10} equivalent per kWh of electricity generated while the thermochemical-biorefinery (BIG-GT/CC SC3) contributes to PMFP for 5.67E-4 kg of PM_{10} equivalent per kWh of electricity generated (about 10.6% less PM_{10}).

Ecotoxicity potentials impacts (HTP, FEP and MECT) there is higher for the Brazil mix scenario they are accounted the impacts of nuclear power plants (corresponding to 2.4% of the Brazil’s total electricity consumption in 2013) and the thermo-power plants.

Nuclear power plant use large amount of water and emit nuclear hazard waste (also contributes to IRP), and fuels burned form NO_x, SO_x and VOCs (present in the flue-gas). The thermochemical-biorefineries have a similar performance, varying only in function of the net-electrical efficiency. Thermochemical-biorefineries contributes at about 65-70% less in this indicator compared whit the Brazilian electricity mix.

The Brazilian electricity mix contributes to HTP of 1.11E-2 kg of 1.4-DB equivalent per kWh of electricity generated while optimized 1G sugarcane biorefinery applying CHP/CEST (SC5) contributes to HTP of 5.08E-3 kg of 1.4-DB equivalent per kWh of electricity generated, that is a reduction of 54.3%.

Thermochemical-biorefineries (BIG-GT/CC SC3) contributes to TETP of 2.48E-4 kg of 1.4-DB equivalent per kWh of electricity generated while Brazilian electricity mix contributes to TETP of 2.85E-5 kg of 1.4-DB equivalent per kWh of electricity generated, a increase of 77.7% over the Brazilian electricity mix. Optimized 1G sugarcane biorefinery applying CHP/CEST (SC5) contributes to TETP of 2.80E-4 kg of 1.4-DB equivalent per kWh of electricity generated, 13.0% more than the thermochemical-biorefineries (BIG-GT/CC SC3)

The nutrient enrichment of the marine water (MEP) and terrestrial (TEP) is due to the use of fertilizer and pesticides in agricultural phase and chemicals in industrial phase with a small contribution of NOx, SOx, NH3 and nitrates present in flue-gas.

The thermochemical-biorefineries (BIG-GT/CC) scenarios contribute to FETP and FEP analogously to HTP. The higher contribution in Brazilian electricity mix is due to the large use of chemicals, emissions, and disposal wastes in petrochemical refinery and nuclear power plant.

Thermochemical-biorefineries (BIG-GT/CC SC3) contribute to MEP of 1.28E-3 kg of N equivalent per kWh of electricity generated while Brazilian electricity mix contributes to MEP of 5.40E-4 kg of N equivalent per kWh of electricity generated.

TAP and MEP is higher for thermochemical-biorefineries due the agricultural phase and by burning biomass/syngas (NO_x, SO_x, NH_3, phosphates, and VOCs). Thermochemical-biorefineries (BIG-GT/CC SC3) contributes to MEP of 1.28E-3 kg of N equivalent per kWh of electricity generated while Brazilian electricity mix contributes to MEP of 5.40E-4 kg of N equivalent per kWh of electricity generated, which is 96.1% lesser.

Optimized 1G sugarcane biorefinery applying CHP/CEST (SC5) contributes to TAP of 2.44E-3 kg of SO_2 equivalent per kWh of electricity generated while Brazilian electricity mix contributes to TAP of 1.92E-4 kg of SO_2 equivalent per kWh of electricity generated, which is 92.1% lesser. The thermochemical-biorefineries have a similar performance, varying only in function of the net-electrical efficiency. Thermochemical-biorefineries contributes at about 5-15% less in this indicator compared whit the optimized 1G sugarcane biorefinery applying CHP/CEST (SC5).

Hydropower plants has a great impact on NLTP and thermo-power plants has a great impact on ULOP, while sugarcane biorefineries and thermochemical-biorefineries (agricultural phase) has a higher impact on ALO, these impacts are characteristic and intrinsic to the production plant-type. The Brazilian electricity mix contributes to NLTP of 2.07E-4 m² of area per kWh of electricity generated and contributes to ULOP of 2.56E-4 m² of area per kWh of electricity generated while thermochemical-biorefinery (BIG-GT/CC SC3) contributes to ALOP of 1.11E-1 m² de area per kWh of electricity generated and on ULOP of 1.44E-4 m² of area per kWh of electricity generated. Thermochemical-biorefineries (BIG-GT/CC SC3) contributes at about 11.5% less in ALOP compared whit the optimized 1G sugarcane biorefinery applying CHP/CEST (SC5).

The large use of water by the optimized 1G sugarcane biorefinery (SC5) contributes to WDP of 1.57E-3 m³ of water per kWh produced while in Brazilian mix contributes to WDP of 4.89E-4 m³ of water per kWh produced (Brazil mix) and in the thermochemical-biorefinery (BIG-GT/CC SC3) contributes to WDP of 1.25E-3 m³ of water per kWh produced (about 2.5 times more than the Brazil mix). The greater water consumption is due the 1G biorefinery technologies and the agricultural phase, thermochemical routes impacts in WDP by use water cooling-cycles applying cooling towers (evaporation and drift effects), a possible optimization to reduce this consumption can be implemented (e.g.: apply air coolers).

The FDP in the Brazilian electricity sector is result of the electricity generation by fossil-fueled thermo-power plants by using mainly natural gas, oil, and coal. Biomass has a great alternative to reduce this impact. Electricity generation based on Brazilian mix contributes to FDP of 2.64E-2 kg of oil equivalent per KWh of electricity generated while thermochemical-biorefineries (BIG-GT/CC SC3) contribute to FDP of 6.01E-3 kg of oil equivalent per KWh of electricity generated, a reduction-difference of 77.3%.

Optimized 1G sugarcane biorefinery applying CHP/CEST (SC5) contributes to FDP of 6.74E-3 kg of oil equivalent per KWh of electricity generated, that is 74,5% less than the Brazilian mix and 2.8% more than the contribution of the thermochemical-biorefineries (BIG-GT/CC SC3).

Figure 105 presents the bar chart of characterized impact indicators performed for electricity generation by optimized 1G sugarcane biorefinery integrate BIG-ICE/CC (SC1) route. Using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach), in kWh comparative base unit.

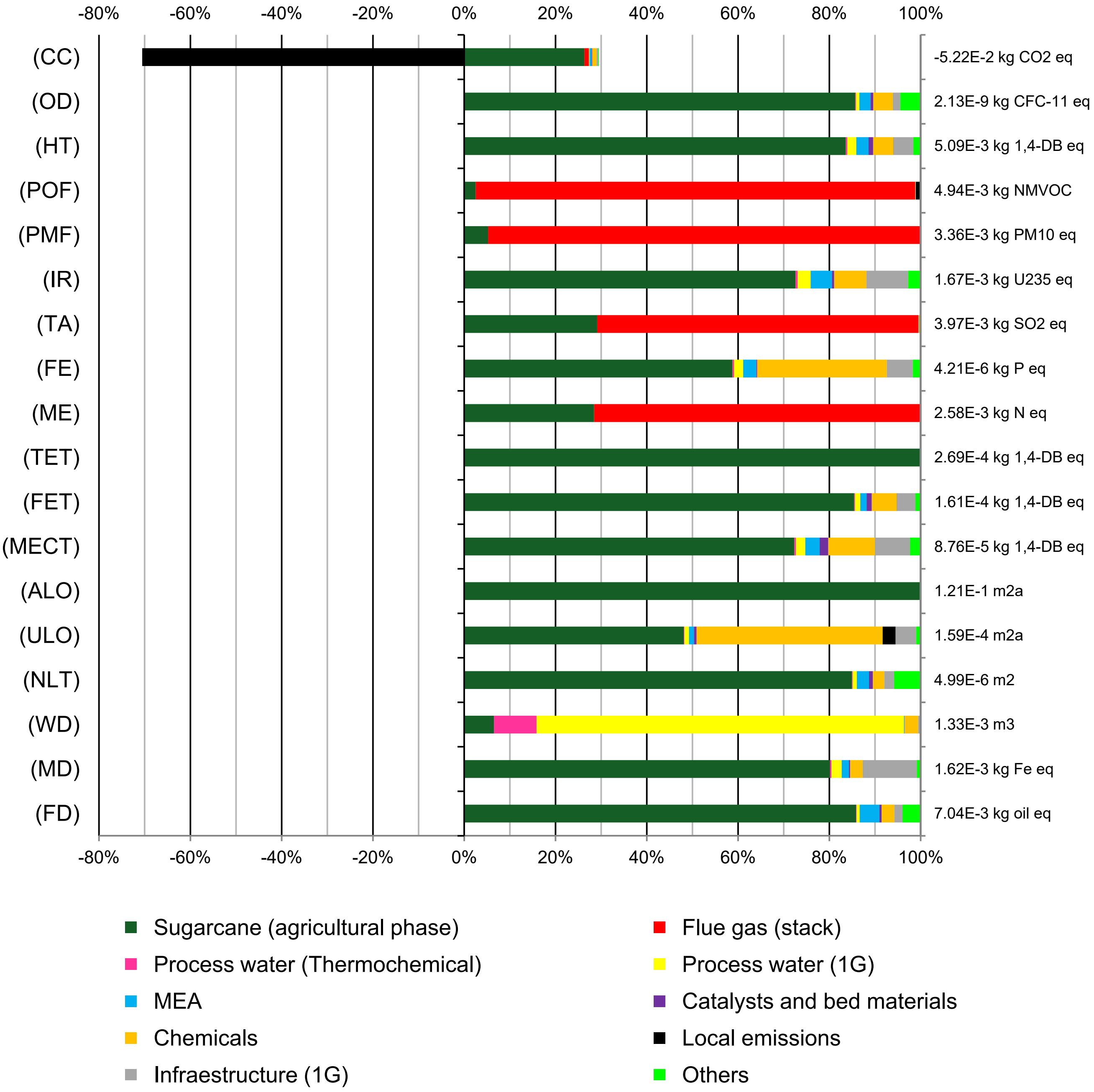

Figure 105 - Characterized impact indicators for electricity generation (kWh) by optimized 1G sugarcane biorefinery integrate BIG-ICE/CC (SC1) route. Method: World ReCiPe (H) midpoint.

As shown in Figure 105, the sugarcane agricultural phase has the largest contribution in the most of the environmental impact indicators and the flue-gas has a significant contribution in some of indicators.

The main positive impacts on GWP came from the agricultural phase emissions, which are related with machinery, transport, and diesel burning impacts (machinery and trucks). The agricultural phase contributes for about 3.34E-2 kg of CO_2 equivalent per kWh of electricity generated (about 88.8% of the positive scores).

Biomass burned in boilers (present in this scenario) considers the emission of biogenic CO_2. And the negative contribution on GWP from local emissions group is due to the co-capture of CO_2 and H_2S system and geological storage or injected into oil reservoirs (CCS), storage consideration contributes for -8.97E-2 kg of CO_2 equivalent per kWh of electricity generated (credits). The thermochemical-biorefinery (BIG-ICE/CC SC1) can reduce the potential impacts on CC indicator, considering the CCS system is possible contribute for -5,22E-2 kg of CO_2 equivalent per kWh of electricity generated (negative emissions).

BIG-ICE/CC SC1 impact on WDP due to the need of a cooling tower system (evaporative and drift losses), process losses and consumptions (gasification agent and CO_2 and H_2S PZ/MDEA blend-based co-capture system), but main thermochemical-biorefinery WDP impacts come from the 1G biorefinery technologies and agricultural phase. Thermochemical process water group contributes to WDP for 1.24E-4 m^3 of water per kWh of electricity generated (about 9.3% of the total score) and the 1G-process water group contributes to WDP for 1.07E-3 m^3 of water per kWh of electricity generated (about 80.5% of the total score).

The formation of NO_x, SO_x and VOCs present in the flue-gas (stack) from the biomass burning in 1G-boiler CHP/EBPST (SC1) and from synthesis gas burning in ICE (exhaust-gas) are the major contributors on POFP. The total flue-gas emissions contribute to POFP for 9.51E-4 kg of NMVOC per kWh of electricity generated (about 83.8% of the total score).

Use of MEA in the co-capture of CO_2 and H_2S system in the thermochemical-biorefinery (BIG-ICE/CC SC1) contributes to FDP for 3.06E-4 kg of oil equivalent per KWh of electricity generated (about 4.2% of the total score) while agricultural phase contributes for 6.05E-3 kg of oil equivalent per KWh of electricity generated (about 83.2% of the total score).

The flue-gas emissions (NO_x, SO_x and NH_3) contribute to TAP for 5.59E-4 kg of SO_2 per kWh of electricity generated (about 32.2% of the total score).

Impacts on MEP is due to the emission of NOx, SOx, NH3 and nitrates present in flue-gas, agricultural phase emissions and smaller emissions of volatile chemicals formed en vent streams, which are mainly phosphoric acid, phosphates, and nitrates. The flue-gas emissions contribute to MEP for 3.68E-4 kg of N equivalent per kWh of electricity generated (about 33.3% of the total score).

The others group was a significant contribution in the impact indicators for this Thermochemical-biorefinery (BIG-ICE/CC SC1) resulting from the large use of lubricating oil by ICE lubricating system, which contribute to FDP for 5.05E-4 kg of oil equivalent per kWh of electricity generated (about 6.9% of the total score).

The thermochemical-biorefinery (BIG-ICE/CC SC1) contributes to ALOP for about 1,21E-1 m^2 of area per KWh of electricity generated, ALOP is directly dependent on the net-electrical efficiency, higher electrical efficiency results in lower amount of raw biomass to produce 1 kWh, and therefore, the potential impacts on ALO indicator are lower.

Figure 106 presents the bar chart of characterized impact indicators performed for electricity generation by optimized 1G sugarcane biorefinery integrate BIG-GT/CC (SC1) route. Using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach), in kWh comparative base unit.

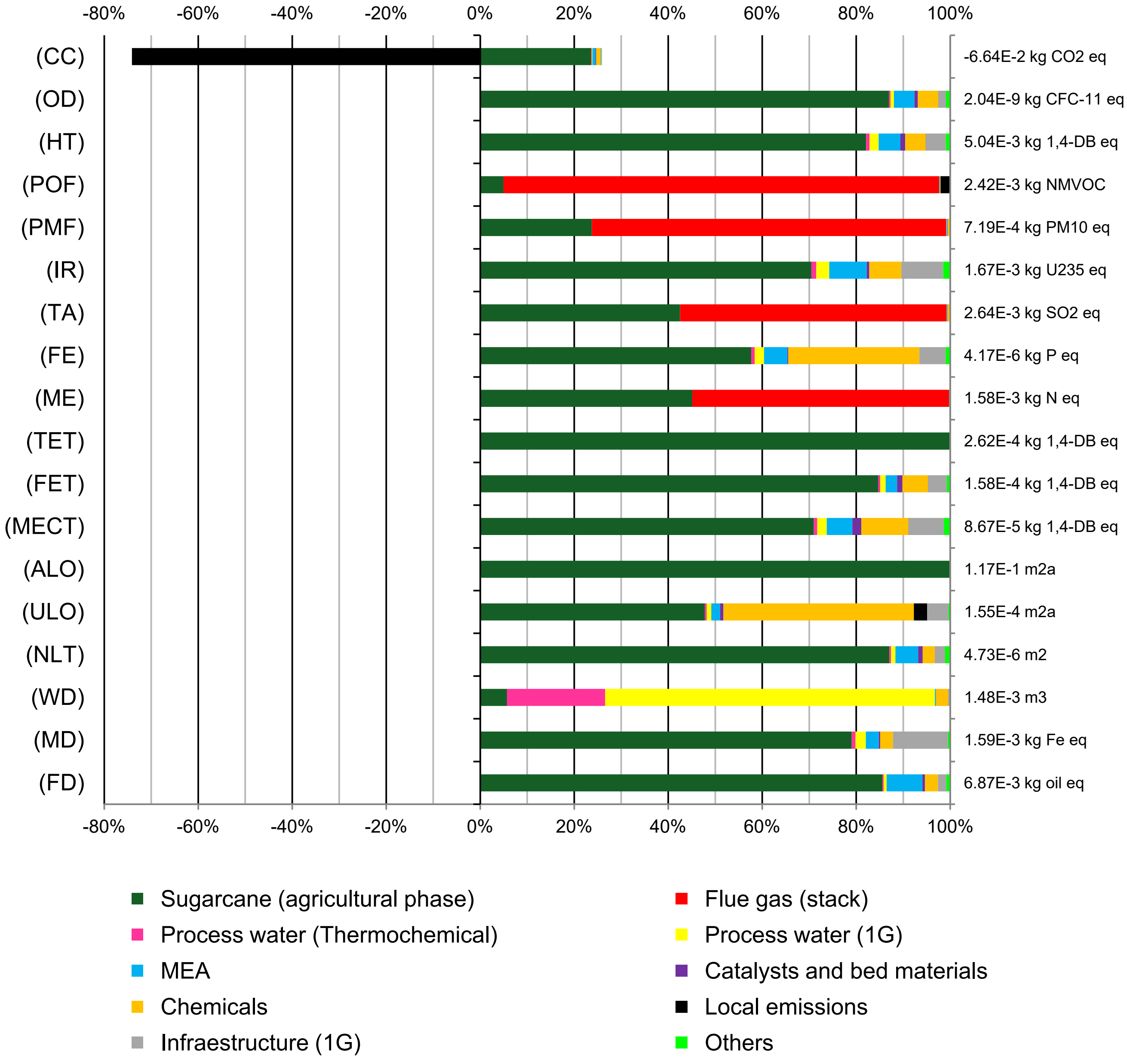

Figure 106 - Characterized impact indicators for electricity generation (kWh) by optimized 1G sugarcane biorefinery integrate BIG-GT/CC (SC1) route. Method: World ReCiPe (H) midpoint.

Figure 107 presents the bar chart of characterized impact indicators performed for electricity generation by optimized 1G sugarcane biorefinery integrate BIG-GT/CC

(SC2) route. Using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach), in kWh comparative base unit.

Figure 107 - Characterized impact indicators for electricity generation (kWh) by optimized 1G sugarcane biorefinery integrate BIG-GT/CC (SC2) route. Method: World ReCiPe (H) midpoint.

As shown in Figure 106 and Figure 107 for electricity generation by thermochemical-biorefineries (BIG-GT/CC SC1 and BIG-GT/CC SC2) they have a similar behavior profile (similar thermochemical technologies) with small differences in the impact indicator scores, which is resultants from the different energetic integrations of thermochemical route with 1G sugarcane biorefinery (with or without CHP/EBPST system). Also shows that the sugarcane agricultural phase has the largest contribution in the most of the environmental impact indicators and the flue-gas have a significant contribution in some of the indicators.

BIG-GT/CC (SC1) is integrated as partially-integrated mode with the 1G sugarcane biorefinery (CHP/EBPST SC1), and BIG-GT/CC (SC2) is integrated as fully-integrated mode with the 1G sugarcane biorefinery.

The main positive impacts on GWP came from the agricultural phase emissions are related with machinery, transport and diesel burning impacts (machinery and trucks). For the thermochemical-biorefinery (BIG-GT/CC SC2) the agricultural phase contributes for 3.12E-2 kg of CO_2 equivalent per kWh of electricity generated (about 90.9% of the positive scores).

And the negative contribution on GWP from local emissions group is due to the co-capture of CO_2 and H_2S system and geological storage or injected into oil reservoirs (CCS), storage consideration for the thermochemical-biorefinery (BIG-GT/CC SC2) contributes for -1.18E-1 kg of CO_2 equivalent per kWh of electricity generated (credits). The thermochemical-biorefinery (BIG-GT/CC SC2) can reduce the potential impacts on CC indicator, considering the CCS system is possible contribute for -8,37E-2 kg of CO_2 equivalent per kWh of electricity generated (negative emissions).

BIG-GT/CC SC2 impact on WDP due to the need of a cooling tower system (evaporative and drift losses), process losses and consumptions (gasification agent and CO_2 and H_2S PZ/MDEA blend-based co-capture system), thermochemical-biorefinery WDP impacts come from the 1G biorefinery technologies and agricultural phase. Thermochemical process water group contributes to WDP for 3.54E-4 m^3 of water per kWh of electricity generated (about 23.9% of the total score) and the 1G-process water group contributes to WDP for 9.98E-4 m^3 of water per kWh of electricity generated (about 67.4% of the total score).

The formation of NO_x, SO_x and VOCs present in the flue-gas (stack) from the biomass burning in 1G-boiler CHP/EBPST (SC1) and from synthesis gas burning in EvGT (exhaust-gas) are the major contributors on POFP. The total flue-gas emissions contribute to POFP for 8.88E-4 kg of NMVOC per kWh of electricity generated (about 83.9% of the total score).

Use of MEA in the co-capture of CO_2 and H_2S system in the thermochemical-biorefinery (BIG-GT/CC SC2) contributes to FDP for 5.88E-4 kg of oil equivalent per KWh of electricity generated (about 8.8% of the total score) while agricultural phase contributes for 5.64E-3 kg of oil equivalent per KWh of electricity generated (about 84.3% of the total score).

The flue-gas emissions (NO_x, SO_x and NH_3) contribute to TAP for 7.20E-4 kg of SO_2 per kWh of electricity generated (about 39.6% of the total score).

The thermochemical-biorefinery (BIG-GT/CC SC2) contributes on ALOP for about 1.13E-1 m^2 of area per KWh of electricity generated, ALOP is directly dependent on the net-electrical efficiency.

Figure 108 presents the bar chart of characterized impact indicators performed for electricity generation by optimized 1G sugarcane biorefinery integrate BIG-GT/CC (SC3) route. Using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach), in kWh comparative base unit.

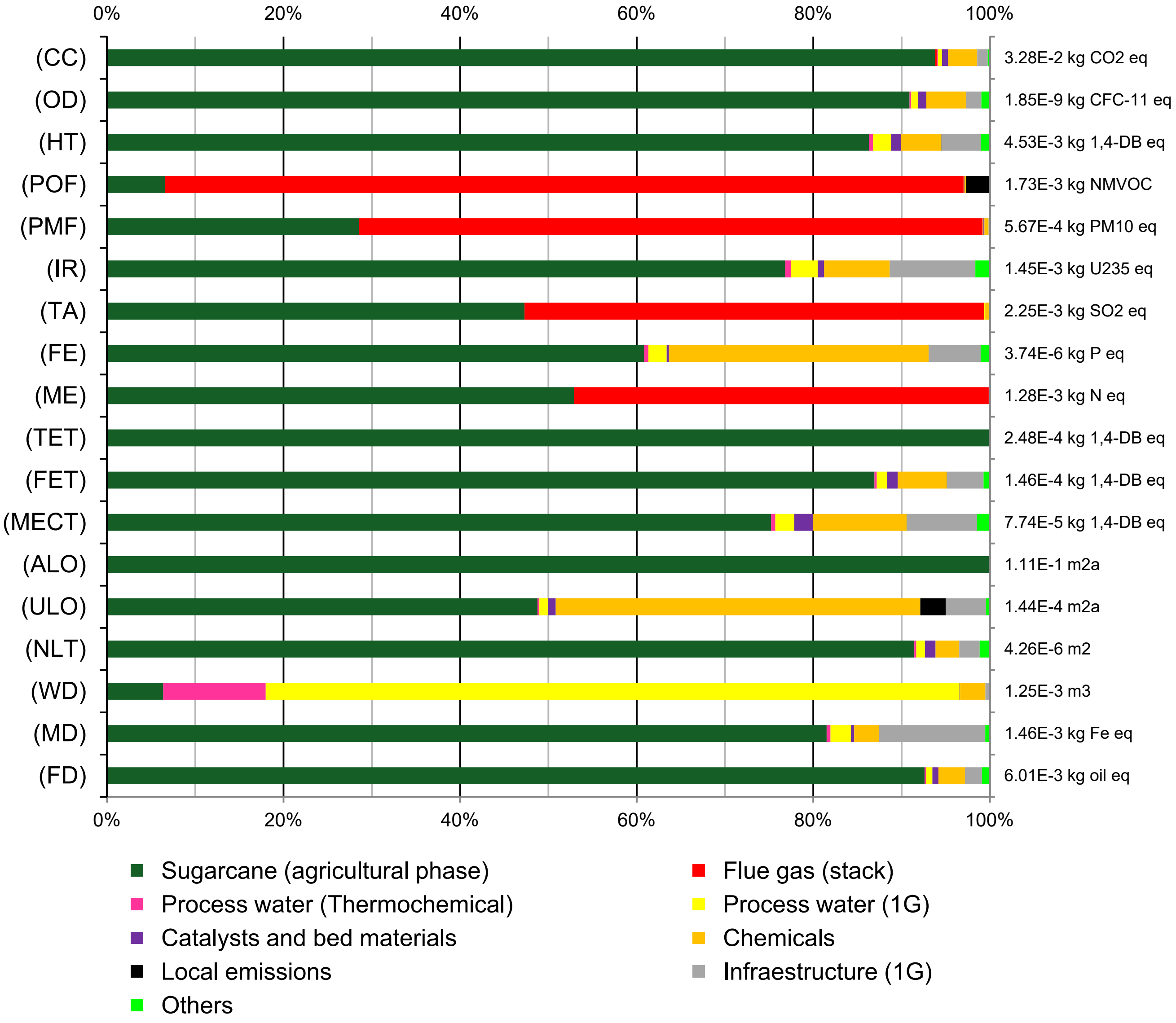

Figure 108 - Characterized impact indicators for electricity generation (kWh) by optimized 1G sugarcane biorefinery integrate BIG-GT/CC (SC3) route. Method: World ReCiPe (H) midpoint.

As shown in Figure 108, the sugarcane agricultural production phase has the largest contribution in the environmental impacts indicators and that the flue-gas has a significant contribution in some of the indicators.

Thermochemical-biorefinery (BIG-GT/CC SC3) not have the co-capture of CO_2 and H_2S system, the CO_2 generated in the gasification process and in the EvGT burning synthesis gas is considers as biogenic CO_2 emission content in the flue-gas (stack).

The main contribution on GWP came from the agricultural phase emissions, which are related with machinery, transport, and diesel burning impacts (machinery and trucks). For thermochemical-biorefinery (BIG-GT/CC SC3) the agricultural phase contributes for about 3.08E-2 kg of CO_2 equivalent per kWh of electricity generated (about 93.8% of the positive scores), while the chemicals group only for 1.09E-3 kg of CO_2 equivalent per kWh of electricity (about 3.3% of the total score).

BIG-GT/CC SC3 has less contribution on WDP than the BIG-GT/CC SC1 and BIG-GT/CC SC2, due not have the co-capture of CO_2 and H_2S system. BIG-GT/CC SC3 impact on WDP due to the need of a cooling tower system (evaporative and drift losses), process losses and consumptions, but main thermochemical-biorefinery WDP impacts come from the 1G biorefinery technologies and agricultural phase. Thermochemical process water group contributes to WDP for 1.45E-4 m^3 of water per kWh of electricity generated (about 11.6% of the total score) and the 1G-process water group contributes to WDP for 9.83E-4 m^3 of water per kWh of electricity generated (about 78.6% of the total score).

The formation of NO_x, SO_x and VOCs present in the flue-gas (stack) from the biomass burning in 1G-boiler CHP/EBPST (SC1) and from synthesis gas burning in ICE (exhaust-gas) are the major contributors on POFP. The total flue-gas emissions contribute to POFP for 9.51E-4 kg of NMVOC per kWh of electricity generated (about 83.8% of the total score).

The impact scores (POFP, PMFP, TAP and MEP) resultant from the emissions of content pollutants (main SOx and carbonates) in the flue-gas are higher in thermochemical-biorefinery (BIG-GT/CC SC3) than in thermochemical-biorefinery (BIG-GT/CC SC1 and SC2), because the synthesis gas is directly sent to the EvGT without prior co-capture of CO_2 and H_2S system, burning without upstream capture of sulfur compounds.

The formation of NO_x, SO_x and VOCs present in the total flue-gas (stack) from the synthesis gas burning in EvGT contributes on POFP for 1.57E-3 kg of NMVOC per kWh of electricity generated (about 90.5% of the total score). The flue-gas emissions (NO_x, SO_x and NH_3), also contribute on TAP for 1.17E-3 kg of SO_2 per kWh of electricity generated (about 52.1% of the total score). The flue-gas emissions also contribute to MEP for 5.99E-4 kg of N equivalent per kWh of electricity generated (about 47.0% of the total score).

Agricultural phase in the thermochemical-biorefinery (BIG-GT/CC SC3) contributes to FDP for 5.56E-3 kg of oil equivalent per KWh of electricity generated (about 92.6% of the total score).

The thermochemical-biorefinery (BIG-GT/CC SC2) contributes to ALOP for about 1.44E-1 m^2 of area per KWh of electricity generated, ALOP is directly dependent on the net-electrical efficiency.

9.8 Comparative potential environmental impacts for methanol (kg): by sugarcane biorefinery integrate Biomass-to-Methanol routes (SC1 and SC2) - (renewable resource); and by Steam methane reforming (SMR) of natural gas - (fossil resource)

Methanol is traditionally produced in large scale from natural gas by autothermal reforming (ATR) or by Steam methane reforming (SMR) of the natural gas to synthesis gas and subsequent catalytic-conversion of the synthesis gas to grade AA methanol (natural gas-derived methanol).

Thermochemical-biorefineries scenarios applying Biomass-to-Methanol route were compared with regard to their potential environmental impacts and faced with the potential environmental impacts for the life-cycle of methanol derived from fossil resource (in this case natural gas). This comparison can show how a technological evolution can change the commodity-sector from an environmental point of view, reflecting the impacts from different feedstock's (fossil or renewable resources).

The production of biomass-derived methanol by thermochemical conversion route of biomass (Biomass-to-Methanol) can decentralize and improve the methanol production by using local and renewable resources, as well reduce the potential environmental impacts of methanol.

In the case of Brazil the use of methanol as liquid transportation fuel is mandatory-prohibited, and all of methanol used as chemical for synthesis is imported, Brazil does not produce methanol (2015) due to market costs&prices. The distribution, logistics and commercialization factors are very important influence over the impact scores, since all methanol consumed in Brazil is imported (2015). This factor is not taken into account in this comparison, since it requires more data and specific studies for the biomass-derived methanol (local factors), this aspects need be evaluated in future studies.

The potential environmental impacts for natural gas derived methanol are obtained from the Ecoinvent LCA database (Methanol, at plant, GLO) in the SimaPro®7.3.3 software.

Comparative potential environmental impacts (comparative bar chart) for the methanol production (kg) by 1G sugarcane biorefinery integrate Biomass-to-Methanol

(SC1 and SC2) routes are presented in the APPENDIX B as supplementary materials.

Figure 109 presents the bar chart of comparative potential environmental impacts performed for methanol grade AA production by optimized 1G sugarcane biorefinery integrate Biomass-to-Methanol (SC1 and SC2) routes and methanol grade AA production by large-scale SMR of natural gas. Using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach), in kg comparative base unit.

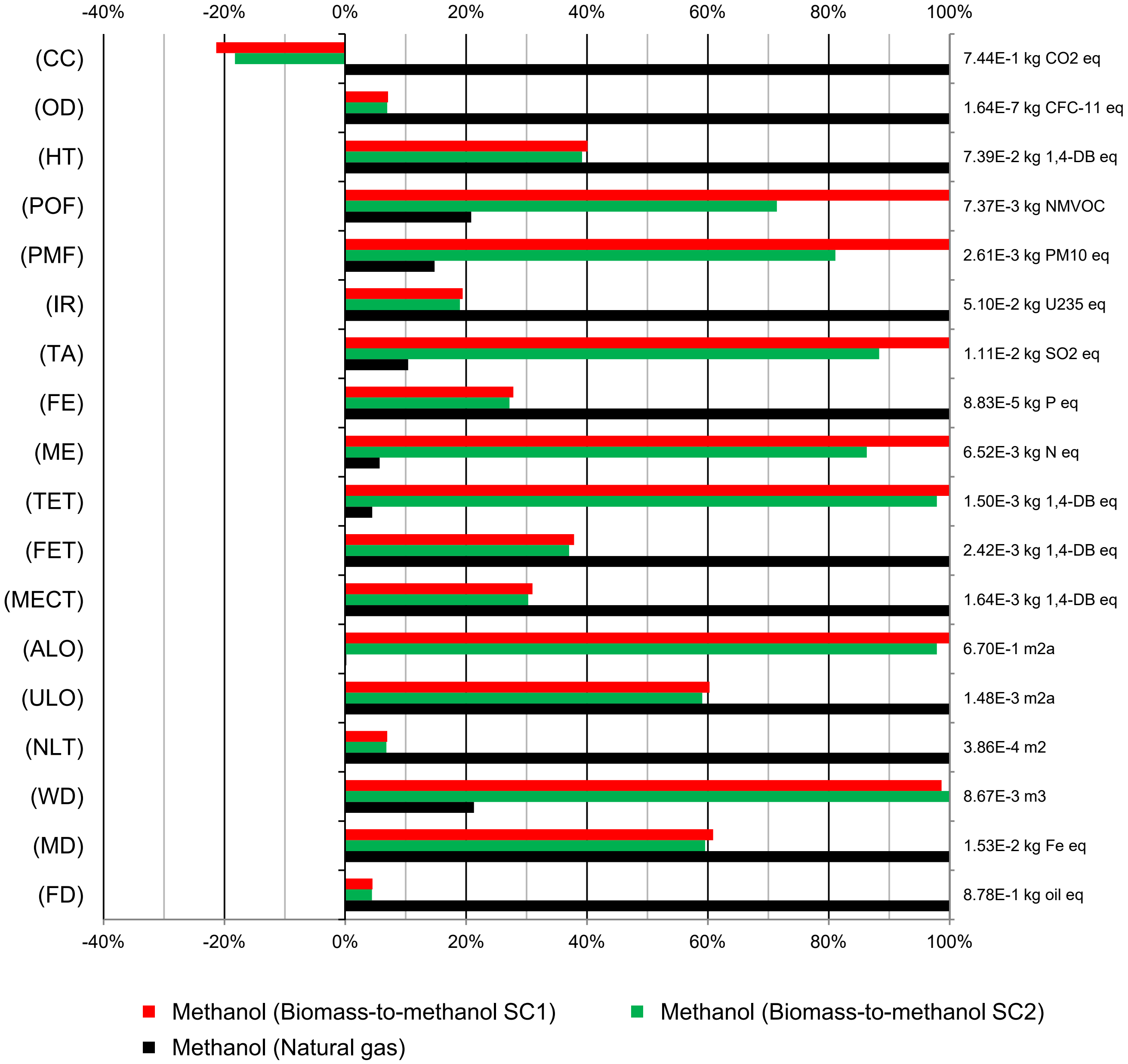

Figure 109 - Comparative potential environmental impacts for methanol production (kg) by optimized 1G sugarcane biorefinery integrate Biomass-to-Methanol (SC1 and SC2) routes; and Methanol from SMR of natural gas (fossil). Method: World ReCiPe (H) midpoint.

The comparative potential environmental impacts (Figure 109) clearly show the differences between the potential environmental impacts of a ‘purely’ industrial plant (fossil fuel based) and an agricultural plant-based (renewable based) for grade AA methanol production, these characteristics is evident in ALO and FD impact indicators.

Biomass-to-Methanol (SC1) is integrated as partially-integrated mode with the 1G sugarcane biorefinery (CHP/EBPST SC1), and Biomass-to-Methanol (SC2) is integrated as fully-integrated mode with the 1G sugarcane biorefinery. Thermochemical-biorefinery (Biomass-to-Methanol SC1) and thermochemical-biorefinery (Biomass-to-Methanol SC2) integrates a double-column cryogenic air separation unit (ASU) to supply high-purity oxygen to the directly-heated gasifier (system-boundary). The environmental potential impacts considers the liquid N_2 (LNG) and liquid Ar (LAR) as products allocating part of the environmental impacts according to economic allocation approach in the section 3.1.4.2 (Economic allocation approach).

As shown in Figure 109, thermochemical-biorefinery (Biomass-to-Methanol SC1 and Biomass-to-Methanol SC2) scenarios they have a similar behavior profile (similar thermochemical technologies) with small differences in the impact indicator scores, which is resultants from the different energetic integrations of thermochemical route with 1G sugarcane biorefinery (with or without CHP/EBPST system). Also, shows that for all most potential environmental impacts (scores) for the thermochemical-biorefinery (Biomass-to-Methanol SC1) and thermochemical-biorefinery (Biomass-to-Methanol SC2) there is a tendency to decrease with increasing net-energy efficiency (methanol productivity) of the technologies/routes, showing a direct proportionality with the environmental impact allocations.

GWP depend of bagasse fraction that is gasified in the thermochemical route and in the fraction that is burned in the traditional CHP/PEST system (auxiliary). In the scenario Biomass-to-Methanol (SC1) 71.2% of available bagasse is sent to gasifier and in the Biomass-to-Methanol (SC2) 100% is sent to gasifier. Large-scale SMR of natural gas contributes to GWP for 7.44E-1 kg of CO_2 equivalent per kg of methanol produced while the thermochemical-biorefinery (Biomass-to-Methanol SC1) contributes to GWP for -1.59E-1 kg of CO_2 equivalent per kg of methanol produced (negative emissions) and the thermochemical-biorefinery (Biomass-to-Methanol SC2) contributes to GWP for -1.36E-2 kg of CO_2 equivalent per kg of methanol produced (negative emissions), 14.5% less carbon sequestration potential than the thermochemical-biorefineries (Biomass-to-Methanol SC1).

