UNIVERSIDADE ESTADUAL DE CAMPINAS
Faculdade de Engenharia Mecânica

JORGE VINÍCIUS DA SILVA NETO

Prospective Study on Production and Use of Biogas from Vinasse: Technological, Energetic and GHG Emissions Aspects

Estudo Prospectivo da Produção e Uso de Biogás de Vinhaça: Aspectos Tecnológicos, Energéticos e de Emissões de GEE

CAMPINAS
2020

JORGE VINÍCIUS DA SILVA NETO

Prospective Study on Production and Use of Biogas from Vinasse: Technological, Energetic and GHG Emissions Aspects

Estudo Prospectivo da Produção e Uso de Biogás de Vinhaça: Aspectos Tecnológicos, Energéticos e de Emissões de GEE

Thesis presented to the School of Mechanical Engineering of the University of Campinas in partial fulfillment of the requirements for the degree of Doctor in Energy Systems Planning.

Tese apresentada à Faculdade de Engenharia Mecânica da Universidade Estadual de Campinas como parte dos requisitos exigidos para a obtenção do título de Doutor em Planejamento de Sistemas Energéticos

Orientador: Prof. Dr. WALDYR LUIZ RIBEIRO GALLO
Coorientador: Prof. Dr. ÉDSON APARECIDO ABDUL NOUR

ESTE EXEMPLAR CORRESPONDE À VERSÃO FINAL DA TESE DEFENDIDA PELO ALUNO JORGE VINÍCIUS DA SILVA NETO, E ORIENTADA PELO PROF. DR. WALDYR LUIZ RIBEIRO GALLO.

....

ASSINATURA DO ORIENTADOR

CAMPINAS
2020

Ficha catalográfica
Universidade Estadual de Campinas
Biblioteca da Área de Engenharia e Arquitetura
Rose Meire da Silva - CRB 8/5974

Si38p

Silva Neto, Jorge Vinicius, 1967-
Prospective study on production and use of biogas from vinasse: technological, energetic and GHG emissions aspects / Jorge Vinicius da Silva Neto. – Campinas, SP : [s.n.], 2020.

Orientador: Waldyr Luiz Ribeiro Gallo.
Coorientador: Edson Aparecido Abdul Nour.
Tese (doutorado) – Universidade Estadual de Campinas, Faculdade de Engenharia Mecânica.

1. Vinhaça. 2. Biogás. 3. Digestão anaeróbia. 4. Cana-de-açúcar - Biomassa. 5. Sulfeto de hidrogênio. I. Gallo, Waldyr Luiz Ribeiro, 1954-. II. Nour, Edson Aparecido Abdul, 1961-. III. Universidade Estadual de Campinas. Faculdade de Engenharia Mecânica. IV. Título.

Informações para Biblioteca Digital

Título em outro idioma: Estudo prospectivo da produção e uso do biogás de vinhaça: aspectos tecnológicos, energéticos e de emissões de GEE
Palavras-chave em inglês:
Vinasse
Biogas
Anaerobic digestion
Sugarcane - Biomass
Hydrogen sulfide
Área de concentração: Planejamento de Sistemas Energéticos
Titulação: Doutor em Planejamento de Sistemas Energéticos
Banca examinadora:
Waldyr Luiz Ribeiro Gallo [Orientador]
Suani Teixeira Coelho
Antonio Maria Francisco Luiz José Bonomi
Telma Teixeira Franco
Joaquim Eugênio Abel Seabra
Data de defesa: 03-07-2020
Programa de Pós-Graduação: Planejamento de Sistemas Energéticos

Identificação e informações acadêmicas do(a) aluno(a)
- ORCID do autor: https://orcid.org/0000-0002-2194-9309
- Currículo Lattes do autor: http://lattes.cnpq.br/5552706126624641

UNIVERSIDADE ESTADUAL DE CAMPINAS
FACULDADE DE ENGENHARIA MECÂNICA

TESE DE DOUTORADO

Prospective Study on Production and Use of Biogas from Vinasse: Technological, Energetic and GHG Emissions Aspects

Estudo Prospectivo da Produção e Uso de Biogás de Vinhaça: Aspectos Tecnológicos, Energéticos e de Emissões de GEE

Autor: Jorge Vinícius da Silva Neto

Orientador: Prof. Dr. Waldyr Luiz Ribeiro Gallo
Coorientador: Prof. Dr. Édson Aparecido Abdul Nour

A Banca Examinadora composta pelos membros abaixo aprovou esta Tese:

Prof. Dr. Waldyr Luiz Ribeiro Gallo, Presidente
Faculdade de Engenharia Mecânica – UNICAMP

Prof^a. Dr^a. Suani Teixeira Coelho
Programa de Pós-graduação em Energia – Instituto de Energia e Ambiente/USP

Prof. Dr. Antonio Maria Francisco Luiz José Bonomi
Laboratório Nacional de Biorrenováveis – LNBR

Prof^a. Dr^a. Telma Teixeira Franco
Faculdade de Engenharia Química – UNICAMP

Prof. Dr. Joaquim Eugenio Abel Seabra
Faculdade de Engenharia Mecânica – UNICAMP

A Ata da defesa com as respectivas assinaturas dos membros encontra-se no processo de vida acadêmica do aluno.

Campinas, 03 de julho de 2020.

Dedication

To my son, Luis

Acknowledgements

I would like to thank Dr. Jose Tomaz Vieira Pereira, who helped me getting back on the academic track. Many thanks also to my advisors, Dr. Waldyr Luiz Ribeiro Gallo and Dr. Edson Aparecido Abdul Nour, for their patience and insights. Special thanks to Dr. Marcelo Elauiy who helped me a lot in putting thousands of numbers and dozens of ideas into one single paper.

I would like to express my gratitude to all professors, researchers and colleagues at UNICAMP's Energy Systems Planning Program (PSE) and Interdisciplinary Center for Energy Planning (NIPE), who helped me "connecting the dots" of the energy as a whole. I guess here I could extend this acknowledgment to all professors I had and to the Campinas State University.

Many tanks to many people in the biogas, energy and sugarcane industries. So many people that I'm afraid to forget mentioning someone and be unfair, so, to all of you, biogas people, thanks for the opportunity of learning and discussing ideas, concepts and concrete projects to promote this energy source. Still trying to be fair, I should nominally mention Mr. Thorkil Dahlgreen and Mr. Peter Thygesen from Biogasclean, who support me since the early concept of the Ester Biogas Project, thank you.

Resumo

Este trabalho foca na produção de biogás a partir da vinhaça (subproduto derivado da destilação de etanol) no contexto brasileiro, com os objetivos de: apresentar um modelo matemático da digestão anaeróbica da vinhaça mais preciso; avaliar os balanços de gases de efeito estufa e de energia do etanol quando biogás da vinhaça é produzido e usado; e avaliar os benefícios do biogás da vinhaça quando utilizado como substituto ao óleo fóssil e gás natural como fonte de energia. São apresentados conceitos de digestão anaeróbica e revisão de tecnologias para produzir, dessulfurizar e purificar o biogás, com foco à vinhaça como substrato e ao H_2S, contaminante encontrado em grandes quantidades no biogás da vinhaça. Apresenta-se um modelo matemático da digestão anaeróbica que inclui o H_2S no biogás, além do CH_4 e do CO_2, e calcula a eficiência dos reatores com base na retenção da biomassa anaeróbica. O modelo foi calibrado e validado com dados de um reator de grande escala processando vinhaça. Diferentes cenários foram simulados avaliando vazão de biogás, teor de metano e desempenho com e sem decantador, além do teor de H_2S. O modelo mostrou alta precisão para o teor de CH_4 e média precisão para o teor H_2S. O reator otimizado foi capaz de produzir 83% mais metano por volume de reator com metade do tempo de retenção. Nas destilarias, balanços energéticos (EB) e emissões de gases de efeito estufa evitadas (GHGEA) do etanol foram recalculados incluindo o biogás da vinhaça para avaliar seus benefícios. O biogás da vinhaça foi considerado produzindo eletricidade ou biometano. Os resultados mostram que o biogás da vinhaça pode representar melhorias nos indicadores, variando de melhora de 3,5% no EB na geração de eletricidade à melhora de 27,5% na GHGEA pela substituição do diesel nas operações da usina. Também, o potencial do biogás de vinhaça para geração elétrica é examinado e comparado a termelétricas a óleo fóssil em termos de energia, custos e emissões de gases de efeito estufa no Brasil, sugerindo um programa para substituir usinas a óleo por usinas de biogás com benefícios econômicos e ambientais. A possibilidade de uso do biometano da vinhaça em substituição ao gás natural no Estado de São Paulo foi também avaliada, apresentando um programa de incentivo ao biometano que poderia promover reduções de emissões. Por fim, é avaliada a relação do biogás com o etanol em termos de suprimento de energia nos próximos anos, mostrando que energia adicional substancial pode ser obtida e quantidades ainda maiores de combustíveis fósseis poderiam ser substituídas.

Palavras Chave:

Vinhaça de Cana-de-Açúcar, Biogás, ADM1, Redução de Sulfato, H_2S, Biometano, Substituição de Diesel, Energia Renovável

Abstract

This work focusses on biogas production from vinasse (by-product derived from ethanol distillation) with objectives of: presenting a more accurate mathematical model of anaerobic digestion of vinasse; assessing greenhouse gases and energy balances of ethanol when vinasse biogas is produced and used; and assessing the benefits of vinasse biogas used as a substitute for fossil oil and natural gas as energy source. A mathematical model of the anaerobic digestion that includes, besides methane and carbon dioxide, the hydrogen sulfide content on biogas and calculates reactors efficiency based on anaerobic biomass retention is presented. The model was calibrated and validated against data from a large-scale anaerobic reactor processing sugarcane vinasse. Comparative scenarios and set-ups were simulated to investigate the reactor's performance. Biogas flow, methane content, and yield with and without a settler were evaluated. Quality of predictions was assessed, showing high accuracy for CH_4 predictions and medium accuracy for H_2S and biogas flow predictions. The optimised modelled reactor was able to produce 83% more methane per volume of reactor with half the retention time. Within the distilleries, the Energy Balance (EB) and Greenhouse Gases Emissions Avoided (GHGEA) of sugarcane ethanol were calculated, including the vinasse biogas, to assess potential benefits. Biogas from vinasse was considered producing electricity or biomethane. Results show that biogas from vinasse can represent improvement in both indicators, which ranges from 3.5% improvement in EB by electricity generation with biogas to 27.5% improvement in GHGEA by replacing diesel in the mill operations. After, the use of vinasse biogas for power generation is examined and compared with fossil oil power plants in terms of energy, costs and greenhouse gas emissions in Brazil, suggesting a program to replace expensive oil power plants by biogas plants with expressive benefits in all aspects. Also, the possibility of using vinasse biomethane to replace natural gas in São Paulo State is evaluated, presenting an incentive program to this new source of energy that could promote considerable emissions reductions. Furthermore, the relation of biogas to ethanol in terms of energy supply in the next years is evaluated, showing that substantial additional energy can be obtained, and larger amounts of fossil fuels can thus be replaced.

Key Words:
Sugarcane Vinasse, Biogas, ADM1, Sulfate Reduction, H_2S, Biomethane, Diesel Replacement, Renewable Energy

List of Figures

List of Tables

List of Abbreviations and Acronyms

AD	Anaerobic Digestion
ADM1	Anaerobic Digestion Model no. 1
ACP	Anaerobic Contact Process
ANEEL	Brazilian Electricity Agency - Agência Nacional de Energia Elétrica
ANP	National Agency of Oil, Natural Gas and Biofuels - Agência Nacional de Petróleo, Gás Natural e Biocombustíveis
BBL	Barrel
BI	Billion - 10^9
Biomethane	Biogas purified to achieve ANP’s 8/2015 Resolution specifications
CAPEX	Capital Expenditure
CBIO	Decarbonization credits created by Renovabio, equivalent to one metric ton of carbon dioxide equivalent emissions avoided
CCEE	Chamber of Electric Energy Commercialization
CETESB	Environmental Agency of São Paulo State - Companhia Ambiental de São Paulo
CI	Carbon Intensity of fuels
CIGAR	Covered In-Ground Anaerobic Reactor
CO_{2e}	Carbon Dioxide Equivalent
COD	Chemical Oxygen Demand
CSTR	Continuous Stirred Tank Reactor
CTC	Sugarcane Technology Center - Centro de Tecnologia Canavieira
EPE	Energy Research Office - Empresa de Pesquisa Energética
ESR	Energy Substitution Ratio
FAO	Food and Agriculture Organization of The United Nations
GHG	Greenhouse Gases
GJ	Giga Joules - 10^9 Joules
GW	Giga Watts - 10^9 Watts
HDPE	High Density Polyethylene
HHV	Higher Heating Value
HRT	Hydraulic Retention Time
HSC	Half Saturation Constant
IEA	International Energy Agency
IPCC	Intergovernmental Panel for Climate Change
IPT	Instituto de Pesquisas Tecnológicas - Technological Research Institute
IWA	International Water Association
LCA	Life Cycle Analysis
LHV	Lower Heating Value
m^3/d	cubic meters per day
MAPA	Ministry of Agriculture, Cattle and Supplying
MCF	Methane Conversion Factor
MI	Million – 10^6
MJ	Mega Joule – 10^6 Joules
MMBTU	Million BTUs
MME	Ministry of Mines and Energy
MSUR	Maximum Substrate Uptake Rate
NG	Natural Gas
NGL	Liquefied Natural Gas
ONS	National Electrical System Operator - Operador Nacional do Sistema Elétrico
OPEX	Operational Expenditure

ORL	Organic Loading Rate
Proálcool	National Alcohol Program
Renovabio	National Biofuels Policy Act
SIN	National Interconnected Electrical System - Sistema Interligado Nacional
SRB	Sulfate Reducing Bacteria
SRT	Solids Retention Time
SV	Sugarcane Vinasse
t	Metric ton; equivalent to 1,000kg
TC	Ton of Sugarcane
tCO_{2e}	One metric ton of carbon dioxide equivalent
TAN	Total ammonia nitrogen
ThOD	Theoretical Oxygen Demand
TKN	Total Kjeldahl nitrogen
TS	Total Solids
TSS	Total Suspended Solids
TVS	Total Volatile Solids
TOE	Ton of Oil Equivalent
UASB	Upflow Anaerobic Sludge Blanket
UNICA	Brazilian Sugarcane Industry Association
VBG	Vinasse Biogas: Biogas obtained from anaerobic digestion of vinasse
VBM	Vinasse Biomethane: Biomethane produced from vinasse biogas
VFA	Volatile Fatty Acids
VSS	Volatile Suspended Solids
VUC	Variable Unitary Cost

Table of Contents

1 Introduction

1.1 Brief historical panorama of Energy

Energy consumption by humanity has increased dramatically in the past few centuries and maintains a relevant growth trajectory in current times (Figure 1-1). Most of the energy utilized in global scale is originated from fossils fuels and its usage has resulted in the increase of greenhouse gases concentration in the atmosphere, leading to global warming and climate change.

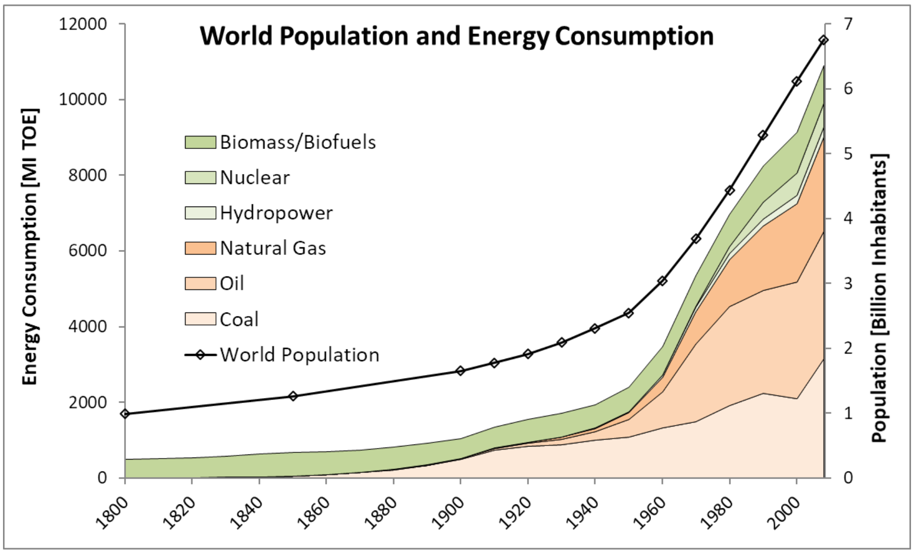


Figure 1-1: World energy consumption (SMIL, 2010); world population (GOLDEWIJK, 2005).

1.2 Brief world panorama of energy and electricity

Currently, the world’s primary energy supply is mostly fossil, with coal, oil and natural gas accounting for 81% of the 13,761 million TOE offered in 2016 (IEA, 2018).

The outlook in countries such as China, regarding the supply of fossil energy, is even more intense, with 89% of energy supply from fossil, 63% originated from coal, as shown in Figure 1-2. Brazil has 43.2% of its energy supply from renewable sources (EPE, 2018a).

Worldwide, 73% of electricity is generated from fossil sources, coal corresponding to 44.5% and natural gas corresponding to 23.8% of energy generation (IEA, 2018). In Brazil 80.4% of electricity is generated through renewable sources, of which 65.2% hydroelectric sources, 8.2% biomass originated and 6.8% from wind (EPE, 2018a).

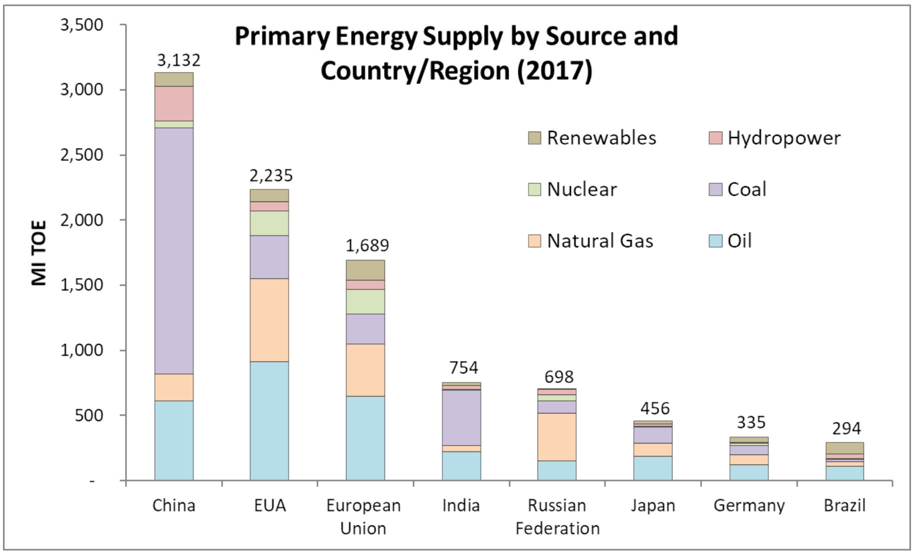


Figure 1-2: Primary energy supply by source and country/region. Source: (BP, 2018; EPE, 2018a)

1.3 Recent Energy Evolution in Brazil

The domestic energy supply in Brazil in 2017 was 294 MI TOE, 56.8% of which corresponded to non-renewable sources and 43.2% to renewable sources. Oil and its products accounted for 36.2% of total internal supply, the country's main source, followed by sugarcane products, natural gas, and hydropower with 17.4%, 12.9% and 11.9% of the total internal supply respectively. ONS (National Electrical System Operator) Energy Operation Plan for 2018/2022 recognizes that the increase of electricity generated by solar and wind sources and the reduction of hydroelectric reserve capacity in the Brazilian electrical system, associated with recurrent unfavourable climatic conditions, lead to an increased dispatch of high cost fossil power plants (ONS, 2018). Most fossil power plants in Brazil use fuel oil, diesel and natural gas as fuel and are mainly demanded when the country's rainfall regime is unfavourable, which occurred frequently in the last five years, especially 2014 and 2015 (CCEE, 2018).

1.4 The history and role of sugarcane in Brazil's energy

A significant share of the energy produced and consumed in Brazil comes from sugarcane products, mainly ethanol and bagasse.

Throughout Brazilian history, sugarcane went through several periods of strength followed by slowdowns caused by internal and external factors, with the sugar as its main product until recently. In 1931 President Getúlio Vargas' Decree number 19717 determines the mixture of 5% ethanol in imported gasoline, starting this fuel's trajectory in Brazil (BRASIL, 1931). In 1975, triggered by rise in international oil prices, the National Alcohol Program (Proálcool) is created to meet the needs of the domestic and foreign automotive fuel market and the Brazilian sugarcane industry enters a period of substantial increase in production and productivity. Ethanol production grew from 600 million litres in 1975 to 3.4 billion litres in 1979, with the expansion of existing distilleries at the sugar mills and the construction of 180 autonomous distilleries (GORDINHO, 2010; VIEIRA; LIMA; BRAGA, 2007).

The 2000s mark the beginning of a period of substantial increase in the perception of relevance by society and governments of environmental sustainability, climate issues and the consequences of GHG emissions. This period also marks the beginning of a new cycle of rising in international oil prices.

In 2003, flex-fuel technology emerged, allowing the indistinct use of gasoline or ethanol mainly in light vehicles, leading to a substantial increase in ethanol consumption. Between 2002 and 2010 hydrous ethanol consumption increased from 5.6 billion litres to 19 billion litres, an increase of 240% in the period. Between 2005 and 2009 more than 100 new sugarcane mills and distilleries are inaugurated (PINTO, 2011).

The sugar-energy[1] industry represents today one of the largest businesses in the national economy. There are currently approximately 360 mills in operation (MAPA, 2019), having reached its highest number in 2010/2011, when there were approximately 430 mills in operation.

In the 2017/2018 season, 641 million tons of sugarcane were processed, harvested on 10.1 million hectares. Total production was 38.6 million tons of sugar, 16.5 billion litres of hydrous ethanol and 11.4 billion litres of anhydrous ethanol. In 2017, 21.4 TWh of electricity produced in sugar-energy units were exported to national interconnected grid (SIN) (EPE, 2018a; UNICA, 2019a).

1.5 Vinasse biogas and its benefits

The vinasse, by-product originated in the distillation stage of ethanol production, is generated in volume usually more than ten times greater than the ethanol itself, contains polluting potential twenty times greater than domestic effluent and can be used for biogas production through the anaerobic digestion process.

---

[1] “Sugar-energy” is a free translation of the neologism “Sucroenergético”, term created to reflect the fact that from sugarcane much more than sugar is produced, but also relevant quantities of energy as fuel (ethanol and bagasse) and electricity. Vinasse biogas makes this term even more meaningful.

Biogas generated by anaerobic digestion of vinasse is a source of energy with considerable potential, obtained without increasing the sugarcane planted area, without competition with food and has versatile usage.

After biogas' impurities removal, such as H_2S (a particularly important contaminant in the case of vinasse biogas), electricity can be produced by burning it in the existing boilers at the mills or in biogas burning Otto cycle generator sets. From biogas, through its purification, by CO_2, other contaminants and moisture removal, a renewable substitute of natural gas can be obtained, called biomethane, and whose origin and specifications have already been regulated by ANP.

Vinasse biomethane can be injected into the natural gas pipe network, directly replacing this fossil fuel. It can also be used as fuel in diesel cycle vehicles and other equipment provided with systems called "Dual-Fuel", which allow the partial replacement of diesel oil by gas (natural gas or biomethane), a particularly attractive possibility if these vehicles and equipment integrate the operations of the plant where vinasse biogas was obtained.

Vinasse biomethane could also replace gasoline, and even ethanol itself, as light vehicles Otto cycle fuel, although vehicles must be adapted for its use and distribution of the biomethane may be challenging. The latter is an interesting approach, since by producing additional renewable fuel from the same sugarcane biomass, the expansion of sugarcane plantation area and the high costs associated with this expansion can be reduced.

In any case, producing renewable electricity or fuel, vinasse biogas can reduce the carbon footprint and improve the energy balance of all sugarcane products (sugar, ethanol, bagasse, electricity) because of the better usage of sugarcane biomass.

Although the vinasse biogas will be seasonally produced, during the sugarcane crop season it will be a firm, non-intermittent source of energy, differently from solar or wind energy, and will be produced during the low rainfall period of the year for most hydropower plants in the country, helping to save water in their reservoirs and avoiding the dispatch of fossil power plants.

Vinasse biogas projects would be built close to the distilleries which are, by their turn, mostly close to high energy demand more populated areas, although still in the countryside, bringing the benefits of distributed electricity generation. Vinasse biomethane is the analogue of the distributed generation for natural gas.

The operation of vinasse biogas projects should create new jobs and demand more skilled people compared to usual rural opportunities. Also, during construction, they will demand engineering, equipment, services, and materials, mostly local supplied, thus the vinasse biogas products will be largely decoupled from foreign currencies exchange rates and international oil prices.

The current more frequent use of vinasse is its application in the crop field, a process called fertirrigation, as a way of recycling potassium and other nutrients contained in the vinasse, but this process would not be compromised by the production of vinasse biogas.

Summarizing, the production of biogas/biomethane from sugarcane ethanol vinasse can bring many benefits:

- Reduction of Greenhouse Gas (GHG) emissions by replacing natural gas, diesel or by generating renewable electricity.
- Improvement of energy and GHG balances of sugar and ethanol obtained from sugarcane.
- Generation of new source of income to the mills and potential reduction of the operation costs by the substitution of diesel oil.
- Better use of sugarcane biomass and consequent increase in productivity of the entire sugarcane chain.
- Decreased demand for sugarcane planting area from its better energy use.
- Technological and infrastructure development in interior locations of the country.
- Increased biofuel production in the country and decreased consumption and importation of fossil fuels.

1.6 Barriers to development

Biogas from vinasse presents some challenges for its production and commercialization: 1) vinasse is very acidic and biogas production only occurs when pH is close to neutrality; 2) vinasse contains a large amounts of sulfur compounds introduced in the production processes of the mills (sulfate used for yeast treatment, and sulfite used for sugar colour removal) that generates hydrogen sulfide, which impairs the methane production, may be inhibitory to bacteria and archaea and is a toxic and corrosive gas that should have its content substantially reduced for energetic use of biogas; and 3) its production is seasonal, following the production of ethanol itself, and its storage is not in principle practical or economic, which brings economic, financial and commercial impacts to its use.

Although several academic studies and some commercial and demonstration scale projects for the production and use of vinasse biogas have already been undertaken, this practice has not been widely adopted in Brazil. There are also other barriers among which we highlight the perceived technology risk and the lack of public policies that would allow the wide insertion of vinasse biogas in the Brazilian energy matrix.

1.7 Justification for the work

The still existing lack of technological knowledge (or the lack of transfer of this knowledge from academia to industry), together with perceived risks of vinasse biogas projects justifies the development of this work, which aims to increase the assertiveness in the evaluation of potential production of biogas in quantity and quality terms, which, by its turn, may help in closing some of the technological gaps of such projects.

The under evaluated benefits of vinasse biogas for the existing ethanol industry, as well the benefits of vinasse biogas replacing fossil fuels, such as diesel and heavy oil in power generation, or diesel, mainly used in transport sector, or even replacing natural gas (through a blend with purified biogas), is also a relevant justification for this work.

A better evaluation of the potential of the above-mentioned replacements as well as discussions of incentive schemes for wide adoption of vinasse biogas as energy source reinforces the justification of this work.

In essence, the size of the potential biogas/biomethane market from sugarcane ethanol vinasse and its energetic relevance - compared to that obtained from ethanol and electricity from sugarcane bagasse, or to other energy sources - fossil or otherwise, besides the benefits presented in the previous section summarizes the justification of the present work.

1.8 Objectives

1.8.1 Overall Objective

The general objective of this work is to contribute to close some of the knowledge gaps of the production and use of vinasse biogas: by increasing the accuracy of the prediction of its production in quantitative and qualitative terms; by assessing the benefits of vinasse biogas production and use for the ethanol produced in terms of greenhouse gases and energy balances and; by assessing the benefits of vinasse biogas used as a substitute for fossil oil in power generation and natural gas, in addition to incentive schemes that could promote its adoption on a large scale.

1.8.2 Specific objectives

The overall objective of this work is divided in specific objectives, addressed in different chapters/sections, and include the following topics:

- Presentation and description of technologies used for biogas production, desulfurization and purification considering the specificities of its production from vinasse,
- Present a novel, improved mathematical model of anaerobic digestion to calculate the quantity and quality of biogas (including H_2S), calibrated and validated with operational data of a commercial scale biogas production project using vinasse as substrate,
- Present an original study about improvement on energy and greenhouse gases balances of the ethanol produced in plants using vinasse biogas as a source of electricity or biomethane production, the later injected into the natural gas network or replacing diesel oil used in its agricultural operations,
- Evaluation of economic and environmental benefits associated with the use of vinasse biogas in replacement of fossil oil and natural gas and proposition of mechanisms and incentives for the wide adoption of vinasse biogas in different scenarios and markets.

1.9 Methodological Aspects

In order to achieve this work’s overall and specific objectives, it was constructed based on a methodology that consists of a first section with a technological review of methods and process for production and use of biogas from vinasse, which give the basis of vinasse to energy projects. This review is them followed by three articles, which are interrelated and focused on different aspects of vinasse biogas production and use. The first article looks after technological aspects of vinasse anaerobic digestion, the second evaluates the energetic and environmental benefits of vinasse biogas on the ethanol from where it was originated and the third looks at benefits of vinasse biogas on the Brazilian energy sector in a wider scope.

The technological review consists of a survey of the technologies, process and methods used in the production of vinasse biogas and its decontamination and purification for energetic use, considering the efficiencies of these technologies, their demands for inputs and energy, among other aspects. This information was obtained through bibliographic survey, consultations with specialized suppliers and designers and data collected in pilot project operation.

After this technological review, a first article looks after the vinasse anaerobic digestion in technological terms, showing actual operational data of a commercial scale plant, a mathematical model for vinasse anaerobic digestion and possible improvements of this type of project, based on technologies suitable for projects in Brazilian conditions. The model presented on the article was calibrated with data from the above-mentioned commercial scale plant operation and calculates the quantity and composition of vinasse biogas, including H_2S, which serves also as optimization tool. This chapter has its own methodology, results and discussion detailed therein. This chapter also has additional information, in the form of supplemental material, for those not familiar with mathematical models of anaerobic digestion.

In the next chapter, also in the form of an article, an original study presents the positive energy and environmental effects of vinasse biogas when allocated on the ethanol from where it was originated. There, the potential of vinasse biogas and its use for electricity or biomethane production, the latter injected into the grid or used as a substitute for diesel oil in plant’s operations, are evaluated and the vinasse biogas effects on ethanol’s energy and GHG balances are calculated for each case in different scenarios. As the previous article, this chapter also has its methodology, results and discussion accordingly detailed.

Finally, a third article presents possible vinasse biogas effects in a boarder sense in the Brazilian energy matrix, showing market opportunities for vinasse biogas replacing fossil fuels, by electricity or biomethane production, are evaluated and incentive mechanisms are suggested for the large adoption of this source of energy. This chapter also has its methodology, results and discussion detailed along its course of development.

1.10 Work Structure

This thesis is structured as follows:

- Chapter 1 presents introduction, rationale, objectives, methodological notes, and this work structure.
- Chapter 2 discusses anaerobic digestion, introducing the principles of the process of transforming organic matter into biogas with particular focus on vinasse as a substrate and deals with the technologies designed for desulfurization and purification of vinasse biogas. This chapter also presents vinasse as substrate for biogas production and projects in Brazil.
- Chapter 3 is a transcription of article published by the journal “Water Science and Technology” in December 2019, where a mathematical model of anaerobic digestion of vinasse including the H_2S production and decoupling the solids retention time from the hydraulic retention time is presented. This chapter has supplemental material that presents

the basic concepts of the mathematical modelling of biogas production and its application in anaerobic digestion of vinasse, which is presented on Appendix 1.