Process biomass trough different transformation stages (e.g.: handling, transport, drying, milling/crushing and burning) contribute for PMFP due generate large amounts of fines particulates, burning biomass emits NOx, SOx, NH3, and particulate matter (fly-ashes), that also contribute to PMFP. The impact of process sugarcane bagasse depends on the fractions of the available biomass is processed by the thermochemical route and the fraction of biomass is processed by the CHP/EBPST, milling and drying processes emits fine-matter particles PM_{10} less than the burning process in solid-fuel fired boilers (considering the two systems with control of particulate emissions).

Thermochemical-biorefinery (Biomass-to-Methanol SC1) contributes to PMFP for 2.61E-3 kg of PM_{10} equivalent per kg of methanol produced while the thermochemical-biorefinery (Biomass-to-Methanol SC2) contributes to PMFP for 2.12E-4 kg of PM_{10} equivalent per kg of methanol produced (about 18.9% less PM_{10}). Large-scale SMR of natural gas contributes to PMFP for 3.85E-3 kg of PM_{10} equivalent per kg of methanol produced, which is about 81.8% less PMFP.

HTP and FETP there is higher for large-scale SMR of natural gas they are accounted the impacts of the fossil resource use (burned). Large amount of natural gas consumed contributing for IRP and FEP. The thermochemical-biorefineries (Biomass-to-Methanol SC1 and SC2) have a similar performance, varying only in function of the net-electrical efficiency. Thermochemical-biorefineries contributes at about 70-80% less in this indicators compared whit the large-scale SMR of natural gas.

TETP is higher for thermochemical-biorefineries due the agricultural phase and the burning biomass/syngas processes (NO_x, SO_x, NH_3, phosphates, and VOCs).The nutrient enrichment of the marine water (MEP) and terrestrial (TEP) is due to the use of fertilizer and pesticides in agricultural phase and chemicals in industrial phase with a small contribution of NOx, SOx, NH3 and nitrates present in flue-gas.

Large-scale SMR of natural gas plants have a higher NLTP and ULOP (not considered ALOP) than thermochemical-biorefineries which have a major impact on ALO. Thermochemical-biorefinery (Biomass-to-Methanol SC1) contributes to ALOP of 6.70E-1 m² de area per kg of methanol produced and thermochemical-biorefinery (Biomass-to-Methanol SC2) contributes to ALOP of 6.56.70E-1 m² de area per kg of methanol produced, while large-scale SMR of natural gas plants contribute to ALOP of 1.18E-3 m² de area per kg of methanol produced, that is about 1.8% of the ALOP for the thermochemical-biorefinery (Biomass-to-Methanol SC2).

Large-scale SMR of natural gas plants contribute to NLTP of 3.86E-4 m² de area per kg of methanol produced while thermochemical-biorefinery (Biomass-to-Methanol SC1) contributes to NLTP of 2.68E-5 m² de area per kg of methanol produced, which is about 81.8% less, and thermochemical-biorefinery (Biomass-to-Methanol SC2) contributes to NLTP of 2.62E-1 m² de area per kg of methanol produced,

Thermochemical-biorefinery (Biomass-to-Methanol SC1) contributes to WDP of 8.55E-3 m³ of water per kg of methanol produced and thermochemical-biorefinery (Biomass-to-Methanol SC2) contributes to WDP of 8.67E-3 m³ of water per kg of methanol produced, 13.6% more than the thermochemical-biorefinery (Biomass-to-Methanol SC1), while large-scale SMR of natural gas plants contribute to 1.85E-4 m³ of water per kg of methanol produced, 78.7% more than the thermochemical-biorefinery (Biomass-to-Methanol SC2)

Large-scale SMR of natural gas plants contribute to FDP of 8.78E-1 kg of oil equivalent per kg of methanol produced while thermochemical-biorefinery (Biomass-to-Methanol SC2) contributes to FDP of 3.87E-2 kg of oil equivalent per kg of methanol produced, a reduction of 96.8% on FDP. Thermochemical-biorefinery (Biomass-to-Methanol SC1) has practically the same impact of the thermochemical-biorefinery (Biomass-to-Methanol SC2), contributing to FDP of 3.96E-2 kg of oil equivalent per kg of methanol produced, that is 0.09% more.

Figure 110 presents the bar chart of characterized impact indicators performed for methanol production by optimized 1G sugarcane biorefinery integrate Biomass-to-Methanol (SC1) route. Using the World 2008 midpoint ReCiPe model in SimaPro®7.3.3 software (economic allocation approach), in kg comparative base unit.

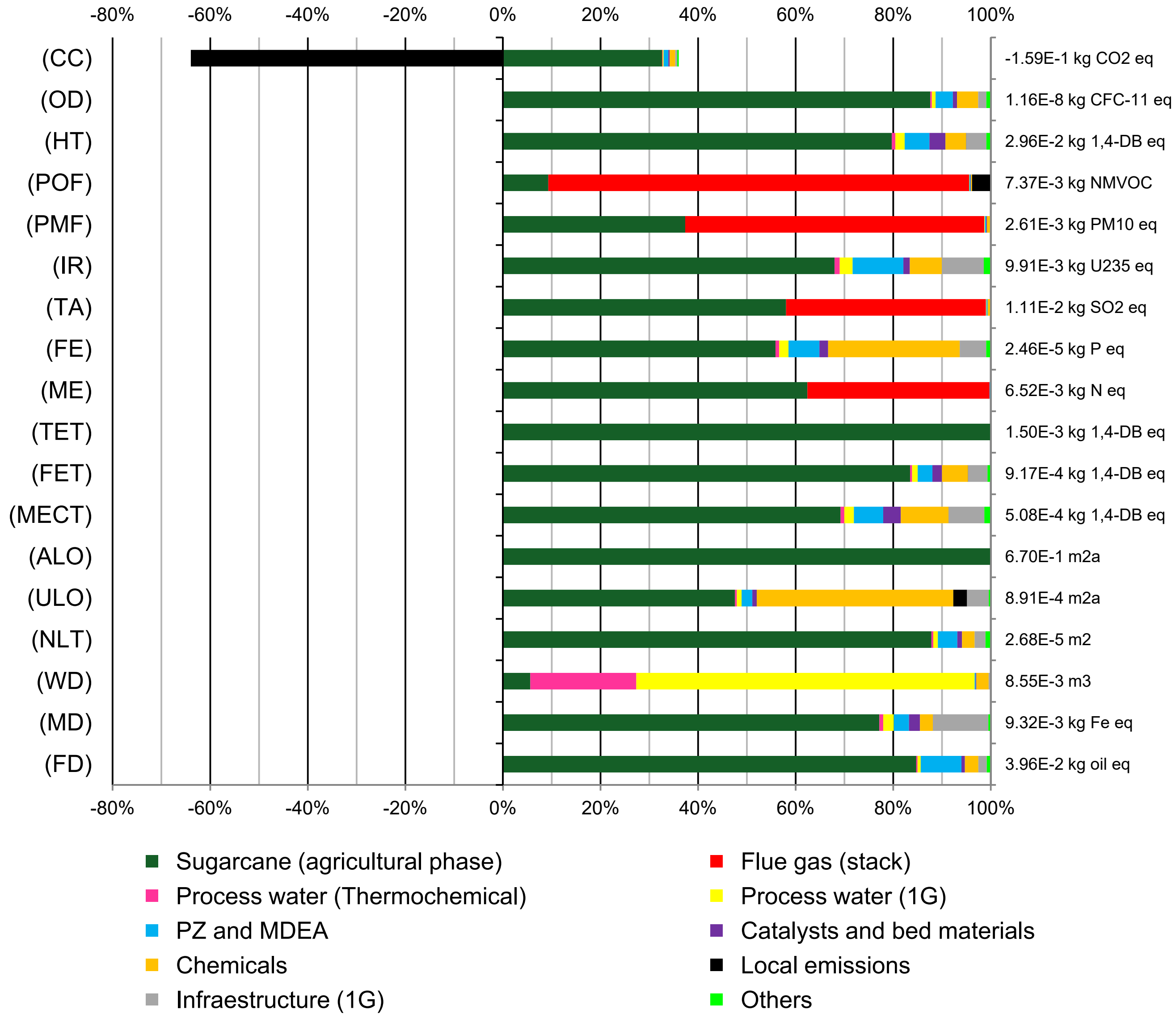

Figure 110 - Characterized impact indicators for methanol production (kg) by optimized 1G sugarcane biorefinery integrate Biomass-to-Methanol (SC1) route. Method: World ReCiPe (H) midpoint.

Figure 111 presents the bar chart of characterized impact indicators performed for methanol production by optimized 1G sugarcane biorefinery integrate Biomass-to-Methanol (SC2) route. Using the World 2008 midpoint ReCiPe model in SimaPro®7.3.3 software (economic allocation approach), in kg comparative base unit.

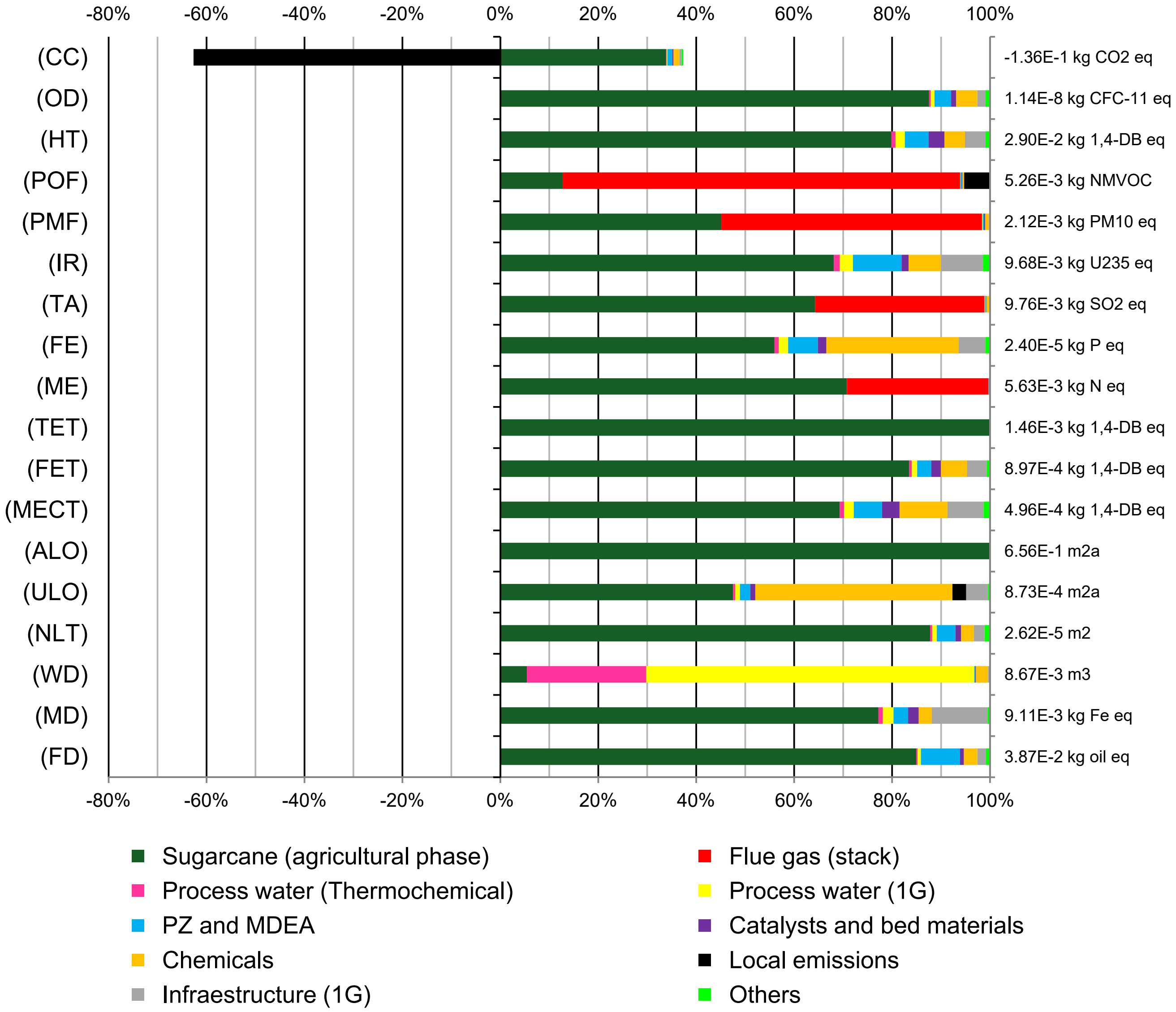

Figure 111 - Characterized impact indicators for methanol production (kg) by optimized 1G sugarcane biorefinery integrate Biomass-to-Methanol (SC2) route. Method: World ReCiPe (H) midpoint.

As shown in Figure 110, the results of characterized impact indicators for methanol production by thermochemical-biorefinery (Biomass-to-Methanol SC1), and as shown in and Figure 111, by thermochemical-biorefinery (Biomass-to-Methanol SC2) they have a similar behavior profile with small differences in the impact indicator scores resultants from the different energetic integrations of thermochemical route with 1G sugarcane biorefinery (with or without CHP/EBPST system). Also shows that the sugarcane agricultural phase has the largest contribution in the most of the environmental impact indicators and the flue-gas have a significant contribution in some of the indicators.

Biomass-to-Methanol (SC1) is integrated as partially-integrated mode with the 1G sugarcane biorefinery (CHP/EBPST SC1), and Biomass-to-Methanol (SC2) is integrated as fully-integrated mode with the 1G sugarcane biorefinery.

The main positive impacts on GWP came from the agricultural phase emissions are related with machinery, transport and diesel burning impacts (machinery and trucks). For the thermochemical-biorefinery (Biomass-to-Methanol (SC1) the agricultural phase contributes to GWP for 1.86E-1 kg of CO_2 equivalent per kg of methanol produced (about 90.6% of the positive scores). And the negative contribution on GWP, from local emissions group, is due to the co-capture of CO_2 and H_2S system and geological storage or injection into oil reservoirs (CCS), storage consideration for the thermochemical-biorefinery (Biomass-to-Methanol SC1) contributes to GWP for -3.64E-1 kg of CO_2 equivalent kg of methanol produced (credits).

Biomass-to-Methanol (SC1) impact on WDP due to the need of a cooling tower system (evaporative and drift losses), process losses and consumptions (gasification agent and CO_2 and H_2S PZ/MDEA blend-based co-capture system), but main thermochemical-biorefinery WDP impacts come from the 1G biorefinery technologies and agricultural phase. Thermochemical process water group contributes to WDP for 1.86E-3 m^3 of water per kg of methanol produced (about 21.7% of the total score) and the 1G-process water group contributes to WDP for 5.93E-3 m^3 of water per kg of methanol produced (about 69.3% of the total score).

Process biomass trough different transformation stages (e.g.: handling, transport, drying, milling/crushing and burning) contribute for PMFP due generate large amounts of fines particulates, burning biomass emits NOx, SOx, NH3, and particulate matter (fly-ashes), that also contribute to PMFP. The impact of process sugarcane bagasse depends on the fractions of the available biomass is processed by the thermochemical route and the fraction of biomass is processed by the CHP/EBPST, milling and drying processes emits fine-matter particles PM_{10} less than the burning process in solid-fuel fired boilers (considering the two systems with control of particulate emissions).

Thermochemical-biorefinery (Biomass-to-Methanol SC1) applying CHP/CEST (SC5) contributes to PMFP for 2.61E-3 kg of PM_{10} equivalent kg of methanol produced, the total flue-gas from stack and dryers contribute to PMFP for 1.06E-3 kg of PM_{10} equivalent per kg of methanol produced (about 61.3% of the total score). Thermochemical-biorefinery (Biomass-to-Methanol SC2) fully-integrated (without solid-fuel fired boilers) contributes to PMFP for 2.12E-3 kg of PM_{10} equivalent kg of methanol produced (18.9% less PM_{10}), the total flue-gas from stack and dryers contribute to PMFP for 1.13E-3 kg of PM_{10} equivalent per kg of methanol produced (about 53.2% of the total score).

The formation of NO_x, SO_x and VOCs present in the flue-gas (stack) from the biomass burning in 1G-boiler CHP/EBPST (SC1) and from synthesis gas burning in EvGT (exhaust-gas) are the major contributors on POFP. The total flue-gas emissions by thermochemical-biorefinery (Biomass-to-Methanol SC1) contributes to POFP for 6.35E-3 kg of NMVOC per kg of methanol produced (about 86.2% of the total score) while for thermochemical-biorefinery (Biomass-to-Methanol SC2) contributes to POFP for 4.27E-3 kg of NMVOC per kg of methanol produced (about 81.1% of the total score).

Use of PZ and MDEA in the co-capture of CO_2 and H_2S system in the Biomass-to-Methanol SC1) contributes to FDP for 3.32E-3 kg of oil equivalent per kg of methanol produced (about 8.4% of the total score) while agricultural phase contribute for 3.36E-2 kg of oil equivalent per kg of methanol produced (about 84.7% of the total score). Use of PZ and MDEA in the co-capture of CO_2 and H_2S system in the Biomass-to-Methanol (SC2) contributes to FDP for 3.10E-3 kg of oil equivalent per kg of methanol produced (about 8.0% of the total score) while agricultural phase contributes for 3.87E-2 kg of oil equivalent per kg of methanol produced (about 84.9% of the total score)

The flue-gas emission (NO_x, SO_x and NH_3) by thermochemical-biorefinery (Biomass-to-Methanol SC1) contributes to TAP for 4.52E-3 kg of SO_2 per kg of methanol produced (about 40.9% of the total score) while the flue-gas emission by thermochemical-biorefinery (Biomass-to-Methanol SC2) contributes to TAP for 3.37E-3 kg of SO_2 per kg of methanol produced (about 34.5% of the total score).

The thermochemical-biorefinery (Biomass-to-Methanol SC1) contributes to ALOP for about 6.70E-1 m^2 of area per kg of methanol produced while the thermochemical-biorefinery (Biomass-to-Methanol SC2) contributes to ALOP for about 6.56E-1 m^2 of area per kg of methanol produced, that is 14.1% less.

The main differences between thermochemical-biorefinery (Biomass-to-Methanol SC1) and thermochemical-biorefinery (Biomass-to-Methanol SC2) are caused by burning biomass (solid fuel) in the solid-fuel fired boilers or burning gas (gaseous fuel) in the EvGT, a little better environmental performance of the is due to the fact that the combined cycle has higher energy efficiency than the thermochemical-biorefinery (Biomass-to-Methanol SC2) is due to the fact that the EvGT/CC has higher energy efficiency than the traditional solid-fuel fired boiler system.

9.9 Comparative potential environmental impacts for anhydrous ethanol (kg): by first generation sugarcane biorefinery (SC5); by sugarcane biorefinery integrate Biomass-to-Mixed alcohols routes (SC1 and SC2) - (renewable resource); and gasoline by Brazil's petroleum refineries - (fossil resource)

Anhydrous ethanol is an important liquid transportation fuel in Brazil, and this comparison shows how a technological evolution in sugarcane biorefineries can change the Brazil's sugar-energy sector from an environmentally point of view reflecting the impacts from the use of different fuel-options (sources and types).

To assess and compare different liquid transportation fuels is necessary perform a cradle-to-grave assessment, at least partially. Ethanol and gasoline have different energy densities and one of the major steps with great influence undergoes the evaluation of environmental impacts is the fuel end-uses (i.e.: combustion) and their emissions. Only the use models are applied, not being evaluated logistics, transportation and commercialization steps (future works when the VSB tool consider the models for it).

Comparative potential environmental impacts (comparative graph bars) for anhydrous ethanol production (kg) by 1G sugarcane biorefinery integrate Biomass-to-mixed alcohols (SC1 and SC2) routes and 1G sugarcane biorefinery with CHP/CEST (SC5) route are presented in the APPENDIX B as supplementary materials.

The comparative analysis of potential environmental impacts for liquid transportation fuels (renewable and fossil-derived) take into account the impacts from the use of the bio-based ethanol (anhydrous form) produced by thermochemical-biorefineries and the use of pure-gasoline (equivalent fossil product) produced in petroleum refineries (Brazil case). This comparison is carried out for cradle-to-gate system boundary and applying end-use models (2013 base year) for Brazilian case-scenario (without logistic/distribution models) developed using the VSB tool by the division of AIB of the CTBE/CNPEM.

LCA data for gasoline were obtained from Ecoinvent database taking into account the entire life cycle, that is from the extraction and processing of crude oil (adapted to Brazil case) to the end-use in Brazilian vehicles. The end-use models for fossil-derived pure-gasoline and ethanol (hydrous or anhydrous form – comparison based on potential energy) are based on the energy content equivalence measured as potential energy per mass/volume of fuel (MJ/kg or MJ/L).

The comparison is performed considering the different energy density between fossil-gasoline and ethanol in combustion process and their impacts are compared per MJ of potential energy generated.

Figure 112 presents the bar chart of comparative potential environmental impacts performed for ethanol (renewable resource) and for pure-gasoline (fossil resource), considering the use in Brazil's passenger average-vehicles (2013) as end-use model. The impact scores are obtained by using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach) in MJ comparative base unit for gasoline (44.2 MJ/kg) and ethanol (26.4 MJ/kg).

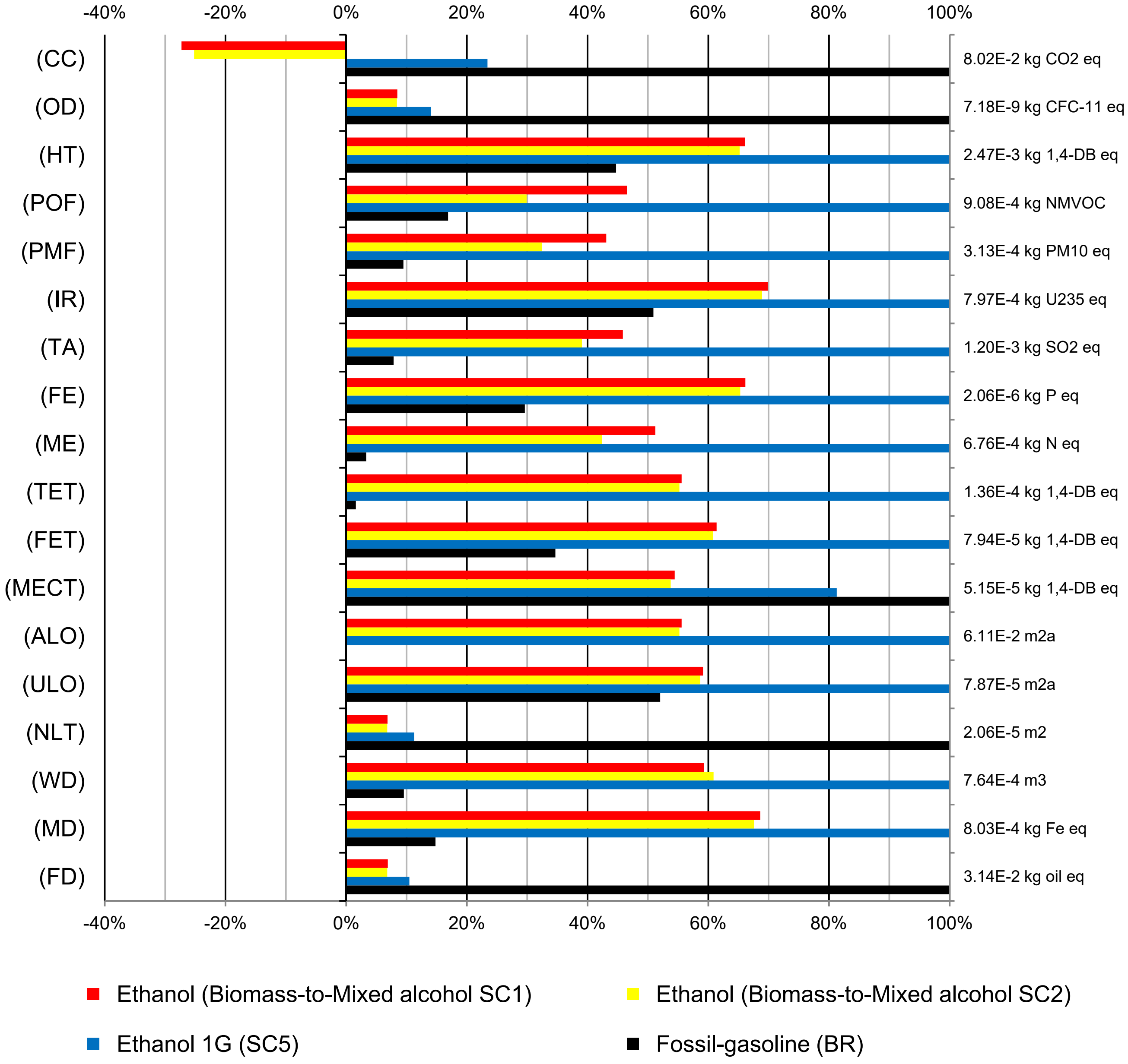

Figure 112 - Comparative potential environmental impacts for: ethanol (MJ) derived from optimized 1G sugarcane biorefinery integrate Biomass-to-Mixed alcohols (SC1 and SC2) routes; ethanol (MJ) derived from optimized 1G sugarcane biorefinery with traditional CHP/CEST (SC5) route (renewable resources); and for Brazilian market pure-gasoline derived from petroleum refinery (fossil resource). Method: World ReCiPe (H) midpoint. Analyze considering the use in Brazil's passenger average-vehicles (2013) as end-use model.

In the APPENDIX B are presented as supplementary materials the comparative potential environmental impacts for ethanol end-use (MJ) derived from optimized 1G sugarcane biorefinery integrate Biomass-to-Mixed alcohols (SC1 and SC2) routes; 1G sugarcane biorefinery with traditional CHP/CEST (SC1) system; and for Brazilian (market based) pure fossil-derived gasoline use, derived from petroleum refinery (at plant) (without adding ethanol in the composition).

The comparative potential environmental impacts (Figure 109) clearly show the differences between the potential environmental impacts of a ‘purely’ industrial plant (fossil fuel based) and an agricultural plant-based (renewable based).

Ethanol produced by the thermochemical-biorefinery (1G/2G ethanol) is the sum of the 1G ethanol produced in the 1G sugarcane biorefinery with the 2G ethanol produced in the thermochemical route (Biomass-to-Mixed alcohols).

As shown in Figure 112, the results of comparative potential environmental impacts shows major potential environmental impacts of ethanol produced by 1G sugarcane biorefinery with traditional CHP/CEST (SC5) system (high-efficiency system) and used in Brazil’s passenger average-vehicles (fuel consumption and emission databank) in many indicators in comparison with pure-gasoline produced by petroleum refinery and used in Brazil’s passenger average-vehicles (fuel consumption and emission databank). This difference is much more pronounced when compared to a 1G sugarcane biorefinery with traditional CHP/CEST (SC1) system, low efficiency energetic system (APPENDIX B).

From the production-chain to end-use ethanol in MJ comparative base unit has the greatest impact scores on the indicators HTP, POFP, PMFP, IRP, TAP, FEP, MEP, TETP, FETP, ALOP, ULOP, WDP, and MDP (13/18 indicators). These indicators represent mostly local potential impacts.

From the production-chain to end-use pure-gasoline in MJ comparative base unit has the greatest impact scores on the indicators GWP, ODP, MECTP, NLTP, and FDP. These indicators represent mostly global potential impacts.

As shown in Figure 109, thermochemical-biorefinery (Biomass-to-Mixed alcohols SC1 and Biomass-to-Mixed alcohols SC2) scenarios they have a similar behavior profile (similar thermochemical technologies) with small differences in the impact indicator scores, which is resultants from the different energetic integrations of thermochemical route with 1G sugarcane biorefinery (with or without CHP/EBPST system).

Also, shows a very interesting results, thermochemical-biorefinery (Biomass-to-Mixed alcohols SC2) was expected to result in better environmental performance, but turned upside down due the fat of the Biomass-to-Mixed alcohols (SC2) apply an EvGT with TIT at 1300.0ºC and not an EvGT with TIT at 1500.0ºC (Biomass-to-Mixed alcohols SC1). EvGT - TIT at 1500.0ºC in CC has net-energy efficiency higher than EvGT – TIT at 1300.0ºC in CC. In addition, the double-column cryogenic air separation unit (ASU) has different size, requiring more electricity in the Biomass-to-Mixed alcohols (SC2) to produce more high-purity oxygen to directly-heated gasifier and to liquefy and produce more LNG (economic allocation effect).

Biomass-to-Mixed alcohols (SC2) route fully-integrated produces 12.94 tonnes/hr of 2G ethanol, and the Biomass-to-Mixed alcohols (SC1) route produces 13.89 tonnes/hr of 2G ethanol, the plant-energy efficiency (thermal and electrical energy) is higher for the Biomass-to-Mixed alcohols (SC1).

Thermochemical-biorefinery (Biomass-to-Mixed alcohols) scenarios there is smaller significant differences between them, the main differences are related to flue-gas emissions owing difference between the biomass burning in boiler (CHP/EBPST SC1) and burning synthesis gas (light-gas) in EvGT and by economic allocation approach (productivity).

Biomass-to-Mixed alcohols (SC1) is integrated as partially-integrated mode with the 1G sugarcane biorefinery (CHP/EBPST SC1), and Biomass-to-Mixed alcohols (SC2) is integrated as fully-integrated mode with the 1G sugarcane biorefinery. Thermochemical-biorefinery (Biomass-to-Mixed alcohols SC1) and thermochemical-biorefinery (Biomass-to-Mixed alcohols SC2) integrates a double-column cryogenic air separation unit (ASU) to supply high-purity oxygen to the directly-heated gasifier (system-boundary). The environmental potential impacts considers the liquid N_2 (LNG) and liquid Ar (LAR) as products allocating part of the environmental impacts according to economic allocation approach in the section 3.1.4.2 (Economic allocation approach).

Thermochemical-biorefineries GWP depend of bagasse fraction that is gasified in the thermochemical route and in the fraction that is burned in the traditional CHP/PEST system (auxiliary). In the scenario Biomass-to-Mixed alcohols (SC1) 73.0% of available bagasse (partially-integrated mode) is sent to gasifier and in the Biomass-to-Mixed alcohols (SC2) 100% is sent to gasifier (fully-integrated mode).

Consumption of fossil-derived pure-gasoline contributes to GWP for 8.02E-2 kg of CO_2 equivalent per MJ of gasoline-energy consumed.

Consumption of 1G ethanol derived from 1G biorefinery (CHP/CEST SC5) contributes to GWP for 1.88E-2 kg of CO_2 equivalent per MJ of ethanol-energy consumed, reduction of 76.6% front the GWP of the consumption of fossil-derived pure-gasoline.

Consumption of 1G/2G ethanol derived from thermochemical-biorefinery (Biomass-to-Mixed alcohols SC1) contributes to GWP for -2.02E-2 kg of CO_2 equivalent per MJ of ethanol-energy consumed, reduction of 127.0% front the GWP of the consumption of fossil-derived pure-gasoline (negative emissions). Obviously, means the sequestration of 27% of the CO_2 equivalent per MJ of gasoline-energy consumed (CCS).

Consumption of 1G/2G ethanol derived from thermochemical-biorefinery (Biomass-to-Mixed alcohols SC2) contributes to GWP for -2.19E-2 kg of CO_2 equivalent per MJ of ethanol-energy consumed, reduction of 125.0% front the GWP of the consumption of fossil-derived pure-gasoline (negative emissions). Obviously, means the sequestration of 25% of the CO_2 equivalent per MJ of gasoline-energy consumed (CCS).

Consumption of fossil-derived pure-gasoline contributes to FDP for 3.14E-2 kg of oil equivalent per MJ of gasoline-energy consumed.

Consumption of 1G ethanol derived from 1G biorefinery (CHP/CEST SC5) contributes to FDP for 3.29E-3 kg of oil equivalent per MJ of ethanol-energy consumed, reduction of 89.5% front the FDP of the consumption of fossil-derived pure-gasoline.

Consumption of 1G/2G ethanol derived from thermochemical-biorefinery (Biomass-to-Mixed alcohols SC1) contributes to FDP for 2.16E-2 kg of oil equivalent per MJ of ethanol-energy consumed, reduction of 93.1% front the FDP of the consumption of fossil-derived pure-gasoline (from fossil to renewable biomass resources).

Consumption of 1G/2G ethanol derived from thermochemical-biorefinery (Biomass-to-Mixed alcohols SC2) contributes to FDP for 2.13E-2 kg of oil equivalent per MJ of ethanol-energy consumed, reduction of 93.2% front the FDP of the consumption of fossil-derived pure-gasoline.

Process biomass trough different transformation stages (e.g.: handling, transport, drying, milling/crushing and burning) contribute for PMFP due generate large amounts of fines particulates, burning biomass emits NOx, SOx, NH_3, and particulate matter (fly-ashes), and burning the fuel in the engines emits NOx, Sox and fine-particles of catalyst or impurities, that also contribute to PMFP. The impact of process sugarcane bagasse depends on the fractions of the available biomass is processed by the thermochemical route and the fraction of biomass is processed by the CHP/EBPST, milling and drying processes emits fine-matter particles PM_{10} less than the burning process in solid-fuel fired boilers (considering the two systems with control of particulate emissions).

Consumption of 1G/2G ethanol derived from thermochemical-biorefinery (Biomass-to-Mixed alcohols SC1) contributes to PMFP for 1.35E-3 kg of PM_{10} equivalent per MJ of ethanol-energy consumed while the consumption of 1G/2G ethanol derived from thermochemical-biorefinery (Biomass-to-Mixed alcohols SC2) contributes to PMFP for 1.01E-4 kg of PM_{10} equivalent per MJ of ethanol-energy consumed (about 24.7% less PM_{10}). Consumption of fossil-derived pure-gasoline contributes to PMFP for 2.96E-5 kg of PM_{10} equivalent per MJ of gasoline-energy consumed, which is about 70.0% to 80.0% less PMFP than the PMFP by the consumption of 1G/2G ethanol derived from thermochemical-biorefinery. Consumption of 1G ethanol derived from 1G biorefinery (CHP/CEST SC5) contributes to PMFP for 3.13E-4 kg of PM_{10}

equivalent per MJ of ethanol-energy consumed, which is about 78.0% to 105.0% more PMFP than the PMFP by the consumption of 1G/2G ethanol derived from thermochemical-biorefinery

While for the consumption of 1G/2G ethanol derived from thermochemical-biorefinery emits more fine-particulate materials (PM_{10}) in the industrial phase the (industrial park) consumption of fossil-derived pure-gasoline emits more fine-particulate materials (PM_{10}) in the end-use phase (e.g.: city roads).

Ecotoxicity, acidification and eutrophication (e.g.: TAP, FEP, MEP, TETP, and FETP) is higher for biorefineries than for petroleum refineries due the agricultural phase and the burning biomass/syngas processes (NO_x, SO_x, NH_3, phosphates, and VOCs).The nutrient enrichment of the marine water (MEP) and terrestrial (TEP) is due to the use of fertilizer and pesticides in agricultural phase and chemicals in industrial phase with a small contribution of NOx, SOx, NH3 and nitrates present in flue-gas.

Fossil-derived pure-gasoline has a higher impact on NLTP and ULOP than 1G/2G ethanol derived from thermochemical-biorefineries (Biomass-to-Mixed alcohols SC1 and SC2) and then 1G ethanol derived from 1G biorefinery (CHP/CEST SC5). Intend, 1G ethanol derived from 1G biorefinery (CHP/CEST SC5) and 1G/2G ethanol derived from thermochemical-biorefineries (Biomass-to-Mixed alcohols SC1 and SC2) has a higher impact on ALOP than fossil-derived pure-gasoline.

Consumption of 1G ethanol derived from 1G biorefinery (CHP/CEST SC5) contributes to ALOP of 6.11E-2 m² de area per MJ of ethanol-energy consumed, consumption of 1G/2G ethanol derived from thermochemical-biorefinery (Biomass-to-Mixed alcohols SC1) contributes to ALOP of 3.40E-2 m² de area per MJ of ethanol-energy consumed, that is about 44.4% of the ALOP for the 1G biorefinery (CHP/CEST SC5), and consumption of 1G/2G ethanol derived from thermochemical-biorefinery (Biomass-to-Mixed alcohols SC2) contributes to ALOP of 3.37E-1 m² de area per MJ of ethanol-energy consumed, that is about 44.8% of the ALOP for the 1G biorefinery (CHP/CEST SC5).