- Chapter 4 is a transcription of article published by the journal "Environmental Progress & Sustainable Energy" in April 2019, which presents projections of energy and greenhouse gas balances of ethanol obtained from distilleries using vinasse biogas.
- Chapter 5 is a transcription of the article accepted by the journal "Sustainable & Renewable Energy Reviews" in August 2020, which shows programs and mechanisms for accelerating the introduction of vinasse biogas, used for electric generation and biomethane production, the impacts of this source of energy in terms of fossil fuels replacement and greenhouse gases emissions and regulatory issues involving the subject.
- Chapter 6 presents the conclusion of the work and suggestions of future developments in the subject of anaerobic digestion of vinasse.

2 Biogas and Anaerobic Digestion

Biogas is the name given to a gas mixture produced during the decomposition of organic matter in the absence of oxygen. This gas mixture is mainly formed of methane (CH_4) and carbon dioxide (CO_2) and may contain other substances, depending on the composition of the material that originated the gas (called substrate) and operating conditions, such as hydrogen sulfide (H_2S), found in significant concentrations in vinasse biogas.

The degradation of organic matter in the absence of oxygen and the consequent generation of biogas is a naturally occurring process, without the need for human intervention, provided that there are adequate environmental conditions and sufficient time for the microorganisms responsible for the process to develop and takes place in swamps, marine sediments, soil and digestive tract of ruminants (CHERNICHARO, 2007a). The generation and release of methane to the atmosphere, however, introduces a disturbance in the carbon cycle, as this compound, once released into the atmosphere, cannot be utilized directly in the plants' photosynthetic metabolism of carbon fixation, it must be degraded, mainly by reaction with hydroxyl in the troposphere and while its degradation is not complete, until it is transformed into CO_2, methane will significantly contribute for global warming (ALVALÁ; KIRCHHOFF; PAVÃO, 1995; MAHONY, 2002).

Anaerobic digestion is the process in which organic matter is decomposed by a bacteria and archaea pool in the absence of oxygen. This process is largely utilized in anaerobic phases of wastewater treatment plants, aiming at reducing the pollutant load of domestic, industrial and agro-industrial effluents and also occurs when solid waste - urban, agricultural and sewage sludge - is disposed in landfills or waste treatment plants that utilize anaerobic processes.

As a result of the degradation process of organic matter contained in effluents and waste, besides the reduction of its pollution load, there is the formation of biogas, which is frequently seen simply as a disposable by-product, even though it is a fuel of significant value and can be used in the production of thermal, electrical or mechanical energy. The methane and carbon dioxide content in biogas are also dependent on the substrate and process of production, varying roughly from 55 to 70% of CH_4 and 45 to 30% of CO_2, besides contaminants. Given its high content of methane, it is a good quality fuel for a variety of applications and may be purified to suit more demanding uses.

Recently, the anaerobic digestion process has been used to obtain biofuels, where instead of using other industries' by-products as substrate for the process, biomass is produced dedicated and specifically for methane production in projects specifically designed for this purpose.

Table 2-1 below shows the typical characteristics of biogas obtained from different sources.

Table 2-1: Biogas composition from different sources.

Biogas				
Parameter	Domestic Wastewater treatment plant $^{(1)}$	Agroindustry Residues & Products$^{(1)}$	Landfill$^{(1)}$	Vinasse Biogas$^{(2)}$
CH_4 (% volume)	65-75%	45-75%	45-55%	55-64.5%
CO_2 (% volume)	20-35%	25-55%	25-30%	34-43%
N_2 (% volume)	3-4%	0-5%	10-25%	N/A
O_2 (% volume)	0.5%	0-2%	1-5%	N/A
H_2 (% volume)	Trace	0.5%	0	N/A
H_2S (ppm_v)	<8,000	10,000-30,000	<8,000	17,500-30,000
NH_3 (mg/m^3)	Trace	0,01-2,50	Trace	N/A
Siloxanes (mg/m^3)	<0.1-5.0	Trace	<0.1-5.0	N/A
Humidity	Saturated	Saturated	<100%	Saturated
LHV (kWh/Nm^3)	6.5-7.5	4.5-7.5	4.5-5.5	5.5-6.0

(1) (DEUBLEIN; STEINHAUSER, 2011); (2) (BARRERA et al., 2015; CORTES PIRES et al., 2015; LEME; SEABRA, 2017; NANDY; SHASTRY; KAUL, 2002; YASAR et al., 2015); N/A: Not Available

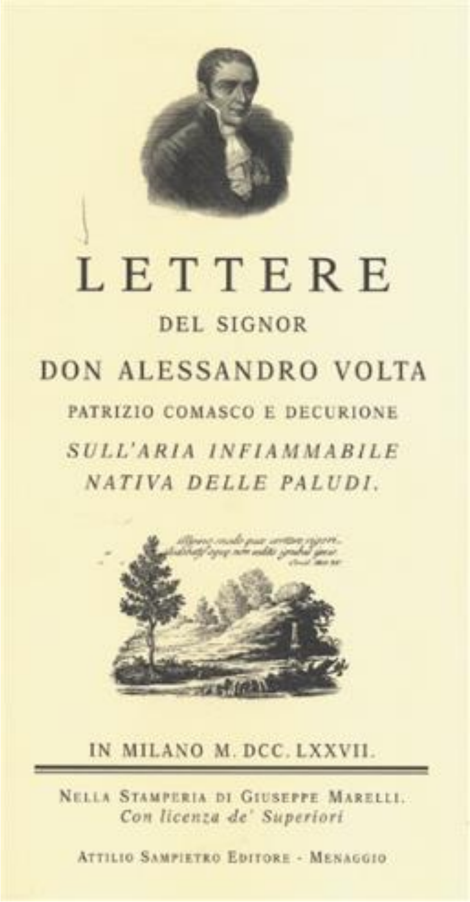
2.1 Historical Development

In a letter attached to Joseph Priestley's work “Experiments and observations on different kinds of air”, Benjamin Franklin describes the observation, made in 1764, of flames spreading through a river surface and declares such effect could be recreated by revolving a lake muddy soil with a stick, from which gas bubbles would rise to the water surface and, in the presence of a lit candle, a strong and sudden flame would be created (PRIESTLEY, 1775).

In 1776 Alessandro Volta, having had access to Priestley's works, collected samples of gas released by Maggiore Lake's bed and, after analysing them, concludes this gas, which he called "inflammable marsh air", had distinct characteristics of the "inflammable air" described by Henry Cavendish (hydrogen - obtained from the reaction of acid with metal), such as different flame colour and speed and different atmospheric air proportion to form an inflammable mixture (ABBASI; TAUSEEF; ABBASI, 2011; TOMORY, 2009). Volta was the first to recognize that "inflammable air" formation was resulting of the conversion of organic matter contained in lakes and rivers' sediments (KHANAL, 2008). Figure 2-1 bellow shows Volta's work cover, in which he relates the "inflammable marsh air".

Faraday also did experiments with swamp gases, concluding there were hydrocarbons in its composition. In the beginning of the 1800s, John Dalton, Willian Henry and Humphrey

Davy worked independently on the description of methane's chemical structure, which was finally elucidate by Avogadro in 1821 (ABBASI; TAUSEEF; ABBASI, 2011; DEUBLEIN; STEINHAUSER, 2011).



LETTERE
DEL SIGNOR
DON ALESSANDRO VOLTA
PATRIZIO COMASCO E DECURIONE
SULL'ARIA INFIAMMABILE
NATIVA DELLE PALUDI.

IN MILANO M. DCC. LXXVII.

NELLA STAMPERIA DI GIUSEPPE MARELLI.
Con licenza de' Superiori

ATTILIO SAMPIETRO EDITORE - MENAGGIO

Figure 2-1: Cover of Italian edition of 1777 Volta's work "Lettere sull'aria infiammabile nativa delle paludi"

The anaerobic digestion process started being systematically studied on the second half of the 19th century, in France, initially aiming to supress the unpleasant odour exhaled by wastewater lagoons. At that time, researches detected the presence of microorganisms, today known as responsible for the anaerobic digestion process (DEUBLEIN; STEINHAUSER, 2011).

The first record of an anaerobic system was made at around 1860, alike to a sceptic tank, used in wastewater treatment in the city of Vesoul, France, called "Mouras' Automatic Scavenger" (KHANAL, 2008). In 1884 Louis Pasteur produced 100 litres of methane from 1m³ of horse manure and come to the conclusion that this source could supply Paris' lighting needs at the time (DEUBLEIN; STEINHAUSER, 2011). In 1895, the city of Exeter - England is equipped with a domestic effluent treatment system designed by Donald Cameron, which harnessed biogas for lighting and heating of the site itself (KHANAL, 2008).

In 1897, in Matunga, India, biogas generated in wastewater disposal tanks of a leper colony was collected and directed to feed internal combustion engines (ABBASI; TAUSEEF; ABBASI, 2011). In 1923 the first sale of biogas took place, to the gas public service in Germany, by that time biogas was already used for heating and electricity generation. Also in Germany, by 1930, biogas was compressed in steel cylinders and used as vehicle fuel (MCCARTY, 2001).

In the 1940s and 1950s the anaerobic digestion of agricultural residues and industrial wastewater investigations began by Imhoff (who since 1906 had been building effluent treatment systems and is inventor of the so-called “Imhoff Tank”) in Germany and Buswell in the United States (MCCARTY, 2001)

There are reports from late 1940s of biogas obtained from sewage sludge digestion being used to drive air blowers and pumps through dual-fuel (diesel-gas) engines in wastewater treatment plants in New York, USA (BOEHM, 1947; GOULD, 1947).

In the 1950s the importance of bacterial biomass retention is acknowledged, allowing smaller and more efficient systems. Also in this decade methane-forming bacteria are detected. In the 1970s the concept of the Up-flow Anaerobic Sludge Blanket (UASB) reactor emerged, which guides the subsequent evolution of anaerobic wastewater treatment systems (MCCARTY, 2001).

2.2 Anaerobic Digestion – Principles of the process

Anaerobic digestion is a biological process of converting complex molecules into the simplest substances containing carbon, CO_2 e CH_4, which occurs in the absence of oxygen and in the presence of microorganisms (bacteria and archaea) in a sequence of steps. In addition to methane and carbon dioxide, there is the production of microorganisms, and, depending on the substrate composition and operating conditions, hydrogen sulfide, nitrogen, hydrogen, and other gases in smaller quantities are also produced. Gaseous components have low solubility in water and biomass can be removed from the liquid phase by settling, thus polluting compounds are converted into products that can be removed from the effluent, making it less harmful to nature. In context of this work, the main interest in the anaerobic digestion process lies in the fact that the gas generated is combustible and less in the fact that the effluent has its polluting potential minimized.

Much of the energy contained in the original substrate components is transformed into biogas and a small portion is transformed into new biomass[2]. At the same time, the energy demand for the process to occur is quite low, and many (often all) of the nutrients needed for the transformation are already present in the substrate, so by simply promoting environmental conditions and contact between the biomass of microorganisms and substrate, the anaerobic process shall occur.

The anaerobic digestion process is mediated by a complex, spontaneous arrangement of many different microorganism families (bacteria and archaea), that co-inhabit the digesters and chain the whole process. One microorganism's metabolism product is substrate for the microorganism of a subsequent step and the physicochemical effect produced by the metabolism of some microorganism is essential for the metabolism of other families of microorganisms.

2.2.1 The anaerobic digestion process stages

The anaerobic digestion process stages are:

2.2.1.1 Hydrolysis

The first step of the process is the solubilization of particulate compounds through hydrolysis. Complex proteins, fats and carbohydrates molecules are converted respectively to amino acids, long chain fatty acids and glycerine and sugars (mono and disaccharides) through exoenzymes produced by hydrolytic bacteria. The original components are converted into simpler molecules that can cross the cell membrane of the microorganisms responsible for subsequent steps, thus continuing the process. Depending on the type of substrate, hydrolysis may be limiting step of the whole anaerobic digestion process and distinct groups of hydrolytic bacteria will occur in greater or lesser amount depending on the quality of the substrate (CHERNICHARO, 2007a; SEADI et al., 2008).

---

[2] This is an important counterpoint to the aerobic effluent treatment process, which requires large amounts of oxygen, only achieved through the use of high energy consumption equipment (aerators, compressors, etc.). A second highlight in the comparison is that aerobic systems produce only CO_2, and therefore has no energy value. Lastly, it is noted that in aerobic systems much of the substrate is converted into new microbiological biomass, which must be removed from the effluent liquid phase and discarded, usually to landfills. These aspects stand as the main advantages of anaerobic systems over aerobic systems.

2.2.1.2 Acidogenesis

In this step, amino acids, fatty acids, and sugars are converted to simpler compounds in a fermentative process within the bacteria cells. Intermediate molecules are produced, such as short chain organic acids (acetic, butyric, propionic), alcohols, ketones, carbon dioxide and hydrogen, and will take part in subsequent process steps: they are substrates for acetogenic and methanogenic bacteria. Most acidogenic bacteria are mandatory anaerobic, but some facultative species consume any free oxygen available, avoiding toxicity to methanogenic archaea.

2.2.1.3 Acetogenesis

At this stage, the compounds produced by acidogenic bacteria are converted into products that will be assimilated by methanogenic archaea: CO_2, H_2 and acetic acid. Organic acids are converted to acetic acid. Reactions mediated by acetogens bacteria produce hydrogen and acetic acid, but these reactions are thermodynamically unfavourable under standard conditions. These reactions would not occur unless hydrogenotrophic and acetotrophic methanogenic archaea, which, by consuming hydrogen and acetate, create environment conditions for reactions mediated by acetogenic bacteria to take place.

2.2.1.4 Methanogenesis

There are two groups of strict anaerobic archaea, the acetoclastic methanogens and the hydrogenotrophic methanogens. The first group produces methane and carbon dioxide from acetate and the second group produces methane and water from carbon dioxide and hydrogen, all substrates resulting from the steps described above. Approximately 70% of methane is produced by the first group and 30% by the second, although the second group’s hydrogen consumption is what makes acetogenesis possible, without which the whole process would not occur. Among acetoclastic, two distinct families stand out: metanosarcina, which are not restrict acetoclastic, they can metabolize hydrogen, methanol and methylamines, and have lower affinity for acetate than methanosaeta, but higher growth rate; and methanosaeta that only consume acetate, having higher affinity to it and slower growth rate than methanosarina.

In addition to the steps already described, in the case of biogas obtained from sulfate rich substrates, such as vinasse, there is an additional and parallel step of great importance, sulfidogenesis.

2.2.1.5 Sulfidogenesis

In this stage, bacteria called sulfate reducing bacteria (SRB), reduce sulfate or sulfite to sulfide, using hydrogen, propionate and acetate, among other substrates, thus competing for the same substrates as methane forming archaea. Sulfate-reducing bacteria operate the disassimilative reduction of sulfur, where sulfate ion acts as an oxidizing agent for the metabolism of organic matter (such as oxygen in respiration), and much of sulfate sulfur is excreted as H_2S (CHERNICHARO, 2007a; RIZZO; LEITE, 2004).

Figure 2-2 below depicts schematically the anaerobic digestion process.

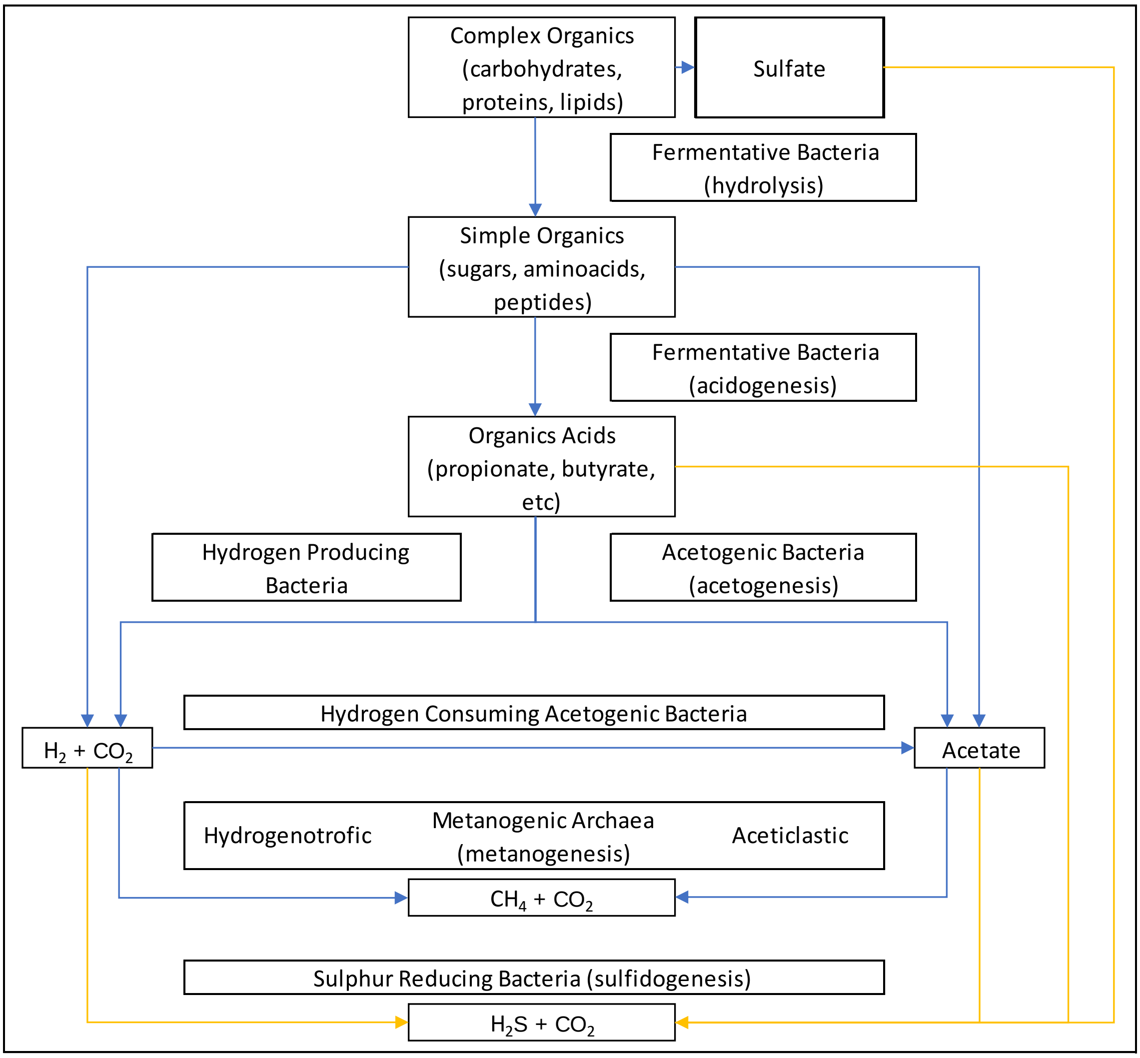


Figure 2-2: Diagram of metabolic routes of anaerobic digestion. Source: adapted from (CHERNICHARO, 2007a)

Sulfidogenesis has harmful consequences for the biogas energy utilization: by reducing part of the methane production potential, since a portion of the substrate for methane production is consumed in the reduction of sulfate; by the generation of hydrogen sulfide itself, which has low solubility in the liquid medium is incorporated into biogas and must be subsequently treated for the biogas energetic use; and the fact that H_2S generated in its non-ionized form may inhibit the biological activity of several species involved in anaerobic digestion (BARRERA et al., 2013; CIRNE et al., 2008; FEDOROVICH; LENS; KALYUZHNYI, 2003).

Theoretically, one of the negative aspects of sulfidogeneis, the consumption of methane precursors by sulfate reducers, can be minimized. Rizzo & Leite (2004) describe the existence of acetate-producing sulfate-reducing bacteria (e.g. Desulfovibrio and Desulfotomaculum) and acetate-consuming species (e.g. Desulfobacter), and indicate that the growth rate of the former (doubling time at 30°C around 3 to 6 hours) may be much higher than the last one (with doubling time around 20 hours). The authors stress that acetate-producing sulfate reducers usually occur in environments with low sulfate concentrations (RIZZO; LEITE, 2004). Although CO_2 is formed in the metabolism of acetate-producing sulfate reducers, the carbon potentially available for further methane production is not fully converted to CO_2, which may in principle lessen part of the damage caused in methane production (KHANAL, 2008).

2.2.2 Operating Conditions

In a reactor operated under stable conditions, the production and consumption rates of each of the products of the different families of microorganisms described above are in equilibrium, so that no intermediate product accumulates (AQUINO; CHERNICHARO, 2005). For this entire sequence of reactions to occur, several conditions must be kept simultaneously within reactors.

2.2.2.1 Temperature

It affects the speed of the microorganisms’ metabolism (therefore reactions’ speed), the substrate and products’ solubility and the ionic equilibrium conditions.

There are three temperature ranges for the operation of microbial consortia: psychrophilic, mesophilic and thermophilic. The performance of the process is quite different in each of these ranges. In each temperature range there are minimum and maximum values and an optimum operating range (CHERNICHARO, 2007a).

For mesophilic systems, the optimum operating temperature range is 35ºC to 40ºC and for thermophilic systems the optimum range is 50ºC to 55ºC (KHANAL, 2008). Exceeding the optimum working temperature for a given range results in a sharp drop of microorganism growth rate and methane production.

Although the rate of metabolism of the microorganisms in the thermophilic range is between 25 and 50% higher than the performance obtained in the mesophilic range (which allows the design of smaller reactors) (KHANAL, 2008), the use of biogas to heat reactors to increase the temperature range from mesophilic to thermophilic limits the availability of biogas itself to produce electricity or biomethane and should be carefully evaluated to achieve positive results. The net yield of thermophilic microorganisms is lower than in the mesophilic ones, which implies longer starting times and make them more susceptible to substrate (in load and quality terms) variations (KHANAL, 2008).

Chernicharo (2007) states that perhaps more important than working at a temperature close to the maximum of a chosen range, in which the growth rate of microorganisms is maximum, is maintaining the temperature as constant as possible, avoiding sudden variations.

Figure 2-3 displays the relation between temperature and anaerobic biomass growth rate. Most anaerobic reactors currently operate in the mesophilic temperature range (CHERNICHARO, 2007a; KHANAL, 2008).

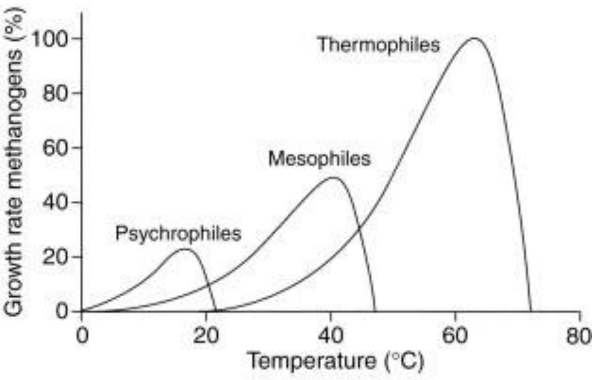


Figure 2-3: Growth rate of methanogenic archaea as a function of temperature. Source: (KHANAL, 2008).

2.2.2.2 pH and Alkalinity

The pH of the environment where anaerobic digestion occurs is of fundamental importance in the process. This parameter directly interferes in reactor's operating conditions, affecting enzyme activity and indirectly, affecting the toxicity of compounds present in reactors (CHERNICHARO, 2007a).

The optimal pH for the combined culture of acidogenic bacteria and methanogenic archaea is in the range of 6.8-7.4 (KHANAL, 2008); however acidogenic bacteria are less sensitive to low pH than archaea, which can be severely inhibited at pH lower than 6.0 (CHERNICHARO, 2007a).

The determination of pH inside the reactor is strongly dependent on the existence of substances that form buffer solutions, the most important being CO_2 and the organic acids produced in the process itself. The dissociation of CO_2 in aqueous medium forms bicarbonate, whose equilibrium occurs at pH 6.3; organic acids have their dissociation equilibrium in the pH range of 4.5. These solutions have the ability to change their balance in the presence of other acids or bases, imposing resistance to pH change. They are of fundamental importance for maintaining the pH in anaerobic reactors, especially the CO_2-bicarbonate pair, whose equilibrium is in the pH range of reactor's operation.

Alkalinity is the term used to indicate the buffering capacity of an acidic solution (SPANJERS, 2011) and is the parameter used for evaluating the buffering capacity of anaerobic systems. It is essential to compensate the acidity arising from the formation of organic acids during anaerobic digestion process, especially when the production of acids exceeds the metabolism capacity of methanogenic archaea, avoiding sudden changes in the systems' pH (MONTEGGIA; LADEMIR; LUCA, 1985).

The continuous production of organic acids by bacteria initially consumes the system's alkalinity, while acetic acid is not consumed by archaea, but under increased load or at low pH levels, archaea activity may be insufficient for the consumption of acetogenesis products, resulting in accumulation of acids and, further, drop in pH, often leading to reactor collapse, a process called acidification or souring (CHERNICHARO, 2007a).

The imbalance between acid production by acetogens bacteria and their consumption by methanogenic archaea initially causes the accumulation of acetate and hydrogen, which in turn thermodynamically limits the processing of longer chain organic acids, such as propionic and butyric by acetogenic bacteria, resulting in their accumulation as well (AQUINO; CHERNICHARO, 2005).

Maintaining pH within acceptable limits within a reactor, in addition to the carbonic acid - bicarbonate system, is often mediated by the production of alkalinity inherent to other reactions: degradation of protein-containing compounds produces ammonia which generates alkalinity in the reactor; reducing sulfate to sulfide produces the same effect (KHANAL, 2008) and the consumption of acetic acid by archaea during methane production also generates alkalinity (VAN HAANDEL; VAN DER LUBBE, 2012).

Sugar degradation, however, does not produce alkalinity to the system. In the specific case of vinasses, part of the acidity of the substrate is due to the presence of sulfate and partly to the presence of organic acids. Both will produce alkalinity when metabolized by methane producing and sulfate reducing microorganisms within the reactors.

The system's pH also changes the quality of the biogas. At lower pH, more CO_2 is unionized and can therefore diffuse into the gas phase of the system, increasing the CO_2 content in biogas (DEUBLEIN; STEINHAUSER, 2011). H_2S suffers the same effect. At the same time, pH levels lower than recommended increases the presence of non-ionized forms of organic acids and hydrogen sulfide, which are inhibitors of microorganisms' metabolism (VAN LIER; MAHMOUD; ZEEMAN, 2008).

The operation of anaerobic reactors is often monitored by the relationship between alkalinity (often called ALK) and the amount of volatile fatty acids (VFA) in the system, and it is almost universally accepted that the ratio in the 0.3 range is indicative of a healthy reactor, although methane production with much higher alkalinity /VFA ratios is possible.

2.2.2.3 Nutrients

For the perfect functioning of the anaerobic digestion process it is necessary to produce and maintain microorganism's biomass, which in their synthesis consume nutrients such as nitrogen, phosphorus, potassium, and numerous other micronutrients.

Knowing that part of the organic matter contained in the effluent will be transformed into biogas and part of it into biomass and knowing that there is a certain proportion in the biomass of various elements (C, N, P, K, etc.), one can estimate the need for nutrients for biomass production. Adopting the typical composition of bacteria and archaea involved in anaerobic digestion of approximately 12 to 10% N and 2% P and assuming a substrate composed of volatile organic acids, and assuming also biomass with a growth rate of 0.02 to 0.05 grams of cell mass per gram of substrate, the N and P requirement should be 1,000mg COD/L to 5mg N/L to 1mg P/L, nutrient supplementation should not be required. This ratio may be quite different depending on the substrate, for example if the substrate is formed of carbohydrates not yet acidified, which would require biomass composed of acidogenic bacteria with higher substrate utilization rate for their own growth (0.15gSSV/gCOD), there should be a relation 350COD:5N:1P in the wastewater (CHERNICHARO, 2007a; SPANJERS, 2011).

Many of the agro-industrial substrates contain the required amounts of nitrogen and phosphorus. Adopting the data presented by Elia Neto et al., (2009), the vinasse has a ratio between 220 and 80 COD:N and between 11 and 3.4N:P, very close to what Spranjers (2011) recommends. Ribas, (2006) presents values varying from 50:1 and 100:1 COD:N. Potassium, sulfur, calcium and magnesium are other nutrients necessary for anaerobic biomass formation.

Micronutrients: In addition to the so-called macronutrients (NPK), some micronutrients are required for the anaerobic digestion process, being fundamental for the growth and metabolism of the reactor flora, although some of them may be toxic at high concentrations. Cobalt and nickel, for example, are present in bacterial and archaeal enzymes. Other elements such as iron, molybdenum, zinc, manganese and copper are also found in the anaerobic biomass elemental composition (SPANJERS, 2011).

2.2.3 Toxicity

Several compounds contained in substrates, or produced during the anaerobic digestion process, may, under some conditions, cause inhibition of methane or intermediates production due to toxicity. Many of the toxicity scenarios are dependent on a systems' pH, which makes this operational parameter even more important. H_2S, organic acids, ammonia in their undissociated forms are compounds that can be toxic, depending on their concentration, and their existence in the nonionized form is pH dependent.

The case of organic acids is noteworthy because the increase in their concentration lowers the pH, which is itself detrimental to archaeal metabolism, while at the same time allows for their existence in nonionized form. For example, at pH 5 a concentration of 44mg COD of acetic acid or 13mg COD of propionic acid results in 50% inhibition of methane production; at pH 7, for the same level of inhibition, 2,800mg Acetic acid or 745 mg propionic acid are required (SPANJERS, 2011).

Hydrogen sulfide is also toxic in its nonionized form and its dissociation is pH dependent. At pH 7 close to 50% of H_2S are unionized and 50% are ionized HS^- (non-toxic form). As pH decreases, the concentration of non-ionized H_2S increases, which may cause archaea and bacteria inhibition, while increases the concentration of H_2S in biogas. Solubility and dissociation of H_2S are also depend on system temperature, imposing an additional variable in the control of this process inhibitor.

Ammonia is processed in the opposite way, the existence of its nonionized form, the more toxic the anaerobic flora, is higher at higher pH, and its equilibrium point is at pH 9.25, a condition that is unlikely to be found in anaerobic digestion of vinasse due to its low initial pH and the small amount of proteins in the process in vinasse. Concentrations of 100mg/L of free ammonia are capable of inhibiting methanogenic archaea, whereas concentrations of more than

7,000mg/L of ammonium ion may not be inhibitory to properly acclimatized biomass (KHANAL, 2008).

2.2.4 Thermodynamics of anaerobic digestion

As stated previously, the anaerobic digestion process is mediated by numerous species of microorganisms that act in sequence, degrading complex polymers to simple forms of carbon-containing compounds, which due to their low solubility in water phase are removed from the liquid effluent.

Reactions occur in the absence of oxygen and provide little additional energy to the microbial community, in fact, some important reactions would not even occur, if not for the syntrophic effect of other steps, since they present positive free energy under standard conditions.

Some important conclusions can be drawn from the analysis of Table 2-2, which shows some of the main reactions in the anaerobic digestion process. Many acetogenic reactions are thermodynamically unfavourable under standard conditions (pH 7, 1Atm pressure, 25ºC, in aqueous solution with 1mol/kg concentration of reactants), presenting positive free energy. They only occur because archaea consume hydrogen and acetate, shifting the equilibrium of acetogenic reactions, making them possible. These reactions are only possible with hydrogen pressure of 10^{-4} to 10^{-3} atm, so it is necessary for hydrogen to be removed from the system for degradation of longer chain organic acids and their conversion to acetate, which is only possible through the existence of an adequate population of hydrogen consuming archaea (CAMPOS, 1999). Sulfur-reducing bacteria and homoacetogenic bacteria also contribute to this process.

It is also interesting to note that sulfate reduction reactions have higher energy than methane production reactions, so that for sulfate-rich wastewaters, sulfate reducing bacteria will have an advantage over methane producing archaea.

It also follows from the analysis of the energies associated with the above reactions that acidogenic processes are the most thermodynamically favourable in the entire anaerobic digestion process.