Consumption of 1G ethanol derived from 1G biorefinery (CHP/CEST SC5) contributes to WDP for 7.64E-4 m³ of water per MJ of ethanol-energy consumed, consumption of 1G/2G ethanol derived from thermochemical-biorefinery (Biomass-to-Mixed alcohols SC1) contributes to WDP for 4.53E-4 m³ of water per MJ of ethanol-energy consumed, that is about 40.7% of the WDP for the 1G biorefinery (CHP/CEST SC5), and consumption of 1G/2G ethanol derived from thermochemical-biorefinery (Biomass-to-Mixed alcohols SC2) contributes to WDP for 4.65E-3 m³ of water per MJ of ethanol-energy consumed, that is about 39.1% of the WDP for the 1G biorefinery (CHP/CEST SC5).

Consumption of fossil-derived pure-gasoline contributes to WDP for 7.31E-5 m³ of water per MJ of gasoline-energy consumed, which is 83.9% less than the WDP for the thermochemical-biorefinery (Biomass-to-Mixed alcohols SC1) and 84.3% less than the WDP for the thermochemical-biorefinery (Biomass-to-Mixed alcohols SC2).

Figure 113 presents the bar chart of characterized impact indicators performed for ethanol production by optimized 1G sugarcane biorefinery integrate Biomass-to-Mixed alcohols (SC1) route. Using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach), in kg comparative base unit

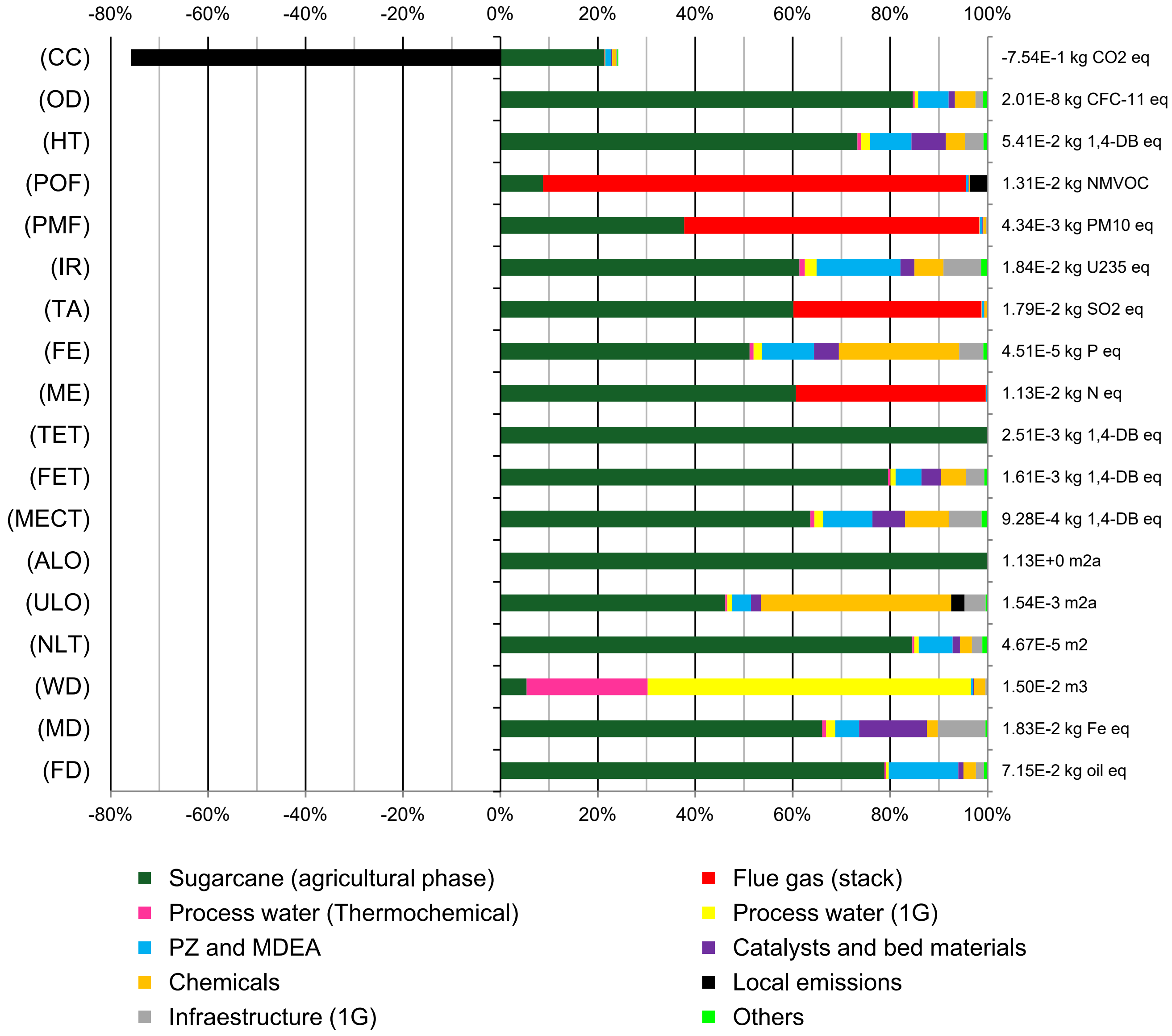

Figure 113 - Characterized impact indicators for ethanol production (kg) by optimized 1G sugarcane biorefinery integrate Biomass-to-Mixed alcohols (SC1) route. Method: World ReCiPe (H) midpoint.

Figure 114 presents the bar chart of characterized impact indicators performed for ethanol production by optimized 1G sugarcane biorefinery integrate Biomass-to-

Mixed alcohols (SC2) route. Using the World midpoint ReCiPe 2008 model in SimaPro$^{®}$7.3.3 software (economic allocation approach), in kg comparative base unit

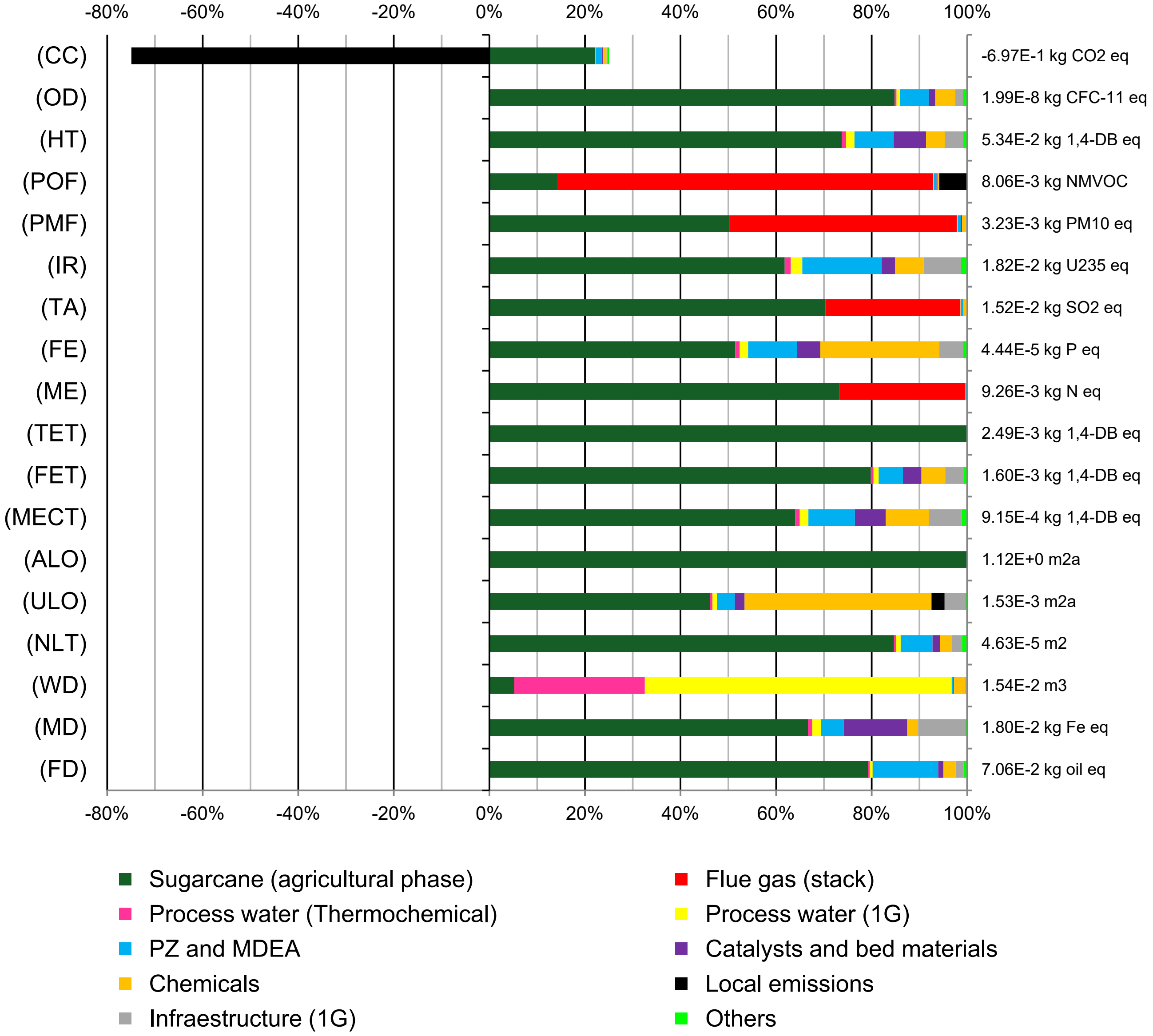

Figure 114 - Characterized impact indicators for ethanol production (kg) by optimized 1G sugarcane biorefinery integrate Biomass-to-Mixed alcohols (SC2) route. Method: World ReCiPe (H) midpoint.

As shown in Figure 113, the results of characterized impact indicators for ethanol production by thermochemical-biorefinery (Biomass-to-Mixed alcohols SC1), and as shown in and Figure 114, by thermochemical-biorefinery (Biomass-to-Mixed alcohols SC2) they have a similar behavior profile with small differences in the impact indicator scores resultants from the different energetic integrations of thermochemical route with 1G sugarcane biorefinery (with or without CHP/EBPST system). Also shows that the sugarcane agricultural phase has the largest contribution in the most of the environmental impact indicators and the flue-gas have a significant contribution in some of the indicators.

Biomass-to-Mixed alcohols (SC1) is integrated as partially-integrated mode with the 1G sugarcane biorefinery (CHP/EBPST SC1), and Biomass-to-Mixed alcohols (SC2) is integrated as fully-integrated mode with the 1G sugarcane biorefinery.

The main positive impacts on GWP came from the agricultural phase emissions are related with machinery, transport and diesel burning impacts (machinery and trucks). For the thermochemical-biorefinery (Biomass-to-Mixed alcohols SC1) the agricultural phase contributes to GWP for 3.12E-1 kg of CO_2 equivalent per kg of ethanol produced (about 88.2% of the positive scores). And the negative contribution on GWP, from local emissions group, is due to the co-capture of CO_2 and H_2S system and geological storage or injection into oil reservoirs (CCS), storage consideration for the thermochemical-biorefinery (Biomass-to-Mixed alcohols SC1) contributes to GWP for -1.11E-1 kg of CO_2 equivalent kg of ethanol produced (credits).

Biomass-to-Mixed alcohols (SC1) impact on WDP due to the need of a cooling tower system (evaporative and drift losses), process losses and consumptions (gasification agent and CO_2 and H_2S PZ/MDEA blend-based co-capture system), but main thermochemical-biorefinery WDP impacts come from the 1G biorefinery technologies and agricultural phase. Thermochemical process water group contributes to WDP for 3.73E-3 m³ of water per kg of ethanol produced (about 24.9% of the total score) and the 1G-process water group contributes to WDP for 9.73E-3 m³ of water per kg of ethanol produced (about 24.8% of the total score).

Process biomass trough different transformation stages (e.g.: handling, transport, drying, milling/crushing and burning) contribute for PMFP due generate large amounts of fines particulates, burning biomass emits NOx, SOx, NH3, and particulate matter (fly-ashes), that also contribute to PMFP. The impact of process sugarcane bagasse depends on the fractions of the available biomass is processed by the thermochemical route and the fraction of biomass is processed by the CHP/EBPST, milling and drying processes emits fine-matter particles PM_{10} less than the burning process in solid-fuel fired boilers (considering the two systems with control of particulate emissions).

Thermochemical-biorefinery (Biomass-to-Mixed alcohols SC1) applying CHP/CEST (SC5) contributes to PMFP for 4.34E-3 kg of PM_{10} equivalent kg of ethanol produced, the total flue-gas from stack and dryers contribute to PMFP for 2.63E-3 kg of PM_{10} equivalent per kg of ethanol produced (about 60.5% of the total score). Thermochemical-biorefinery (Biomass-to-Mixed alcohols SC2) fully-integrated (without solid-fuel fired boilers) contributes to PMFP for 1.54E-3 kg of PM_{10} equivalent kg of ethanol produced (25.6% less PM_{10}), the total flue-gas from stack and dryers contribute to PMFP for 1.54E-3 kg of PM_{10} equivalent per kg of ethanol produced (about 47.5% of the total score).

The formation of NO_x, SO_x and VOCs present in the flue-gas (stack) from the biomass burning in 1G-boiler CHP/EBPST (SC1) and from synthesis gas burning in EvGT (exhaust-gas) are the major contributors on POFP. The total flue-gas emissions by thermochemical-biorefinery (Biomass-to-Mixed alcohols SC1) contributes to POFP for 1.13E-2 kg of NMVOC per kg of ethanol produced (about 86.8% of the total score) while thermochemical-biorefinery (Biomass-to-Mixed alcohols SC2) contributes to POFP for 6.34E-3 kg of NMVOC per kg of ethanol produced (about 78.7% of the total score).

Use of PZ and MDEA in the co-capture of CO_2 and H_2S system in the Biomass-to-Mixed alcohols (SC1) contributes to FDP for 1.02E-2 kg of oil equivalent per kg of ethanol produced (about 14.3% of the total score) while agricultural phase contributes for 5.64E-2 kg of oil equivalent per kg of ethanol produced (about 78.8% of the total score). Use of PZ and MDEA in the co-capture of CO_2 and H_2S system in the Biomass-to-Mixed alcohols SC2) contributes to FDP for 9.68E-3 kg of oil equivalent per kg of ethanol produced (about 13.7% of the total score) while agricultural phase contributes for 5.59E-2 kg of oil equivalent per kg of ethanol produced (about 79.3% of the total score)

The flue-gas emissions (NO_x, SO_x and NH_3) by thermochemical-biorefinery (Biomass-to-Mixed alcohols SC1) contribute to TAP for 6.92E-3 kg of SO_2 per kg of ethanol produced (about 38.6% of the total score) while the flue-gas emissions by thermochemical-biorefinery (Biomass-to-Mixed alcohols SC2) contribute to TAP for 4.29E-3 kg of SO_2 per kg of ethanol produced (about 28.2% of the total score).

The thermochemical-biorefinery (Biomass-to-Mixed alcohols SC1) contributes to ALOP for about 1.13E-0 m^2 of area per kg of ethanol produced while the thermochemical-biorefinery (Biomass-to-Mixed alcohols SC2) contributes to ALOP for about 1.12E-0 m^2 of area per kg of ethanol produced, that is 8.5% less.

The main differences between thermochemical-biorefinery (Biomass-to-Mixed alcohols SC1) and thermochemical-biorefinery (Biomass-to-Mixed alcohols SC2) are caused by burning biomass (solid fuel) in the solid-fuel fired boilers or burning gas (gaseous fuel) in the EvGT, a little better environmental performance of the is due to the fact that the combined cycle has higher energy efficiency than the thermochemical-biorefinery (Biomass-to-Mixed alcohols SC2) is due to the fact that the EvGT/CC has higher energy efficiency than the traditional solid-fuel fired boiler system.

10 Conclusions

This research Master's degree began by asking a major question ***"What is possible to obtain by using all the biomass that is available in sugarcane mills in a sustainable and feasible way?"*** however, in face of a wide range of possibilities that can answer this question, one tool that enable evaluate several technologies that are able to process this available biomass in the Brazilian sugarcane production chain context is the VSB simulation and assessment platform, a tool under development by the division of AIB of CTBE/CNPEM that allows perform assessments on the three pillars of sustainability (economical, environmental, and social).

One of the biomass conversion routes not yet evaluated in detail (2012) by using the VSB tool are the thermochemical conversion routes, this research Master's degree is the pioneer in assess thermochemical technologies for conversion of biomass to value-added bio-based products applying the VSB assessment methodologies (in this preliminary case the environmental aspects).

In the early and initial steps for design the context of this research Master's degree, a broad review was carried out against the numerous thermochemical routes and their possible technologies and characteristic obtained products, starting with the premise that thermochemical routes are simply compost by three-step-stages (blocks) ***"biomass gasification to synthesis gas - synthesis as conditioning – synthesis gas conversion to value-added bio-based products"***.

Obviously, observing the final thermochemical-biorefinery scenarios presented in the APPENDIX A as Aspen Plus$^{®}$v8.4 flowsheet's is not quite like this premise, thermochemical routes can be extremely complex and these simple three-step-stages multiply, turning the understanding of a biorefinery from the point of view as a complete-whole biorefinery system boundary much more complex, thermochemical routes are composed of interconnected-dependent processes, as well theirs parameters, that depend on each other (one set the others) to compose an efficient whole-biorefinery.

A key issue involved in thermochemical conversion routes of biomass is ***"how to represent the characteristic processes of these routes and estimate in an acceptable-accurate way the realistic performance of a thermochemical specific process or technology"***, since many of the thermochemical processes are complex and difficult representability (e.g.: biomass composition complexity, and biomass gasification), two answers are possible: by means of simple models adjusted by technical-realistic-parameters and results obtained from real-operational sized-plants; or by means rigorous and detailed models based on phenomenological models.

In view of all these and many other previous issues, ***thermochemical conversion routes of biomass were proposed considering as targeting-products***: ethanol, due the CTBE context (based on ethanol research and development; electricity, due the biomass competitive end-use (current biomass use); and methanol, comparable to ethanol and a mature-technology developed to convert synthesis gas to a value-added products.

Another key issue is ***"how to integrate these thermochemical routes at a first generation sugarcane biorefinery"***, this is the major key factor of this research Master's degree, and many integration possibilities can be performed, being the most common mass and energy integration: partially-integrated mode; fully-integrated mode; standalone mode; large-scale decentralized mode; cluster's mode; over-sized integrate mode; and combinations.

Initially, only the use of surplus biomass was performed (standalone mode), after this results ***was observed a possibility to improve the interaction between the 1G sugarcane biorefinery and the specific thermochemical conversion route, since the thermochemical route has a great potential to provide more-efficiently thermal and electrical energy than the traditional solid-fuel fired boiler systems***. And then, faced with this improve-possibility, two integration modes were performed, one where only part of the energy required by the 1G sugarcane biorefinery is supplied by the thermochemical route (partially-integrated mode), and another where all the energy required by the thermochemical-biorefinery as a whole are supplied only by the specific thermochemical route (fully-integrated mode).

The environmental performance of the partially-integrated mode or fully-integrated mode thermochemical conversion routes are similar for the targeting-product, differences are directly related to the productive efficiency (economic allocation approach effect) and to the fact that in partially-integrated mode part of the available biomass is burned in solid-fuel fired boiler with greater probability of emit pollutants (e.g.: NOx, SOx, particulate matters, chlorine content compounds, VOCs, and others) due the simple cleaning system normally employed, and in the fully-integrated mode all of the available biomass is gasified to synthesis gas that pass through an advanced selective impurities removal/cleaning system, when part of the sulfur content compounds, chlorine content compounds, and other compounds are removed prior to combustion in the EvGT avoiding their emission directly to atmosphere.

Based on the analysis of the results of these integration modes, it is possible to conclude that some thermochemical routes are able to supply the entire energy requirements of an optimized 1G sugarcane biorefinery, which may not be valid for other biorefinery models (depending on the amount of energy is required).

From the results and technology reviews it is possible to affirm that practically all the ***thermochemical conversion routes of the integral available biomass*** (sugarcane bagasse and straw) with the correct selection of process units and technologies ***can***

supply the entire thermal and electrical requirements of the optimized 1G sugarcane biorefinery with annexed ethanol distillery (integration base scenario). Therefore, it is unnecessary to use solid-fuel fired boiler systems in the sugarcane thermochemical-biorefinery, ***in a future "far away" the current solid-fuel fired boiler systems will be completely replaced by thermochemical conversion routes of biomass***.

The solid-fuel fired boiler systems have low-efficiency and it is possible to observe that the advances contribute with a very-low efficiency gain. This technology is already at the limit of efficiency that is defined by the temperature of the steam generated (material limits). Currently (2015) advanced steam turbines accept superheated-steam up to 540°C at varied pressures.

The most significant pollutant emitted by solid-fuel fired boilers in the gaseous phase is NO_2, N_2O, NO, SO_2, SO_3, NH_3, H_2S, HCL, Cl_2, COS, CHN, VOCs, and particulate matter (salt and solid compounds) with respect to the burning biomass are caused by the turbulent movement of combustion gases, the biomass N, S and Cl content, the incomplete conversion of biomass and carbon as well the air excess employed in the combustion reaction.

As shown in Table 14, for ***CHP/CEST systems with integral use of available biomass to generate surplus electricity to electric power grid*** the installed capacity gain by improving the technology operational parameters is about 40.0MW (CHP/CEST SC1 to CHP/CEST SC5), ***an increase of 67.5% in electricity generation capacity, CHP/CEST SC5 present 99.0 MW of surplus capacity to generate electricity to electric power grid***. As shown in Figure 99, on the environmental point of view, only evaluating the operational conditions (disregarding variations in infrastructure potential environmental impacts) it is observed that ***there is a reduction of only about 7.0% in the main potential environmental impact indicators***, which does not represent a great environmental gain

As an alternative route for electricity generation, BIG-ICE/CC SC1 presents a low-performance. As shown in Table 19, when partially-integrated at an optimized 1G sugarcane biorefinery ***present 121.0 MW of surplus capacity to generate electricity to electric power grid***. An increase at about 21.7 MW on surplus capacity to generate electricity to electric power grid when compared to the 1G biorefinery applying CHP/CEST SC5, which is about 22.0% more than.

As an alternative route for electricity generation, BIG-ICE/CC SC3 presents a high-performance. As shown in Table 20, when fully-integrated at an optimized 1G sugarcane biorefinery ***present 170.0 MW of surplus capacity to generate electricity to electric power grid***. An increase at about 71.0 MW on surplus capacity to generate electricity to electric power grid when compared to the 1G biorefinery applying CHP/CEST SC5, which is about 72.0% more than.

1G sugarcane biorefinery with annexed ethanol distillery (integration base) can produce ***25.6 tonnes per hour of sugar and 13.9 tonnes per hour of 1G anhydrous ethanol***

Biomass integrated directly-heated gasifier and low-pressure methanol catalytic-synthesis (Biomass-to-Methanol), in addition to 1G sugar and anhydrous ethanol production, can produce by ***Biomass-to-Methanol (SC1) 25.6 tonnes per hour of biomass-derived grade AA methanol***, 107.2 tonnes per hour of high-purity liquid nitrogen and 0.64 tonnes per hour of high-purity liquid argon or by ***Biomass-to-Methanol (SC2) 24.3 tonnes per hour of biomass-derived grade AA methanol***, 130.9 tonnes per hour of high-purity liquid nitrogen and 0.79 tonnes per hour of high-purity liquid argon.

Biomass integrated directly-heated gasifier and mixed alcohols catalytic-synthesis (Biomass-to-Mixed alcohols), in addition to 1G sugar and anhydrous ethanol production, can produce by ***Biomass-to-Mixed alcohols (SC1) 13.9 tonnes per hour of biomass-derived anhydrous ethanol, 2.1 tonnes per hour of mixed higher-molecular alcohols***, 108.6 tonnes per hour of high-purity liquid nitrogen and 0.84 tonnes per hour of high-purity liquid argon or by ***Biomass-to-Mixed alcohols (SC2) 13.0 tonnes per hour of biomass-derived anhydrous ethanol, 2.0 tonnes per hour of mixed higher-molecular alcohols***, 130.9 tonnes per hour of high-purity liquid nitrogen and 0.79 tonnes per hour of high-purity liquid argon.

Generalizing, the potential environmental impacts for the main biomass-based value-added products showed advantages over corresponding products derived from fossil resources (Brazil case) in terms of global-type impact indicators (e.g.: CC, OD, IR, ME, NLT, MD, and FD). They also showed disadvantages in terms of local-type impact indicators (e.g.: ALO, PMF, TA, TET, POF, FET, FE, HT, and WD).

The **agricultural phase (cane production) has the greatest contribution in most indicators of potential environmental impacts**.

In the 1G sugarcane biorefinery (CHP/CEST SC5) the ***agricultural phase contributes for more than 80.0% of the total score of the indicators: CC, OD, HT, TET, FET, ALO, NLT,MD, and FD.***

In the 1G sugarcane biorefinery (CHP/CEST SC5) the agricultural phase contributes to GWP for 3.48E-2 kg of CO_2 equivalent per kWh of electricity generated (about 94.5% of the total score).

Thermochemical-biorefinery applying BIG-ICE/CC route scenarios and BIG-GT/CC route scenarios present a reduction of about 72.0% to 77.0% in the score of FDP when compared to Brazilian electric sector (final consumption) in the 2013 situation (Brazilian electricity mix)

Electricity generation based on Brazilian mix contributes to FDP of 2.64E-2 kg of oil equivalent per KWh of electricity generated while thermochemical-biorefineries (BIG-

GT/CC SC3) contribute to FDP of 6.01E-3 kg of oil equivalent per KWh of electricity generated, a reduction-difference of 77.3%.

Thermochemical-biorefinery applying ***BIG-ICE/CC SC1 contributes to GWP for -5.21E-2 kg of CO_2 equivalent per kWh of electricity generated*** (negative emissions), Thermochemical-biorefinery applying ***BIG-GT/CC SC2 contributes to GWP for -8.37E-2 kg of CO_2 equivalent per kWh of electricity generated*** (negative emissions), and Thermochemical-biorefinery applying ***BIG-GT/CC SC1 contributes to GWP for -6.64E-2 kg of CO_2 equivalent per kWh of electricity generated*** (negative emissions).

Electricity from the Brazilian electricity mix contributes to GWP for 2.50E-1 kg of CO_2 equivalent per kWh of electricity generated while the thermochemical-biorefinery (BIG-GT/CC SC3) contributes to GWP for 3.28E-2 kg of CO_2 equivalent per kWh of electricity generated, a difference of 86.9% on GWP (without CCS sequestration technology). The optimized 1G sugarcane biorefinery applying CHP/CEST (SC5) contributes for 3.68E-2 kg of CO_2 equivalent per kWh of electricity generated, that is 12.2% more than the thermochemical-biorefinery (BIG-GT/CC SC3).

Thermochemical-biorefinery applying BIG-GT/CC route scenarios present a reduction of about 5.0% to 18.0% in the score of the almost all of the potential environmental impact indicators (except CC) when compared to Thermochemical-biorefinery applying BIG-ICE/CC route scenarios.

Large-scale SMR of natural gas plants contribute to FDP of 8.78E-1 kg of oil equivalent per kg of methanol produced while ***thermochemical-biorefinery (Biomass-to-Methanol SC2) contributes to FDP of 3.87E-2 kg of oil equivalent per kg of methanol produced, a reduction of 96.8% on FDP***.

Large-scale SMR of natural gas contributes to GWP for 7.44E-1 kg of CO_2 equivalent per kg of methanol produced while the thermochemical-biorefinery (Biomass-to-Methanol SC1) contributes to GWP for -1.59E-1 kg of CO_2 equivalent per kg of methanol produced (negative emissions) and the thermochemical-biorefinery (Biomass-to-Methanol SC2) contributes to GWP for -1.36E-2 kg of CO_2 equivalent per kg of methanol produced (negative emissions)

From the ***production-chain to end-use ethanol in MJ comparative base unit has the greatest impact scores on the indicators HTP, POFP, PMFP, IRP, TAP, FEP, MEP, TETP, FETP, ALOP, ULOP, WDP, and MDP (13/18 indicators)***. These indicators represent mostly local potential impacts.

From the **production-chain to end-use pure-gasoline in MJ comparative base unit has the greatest impact scores on the indicators GWP, ODP, MECTP, NLTP, and FDP.** These indicators represent mostly global potential impacts.

As shown in Figure 112, the results of comparative potential environmental impacts shows that the consumption of **ethanol derived from 1G biorefinery (CHP/CEST**

SC5) dramatically reduces the potential global environmental impacts (e.g.: CC and FD), but there is an significant increase in potential local environmental impacts (e.g.: WD, PMF, and HT). Also shown that the cconsumption of ***1G/2G ethanol derived from thermochemical-biorefinery (Biomass-to-Mixed alcohols) contributes to about 30.0% to 60.0% less in all of the potential environmental impact indicators then the 1G ethanol derived from 1G biorefinery (CHP/CEST SC5).***

Consumption of ***fossil-derived pure-gasoline contributes to GWP for 8.02E-2 kg of CO_2 equivalent per MJ of gasoline-energy consumed***.

Consumption of **1G ethanol derived from 1G biorefinery (CHP/CEST SC5)** contributes to GWP for 1.88E-2 kg of CO_2 equivalent per MJ of ethanol-energy consumed, **reduction of 76.6% front the GWP of the consumption of fossil-derived pure-gasoline.**

Consumption of ***1G/2G ethanol derived from thermochemical-biorefinery (Biomass-to-Mixed alcohols SC1)*** contributes to GWP for -2.02E-2 kg of CO_2 equivalent per MJ of ethanol-energy consumed, ***reduction of 127.0% front the GWP of the consumption of fossil-derived pure-gasoline (negative emissions).*** Obviously, means the sequestration of 27% of the CO_2 equivalent per MJ of gasoline-energy consumed (CCS).

Consumption of ***1G/2G ethanol derived from thermochemical-biorefinery (Biomass-to-Mixed alcohols SC2)*** contributes to GWP for -2.19E-2 kg of CO_2 equivalent per MJ of ethanol-energy consumed, ***reduction of 125.0% front the GWP of the consumption of fossil-derived pure-gasoline (negative emissions).*** Obviously, means the sequestration of 25% of the CO_2 equivalent per MJ of gasoline-energy consumed (CCS).

Consumption of ***fossil-derived pure-gasoline contributes to FDP for 3.14E-2 kg of oil equivalent per MJ of gasoline-energy consumed***.

Consumption of ***1G ethanol derived from 1G biorefinery (CHP/CEST SC5)*** contributes to FDP for 3.29E-3 kg of oil equivalent per MJ of ethanol-energy consumed, ***reduction of 89.5% front the FDP of the consumption of fossil-derived pure-gasoline***.

Consumption of ***1G/2G ethanol derived from thermochemical-biorefinery (Biomass-to-Mixed alcohols SC1)*** contributes to FDP for 2.16E-2 kg of oil equivalent per MJ of ethanol-energy consumed, ***reduction of 93.1% front the FDP of the consumption of fossil-derived pure-gasoline (from fossil to renewable biomass resources)***.

Consumption of ***1G/2G ethanol derived from thermochemical-biorefinery (Biomass-to-Mixed alcohols SC2)*** contributes to FDP for 2.13E-2 kg of oil equivalent per MJ of ethanol-energy consumed, ***reduction of 93.2% front the FDP of the consumption of fossil-derived pure-gasoline***.

10.1 Recommendations for future works

The logical framework approach (Figure 1) developed to assess the environmental aspects of thermochemical-biorefinery scenarios can be extended to technical, economic and social assessments for a complete sustainability assessment, it is necessary for a decision-making process.

The environmental impacts related to the infrastructure of the thermochemical conversion routes of biomass must be evaluated and added to the results (scores), since these impacts must be significant in the industrial phase environmental assessment. To achieve the environmental impacts related to infrastructure, a deeper evaluation of the technologies involved in the thermochemical conversion routes of biomass is necessary.

In this research Master's degree was evaluated scenarios for 2.0 Mtonnes of cane processed by thermochemical-biorefineries scenarios on-season with integral use of available biomass (i.e.: sugarcane bagasse and straw). However, it is necessary assess scenarios that have operation during the off-season period, because these advanced-technologies must operate efficiently all-year-round.

The standalone, decentralized or cluster's configurations should be comparatively assessed. Specifically considering the local effects over the sustainability, only the gain associated with scale factors may be not better than fully-integrated modes. In this research Master's degree the standalone thermochemical-biorefinery scenarios are not analyzed, there can be used for comparative analysis front literature comparable scenarios.

Evaluate the impact of the implementation of thermochemical-biorefinery scenarios in the Brazil's sugar-energy sector through the macro-indicators in order to estimate the potential advantages and disadvantages in a broader scenario and context.

A technical assessment is essential and necessary to determine process operational parameters and real technical limitations, allowing validate the processes models and to limit/reduce possible unrealistic estimative made in the Aspen Plus®v8.4 process simulation platform. Is not an easy task, many of the technologies related to thermochemical route technologies for the processing of biomass are only in research and/or development phase.

To assess thermochemical conversion routes of biomass integrated at 1G sugarcane biorefinery is required and mandatory perform the mass and energy integration, the energy demand and supply (heat and power consumption and generation) has a major impact factor on setting-up operational parameters.

The Aspen Plus®v8.4 process simulation models take into account the formation of particulate materials in several process steps by applying simplified models of particle size distribution (PSD). Data for particle diameters in the plant key points should be estimated (theoretical or experimental) to obtain more accuracy in the models.

In this research Master's degree was evaluated only atmospheric CFB directly-heated gasifier type. However, other gasifier types should be assessed and compared to determine advantages and disadvantages of each technologies-type. Gasifiers with the greatest potential for application in the Brazil's sugarcane-context are:

a) atmospheric CFB directly-heated gasifier;
b) atmospheric DFB indirectly-heated gasifier;
c) pressurized entrained flow gasifier.

Future works

This research presented in the Master's degree is only part of the full sustainability assessment. And, the environmental assessment presented requires complementation (e.g.: installed infrastructures and off-season operations). Many of the issues observed in the processes technologies and some of the open questions reported in the recommendations for future works will be studied in the research Doctoral degree.

The proposed title for the future research (Doctoral degree) is:

Technical, economic and environmental assessment of advanced biorefineries based on sugarcane (on-season) and energy cane (off-season) for sustainable co-production of sugar, thermal energy, electricity, liquid biofuels, and chemicals.

Avaliação técnica, econômica e ambiental de biorrefinarias avançadas baseadas em cana-de-açúcar (safra) e cana energia (entressafra) para a coprodução sustentável de açúcar, energia térmica, eletricidade, combustíveis líquidos e produtos químicos.

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The main objective of this research Doctoral degree will be **propose** (select technologies and design scenarios), **assess** (technical, economic and environmental assessment) and **compare** (scenarios, technologies, and products) **scenarios of fully-integrated thermochemical-based biorefineries operating all year round**, based on **integral use** of **conventional sugarcane** (on-season) and **energy cane** (off-season) mainly targeting the co-production (Brazilian sugar-energy sector) of sugar, thermal energy, electricity, liquid fuels, and chemicals (multi-product plants).

Notes

Reproduction and the use of information presented in this Master dissertation regarding the thermochemical routes are authorized provided the source is acknowledged. The use and disclosure of information regarding first-generation technologies must respect the precepts of CTBE and CNPEM.

The author of this Master dissertation reserves the right to not provide/distribution the original software files (Aspen Plus® process simulation platform and SimaPro® software files) performed in this research Master's degree. Only the division of AIB of the CTBE/CNPEM is authorized to access for read/write and use/modify the original software files resultants from this research Master's degree, without prior permission of the author, provided the source is acknowledged.

Some of the production processes of biomass-derived products (e.g.: sugar, thermal energy, electricity, liquid biofuels, and chemicals) by thermochemical routes integrated at an optimized 1G sugarcane biorefinery with integral use of biomass available developed in this research Master's degree will be improved and subsequently able to be submitted to patent application for idea and production process.

Additional information, data, and results about first-generation technologies (complete production chain) and about the VSB simulation and assessment tool are not the responsibility of the author of this research Master's degree, more information about can be found in several publications of the division of AIB of the CTBE/CNPEM.

References made in this Master's dissertation to any specific commercial products, processes, or services by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the author of this research Master's degree.

Details about the processes, component/substances, and materials implemented in SimaPro®7.3.3 software for LCA can be consulted in the database (CTBE), with the consent of the division of AIB of the CTBE/CNPEM.

The VSB simulation and assessment platform (tool) uses Aspen Plus® process simulation platform and SimaPro® software licensed and available for use by authorized research`s students with concern and knowledge of the division of AIB of the CTBE/CNPEM.