Table 2-2: Main reactions of anaerobic digestion and its associated energies

Process	**Equation**	**Free Energy $\Delta G^{0\prime}$ (kJ/mol)**	**Reference**
Acidogenesis			
Glucose to acetate	$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COO^- + 2CO_2 + 2H^+ + 4H_2$	-206	(AQUINO; CHERNICHARO, 2005)
Glucose to propionate	$C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COO^- + 2H^+ + 2H_2O$	-358	(AQUINO; CHERNICHARO, 2005)
Glucose to butyrate	$C_6H_{12}O_6 + 2H_2 \rightarrow CH_3CH_2CH_2COO^- + 2CO_2 + H^+ + 2H_2$	-255	(AQUINO; CHERNICHARO, 2005)
Acetogenesis			
Propionate to acetate	$CH_3CH_2COO^- + 3H_2O \rightarrow CH_3COO^- + H^+ + HCO_3^- + 3H_2$	+76.1	(CAMPOS, 1999)
Propionate to acetate	$CH_3CH_2COO^- + 2HCO_3^- \rightarrow CH_3COO^- + H^+ + 3HCOO^-$	+72.2	(AQUINO; CHERNICHARO, 2005)
Butyrate to acetate	$CH_3CH_2CH_2COO^- + 2H_2O \rightarrow 2CH_3COO^- + H^+ + 2H_2$	+48.1	(CAMPOS, 1999)
Benzoate to acetate	$C_7H_5CO_2^- + 7H_2O \rightarrow 3CH_3COO^- + 3H^+ + 3H_2 + HCO_3^-$	+53	(KHANAL, 2008)
Ethanol to acetate	$CH_3CH_2OH + H_2O \rightarrow CH_3COO^- + H^+ + 2H_2$	+9.6	(CAMPOS, 1999) (AQUINO; CHERNICHARO, 2005)
Lactate to acetate	$CH_3CHOHCOO^- + 2H_2O \rightarrow CH_3COO^- + H^+ + HCO_3^- + 2H_2$	-4.2	(CAMPOS, 1999)
Palmitate to acetate	$CH_3(CH_2)_{14}COO^- + 14H_2O \rightarrow 8CH_3COO^- + 7H^+ + 14H_2$	+354.6	(VAN LIER; MAHMOUD; ZEEMAN, 2008)
Homoacetogenesis			
Bicarbonate to acetate	$2HCO_3^- + 4H_2 + 4H^+ \rightarrow CH_3COO^- + 4H_2O$	-104.7	(CAMPOS, 1999; CHERNICHARO, 2007b)
Methanogenesis			
Bicarbonate to methane	$HCO_3^- + 4H_2 + H^+ \rightarrow CH_4 + 3H_2O$	-135.6	(CAMPOS, 1999) (AQUINO; CHERNICHARO, 2005)
Acetate to methane	$CH_3COO^- + H_2O \rightarrow HCO_3^- + CH_4$	-31.0	(CAMPOS, 1999) (AQUINO; CHERNICHARO, 2005)
Formate to methane	$HCOO^- + \frac{1}{4}H_2O + \frac{1}{4}H^+ \rightarrow \frac{1}{4}CH_4 + \frac{3}{4}HCO_3^-$	-32.6	(AQUINO; CHERNICHARO, 2005)
Sulfidogenesis			
Acetate + Sulfate to sulfide	$CH_3COO^- + SO_4^{2-} \rightarrow HS^- + 2HCO_3^-$	-48	(BARRERA et al., 2015; SOLON, 2015; VAN LIER; MAHMOUD; ZEEMAN, 2008)
Acetate + sulfate to sulfide	$CH_3COO^- + SO_4^{2-} \rightarrow H_2O + CO_2 + S^{2-} + HCO_3^-$	-12.41	(RIZZO; LEITE, 2004)
Hydrogen + Sulfate to sulfide	$SO_4^{2-} + 4H_2 + H^+ \rightarrow HS^- + 4H_2O$	-151.9	(CHERNICHARO, 2007b)
Hydrogen + Sulfate to sulfide	$SO_4^{2-} + 4H_2 \rightarrow S^{2-} + 4H_2O$	-129.98	(BARRERA et al., 2015; RIZZO; LEITE, 2004; SOLON, 2015)
Pyruvate + Sulfate to sulfide	$4CH_3COCOO^- + SO_4^{2-} \rightarrow S^{2-} + 4CO_2 + 4CH_3COO^-$	-331.06	(RIZZO; LEITE, 2004)
Lactate + Sulfate to sulfide	$2CH_3CHOHCOO^- + SO_4^{2-} \rightarrow S^{2-} + 2CO_2 + +H_2O + 2CH_3COO^-$	-140.45	(RIZZO; LEITE, 2004)
Propionate + Sulfate to sulfide	$CH_3CH_2COO^- + 0{,}75SO_4^{2-} \rightarrow 0{,}75HS^- + HCO_3^- + 0{,}25H^+ + CH_3COO^-$	-37.7 (at 37ºC)	(BARRERA et al., 2015; COLTURATO, 2015; SOLON, 2015)
Propionate + Sulfate to sulfide	$CH_3CH_2COO^- + 1{,}75SO_4^{2-} \rightarrow 1{,}75HS^- + 3HCO_3^- + 0{,}5H^+ + 0{,}25_3OH^-$	-88.9 (at 37ºC)	(COLTURATO, 2015)

2.2.5 Kinetics of microorganisms

The process of anaerobic digestion depends on series of intricate reactions and relationships between different species of bacteria and archaea, which in turn depend on very strict environmental conditions to occur. In addition to the conditions already presented, considerations should be made regarding the kinetic parameters of different species and families of microorganisms. These parameters refer to the speeds at which microorganisms consume substrates, produce biomass, metabolites, and decay. These parameters are established for calculation and modelling purposes and depends on the microorganisms and substrate concentrations.

Several different models to represent the kinetics of microorganism-mediated transformations have been developed over the years. Generally, the description of these phenomena is based on the model proposed by Monod in the late 1940s. This model admits simplifications, such as the existence of all substances necessary to the process, except the so-called limiting substrate, that there are no limitations of diffusion of this substrate in the process, non-accumulation of products, no existence of inhibitions and is based on the following relationships: (CAMPOS, 1999; CHERNICHARO, 2007b):

1- The gross growth rate of microorganisms is proportional to the substrate utilization rate and biomass production coefficient, given as follows:

$$dX/dT = Y \times dS/dT \qquad \text{Equation 2-1}$$

Where:

dX/dT = microorganism generation rate (mgSSV/L.d)

dS/dT = substrate utilization rate (mgDQO/L.d)

Y = biomass production coefficient (mgSSV/mgDQO)

2- The growth of microorganism biomass relies on the concentration of the biomass itself and its specific growth rate:

$$dX/dT = \mu \times X \qquad \text{Equation 2-2}$$

Where:

dX/dT = microorganism generation rate (mgSSV/L.d)

X = concentration of microorganisms (mgSSV/L)

μ = specific growth rate (d-1)

3- Specific growth rate:

$$\mu = \mu_{max} \times \frac{S}{K_s + S}$$ Equation 2-3

Where:

μ = specific growth rate (d-1)

μ_{max} = maximum specific growth rate (d-1)

S = Limiting substrate concentration (mgDQO/L)

K_s = substrate concentration, in which $\mu = 1/2\ \mu_{max}$(mgDQO/L)

4- From the existing biomass, a portion of microorganisms perishes, as Equation 2-4:

$$dX/_{dT} = K_d \ \times X$$ Equation 2-4

Where:

K_d = decay coefficient (d-1)

X = concentration of microorganisms (mgSSV/L)

$dX/_{dT}$ = decay rate of microorganisms (mgSSV/L.d)

5- The substrate consumption is given by the biomass growth divided by the biomass production coefficient, according to Equation 2-5

$$dS/_{dT} = \mu_{max} \times S/_{(K_s + S)} \times X/_{Y}$$ Equation 2-5

Where:

$dS/_{dT}$ = substrate utilization rate (mgDQO/L.d)

μ_{max} = maximum specific growth rate (d^{-1})

S = Limiting substrate concentration (mgDQO/L)

K_s = Substrate concentration in which $\mu = 1/2\ \mu_{max}$(mgDQO/L)

Y = biomass production coefficient (mgSSV/mgDQO)

X = concentration of microorganisms (mgSSV/L)

6- Besides biomass, the degradation of the substrate produces methane, according to Equation 2-6 (CHERNICHARO, 2007a).

$$dCH_4/_{dt} = (1 - Y)\ dS/_{dt}$$ Equation 2-6

Where:

$dCH_4/_{dt}$ = methane production rate (mgDQO/L.d)

7- Equation 2-1 combined with equation 2-5 results in equation 2-7:

$$ {}^{dS}/_{dt} = {}^{dCH_4}/_{dt} + {}^{dX}/_{dT} $$ Equation 2-7

Which shows that from the consumption of substrate Methane and Biomass are produced.

In many cases, one same substrate may limit biomass growth in low concentrations and impose inhibition in higher concentration. To address this aspect different models may be applied (such as Haldane model and others), or inhibition functions may be used multiplying the Monod function (CHERNICHARO, 2007b; KHANAL, 2008).

Table 2-3: Kinetic constants of bacterial and archaeal species under different conditions

Process/Stage/ Microorganism	**Substrate**	**k_m** (gDQO/gSSV.d) Maximum Substrate Utilization Rate	**Y** (gSSV/gDQO) Coefficient of biomass production	**K_s** (mgDQO/L) Saturation Constant	**μ_{max}** (d^{-1}) Maximum growth rate	**K_d** (d^{-1}) Endogenous respiration coefficient
Acidogenic (a)	Carbohydrates	1.33-70.6	0.14-0.17	22.5-630	7.2-30	6.1
Acetogenic (a)	Long chain organic acids	0.77-6.67	0.04-0.11	105-3.180	0.085-0.55	0.01-0.015
Acetogenic (a)	Short-chained organic acids	6.2-17.1	0.025-0.047	12-500	0.13-1.2	0.01-0.027
Acetoclastic Methanogenic (a)	Acetate	2.6-11.6	0.01-0.054	11-421	0.08-0.7	0.04-0.037
Hydrogentrophic methanogenic (a)	H2/CO_2	1.92-90	0.017-0.045	0.6	0.05-4.07	0.088
Acidogenic (b)	n.d.		0.15			
Methanogenic (b)	n.d.		0.03			
Anaerobic Filter (b)	n.d.		0.115-0.121			
Anaerobic treatment (b)	n.d.		0.05-0.15			
n.d. (b)	Carbohydrates		0.35			
n.d. (b)	Proteins		0.0205			
n.d. (b)	Fats		0.038			
n.d. (b)	Butyrate		0.058			
n.d. (b)	Propionate		0.037			
n.d. (b)	Acetate		0.032			
n.d. (b)	Hydrogen		0.038			
Methanosaeta (b)	Acetate	10.1	0.019	49		
Methanosarcina (b)	n.d.	12.2	0.048	280		
Acidogenic Bacteria (c)		13	0.15	200	2.0	
Methanogenic Archaea (c)		13	0.03	50	0.4	
Mixed culture (c)		2	0.18	-	0.4	
Acidogenesis (d)		13	0.15	200	2	
Methanogenesis (d)		3	0.03	30	0.12	
Mixed culture (d)		2	0.03-0.18	-	0.12	
Methanosaeta (d)				300	0.12	
Methanosarcina (d)				30	0.71	
Hydrogentrophic methanogenic (d)				0.06	2.85	

(a) (AQUINO; CHERNICHARO, 2005); (b) (KHANAL, 2008); (c) (CAMPOS, 1999); (d) (VAN LIER; MAHMOUD; ZEEMAN, 2008)

Each specie or family has distinct characteristics of growth rate, decay, substrate affinity, metabolite production rate, etc. which will depend on environmental conditions, substrate type, among other variables some of which are presented in Table 2-3.

From the understanding of these kinetic relationships and from experimentally obtained values for the constants, rates and coefficients of several species, cultures and systems and considering limiting conditions, we can extract important knowledge.

The most favourable reactions in anaerobic digestion are those of the acidic phase, which also have the species with the highest biomass production coefficient and growth rate, and are also less limited by pH (VAN LIER; MAHMOUD; ZEEMAN, 2008), such way loading shocks in reactors are accompanied by large production of short chain organic acids, result of the acidogenic phase. Due to their high growth rate, acidogenic bacteria are also more resistant to flow shocks in reactors.

On the other hand, methanogenic archaea, especially methanosaeta, given their low biomass production and growth rates, can be “flushed” from reactors subjected to flow rates higher than design conditions. From the kinetic constants of methanosaeta and methanosarcina species it can be concluded that systems with low substrate concentrations favour the predominance of methanosaeta, systems operating with high acetate concentrations or low cell retention times methanasarcina prevail, which due to its ability to process various substrates, besides acetate, provides stability to the operation.

Sulfate-reducing bacteria have thermodynamic and environmental advantages over methanogenic archaea, so they prevail when competing for the same substrates. This predominance of sulfate-reducing leads to lower methane production.

Acetogenic bacteria, given the thermodynamic limitations of their reactions, depend on other species that consume hydrogen they release themselves, a task performed mainly by methanogenic archaea but also by sulfate reducers.

2.2.6 Methane Production

2.2.7 Buswell Equation

Through the chemical composition of a substrate it is possible to calculate the theoretical potential for methane production by the Buswell equation (1952) (Equation 2-8). Buswell's formula does not consider that part of the substrate is used for biomass growth or other competing biochemical pathways and considers that the substrate is fully biodegradable, thus being a maximum potential calculation. Computing the culture biomass production coefficients and considering the recalcitrance of compounds, is useful for estimating biogas quantity and quality, giving indications of biogas composition (methane and carbon dioxide mainly). The equation also does not take into account the solubility of the different biogas components in the liquid phase of the system, which can significantly change the methane, carbon dioxide and hydrogen sulfide volumes generated by the microorganisms and those actually present in the biogas (CHERNICHARO, 2007a; KHANAL, 2008; VAN LIER; MAHMOUD; ZEEMAN, 2008).

$$C_nH_aO_bN_cS_d + \left(n - \frac{a}{4} - \frac{b}{2} + \frac{3 \times c}{4} + \frac{d}{2}\right) H_2O \rightarrow \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4} + \frac{3 \times c}{8} + \frac{d}{4}\right) CO_2 + \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3 \times c}{8} - \frac{d}{4}\right) CH_4 + cNH_3 + dH_2S$$

Equation 2-8

2.2.7.1 COD – Chemical Oxygen Demand

COD is the measure of the amount of oxygen required for complete oxidation of organic matter present in a wastewater or substrate, and is, therefore, directly related to its oxidation state. COD is often used as a parameter to evaluate the polluting potential of effluents. The higher the oxidation state of the compound, the greater the amount of CO_2 and the lower the amount of CH_4 biogas obtained from its anaerobic degradation. Considering that the most reduced carbon state is found in methane and the most oxidized state is found in carbon dioxide, the methane COD is the highest possible (4g O_2 / g CH_4) and the COD of carbon dioxide is equal to zero (obviously), thus COD serves as an indirect measure of the methane production potential of a given compound subjected to anaerobic digestion.

If the chemical composition of the substrate is known, its COD can be calculated from the reaction of its complete oxidation as follows in Equation 2-9:

$$C_nH_aO_bN_c + \left(n + \frac{a}{4} - \frac{b}{2} - \frac{3 \times c}{4}\right) O_2 \rightarrow nCO_2 + \left(\frac{a}{2} - \frac{3 \times c}{2}\right) H_2O + cNH_3$$

Equation 2-9

The COD in grams of O_2 per gram of product is given by Equation 2-10:

$$DQO_{CnHaObNc} = 32 \times \left(n + \frac{a}{4} - \frac{b}{2} - \frac{3 \times c}{4}\right) / (12n + a + 16b + 14c)$$

Equation 2-10

The COD is also commonly evaluated in laboratory by reacting the product to be analysed with a strong oxidizer at high temperature, so that virtually all organic matter is converted to carbon dioxide and water.

From the COD value, calculated or measured in a laboratory test, the amount of methane that could theoretically be produced can be calculated (assuming the entire substrate to be biodegradable and no substrate is used for microorganisms growth) by the ratio of 4 grams of COD of substrate equals 1 gram of methane produced, i.e.: 1 gram of COD equals 0.25g of methane. Given the methane density at standard conditions of 0.7157 kg/Nm³, we have that for each kilogram of COD consumed in anaerobic process results in 0.35Nm³ of methane.

Otherwise, the difference between the substrate COD at the inlet of an anaerobic system and the sum of the COD of the anaerobic digestion products (biomass and biogas) plus the effluent COD at the outlet of this same system creates the system's COD balance, as shown in Figure 2-4: below:

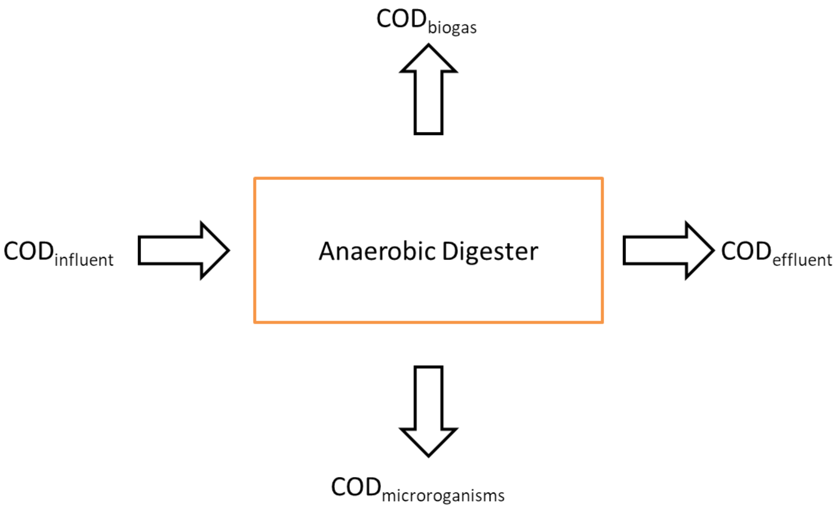


Figure 2-4: COD balance in anaerobic process

Considering biogas as a mixture of CO_2 and CH_4 and knowing that CO_2 has zero COD, the biogas COD is equal to the methane COD produced. The COD of microorganisms can be calculated by their estimated typical composition ($C_5H_7O_2N_1$), equivalent to 1.415 kg DQO/kg VSS (VAN HAANDEL; VAN DER LUBBE, 2012; VAN LIER; MAHMOUD; ZEEMAN, 2008). Influent and effluent CODs can be verified in laboratory, or if the substrate composition is known, input COD can be calculated.

2.2.7.2 Sulfate Effect

For sulfate-containing substrates, sulfate-reducing bacteria tend to prevail over methanogenic in competition for acetate, hydrogen and other methane precursors, causing a decrease in methane production. By the stoichiometry of the sulfide oxidation reaction, per Equation 2-11, we can calculate the sulfide's COD:

$$S^{2-} + O_2 \rightarrow SO_4^{2-} \qquad \text{Equation 2-11}$$

From this reaction, we have that each 96 grams of sulfate requires 64 grams of COD for sulfide reduction and this COD will not be available for methanogenic archaea to produce methane. In other words, there is a ratio of 1g COD for every 1.5g SO_4^{-2} that cannot be used for methane production, from what follows that if the COD:SO_4^{-2} ratio of a substrate is less than 0.67, there will be no methane production (CHERNICHARO, 2007a; KHANAL, 2008; VAN LIER; MAHMOUD; ZEEMAN, 2008).

It should be considered, however, that acetate-producing sulfate-reducing bacteria would not fully consume the above-referenced COD, but part of it would be contained in the acetate produced, however, this route should only prevail at low sulfate concentrations (RIZZO; LEITE, 2004). Khanal (2008) also notes that acetate-producing sulfate-reducing bacteria may be favoured at low pH, which is not favourable for methane production (KHANAL, 2008).

2.3 Technologies for biogas production

As seen in previous sections, for biogas production through anaerobic degradation of organic substrates to occur, several physicochemical conditions must be met, without which the end product may eventually not be produced or the process' yield may be greatly impaired. The engineering task in biogas production and use projects is, based on a wide scope of knowledge accumulated over the years, result of experiences and development that today translate into mature and low risk technology, to evaluate the particular conditions imposed by projects, deciding on the best way to obtain and use biogas at the lowest possible cost, while ensuring longevity, robustness, predictability and high availability to enterprises, important attributes to energy projects. This section will address the technological aspects of biogas production and use, especially focusing on vinasse as a substrate.

2.3.1 Gas production

The transformation of organic matter contained in various substrates into biogas through the anaerobic digestion process occurs in equipment commonly called anaerobic reactors, also referred as digester, anaerobic digester or biodigester.

An anaerobic reactor is a device in which the substrate to be digested is introduced, and where microorganisms, that will be fed on the organic matter contained in the substrate, are cultivated and kept, producing biogas and increasing its population. Biogas, surplus biomass and digested substrate will be withdrawn from the reactor. It is an enclosed container to avoid contact with oxygen - harmful to most microorganisms responsible for anaerobic digestion, with volume dependent on substrate quality, flow and organic load rate, whose format and construction method will vary depending on the technology employed and other particularities of the project such as substrate used, characteristics of the location, including climate, available area, and others.

Intimate contact between the substrate and the microorganisms shall be achieved in the anaerobic reactor. For the maintenance of a balanced flora and for the reactions to occur efficiently, temperature, pH, nutrient existence, absence of inhibitors, hydraulic and organic loading, cell retention time among other conditions must be met.

Van Lier (2008) highlights some conditions that must be met for anaerobic digestion process performance be adequate:

- High retention of viable biomass on the reactor under operating conditions
- Sufficient contact between substrate and biomass
- Adaptation of biomass to substrate
- Maintaining favourable environmental conditions for microorganisms under all operating conditions, with special focus on limiting process steps.

2.3.2 Design parameters for anaerobic reactors

Initially, two concepts are fundamental for understanding the performance of anaerobic reactors: hydraulic retention time and cell retention time. Decoupling the hydraulic retention time from the cell retention time was one of the developments that allowed the success of anaerobic digestion systems.

a. **The Hydraulic Retention Time (HRT)**: is the average time the liquid remains inside the reactor, being defined by Equation 2-12:

$$\theta_h = \frac{V}{Q}$$

Equation 2-12

Where:
θ_h = Hydraulic Retention Time [d]

V = Reactor volume [m^3]

Q = Flow rate [m^3/d]

b. **Cell Residence Time (CRT)**: is the average residence time of the microbiological biomass inside the reactor, called sludge age, being defined by Equation 2-13:

$$\theta_c = \frac{X}{\Delta X / \Delta t}$$

Equation 2-13

Where:
θc = *Cell Residence Time [d]*

X = *Concentration of microorganisms in the reactor [kg/m^3]*

$\Delta X/\Delta t$ = *Reactor microorganism withdrawal rate [kg/m^3/d]*

In the 1950s the importance of the decoupling between hydraulic retention time and cell retention time for the effective application of anaerobic digestion technology is recognized (MCCARTY, 2001). This development led to an increase in the loading rate of material to be digested in the reactors, which implies shorter hydraulic detention times, higher flow rates and, therefore, smaller reactors, without, however, losses of biomass by dragging cells out of the reactor.

According to McCarty (2001), G. J. Schroepfer et al. in 1955 used a conventional CSTR reactor followed by a sedimentation tank, with retained microorganisms returning to the reactor, achieving very short hydraulic retention times to the standards of the time (less than one day treating effluent from a meat packer), creating what we call today the Anaerobic Contact Process (ACP). Difficulties with sedimentability caused by sludge-attached gas bubbles leading to float and with very intense mixing in the reactor (and its deleterious effect on anaerobic sludge flocculation) have been resolved with less intense agitation and the use of degassing systems (MCCARTY, 2001; VAN LIER; MAHMOUD; ZEEMAN, 2008).

Just as the ACP, the subsequent development of anaerobic reactors was also inspired by aerobic processes. Attached growth reactors use fixed support material inside the reactors to which biomass grow adhered. They are called anaerobic filters and can operate in downflow or upflow. These reactors are especially effective with soluble substrates and in conditions where sludge granulation is difficult to obtain. Problems with biomass accumulation at the bottom of the reactors (in upflow reactors), clogging and short-circuiting caused the number of new installations with this technology to fall substantially in the early 2000s (CHERNICHARO, 2007a; MCCARTY, 2001; VAN LIER; MAHMOUD; ZEEMAN, 2008). Using much smaller particles to support biomass growth than fixed bed reactors and very high upward speeds, fluidized and expanded bed reactors treat with good efficiency and low hydraulic retention times diluted effluents without inconveniences such as clogging and short-circuits.

In the early 1970s, Lettinga proposed two strategies for maintaining long cell retention times: 1 - keep agitation within the reactor to the minimum possible, seeking to increase sludge sedimentability and 2 – install a gas release and solid (sludge) sedimentation devices internally to the reactor. It was the beginning of one of the most widespread and probably the most successful anaerobic wastewater treatment technique known as UASB (Upflow Anaerobic Sludge Blanket) (MCCARTY, 2001). The technique promoted the formation of granulated sludge with high sedimentation capacity, which further increase the efficiency of the system. As with fixed bed reactors, UASB followed variations such as the Expanded Granular Sludge Blanket (EGSB) - basically a UASB with upflow speeds that allow the expansion of the sludge blanket, recirculating reactors for reducing organic load, use of two sets of separators, and many others.

The increase in cell retention time in so-called high-rate anaerobic reactors is due to the recovery and return of effluent-contained biomass in settlers outside the reactor, by the retention of biomass by separators installed internally in the reactor - which is enhanced by the increase in its density by flocculation or granulation or by growing of biomass adhered to support material internally to the reactor.

Although the wastewater treatment sector makes use of numerous technologies, arrangements and designs for anaerobic digestion, not all of these are usual when the goal is to maximize biogas production and minimize construction costs instead of focusing in effluent quality, such as vinasse, which will later be applied to crops and not disposed of in water bodies.

Among the anaerobic digestion technologies of interest for the production and energy use of biogas, we can highlight the following:

1- Continuous stirred-tank reactor (CSTR)
2- Upflow anaerobic sludge blanket reactors (UASB)
3- Anaerobic lagoons

2.3.3 Continuous Stirred Tank Reactors

These reactors are usually cylindrical in shape, made of concrete or steel, with mixing systems and, in the case of cold climate countries, also with heating systems and thermal insulation. Tank coverings often serve as reserve of biogas. CSTR reactors are used mostly in the mesophilic temperature range, continuously fed and do not have anaerobic biomass recovery or retention devices.

The process consists of receiving the substrate and mix it inside the reactor, allowing contact between the active biomass and the substrate, promoting the substrate degradation and biogas production. There is no device for separating the active biomass from the substrate, so that a mixture containing active biomass and partially degraded substrate is discarded. A simplified scheme of a CSTR reactor is shown in Figure 2-5: below.

According to Weiland (2010), most biogas production projects in Germany use this technology, especially well-suited to substrates with solids content around 10%. Cabral (2015) considers the solids content of 15 to 20% is suitable for CSTR reactors, depending on the substrate and the technological intensity level of the reactor (CABRAL, 2015). The form of mixing may be mechanical, hydraulic, or pneumatic. The most common mechanical mixing being provided with radial, axial or diagonal propellers or impellers whose operation may vary in speed and frequency. Systems operating at lower solids often employ submersible mixers tangentially mounted to the reactor that can have their position and angle adjusted. The mixing device also lends itself to preventing the formation of supernatant layers in the reactor. (WEILAND, 2010). Axial mixers often prevent the use of the digester cover as a biogas reservoir (CABRAL, 2015).

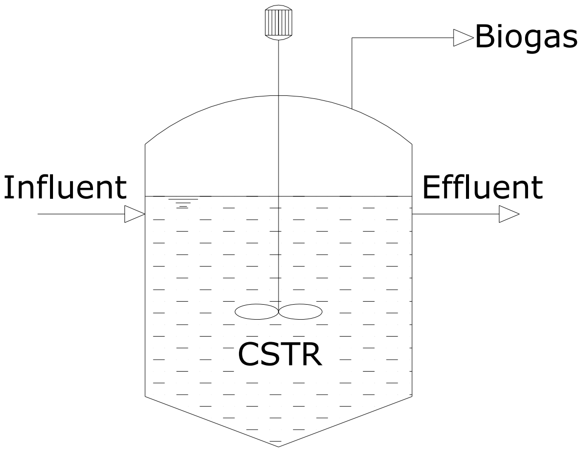


Figure 2-5: Continuous Stirred Tank Reactor - CSTR

Arrangements with two reactors are also frequent, one of higher technology intensity, working with higher loading rate and a second reactor which has longer retention time taking advantage of residual potential of biogas production, these arrangements result in higher overall biogas productivity.

For a continuous stirred-tank reactor with no form of biomass retention, the hydraulic retention time is equal to the cellular retention time. In this case, the minimum hydraulic retention time, according to Chernicharo (2007), is a function of the slowest reproducing microorganism growth rate and is given by equation 2-14. If this condition is not met, there will not be microorganisms of the considered specie to carry the substrate metabolism.

$$\theta_{min} = t_{dup} = \frac{\ln(2)}{\mu}$$ Equation 2-14

CSTR reactors can be provided with external settlers to recover anaerobic biomass and return them to the reactor, configuring the already mentioned ACP, Anaerobic Contact Process, (Figure 2-6) (CHERNICHARO, 2007a; DEUBLEIN; STEINHAUSER, 2011). However, this arrangement is not frequent in biogas projects in Germany and Europe in general. The effluent of these systems operating with high solids substrates (animal waste, for example), is composed of, besides water and microorganisms, undigested material and used as fertilizer (PELL FRISCHMANN, 2012).

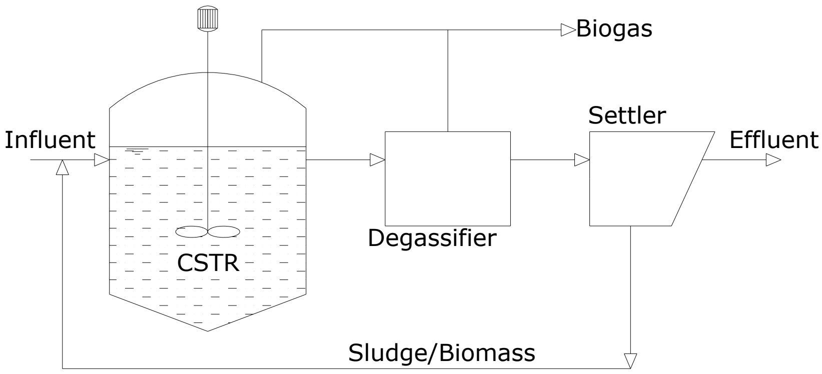


Figure 2-6: Anaerobic Contact Process - ACP

2.3.4 Upflow anaerobic sludge blanket reactors (UASB)

Upflow anaerobic sludge blanket reactors (and variants) represent the largest number of anaerobic treatment systems in operation today (VAN LIER; MAHMOUD; ZEEMAN, 2008). The process, shown in Figure 2-7, consists of moving the substrate upstream through a dense anaerobic sludge blanket of high metabolic activity (CHERNICHARO, 2007a).

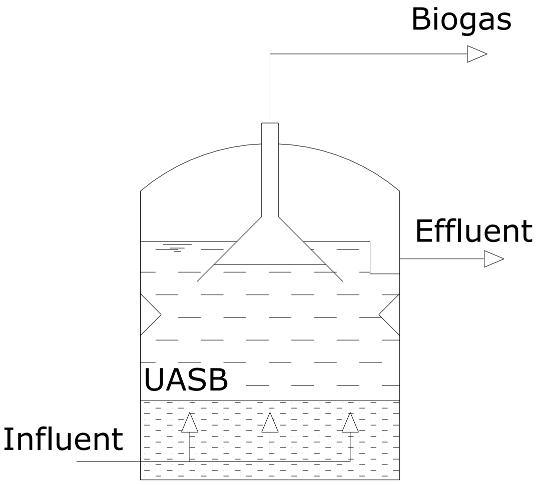


Figure 2-7: UASB Reactor

These reactors are constructed in the form of cylindrical or prismatic concrete or steel tanks and contain an influent distribution system that promotes the uniform distribution over the entire base area of the tank and also a device called a three-phase separator or gas-liquid-solid separator (also known as GLSS). The phase separators promote the retention of solids particles that eventually reach the top of the reactor, recovering active biomass (CHERNICHARO, 2007a).