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APPENDIX A - Aspen Plus®v8.4 complete flowsheet of thermochemical routes scenarios and traditional CHP/CEST and CHP/EBPST scenarios developed to obtain mass and energy balances (input/output) for LCA

Contents

Combined heat and power (CHP) generation applying condensing-extraction steam turbine (CEST):
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Combined heat and power (CHP) generation applying extraction back-pressure steam turbine (EBPST)
Figure A2- 22 bar and 320ºC: Scenario 1 (SC1); Figure A4 - 45 bar and 450ºC: Scenario 2 (SC2); Figure A6 - 65 bar and 480ºC: Scenario 3 (SC3); Figure A8 - 85 bar and 520ºC: Scenario 4 (SC4); Figure A10 - 90 bar and 530ºC: Scenario 5 (SC5); Figure A11 - 96 bar and 530ºC: Scenario 6 (SC6); Figure A14 - 120 bar and 530ºC: Scenario 7 (SC7).

Biomass integrated directly-heated gasifier and internal combustion engine in combined-cycle (BIG-ICE/CC)
Figure A15 - Scenario 1 (SC1); Figure A16 - Scenario 2 (SC2).

Biomass integrated directly-heated gasifier and gas turbine in combined-cycle (BIG-GT/CC)
Figure A17 - Scenario 1 (SC1); Figure A18 - Scenario 2 (SC2); Figure A19 - Scenario 3 (SC3); Figure A20 - Scenario 4 (SC4); Figure A21 - Scenario 5 (SC5).

Biomass to methanol production by biomass integrated directly-heated gasifier and low-pressure methanol catalytic-synthesis (Biomass-to-Methanol)
Figure A22 - Scenario 1 (SC1); Figure A23 - Scenario 2 (SC2); Figure A24 - Scenario 3 (SC3);

Biomass to mixed alcohols production by biomass integrated directly-heated gasifier and mixed-alcohols catalytic-synthesis (Biomass-to-Mixed alcohols)
Figure A25 - Scenario 1 (SC1); Figure A26 - Scenario 2 (SC2); Figure A27 - Scenario 3 (SC3);

Combined heat and power (CHP) production applying condensing-extraction steam turbine (CEST) 22 bar and 320ºC

Scenario 1 (SC1)

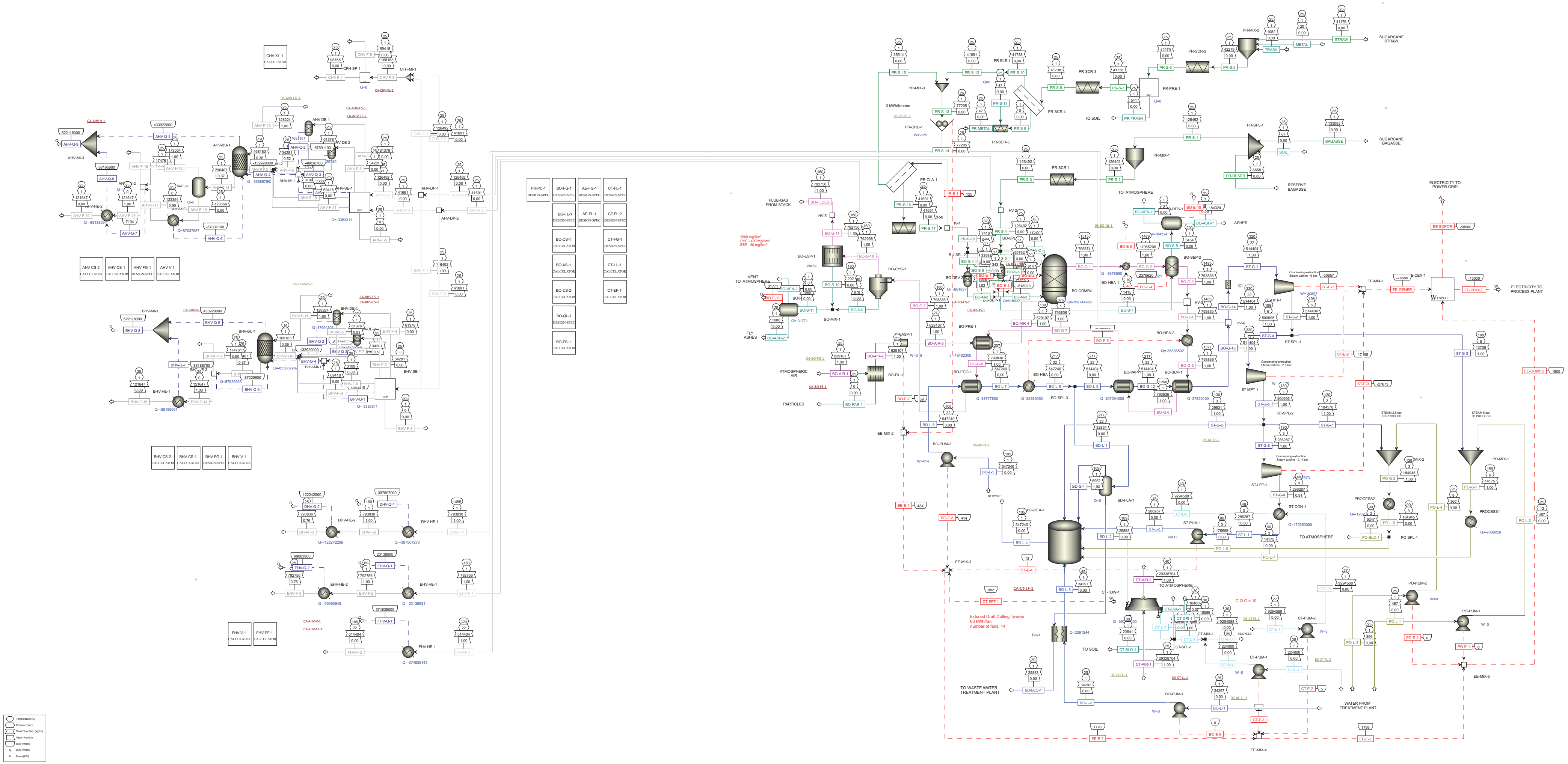

Figure A1 / Aspen Plus®v8.4 flowsheet - Combined heat and power (CHP) production applying condensing-extraction steam turbine (CEST - 22 bar/320ºC: Scenario 1 (SC1)

Combined heat and power (CHP) production
applying extraction back-pressure steam turbine (EBPST)
22 bar and 320ºC

Scenario 1 (SC1)

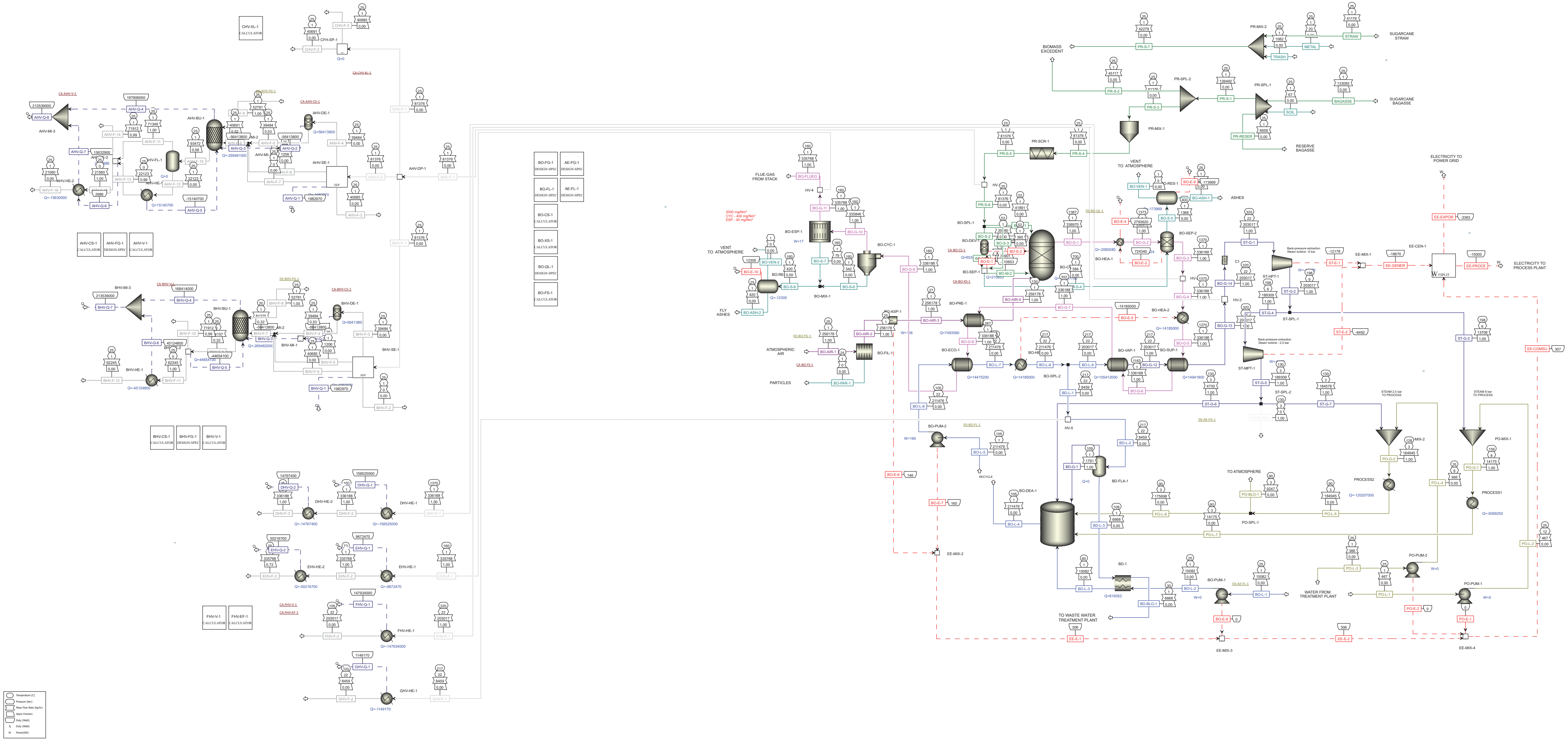

Figure A2 / Aspen Plus®v8.4 flowsheet - Combined heat and power (CHP) production applying extraction back-pressure steam turbine (E PST) - 22 bar/320ºC: Scenario 1 (SC1)

Combined heat and power (CHP) production applying condensing-extraction steam turbine (CEST)
45 bar and 450ºC

Scenario 2 (SC2)

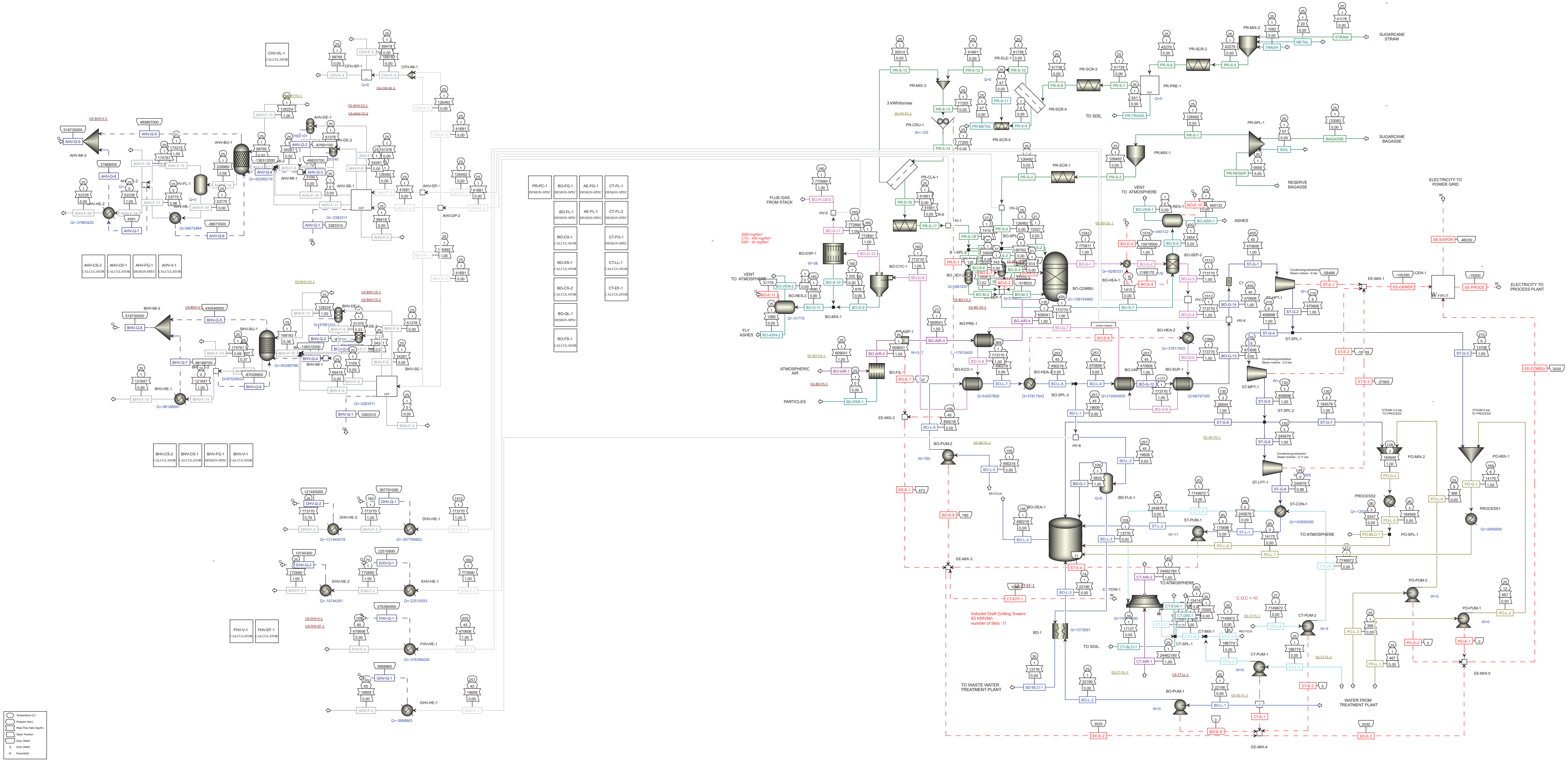

Figure A3 / Aspen Plus®v8.4 flowsheet - Combined heat and power (CHP) production applying condensing-extraction steam turbine (CEST - 45 bar/450ºC: Scenario 2 (SC2)

Combined heat and power (CHP) production
applying extraction back-pressure steam turbine (EBPST)
45 bar and 450ºC

Scenario 2 (SC2)

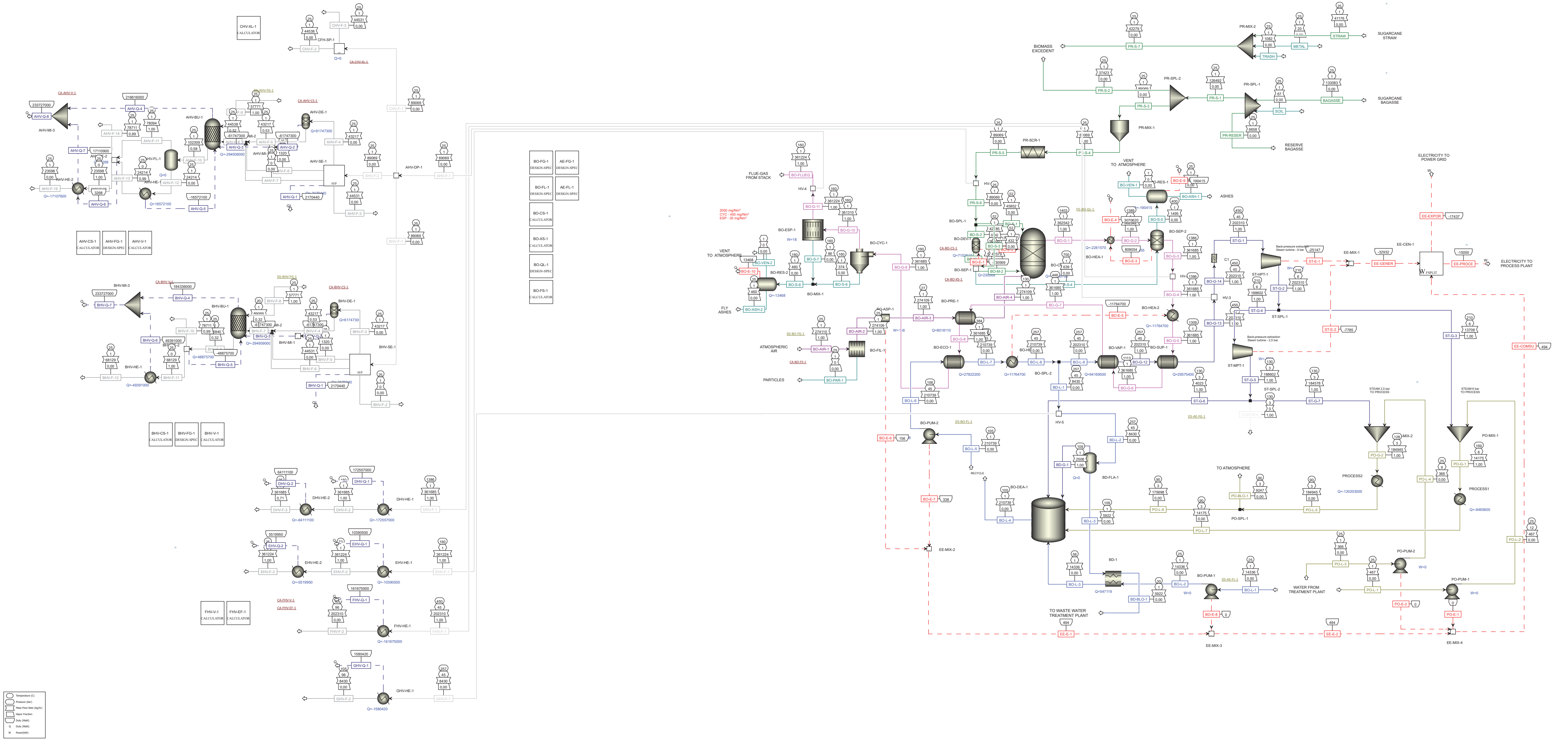

Figure A4 / Aspen Plus®v8.4 flowsheet - Combined heat and power (CHP) production applying extraction back-pressure steam turbine (E PST) - 45 bar/450ºC: Scenario 2 (SC2)

Combined heat and power (CHP) production applying condensing-extraction steam turbine (CEST) 65 bar and 480ºC

Scenario 3 (SC3)

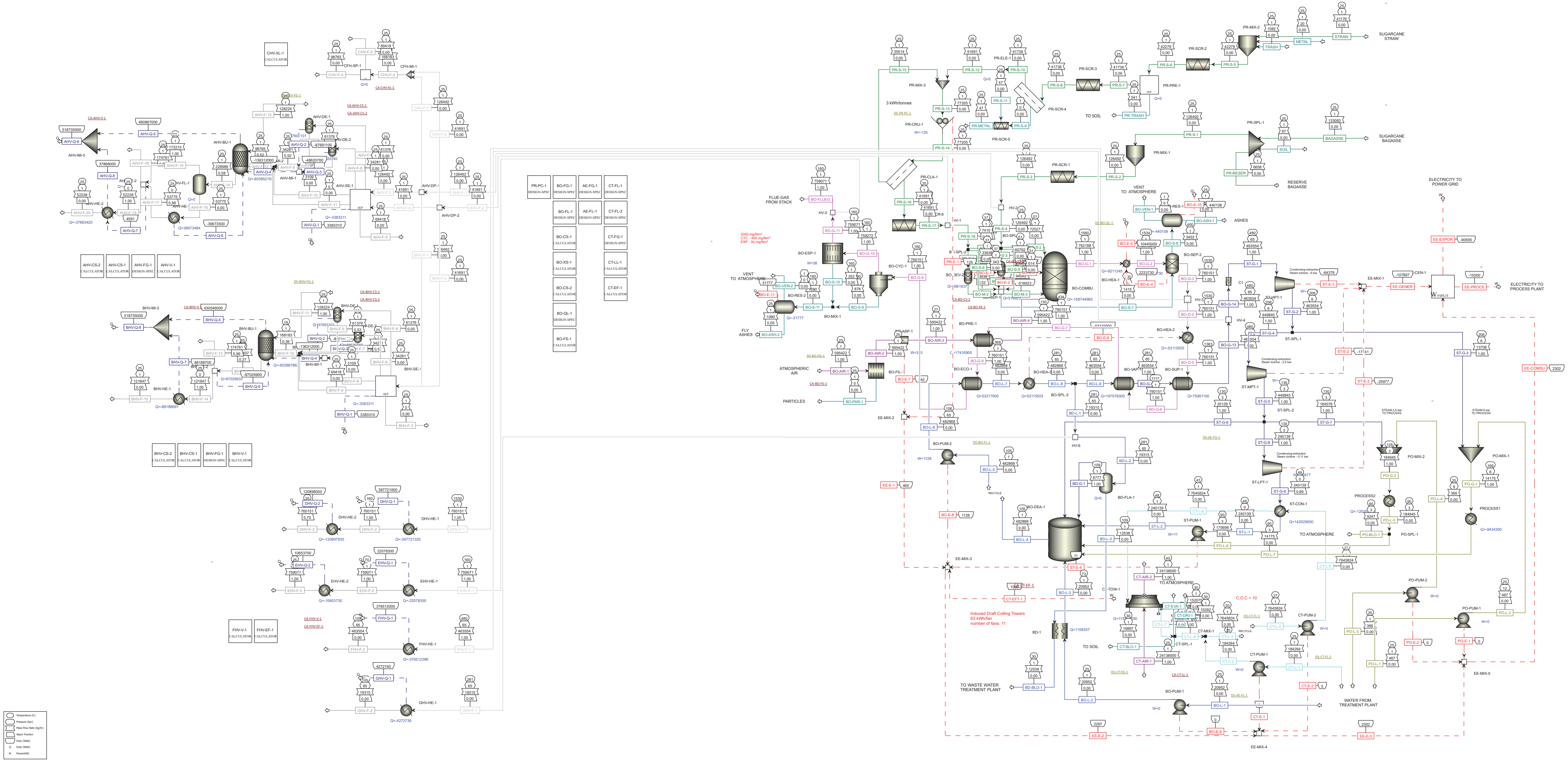

Figure A5 / Aspen Plus®v8.4 flowsheet - Combined heat and power (CHP) production applying condensing-extraction steam turbine (CEST - 65 bar/480ºC: Scenario 3 (SC3)

Combined heat and power (CHP) production
applying extraction back-pressure steam turbine (EBPST)
65 bar and 480°C

Scenario 3 (SC3)

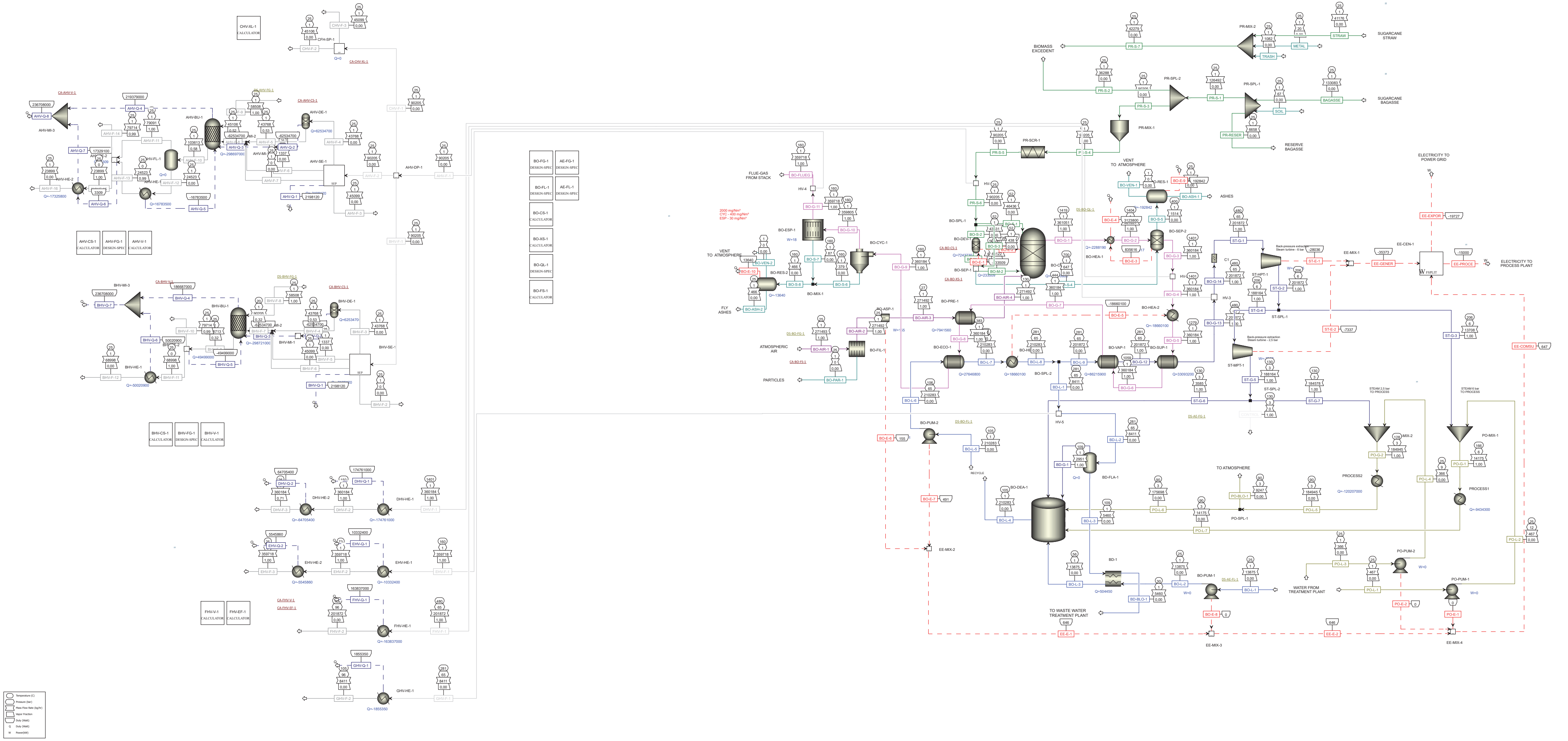

Figure A6 / Aspen Plus®v8.4 flowsheet - Combined heat and power (CHP) production applying extraction back-pressure steam turbine (E PST) - 65 bar/480ºC: Scenario 3 (SC3)

Combined heat and power (CHP) production applying condensing-extraction steam turbine (CEST)
85 bar and 520ºC

Scenario 4 (SC4)

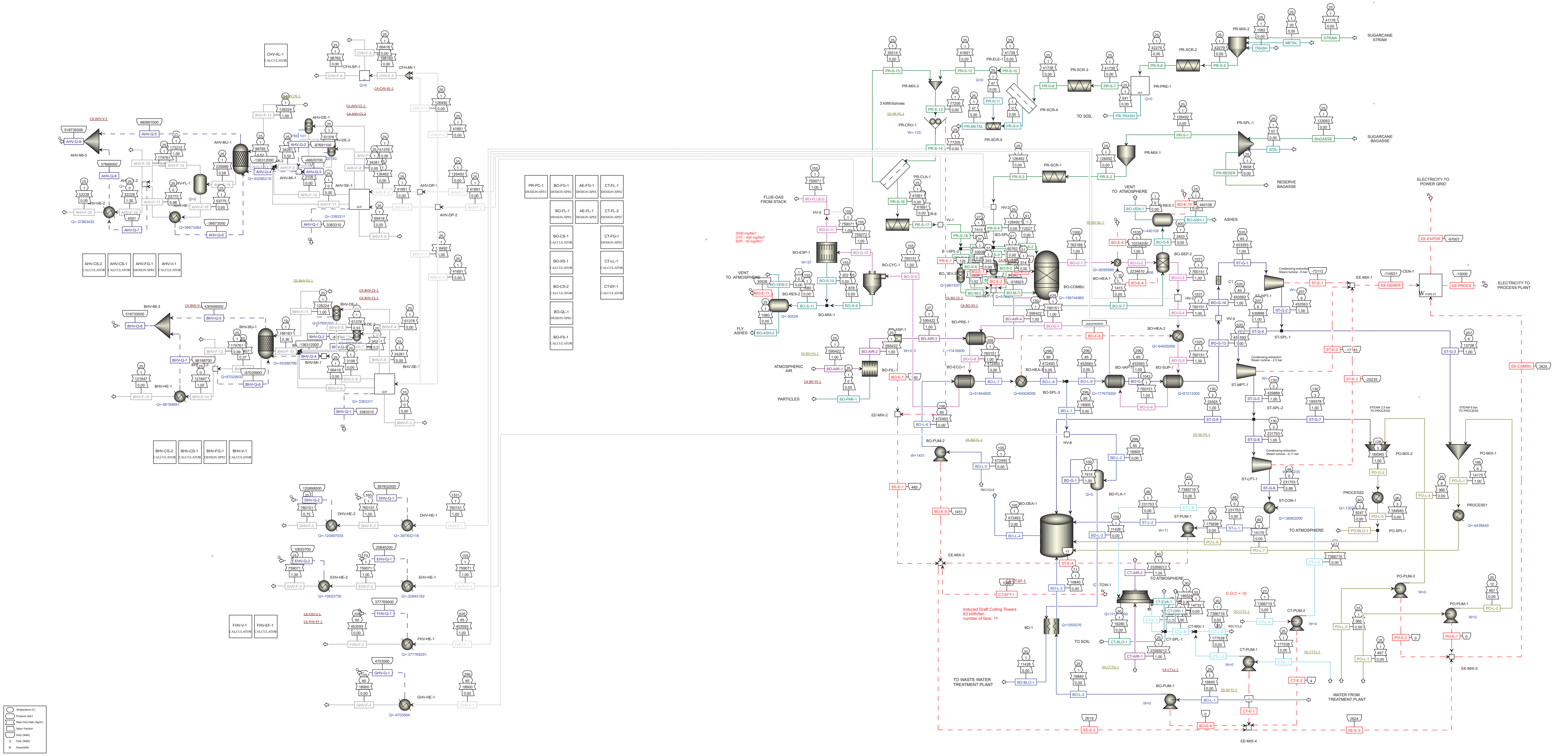

Figure A7 / Aspen Plus®v8.4 flowsheet - Combined heat and power (CHP) production applying condensing-extraction steam turbine (CEST - 85 bar/520ºC: Scenario 4 (SC4)

Combined heat and power (CHP) production applying extraction back-pressure steam turbine (EBPST) 85 bar and 520ºC

Scenario 4 (SC4)

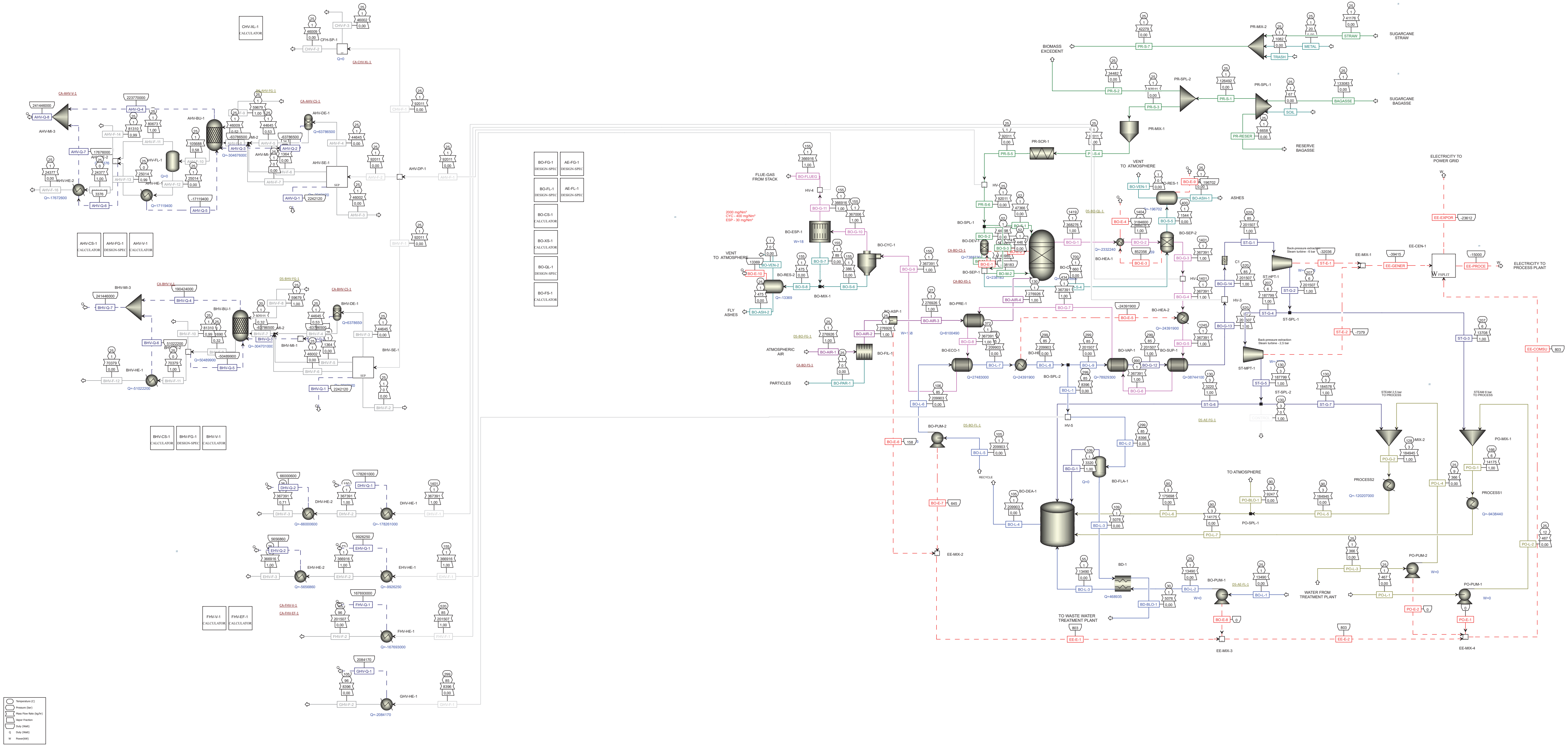

Figure A8 / Aspen Plus®v8.4 flowsheet - Combined heat and power (CHP) production applying extraction back-pressure steam turbine (E PST) - 85 bar/520ºC: Scenario 4 (SC4)

Combined heat and power (CHP) production applying condensing-extraction steam turbine (CEST) 90 bar and 530ºC

Scenario 5 (SC5)

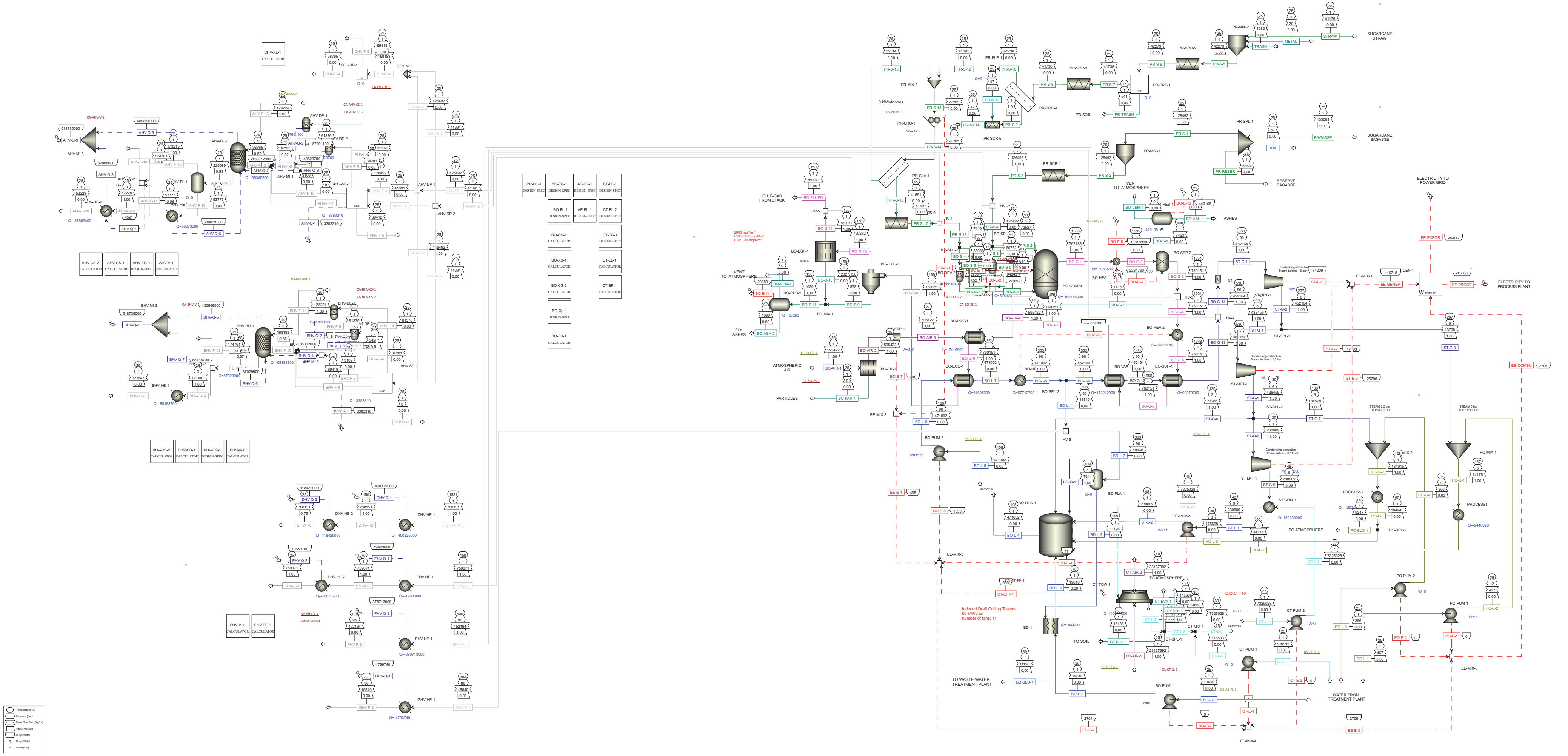

Figure A9 / Aspen Plus®v8.4 flowsheet - Combined heat and power (CHP) production applying condensing-extraction steam turbine (CEST - 90 bar/530ºC: Scenario 5 (SC5)

Combined heat and power (CHP) production
applying extraction back-pressure steam turbine (EBPST)
90 bar and 530ºC

Scenario 5 (SC5)

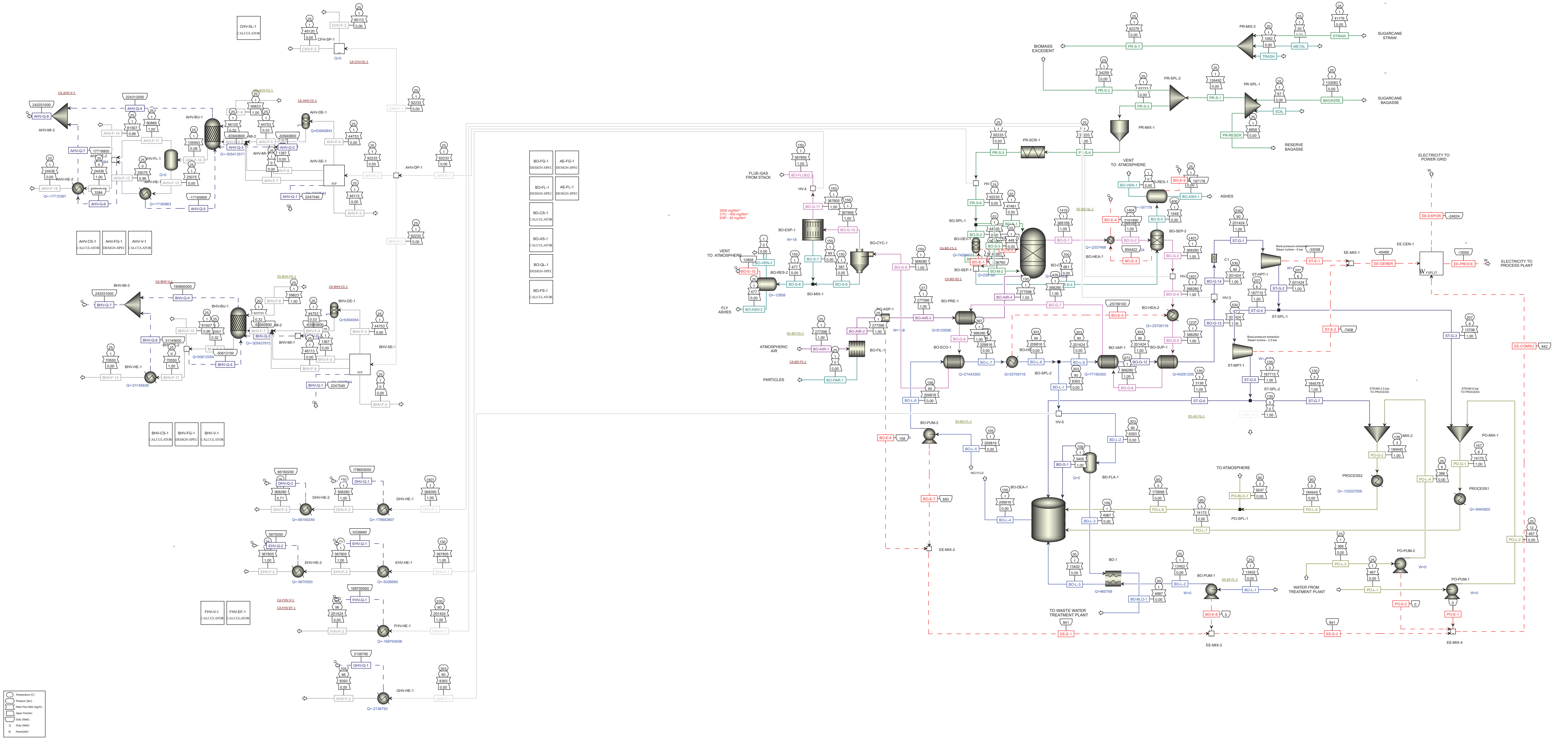

Figure A10 / Aspen Plus®v8.4 flowsheet - Combined heat and power (CHP) production applying extraction back-pressure steam turbine (BPST) - 90 bar/530ºC: Scenario 5 (SC5)

Combined heat and power (CHP) production applying condensing-extraction steam turbine (CEST) 96 bar and 530ºC

Scenario 6 (SC6)

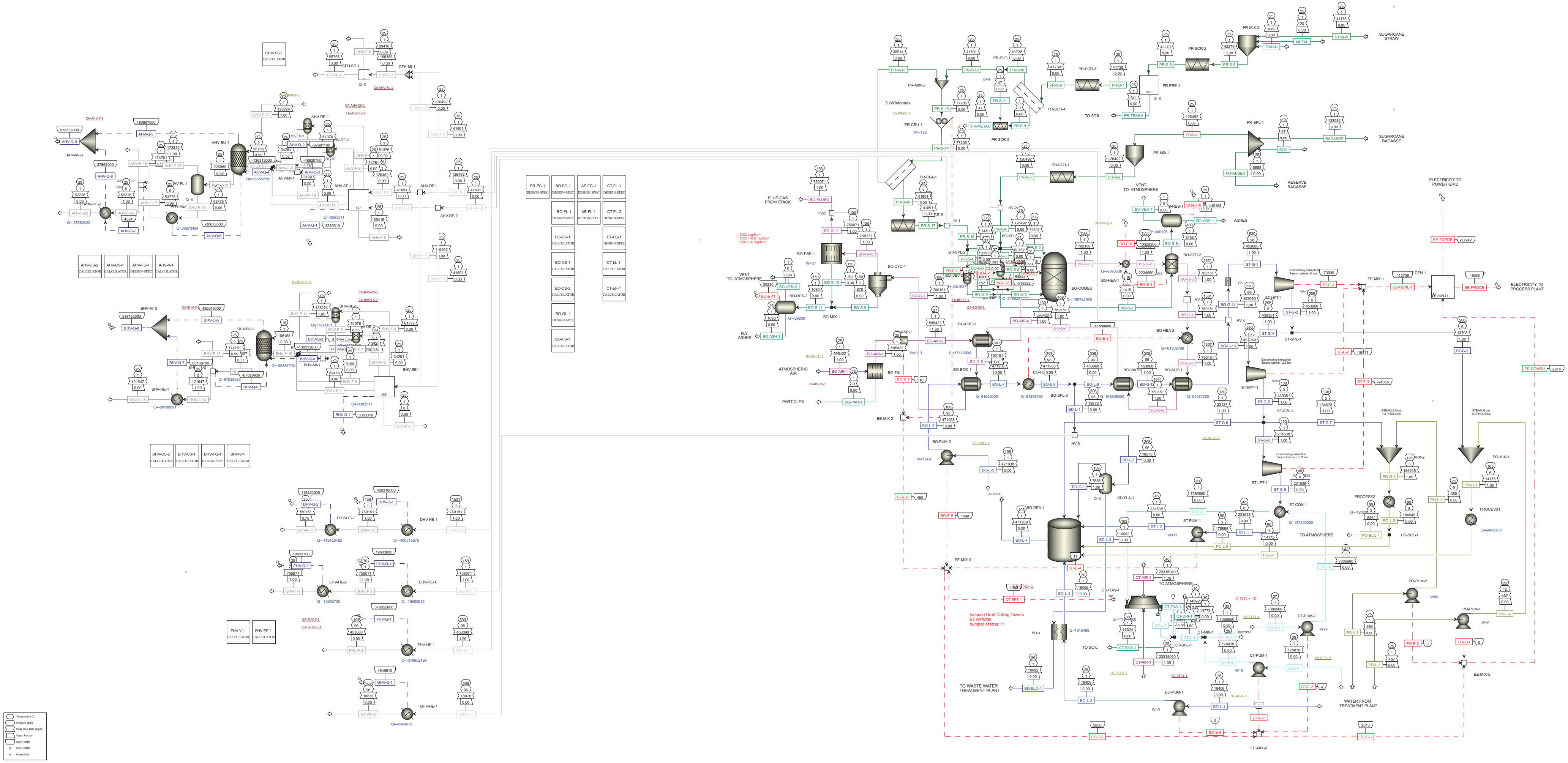

Figure A11 / Aspen Plus®v8.4 flowsheet - Combined heat and power (CHP) production applying condensing-extraction steam turbine (CES) - 96 bar/530ºC: Scenario 6 (SC6)

Combined heat and power (CHP) production applying extraction back-pressure steam turbine (EBPST) 96 bar and 530ºC

Scenario 6 (SC6)

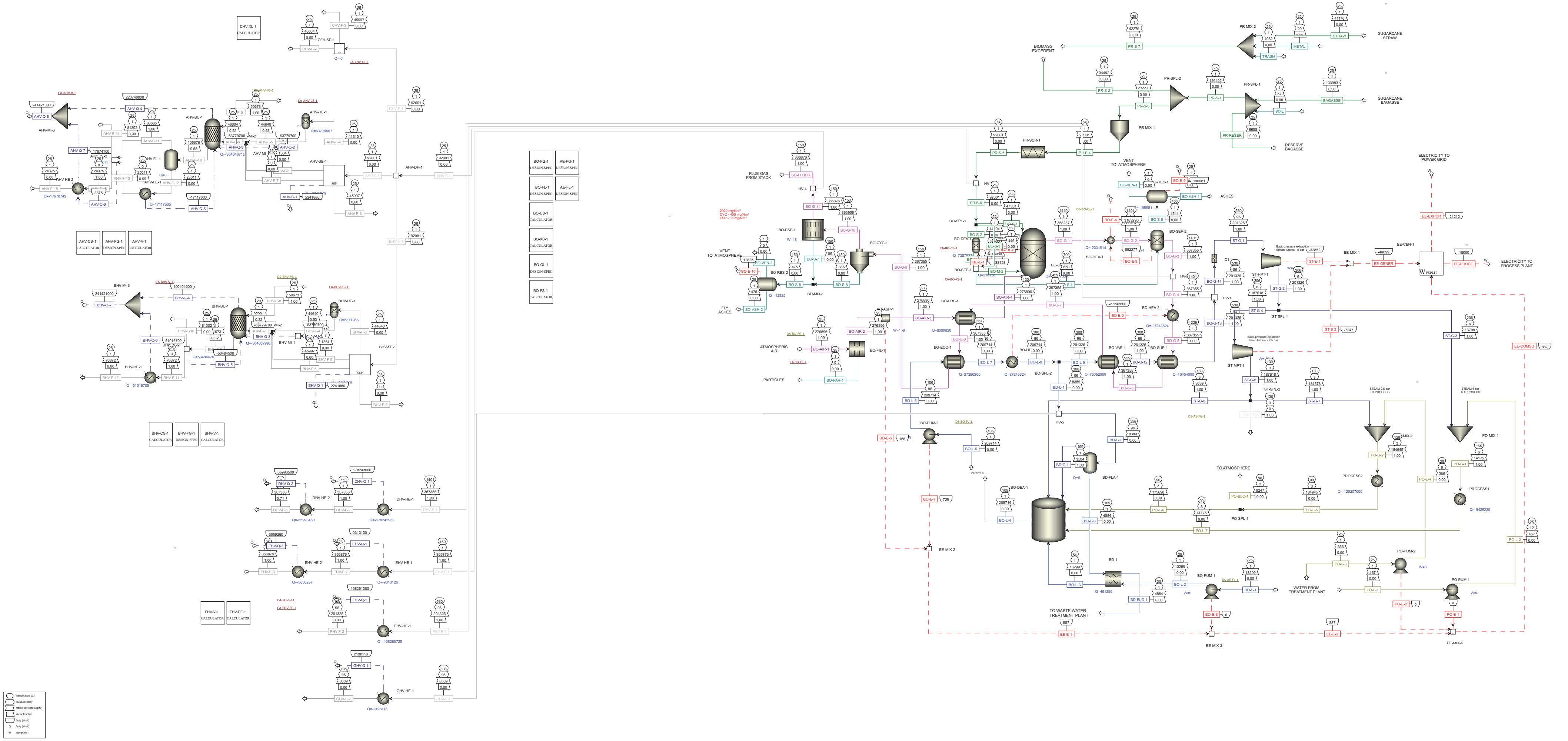

Figure A12 / Aspen Plus®v8.4 flowsheet - Combined heat and power (CHP) production applying extraction back-pressure steam turbine (BPST) - 96 bar/530ºC: Scenario 6 (SC6)

Combined heat and power (CHP) production applying condensing-extraction steam turbine (CEST) 120 bar and 530ºC

Scenario 7 (SC7)

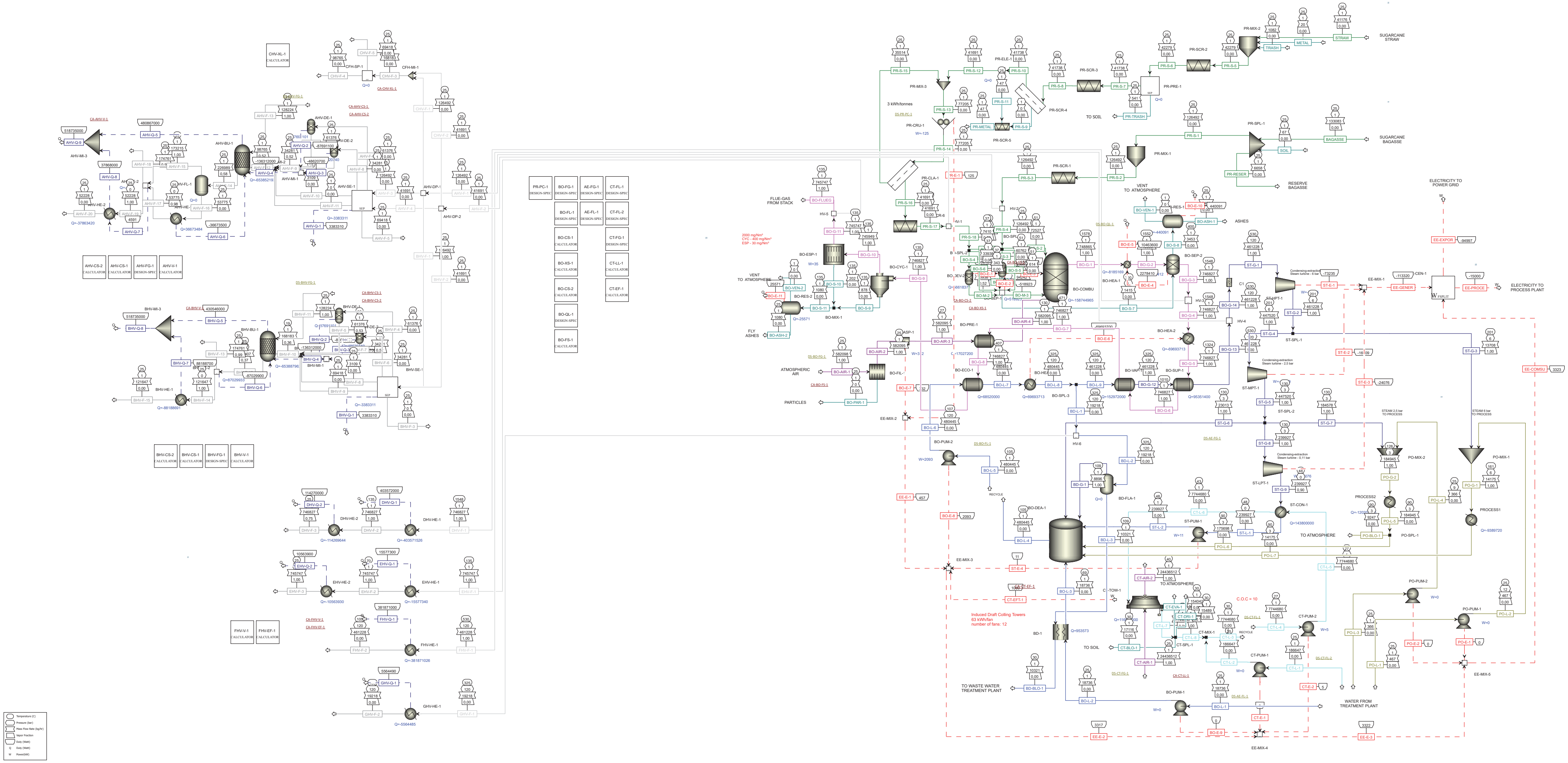

Figure A13 / Aspen Plus®v8.4 flowsheet - Combined heat and power (CHP) production applying condensing-extraction steam turbine (CES) - 120 bar/530ºC: Scenario 7 (SC7)

Combined heat and power (CHP) production
applying extraction back-pressure steam turbine (EBPST)
120 bar and 530ºC

Scenario 7 (SC7)

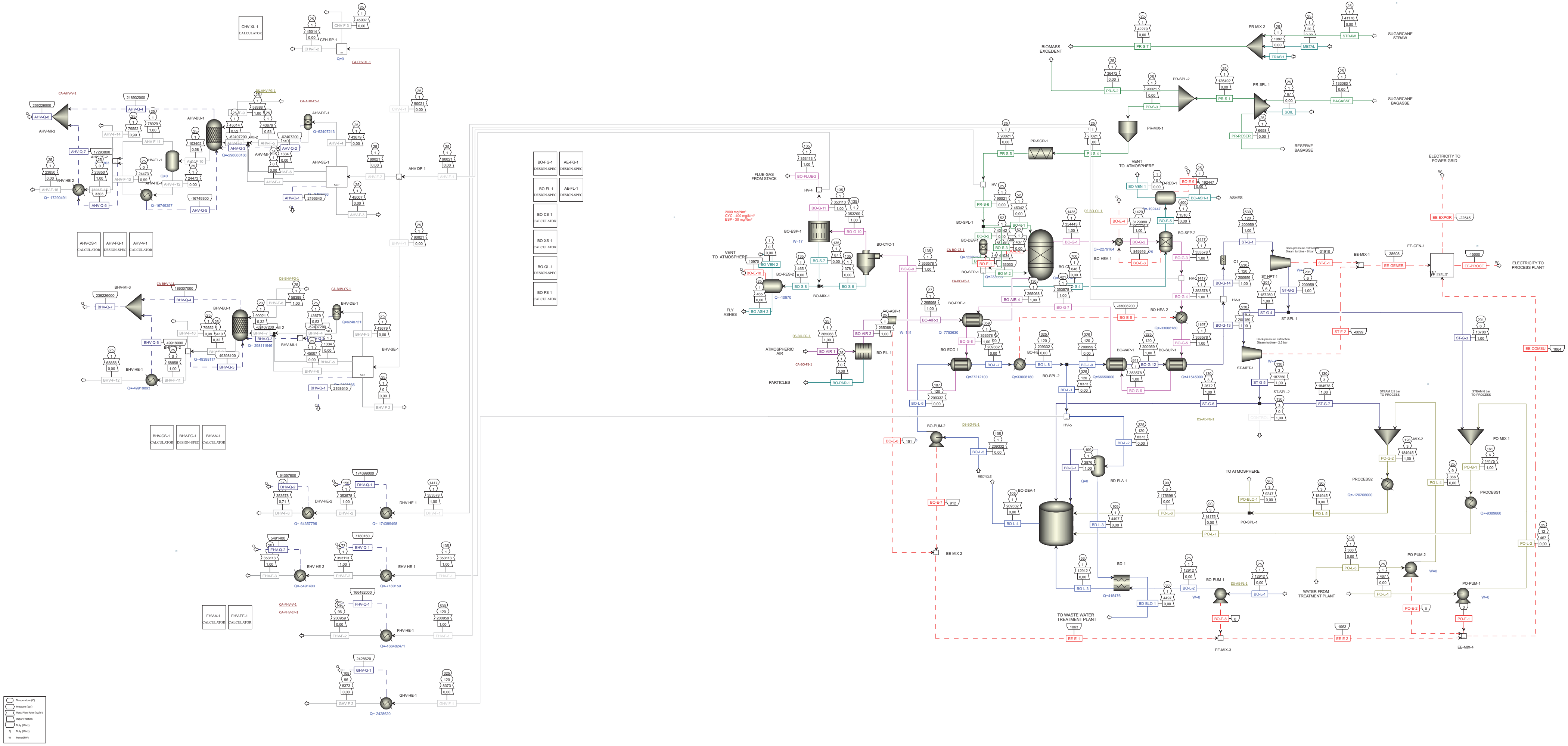

Figure A14 / Aspen Plus®v8.4 flowsheet - Combined heat and power (CHP) production applying extraction back-pressure steam turbine (BPST) - 120 bar/530ºC: Scenario 7 (SC7)

Biomass integrated directly-heated gasification and internal combustion engine in combined cycle (BIG-ICE/CC)

Scenario 1 (SC1)

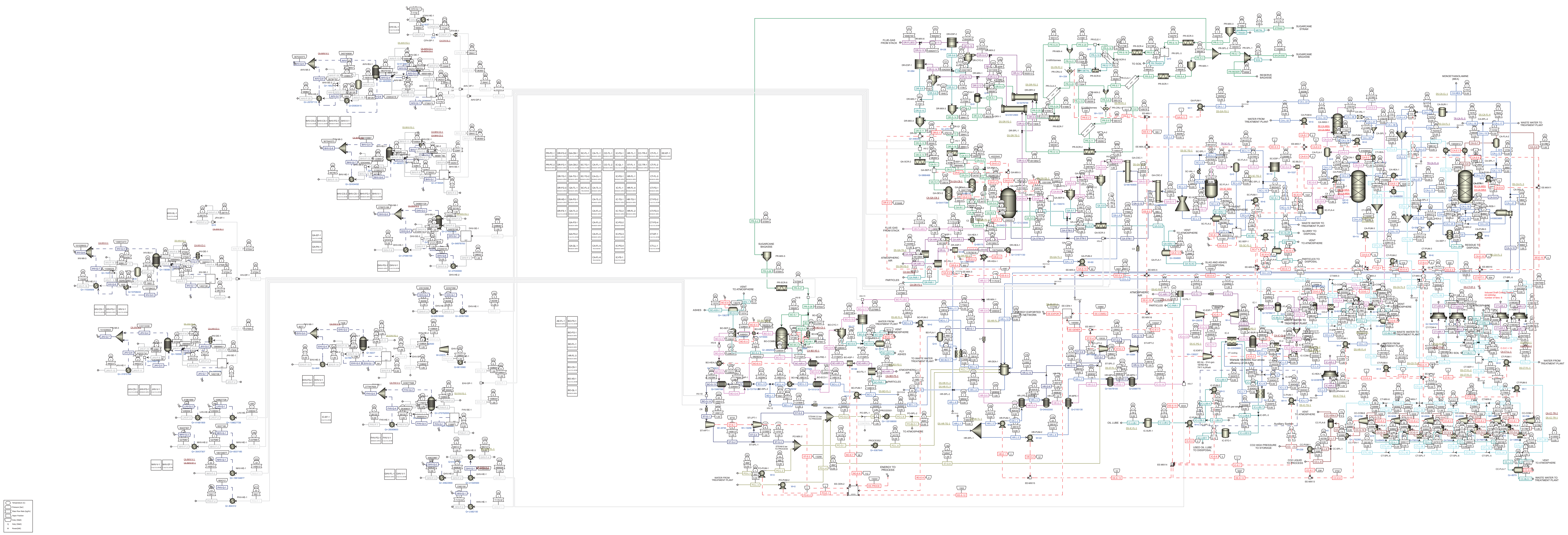

Figure A15 / Aspen Plus®v8.4 flowsheet - Biomass integrated directly-heated gasification and internal combustion engine in combined cycle (BIG-ICE/CC): Scenario 1 (SC1)

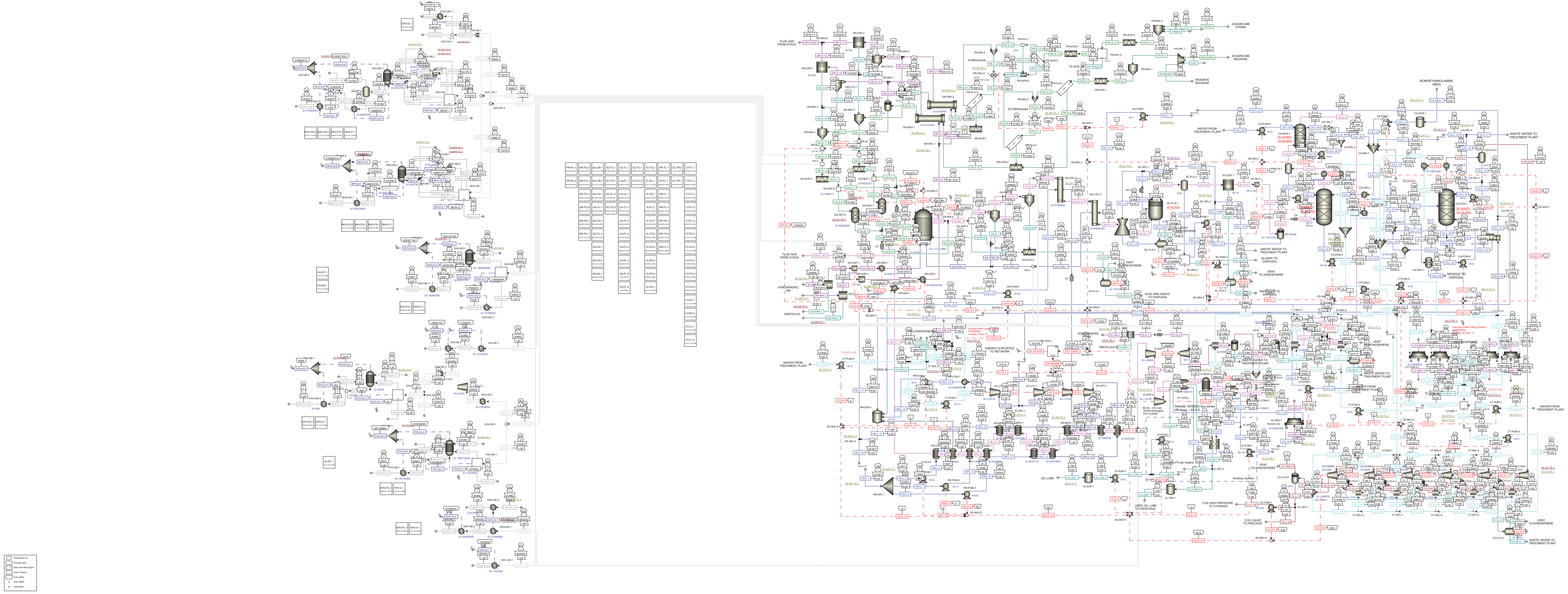

Figure A16 / Aspen Plus®v8.4 flowsheet - Biomass integrated directly-heated gasification and internal combustion engine in combined cycle (BIG-ICE/CC): Scenario 2 (SC2)

Biomass integrated directly-heated gasification and gas turbine in combined cycle
(BIG-GT/CC)

Scenario 1 (SC1)

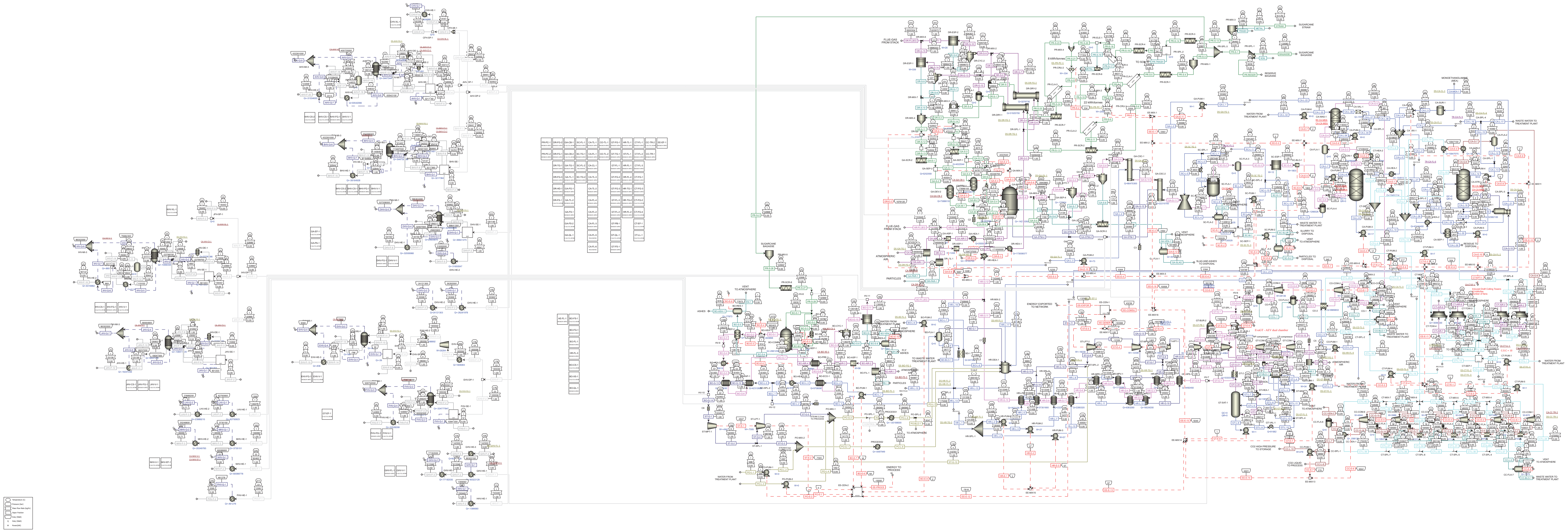

Figure A17 / Aspen Plus®v8.4 flowsheet - Biomass integrated directly-heated gasification and gas turbine in combined cycle (BIG-GT/CC): Scenario 1 (SC1)

Biomass integrated directly-heated gasification and gas
turbine in combined cycle
(BIG-GT/CC)

Scenario 2 (SC2)

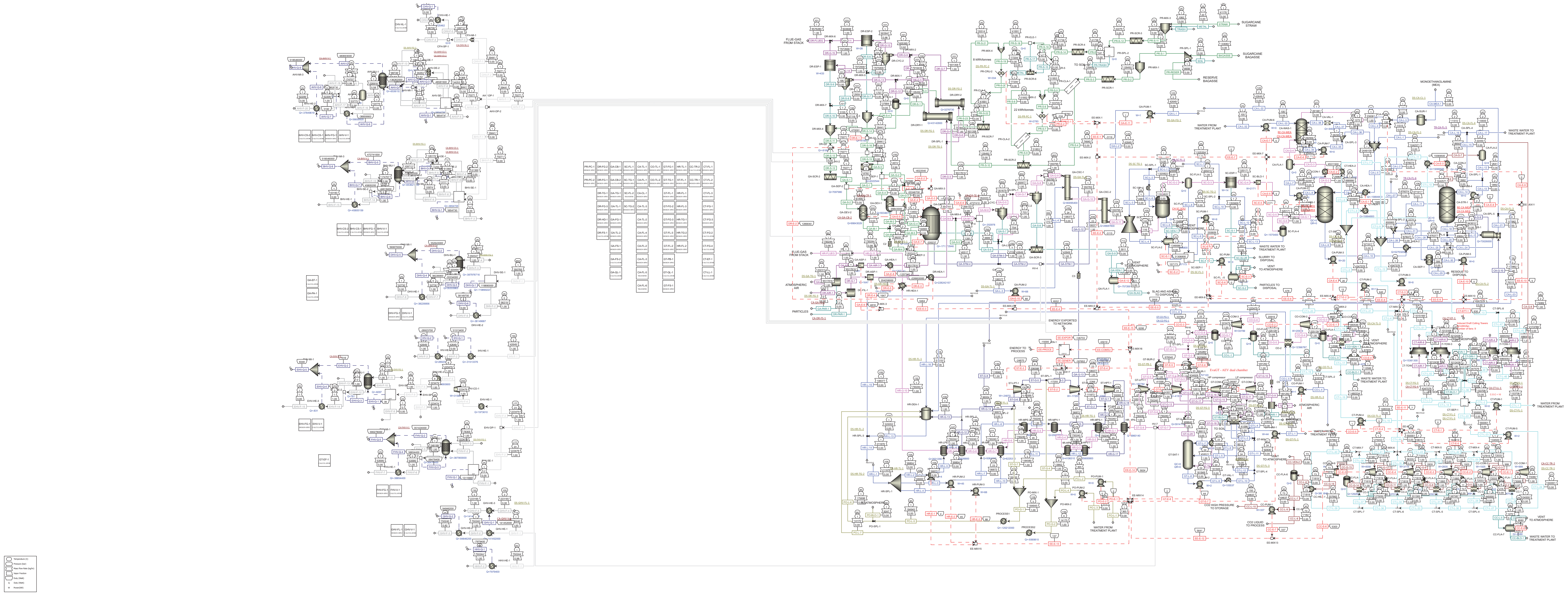

Figure A18 / Aspen Plus®v8.4 flowsheet - Biomass integrated directly-heated gasification and gas turbine in combined cycle (BIG-GT/CC): Scenario 2 (SC2)

Biomass integrated directly-heated gasification and gas turbine in combined cycle (BIG-GT/CC)

Scenario 3 (SC3)

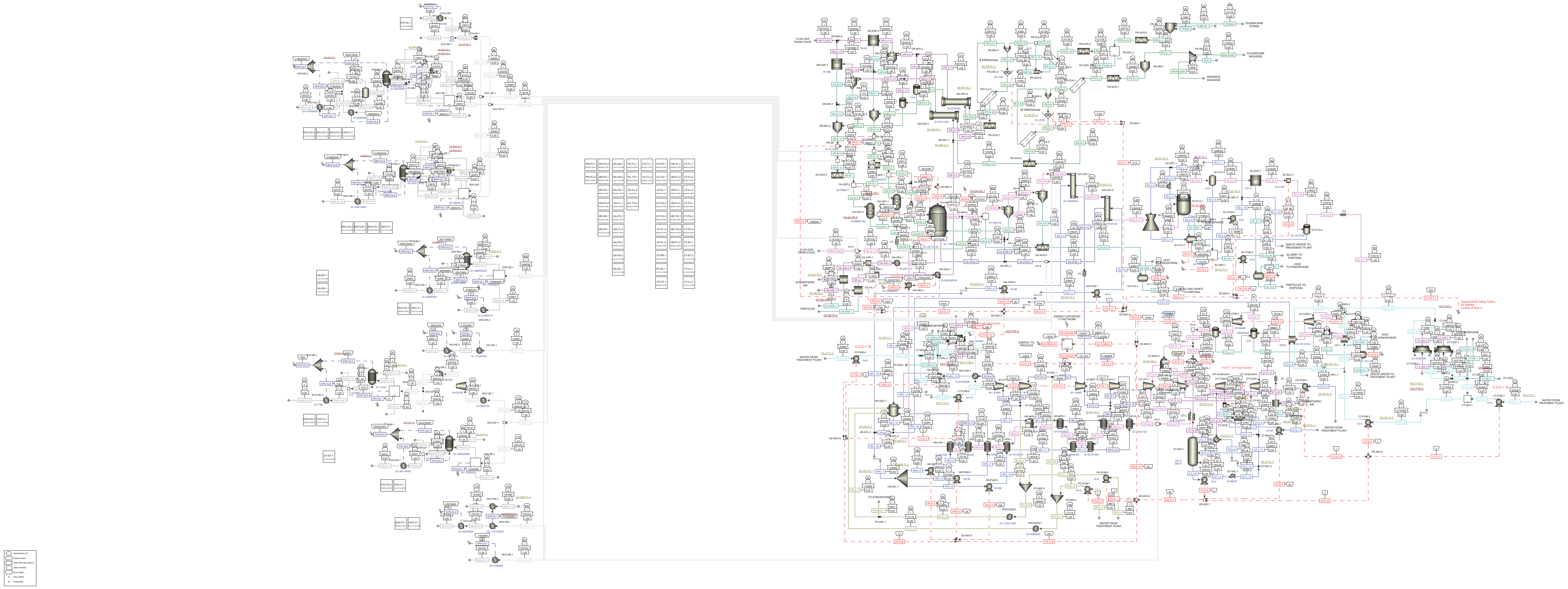

Figure A19 / Aspen Plus®v8.4 flowsheet - Biomass integrated directly-heated gasification and gas turbine in combined cycle (BIG-GT/CC): Scenario 3 (SC3)