The presence of high density granular or flocculent sludge is of great importance for the performance of these reactors, according to McCarty (2001) “dense particles constituted by interwoven mixture of symbiotic anaerobic microorganisms", which has extremely good sedimentability and maintains the organisms inside the reactor. Chernicharo (2007) points out that the formation of the granules occurs through a careful start-up process, in which an artificial selection mechanism is applied, where the organisms less prone to sedimentation are removed, keeping in the reactor the ones that have the necessary qualities for good process performance.

UASB sludge density is in the range of 40-100g of total solids per litre, for this reason high upward speeds are possible without risk of biomass wash-out from the reactor, which is also prevented by the existence of a three phase separator at the top of the tank (CHERNICHARO, 2007a). Mechanical mixing devices in the reactor is not provided given the deleterious effect of very intense mixing on the increase of sludge density and also as a way to decrease reactor costs (VAN LIER; MAHMOUD; ZEEMAN, 2008).

Contact between substrate and active biomass is made by uniform distribution at the bottom of the reactor and as a result of agitation caused by biogas generation. High upflow speed also contributes to better contact between active biomass and substrate.

Chernicharo (2007) considers that the design of this type of reactor is fundamentally related to up-flow speed, which should be low enough to avoid washing the active biomass. When dealing with relatively dilute substrates such as domestic sewage, the reactor area should be larger in order to decrease this speed. With higher COD substrates, such as agro-industrial effluents, the reactor area may be smaller, while keeping the upward velocity within the recommended limits.

Souza et. al., (1992) operating a thermophilic UASB reactor fed with sugarcane vinasse, maintained effluent recirculation and addition of sodium hydroxide (average 4 g NaOH/kg COD) and after achieving satisfactory sludge granulation, obtained 71.7% COD removal with 26.5kgCOD/m^3/day, resulting in the production of 0.22m^{3}CH$_4$/kgCOD loaded in the reactor and 98% removal of sulfate from the vinasse. The authors also reported, besides the need of sodium hydroxide, the addition of nutrients (7. 4 g N/kg COD and 1.7 g P/kg COD) to maintain stable operation. It is also interesting to note that the design of this UASB reactor includes settling tank for biomass recover after the digester (SOUZA; FUZARO; POLEGATO, 1992).

Vlissidis & Zoubuolis (1993), described the operation of a sugar beet ethanol vinasse digester composed of two 1,000m^3 tanks which had the process' pH controlled by the addition of lime in a second settling tank that had its content recirculated to the first two reactors. The system operated in thermophilic range with OLR of approximately 7kgCOD/m³/day (VLISSIDIS; ZOUBOULIS, 1993).

Blaszczyk et. al., (1994) report the operation of an UASB reactor treating effluent from a corn wet milling facility. The reactor subject to simultaneous shock loading of pH, temperature and COD experienced biomass wash-out, since it lost the ability to settle, and the effectiveness of digestion was greatly diminished (BLASZCZYK; GARDNER; KOSARIC, 1994).

Ahn et. al., (2001) describe a long-term operation of an UASB reactor treating brewery wastewater and report frequent reseeding (once or twice a year) due to granule wash-out, which represented considerable expense. The authors have also interesting observation that when considering the pre-acidification tank in the OLR calculations, this value drops from 7.5kgCOD/m³/d to 3.5kgCOD/m³/d. Other interesting aspect in this paper is the fact that the pre-acidification tank consumed 41% of COD but produced a low quality biogas, with only 46% methane (AHN; MIN; SPEECE, 2001).

Leitão, et al (2006) describe the behavior of UASB reactor under organic load and hydraulic shocks, pointing to the possibility of excessive generation and accumulation of volatile organic acids, pH drop, alteration of biogas composition, changes in the characteristic of the sludge blanket, among other effects (LEITÃO et al., 2006).

Yamada et. al., (2013) reports a reduction in alkali supplementation in a UASB treating shochu (Japanese distilled beverage) wastewater from 0.020 kgCaCO3/kgCOD to zero by effluent recycle strategy of 10:1 ratio (recycle to effluent) (YAMADA et al., 2013).

Kobayashi et al., (2015) describes an UASB fed with wastewater with different concentrations of sulfide, showing granules with lower strength and decreased diameter, as well as effluent with increased turbidity at high sulfide concentration. The study concludes that sulfide affected negatively methane production, chemical oxygen demand removal and sludge retention (KOBAYASHI; XU; CHIKU, 2015). This conclusion is especially important when considering the vinasse anaerobic digestion, because of its high sulfate concentration which will become sulfide in the anaerobic environment.

Lopez et. al., (2015) tested a UASB reactor operating with tequila vinasse, managing to eliminate the need for external alkali addition by recirculating the effluent at a 10:1 ratio, which, however, caused changes in the sludge characteristics. The sludge became partially flocculent and with smaller granules, condition that can lead to sludge washing. The Organic Loading Rate (OLR) reached 20kgCOD/m³/day and the reactors' alkalinity varied from 2,000 to 6,000 mg/L. While the VFA/ALK ratio was kept between 0.1 e 0.5 the reactor operated with stability, whereas as the ratio surpassed 0.8 sodium carbonate had to be added (LÓPEZ-LÓPEZ et al., 2015).

Barros et. al., (2016) using two bench scale UASB reactors operating with sugarcane ethanol vinasse with variable OLR regimes used sodium hydroxide (NaOH) for pH control and replaced the alkali with effluent recirculation strategy after a certain testing period. Influent alkalinity increased significantly with recirculation, although COD removal efficiency dropped, as did methane production and methane content in biogas for OLR above 7.5kgCOD/m^3/day with recirculation (BARROS; DUDA; OLIVEIRA, 2016).

Ferraz Junior. et. al., (2016) report that was impossible to have stable biogas production in a lab scale UASB reactor treating sugarcane vinasse without external source of alkali. It was required sodium bicarbonate (NaHCO3) solution at concentrations of 12.5 g /L to achieve adequate pH for biogas production (FERRAZ JÚNIOR et al., 2016).

Janke et. al., (2016) also report the addition of alkalizing substances to UASB reactors operating with sugarcane vinasse for pH adjustment or recovery from inhibitory states (JANKE et al., 2016).

According to Chamy et. al., (2017), granulation phenomenon is an important aspect in stable performance of UASB reactors. In this study, granules deterioration led to destabilization of UASB operation when lowering the reactor influent COD and increased influent flow of Pisco (Chilean distilled beverage) vinasse (CHAMY et al., 2007).

Macarie et al., (2018) consider that granulation of biomass is the basis of operation of anaerobic systems such as UASB, but problems in granulation may result in loss of biomass, poor treatment efficiencies and even complete reactor wash-out. According to the authors, possible causes to a granulation problem can be related to effluent quality (deficiency or excess of macronutrients or micronutrients, high COD, high sulfate, etc.), to operational factors (loading rate, upflow velocity) or poor engineering design (MACARIE et al., 2018).

Borzacconi et al., (2018) report an UASB reactor that suffered of sudden drop in pH which caused sudlge to acquire poor settlement proprieties with simultaneous loss of COD removal efficiency. In an attempt to eliminate the poor settling sludge by increasing the upflow velocity, a complete wash-out of biomass was observed (BORZACCONI et al., 2008).

2.3.5 Anaerobic lagoons

Domestic and industrial wastewaters are often treated by anaerobic lagoons, which according to EPA (2011) are reservoirs dug into the ground at least 2.4m deep, to minimize the effect of atmospheric oxygen diffusion into the pond's liquid environment, allowing anaerobic microorganisms to prevail. Campos (1999) describes them as simple and low cost systems in terms of construction and operation, with satisfactory efficiency and depth of 3 to 5 meters, to which Chernicharo (2007) adds are devoid of mixing and heating systems and constitute an appropriate alternative to wastewater treatment in warm climates (CAMPOS, 1999; CHERNICHARO, 2007a; EPA, 2011). Figure 2-8 schematically shows an anaerobic lagoon.

Anaerobic lagoons are, however, systems with low ORL and long HRT, thus occupy more space compared to other types of reactors. They are also often open to weather, which causes smell problems, insect proliferation and loss of heat. The functioning mechanism of an anaerobic lagoon consists of sedimentation of the solids present in the effluent to the bottom of the lagoon, where the organic fraction of these solids decomposes anaerobically. The effluent, free of solids, is removed from the pond from the opposite side to which the substrate was introduced. The high loads in relation to the ponds surface, associated with their depth, makes the environment oxygen free, allowing an anaerobic process of organic matter purification (CAMPOS, 1999; CHERNICHARO, 2007a; EPA, 2011).

In Brazil anaerobic lagoons are widely used for domestic wastewater treatment, but are also used in industrial wastewater treatment systems, especially in the food industry (slaughterhouses, cassava starch factories, etc.) and in the treatment of animal waste, a sector that, favoured by the carbon credits of the clean mechanisms of the Kyoto Protocol, has installed more than 1,850 digesters in the country, mostly anaerobic lagoons (MARIANI, 2015).

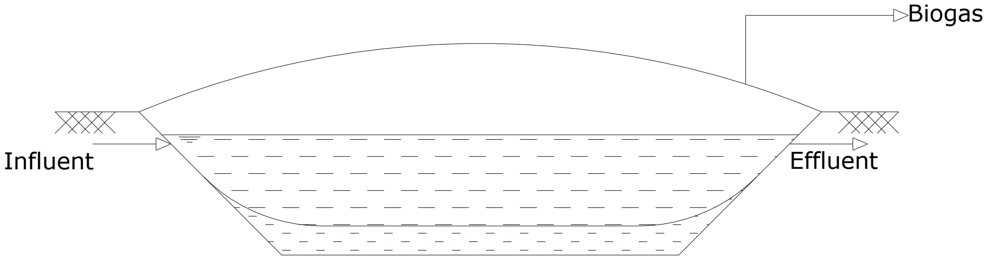


Figure 2-8: Anaerobic Lagoon

2.3.6 High-Rate Anaerobic Lagoons

Chernicharo states that while the minimum cell residence time of methanogenic archaea in wastewater treatment is more than 3.3 days at 30°C, shorter hydraulic retention times can be achieved by evenly distributing the effluent across the bottom of the lagoon, mimicking a UASB reactor, which favours the increase of microbial biomass density and its retention inside the lagoon (CHERNICHARO, 2007a). In 1967, Oswald et al. designed a lagoon with a deeper well which received effluent and showed greater reduction of suspended solids and COD than other lagoons working with similar loads (OSWALD; GREEN; LUNGDIST, 1994). Campos (1999), who describes Oswald's concept, suggests dividing anaerobic lagoons into two categories: low loading rate (conventional) and high loading rate, emphasizing the fact that this technique allows the digestion of solid matter, enabling lower sludge accumulation and also the use of biogas collection covers (CAMPOS, 1999).

UNSW (1998) states that anaerobic lagoons acting as a fully mixed reactor, known as a "Bulk Volume Fermenter", can achieve treatment performance similar to an UASB reactor, while being a lower cost option. The report also suggests these reactors could have OLR up to six times greater than a conventional pond. The report states that the use of lagoon covers, which was put into practice in the 1980s, aiming to collect biogas and control odours, has the additional advantage of maintaining reactor's temperature, notably in places with lower ambient temperature (UNSW-CRC, 1998).

Wall (2000) describes a "HRAL - High Rate Anaerobic Lagoon" anaerobic lagoon system as a reactor that incorporates principles similar of an UASB, where the raw affluent is introduced by the reactor base through a large number of points, causing the affluent to pass through a sludge blanket, allowing substrate and microorganisms contact. The system is provided with effluent recycling, to assist the reactor's pH maintenance with the alkalinity generated in the anaerobic process and to increase substrate and active biomass contact by the increased flow rate. The described system also incorporates plastic cover and biogas collection devices consisting of channels formed by the existence of floats mounted on the cover itself, creating voids between the cover and the liquid surface in the reactor (WALL et al., 2000).

There are numerous companies on the market today that offer pond-based anaerobic systems with proprietary technologies configured as high-rate lagoons. Some of these are global, larger companies, but also numerous small regional companies apply similar concepts. This technology has been used in several sectors that generate high organic load effluents, especially in warm climate countries without severe space limitations. Areas of application of this concept of high-rate lagoons include palm oil mill effluent, cassava starch and ethanol production in Southeast Asia, Central and South America.

The configurations of these reactors vary, some designers endow the lagoons with distinct reaction and sedimentation zones, separated by baffles mounted internally to the lagoons. Other arrangements provide for more than one reaction zone, similar to what occurs in sequential baffled reactors.

The reactors are provided with influent distribution systems throughout the base of the reactor, often made by network of pipes which have holes or nozzles in order to provide homogenous distribution of the substrate in the reaction zone. Given the higher density of sludge than reactor liquid and the long hydraulic residence times of this type of reactor, there is a tendency to form a sludge blanket at the bottom of the reactor, similar to UASB reactors, but not necessarily composed of granulated sludge. In addition to the effluent distribution system, high-rate lagoons often have piping systems for anaerobic sludge management, allowing their removal or inoculation as needed.

Depending on the characteristics of the sludge generated in terms of sedimentability, anaerobic lagoons may be provided with settlers at their outlet, aiming to recover part of the sludge that may be present in the effluent for re-inoculation in the reactor reaction zone or for disposal, which makes it an arrangement somewhat similar to anaerobic contact process (ACP), with a high-rate pond in place of a CSTR. For low pH wastewaters, such as vinasse and starch effluents, the reactor effluent can be recirculated to increase alkalinity, assist in balancing alkalinity and volatile acids and to maintain pH in the appropriate level to anaerobic digestion.

Lagoon covers are generally made of plastic material such as HDPE (High Density Polyethylene), LLDPE (Low Density Linear Polyethylene), flexible PVC but also EPDM rubber sheets. The lagoons are usually lined with the same materials used in the covers. Vinasse lagoons in Brazil shall comply with standards such as CETESB 4.231. The cover can work under positive pressure (creating a large volume of biogas between the lagoon and the cover) or slight vacuum, which reduces incident risks in case of strong winds. Positive pressure covers often have belts or net arrangements for holding the cover to prevent damage from strong winds.

Positive pressure lagoon covers may be subject to fugitive emissions in case of any defect on the cover, which should be a key point of attention due to global warming potential of methane. On the other hand, covers under vacuum may be subject of air contamination of the biogas in case of openings, which may lead to explosive mixture formation”

Different methods of anchoring the cover are proposed, such as burying its end in a ditch dug at the periphery of the lagoon and backfilling it with earth, or the construction of a concrete wall along the entire perimeter of the lagoon to fix the cover in it.

Gas collection methods also vary, which may be through channels formed between floats installed on the cover and reactor liquid for systems operating under vacuum, perforated piping around the reactor or even connecting a pipe directly to the cover. In case of anchoring the cover to concrete wall, if the wall is sufficiently high, there will be an empty space throughout the reactor periphery, between the wall and the cover, from where biogas can be removed. Cabral, (2015) recommends substrates with less than 5% total solids for high-rate ponds.

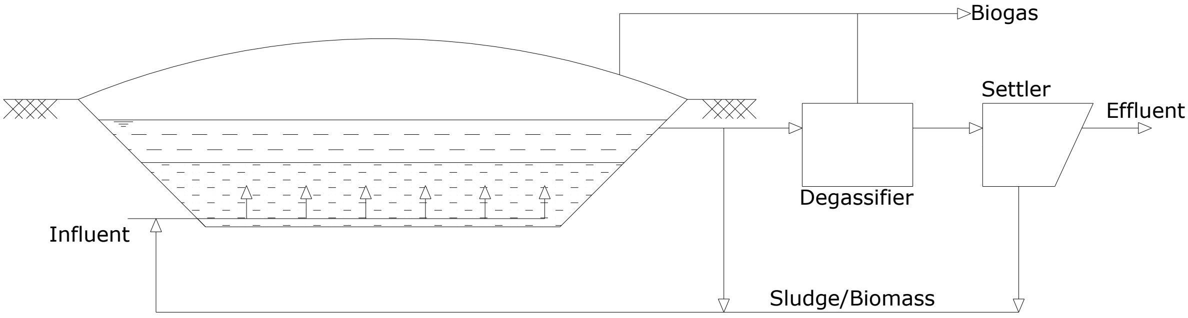


Figure 2-9: High Rate Lagoon

Figure 2-9 shows a schematic arrangement of a high rate lagoon with degassing system and settler.

2.4 Biogas Conditioning for Energy Use

Biogas is a very versatile energy source and can be used for electrical generation in Otto cycle generator sets, burned in boilers for steam and electricity production or it can be purified, by removal of CO_2, H_2S and other contaminants, to generate the so called biomethane, which can be used as a natural gas blending renewable.

The composition of biogas may vary depending on the substrate used for its production and with respect to the scope of this work, the biogas of vinasse, no contaminants other than hydrogen sulfide are reported in literature. The composition of vinasse biogas found in literature is presented in Table 2-4: below (BARRERA et al., 2015; CORTES PIRES et al., 2015; LEME; SEABRA, 2017; NANDY; SHASTRY; KAUL, 2002; YASAR et al., 2015).

Table 2-4: Volumetric composition of vinasse biogas found in literature.

Author	*CH_4*	*CO_2*	*H_2S*
*Leme; Seabra (2017)**	*60%*	*38.1%*	*1,9%*
Yasar et al. (2015)	*58–61%*	*36–38%*	*3%*
Barrera et al. (2015)	*-*	*-*	*1,75%*
Nandy; Shastry; Kaul (2002)	*62.4–64.5%*	*34.0–36.0*	*1.5–1.6%*
Cortes Pires et al. (2015)	*55%*	*43%*	*2%*
** Theoretical data*			

Given the origin of vinasse, practically free of silicon-containing compounds, normally associated with anthropogenic substrates, such as domestic sewage and urban waste, and low protein, normally associated with animal waste (DEUBLEIN; STEINHAUSER, 2011), contaminants such as siloxanes and ammonia in biogas obtained from vinasse are not expected.

For biogas burning in engines or boilers it is recommended a maximum of 80% relative humidity, easily obtained by biogas cooling, condensate removal and subsequent reheating. To comply with the Brazilian standard for biomethane, it must have dew point of -45ºC (at 1Atm), for what adsorption processes with alumina, silica gel or activated carbon or absorption with triethylene glycol or glycol should be carefully evaluated (ALLEGUE; HINGE, 2012).

The purpose of this section is to cover the main technologies employed to remove acid gases found in biogas (H_2S and CO_2). The removal or decrease of H_2S concentration is essential for the use of biogas for electricity and steam generation and the almost total removal of both H_2S and CO_2, is a necessary condition to obtain biomethane. This section is divided into processes to remove CO_2 and H_2S form biogas for biomethane production and biogas desulfurization processes for Otto cycle power generation.

2.4.1 H_2S

Hydrogen sulfide is flammable, colourless, reasonably soluble in various liquids, including water, which has a rotten egg odour and can be extremely harmful to human health, causing death in relatively low concentrations (CHOU, 2003). In concentration above approximately 100 ppm, it causes olfactory paralysis, giving the false impression that the risk has dissipated (KHANAL, 2008), for this reason, it is always recommended to use H_2S detectors in places where there is a possibility of existence of H_2S, such as biogas plants. Table 2-5: summarizes the effects of sulfur gas on humans.

Hydrogen sulfide (H_2S) corrodes tanks, pipelines and equipment such as valves, blowers, compressors and engines that contain metallic parts exposed to this gas, imposing high maintenance and operation costs on biogas plants. The reactivity of the hydrogen sulfide gas is amplified in the presence of moisture (WELLINGER; ANNA, 1999). Hydrogen sulfide is converted into sulfur oxides during combustion, contaminating lubricating oil from generator sets and causing damage to catalysts and heat exchangers (DEUBLEIN; STEINHAUSER, 2011; KHANAL, 2008).

Table 2-5: Hydrogen Sulfide: Established dose-effect relationships. Adapted from WHO (2003).

Concentration		*Effect*
mg/Nm³	*ppm*	
>700	*>494*	*Death*
>560	*>395*	*Breathing difficulty*
>140	*>99*	*Olfactory paralysis*
28	*20*	*Fatigue, loss of appetite, headache, irritability, dizziness.*
5 – 29	*3,5 – 20*	*Eye irritation*
7 – 14	*4,9 – 10*	*Increased blood lactate concentration, decreased oxygen uptake*
2,8	*2*	*Bronchial constriction in asthmatic individuals*
0,011	*0,008*	*Odor detection threshold*

After combustion, in contact with water, it forms extremely corrosive sulfuric acid, so special attention should be paid to the exhaust gas temperature of boilers and generator sets, especially working with some sort of heat recovery, so that condensation is avoided. Furthermore, the emission of sulfur oxides to atmosphere through the exhaust of thermal machines using high H_2S biogas is harmful to the environment, causing acid rain, among other effects (ALLEGUE; HINGE, 2014).

Sugarcane ethanol vinasse usually contains significant amounts of sulfur derived compounds, mainly sulfite to reduce the of sugarcane juice color and sulfuric acid in the treatment of yeast. In the anaerobic digestion process, sulfite and sulfate present in vinasse are converted to sulfide by sulfur-reducing bacteria (RIZZO; LEITE, 2004), as explained ahead in this work.

Biogas' sufide content will be dependent on the vinasse's COD, sulfate content, substrate degradability, the conversion efficiency of oxidized sulfur compounds as well as the reactor's operating pH and temperature. Sulfide content in biogas is normally expressed in parts per million (ppm), ranging from a few hundred parts per million for low sulfur substrates to few tens of thousands parts per million, for sulfur-rich substrates such as biogas from sugarcane ethanol vinasse (BARRERA et al., 2015; YASAR et al., 2015).

The reactor's operating pH requires attention, since the H_2S content in its gas phase is lower for higher reactor pH values, which allows its dissociation. At same time, the undissociated form of H_2S is toxic to the anaerobic community: at pH 7, 50% of sulfide is in its volatile, non-ionized form, potentially toxic and available to biogas contamination, while at pH 8, 91% of H_2S is dissociated, as Figure 2-10 shows. The increase of reactor's operating pH, within acceptable technical and economical limits, will reduce H_2S content in biogas (CIRNE et al., 2008).

The harmful effects on the anaerobic digestion of high sulfate wastewaters are the decrease of potential methane production by the competition of sulfur-reducing bacteria and methanogenic archaea by the same substrates; the likely inhibition of bacteria and archaea by hydrogen sulfide in its non-dissociated form; and the need of hydrogen sulfide removal from biogas for its use as energy source. In this section it will be discussed the means through which hydrogen sulfide concentration on biogas can be reduced.

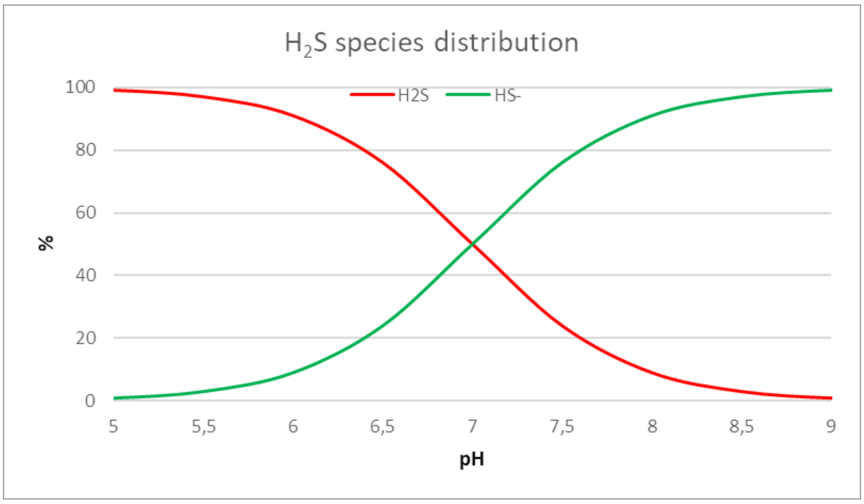


Figure 2-10: Species Distribution Diagram for H_2S in water.

2.4.2 Hydrogen sulfide removal from biogas

The removal or decrease of H_2S concentration in biogas, a process called desulfurization can occur in two locations in a biogas plant:

a) Internally to the anaerobic reactor where biogas is produced or
b) In additional equipment, external and independent of the anaerobic digestor, after biogas production.

H_2S removal methods can also be classified according to principles and technology employed, namely:

a) Physicochemical Processes: adsorption, absorption, precipitation by addition of salts/iron hydroxide.
b) Biological Processes: oxygen addition in the digester; biofilters, bioscrubbers and bio trickling filters.

The desulfurization technology to be employed will depend on the intended use of biogas, the raw biogas H_2S content, and the volume of biogas to be treated. In terms of intended use, for burning biogas in steam boilers the recommended H_2S levels are relatively high, turbines and microturbines can operate at even higher H_2S levels, possibly without the need of desulfurization systems (limited mainly by sulfur oxides emissions on exhaust gas) and generator sets (spark ignition engines) have more restrict requirement. Generator sets manufacturers usually establish different warranty conditions and maintenance programs depending on the quality of the gas where the H_2S content is an important parameter of consideration. For purposes of biomethane production, by ANP Resolution No. 8/2015 (ANP, 2015) must have a maximum of $10 mgH_2S/m^3$ at 20ºC, 1Atm (or 6.58ppm at 0ºC, 1Atm). Depending on the case, the H_2S removal process may require more than one step based on different technologies. It is also important to note that CO_2 removal processes for biomethane can also remove H_2S in some cases, which may work as H_2S main or polishing step.

Usual recommended limits for H_2S content depending on biogas use are summarized in Table 2-6 below:

Table 2-6: Usual H_2S limits, adapted from (ALLEGUE; HINGE, 2014)

Biogas Use	*Recommended H_2S content*	*Rem.:*
Biomethane	*6,58ppm (10mg/m³ to 20ºC, 1 Atm)*	*To comply to ANP nº8/2015*
Internal combustion engines	*<500ppm*	*Usually measured in mg/MJ or mg/kWh to compensate for different methane content in biogas*
Boilers, steam generators	*<1.000ppm*	
Turbines	*<10.000ppm*	
Microturbines	*Some models <70.000ppm* *usually <5.000ppm*	

2.4.2.1 Chemical Precipitation: Addition of iron salts/hydroxide

One of the ways to reduce the H_2S content in biogas is to reduce its concentration in the liquid phase, where the gas is originated, turning it into a non-volatile compound, a stable precipitate out of the aqueous phase. By the addition of compounds which react with aqueous H_2S to form a sulfur-based component which will not come off into the gas phase, the biogas H_2S content will decrease. Iron-based compounds such as iron chlorides or hydroxides have this property. Ferric chloride ($FeCl_3$) has good market offer and low costs (ALVES et al., 2004), and is available in aqueous solution, which facilitates application and handling (ALLEGUE; HINGE, 2014). The following equations represent the process:

$FeCl_2 + H_2S \rightarrow FeS\downarrow + 2HCl$ Equation 2-15

$2FeCl_3 + 3\ H_2S \rightarrow Fe_2S_3\downarrow + 6HCl$ Equation 2-16

$2Fe(OH)_3 + H_2S \rightarrow 2Fe(OH)_2\downarrow + S\downarrow + 2H_2O$ Equation 2-17

$Fe(OH)_2 + H_2S \rightarrow FeS\downarrow + 2H_2O$ Equation 2-18

Among the disadvantages of the process are the formation of sludge by precipitation of ferric sulfide, which leads to clogging of tanks and the high acquisition costs. Iron chlorides usage in large quantities leads to reactor pH drop by formation of hydrochloric acid (ALLEGUE; HINGE, 2014; ALVES et al., 2004; CIRNE et al., 2008).

The use of f iron chlorides is very effective for coarser H_2S removal off the liquid phase, however, it is not a stable process and is not indicated to obtain low levels of H_2S in the biogas, such as those required to obtain biomethane, and may be used in combination with other methods for removal of hydrogen sulfide from biogas. Obtaining 100 to 200ppm H_2S in biogas with this method has been reported in literature (ALLEGUE; HINGE, 2014). Systems based on chemical precipitation to reduce H_2S levels are considered to be of low capital and high operating costs (CHERNICHARO et al., 2011).

Given the high H_2S levels usually obtained in vinasse biogas, the use of iron chloride as the main control mechanism has limited applicability due to acquisition costs.

2.4.3 Biological desulfurization systems

The removal of hydrogen sulfide from biogas can be done by microorganisms by injecting controlled quantities of oxygen directly into the anaerobic digestor or in separate equipment. This process occurs in presence of so-called sulfide-oxidizing bacteria, most of them belonging to the *Thiobacillus* family. Through their metabolism, these bacteria oxidize sulfide to elemental sulfur or sulfate and generally do not require inoculation since they are ubiquitous. Oxygen injection, usually between 2% and 6% air in biogas, should be done carefully to avoid the formation of explosive mixture. The amount of oxygen injected will depend on the sulfur content on the biogas (PETERSSON; WELLINGER, 2009; SEADI et al., 2008; WELLINGER; ANNA, 1999).

Air addition may be a disadvantage if the biogas will be purified to biomethane. Nitrogen introduced to biogas stream and unreacted oxygen are components that are not removed by traditional purification processes. In this case, purified oxygen may be an alternative to minimize the problem (PERSSON, 2003; PETERSSON; WELLINGER, 2009).

The microorganisms of interest for the biological desulfurization of biogas are chemotrophic[3], they use CO_2 as a carbon source and inorganic sulfur as energy source. The H_2S degradation by these organisms occurs under aerobic conditions, in which oxygen is the electron acceptor. *Thiobacillus sp.* have the ability to grow under different conditions, even in some extreme cases, such as *Thiobacillus thiooxidans* which tolerate pH below 1 (SYED et al., 2006). Depending on the conditions, sulfide oxidation may be complete to sulfate (under excess oxygen) or incomplete to molecular sulfur (under limited oxygen supply) (CIRNE et al., 2008). Technologies based on aerobic desulfurization are attractive due to their simple design, low operating costs and reduced need for supplies (SOREANU; AL-JAMAL; BÉLAND, 2005).

2.4.3.1 Oxygen addition to anaerobic digestors

The introduction of micro-aerobic conditions in the digester to oxidize sulfide is one of the simplest methods used for H_2S removal from biogas, used in thousands of small-scale plants where gas is used to generate electricity and heat in Otto cycle engines (ALLEGUE; HINGE, 2014; CIRNE et al., 2008).

The addition of air in the digester by a small blower promotes the proliferation of sulfur oxidizing bacteria that form elemental sulfur and sulfate from sulfide and lodge on the inner surfaces of the reactor. Although in some cases the efficiency may be quite high, the recommended H_2S levels for the most common thermal machines are usually not reached (ALLEGUE; HINGE, 2014). Wood beams and rope nets are sometimes installed inside reactor to increase the support area for bacterial growth (ABATZOGLOU; BOIVIN, 2008; BEIL; HOFFSTEDE; HAHN, 2010). Additional care must be taken to avoid excessive oxygen dosing inside the reactor, reaching the explosive limit (ABATZOGLOU; BOIVIN, 2008).

The major disadvantage of this form of control of biogas H_2S content is precisely the introduction of oxygen inside an anaerobic reactor which can compromise methane formation, since methanogenic bacteria are strict anaerobic. Evidence of this is found in reports by Cirne (2008) and Khanal and Huang (2003) where significant COD removal by facultative bacteria under micro-aerobic conditions are describe (CIRNE et al., 2008; KHANAL; HUANG, 2003). High sulfate substrates, such as vinasse, should receive large amounts of oxygen for sulfide

---

[3] H_2S-degrading microorganisms can be autotrophic (chemoautotrophic or photoautotrophic) or myxtrophic. Autotrophic microorganisms use CO_2 as a carbon source and light or chemical energy from the oxidation of reduced compounds as an energy source. Mixotrophic ones can use organic carbon as a carbon source. Chemoautotrophic microorganisms can be strict anaerobes, microaerophils and facultative anaerobes, using, for example, nitrate as the final electron acceptor.

oxidation. Khanal and Huang (2003) report a significant reduction in methane formation from a substrate with 1000mg/L of sulfate in a reactor subjected to micro-aerobic conditions. The effect of oxygen becomes beneficial to methane production when increasing sulfate concentration to 5000mg/L, although methane production in this condition with aeration was significantly lower compared to the condition of lower sulfate concentration without aeration.

Air injection in the anaerobic reactor does not remove the sulfur from the reactor immediately, but forms sulfate or elemental sulfur that remain within the reactor and may, once again, form sulfide. Elemental sulfur forms deposits that can cause corrosion and imposes periodic maintenance on reactors for the removal of such deposits. In addition, this process does not handle H_2S peaks well, is difficult to control and introduces nitrogen (and the portion of oxygen that did not react with H_2S) to biogas, which limits or hinders its later use for biomethane production (ALLEGUE; HINGE, 2014; BEIL; HOFFSTEDE; HAHN, 2010). The nitrogen issue can in principle be solved by using a PSA unit to remove it from air used for desulfurization, although this strategy isn’t commonly used (BEIL; HOFFSTEDE; HAHN, 2010).

The addition of oxygen inside the anaerobic reactor may also alter the characteristics of anaerobic sludge and eventually impair its sedimentability (CIRNE et al., 2008).

2.4.3.2 Biological desulfurization external to the digester

In these processes, sulfide contained in biogas is biologically oxidized to sulfate and elemental sulfur in an external column downstream of the anaerobic reactor.

These columns are usually packed to provide increased contact between biogas and process liquid, also providing surface where the sulfur oxidizing bacteria can grow, forming a biofilm (ALLEGUE; HINGE, 2014). Biogas, with the addition of air, and liquid flows through the column are put in contact, usually in counter current (PETERSSON; WELLINGER, 2009). H_2S is absorbed by the scrubbing liquid and, in contact with the bacteria responsible for oxidation and in the presence of oxygen contained in the admitted air, is converted to elemental sulfur or sulfate, which is dissolved in the process liquid, thus absorption and biological oxidation occur in the same column (CHERNICHARO et al., 2011).

The process has the drawback of adding N_2 to desulfurized biogas which can be minimized by the use of purified oxygen in addition to excess oxygen that has not reacted with H_2S (BEIL; HOFFSTEDE; HAHN, 2010; PETERSSON; WELLINGER, 2009).

These systems also apply to desulfurization of off-gas resulting from biogas purification systems.

2.4.3.2.1 Biofilters and Biotrickling Filters

Biofilters and biotrickling filters are reactors operating in three phases, solid, liquid and gaseous, consisting of columns filled with organic or inert support material to the growth of the biofilm-forming sulfur-oxidizing bacteria and through which the biogas to be treated is passed and in which, continuously or discontinuously, an aqueous solution containing nutrients is sprayed (SYED et al., 2006). H_2S is transferred from the gas phase to the liquid phase and is absorbed by biofilm (ALLEGUE; HINGE, 2014; PANTOJA FILHO, 2008) in which the biological sulfur transformations are processed as shown in Equations 2-19 and 2-20 (COLTURATO, 2015; ZICARI, 2003).

$$HS^- + 1/2\ O_2 + H^+ \rightarrow S_0 + H_2O \qquad \text{Equation 2-19}$$

$$S_0 + H_20 + 1/2\ O_2 \rightarrow SO_4^{-2} + 2H^+ + H_2O \qquad \text{Equation 2-20}$$

It is an aerobic process in which oxygen is usually obtained by injecting air along with biogas at the column inlet (ALLEGUE; HINGE, 2014).

Allengue (2014) distinguishes systems by the nature of the packing material, being the organic nature for biofilters and the inert nature for biotrickling filters. Syed (2006) considers that the difference stems from the fact that biotrickling filters continually receive process liquid sprayed into the column, although systems that work inert support material and have discontinuous percolation are commercially available, and do not fully fit to neither definitions.

Process liquid pH may drop due to sulfate production within the reactors, although this usually does not cause process performance to drop, given the acidophilic characteristics of some species, such as *Thiobacillus thiooxidans*, whose optimum pH of operation is within 2.0 and 3.5 (SOREANU; AL-JAMAL; BÉLAND, 2005; SYED et al., 2006; ZICARI, 2003). The process liquid containing sulfate and elemental sulfur is discarded and replaced as its pH falls below established levels (ALLEGUE; HINGE, 2014; PETERSSON; WELLINGER, 2009).

The desired characteristics in the support material are: high surface area to volume ratio, low density, low head losses, good moisture retention characteristics, ability to support the development and provide nutrients to the bacterial community in the biofilm, being durable in its work environment, neutral or alkaline character and buffering capacity, among others (PANTOJA FILHO, 2008; ZICARI, 2003). Zicari (2003) points out that there is a compromise solution in the selection of the support material for microorganisms, while organic products provide good moisture retention, buffering capacity and nutrient source, they quickly degrade in acidic conditions usually found (and should be replaced with certain frequency) and have higher head losses.

The amount of air to be injected into the system varies according to the biogas H_2S content, the final product to be obtained (elemental sulfur or sulfate) and the desired amount of oxygen remaining in the biogas after its passage through the desulfurization unit. The last two conditions are closely related, since excess air tends to produce sulfate and lack of oxygen (or excess H_2S) tends to produce elemental sulfur (ZICARI, 2003). Production of elemental sulfur can cause fouling problems in the support media, generate preferential pathways and column clogging, leading to cleaning procedures.

These systems provide low capital and operating costs, because they usually work at ambient pressure and temperature, low electricity consumption and do not require chemical supplies, at same time provide better control than the simple air injection in the digesters (BEIL; HOFFSTEDE; HAHN, 2010; COLTURATO, 2015). In many cases nutrients for sulfur-oxidizing bacteria can be obtained by the internal recycling of nutrients from dead cells (PANTOJA FILHO, 2008).

There are several companies in the market supplying biological desulfurization systems as described in this item. Commercial-scale projects, operating with up to 50,000ppm of biogas H_2S and loads of up to 5,500 kg/h with 90-99% H_2S removal efficiencies are described in literature (ALLEGUE; HINGE, 2014).

2.4.3.2.2 Bioscrubbers

Some biological desulfurization systems are actually configured as two reactors: an absorption tower with alkaline process liquid, usually with the addition of caustic soda, which absorbs H_2S and a second reactor, aerated and biological, where the process liquid is sent after absorption and where the production of mostly elemental sulfur occurs (small portion of the sulfur is completely oxidized to sulfate) by biological means, being called *"Bioscrubbers",* (ALLEGUE; HINGE, 2014; BEIL; HOFFSTEDE; HAHN, 2010). In these systems, nutrient addition is required, and the pH is continuously monitored, excess biomass as well as elemental sulfur are continuously removed from the process. In the aerobic biological reactor, sodium-bound sulfur is oxidized to elemental sulfur and sodium hydroxide is partially regenerated, so that the soda required for its operation is lower than the used by strict chemical absorption desulfurization systems. The regenerated solution is recirculated to the absorber (ALLEGUE; HINGE, 2014; PANTOJA FILHO, 2008; SYED et al., 2006).

Since air is introduced only in the biological regeneration process, N_2 and O_2 will not be present in the biogas (SYED et al., 2006). Commercial systems reducing H_2S content from 20,000ppm to 10 or 100ppm with flow rates of up to 2,500m³/h are reported, some manufacturers claim more than 99% H_2S removal by this process (ALLEGUE; HINGE, 2014). Consumption of caustic soda is the main disadvantage of bioscrubbers.

Figure 2-11 shows generic arrangements of biological desulfurization systems external to anaerobic reactors.

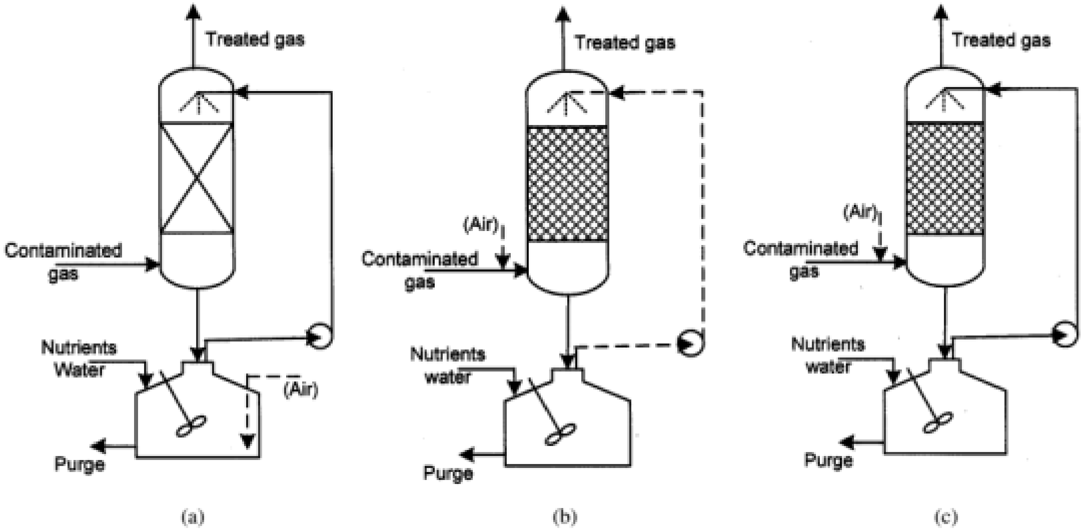


Figure 2-11: Biological desulfurization arrangements: a) bioscrubber, b) biofilter, c) biotrickling filter. Source: (SYED et al., 2006)

2.4.4 Adsorption

Adsorption processes are based on the adhesion of H_2S on the surface of a solid material (the adsorbent) when biogas flows through it. The absorbent retains H_2S molecules while allows the passage of other components, such as methane. The adsorbents are usually porous material with high surface to volume ratio, which improves the contaminant removal capacity (ONG; WILLIANS; KAFFKA, 2014). The capture can happen through weak intermolecular forces, by physically trapping compounds or by chemical reaction with the adsorbent material. The adsorbent material becomes saturated during the operation and must be discarded or regenerated. The process is simple and well-known, although recommended for smaller H_2S loads (up to 200kg/day). The process physical arrangement basically consists of columns filled with the adsorbent through which contaminated gas flows. Two columns can be used in parallel for continuous operation. In this case, when the first column’s material is replaced or regenerated the second column is used (ABATZOGLOU; BOIVIN, 2008; ALLEGUE; HINGE, 2014; ZICARI, 2003).

2.4.4.1 Iron oxide adsorption

One of the oldest and best-known materials used for biogas H_2S removal is the impregnation of wood chips with iron oxides, called iron sponge. The hydrogen sulfide gas passing through this material undergoes a reaction and becomes iron sulfide. In contact with oxygen, iron sulfide reacts by converting to iron oxide again and elemental sulfur (ZICARI, 2003).

The filter bed is usually composed of wood chips primarily impregnated with ferric oxide hydrates (Fe_2O_3) (ZICARI, 2003) which provides greater contact area to volume ratio, lower weight, and lower pressure losses compared to iron swarf filings (MERCADO, 2010). Material regeneration may occur by the continuous intake of small amount of air with the biogas, causing the iron sulfide to continually convert to elemental sulfur, but the bed will inevitably become clogged. This method also involves introducing nitrogen to biogas (ALLEGUE; HINGE, 2014; ZICARI, 2003).

For regeneration of the absorbing material when out of operation, one may opt for continuous passage of air or laying the material in the soil in defined thickness layers and continuously humidify for a few days. The disposal or regeneration process must be done with care, as the regeneration reaction is highly exothermic, which may cause material combustion (ALLEGUE; HINGE, 2014; ZICARI, 2003).

At each regeneration, the material loses approximately 1/3 of its effectiveness, so that only two or three regenerations are employed, after which the material must be discarded. The used material disposal may be problematic, not only due to combustion hazards, but, depending on local environmental legislation, the material may be considered hazardous. It is convenient that the gas admitted to the iron oxide purification system is not completely dry, as moisture contributes to its performance, although condensation should be avoided (ALLEGUE; HINGE, 2014; MERCADO, 2010; ZICARI, 2003).

Because it is well-known technology, design parameters have already been perfectly established. Iron oxide H_2S adsorption has high efficiency and selectivity in H_2S removal (up to 99.98% removal), consists of simple systems which operate at low pressure and temperature. In contrast, the difficulties and risks associated with the regeneration and disposal of the material, as well as the high operating cost, especially for high sulfur loads (result of continuous adsorbent material replacement) are negative points. Several companies market proprietary products and formulations with claims of better performance.

Equations 2-21 and 2-22 show H_2S reactions with iron oxide and its regeneration.

Purification:

$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O$ (ΔH= -22 kJ/g-mol H_2S) Equation 2-21

Regeneration:

$2Fe_2S_3 + O_2 \rightarrow 2Fe_2O_3 + 3S_2$ (ΔH= -198 kJ/g-mol H_2S) Equation 2-22

2.4.4.2 Activated Carbon Adsorption

Activated carbon is widely used in biogas plants where low H_2S content is required and is used mainly for polishing processes or under low flow and/or low H_2S content of raw biogas (BEIL; HOFFSTEDE; HAHN, 2010; COLTURATO, 2015; ZICARI, 2003). There are three common types of activated carbon: Non-impregnated, impregnated and impregnated with catalysts. When impregnated, they have higher adsorption rates, promoting the oxidation of sulfide to elemental sulfur, which is the product effectively adsorbed (ABATZOGLOU; BOIVIN, 2008; MUÑOZ et al., 2015).

Muñoz et. al., (2015) present research results relating the acidity of the medium to the performance of H_2S adsorption by non-impregnated activated carbon, in which pH above 5 promotes considerable performance increase (MUÑOZ et al., 2015). Several substances are used to impregnate activated carbon, but only potassium iodide (KI) and potassium permanganate ($KMnO_4$) allow the H_2S oxidation to elemental sulfur without introducing oxygen to the gas stream, which gives the process an advantage if the biogas will be used for biomethane production. Other substances used in the impregnation of activated carbon, such as sodium bicarbonate (NaHCO3), sodium carbonate (Na2CO3), sodium hydroxide (NaOH) and potassium hydroxide (KOH) must have the presence of water and oxygen for the conversion of sulfide to elemental sulfur (PETERSSON; WELLINGER, 2009).

The process operates at low pressure and temperature from 50º to 70ºC, humidity preferably up to 90%, without condensation, and oxygen at 4:1 stoichiometric ratio with H_2S. Activated carbon desulfurization systems are usually designed for a 4,000 to 8,000-hour media exchange cycle (ALLEGUE; HINGE, 2014; MUÑOZ et al., 2015; WELLINGER; ANNA, 1999). On-site regeneration is possible for impregnated systems, but they are difficult and risky to execute due to fire hazard. The discarded product after use may be considered hazardous and require proper disposal procedure. Although Activated carbon desulfurization systems are simple in terms of construction and operation, the frequent exchange of expensive active material impose high operational costs, being recommended for polishing situations or at low H_2S loads (ABATZOGLOU; BOIVIN, 2008; ALLEGUE; HINGE, 2014; BEIL; HOFFSTEDE; HAHN, 2010).

2.4.5 Chemical absorption by Iron Chelates

H_2S can be absorbed by iron chelate solutions, in this process Fe^{3+} ions are reduced to Fe^{2+} while H_2S is oxidized to elemental sulfur. The solution is regenerated in a second reactor by the addition of oxygen and water (ALLEGUE; HINGE, 2014; PETERSSON; WELLINGER, 2009). This process has high efficiency and selectivity in H_2S removal under ambient temperature and low pressure conditions and produces as by-product elemental sulfur which is stable and may have commercial value (COLTURATO, 2015; FRARE et al., 2010; MUÑOZ et al., 2015). The process was originally developed for the natural gas industry and appears to be best suited for high gas flow rates or high H_2S content, the reagent can be almost fully regenerated and the system produces biogas at 1-10ppm H_2S (MUÑOZ et al., 2015).

According to Horikawa (2004), EDTA (ethylenediaminetetraacetic acid) is the most used agent. Reactions with Fe/EDTA (Iron/ Ethylenediaminetetraacetic Acid) and H_2S are processed as shown in Equations 2-23 to 2-26 (FRARE et al., 2010; HORIKAWA et al., 2004).

H_2S absorption:

$$H_2S(g) \rightarrow H_2S(aq) \qquad \text{Equation 2-23}$$

$$H_2S(aq) + 2Fe^{3+}/EDTA \rightarrow S\downarrow + 2H^{+} + 2Fe^{2+}/EDTA \qquad \text{Equation 2-24}$$

Iron chelate regeneration:

$$O_2(g) \rightarrow O_2(aq) \qquad \text{Equation 2-25}$$

$$O_2(aq) + 4Fe^{2+}/EDTA + 2H_2O \rightarrow 4Fe^{3+}/EDTA + 4OH^{-} \qquad \text{Equation 2-26}$$

Product regeneration happens by introducing air into a column at ambient temperature and pressure, promoting the oxidation of Fe^{2+} to Fe^{3+}, giving the reagent the condition to perform its function in the absorption column again.

Figure 2-12 shows a diagram of the H_2S removal process by iron chelates.

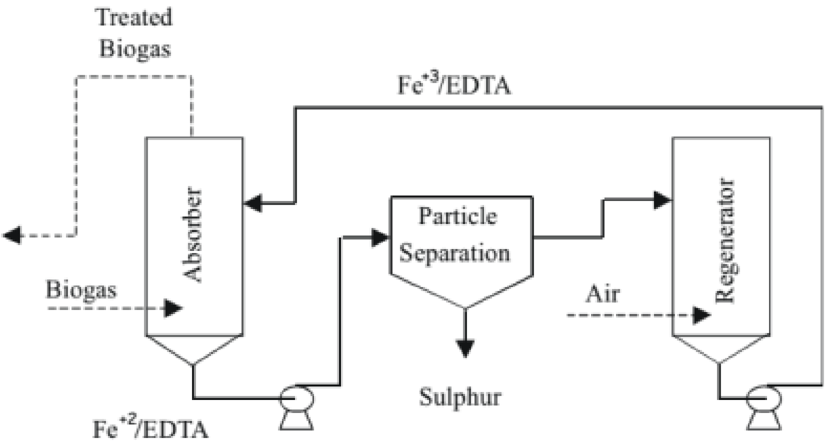


Figure 2-12: Simplified iron chelate process diagram. Source: (HORIKAWA et al., 2004).

2.5 Biomethane Production - Biogas Purification

2.5.1 Physicochemical Systems - Absorption

Absorption processes occur by the difference in solubility of biogas components in absorbing liquid, shown in Figure 2-13 for water.

The absorption process usually occurs in a counter-current column, with biogas being fed from the bottom of the column and the washing liquid from the top of the column. The absorption processes may be purely physical, based solely on the difference in solubility of the different biogas components in the absorber liquid, or may be chemical, where reactions transform contaminants into more soluble forms in the absorber liquid, which is later regenerated.

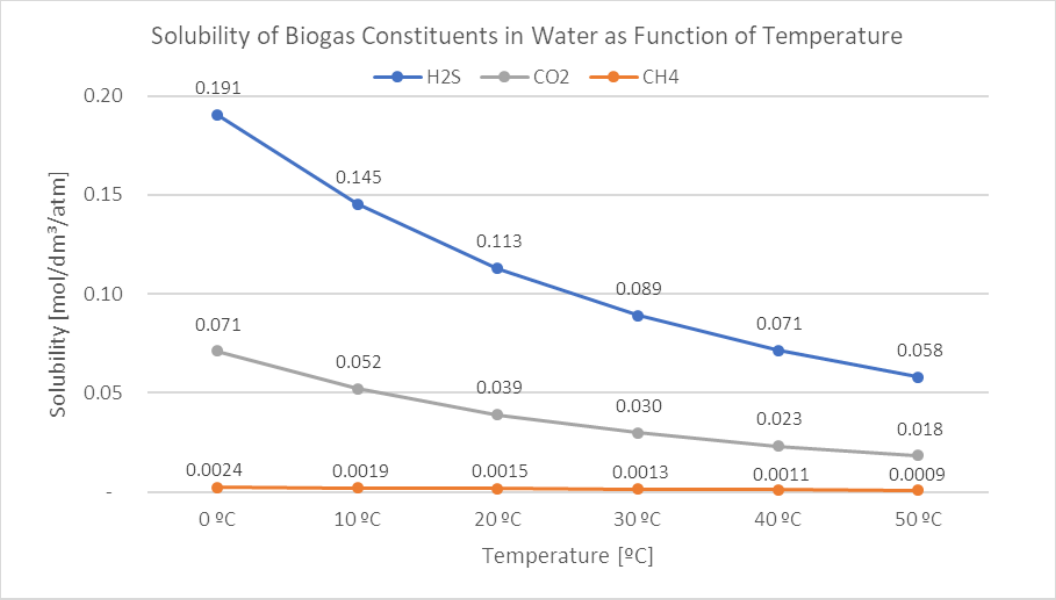


Figure 2-13: Solubility of the main constituents of biogas in water. Source: Sander (1999)

The columns are filled with inert material that promotes larger contact area between gas and liquid. With the transfer of the most soluble contaminants into the liquid phase (usually acid gases such as CO_2 and H_2S) biogas exits from the top of the column largely free of one or both contaminants. The absorbing liquid, containing the contaminants in their original form or after the reaction with additives contained therein, is removed from the base of the column and sent to a stripping/desorption stage, where contaminants are released to a new gas stream.

2.5.1.1 Water Scrubbing

Water scrubbing is the most common process used for biogas upgrading to biomethane (STAMBASKY, 2017). This process is based on the difference in water solubility of H_2S, CO_2 and methane. Water is circulated in a column filled with high surface to volume ratio packing media under controlled pressure and temperature, through which biogas also circulates, usually in counter current. H_2S and CO_2 are simultaneously absorbed by the liquid stream, since both are more soluble in water than methane.

Biogas, mostly free of H_2S and CO_2, leaves the absorption column from the its top. Water with dissolved CO_2 and H_2S is sent to a desorption column, where H_2S and CO_2 are released and transferred back to the gas phase in a new gas stream called “off-gas”. Before the desorption column, water passes a flash tank, in order to minimize methane losses. The emitted gaseous stream released in the desorption column must be further treated to avoid the emission of reduced sulfur (H_2S) to the atmosphere, which can be accomplished by a biological system such as biofilter, biotrickling filter or bioscrubber. Normally the water circulates in a closed circuit, and a small part of it is lost in the desorption column. In particular situations, such as effluent treatment plants, water may be used only once without the adoption of closed circulation.

This process is only applied when the goal is biomethane production, it is not used for selective H_2S removal. Biogas should be compressed to 5-10 Bar to increase H_2S and CO_2 solubility in the water. Temperature is also important in the process as gas solubility increases as temperature drops. The absorption water cooling process can consume significant amounts of energy. Sulfate formation in the desorption column may acidify the wash water and cause corrosion of system components. Foaming and microbial growth are other problems that may occur (BAUER et al., 2013a).

In some circumstances high H_2S content of 20,000ppm or more may be allowed in water scrubbing systems, but careful selection of biogas blower and equipment materials should be realized (PRESSURE WORX, 2018). Figure 2-14 shows a diagram illustrating the process.

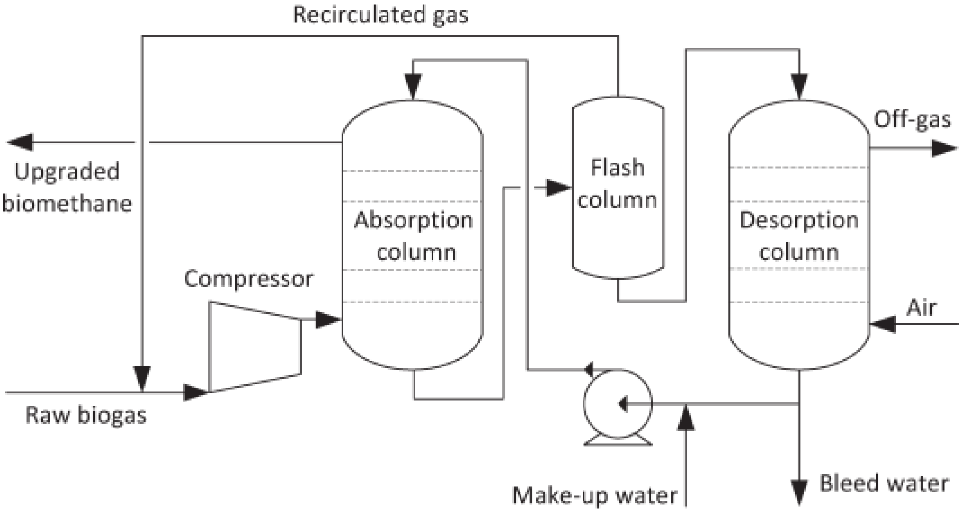


Figure 2-14: Simplified diagram of the water scrubbing process. Source (BAUER et al., 2013a)

2.5.1.2 Absorption in organic solvents

This is a similar process to absorption in water, except that instead of water, a chemical in which CO_2 and H_2S have greater solubility is used, with no reactions occurring between the absorbing liquid and the absorbed products. The process can be quite selective over H_2S and CO_2 and requires less heat for regeneration of the absorbing liquid when compared to amines. Among absorbing liquids, polyethylene glycol dimethyl ether or refrigerated methanol are used (to decrease its vapor pressure and thus product losses) in commercial processes. In these processes, water is also removed and methane losses are relatively low (KORENS; SIMBECK; WILHELM, 2002).

The H_2S and CO_2 solubility in organic solvents is much higher than in water, causing the absorber volumes to be circulated in the system to be significantly lower, which entails lower energy consumption compared to water absorption systems. When operating as a biomethane purification system, this process usually has H_2S removed by other methods previously (BAUER et al., 2013a; BEIL; HOFFSTEDE; HAHN, 2010), but this arrangement should be evaluated for H_2S content and final biogas use. This technology is best suited for higher gas flows to be treated and selective H_2S removal has not yet proved competitive (ALLEGUE; HINGE, 2014).

Most biomethane plants using this process employ the Genosorb® 1753 absorber, minor solvent replacement is required to compensate for losses due to product vaporization and there is no water consumption (BAUER et al., 2013a). The pressure in the absorption column is usually about 8 bar and the required desorption temperature is 50°C. Final product biomethane concentrations in the 93-98% range can be obtained and methane losses are around 2%, which may require special offgas treatment. Nitrogen and oxygen are not removed by this process, so the use of air in biological desulfurization systems for biogas pretreatment should be carefully evaluated (BEIL; HOFFSTEDE; HAHN, 2010).

Figure 2-15 shows a diagram illustrating the process.

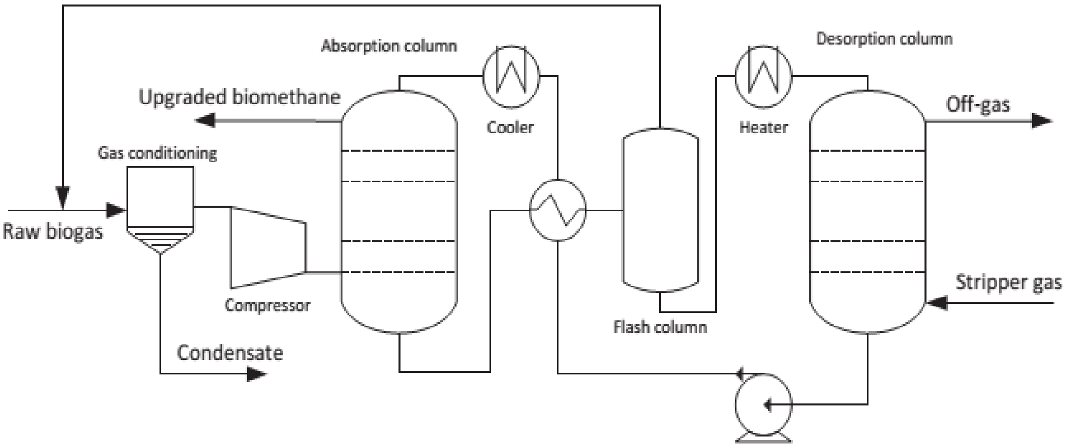


Figure 2-15: Simplified diagram of organic solvents process. Source (BAUER et al., 2013a)

2.5.1.3 Chemical Absorption by Amines

Process employed in the natural gas industry and synthesis gas treatment plants which is based on the creation of weak chemical bonds between acid gas components (CO_2 e H_2S) and amines. Primary (usually monoethanolamine - MEA), secondary (usually diethanolamine - DEA) and tertiary (usually methyldiethanolamine - MDEA) amines are employed, which form gradually weaker bonds with the acidic gas components in the presented order (KORENS; SIMBECK; WILHELM, 2002). Currently the most commonly applied amine is a mixture of MDEA with piperazine (PZ), called activated MDEA or aMDEA (BAUER et al., 2013a; HOYER et al., 2016).

One of the advantages of amines is their selectivity for reactions with H_2S and CO_2: while the reaction with the former is virtually instantaneous, the latter is much slower and dependent on the amine used (CO_2 absorption through MEA is 1,000 times faster than through MDEA), making selective H_2S removal possible (KORENS; SIMBECK; WILHELM, 2002). This is especially relevant in the Natural Gas industry to allow sulfur recovery units operations.

Korens et al., (2002) report two cases in the synthesis gas industry with MDEA-based for acid gas removal in which one achieved 30% CO_2 removal while reducing 7,800 ppm to 4ppm H_2S, and the other obtained 100-200ppm H_2S with only 15% CO_2 removal. Korens et. al.,

(2002) also report a case in the natural gas industry that CO_2 removal was 30% while H_2S removal was 99%.

Tertiary amines have the highest H_2S selectivity, they are the most stable concerning degradation and produce the lowest corrosive effects. The bonds between the amine and CO_2 and H_2S are broken by supplying heat to the solution, implying significant process thermal demand, being indicated from 120ºC to 150ºC (BAUER et al., 2013a). Methane losses in the process of removing H_2S by amines are quite small and electricity consumption is reduced compared to other methods as it works at lower pressures on the absorption column (1-2 Bar) and desorption column (1.5-3 Bar) (BAUER et al., 2013a). Persson (2003) recommends H_2S removal before the CO_2 removal process by amines, since the energy required for absorbent regeneration is higher when reacting with H_2S (PERSSON, 2003). In addition to possible corrosion, amine losses and foaming are the most common problems (BAUER et al., 2013a).

Figure 2-16 shows a diagram illustrating the amine process.

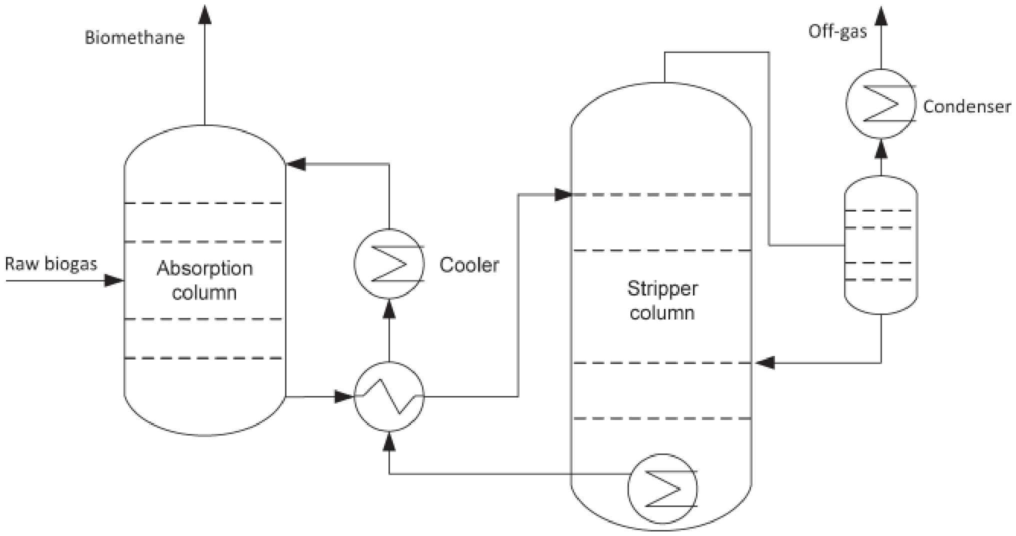


Figure 2-16: Simplified diagram of amines process. Source (BAUER et al., 2013a)

2.5.2 PSA (Pressure Swing Adsortion)

PSA is one of the most common biogas purification process (STAMBASKY, 2017). The process can be described simply as follows: crude biogas is compressed at relatively high pressures (up to 10 Bar, usually 7 to 8 Bar) and introduced into a column where adsorbent material retains CO_2, but does not retain CH_4, when the column material is saturated with CO_2, pressure is relieved and CO_2 is released from the adsorber leading to an offgas stream (BAUER et al., 2013a). For continuous biomethane production, systems are composed of a series of columns, usually 4 or 6, operating simultaneously in the different process phases:

pressurization, feed, blowdown and purge (ALLEGUE; HINGE, 2014; BAUER et al., 2013a; GRANDE, 2011).