Biomass integrated directly-heated gasification and gas turbine in combined cycle (BIG-GT/CC)

Scenario 4 (SC4)

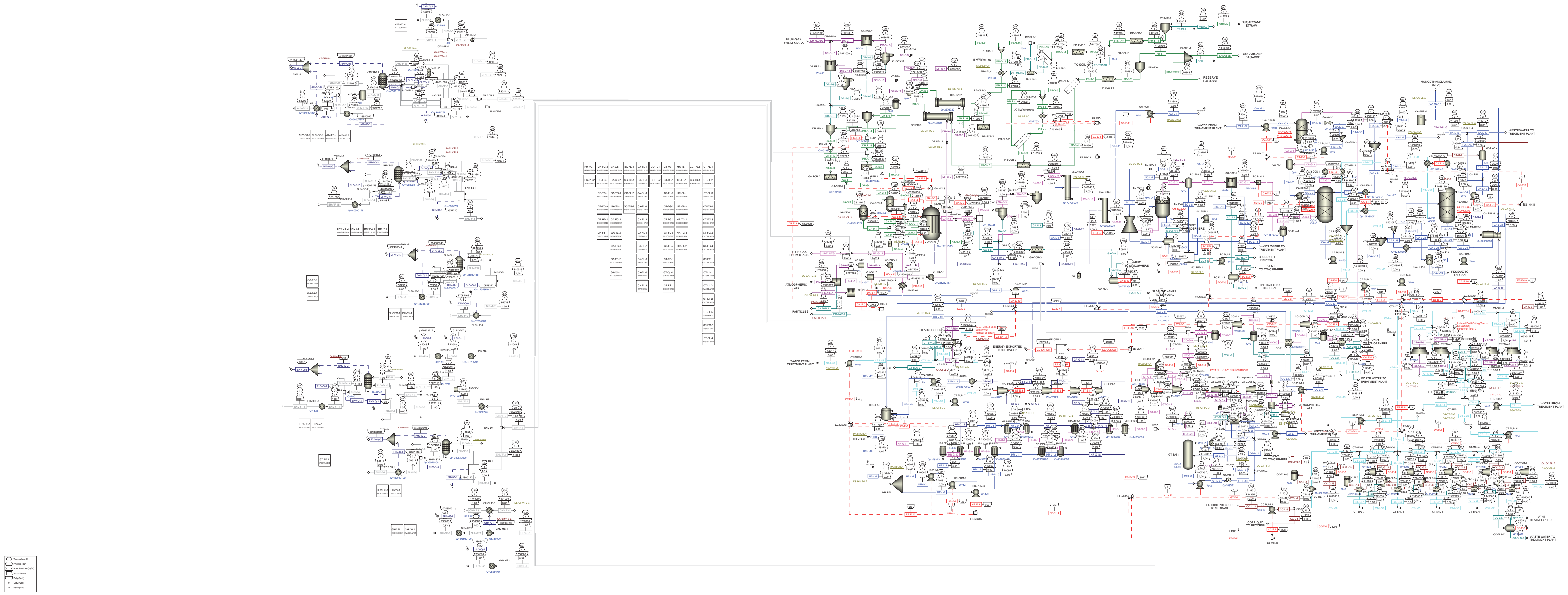

Figure A20 / Aspen Plus®v8.4 flowsheet - Biomass integrated directly-heated gasification and gas turbine in combined cycle (BIG-GT/CC): Scenario 4 (SC4)

Biomass integrated directly-heated gasificatio and gas turbine in combined cycle
(BIG-GT/CC)

Scenario 5 (SC5)

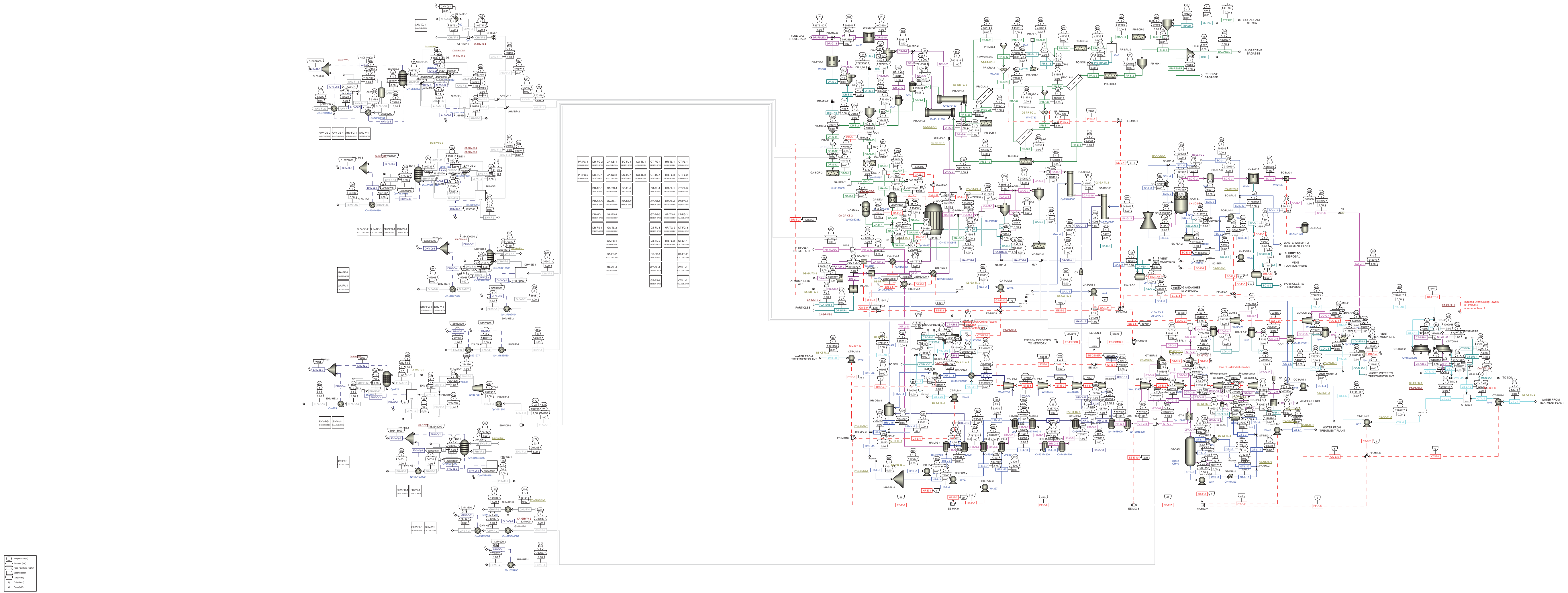

Figure A21 / Aspen Plus®v8.4 flowsheet - Biomass integrated directly-heated gasification and gas turbine in combined cycle (BIG-GT/CC): Scenario 5 (SC5)

Figure A22 / Aspen Plus®v8.4 flowsheet - Biomass to methanol production by biomass integrated directly-heated gasification and low ressure methanol catalytic-synthesis (Biomass-to-Methanol): Scenario 1 (SC1)

Biomass integrated directly-heated gasification an
low-pressure methanol catalytic-synthesis
(Biomass-to-Methanol)

Scenario 2 (SC2)

Figure A23 / Aspen Plus®v8.4 flowsheet - Biomass to methanol production by biomass integrated directly-heated gasification and low ressure methanol catalytic-synthesis (Biomass-to-Methanol): Scenario 2 (SC2)

Biomass integrated directly-heated gasification an low-pressure methanol catalytic-synthesis (Biomass-to-Methanol)

Scenario 3 (SC3)

Figure A24 / Aspen Plus®v8.4 flowsheet - Biomass to methanol production by biomass integrated directly-heated gasification and low ressure methanol catalytic-synthesis (Biomass-to-Methanol): Scenario 3 (SC3)

Figure A25 / Aspen Plus®v8.4 flowsheet - Biomass to mixed alcohols production by biomass integrated directly-heated gasification an mixed alcohol catalyst-synthesis (Biomass-to-Mixed alcohol): Scenario 1 (SC1)

Biomass to mixed alcohols production by
biomass integrated directly-heated gasificatio
and mixed alcohol catalyst-synthesis
(Biomass-to-Mixed alcohol)

Scenario 2 (SC2)

Figure A26 / Aspen Plus®v8.4 flowsheet - Biomass to mixed alcohols production by biomass integrated directly-heated gas fication an mixed alcohol catalyst-synthesis (Biomass-to-Mixed alcohol): Scenario 2 (SC2)

Figure A27 / Aspen Plus®v8.4 flowsheet - Biomass to mixed alcohols production by biomass integrated directly-heated gasification an mixed alcohol catalyst-synthesis (Biomass-to-Mixed alcohol): Scenario 3 (SC3)

APPENDIX B - Additional and supplementary bar charts obtained from Life Cycle Inventory Assessment (LCIA)

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Figure B2 - Comparative potential environmental impacts for ethanol production (kg) by 1G sugarcane biorefinery integrate Biomass-to-Mixed alcohols (SC1, SC2) routes. Method: World ReCiPe (H) midpoint.

Figure B3 - Comparative potential environmental impacts for ethanol production (kg) by 1G sugarcane biorefinery integrate Biomass-to-Mixed alcohols (SC1, SC2) routes and 1G sugarcane biorefinery with CHP/CEST (SC5) route. Method: World ReCiPe (H) midpoint.

Figure B4 - Comparative potential environmental impacts for methanol production (kg) by 1G sugarcane biorefinery integrate Biomass-to-Methanol (SC1, SC2) routes. Method: World ReCiPe (H) midpoint.

Figure B5 - Comparative potential environmental impacts for ethanol production (kg) by 1G sugarcane biorefinery integrate Biomass-to-Mixed alcohols (SC1, SC2) routes. Method: World ReCiPe (H) midpoint

Figure B6 - Characterized impact indicators for electricity generation (kWh) based on Brazil’s total electricity final consumption (2013) – Electricity (Mix Brazil). Method: World ReCiPe (H) midpoint.

Figure B7 - Characterized impact indicators for sugarcane production (kg) - Sugarcane (agricultural phase). Method: World ReCiPe (H) midpoint.

Figure B8 - Characterized impact indicators for electricity generation (kWh) - industrial phase of 1G sugarcane biorefinery applying CHP/CEST (SC5). Method: World ReCiPe (H) midpoint.

Characterized impact indicators for electricity generation (kWh) by 1G sugarcane biorefinery with CHP/CEST
Figure B9 - CHP/CEST (SC1); Figure B10 - CHP/CEST (SC2); Figure B11 - CHP/EBPST (SC2); Figure B12 - CHP/CEST (SC3); Figure B13 - CHP/EBPST (SC3); Figure B14 - CHP/CEST (SC4); Figure B15 - CHP/EBPST (SC4); Figure B16 - CHP/CEST (SC6); Figure B17 - CHP/EBPST (SC6); Figure B18 - CHP/CEST (SC7); Figure B19 - CHP/EBPST (SC7).

Figure B1 presents the bar chart of comparative potential environmental impacts performed using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach) for electricity generation in kWh comparative base unit by 1G sugarcane biorefinery integrate BIG-GT/CC routes.

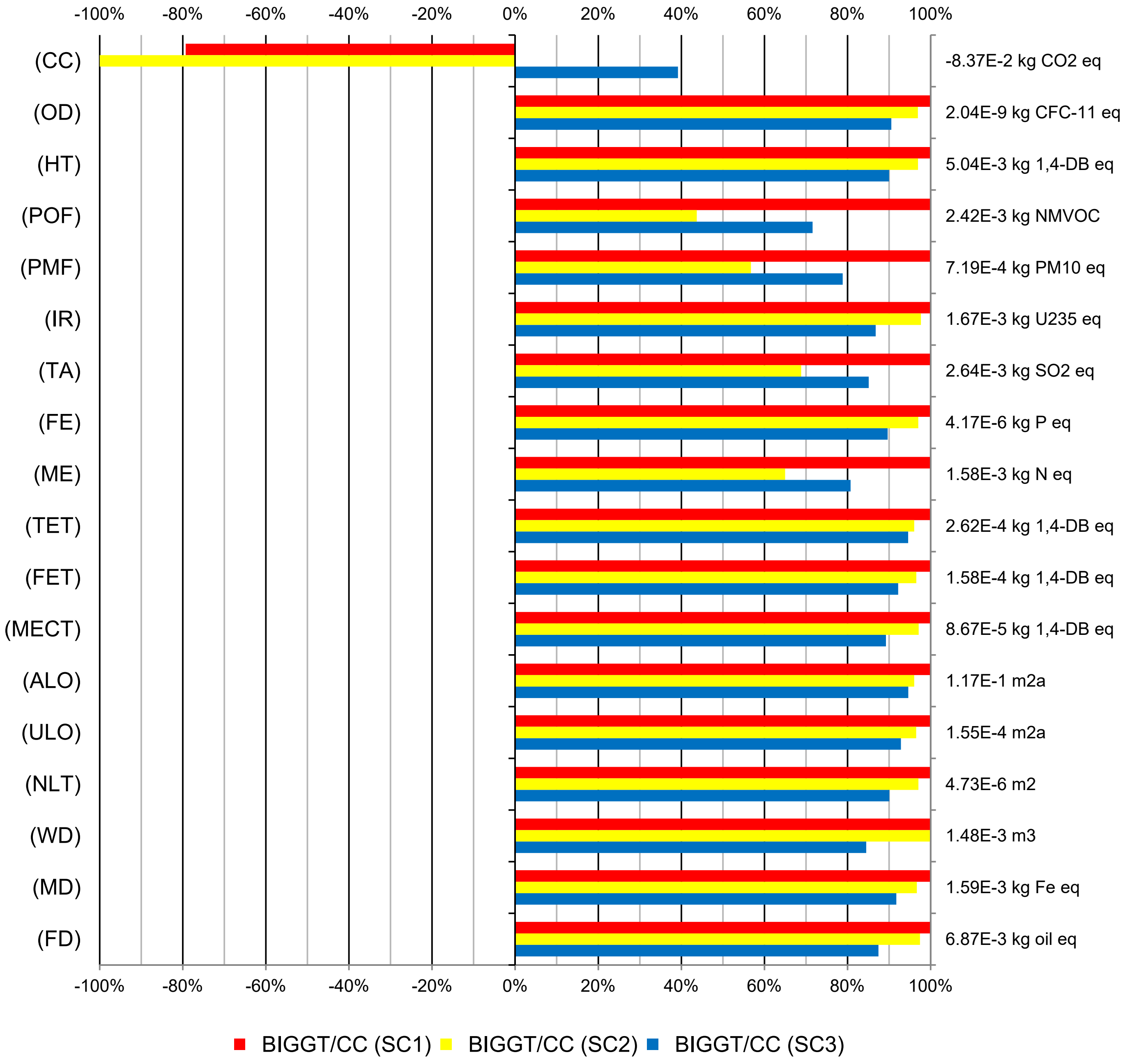

Figure B1 - Comparative potential environmental impacts for electricity generation (kWh) by 1G sugarcane biorefinery integrate BIG-GT/CC (SC1, SC2 and SC3) routes. Method: World ReCiPe (H) midpoint.

Figure B2 presents the bar chart of comparative potential environmental impacts performed using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach) for ethanol production in kg comparative base unit by 1G sugarcane biorefinery integrate Biomass-to-Mixed alcohols routes.

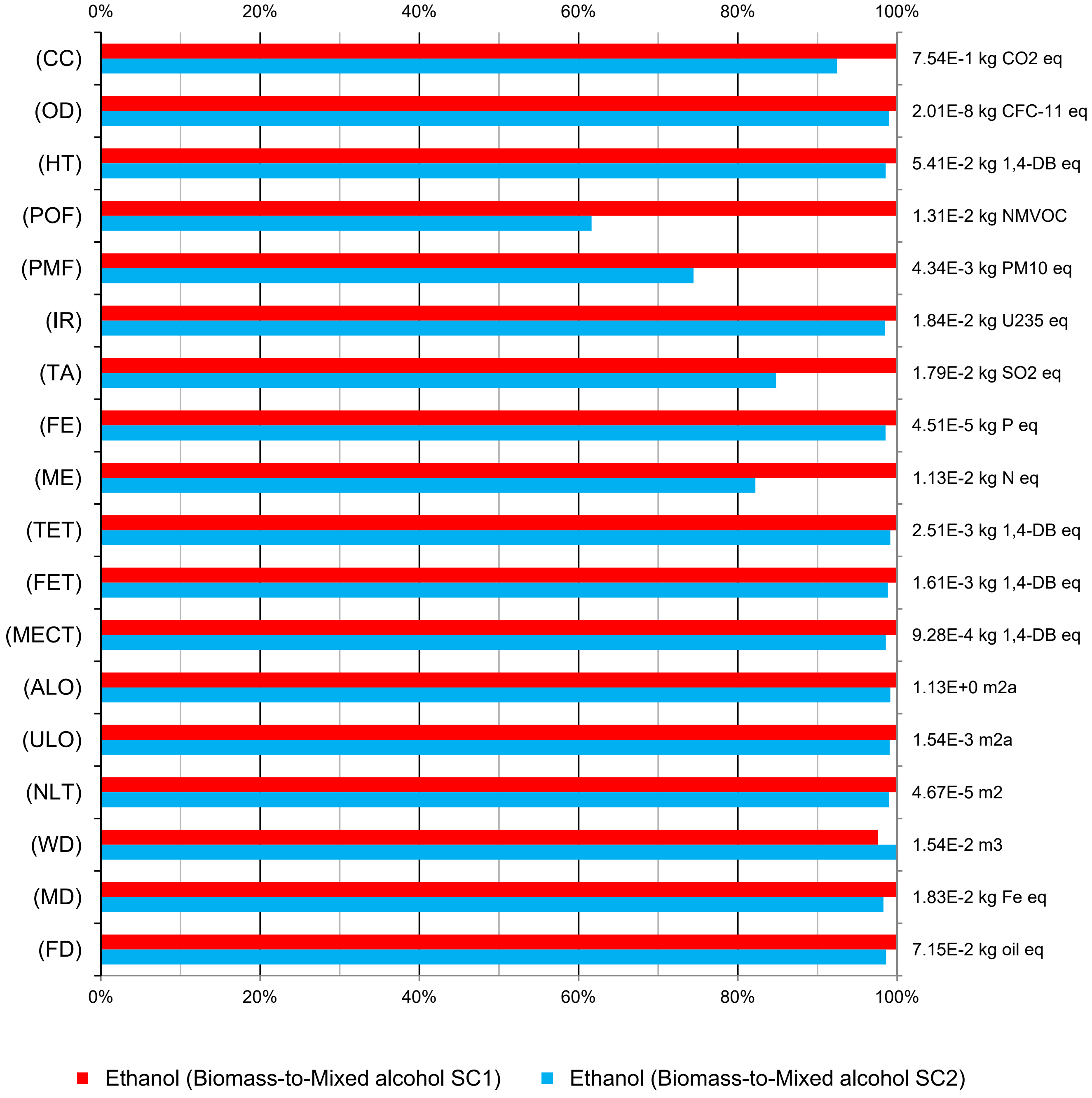

Figure B2 - Comparative potential environmental impacts for ethanol production (kg) by 1G sugarcane biorefinery integrate Biomass-to-Mixed alcohols (SC1, SC2) routes. Method: World ReCiPe (H) midpoint.

Figure B3 presents the bar chart of comparative potential environmental impacts performed using the World midpoint ReCiPe model in SimaPro®7.3.3 software (economic allocation approach) for ethanol production in kg comparative base unit by 1G sugarcane biorefinery with CHP/CEST (SC5) and by 1G sugarcane biorefinery integrate Biomass-to-Mixed alcohols routes.

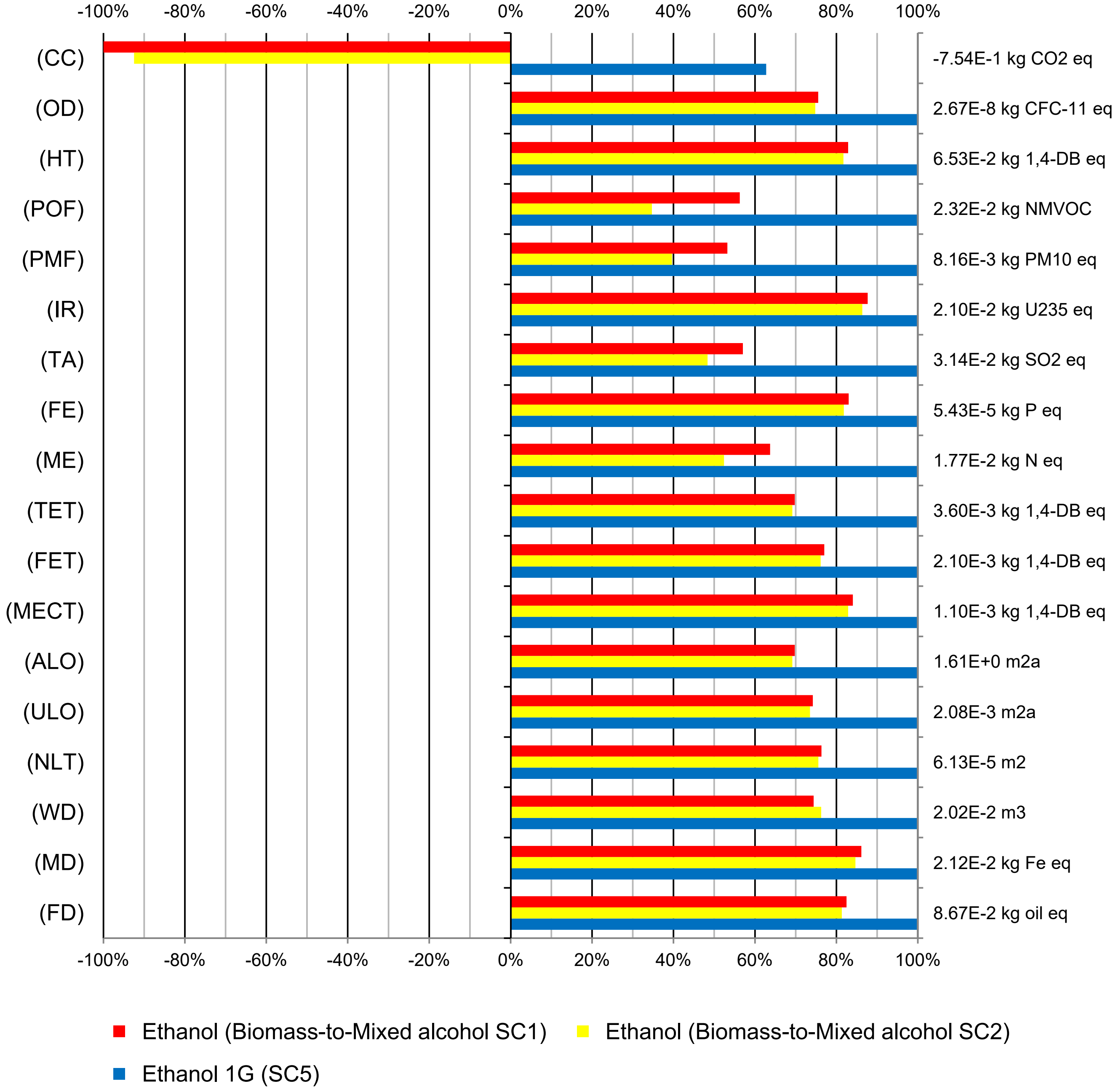

Figure B3 - Comparative potential environmental impacts for ethanol production (kg) by 1G sugarcane biorefinery integrate Biomass-to-Mixed alcohols (SC1, SC2) routes and 1G sugarcane biorefinery with CHP/CEST (SC5) route. Method: World ReCiPe (H) midpoint.

Figure B4 presents the bar chart of comparative potential environmental impacts performed using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach) for grade AA methanol production in kg comparative base unit by 1G sugarcane biorefinery integrate Biomass-to-Methanol routes.

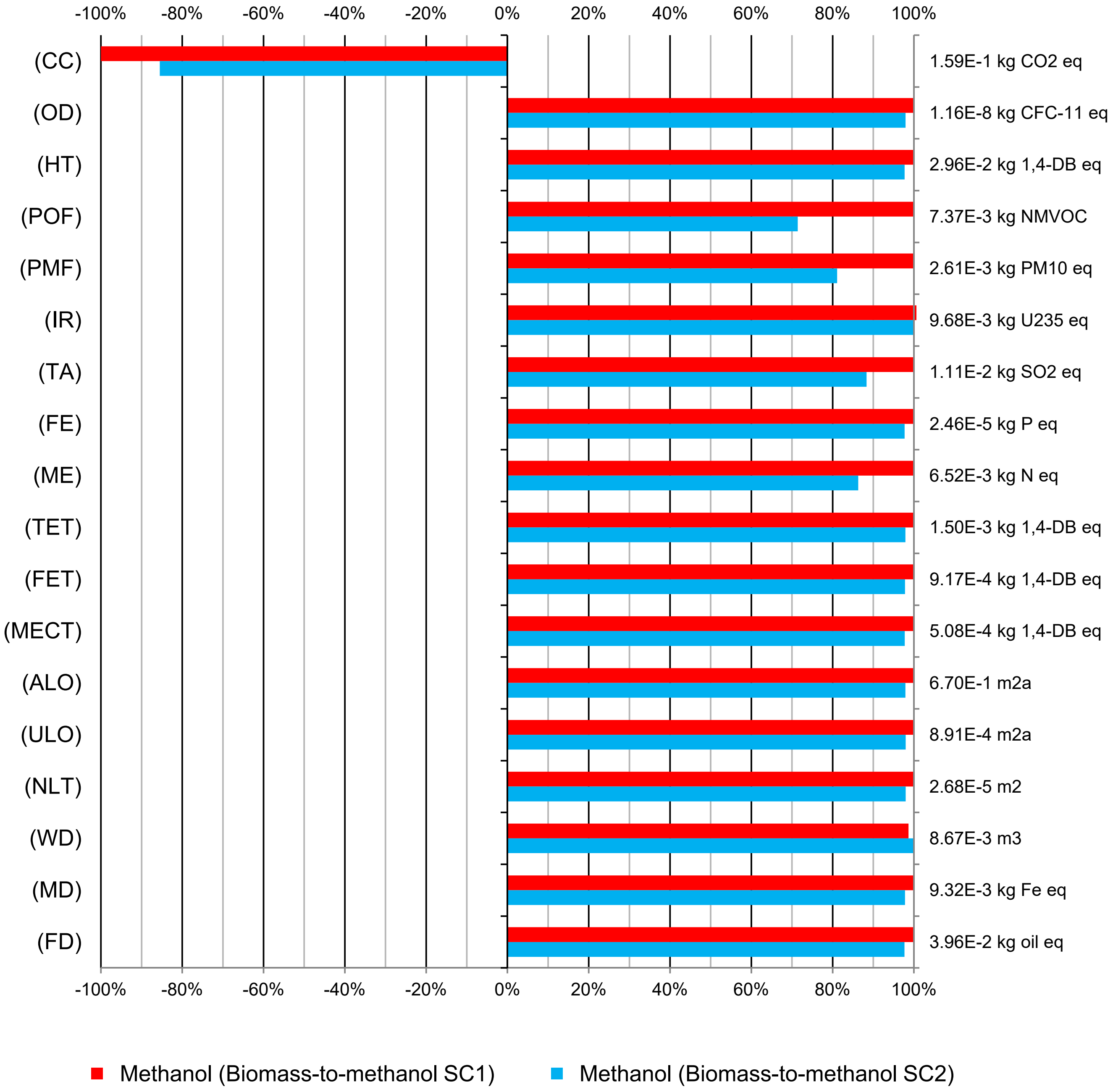

Figure B4 - Comparative potential environmental impacts for methanol production (kg) by 1G sugarcane biorefinery integrate Biomass-to-Methanol (SC1, SC2) routes. Method: World ReCiPe (H) midpoint.

Figure B5 presents the bar chart of comparative potential environmental impacts performed using the World midpoint ReCiPe model in SimaPro®7.3.3 software (economic allocation approach) for ethanol production in kg comparative base unit by 1G sugarcane biorefinery integrate Biomass-to-Mixed alcohols routes.

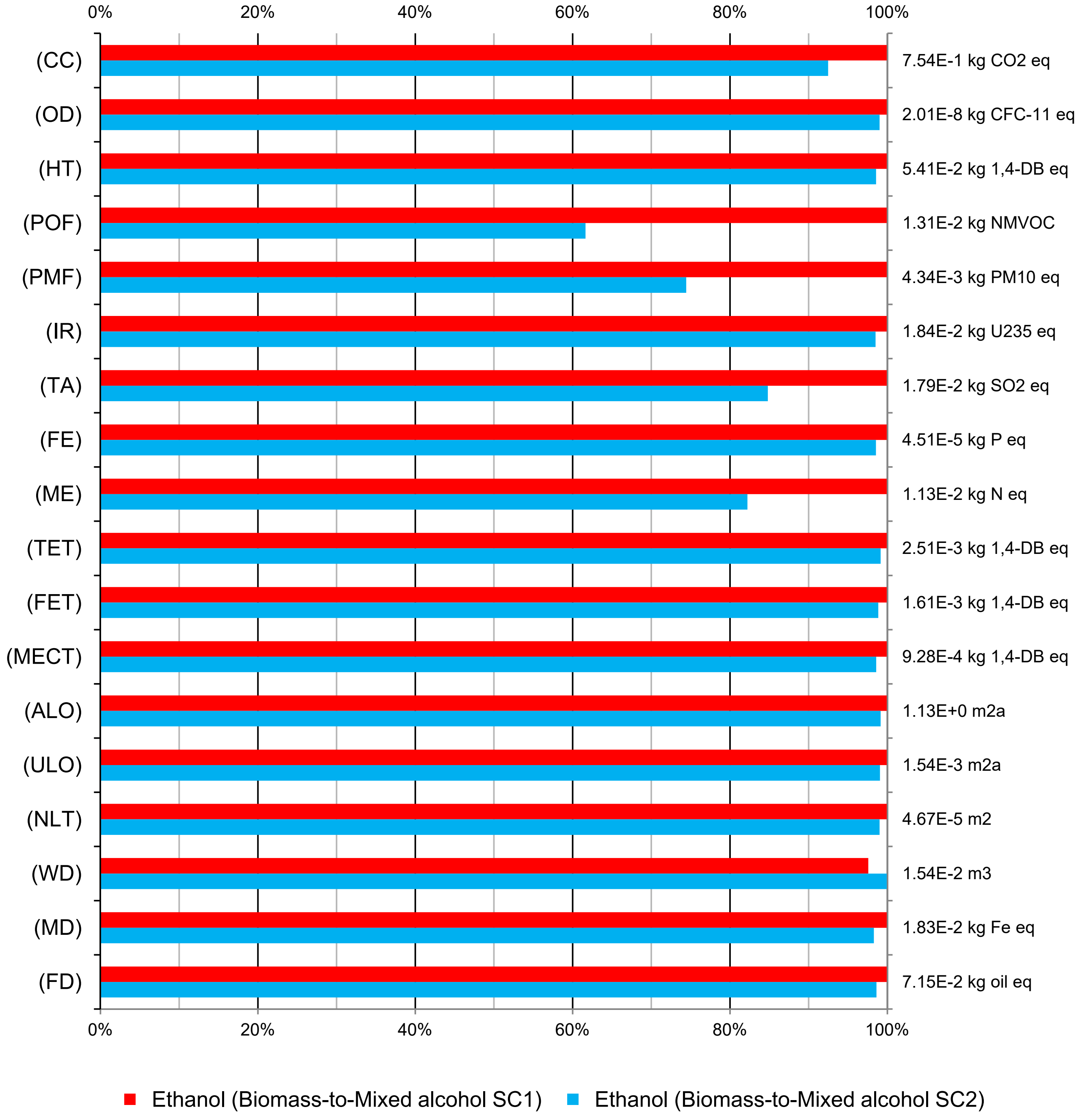

Figure B5 - Comparative potential environmental impacts for ethanol production (kg) by 1G sugarcane biorefinery integrate Biomass-to-Mixed alcohols (SC1, SC2) routes. Method: World ReCiPe (H) midpoint

Figure B6 presents the bar chart of characterized impact indicators performed using the World midpoint ReCiPe model in SimaPro®7.3.3 software for electricity generation in kWh comparative base unit based on Brazil's total electricity final consumption (2013) – Electricity (Mix Brazil).

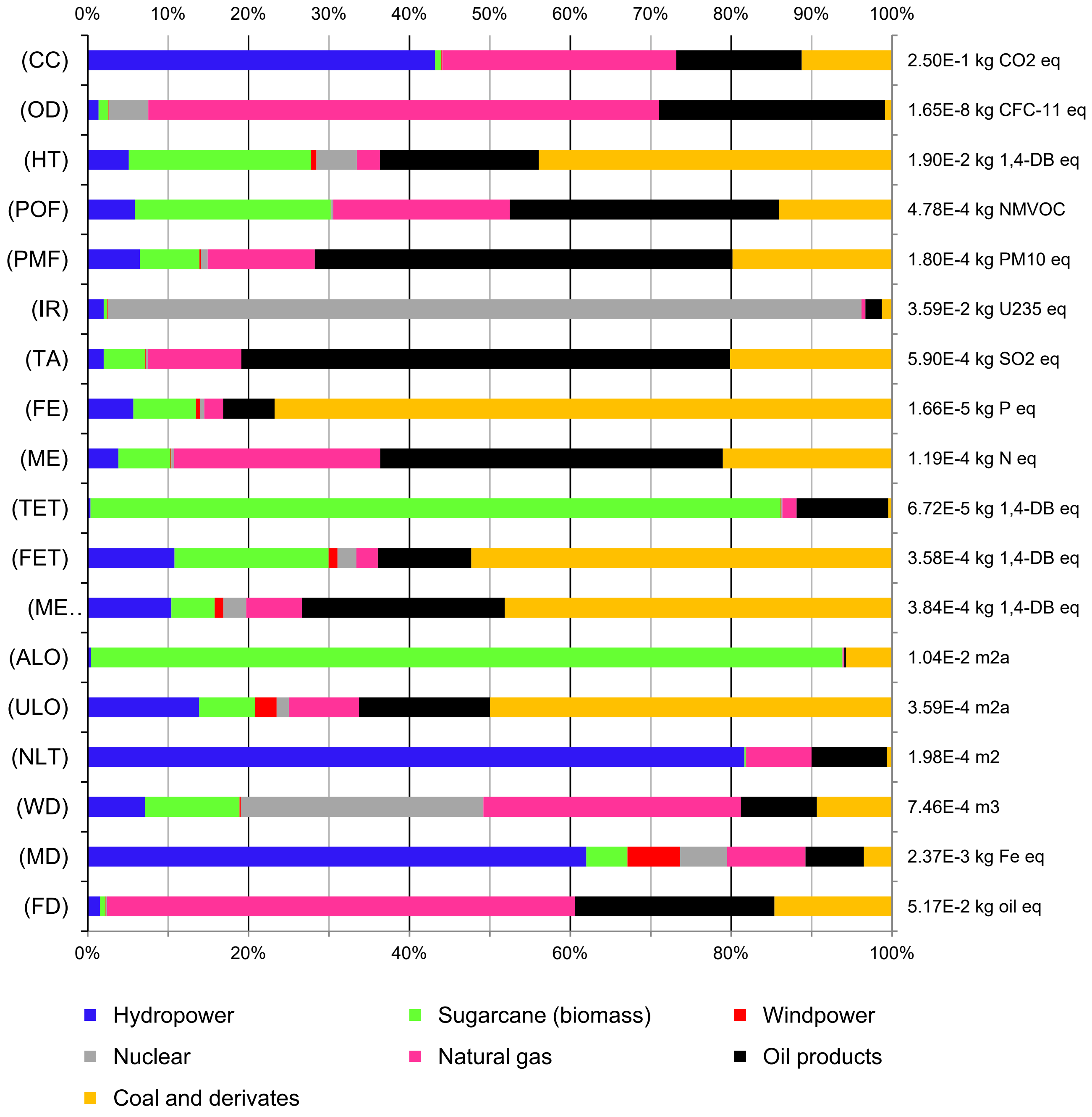

Figure B6 - Characterized impact indicators for electricity generation (kWh) based on Brazil's total electricity final consumption (2013) – Electricity (Mix Brazil). Method: World ReCiPe (H) midpoint.

Figure B7 presents the bar chart of characterized impact indicators performed using the World midpoint ReCiPe model in SimaPro®7.3.3 software for sugarcane production in kg comparative base unit – Sugarcane (agricultural phase.