The adsorbent is a high porosity solid material with large surface area. Molecular sieves of carbon are usually commercially employed, but activated carbon, zeolites, titaniosilicates are also employed (GRANDE, 2011). In addition to CO_2, water, hydrogen sulfide gas, nitrogen and oxygen can also be separated by the PSA process, however it is recommended that desulfurization be carried out before the purification unit, as sulfide can irreversibly contaminate some adsorbing materials. Zeolites are not recommended for operation with moisture-containing biogas (BEIL; HOFFSTEDE; HAHN, 2010; GRANDE, 2011).

In more sophisticated cycles there are pressure equalization steps between columns in different stages which are of great importance for reducing process methane losses, usually in range of 3 to 12%. A pressure equalization step is capable of increasing methane recovery from 79.4% to 86.3% obtaining 97.1% purity biomethane. Equalization steps increase biomethane production, but at the expense of increased capital and equipment complexity (GRANDE, 2011). A compromise solution is typically achieved with four column systems and two pressure equalization processes (Wellinger 2009 *apud* Grande 2011).

Figure 2-17 shows a diagram illustrating the PSA process.

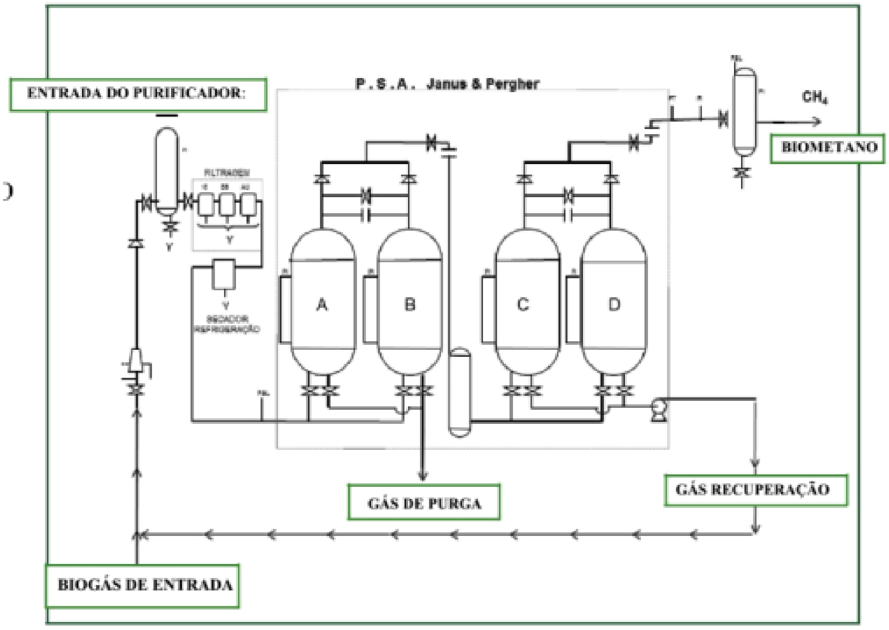


Figure 2-17: PSA simplified Diagram. Source: Janus & Pergher

Adler (2014) and IRENA (2017) bring comparative costs of implementing biogas purification systems to biomethane, presented in Figure 2-18 below.

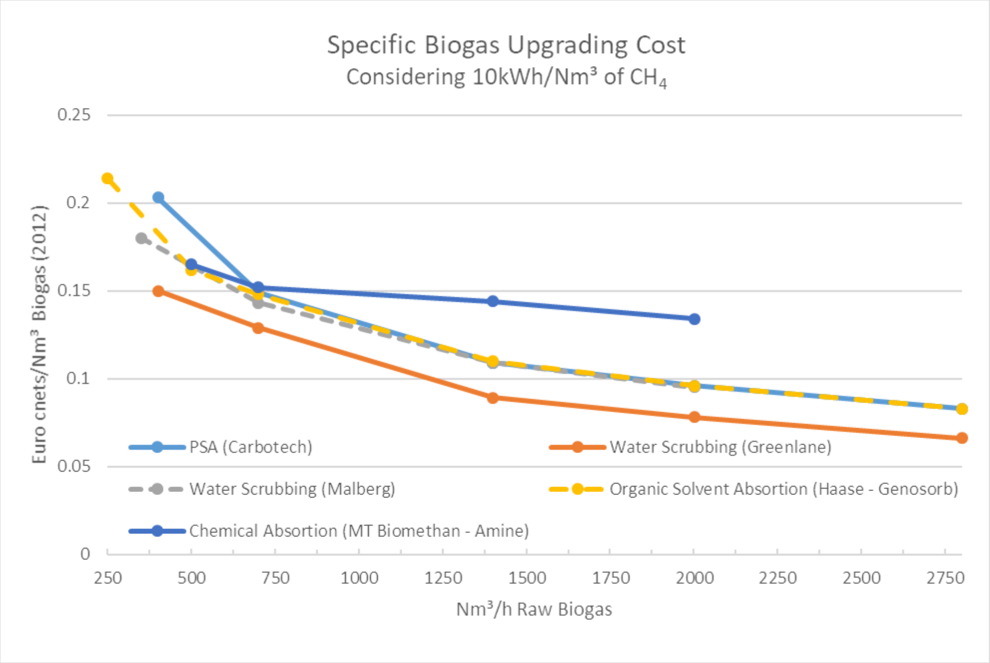


Figure 2-18: Specific cost of biogas purification to biomethane as a function of the scale of the project and the technology employed. Source: (ADLER et al., 2014; IRENA, 2017).

Table 2-7 summarizes data from biogas purification systems.

Table 2-7: Comparison of biogas purification technologies, self-elaboration based on data from (ALLEGUE; HINGE, 2014; BAUER et al., 2013a; BIEL et al., 2013; FRARE et al., 2010; IRENA, 2017).

	PSA	*Water absorption*	*Physical absorption*	*Chemical Absorption (amines)*
Electricity kWh/Nm³ biogas	*0.19-0.25*	*0.17-0.30*	*0.20-0.33*	*0.06-0.15*
Regeneration Temperature	*-*	*-*	*40-80ºC*	*110-160ºC*
Thermal Demand (kWh_{th}/Nm³ biogas)			*0.3*	*0.5-0.8*
Water L/Nm³ biogas	*0*	*0.04-0.4*	*0*	*0.03*
H_2S inlet (Max.)		*300-20,000*		*300ppm*
Fine Desulfurization Required on Inlet	*Yes*	*No*	*No*	
Methane Losses	*1-10%*	*0.5-2%*	*1-4%*	*0.1-0.2%*
Operating pressure	*4-10 Bar*	*4-10 Bar*	*4-8 Bar*	*0.1-4 Bar*
Operation and maintenance			*2-3% of CAPEX; Absorbent replacement*	*Amine: 0.00003 kg/Nm3*

Table 2-8 presents biomethane specifications in various countries.

Table 2-8: Biomethane specs in some countries and regions of the world. Adapt from de (ALLEGUE; HINGE, 2014)

Country / Characteristic	Austria	France	Germany	Netherland	Spain	Sweden	Switzerland	British Columbia	California	Michigan	Brasil North	Brasil Other Areas
HHV (MJ/Nm³)	*38.5–46.1*	*38.5–46.1 (H gas) 34.2–37.8 (L gas)*	*30.2–47.2*	*31.6–38.7*			*38.5–47.2 (limited injection)*		*36.9–42.8*		*34.0 - 38.4 At 20ºC*	*35.0 - 43.0 At 20ºC*
CH_4 (%)	*> 96*			*> 80*	*> 95*	*97±1* (1) *97±2* (2)	*> 96 (unlimited) > 50 (limited)*	*> 95.5*		*> 93.5*	*>90.0*	
CO_2 (%)	*< 2*	*< 2.5 <11.3* (3)	*< 6*	*< 6 (< 10–10.3 para rede regional)*	*< 2.5*	*< 3*	*<6 (unlimited) <4 (limited)*	*< 2*	*3*	*<3.0*	*<3.0*	
$CO_2+O_2+N_2$ (%)						*< 4* (1) *< 5* (2)			*4 (incl. H_2 and CO)*		*<10.0*	
H_2 (%)	*< 4*	*< 6*	*< 5*	*< 12*	*< 5*	*< 0.5*	*< 4*		*0.1*			
O_2 (%)	*< 0.5*	*< 0,01 3 %* (3)	*< 3*	*< 0.5*	*< 0.01 < 0.3* (3)	*< 1*	*< 0.5*	*<0.2*	*< 0.2*	*<3*	*<0.8*	
Water max. (mg/Nm³)				*< 32*		*< 32*		*< 65*		*No condensation*		
Dew Point (°C)	*< -8 at 40 bar*	*< -5 at max. pipe pressure*	*Soil Temperature*	*< -10 at 8 bar*	*< +2 at 70 bar*	*< T Amb. – 5 < -9 at 200 bar*	*-8 at max. pipe pressure*				*-39 (also in NE Brazil)*	*-45*
Total Sulfur (mgS/m³)	*< 10*	*< 30*	*< 30*	*< 45*	*< 50*	*< 23*	*<30*		*265*		*<70*	
H_2S	*< 5 mg/m³*	*< 5 mg/m³ (H_2S+COS)*	*< 5 mg/m³*	*< 5 mg/m³*	*< 15 mg/m³ (incl. COS)*	*< 10 ppm = < 15.2 mg/m³*	*< 5 mg/m³*	*4.3 ppm*	*88 mg/m³*	*4.1ppm*	*<10 mg/m³*	
Ammonia	*Technically Free*	*< 3 mg/m³*	*< 20 mg/m³*	*< 3 mg/m³*	*< 3 mg/m³*	*< 20 mg/m³*	*< 20 mg/m³*		*< 0.001 mol.%*			
Siloxane	*< 10 mg/m³ silicon total*			*< 5 ppm*	*< 10 mg/m³*				*Free or < 0.1 mgSi/m³*		*0,3 mgSi/m³*	
Particulate	*Technically Free*	*< 5 mg/Nm³*		*Technically Free*	*Technically Free*	*< 1 µm*	*Technically Free*		*Free*		*Filter 0,2 µm at producer; 1,0 µm at retailer*	
(1) Type A: biogas as vehicle fuel – Engines without lambda control; (2) Type B: biogas as vehicle fuel – Engines with lambda control; (3) Under specific conditions												

2.6 Vinasse

During the ethanol production process, in the distillation stage, the wine (fermented must) is separated into three components: secondary ethanol, phlegm and vinasse. The phlegm is sent to a second column, where hydrated ethanol, fusel oils and phlegmasse are separated. The residue from the first distillation column is called vinasse. CETESB (São Paulo State Environmental Agency) defines vinasse simply as “liquid derived from the distillation of wine resulting from the fermentation of sugarcane juice or molasses” (CETESB, 2015).

Vinasse is a liquid with colour that varies from pale yellow to reddish brown, generated at high temperature (natural requirement of the distillation process), which contains large amounts of salts and organic matter, which endows it with high polluting potential. It is generated in large volumes, from 8 to 12 litres of vinasse per litre of ethanol. Its physicochemical characteristics, as well as its production volume, vary widely, depending on some characteristics of the process that originated it, such as must (sugarcane juice, molasses or mixed), alcohol content of the wine, type of heating in the distillery (direct or indirect steam), among others. It is also commonly called in Portuguese “vinhaça”, “vinhoto”, “restilo” and “garapão”. In English, it can also be called “stillage” (ELIA NETO et al., 2009).

The disposal of vinasse became a point of environmental attention with the Proalcool[4] program and the rise of renewable fuel production, given its high polluting potential and possible disastrous consequences of its improper disposal. Until the late 1970s vinasse was disposed directly in waterbodies or in locations called “sacrifice areas”. With the ban on the discharge of vinasse into waterbodies and the limitation, and subsequent prohibition, of the use of sacrifice areas, the practice of fertigation, the application of *in natura* vinasse in the sugarcane fields, was developed following technical criteria to prevent damage to the water table, the soil and the crop itself (CORAZZA; SALLES-FILHO, 2000; GORDINHO, 2010).

In 2005, CETESB published the regulation number 4231, which regulates the application of vinasse to agricultural fields in São Paulo state, based on parameters such as vinasse composition (especially potassium) and soil characteristics, among others, to define the maximum quantities of vinasse to be applied per area (CETESB, 2015). Compared to other

---

[4] The National Ethanol Program, known as Proalcool, was created in 1975 by Brazilian federal government to reduce the country’s dependence on imported fossil fuels and resulted in a 5.6 fold increase in ethanol production in five years, from 600 million litres in 1975 to 3.4 billion litres in 1979.

solutions to vinasse disposal, fertigation is the least expensive, nevertheless implies in very significant expenses for the distilleries, reaching R$7.80/m³ applied to the crop in some cases (FERMENTEC, 2016).

Fertigation promotes the increase of sugarcane productivity, presenting itself as an interesting mechanism of nutrient recycling for the crop, especially potassium, given its high concentration in vinasse and its large demand for sugarcane development (ELIA NETO et al., 2009; PENATTI, 2007; UNESP, 2007).

Figure 2-19 below shows the vinasse to ethanol ratio of production according to Elia Neto et al., (2009).

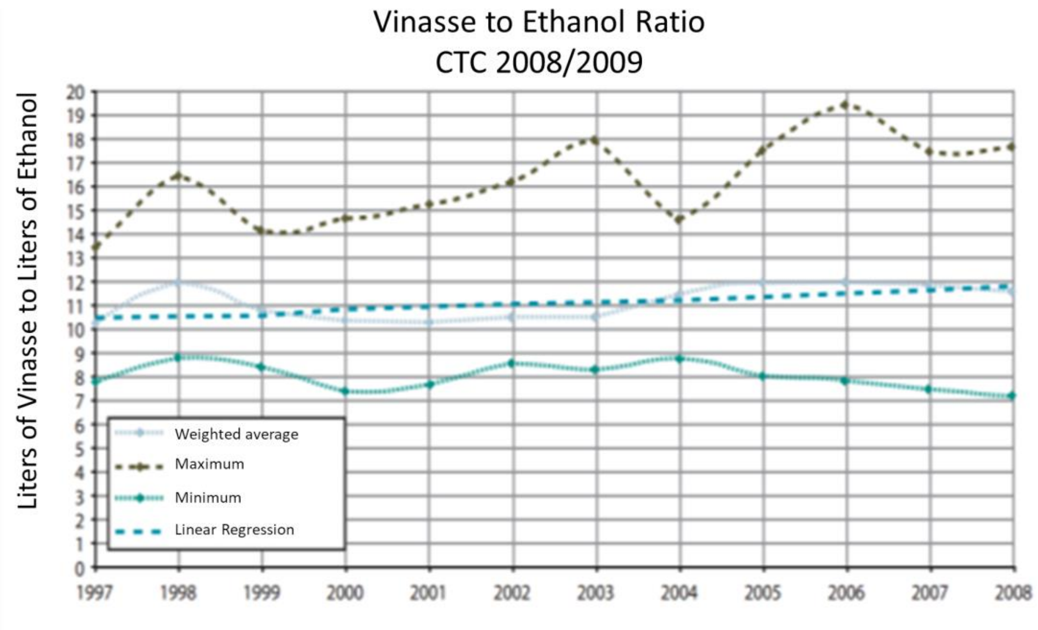


Figure 2-19: Vinasse/Ethanol ratio. Adapted from (ELIA NETO et al., 2009).

The main characteristics of vinasse are summarized in Table 2-9 below:

Table 2-9: Vinasse characteristics. Adapted from (ELIA NETO et al., 2009).

Parameter	*CTC 1995*	*CTC 2008*	*CETESB 1982 Sugarcane Juice*	*CETESB 1982 Mixed Molasses + Sugarcane Juice*
pH	*4.15*	*4.80*	*3.7-4.6*	*4.4-4.6*
Temperature (ºC)	*89*		*80-100*	*80-100*
COD (kgO_2/m^3)	*28,450*	*31,505*	*15,000-33,000*	*45,000*
Total Solids (mg/L)	*25,155*	*29,596*	*23,700*	*52,700*
Total Volatile Solids (mg/L)	*10,211*	*21,905*	*20,000*	*40,000*
Total Fixed Solids (mg/L)	*18,420*	*24,520*	*3,700*	*12,700*
Nitrogen (mg/L - N)	*357*	*353*	*150-700*	*480-710*
Phosphorous (mg/L - P)	*60*	*32*	*2.1-44.1*	*1.89-42*
Potassium (mg/L - K)	*2,035*	*2,667*	*991-1,735*	*2,759*
Sulfate (mg/L - S)	*1,538*	*861*	*300-380*	*1,850-1,865*

Studies presenting characteristics of vinasse in terms of its composition indicate presence of organic acids, sugars, ethanol among other substances (BENKE; MERMUT; CHATSON, 1997; DOELSCH et al., 2009; JANKE et al., 2016; PARNAUDEAU et al., 2008).

The important consideration to be made regarding vinasse in this work is that given its high COD, which can be transformed into biogas, and the large production volume, an equally large amount of energy through its anaerobic digestion can be produced.

Other sugarcane mill's by-products, such as filter cake (or press-mud) and plant's tops and dry leaves left on the field may be used as substrate for biogas production also with significant potential, but these discussions are outside this work's scope.

2.6.1 Vinasse as a substrate for biogas production

Vinasse contains organic matter that can be transformed into biogas, in addition to the nutrients needed to grow the biomass responsible for the transformation. It is generated at high temperatures, thus, to maintain the operating temperature of the reactors, whether mesophilic or thermophilic, the vinasse must be cooled, imposing no energy penalty for heating purposes. The organic matter of vinasse is already largely hydrolysed, being in the form of soluble compounds (mainly sugars and organic acids) in aqueous solution, thus the hydrolysis step, which in many cases is the limiting process of anaerobic digestion, is not a problem for vinasse anaerobic digestion.

On the other hand, vinasse contains significant amounts of sulfate and organic acids, which makes its pH much lower than recommended for anaerobic digestion. The existence of sulfate also means that part of the vinasse COD is not used for methane production but for sulfate reduction, reducing methane production and implying the treatment of biogas for H_2S removal.

Another important factor concerns the seasonality of vinasse production, typically between April and November in the centre-south region of Brazil, coinciding with the sugarcane crop season, thus during off-season period there is no gas production, which brings sales, biological and financial impacts to vinasse biogas projects.

Also an aspect of concern when dealing with vinasse biogas production, is the usage by the distilleries of antibiotics to treat the yeast. Some antibiotics will not degrade at distillation column's temperature and will remain in the vinasse after distillation. These antibiotics, if reach the anaerobic digestor may severely impair biogas production and even completely collapse the anaerobic population in the digestor.

Although facing the difficulties above described, some projects developed in Brazil have already proven the technical feasibility of vinasse biogas production.

Wilkie et al., (2000) present a list of 149 commercial-scale projects producing biogas from vinasse of various sources, of which only three are in Brazil. Most of those projects are molasses' ethanol vinasse projects in India, where very strict rules impose the treatment of wastewater from distilleries prior to disposal (TEWARI; BATRA; BALAKRISHNAN, 2007).

Separating the full-scale vinasse anaerobic digestion projects of several sources listed by Wilkie (2000) by the technology used, 27 of them are from high-rate lagoons working with organic loading rates of up to 3.6kgCOD/m³/day; 10 projects are Anaerobic Contact Process reactors working with loading rates within 3 and 15kgCOD/m³/day and 81 projects use UASB reactors with rates up to 20kgCOD/m³/day when operating in mesophilic range. Among the projects presented in this paper, the average production of methane from sugarcane vinasse is 0.26m³CH_4/kgCOD (WILKIE; RIEDESEL; OWENS, 2000).

Numerous scientific articles describe laboratory apparatus and large-scale projects for the production of biogas from sugarcane ethanol vinasse in Brazil and other countries, whose COD to Methane Conversion Factors (MCF - expressed as Nm³CH_4/kgCOD) are shown in Table 2-10 below (CORTES PIRES et al., 2015; CRAVEIRO; SOARES; SCHMIDELL, 1986; DRIESSEN; TIELBAARD; VEREIJKEN, 1994; PINTO, 1999; SOUZA; FUZARO; POLEGATO, 1992; VLISSIDIS; ZOUBOULIS, 1993; WILKIE; RIEDESEL; OWENS, 2000).

Table 2-10: Methane Conversion Factors (MCF) of vinasse found in literature in Nm³CH_4/kg COD.

Author	*MCF (Nm³CH_4/kgCOD)*
Cravieiro (1986)	*0.216*
Souza et al., (1992)	*0.222*
Vlissidis (1993)	*0.182*
Driessen (1994)	*0.260*
Barbelli (1998) apud PINTO C P (1999)	*0.240*
Wilkie (2000)	*0.260*
Pires (2015)	*0.196*
Average	*0.225*
** Laboratory studies and methanogenic potential tests are not included in the table above, which only presents large scale project results.*	

2.6.2 Production of vinasse biogas - Brazilian cases

According to Pinto, (1999), the first initiative to produce biogas from vinasse in Brazil took place in Rio de Janeiro State, in the city of Campos at Jacques Richer Central Distillery in early 1980's. It was an Indian model digester, in a joint project between Eletrobras (state owned electricity company) and the cooperative of sugar and alcohol producers of Rio de Janeiro State. The process promoted a significant MCF approximately 0.22 $Nm^3CH_4/kgCOD$ (assuming $40kgO_2/m^3$ COD vinasse) with hydraulic retention time of 11 days and 62% COD removal.

IPT, (1990) apud Pinto, (1999) reports another project developed in Penedo, Alagoas State, at the Paisa Distillery with IPT's technical support and financial support from BNDE (now BNDES) in 1981. Although the project had very positive results regarding the conversion of vinasse to methane, with MCF of up to $0.24Nm^3CH_4/kgCOD$ and 95% COD removal, the project was not continued. The reactor used was a UASB.

In 1984, an anaerobic reactor and a biogas purification plant were installed at the São João Mill, in Pirassununga, State of São Paulo. The anaerobic reactor was a UASB and the biogas purification was based on water scrubbing technology. The project operated for 10 years and produced biomethane with 98% methane reaching 1.48 million m^3 of CH_4 in the 92/93 harvest season. The project aimed replacing diesel from the sugarcane truck fleet and ceased activities due to the difficulties encountered in operating a gas-powered fleet with increasingly powerful vehicles and falling oil prices (BARBELI, 1998; BARBOSA CORTEZ et al., 2016; PINTO, 1999).

The São Martinho Mill began developing a biogas production project from vinasse with a $75m^3$ of volume pilot UASB reactor in 1992. Following a successful commissioning, the project was expanded to a commercial scale UASB reactor of approximately $5,000m^3$ volume with settlers installed on the UASB outlet. The gas produced is used for yeast drying and is still in operation today (SOUZA; FUZARO; POLEGATO, 1992).

Table 2-11 below summarizes available operating data of the anaerobic reactors of the Paisa distillery and the São Martinho mill.

Table 2-11: Data from Paisa and São Martinho biogas production operations

	São Martinho Mill Souza et al., (1992)		*Penedo Distillery IPT (1990)*	
	Influent	*Effluent*	*Influent*	*Effluent*
pH	*3.7*	*6.9*	*3.73*	*7.3*
COD (kg O2/m³)	*31.80*	*9.00*	*31.35*	*6.14*
Sulfate (mg/L - S)	*480*	*10*	*857*	*-*
N	*460*	*660*	*412*	*343*
P	*27*	*44*	*109*	*108*
K	*1500*	*1400*	*1473*	*1221*
TRH (h)	*10.8*		*18*	
Organic Loading Rate	*26.5*		*18.7*	
COD Removal	*71.7%*		*80.5%*	
Methane Content	*60%*		*60-65%*	
Biogas Conversion Factor m³biogas/kgCOD	*0.37*		*0.4*	
Methane Conversion Factor $m^3CH_4/kgCOD$	*0.22*		*0.24-0.26*	

Recently other vinasse biogas production initiatives have started up, some of them widely publicized but with little technical content presented, so it is difficult to evaluate the performance of these projects. These projects include the plant installed next to Coopcana Mill in Tamboara – Paraná State , the plant installed next to Companhia Alcoolquímica Nacional, in Vitória de Santo Antão – Pernambuco State and the plant installed next to Monte Alegre Mill – Minas Gerais State (ELIA NETO; SOUZA, 2016). More recently, still under construction, the first large scale biogas project to produce electricity with sugarcane byproducts at Bonfim Mill uses high rate anaerobic lagoons to digest the vinasse, along with CSTR system to produce gas from filter cake. In addition, the plant next to Ester Mill – São Paulo State will be described in more details ahead.

2.6.3 Usina Açucareira Ester Vinasse to Electricity Project

This project consisted of an anaerobic reactor designed by New Zealander company Waste Solutions. It was designed in the form of a covered anaerobic lagoon, with internal chambers, vinasse distribution pipes and a vinasse mixing, among other features. The biogas had the H_2S removed by a biological desulfurization unit made by Danish company Biogasclean and was further used to produce electricity by an Austrian-made 1MWe genset. The plant utilized an existing vinasse lagoon as collection, cooling and pumping station of vinasse, which also served as reservoir for *in natura* vinasse for biogas plant operation whenever the distillery for any reason was unable to supply vinasse. The digested vinasse was discarded into a second tank, also owned by the mill, from where it proceeded for the fertigation process.

The plant was installed in an area of 10,000m² where previously sugarcane was planted. Figure 2-20 and figure 2-21 show images of the unit.

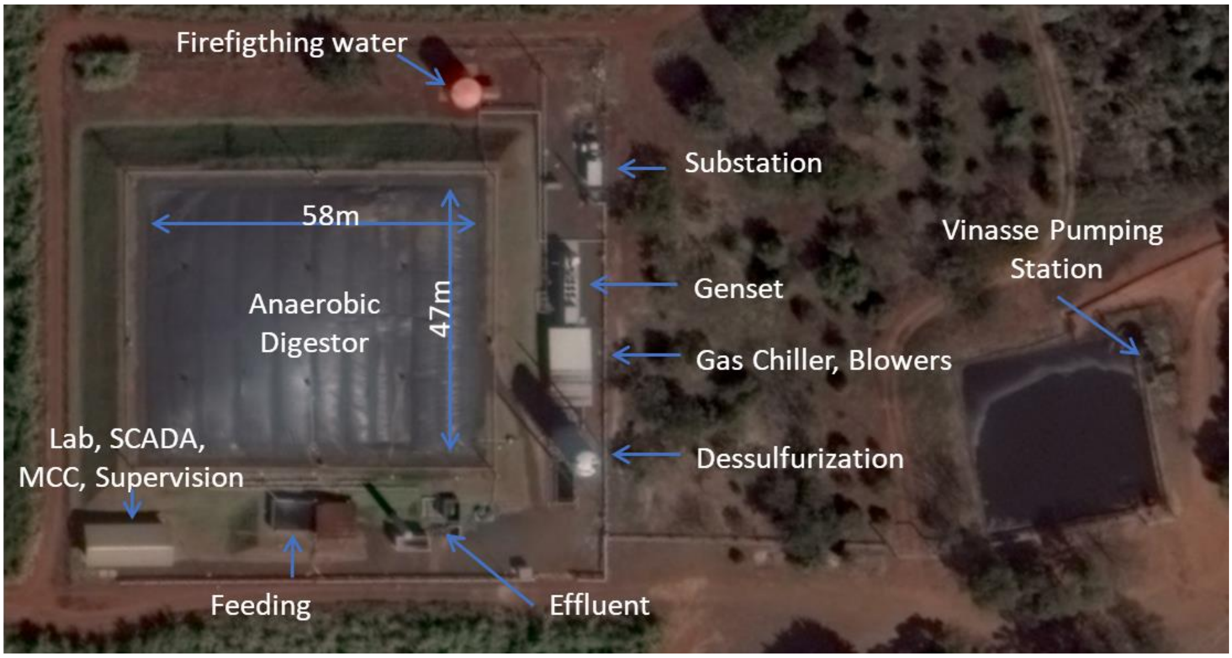


Figure 2-20: Satellite image of the vinasse biogas plant built at the Ester Mill in 2014.

Figure 2-21: View of the Vinasse Biogas Plant in October 2012

Following the survey of the land, the execution of the engineering design, obtaining the environmental licenses and contracts signed by the companies involved, in January 2010, construction began, which had the biogas production and desulfurization modules completed respectively in October and December 2010. The generator set was installed only two years later, in 2012.

Throughout the 2011, 2012 and 2014 harvest seasons, biogas was produced and desulfurized to obtain data and establish operational parameters and validate project assumptions. The plant's operation was certified by ISO 9001:2008 quality standard for the scope "Process Development and Production of Biogas for Electric Power Generation". Tens of thousands of physicochemical analyses of influent (vinasse), effluent, liquid in process and biogas were performed and recorded, which constitutes a significant amount of operational data.

3 Article 1 - ADM1 approach to the performance optimisation and biogas H_2S prediction of a large-scale anaerobic reactor fed on sugarcane vinasse[5]

Abstract

In this paper, we present extensions to the Anaerobic Digestion Model No.1 (ADM1) to simulate hydrogen sulfide in biogas and solids retention efficiency. The extended model was calibrated and validated against data from a large-scale covered in-ground anaerobic reactor (CIGAR), processing sugarcane vinasse.

Comparative scenarios and set-ups of a CIGAR with and without a settling tank unit (settler) were simulated to investigate the reactor's performance. Biogas flow, methane content, and yield with settler were 15,983 Nm3/d, 57%, and 0.198 Nm3CH_4/kgCOD, respectively, which were 9.4%, 1.8%, and 11.64%, higher than without the settler. Improvements are combination of influent flow rate 116% higher and increased solids retention time by using a settler. The optimised modelled reactor, which volume was reduced by 50%, was able to produce 83% more methane per volume of reactor with half the retention time. After model calibration and validation, we assessed the quality of predictions and its utility. The overall quality of predictions was assessed as high accuracy quantitative for CH_4 and medium for H_2S and biogas flow.

A practical demonstration of ADM1 to industrial application is presented here to identify the potential optimisation and behaviour of a large-scale anaerobic reactor, reducing, consequently, expenditure, risk, and time.

Keywords: Sugarcane Vinasse, Biogas, ADM1, Sulfate Reduction, H_2S, Solid Retention.

---

[5] This chapter is an *ipsis litteris* reproduction of the paper published by the Journal *Water Science & Technology* in November 2019.

Silva Neto, J.V., Elaiuy, M.L.C., Nour, E.A.A., 2019. ADM1 approach to the performance optimisation and biogas H_2S prediction of a large-scale anaerobic reactor fed on sugarcane vinasse. Water Sci. Technol. 80, 1774–1786. https://doi.org/10.2166/wst.2019.434

3.1 Introduction

Vinasse is a wastewater with high chemical oxygen demand (COD) and high sulfate, produced in large volumes during sugarcane ethanol distillation. Anaerobic digestion (AD) is a sustainable bioprocess to unlock the value of sugarcane vinasse (SV) as an energy feedstock through biogas recovery, from which additional bioenergy can be produced, generating electricity in gas engines, steam in boilers or even replacing diesel in sugarcane agricultural operations. There is lack of retrofitted technology from pilot to large-scale (FUESS; ZAIAT, 2018) and current stage of research on AD of SV is still scarce in Brazil (MORAES; ZAIAT; BONOMI, 2015).