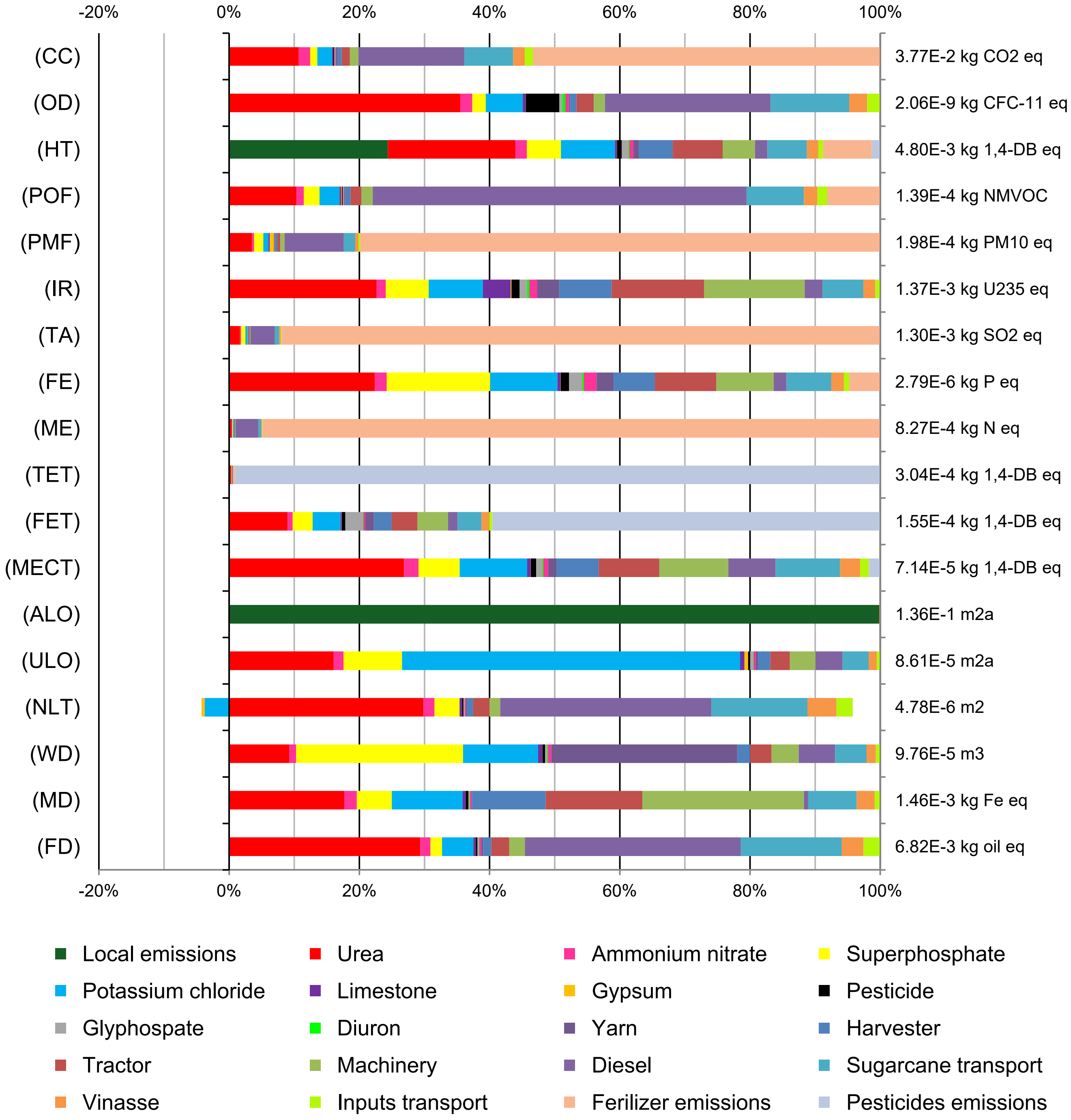

Figure B7 - Characterized impact indicators for sugarcane production (kg) - Sugarcane (agricultural phase). Method: World ReCiPe (H) midpoint.

* ALO impact from Local emissions group is equivalent to Sugarcane (kg) impact

Figure B8 presents the bar chart of characterized impact indicators performed using the World midpoint ReCiPe model in SimaPro®7.3.3 software for electricity generation in kWh comparative base unit - industrial phase of the 1G sugarcane biorefinery applying CHP/CEST (SC5).

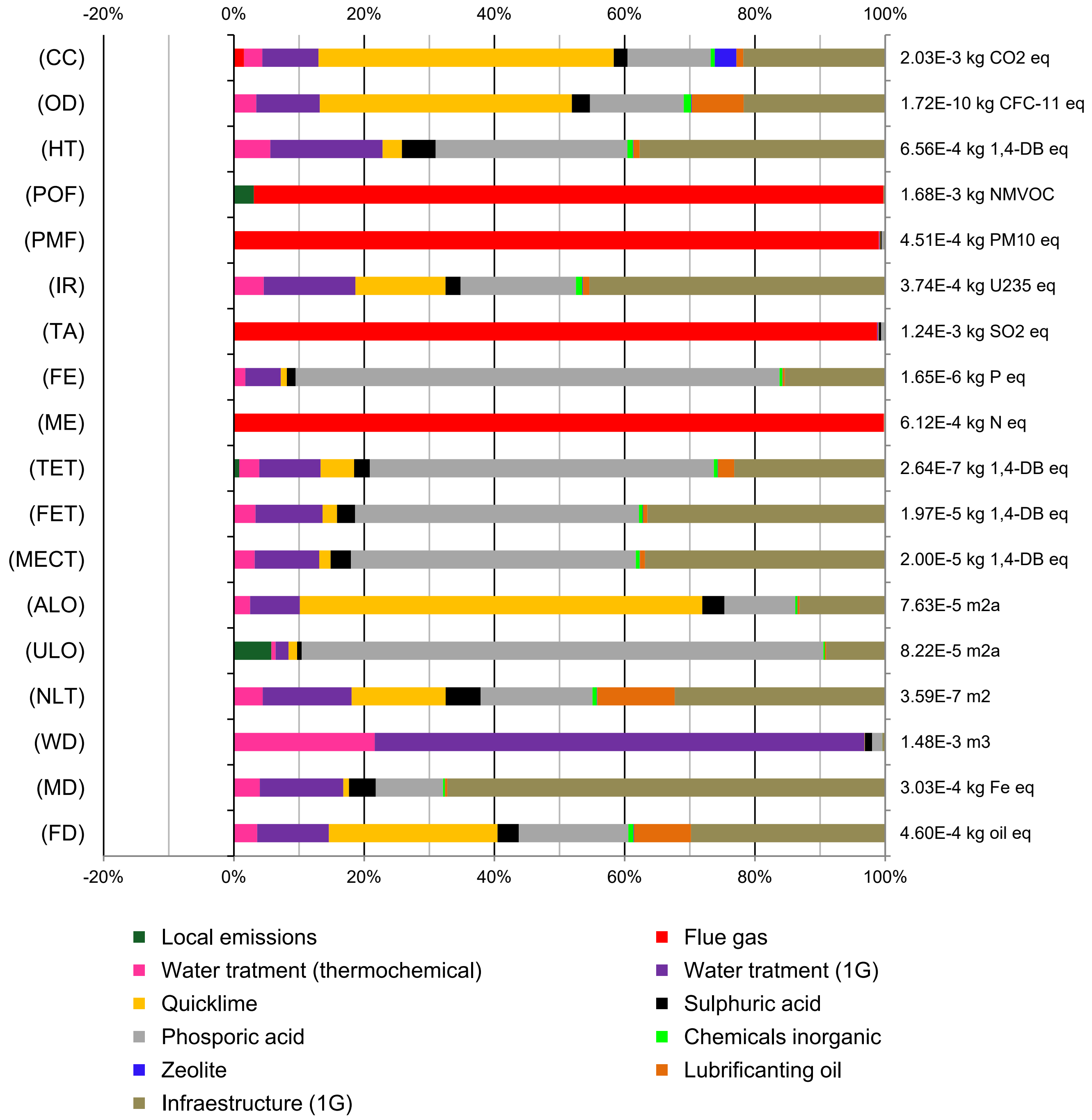

Figure B8 - Characterized impact indicators for electricity generation (kWh) - industrial phase of 1G sugarcane biorefinery applying CHP/CEST (SC5). Method: World ReCiPe (H) midpoint.

Figure B9 presents the bar chart of characterized impact indicators performed using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach) for electricity generation in kWh comparative base unit by 1G sugarcane biorefinery applying CHP/CEST operating at 22 bar and 320ºC (SC1).

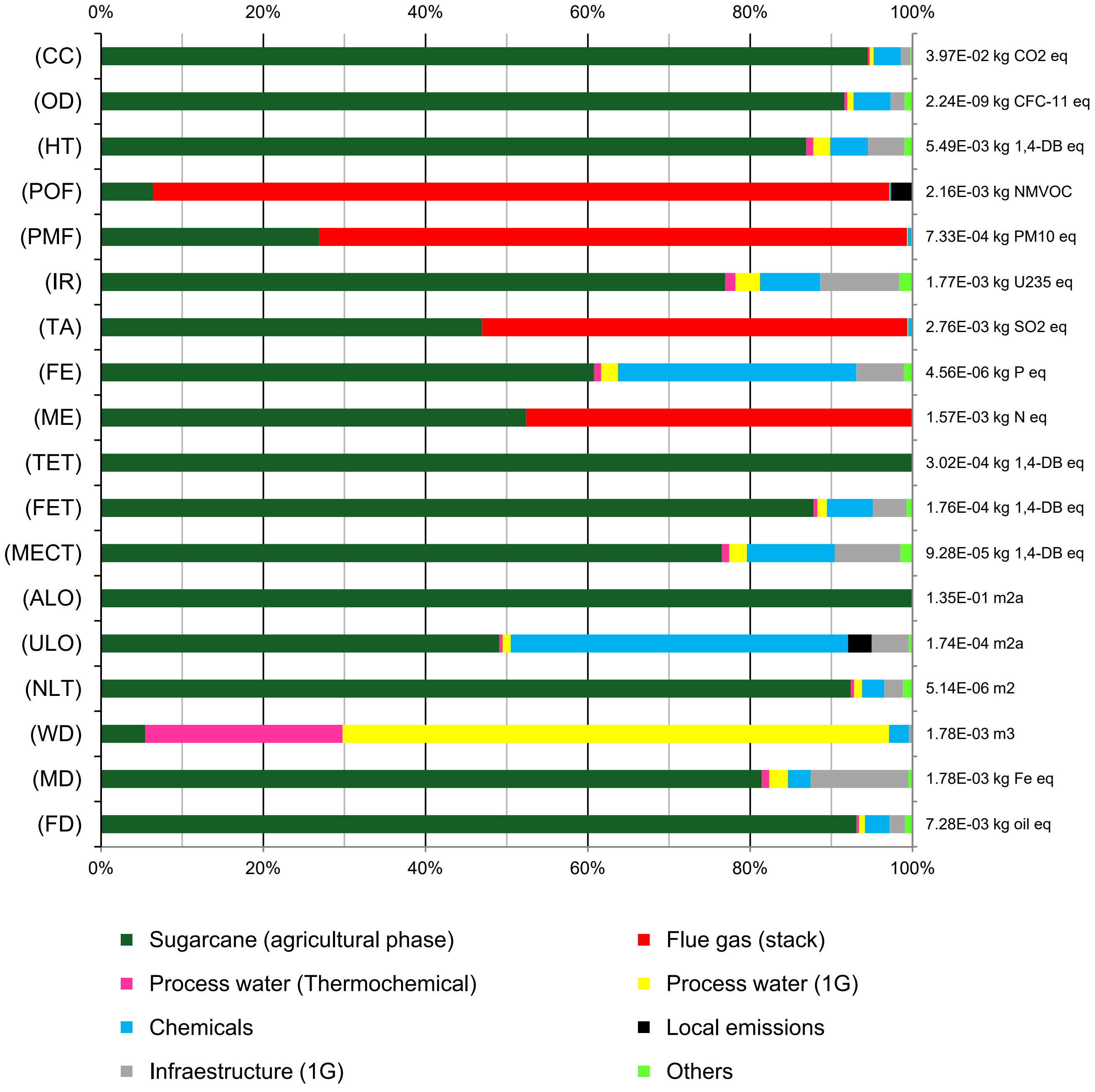

Figure B9 - Characterized impact indicators for electricity generation (kWh) by 1G sugarcane biorefinery with CHP/CEST (SC1) system. Method: World ReCiPe (H) midpoint.

Figure B10 presents the bar chart of characterized impact indicators performed using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach) for electricity generation in kWh comparative base unit by 1G sugarcane biorefinery applying CHP/CEST operating at 45 bar and 450ºC (SC2).

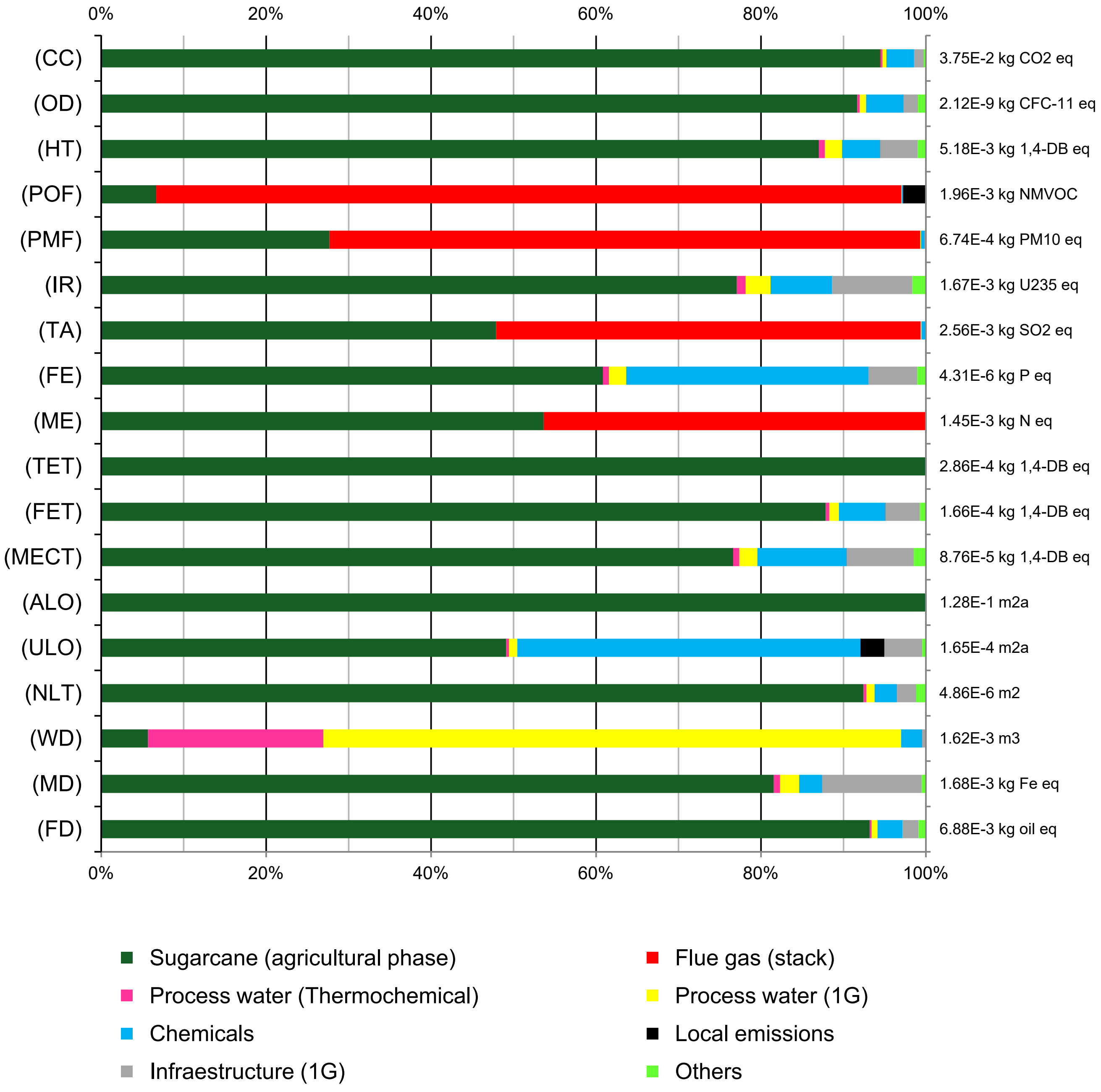

Figure B10 - Characterized impact indicators for electricity generation (kWh) by 1G sugarcane biorefinery with CHP/CEST (SC2) system. Method: World ReCiPe (H) midpoint.

Figure B11 presents the bar chart of characterized impact indicators performed using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach) for electricity generation in kWh comparative base unit by 1G sugarcane biorefinery applying CHP/EBPST operating at 45 bar and 450ºC (SC2).

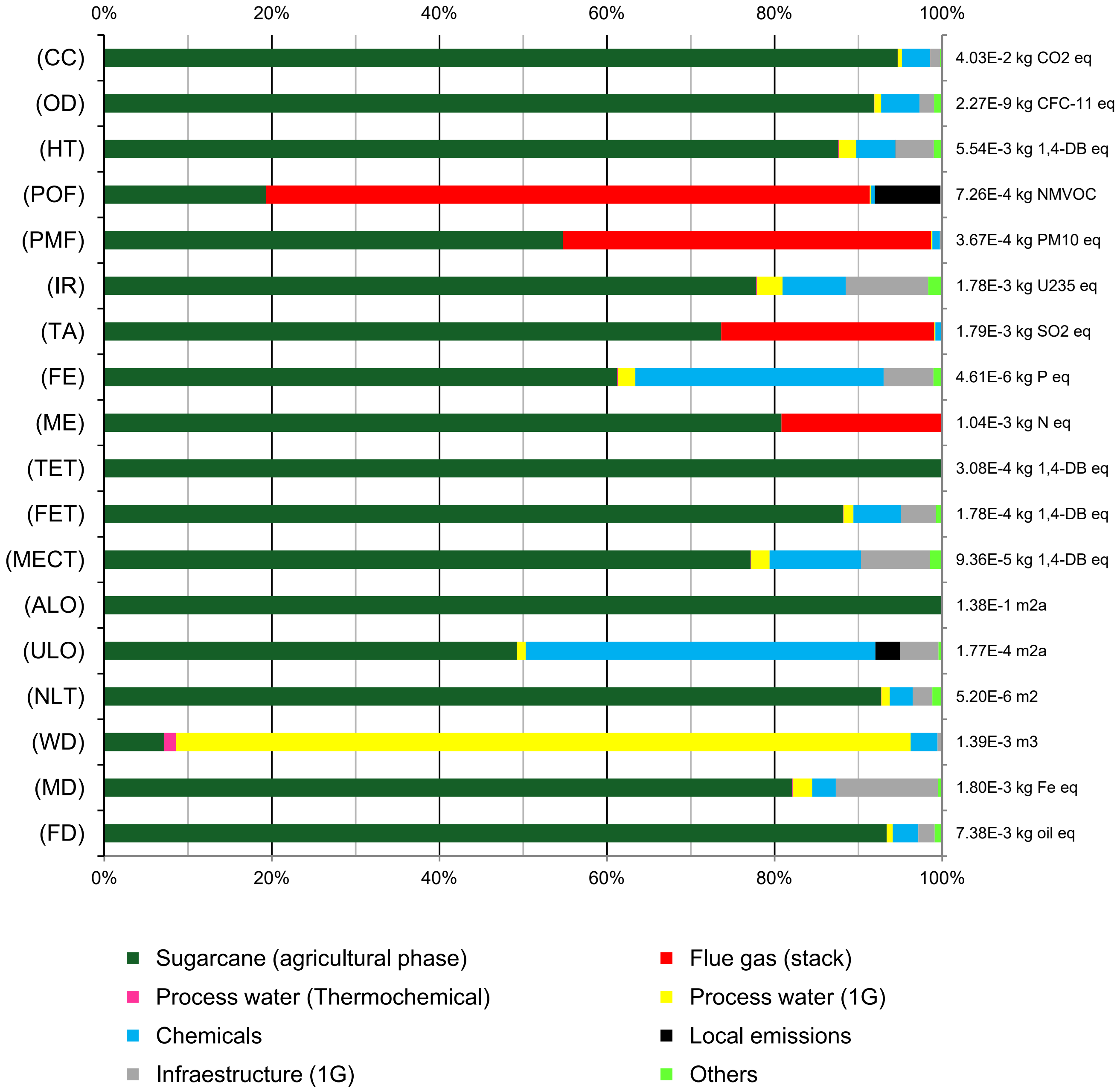

Figure B11 - Characterized impact indicators for electricity generation (kWh) by 1G sugarcane biorefinery with CHP/EBPST (SC2) system. Method: World ReCiPe (H) midpoint.

Figure B12 presents the bar chart of characterized impact indicators performed using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach) for electricity generation in kWh comparative base unit by 1G sugarcane biorefinery applying CHP/CEST operating at 65 bar and 480ºC (SC3).

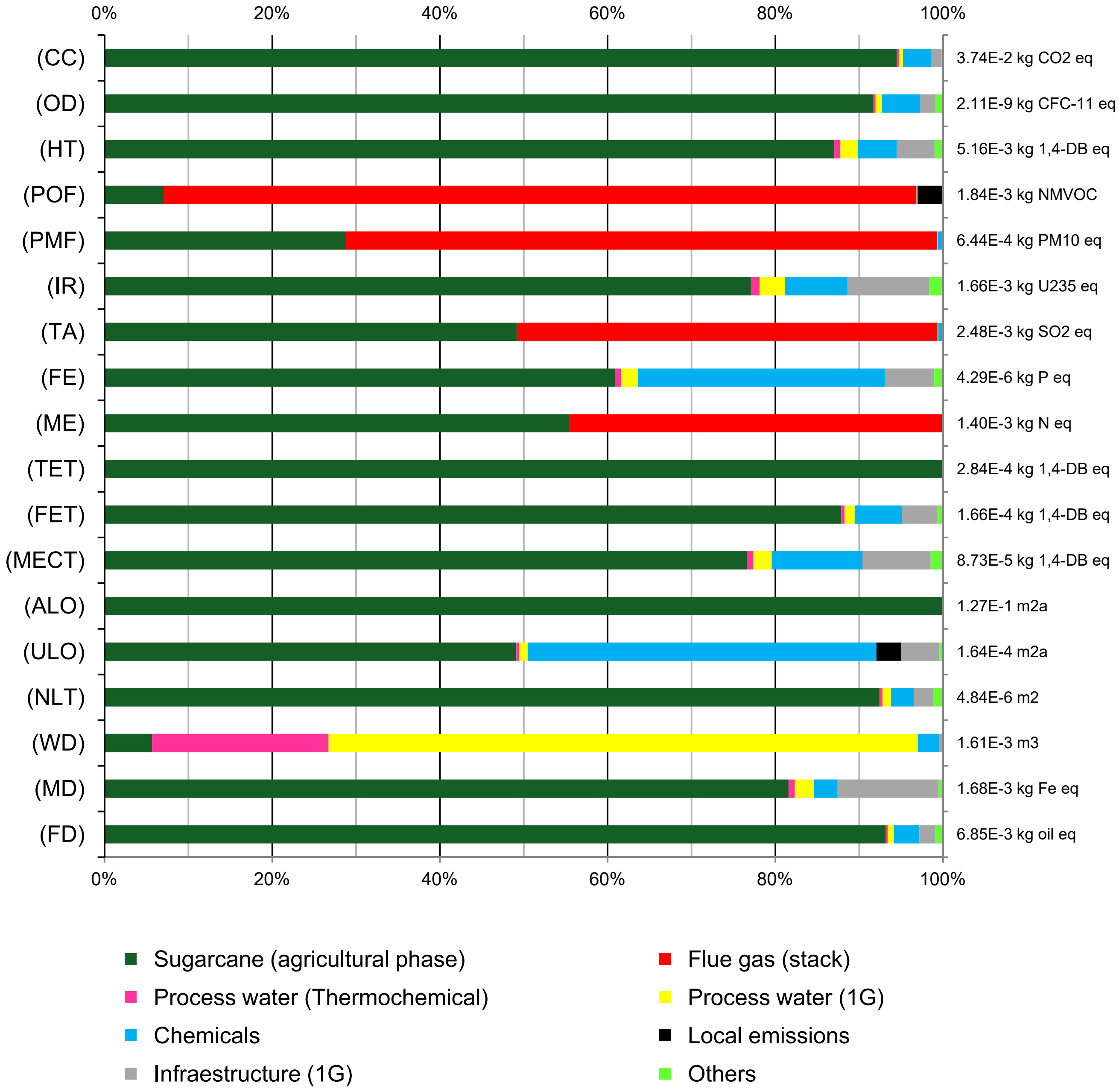

Figure B12 - Characterized impact indicators for electricity generation (kWh) by 1G sugarcane biorefinery with CHP/CEST (SC3) system. Method: World ReCiPe (H) midpoint.

Figure B13 presents the bar chart of characterized impact indicators performed using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach) for electricity generation in kWh comparative base unit by 1G sugarcane biorefinery applying CHP/EBPST operating at 65 bar and 480ºC (SC3).

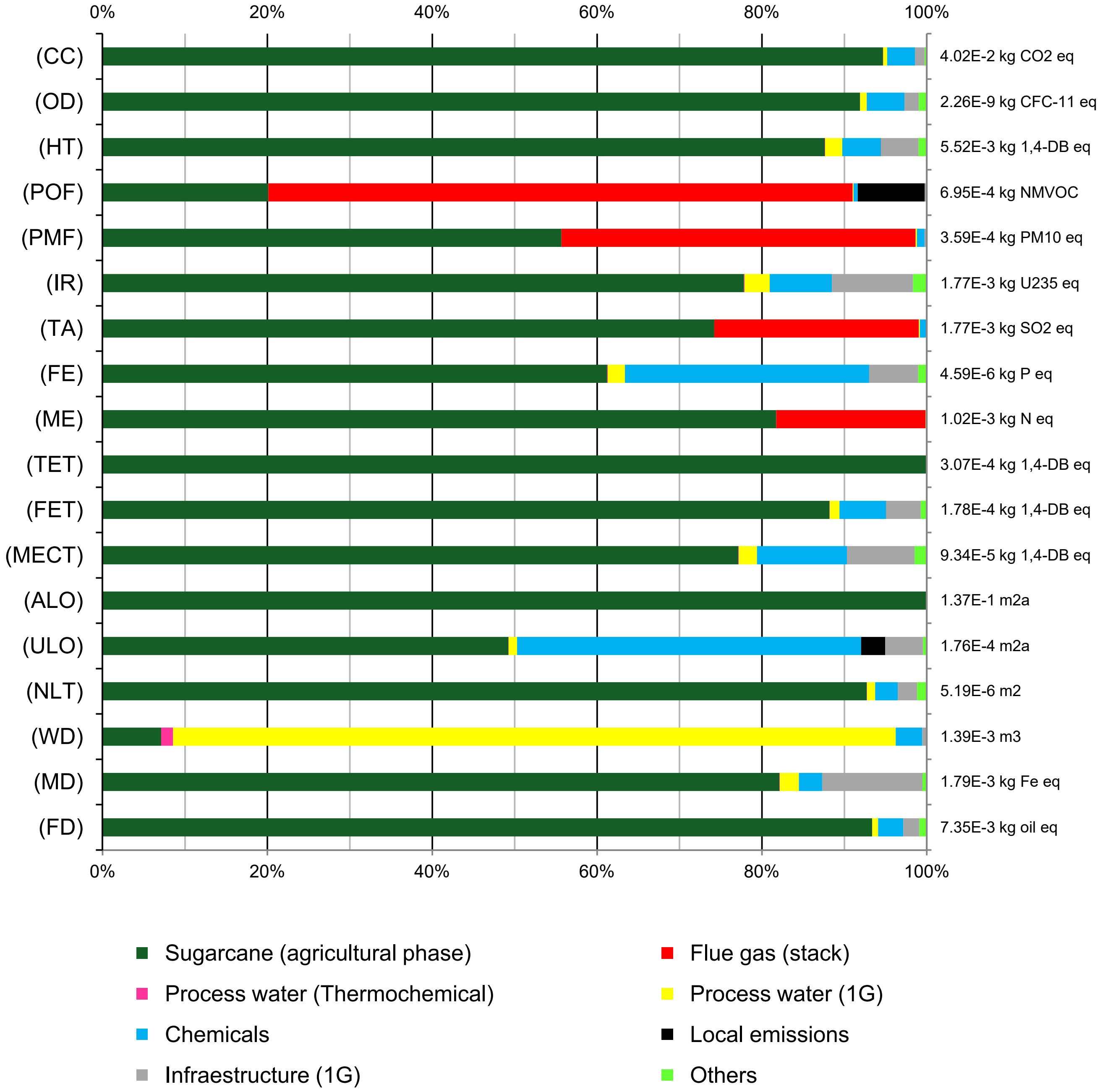

Figure B13 - Characterized impact indicators for electricity generation (kWh) by 1G sugarcane biorefinery with CHP/EBPST (SC3) system. Method: World ReCiPe (H) midpoint.

Figure B14 presents the bar chart of characterized impact indicators performed using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach) for electricity generation in kWh comparative base unit by 1G sugarcane biorefinery applying CHP/CEST operating at 85 bar and 520ºC (SC4).

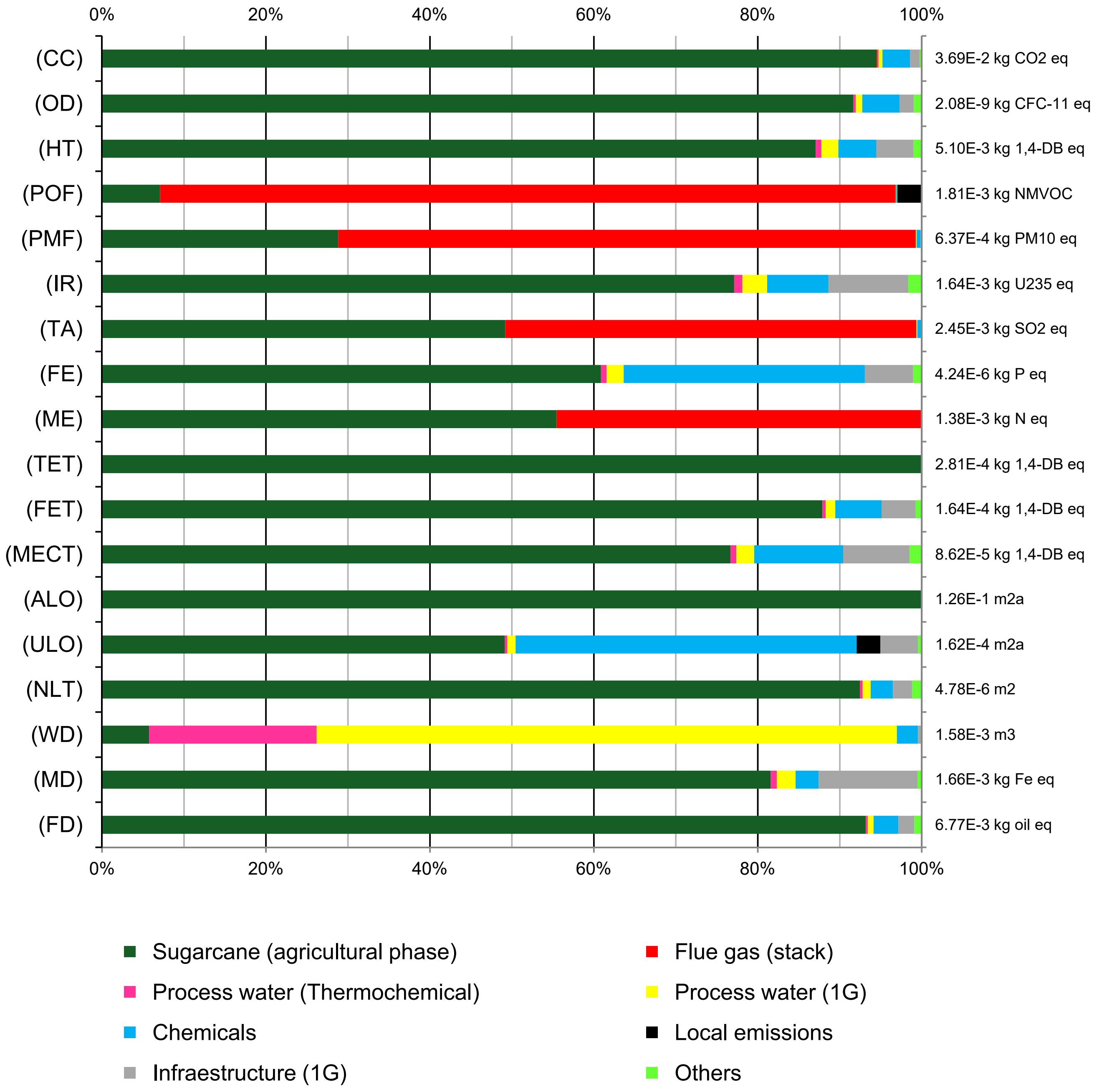

Figure B14 - Characterized impact indicators for electricity generation (kWh) by 1G sugarcane biorefinery with CHP/CEST (SC4) system. Method: World ReCiPe (H) midpoint.

Figure B15 presents the bar chart of characterized impact indicators performed using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach) for electricity generation in kWh comparative base unit by 1G sugarcane biorefinery applying CHP/EBPST operating at 85 bar and 520ºC (SC4).

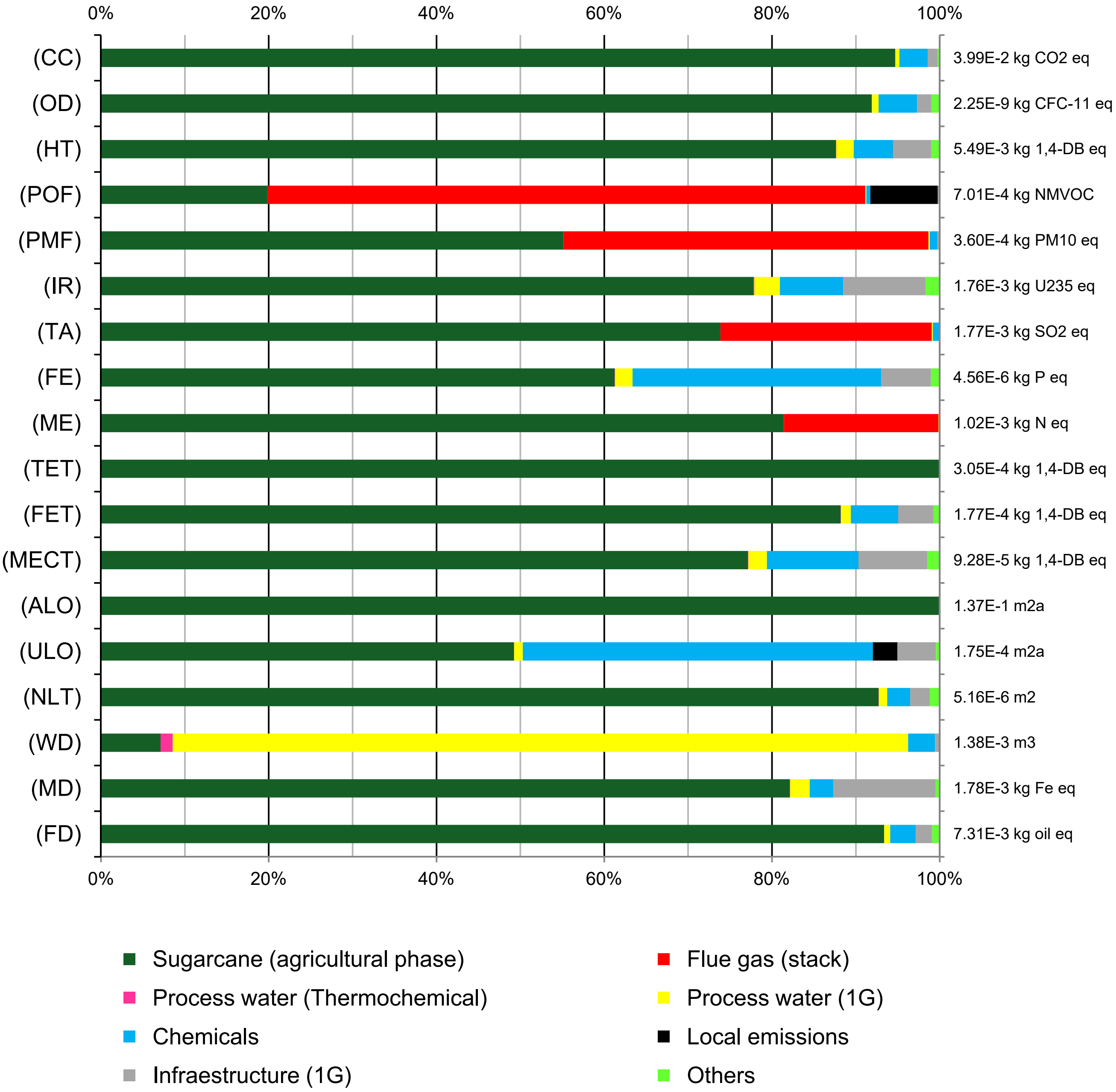

Figure B15 - Characterized impact indicators for electricity generation (kWh) by 1G sugarcane biorefinery with CHP/EBPST (SC4) system. Method: World ReCiPe (H) midpoint.

Figure B16 presents the bar chart of characterized impact indicators performed using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach) for electricity generation in kWh comparative base unit by 1G sugarcane biorefinery applying CHP/CEST operating at 96 bar and 530ºC (SC6).

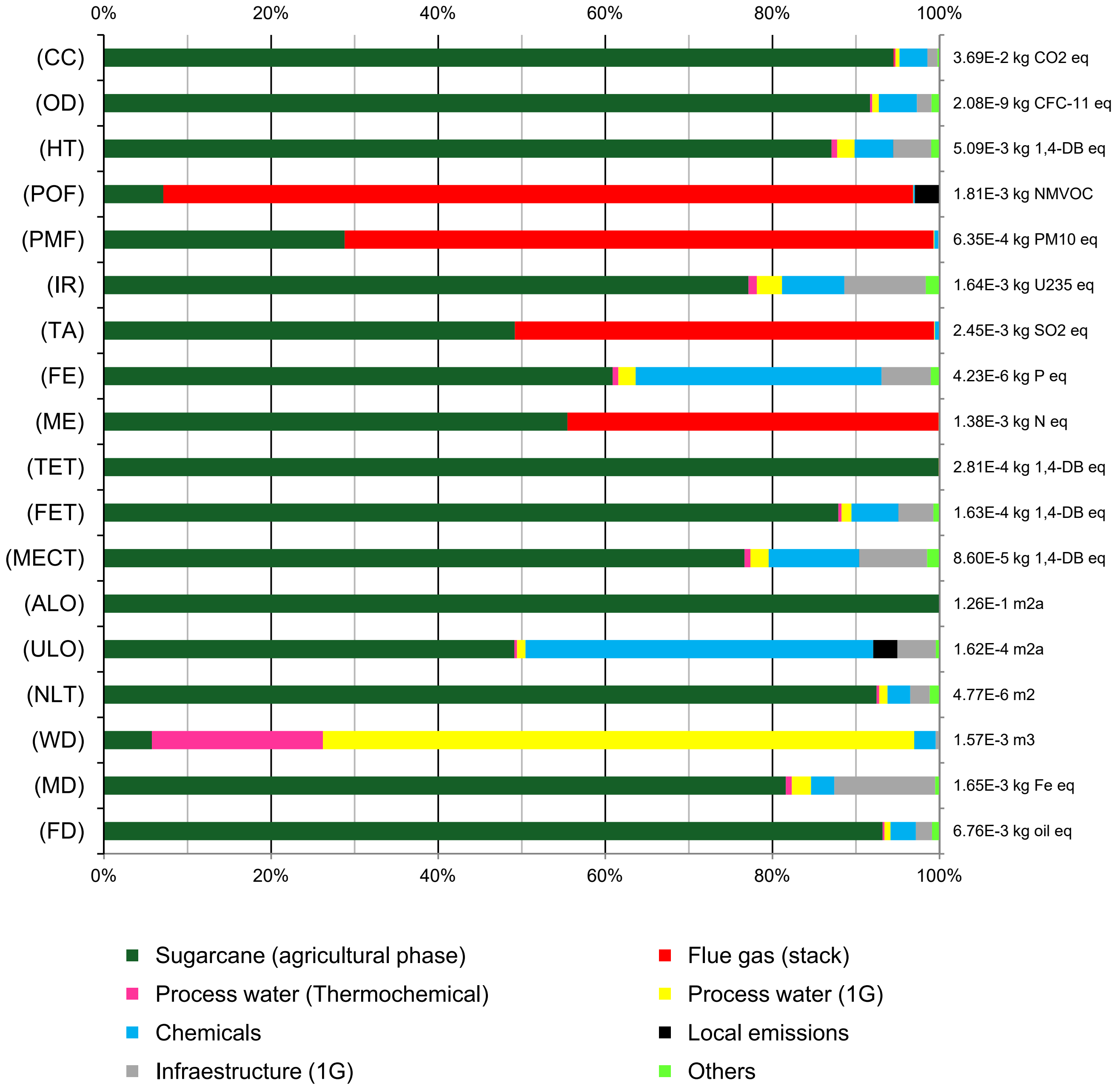

Figure B16 - Characterized impact indicators for electricity generation (kWh) by 1G sugarcane biorefinery with CHP/CEST (SC6) system. Method: World ReCiPe (H) midpoint.

Figure B17 presents the bar chart of characterized impact indicators performed using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach) for electricity generation in kWh comparative base unit by 1G sugarcane biorefinery applying CHP/EBPST operating at 96 bar and 530ºC (SC6).

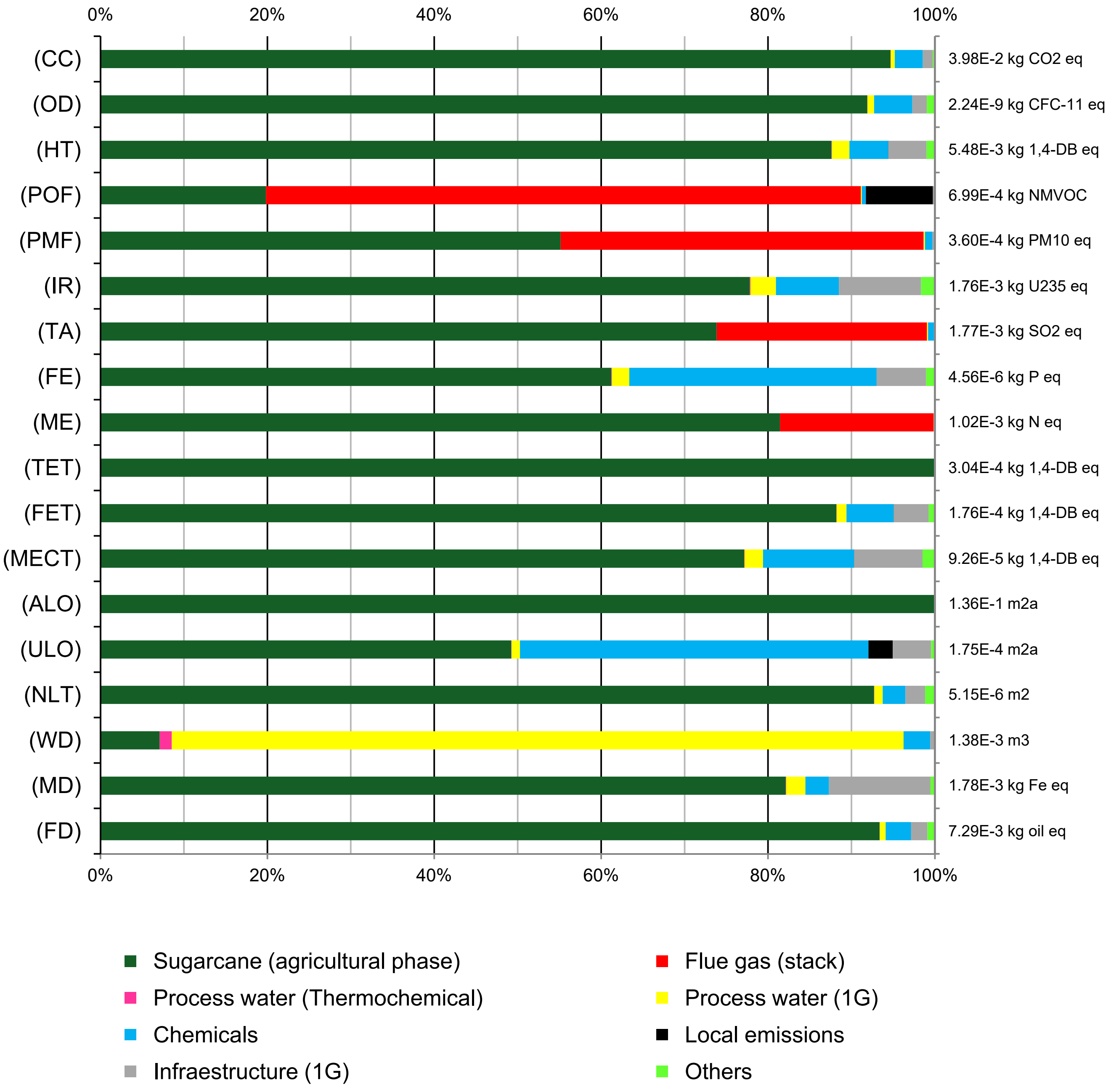

Figure B17 - Characterized impact indicators for electricity generation (kWh) by 1G sugarcane biorefinery with CHP/EBPST (SC6) system. Method: World ReCiPe (H) midpoint.

Figure B18 presents the bar chart of characterized impact indicators performed using the World midpoint ReCiPe 2008 model in SimaPro$^{®}$7.3.3 software (economic allocation approach) for electricity generation in kWh comparative base unit by 1G sugarcane biorefinery applying CHP/CEST operating at 120 bar and 530ºC (SC7).

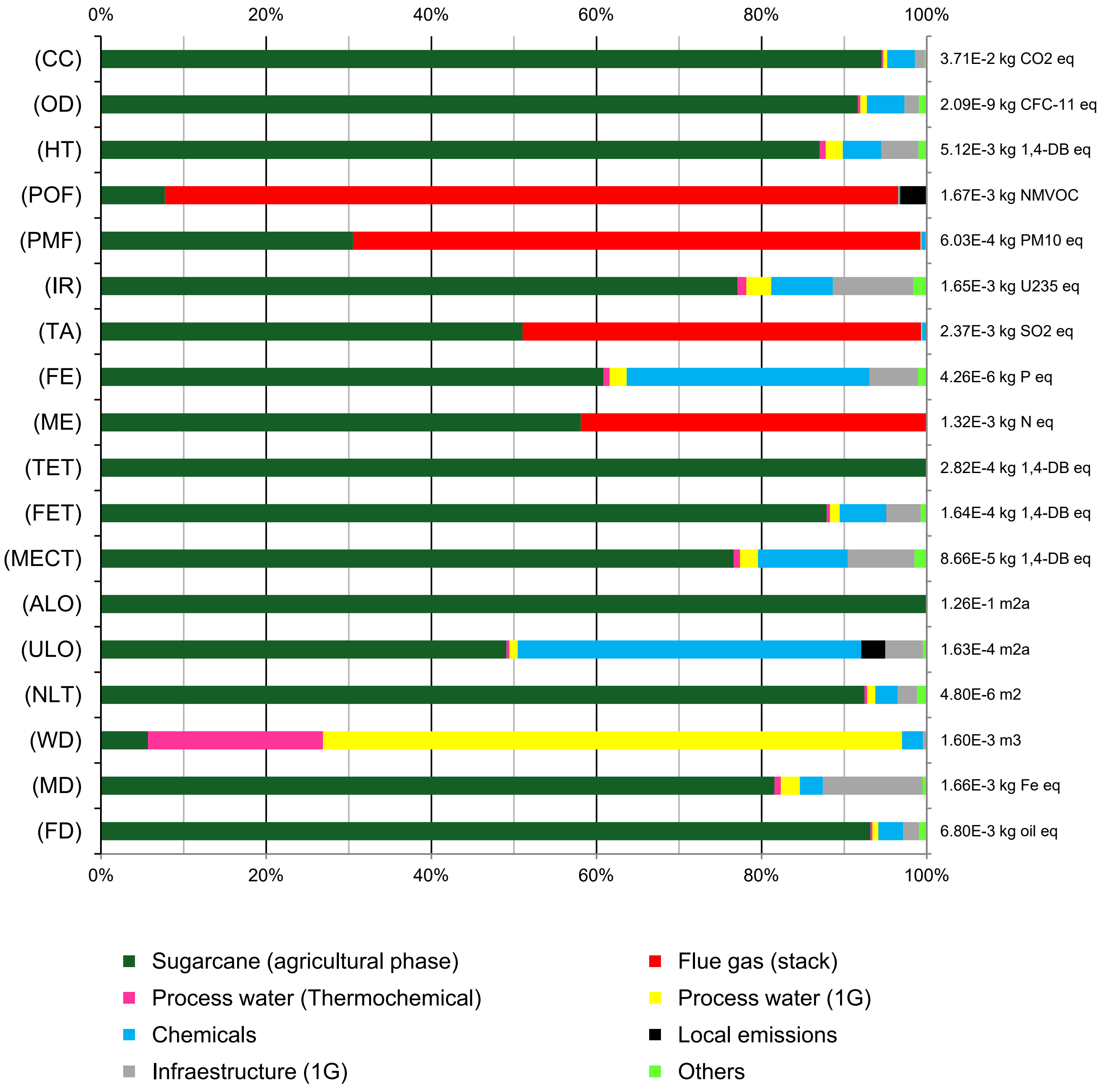

Figure B18 - Characterized impact indicators for electricity generation (kWh) by 1G sugarcane biorefinery with CHP/CEST (SC7) system. Method: World ReCiPe (H) midpoint.

Figure B19 presents the bar chart of characterized impact indicators performed using the World midpoint ReCiPe 2008 model in SimaPro®7.3.3 software (economic allocation approach) for electricity generation in kWh comparative base unit by 1G sugarcane biorefinery applying CHP/EBPST operating at 120 bar and 530ºC (SC7).

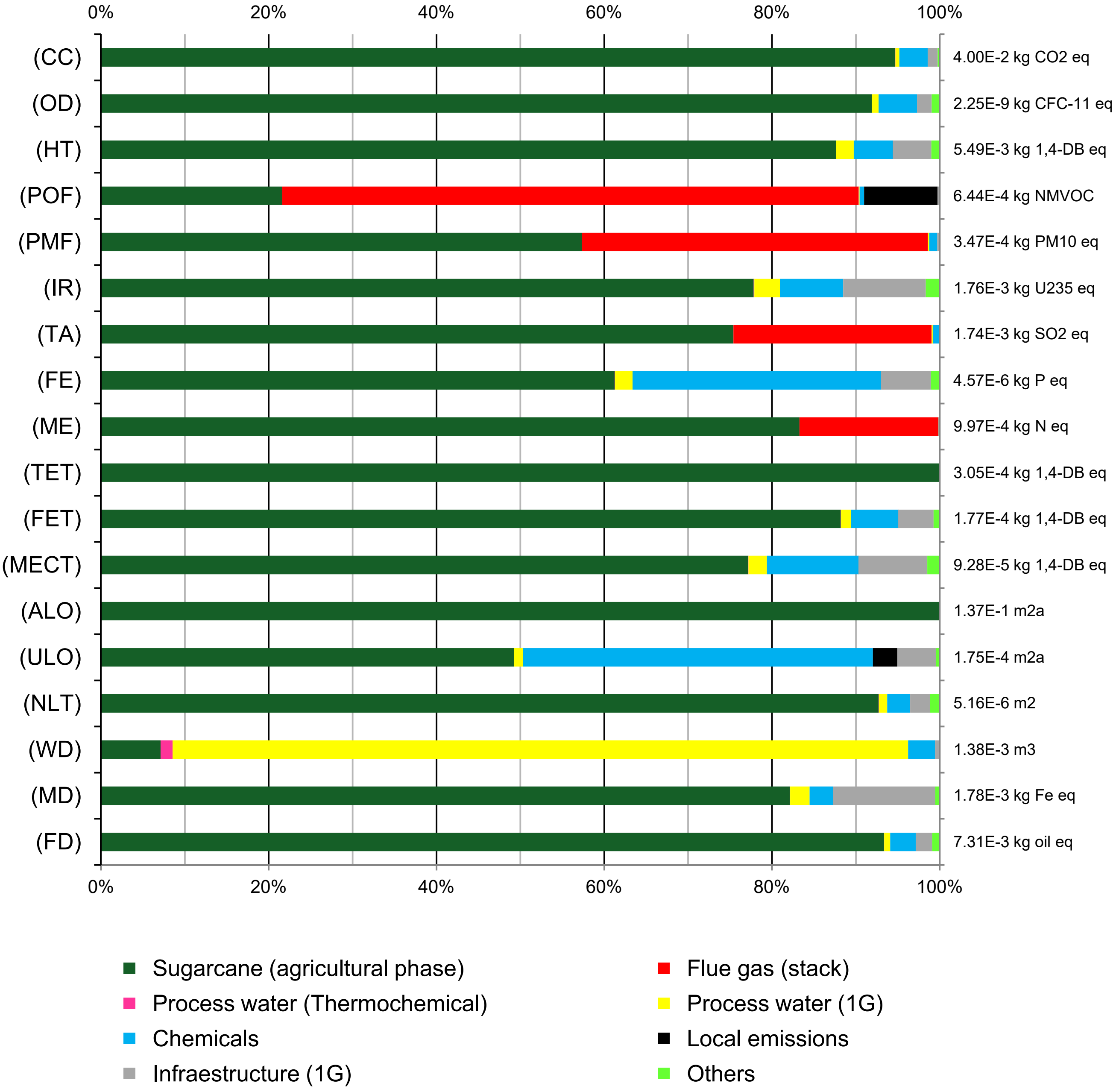

Figure B19 - Characterized impact indicators for electricity generation (kWh) by 1G sugarcane biorefinery with CHP/EBPST (SC7) system. Method: World ReCiPe (H) midpoint.

APPENDIX C - Publication proposals (to be submitted)

Contents

Process simulation and evaluation of different cogeneration system configurations to Combined Heat and power (CHP) generation at a Brazilian first generation sugarcane biorefinery

Bagasse and straw can be used as feedstock for bio-based products by chemical, biochemical or thermochemical conversion routes. The amount of surplus biomass available for use depends on the energetic efficiency of the biorefinery. The combined heat and power (CHP) generation (Rankine-cycle cogeneration system) from sugarcane bagasse and straw is used to supply steam and electricity to the first generation (1G) sugarcane biorefinery, making it self-sufficient in energy terms by solid-fuel fired low-pressure boiler (low efficiency). The different configurations of commercial cogeneration systems currently used in the Brazilian 1G sugarcane biorefinery scenario were evaluated for supply thermal and electric energy to the plant while producing electricity outputs and/or surplus sugarcane bagasse and straw. Results are analyzed front of new technologically competitive scenarios for biomass conversion to power and/or biofuels and discuss about the application in integrated future 1G sugarcane biorefinery scenarios with thermochemical routes or with biochemical routes. In this study is considered a two million tonnes of processed cane on-season by optimized 1G (1G) sugarcane biorefinery with annexed ethanol distillery with/without electricity export to the electric power grid. The simulation in steady state of the biorefineries scenarios were carried out using Aspen Plus®v8.4 (AspenTech, USA) process simulation platform to calculate mass and energy balances for CHP applying condensing-extraction steam turbine (CEST) system with integral use of available lignocellulosic biomass (bagasse and straw) and for CHP applying extraction back-pressure steam turbine (EBPST) system with partial use of available bagasse (surplus bagasse and straw). 13 biorefinery scenarios based on bagasse and straw available as raw feedstock has been carried out at different operating conditions (22 bar and 320ºC; 45 bar and 450ºC; 65 bar and 480ºC; 85 bar and 520ºC; 90 bar and 530ºC; 96 bar and 530ºC; 120 bar and 530ºC) of the cogeneration systems. The increases in the operating parameters (pressure and temperature) and cogeneration cycle efficiency resulted increases of electrical energy generation for the electric power grid and a reduction of the rate of water circulating in the system. The best 1G sugarcane biorefinery scenario for surplus bagasse is the scenario with lower operational parameters (EBPST at 22 bar and 320°C) and the best 1G sugarcane biorefinery scenario for electricity generation is the scenario with EBPST operating at 90 bar and 530°C.

Keywords: Aspen Plus® simulation. Atmospheric CFB gasifier. Bagasse. Combined heat and power generation. Straw. Sugarcane biorefinery. Surplus biomass.

Process simulation and evaluation of Biomass integrated directly-heated gasifier and Internal Combustion Engine in Combined-cycle (BIG-ICE/CC) route integrated at a Brazilian first generation sugarcane biorefinery

Biomass integrated directly-heated gasifier and Internal Combustion Engine in Combined-cycle (BIG-ICE/CC) route integrated at a first generation (1G) sugarcane biorefinery are evaluated for electricity generation and the results are compared with the combined heat and power generation (CHP) applying condensing-extraction steam turbine (CEST) system in a 1G sugarcane biorefinery and with the biomass integrated directly-heated gasifier with gas turbine in combined-cycle (BIG-GT/CC) integrated at a 1G sugarcane biorefinery. In this study is considered a two million tonnes of processed cane on-season by optimized 1G sugarcane biorefinery with annexed ethanol distillery with integral use of available biomass. The simulation in steady state of the thermochemical-biorefineries scenarios were carried out using Aspen Plus®v8.4 (AspenTech, USA) process simulation platform aiming evaluating electricity generation while supply the thermal and electric energy need to the thermochemical-biorefinery, applying the gasification of biomass by using air and steam agents in an atmospheric circulating fluidized bed (CFB) directly-heated gasifier. The low-medium LHV synthesis gas and its potential use for electricity generation was evaluating in a single-fueled (SG) internal combustion engine (ICE) with turbo charging system. This engine works according to lean-burn four-stroke Otto-cycle spark-ignited (SI) gas engine operating in combined-cycle (CC) mode with steam turbine (ST) system (Rankine-cycle cogeneration system). Two thermochemical-biorefinery scenarios based on bagasse and straw as raw feedstock available to thermochemical route was evaluated considers the energy integration (thermal and electrical) possibilities between BIG-ICE/CC and 1G technologies. Results for the BIG-ICE/CC technology integrated at a 1G sugarcane biorefinery do not have showed an attractive potential to be applied for a large-scale electrical energy production. The steam production in the heat recovery steam generator (HRSG) system is limited and not has the potential to meet the demands of the thermochemical-biorefinery, still dependent on your traditional CHP system (boiler) or in a complementary steam generation system. The increase in electricity output is not so great when compared to a high-pressure efficient Rankine-cycle cogeneration system, and significantly lower when compared to a similar scenario applying the BIG-GT/CC technologies.

Keywords: Aspen Plus® simulation. Atmospheric CFB gasifier. Bagasse. BIG-ICE/CC. Combined heat and power generation. Directly-heated gasification. Straw. Sugarcane biorefinery. Surplus electricity

Process simulation and evaluation of Biomass Integrated direct-heated Gasification and Gas Turbine in Combined-cycle (BIG-GT/CC) route integrated at a Brazilian first generation sugarcane biorefinery

Biomass Integrated direct-heated Gasification and Gas Turbine in Combined-cycle (BIG-GT/CC) route for electricity generation is an attractive alternative for efficient energy (heat and power) production from integral use of available lignocellulosic biomass (bagasse and straw) in a first generation (1G) sugarcane biorefinery. The BIG-GT/CC technology integrated at a 1G sugarcane biorefinery are evaluated for electricity generation and the results are compared with the combined heat and power generation (CHP) applying condensing-extraction steam turbine (CEST) system at a 1G sugarcane biorefinery and with the biomass integrated directly-heated gasifier and internal combustion engine in combined-cycle (BIG-ICE/CC) integrated at a 1G sugarcane biorefinery. In this study is considered a two million tonnes of processed cane on-season by optimized 1G sugarcane biorefinery with annexed ethanol distillery with integral use of available biomass. The simulation in steady state of the thermochemical-biorefineries scenarios were carried out using Aspen Plus®v8.4 (AspenTech, USA) process simulation platform aiming evaluating electricity generation while supply the thermal and electric energy need to the thermochemical-biorefinery, applying the gasification of biomass by using air and steam agents in an atmospheric circulating fluidized bed (CFB) directly-heated gasifier. The low-medium LHV synthesis gas and its potential use for power generation was evaluating in a high-performance advanced class evaporative (humidification tower) gas turbine (EvGT) air cooled blades. The gas turbine cycle has dual combustion chamber (reheated), heat recovery intercooler/after-cooler and exhaust-gas heat recovery system (recuperator), operating in combined-cycle (CC) mode with steam turbine (ST) system (Rankine-cycle cogeneration system). Five thermochemical-biorefinery scenarios based on bagasse and straw as raw feedstock available to thermochemical route was evaluated considers the energy integration (thermal and electrical) possibilities between BIG-GT/CC and 1G technologies and the implementations of pre-combustion (upstream) co-capture of CO_2 and H_2S using MEA solution (co-capture system). Results demonstrate for the integrated biorefinery scenarios an electricity generation capacity range from 135 to 180 MW_e to the electric power grid depending on the configuration of the thermochemical-biorefinery, taking into account the energetic integration. The steam production in the heat recovery steam generator (HRSG) system is able to meet the steam requirements of the biorefinery.

Keywords: Aspen Plus® simulation. Atmospheric CFB gasifier. Bagasse. BIG-GT/CC. Combined heat and power generation. Directly-heated gasification. Straw. Sugarcane biorefinery. Surplus electricity.

Process simulation and evaluation of Biomass integrated directly-heated gasifier and Low-pressure Methanol catalytic-synthesis (Biomass-to-Methanol) integrated at a Brazilian first generation sugarcane biorefinery

Methanol is an important primary chemical commodity in the world as a largest chemical synthesis feedstock and an optional liquid fuel (grade AA), traditionally produced in large scale from natural gas (methane reforming process). The methanol production by thermochemical conversion route of biomass as feedstock (Biomass-to-Methanol) can decentralize and improve the methanol production by using local and renewable resources, as well reduce the environmental impacts and the fossil resources dependence. The first generation (1G) sugarcane biorefinery integrated scenarios with the biomass to methanol technology are evaluated and compared with the literature results for the methanol production from natural gas. In this study is considered a two million tonnes of processed cane on-season by optimized 1G sugarcane biorefinery with annexed ethanol distillery with integral use of available biomass. The simulation in steady state of the thermochemical-biorefineries scenarios were carried out using Aspen Plus®v8.4 (AspenTech, USA) process simulation platform aiming evaluating methanol production while supply the thermal and electrical energy need to the thermochemical-biorefinery, applying the gasification of biomass by using oxygen (from ASU) and steam agents in an atmospheric circulating fluidized bed (CFB) directly-heated gasifier. The low-medium LHV synthesis gas is cleaned in a wet system and compressed, an fraction of this gas is direct destined together with tail-gas to supply heat and power to the thermochemical-biorefinery in a high-performance advanced class evaporative-class gas turbine (EvGT) in combined-cycle (CC) mode with steam turbine (ST), and other fraction is destined to the high-temperature and low-temperature (two stages) water-gas-shift (WGS) system to adjust the hydrogen to carbon ratio to higher yields in the methanol synthesis. For increase the methanol yield and avoid the catalytic deactivation, CO_2 is removed in the pressurized co-capture of CO_2 and H_2S system using a methyl-diethanolamine (MDEA) and piperazine (PZ) solution. The cleaned and conditioned synthesis gas is compressed to 50 bar and converted to methanol in the gas-cooled fixed bed synthesis reactor combined in series with an isothermal water-cooled fixed bed synthesis reactor (two stages) with loop recycle system of unconverted synthesis gas. These reactors are simulated applying Langmuir-Hinschelwood-Hougen-Watson kinetic (LLHW) model for $CuO/ZnO/Al_2O_3$ high active methanol catalyst in plug-flow reactors (PFR). Pressure swing absorption (PSA) system recovery the hydrogen present in the tail-gas, which is recycled to low-pressure methanol catalytic-synthesis reactors. After cooling and separation of the tail-gas, the crude methanol is purified in an energy-saving four-column triple-effect methanol distillation system for grade AA methanol. Three thermochemical-biorefinery scenarios based on bagasse and straw as raw feedstocks available to thermochemical route were evaluated considers the possibilities of energy integration (thermal and electrical) between Biomass-to-Methanol and 1G technologies.

Keywords: Aspen Plus® simulation. Atmospheric CFB gasifier. Bagasse. Biomass-to-Methanol. Cryogenic air separation unit. Directly-heated gasification. Low-pressure methanol catalytic-synthesis. Methanol. Straw. Sugarcane biorefinery.

Process simulation and evaluation of Biomass integrated directly-heated gasifier and mixed alcohols catalyst-synthesis (Biomass-to-Mixed alcohols) integrated at a Brazilian first generation sugarcane biorefinery

The second generation ethanol (E2G) from sugarcane bagasse and straw can be produced a competitive way by biochemical conversion route or by thermochemical conversion routes. The first generation (1G) sugarcane biorefinery integrated scenarios with the biomass to thermochemical mixed alcohols technology are evaluated and compared with the results obtained for the 1G ethanol technology, for biomass to biochemical ethanol technology and for the thermochemical biomass to mixed alcohols technology. In this study is considered a two million tonnes of processed cane on-season by optimized 1G sugarcane biorefinery with annexed ethanol distillery with integral use of available biomass. The simulation in steady state of the thermochemical-biorefineries scenarios were carried out using Aspen Plus®v8.4 (AspenTech, USA) process simulation platform aiming evaluating the mixed alcohols production while supply the thermal and electrical energy needs to the thermochemical-biorefinery, applying the gasification of biomass by using oxygen (from ASU) and steam agents in an atmospheric circulating fluidized bed (CFB) direc-gasifier. The low-medium LHV synthesis gas is cleaned in a wet system and compressed, an fraction of this gas is direct destined together with the tail-gas to supply heat and power to the thermochemical-biorefinery in a high-performance advanced class evaporative-class gas turbine (EvGT) in combined-cycle (CC) mode with steam turbine (ST), and other fraction is destined to the high-temperature and low-temperature (two stages) water-gas-shift (WGS) system to adjust the hydrogen to carbon ratio to higher yields in the mixed alcohols catalyst-synthesis. For increase the alcohol yield and avoid the catalytic deactivation, CO_2 is removed in the pressurized co-capture of CO_2 and H_2S system using a methyl-diethanolamine (MDEA) and piperazine (PZ) solution. The cleaned and conditioned synthesis gas is compressed to 87 bar and converted to higher mixed alcohols in the isothermal water-cooled fixed bed synthesis reactor with loop recycle system for unconverted synthesis gas and distillated methanol. These reactors are simulated applying Langmuir-Hinschelwood-Hougen-Watson kinetic (LLHW) model in plug-flow reactor (PFR) for $KCoMoS_2/C$ catalyst in stoichiometric reactor (RStoic). After cooling and separation of the tail-gas, the mixed alcohols are purified in an three-column double-effect alcohols distillation system (ethanol purification) and molecular sieve dehydration unit (MSDU). The bottom of the second distillation column contain a mixture of high alcohols (propanol, 1-butanol and pentanol), can be used as fuels blend-stock or purified for chemical use, in the top of the third distillation column pure methanol is recovered and recycled to mixed alcohols catalytic-synthesis reactor to increase the ethanol production and in the bottom of the third distillation column is separated anhydrous ethanol. Three thermochemical-biorefinery scenarios based on bagasse and straw as raw feedstocks available to thermochemical route were evaluated considers the possibilities of energy integration (thermal and electrical) between Biomass-to-Methanol and 1G technologies.

Keywords: Aspen Plus® simulation. Atmospheric CFB gasifier. Bagasse. Biomass-to-Mixed alcohols. Cryogenic air separation unit. Directly-heated gasification. Ethanol. mixed alcohols catalyst-synthesis. Straw. Sugarcane biorefinery.

Environmental Life Cycle Assessment (LCA) of electricity generation by advanced cogeneration systems integrated at a Brazilian first generation sugarcane biorefineries

Different advanced cogeneration systems integrated at sugarcane biorefineries are evaluated regarding its environmental impacts. The objective is to evaluate and compare the environmental impacts of electricity generation to the electric power grid while supplying thermal and electrical energy to the pant from the integral use of available biomass (bagasse and straw). Environmental impacts assessment is based on the Life Cycle Assessment (LCA) methodology (ISO14040:2006 and ISO14044:2006) under the scope of the Virtual Sugarcane Biorefinery (VSB) tool (CTBE, Brazil) computational simulation platform and performed using the World midpoint ReCiPe model in SimaPro®7.3.3 (PRé Consultants B.V., Netherlands) software with an economic allocation approach for evaluate the life cycle inventory (LCI) obtained from CanaSoft (CTBE, Brazil) spreadsheet models and mass and energy balances obtained from Aspen Plus®v8.4 (AspenTech, USA) process simulation platform. Biorefinery scenarios based on the integral use of biomass available for electricity generation by thermochemical routes evaluated are: combined heat and power (CHP) generation applying the condensing-extraction steam turbine (CEST) systems; biomass integrated directly-heated gasifier and internal combustion engine in combined-cycle (BIG-ICE/CC) systems; and the biomass integrated directly-heated gasifier and gas turbine in combined-cycle (BIG-GT/CC) systems. These thermochemical technologies were selected because they are commonly discussed alternatives for improving electricity efficiency in thermo electric units. Results indicate that more advanced cogeneration alternatives are able to reduce environmental impacts of the process because more electricity is produced per unit of sugarcane processed.

Keywords: Advanced cogenerations systems. Bagasse. Electricity. Environmental impacts. Life cycle assessment. Straw. SimaPro® software. Straw. Sugarcane biorefinery.

Environmental Life Cycle Assessment (LCA) of methanol and ethanol production by biomass-to-liquid biofuels thermochemical routes integrated at a Brazilian first generation sugarcane biorefineries

Biomass to methanol production and biomass to ethanol (and other mixed alcohols) production from sugarcane bagasse and straw by directly-heated gasification integrated at a first generation (1G) sugarcane biorefinery are evaluated regarding its environmental impacts. The objective is to evaluate and compare the environmental impacts of methanol and ethanol productions in the thermochemical-biorefineries. Environmental impacts assessment is based on the Life Cycle Assessment (LCA) methodology (ISO14040:2006 and ISO14044:2006) under the scope of the Virtual Sugarcane Biorefinery (VSB) tool (CTBE, Brazil) computational simulation platform and performed using the World midpoint ReCiPe model in SimaPro®7.3.3 (PRé Consultants B.V., Netherlands) software with an economic allocation approach for evaluate the life cycle inventory (LCI) obtained from CanaSoft (CTBE, Brazil) spreadsheet models and mass and energy balances obtained from Aspen Plus®v8.4 (AspenTech, USA) simulation platform. Thermochemical-biorefinery scenarios based on the integral use of biomass available for bio-based products by gasification of biomass by using oxygen and steam agents in an atmospheric circulating fluidized bed (CFB) directly-heated gasifier with further chemical catalytic conversion of synthesis gas to methanol by low-pressure methanol catalytic-synthesis and chemical catalytic conversion of synthesis gas to ethanol and other mixed alcohols by mixed alcohols catalyst-synthesis. These thermochemical technologies were selected because they are commonly discussed alternatives for improving the portfolio of products considering in a biorefinery context. Environmental impacts of methanol production by thermochemical conversion route of biomass were compared to the fossil conversion route (natural gas). Environmental impacts of ethanol production by thermochemical conversion route of biomass were compared to the conventional 1G ethanol production and with the second generation ethanol production by biochemical route. Results indicate that thermochemical conversion alternatives are able to reduce environmental impacts of methanol in comparison to the fossil alternatives and of ethanol production in comparison to the fossil equivalent product (gasoline) and renewable alternatives (biochemical route) in some environmental impacts categories.

Keywords: Bagasse. Biomass-to-Methanol. Biomass-to-Mixed alcohols. Environmental impacts. Ethanol. Life cycle assessment. Methanol. SimaPro® software. Straw. Sugarcane biorefinery. Thermochemical conversion routes.

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Comparative technical, economic and environmental assessment of biomass-to-ethanol conversion technologies: biochemical and thermochemical routes integrated at a first generation sugarcane biorefinery

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Second-generation ethanol production from sugarcane bagasse and straw can be produced competitively by biochemical or thermochemical conversion routes in biorefineries. Considering biomass-to-ethanol technologies, this work aims to compare technical, economic, and environmental aspects of biochemical and thermochemical routes. The biochemical route considered is by steam explosion pre-treatment followed by enzymatic hydrolysis and fermentation process to ethanol production of the surplus biomass available. The thermochemical conversion route considered is by integrated directly-heated gasification and mixed alcohols catalytic-synthesis process with gas turbine in combined-cycle to supply the plant energy demand. Both routes are considered integrated in an optimized annexed first generation (1G) sugarcane biorefinery with production of sugar and anhydrous ethanol. Mass and energy balances obtained from computer simulation developed in Aspen Plus®v8.4 platform provide information for the technical, economic, and environmental assessment of each technological route. Economic evaluation impacts are determined using traditional financial metrics (e.g. internal rate of return, net present value, and products production costs). Environmental assessment is carried out using the Life Cycle Assessment methodology to calculate impact categories (e.g. acidification, climate changes, depletion of abiotic resources, ecotoxicity, eutrophication, human toxicity, land use, ozone layer depletion, and photochemical oxidation). Results shows that besides the different mix of products obtained in each conversion route, booth routes present good economic and environmental impacts in comparison to the fossil alternatives. This assessment provides a comparative and critical analysis of the biomass-to-ethanol conversion technologies and elucidates critical points to be better assessed in future studies.

Keywords: Bagasse. Biochemical conversion route. Biomass-to-ethanol. Economic assessment. Environmental assessment. Straw. Sugarcane biorefinery. Technical assessment. Thermochemical conversion routes.