The breakthroughs on AD technologies to new applications are largely guided by mathematical models and to date The Anaerobic Digestion Model No.1 (ADM1) (BATSTONE et al., 2002b) is the state of the art model. However, since its publication substantial extensions have been proposed to ADM1 (BATSTONE; KELLER; STEYER, 2006). Two examples of extensions are sulfate reduction (BARRERA et al., 2013, 2015; BATSTONE, 2006; FEDOROVICH; LENS; KALYUZHNYI, 2003) and decoupling Solids Retention Time (SRT) from Hydraulic Retention Time (HRT) to simulate high rate AD systems (FEDOROVICH; LENS; KALYUZHNYI, 2003; FELDMAN et al., 2018; ZAHER et al., 2003).

The sulfate extension suggested in Batstone et al., (2006) under-predicted H_2S and over-predicted volatile fatty acids, while in Fedorovich et al., (2003) it was not calibrated to predict hydrogen sulfide in biogas. These limitations were overcome in Barrera et al., (2015) where the extension was validated for sulfate-rich vinasse. It included biochemical routes for depleted hydrogen once sulfate reducing bacteria (SRB) use volatile fatty acids as source of electrons. This extension may be applied to model AD of Brazilian SV, which average SO_4^{-2}:COD ratio of 0.055, shows evidence of a sulfate-rich liquid substrate (ELIA NETO et al., 2009). Ascertaining sulfate reduction dynamics in AD by modelling extension to ADM1 is a useful tool to predict undesirable H_2S in biogas and costs with its removal. Unlike model validation in Barrera et al., (2015) for sulfate-rich vinasse using data from lab-scale experiments, we show the applicability of their study on sulfate extension to validate a model against data from industry.

Since 1950 the importance of SRT in AD is recognised as a tool to reduce anaerobic reactors size (MCCARTY, 2001). High rate anaerobic reactors are based on decoupling SRT from HRT by promoting biomass retention within reactors (VAN LIER; MAHMOUD; ZEEMAN, 2008). Biomass retention can be achieved by settling, attachment or granulation

(DERELI et al., 2012), although the formation of granular anaerobic biomass, the core of most efficient anaerobic reactors, is occasionally impossible or unstable. In this case, drawing anaerobic biomass out of the effluent in a settling tank and recycling it back to the reactor, increases SRT irrespective of HRT (MCCARTY, 2001; TAUSEEF; ABBASI; ABBASI, 2013). This hydraulic configuration is called Anaerobic Contact Process (ACP) and is suitable to disperse or flocculent anaerobic biomass. The retention of biomass allows higher microorganism concentration and lower food to microorganism ratios (F/M), resulting in lower biomass and higher methane production (APPELS et al., 2008; LOW; CHASE, 1999; RUIZ et al., 2011; TUROVSKIY; MATHAI, 2006).

In the original ADM1, which is based on a Continuous Stirred Tank Reactor (CSTR), the SRT is equivalent to HRT (BATSTONE et al., 2002a) and is limited to biomass growth rate (ABBASI; TAUSEEF; ABBASI, 2011). To model a high rate process in ADM1, Batstone et al., (2002b) suggest the introduction of a variable to the mass outflow term of the mass balance equation of ADM1 to represent the SRT above HRT in a CSTR (BATSTONE et al., 2002a). Feldman et al., (2018) considered an ideal solids separation unit to model the operation of an anaerobic granular Internal Circulation reactor (FELDMAN et al., 2018). Zaher et al., (2003) suggest in their model a factor (fxout = SRT/HRT) multiplying the outflow term of mass balance equation which adds proportionality to the model (at constant fxout, decreasing HRT will affect SRT proportionally), efficiency adjustments (different values for different solids retention efficiencies) and shock events simulations (ZAHER et al., 2003). Kleerebezem and Loosdrecht (2006) consider that a constant SRT value for AD modelling, as suggested by Batstone et al., (2002a), may lead to unrealistic high solids concentrations and, instead, a maximum solids concentration in the reactors should be considered. Reichert (1994) presents an activated sludge model including a settler and sludge recycle, which is suitable to model solids retention in an ACP. In Reichert (1994) model, since the settler is nonideal (i.e. not all solids are retained in the settler), excessively high solids concentration on the reactor, as decribed by Kleerebezem and Loosdrecht (2006), is avoided.

Two ADM1 key-objectives are optimisation of plant design and operational analysis of AD systems to fulfil industry needs (BATSTONE, 2006; KAZADI MBAMBA et al., 2016; OZKAN‐YUCEL; GÖKÇAY, 2010). Nevertheless, the literature on the application of ADM1 to industrial case studies is scarce (DERELI, 2019) with a few extended benefit-cost analysis.

Modelling sulfate reduction and hydraulic variation in an AD system would address operational analysis and critical issues on design, showing what benefits and limitations are available from industrial application of ADM1.

Recent case study on ADM1 to cover the gaps of its industrial application was published in Elaiuy et al., (2018). In this work, the authors calibrated and validated the model of a large-scale Covered In-Ground Anaerobic Reactor (CIGAR) in Brazil, which processes SV to produce biogas and generate bioelectricity for supply to the local grid. However, neither model extension nor optimisation alternatives were explored in their model.

Thus, the novelty of this paper is to present a further step to the work of Elaiuy et al., (2018) towards the neglected sulfate extension and investigate possible design optimisation by evaluating: (i) sulfate reduction processes in AD of SV and predictions of H_2S in biogas; (ii) extension to ADM1 to incorporate a settler and sludge recycle for the improvement of biomass retention efficiency in the CIGAR reflecting on biogas production and methane yields; (iii) potential CAPEX and OPEX savings.

3.2 Methods

3.2.1 CIGAR configuration and operation

The modelled CIGAR is one of the components of a biogas plant. It is an anaerobic reactor built in 2010 on a sugarcane mill in Brazil. Soil excavation was carried out to fit in-ground the 15,000 m^3 CIGAR, which was lined and covered with HDPE (High Density Polyethylene) to store biogas underneath a headspace of 4,800 m^3. Inside the CIGAR vertical HDPE baffles divided the reactor into three communicating chambers. Chamber 1 (C1 - 60% of total reactor volume) was fed with a mixture of raw vinasse and effluent from C1 (recycle stream) mixed in an external mix tank. This mixture was pumped upwards through pipes at the bottom of the reactor, as in a typical upflow anaerobic sludge blanket (UASB) reactor. The remaining volume of the reactor was split into two chambers, chamber 2 (C2) and chamber 3 (C3). C2 was fed only with effluent from C1, and C3 was designed to settle the anaerobic sludge, which may be recycled back to C1.

The CIGAR was designed to operate under mesophilic conditions (37^{o}C), 39.5 m^3/h flow rate of SV, 1.99 $kgCOD/m^3/d$ organic loading rate (OLR), 15 days HRT, 0.227 $Nm^3CH_4/kgCOD$ methane yield to produce 491 Nm^3/h of biogas with 55% CH_4.

A schematic layout of the reactor is presented in Figure 3-1.

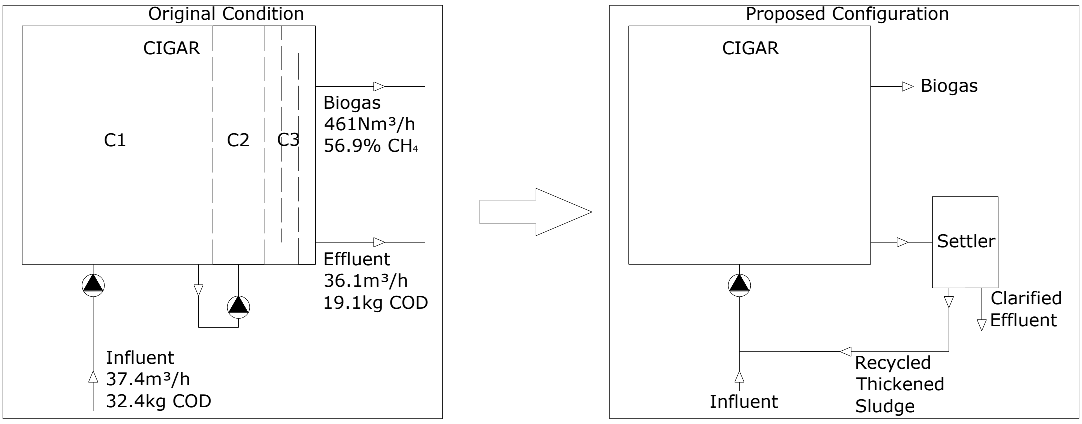


Figure 3-1: CIGAR - Original and proposed configurations.

3.2.2 Analytical Methods

Data was collected from CIGAR operation over the harvest season of 2012 (Season_12) from May to December for 220 days. Eventually data were not available due to operational problems. Physico-chemical analyses were carried out by plant operators according to the protocols described by the Standard Methods for the Examination of Water and Wastewater (APHA, 2005), in an on-site laboratory and included analysis of influent, recycle, and effluent streams (Table 3-1). Biochemical characterization of the substrate as carbohydrates, lipids, and proteins was performed following the analytical methods described in Elaiuy et al., (2018).

Table 3-1: Physico-chemical analyses, method, and frequency.

Parameter	*Method*	*Frequency*
Temperature	*APHA 2550*	*Continuously (online)*
pH	*APHA 4500*	*Continuously (online) for mixed influent, daily for other streams*
COD concentration	*APHA 5,220*	*Daily*
Total solids (TS)	*APHA 2,540B*	*Weekly*
Total volatile solids (TVS)	*APHA 2,540E*	*Weekly*
Total suspended solids (TSS)	*APHA 2,540D*	*Weekly*
Volatile suspended solids (VSS)	*APHA 2,540E*	*Daily*
Volatile fatty acids (VFA)	*APHA 5,560*	*Daily*
Partial alkalinity	*APHA 2,320*	*Daily*
Total Kjeldahl nitrogen (TKN)	*APHA 4,500*	*Biweekly*
Total ammonia nitrogen (TAN)	*APHA 4,500*	*Biweekly*
Sulfate (SO_4^{-2})	*Turbidimetric (APHA 9,038)*	*Randomly*

Influent flow was measured continuously using a magnetic flow meter OPTIFLUX KC1000F/6 (Krohne) with IFC100 signal converter. Biogas flow was continuously measured using a thermal dispersion mass flow meter FT-2 (Contech). H_2S was measured daily with precision detection tubes (Kitagawa manual pump model AP20, tubes model 120SH - range of 0.1% to 4% H_2S). CH_4 was measured 6 times a day with a handheld GEM2000 biogas analyser (Landtec).

3.2.3 Soluble COD removal efficiency

Theoretical Oxygen Demand (ThOD) of 1kg of microorganisms as Volatile Suspended Solids (VSS) with an estimated composition of $C_5H_7O_2N$ can be calculated as 1.42 kgCOD/kgVSS (VAN LIER; MAHMOUD; ZEEMAN, 2008). Subtracting the ThOD of VSS from the total COD results in a *proxy* soluble COD. Thus, the *proxy* of soluble COD can be calculated by the following equation:

$$COD_{proxy\_soluble} = COD_{total} - 1.42\ x\ VSS \qquad \text{Equation 3-1}$$

COD removal efficiency for the proxy soluble COD can be calculated as follows:

$$COD\ Removal\ Efficiency_{proxy\_soluble,i} = 1 - COD_{proxy\_soluble,i}/COD_{Influent} \qquad \text{Equation 3-2}$$

Similarly, total COD removal can be calculated for effluent as follows:

$$COD\ Removal\ Efficiency_{i} = 1 - COD_{i}/COD_{Influent} \qquad \text{Equation 3-3}$$

Where “i” refers to recycle or effluent stream.

During Season_12 high values of VSS in effluent and recycle, from chambers 3 and 1, respectively, denoted anaerobic biomass being washed out from both chambers, which was confirmed by Imhoff cone settleable solids tests. The comparison of *proxy* soluble COD removal efficiency between effluent and recycle, based on operational data from Season_12, will be presented and discussed further on to justify possible optimisation of plant design.

Settler - preliminary test

In 2012 a small settler was connected to the CIGAR to evaluate effluent solids reduction. Its overall performance was an average retention of 53% volatile solids (VS) loaded and 54% COD loaded in a concentrated stream of thickened sludge, corresponding to 20% of settler inflow. Average VS of thickened sludge was 13,792 mg/L, 2.6 times higher than the VS of settler inflow (i.e., CIGAR effluent). Similarly, average COD of thickened sludge was equal to 39,430 mg/L, 2.7 times higher than the settler inflow COD.

Based on this preliminary test, using a settler to clarify the effluent from the CIGAR and return the thickened sludge back to the reactor, would increase the SRT and biomass concentration in the CIGAR. By doing so, it is expected higher methane yield, lower biomass production, and better effluent quality. Besides, we assume that a settler would be more efficient than C3, which was designed for the same purpose, simplifying reactor design, construction, and operation. This assumption is investigated in this paper by the inclusion of a settler and sludge recycle to ADM1 and will be discussed later. Figure 3-1 presents a schematic flow diagram for the original condition and proposed configuration, along with a simplified mass balance.

3.2.4 Modelling framework

The model under study, implemented in Aquasim 2.1G, combines two updates to the previous model described in Elaiuy et al., (2018): the sulfur chain reactions and the sludge retention and recycle. The first update evaluates the H_2S in biogas to better assess its concentration for suitable biogas cleaning process, where Season_12 data was used to calibrate and validate the model. The second update simulates the overall performance of the CIGAR with improved solids retention and possible design modifications, aiming at cost reduction and improved performance, where typical vinasse COD values were used for simulations with the previously validated model.

3.2.4.1 Sulfur chain extension in ADM1

Original ADM1 does not include the sulfur chain processes (BATSTONE et al., 2002a). To account to this chain of reactions, three species of Sulfur Reducing Bacteria (SRB) were added to the model, propionate sulfate reducing bacteria (pSRB), acetate sulfate reducing bacteria (aSRB), and hydrogenotrophic sulfate reducing bacteria (hSRB), including their respective substrates uptake and decay processes.

A simplified extension including only hSRB would not consider volatile fatty acids (VFA) consumption by SRB, limiting the assessment of their impact on methane production (Batstone et al., 2006). On the other hand, included in the model extension, butyrate and valerate seemed unnecessary due to their low concentration in the AD of SV under study, adding unnecessary complexity to the model (BARRERA et al., 2015).

Also, three acid/base dissociation process (H_2SO_4, HSO_4^- and H_2S) and H_2S gas transfer from liquid to gas phase process were added to the original ADM1.

SRBs considered consume, each one, all together with sulfate, hydrogen, propionate and acetate.

Reaction rates were considered as dual Monod kinetics, where rates are simultaneously dependent on two substrates concentration: hydrogen, propionate, and acetate for each one of the species considered and sulfate concentration for all SRB.

SRB kinetic and stoichiometric parameters were adopted from Barrera et al., (2015) and Solon (2015), respectively. The following reactions were added as shown below.

$$C_2H_5COOH + 0.75H_2SO_4 \rightarrow CH_3COOH + CO_2 + H_2O + 0.75H_2S$$ Equation 3-4

$$CH_3COOH + H_2SO_4 \rightarrow 2CO_2 + 2H_2O + H_2S$$ Equation 3-5

$$4H_2 + H_2SO_4 \rightarrow H_2S + 4H_2O$$ Equation 3-6

Sulfide produced by sulfate reduction is found in the gas and liquid stream. In the liquid stream it may be undissociated (H_2S) or dissociated (HS^-) in proportions defined by dissociation constant, Henry's Law constant and environmental conditions, including reactor pressure, temperature and pH. Acid-base equilibrium for both H_2S and H_2SO_4 were implemented as algebraic equations, with the two dissociations of H_2SO_4 included, as suggested by Knobel and Lewis, (2002).

Sulfur was introduced to the model as an input variable, read according to available data for sulfate. The statistical mode was used when data for sulfate was rather sparse. By doing so, misled SO_4^{-2} values interpolated by Aquasim were avoided. H_2S transfer to gas phase was implemented similarly to other gases (CH_4, CO_2 and H_2), with gas constants from Sander (1999).

Inhibition by free H_2S was considered for hydrogen, acetate, butyrate, propionate, and valerate degrading organisms, as well as for all SRB. The formulation used was presented in Fedorovich et al., (2003) as a first order inhibition kinetics. For ease of calculation only one constant for all bacterial groups affected by H_2S inhibition was used.

The model including sulfur consists of 25 biochemical process, 11 of them subject to one or more inhibition process, 9 acid base equilibrium process, and 4 liquid-gas transfer physical process, implemented as differential and algebraical equations system in a completely stirred tank reactor composed of a liquid phase and a headspace.

Parameter estimation and model validation procedure

The model incorporating the sulfur chain processes includes the Maximum Substrate Uptake Rate (MSUR) and half saturation constant (HSC) of the three SRB groups considered.

Before parameter estimation, the model was tested with the same set of parameters that describes the SRB groups in Barrera et al., (2015) against dataset from Season_12. After visual inspection of results, as suggested by Donoso-Bravo et al., (2011), simulations for biogas and methane agreed well with measured data. However, deviations were noted between simulated and measured values for H_2S during the first 70 days and good correlation for the remaining days (data not shown). For this reason, from 220 days of operational data of Season_12, the first 70 days were discarded.

The remaining 150 days of Season_12 were split into two subsets, one for parameter estimation and the other one for cross validation.

The first subset of data, used for parameter estimation, ranged from day 70 to day 150. The initial ten days (70 to 80) were used as a ramp and did not account to model error calculations. The second subset of data, used for cross validation, ranged from day 140 to day 220 and again, the first ten days (140 to 150) used as a ramp were discarded for error calculations.

SRB constants (MSUR and HSC for acetate hydrogen, propionate, and sulfate) were estimated by Aquasim built-in function for parameter estimation. The function target was to minimize the difference between simulated and measured H_2S concentration in biogas.

With respect to model accuracy, the Relative Absolute Error (rAE) was used to evaluate deviations between measured and simulated values.

rAE is calculated following the equation below:

$$\mathrm{rAE} = \frac{\sum_{i=1}^{n}\left(\frac{\left|y_{m,i} - y_i(p)\right|}{y_{m,i}}\right)}{n} \qquad \text{Equation 3-7}$$

Where $y_{m,i}$ is the ith measured value, $y_i(p)$ is the model prediction at the time corresponding to data point i, which by its turn is a function of the set of parameters p to be estimated, and n is the number of observations.

For rAE results, we adopted the following classification from Batstone et al., (2002a), thereby qualifying the model quantitative predictions as high accuracy (rAE ±10%) and medium accuracy (rAE 10% - 30%).

3.2.4.2 Sludge retention

Model inputs and description

Influent COD was set constant to 31.5 kgCOD/m^3, adopted from Elia Neto et al., (2009) who have reported an average characterization of vinasse from 20 ethanol mills across Brazil. The main idea behind setting this value from another author was to assume an average COD for Brazilian SV, in order to avoid specific mill-type influent and project a potential national biogas production.

Disintegration of particulate matter (originated from influent and decayed bacterial biomass) was considered as first order kinetics reaction, resulting in carbohydrates, proteins, lipids and inerts (soluble and particulate). Substrate was biochemically fractionated as 44% carbohydrates (f_{ch}), 30% proteins (f_{pr}), and 26% lipids (f_{li}), according to Elaiuy et al., (2018). Although, particulate composites vary in time, fractions of carbohydrates, proteins, and lipids were assumed constant in the simulations. Besides, their hydrolysis constant was kept the same, 0.66 d^{-1} for all three components.

The degradation extent (f_d) describing the degradable theoretical oxygen demand (ThOD) fraction of substrate converted to methane was set to 50% as estimated in Elaiuy et al., (2018). The kinetic parameters to model sulfate reduction process in the AD of SV were initially kept the same as in Barrera et al., (2015). Apart from these, stoichiometric and kinetic parameters were based on the work of (ROSEN; JEPPSSON, 2006), The charge balance of the influent was determined from measured values of influent pH, VFA concentration, inorganic nitrogen (calculated as TAN), and inorganic carbon (calculated through partial alkalinity measurements) (Elaiuy et al., 2018).

Settler and sludge recycle modelling

To simulate the inflow of sludge recycle from the settler back to the CIGAR an advective link with a bifurcation was implemented in Aquasim, as suggested in Reichert (1994). To model the settler, a variable (*recircX*) defining the solids retention efficiency was implemented in Aquasim and set constant to 43% (10% lower than the real capacity of the tested settler) to allow some uncertainty of model predictions. This variable multiplies each solids concentration in the CIGAR’s effluent, calculating the solids mass flow rate driven to recycle stream. To simplify the implementation the advective link was set only to transport solids. With this modelling structure, there is no need to calculate actual SRT, which is difficult in in-ground anaerobic reactors, where sampling the sludge bed is not practical or accurate.

3.2.5 Proposed CIGAR set-ups

The 40% volume of the CIGAR occupied by C2 and C3 were responsible for only 21% of total biogas over Season_12. These percentages were calculated comparing COD removal between recycle and effluent streams.

This low performance may be due to inefficient biomass retention and to address this problem the following operational set-ups (Setup1, Setup2, Setup3) for the CIGAR were modelled considering the applicability in full-scale system. The optimisation study is based on Setup3.

- Setup1. Chambers are lumped together as a single reactor;
- Setup2. Chambers are lumped together as a single reactor and connected to an external settler;
- Setup3. Volume of the single reactor is reduced by 50% and connected to an external settler.

Modelled scenarios

Setup1 and Setup2 were subject to 6 different scenarios (SC1 to SC6), each one at higher flow rate (Table 3-2). By doing so, we could verify the collapse of the reactor due to biomass washout by increasing the flow rate and assess the performance of Setup1 and Setup2. In each scenario, an initial flow rate ramp of 10 days was undertaken to gradually increase the biomass concentration as the flow increases in a dynamic equilibrium. Therefore, as soon as the flow rate becomes constant, the system will have reached a steady state condition. If the ramp is too steep, chances are the reactor will collapse because biomass growth rate does not follow the increased flow rate.

After the 10 day-ramp, each scenario had a constant flow over 210 days, resulting in a total of 220 days of CIGAR operation for each scenario (average operation period of sugarcane mills in Brazil).

Table 3-2: Characteristics of modelled scenarios.

Scenarios	*Influent flow rate (after 10 days ramp) [m³/d]*	*HRT [d]*	*Increase in influent flow rate compared to nominal value*
SC1	*948*	*15.2*	*0%*
SC2	*1,090*	*13.2*	*15%*
SC3	*1,232*	*11.7*	*30%*
SC4	*1,417*	*10.2*	*50%*
SC5	*1,514*	*9.5*	*60%*
SC6	*2,050*	*7.0*	*116%*

Steady state simulations for methane yield, biogas flow and CH_4 were performed in all set-ups and scenarios. Therefore, variations in biogas production and its composition could be attributed to biomass retention effects and not to other variables.

3.3 Results

3.3.1 CIGAR monitoring

Characteristics of influent, effluent, recycle streams, and biogas composition covering 220 days are shown in Table 3-3. The average of each dataset was calculated ± one standard deviation. The varying characteristics can be noted by the dispersion of datasets relative to their average, indicating dynamic behaviour of loading conditions. It is noteworthy that SV characteristics varies over Season_12, depending on production schedules of ethanol and sugar by the sugarcane mill.

Soluble and total COD values for recycle (C2) and effluent (C3), in Table 4-3, indicate that effluent total COD is 21% lower than recycle total COD, and effluent soluble COD is 11% lower than recycle soluble COD.

Total COD removal efficiency for recycle and effluent streams were 32% and 46% respectively. Soluble COD removal efficiency for recycle and effluent streams were 65% and 69%, respectively, indicating high soluble COD removal efficiency for both streams.

Assuming that the difference between total and soluble COD is due to anaerobic biomass washout, we presume that increased solid retention using a settler could improve the CIGAR overall performance. A settler could replace C2 and C3 in a more efficient way reducing by 40% the volume of the CIGAR, whilst improving its overall performance. Furthermore, both chambers add constructive complexity that affects CAPEX and OPEX due to extra pumps, valves, pipes and HDPE baffles.

Table 3-3: Characteristics of influent, effluent, recycle streams, and biogas composition during entire season_12.

	Minimum	*Average*	*Standard Deviation*	*Maximum*
Influent Total COD (kg/m³)	*4.30*	*30.05*	*10.64*	*71.61*
Effluent Total COD (kg/m³)	*2.51*	*16.17*	*9.87*	*52.46*
Effluent VSS (kg/m³)	*0.40*	*4.58*	*3.52*	*16.70*
Effluent Soluble COD (kg/m³)	*0.84*	*9.36*	*7.54*	*33.61*
Recycle Total COD (kg/m³)	*2.39*	*20.55*	*10.04*	*52.88*
Recycle VSS (kg/m³)	*0.40*	*6.44*	*4.53*	*20.90*
Recycle Soluble COD (kg/m³)	*0.56*	*10.55*	*7.00*	*28.02*
Influent (g SO_4^{-2} /m³)	*250*	*1,357*	*579*	*2,750*
Influent SO_4^{-2}: COD	*0.01*	*0.05*	*0.03*	*0.18*
H_2S (ppm)	*7,500*	*14,856*	*3,889*	*30,000*
CH_4 (%)	*31.5*	*57.2*	*6.5*	*77.5*

3.3.2 Sulfur Chain Modelling

Direct and cross validation

The kinetic parameters to model sulfate reduction process in the AD of SV (Table 3-4) were estimated against the first aforementioned dataset. The results of estimated parameters are mostly similar to Barrera et al., (2015), except for Km_aSRB, Ks_aSRB, Km_pSRB, and Ks_pSRB. A primary driver for these differences is the SO_4^{-2}:COD ratio. Whilst this ratio averaged 0.0502 in this work a higher ratio was found in Barrera et al., (2015). There was competition for acetate between SRB and methanogens as long as inhibition related to COD:SO_4 ratio was not severe (COD:SO_4 < 0.1) (BARRERA et al., 2013). The uptake of acetate and neglected propionate by methanogens reflected in lower Km_aSRB and higher Ks_aSRB. Nonetheless, Ks_SO_4_aSRB, Ks_SO_4_hSRB, and Ks_SO_4_pSRB, which are needed to predict S_{SO4}, are similar to parameters from Barrera et al., (2015).

Table 3-4: Comparison of kinetic parameters reported in Barrera et al (2015) and estimated in this work.

Parameter	*Description*	*Barrera et al. (2015)*	*Estimated in this work*
Km_aSRB	*MSUR$^{(1)}$ for Acetate SRB*	*18.5*	*4.47*
Km_hSRB	*MSUR$^{(1)}$ for hydrogen SRB*	*63*	*65.0*
Km_pSRB	*MSUR$^{(1)}$ for propionate SRB*	*23*	*30.0*
Ks_aSRB	*Acetate HSC$^{(2)}$ for Acetate SRB*	*0.120*	*0.0201*
Ks_hSRB	*Hydrogen HSC$^{(2)}$ for Hydrogen SRB*	*6E-06*	*5.41E-06*
Ks_pSRB	*Propionate HSC$^{(2)}$ for Propionate SRB*	*0.110*	*0.0160*
Ks_SO_4_aSRB	*Sulfate HSC$^{(2)}$ for Acetate SRB*	*0.001*	*0.00100*
Ks_SO_4_hSRB	*Sulfate HSC$^{(2)}$ for Hydrogen SRB*	*0.00105*	*0.00105*
Ks_SO_4_pSRB	*Sulfate HSC$^{(2)}$ for Propionate SRB*	*0.002*	*0.00200*
(1*) Maximum Substrate Uptake Rate, (2) Half Saturation Constant*			

Since other parameters used in the present model were calibrated in previous work for AD of SV, only MSUR and HSC of SRB were selected for calibration.

The simulations shown in Figure 3-2A are split into direct and cross validation of the model for H_2S and there is a good fit between simulated and measured values on both sides. The quality of prediction was sensitive to few kinetic parameters Km_aSRB, Ks_aSRB, Km_pSRB, and Ks_pSRB. Notwithstanding direct validation shows higher quality of prediction (rAE 13.3%) than cross validation (rAE 17.4%), both are in the range of medium (10-30%) accurate quantitative prediction. The same quality of prediction for H_2S was found in Barrera et al., (2015). Furthermore, given the scale and the uncontrolled environment of this work, rAE for both direct and cross validations can be considered satisfactory when compared to other studies, which reported similar rAE under laboratory conditions.

Simulated H_2S concentration in biogas ranged from 0.94% to 2.01% and is close to ranges found in the literature using SV. For example, 1.5% to 3.0%, was reported in Cortes Pires et al., (2015); Leme & Seabra (2017); Nandy et al., (2002); Yasar et al., (2015) and 1.25% to 1.75% in Barrera et al., (2015).

Despite the variability in the influent composition over Season_12, the simulation is consistent after parameter estimation (Figure 3-2A). However, the quality of prediction was less accurate in the cross validation but yet classified as medium accuracy.

Most of H_2S was overestimated by the model. 55% and 62% of simulated values were higher than measured values for direct and cross validation, respectively.

Also, 57% and 46% of simulated values had errors within +/- 10% for direct and cross validation, respectively. However, if we consider the season average H_2S content in biogas the difference between measured and simulated values was 3.08% for the first subset and 8.91% for the second subset.

The rAE for biogas flow in the direct validation of this work was 12.7% (Figure 3-2B), smaller than in Elaiuy et al., (2018), possibly because of free H_2S inhibition to microorganisms, which was the highest among all inhibitions (data not shown).

Similar quality of predictions for biogas flow were presented in Dereli (2019) simulating a full-scale anaerobic reactor.

The same rAE of 6.1% for CH_4 was found in the direct and cross validation, which can be visually confirmed by small deviation between simulated and measured outputs of CH_4 in both sides of Figure 3-2C. Nevertheless, this rAE is higher than the rAE found in Elaiuy et al., (2018), possibly because of the use of methane precursors in the H_2S production instead of CH_4 production. Additionally, compared calculated averages for days 80 to 220 of simulated and measured biogas flow and CH_4 show differences of -4.9% and -2.3%, respectively.

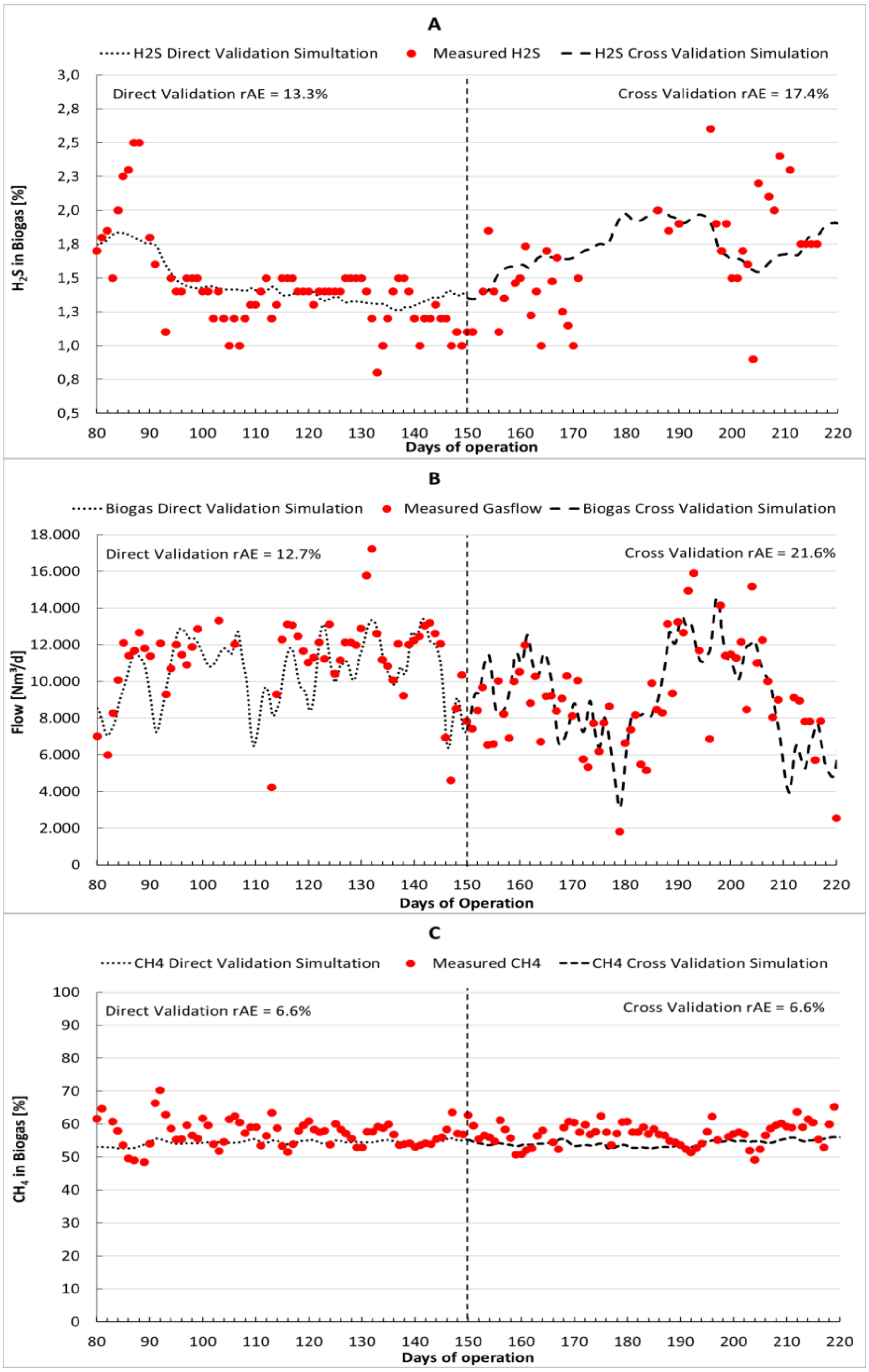


Figure 3-2: rAE of measured and simulated (A) H_2S, (B) biogas flow and (C) CH_4 – direct and cross validation.

3.3.3 Sludge recycle - modelled scenarios

Simulation results of Setup1 and Setup2 for biogas flow, methane content, and methane yield are illustrated in Table 3-5. Comparing results, it was found that Setup2 had better performance than Setup1 in all simulated scenarios.

Table 3-5: Results of biogas flow, methane content, and methane yield from different scenarios and set-ups under study.

Scenario	Setup1 (Without settler)			Setup2 (With settler)			Comparison Setup2 x Setup1		
	Biogas Flow [Nm^3/d]	Methane Content [%]	Methane Yield [Nm^3CH_4/ kgCOD]	Biogas Flow [Nm^3/d]	Methane Content [%]	Methane Yield [Nm^3CH_4/ kgCOD]	Biogas Flow	Methane Content	Methane Yield
SC1	9,858	56.8	0.193	10,593	57.2	0.208	7.5%	0.7%	7.5%
SC2	11,125	56.7	0.190	11,951	57.2	0.205	7.4%	0.8%	8.0%
SC3	12,411	56.6	0.186	13,471	57.1	0.203	8.5%	1.0%	8.8%
SC4	14,047	56.3	0.181	15,287	57.0	0.200	8.8%	1.4%	10.4%
SC5	14,611	56.0	0.178	15,983	57.0	0.198	9.4%	1.8%	11.6%
SC6	Colapse			20,958	56.6	0.189	N/A		

Maximum influent flow rate for SC5 and SC6 were respectively 60 and 116% higher than the nominal reactor design flow rate, meaning above that, imminent biomass washout and reactor collapse. The maximum influent flow rate for Setup2 was higher than for Setup1 before reactor collapse. This is attributed to better biomass retention in Setup2, since it is 52% higher than in Setup1 regarding SC1 (data not shown). We assume that the influent flow rate could be even higher as long as the settler has an improved performance.

It is important to highlight that for Setup1 and Setup2 the stepwise increasing flow rate in each SC, results in a reduction in HRT followed by lower methane yield (Figure 3-3A) and methane content (Figure 3-3B). Nevertheless, these reductions were smaller for Setup2 than for Setup1.

Simulated methane yield of 0.193 $Nm^3CH_4/kgCOD$ for Setup1 was likewise to 0.196 $Nm^3CH_4/kgCOD$ measured in 2012. These figures are smaller than CIGAR projected methane yield of 0.227 $Nm^3CH_4/kgCOD$. However, the amount of methane recovered per kilogram of COD removed is more realistic in the simulations since we adopted 50% of COD removal compared to nominal CIGAR design of 65%.

Average methane yield of 0.225 $Nm^3CH_4/kgCOD$ for large-scale projects has been reported in Silva Neto et al., (2019). Another possible explanation to this discrepancy may be attributed to either higher degradation of substrates or superior SRT. To verify the latter, we simulated a settler with 80% solids retention efficiency and CIGAR influent flow rate of 948m^3/d, resulting in a methane yield of 0.221 $Nm^3CH_4/kgCOD$. This result is 6% higher than simulations where the settler was set to 43% of solids retention efficiency and only 4% lower than average methane yield reported in the literature. The biogas flow was higher for Setup2 than for Setup1 (Figure 3-3C) as a result of increased biomass concentration, thus lower food to microorganism ratio (F/M).

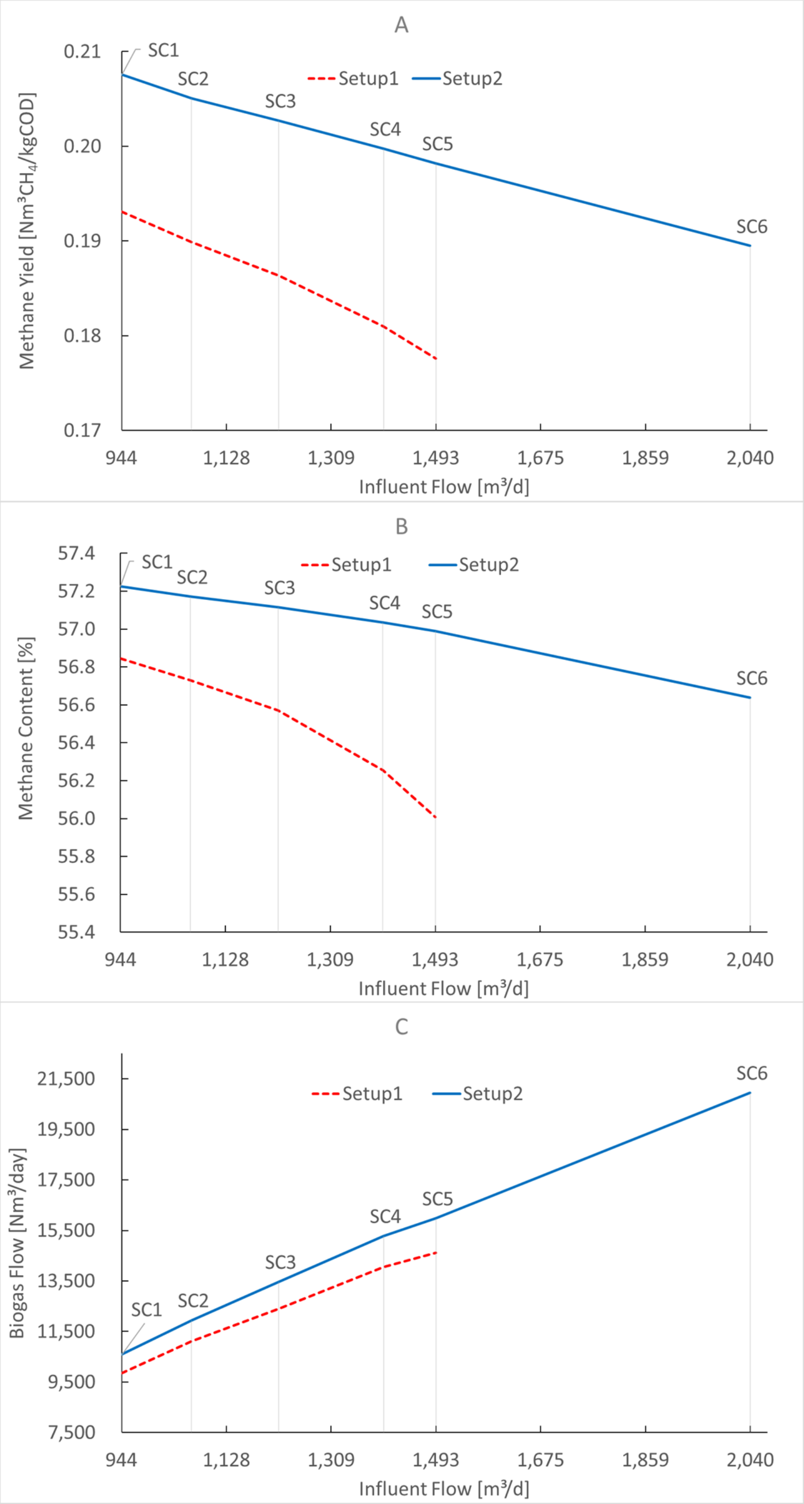


Figure 3-3: A: Methane yield, B: Methane content, C: Biogas flow for modelled scenarios and setups

The OLR was 4.5 kgCOD/m³/d for SC6 and 3.3 kgCOD/m³/d for SC5, which are close to values found in Wilkie et al., (2000), ranging between 4.6 to 5 kgCOD/m³/d for Anaerobic Contact Process digesting sugarcane vinasse. Also, OLRs for SC5 and SC6 were higher than the nominal CIGAR design and Season_12 measured values of 1.99 kgCOD/m³/d and 2.06 kgO$_2$/m³/d, respectively.

3.3.4 CIGAR economics – Setup3 analysis

A comparative analysis between Setup1 and Setup3 after simulations is presented in Table 3-6. The reactor for Setup3 is 50% smaller than Setup1, and yet it was able to produce 83% more methane per cubic meter of reactor at half of HRT of Setup1. However, the methane yield and total biogas flow rate dropped by 7.8% and 8.3%, respectively. Notwithstanding Setup3 has higher biogas production per volume of reactor, it is not possible to achieve the same biogas production as in Setup1. Even though the OLR is higher for Setup 3 the methane yield is smaller.

Table 3-6: Summarised comparison between original (Setup1) and optimised reactor (Setup3).

Parameter	*Unit*	*Original reactor (Setup1)*	*Optimised reactor (Setup3)*	*Comparison Optimised x Original*
HRT	*[d]*	*15.2*	*7.6*	*-50%*
Biogas flow rate	$[Nm^3/d]$	*10,593*	*9,781*	*-8.30%*
Methane Content	*[%]*	*57.2*	*56.8*	*-0.70%*
Methane Yield	$[Nm^3CH_4/kgCOD]$	*0.208*	*0.191*	*-7.80%*
Methane Production	$[Nm^3CH_4/m^3reactor]$	*0.421*	*0.771*	*83%*
Total volume earthworks	$[m^3]$	*20,304* m^3	*10,867* m^3	*-46%*
HDPE liner/cover area	$[m^2]$	*10,204* m^2	*5,109* m^2	*-50%*
Total pipework	*[m]*	*757 m*	*345 m*	*-54%*
Pumping System		*4 pumps,* *2 flow meters,* *4 VSD*$^{(1)}$	*2 pumps, 1 flow meter, 2 VSDs*	*-50%*
(1) VSD = Variable Speed Driver				

By reducing the size of the CIGAR and simplifying its design, as shown in Setup 3, will have an impact on CAPEX planned. Since the majority of capital expenditures occur upfront in the construction stage, costs allocated to land, material, and equipped facilities, for example, will be significantly reduced. OPEX will follow the same trend including for example electricity consumption, staffing, and general overhead. In summary, the optimised CIGAR is a proposed solution that minimises capital and operational expenditures. This involves redesigning not only the reactor but its operation. Whilst there is certainly scope for potential CAPEX and OPEX savings given the size and complexity reductions, in this work we did not take into account expenditures involving the settler.

3.4 Conclusions

Vinasse is a high COD, high sulfate, low pH, seasonally produced wastewater and biogas production from it should be done with special attention in planning, design and operation.

A practical demonstration of ADM1 to industrial application is presented here to identify the potential optimisation and behaviour of a large-scale anaerobic reactor processing SV, reducing, consequently, expenditure, risk, and time.

The modelled higher SRT optimised reactor showed higher biogas production and methane per volume of reactor, followed by a reduced HRT from 15 to 7 days.

By adding an external settler with sludge return substantial savings in materials and services associated with a lagoon-type digestor construction and operation costs can be obtained. Moreover, methane yield, methane concentration and biogas production can be higher when SRT is higher.

The predictions of H_2S levels in biogas by ADM1, based on sulfate and COD content, is a useful tool to assess biogas composition, especially for projects where the gas is not yet under production, but wastewater composition is available.

The quality of predictions of the model allows practitioners and designers of vinasse-to-energy projects to anticipate with reasonable accuracy the H_2S levels in biogas and plan ahead appropriate biogas downstream processing and technology to convert biogas into clean renewable bioenergy. The H_2S model presented small differences between the averages of modelled results and large-scale reactor measured data. The model can be qualified as medium accuracy based on rAE, although majority of calculated values were within a +/-10% error range. The model also improves the accuracy in prediction of energetic value of biogas by reducing errors in biogas flow and CH_4 content compared to previous models.

Electricity or fuel (as biomethane) produced from vinasse biogas are not subject of any premium price or incentives, and treatment of sugarcane vinasse is not compulsory for mills in Brazil. Upon these circumstances the actual scenario of vinasse-to-biogas projects will only be profitable if special attention is given to mathematical models such as ADM1 for evaluation, optimisation, and design of existing and planned biogas plants.

4 Article 2 - Production and use of biogas from vinasse: implications for energy balance and GHG emissions of sugarcane ethanol in the Brazilian context[6]

Abstract

Indicators, such as the Energy Balance (EB) and Greenhouse Gases Emissions Avoided (GHGEA), are frequently used to evaluate the benefits and sustainability of biofuels. Many important papers and reports have been published in recent years to demonstrate the environmental and energetic benefits of biofuels, such as ethanol from sugarcane. EB and GHGEA often include other sugarcane products, such as electricity and bagasse. The anaerobic digestion of vinasse can generate considerable amounts of biogas but is not a common practice in Brazil. This study evaluates the potential benefits to the EB and GHGEA of ethanol by the production of biogas from vinasse and its use to produce electricity or biomethane. Biomethane can be injected on the Natural Gas Grid or used as a fossil diesel oil replacement in the mill operations of harvesting and transportation of sugarcane. The results show that biogas from vinasse can represent improvement in both indicators, which ranges from 3.5% improvement in EB by electricity generation with biogas to 27.5% improvement in GHGEA by replacing diesel in the mill operations.

Novelty: This article aims to present and compare, in terms of the EB and GHGEA of sugarcane ethanol, the effects of producing and using biogas from vinasse in the Brazilian context, which had not been previously analysed. These results contribute to a growing body of research on this incipient form of energy in the Brazilian sugarcane industry.

Keywords: Biogas, Biomethane, Sugarcane Vinasse, Diesel Replacement, Renewable Energy

---

[6] This chapter is an *ipsis litteris* reproduction of the paper published by the Journal *Environmental Progress & Sustainable Energy* in April 2019.

Silva Neto, J.V., Gallo, W.L.R., Nour, E.A.A., 2020. Production and use of biogas from vinasse: Implications for the energy balance and GHG emissions of sugarcane ethanol in the Brazilian context. Environ. Prog. Sustain. Energy 39, 13226. https://doi.org/10.1002/ep.13226

4.1 Introduction

Biofuels production in the world increased by 120% in the past ten years, which is primarily led by USA and Brazilian ethanol. Together, both countries hold 66% of the global biofuel production (BP, 2017). This production expansion triggered an important debate around the sustainability of biofuels in several dimensions.

Greenhouse Gases Emission Avoided (GHGEA) and Energy Balances (EB) are common indicators to evaluate the environmental benefits and sustainability of biofuel production and have been continually revaluated since the late 1970s by numerous researchers (CHUM et al., 2014; WALTER et al., 2015). These indicators are calculated based on the direct and indirect energy and emissions associated with biofuel production against the energetic benefits of the same biofuels that replace their fossil counterparts. Several studies focused on the GHGEA and EB of Brazilian sugarcane ethanol and included the energy and emissions of sugarcane by-products, such as bagasse surpluses and electricity generated in power plants of the mills (CHUM et al., 2014; MACEDO; SEABRA; SILVA, 2008; MACEDO; LEAL; SILVA, 2004; SEABRA et al., 2011; WALTER et al., 2015).

The waste streams from the ethanol production process, such as vinasse, may also be used as a renewable energy source via anaerobic digestion. Although this practice is not common in Brazil, considerable energy can be obtained from vinasse biogas, which can improve both EB and GHGEA of sugarcane ethanol.

The sugarcane industry is a very important economic activity in Brazil with 380 mills in operation in the north-eastern and central-southern regions of the country, which have processed 651 Million tons of sugarcane, resulting in 39.7 Million tons of sugar, 27.1 billion litres of ethanol and 24 TWh of electricity exported to the National Interconnected Grid in 2017 (EPE, 2018b; MAPA, 2017; UNICA, 2018a, 2018b). Sugarcane products were responsible for 17.4% of Brazilian Domestic Energy Supply in 2017. Bagasse and ethanol were responsible for 11.7% and 5.5%, respectively, of the Final Energy Consumption in the country in this same year (EPE, 2018b).

On average, each ton of crushed sugarcane generates 270 kg of bagasse with 50% relative humidity and a lower heating value (LHV) of 7,520 MJ/ton (MACEDO; LEAL; SILVA, 2004). Ethanol yields are reported in the range of 86-92 litres (anhydrous) per ton of sugarcane with an LHV of 22.339 MJ/m^3 (MACEDO; SEABRA; SILVA, 2008; UNICA, 2018b). In addition, in Brazil, for each ton of processed sugarcane, 22.96 kWh of electricity and 2.64-4.39 litres of diesel oil are consumed on average (EPE, 2018b; MACEDO; SEABRA; SILVA, 2008; MACEDO; LEAL; SILVA, 2004; SEABRA et al., 2011). The electricity consumed by the mills is generated by bagasse fuelled steam power plants; thus, it is renewable. However, the diesel oil, which is mainly consumed by sugarcane harvesters and transport trucks, is a fossil fuel (although it contains a biodiesel blend) and negatively affects both EB and GHGEA of the ethanol produced.

Diesel Oil Consumption in the Sugarcane Industry: Studies show that the mechanical harvesting and transportation of sugarcane are important GHG emitters and fossil energy consumers in the ethanol life cycle (MACEDO; SEABRA; SILVA, 2008; MACEDO; LEAL; SILVA, 2004). Diesel consumption varies depending on several factors, such as the percentage of sugarcane mechanically harvested, travelled distance and capacity of sugarcane transportation trucks, different harvest conditions of the operation and crop density. Table 4-1 shows the diesel consumption values according to different authors.

Table 4-1: Diesel oil consumption in cane transport and harvest operation (L/TC)

	Cane Transport	*Cane Harvest*	*Total*
(MACEDO; LEAL; SILVA, 2004)	*0.82 - 0.97*	*1.04 - 1.26*	
(MACEDO; SEABRA; SILVA, 2008)	*0.97*		*4.39*
(SEABRA et al., 2011)	*1.33*	*1.04*	
(SOARES et al., 2009)	*0.98*	*0.9*	*3.5*
(NOVACANA, 2017)	*1.01-1.49*	*0.99*	
(GONÇALVES, 2012)	*0.816 - 0.628*	*0.90*	
(RAMOS, 2013)		*0.82-1.16*	
(BANCHI et al., 2012)		*1.449-2.996*	
(SCHEIDL et al., 2015)	*0.55*	*1.02*	
Author's survey	*0.97-1.04*	*1.19-1.22*	*3.55 - 3.90*

Purified biogas from the vinasse anaerobic digestion can be used to replace diesel in the sugarcane transportation and harvesting process. The conversion of these consumers to biomethane-fuelled Otto cycle engines would impose a decrease in energy efficiency (ATKINS; CENEX, 2016), and a second source of gas should be available offseason, since biomethane is only produced during the sugarcane harvest season, and only a small number of mills are near the natural gas pipeline.

A method to overcome these restrictions is the use of the so-called diesel-gas dual-fuel engines. This technology comprises of a diesel engine (ignition by compression) with a secondary gas fuel injection system, which is usually installed at the air intake manifold and enables the operation of converted consumers at 30-90% Energy Substitution Ratio (ESR). The ESR, i.e., the percentage of diesel replaced by gaseous fuel, depends on the operation regime: more stable operation regimes favour higher substitution rates, and variable regimes lead to more modest substitution rates. This technology enables the operation at 100% diesel when there is no gas supply (ATKINS; CENEX, 2016; STETTLER et al., 2016).

Vinasse: In the ethanol distillation process, large quantities of vinasse are generated (ELIA NETO et al., 2009; HASSUANI; LEAL; MACEDO, 2005). According to a survey by the Brazilian Water Agency, on average, 11.5 litres of vinasse are generated per litre of ethanol produced in the distillation process (ELIA NETO et al., 2009). The vinasse is produced at high temperatures and has low pH (3.7-4.8); its composition varies depending on the source of fermentable substrate (sugarcane juice, molasses, or a mix of both) and the heating method of distillation. Vinasse contains organic carbon components, such as residual fermentable sugars, non-fermentable sugars, and organic acids, which result in high Chemical Oxygen Demand (COD). Vinasse also contains nitrogen, phosphorous, potassium and sulfur, which result in considerable crop fertilizing potential; therefore, it is sent back to the crop area in the fertirrigation process. The vinasse characteristics are shown in Table 4-2 (ELIA NETO et al., 2009).

Table 4-2: Vinasse characterization (Elia Neto 2009)

Parameter	*Value*
pH	*4.80*
COD (kg O2/m^3)	*31.505*
Total Solids (mg/L)	*29.596*
Volatile Solids (mg/L)	*21.905*
Fixed Solids (mg/L)	*24.520*
Nitrogen (mg/L - N)	*353*
Phosphorous (mg/L - P)	*32*
Potassium (mg/L - K)	*2.667*
Sulfate (mg/L - S)	*861*

Anaerobic Digestion: Anaerobic Digestion (AD) is the process by which organic matter is decomposed by a consortium of bacteria and archaea in the absence of oxygen. AD reduces the pollution potential of wastewaters and produces an energy-rich gas. This gas, which is called biogas, is a mixture of mainly CH_4 and CO_2. Because of the presence of sulfur compounds in the vinasse, H_2S (hydrogen sulfide) is also formed in relevant quantities when biogas is produced from this substrate (CORTES PIRES et al., 2015; LEME; SEABRA, 2017; YASAR et al., 2015).

As a bioenergy production process, the anaerobic digestion process relies on a vast array of technologies, such as Covered Anaerobic Lagoons, Continuous Stirred Tank Reactors (CSTR), and Upflow Anaerobic Sludge Blanket (UASB). Covered lagoons can handle low-pH, high-strength wastewaters without the necessity of chemical pH correction, and they have low construction costs, low energy consumption in operation, and good performance under flow and COD load shocks. The anaerobic digestion process is largely applied in agroindustrial plants worldwide to produce alternative energy. Further information about anaerobic digestion can be found elsewhere (DEUBLEIN; STEINHAUSER, 2011; KHANAL, 2008; WEILAND, 2010; WILKIE; RIEDESEL; OWENS, 2000). Vinasse has been used as a substrate for biogas production by anaerobic digestion in several large-scale projects in the world and small and large projects in Brazil, which results in additional bioenergy from the same original amount of sugarcane biomass. The Methane Conversion Factors (MCF) of vinasse in literature are listed in Table 4-3.

Table 4-3: Methane Conversion Factor (MCF) presented in literature* [$Nm^3CH_4/kgCOD$]

Author	*MCF*
(CRAVEIRO; SOARES; SCHMIDELL, 1986)	*0.216*
(SOUZA; FUZARO; POLEGATO, 1992)	*0.222*
(VLISSIDIS; ZOUBOULIS, 1993)	*0.182*
(DRIESSEN; TIELBAARD; VEREIJKEN, 1994)	*0.260*
(PINTO, 1999)	*0.240*
(WILKIE; RIEDESEL; OWENS, 2000)	*0.260*
(CORTES PIRES et al., 2015)	*0.196*
Average	*0.225*

**Laboratory scale tests yields and Biomethane Potential Assay results not included in the presented values, which refer only to large scale projects.*

The anaerobic digestion of vinasse imposes some challenges: 1- The vinasse is produced only during the sugarcane harvest season, which results in five months per year of ociosity with economical and operational implications; 2- Vinasse is very acidic with pH of 3.7 to 4.9, and methane is not produced in pH below 6.0; the reactor operation conditions may imply in relevant operational expenditures if the pH must be corrected using chemicals; 3- Vinasse has a high concentration of sulfate, which decreases its methane yield when it is anaerobically digested and generates H_2S, a contaminant that must be removed from the biogas stream before its use in electricity generation or from the offgas stream after upgrading to biomethane.

Conditioning and treatment of biogas from vinasse: Biogas can be used after the removal of more aggressive contaminants such as H_2S and excessive moisture in electricity generation, which often use Otto cycle engines (DANIEL-GROMKE et al., 2018; VAN FOREEST, 2012). By removing carbon dioxide, other contaminants and the remaining water from the biogas to satisfy specific standards in each country, it can be injected into the natural gas pipe network or directly used as vehicular fuel. After purification, this gas is called biomethane in Brazil and other countries.

Desulfurization: Biogas from vinasse has high levels of hydrogen sulfide (H_2S), which is a poison gas and may damage the equipment that comes in contact with it, especially in the presence of moisture; therefore, it increases the maintenance and operational costs of high H_2S biogas projects (ALLEGUE; HINGE, 2012; ARNOLD, 2009; CHOU, 2003; DEUBLEIN; STEINHAUSER, 2011; FRARE et al., 2010; KHANAL, 2008; WELLINGER; ANNA, 1999). Biological processes are often used to reduce the high levels of H_2S from biogas to the acceptable levels by major genset manufacturers without using chemicals or nutrients (often use digested wastewater as nutrients source) and operate at low pressure and temperature, i.e., low energy consumption. Biofilters and biotrickling filter processes have good efficiency and the lowest operational costs in the literature in removing H_2S from biogas, and they can be used to remove H_2S from the offgas streams from biogas upgrading units (ALLEGUE; HINGE, 2012; ARNOLD, 2009). Table 4-4 presents the biogas composition of vinasse with the H_2S concentration in the literature.

Table 4-4: Volumetric Composition of Biogas from Vinasse

Author	*CH_4*	*CO_2*	*H_2S*
*Leme (2017)**	*60%*	*38.1%*	*1.9%*
Yasar (2015)	*58-61%*	*36-38%*	*3%*
Cortes (2015)	*55%*	*43%*	*2%*
**Theoretical data*			

Upgrading: The basic principle of obtaining biomethane is to concentrate CH_4 of the biogas, usually to above 95%, by removing CO_2, other gases (N_2, O_2) and water in the biogas (ABATZOGLOU; BOIVIN, 2008; SALIHU; ALAM, 2015). High H_2S biogas generally requires treatment before upgrading, but some technologies can be used with this type of gas at a higher cost of more sophisticated materials and components (ONG; WILLIANS; KAFFKA, 2014). Water scrubbing is based on different solubilities of CH_4, CO_2 and H_2S in the water. This technology operates as a pressurized scrubber tower, where CO_2 and H_2S are absorbed by the liquid. The biogas leaves the tower with high CH_4 concentration for further processing (e.g., water removal), and CO_2 and H_2S are desorbed from the water by releasing the pressure in a stripping tower. The offgas is sent for further processing (e.g., desulfurization, CO_2 recover) (ALLEGUE; HINGE, 2012; BAUER et al., 2013b).

Methane loss is an especially important point of attention in the upgrading process, since methane has a Global Warming Potential (GWP) 28 times higher than CO_2 (IPCC, 2014); therefore, the methane released to the atmosphere can eliminate the GHGEA benefit of the produced renewable energy.

Biogas after the purification process to achieve the composition established by ANP (Brazilian Oil, Natural Gas and Renewable Fuels Agency) regulation n°8/2015 can be blended with natural gas in any proportion and be injected into a natural gas distribution network. Biomethane with 96.5% of methane, maximum of 10 mg/m³ H_2S (at 20°C, 1Atm), maximum 0.8% O_2 and balance of CO_2 and N_2 on its composition will satisfy the parameters of the Higher Heating Value, Wobbe Index and others established by the ANP resolution. There is a government-established compulsory blend of the renewable counterparts of diesel oil and gasoline (i.e., biodiesel and ethanol, respectively), but there is no obligation of mixture of biomethane in the natural gases used in Brazil.

4.2 Materials and Methods

The potential benefits in terms of EB and GHGEA of the sugarcane ethanol using vinasse biogas are analyzed. The potential production of methane from the vinasse anaerobic digestion is calculated, and the net productions of electricity and biomethane are estimated for two described process trains.

Biomethane is evaluated in two uses: injecting the final product in the natural gas pipeline or being used as a replacement for diesel oil in the mill operations of harvesting and transportation of sugarcane. Electricity is considered injected into the electrical distribution grid.

The additional energy produced and GHG avoided by the proposed activities for each product and condition are evaluated and compared with the literature values of the indicators of EB and GHGEA of the regular sugarcane ethanol production that does not include biogas production and use.

It is assumed that the proposed activities of production and use of biogas will not affect the steam or electricity production or consumption associated with ethanol production or other existing distillery agroindustry operation, except activities that involve diesel consumption, where the direct emissions from diesel use are reduced in the same proportion of biomethane replacement. With this assumption, the data presented by others for the EB and GHGEA can be used as a base case without extensive recalculations.

The EB indicator considered is the result of the division of all renewable energies produced by the distillery products by the amount of fossil fuel energy directly (sugarcane farming, harvesting and transportation and ethanol production) or indirectly (production of, for instance, fertilizers, lime, herbicides, and seeds) used in the renewable energy production

(MACEDO; SEABRA; SILVA, 2008; SEABRA et al., 2011). The GHGEA is the result of the difference between the amount of fossil CO_2 that is avoided using each product of the distillery and the direct and indirect GHG emissions from the sugarcane and ethanol production activities. A detailed description of energy and GHG balance methodologies in sugarcane ethanol production can be found elsewhere (CHUM et al., 2014; MACEDO; LEAL; SILVA, 2004; RAMÍREZ TRIANA, 2011).

Vinasse is also assumed to be a residue from ethanol processing and has zero life-cycle GHG emissions up to the point of its collection, as suggested by the international carbon and sustainability certification schemes (INTERNATIONAL SUSTAINABILITY & CARBON CERTIFICATION, 2016).

For clarity, the following nomenclature is used:

Methane – refer to 100% pure molecules produced by anaerobic digestion of vinasse

Biogas – Mixture of Methane, Carbon Dioxide and Sufidric Gas

Biomethane – Biogas purified to meet ANP n.8/2015 specifications

To calculate the methane potential, the following equation is used:

$$\text{Methane Potential } [Nm^3CH_4] = \text{Ethanol Production } [m^3_{ethanol}] \times \text{Vinasse Yield } [m^3_{vinasse}/m^3_{ethanol}] \times \text{Vinasse COD } [kg_{COD}/m^3_{vinasse}] \times \text{Methane Conversion Factor } [Nm^3CH_4/Kg_{COD}] \qquad \text{Equation 4-1}$$

To calculate the methane daily or hourly flow, the biogas plant is considered to continuously operate during Brazilian Center-South region sugarcane harvest season period of 210 days per year from April to November.

Methane is the only energy-yielding component considered in biogas and has a Lower Heating Value (LHV) of 802.82 kJ/mol at 0°C (35.818 MJ/Nm³ at 0°C and 1 Atm) according to Brazilian Standard NBR 15213. Biomethane is considered to replace natural gas and diesel by their Lower Heating Value ratios with a 2% decrease in energy efficiency in dual-fuel converted consumers. Methane slips in dual-fuel consumers are considered fully oxidized by the exhaust catalysts. The Lower Heating Value of natural gas and diesel oil were considered as presented at EPE's National Energy Balance (EPE, 2018b) of 39.515 MJ/m³ at 0°C and 1 Atm and 35.497 MJ/L, respectively.

Throughout the results, the references to season 2005/2006 and projections for 2020 are based on the ethanol yields, energy inputs and outputs, GHG emissions and avoidances and other relevant data as presented in MACEDO; SEABRA; SILVA, (2008); references to season

2008 are based on same set of data presented by SEABRA *et al.*, (2011). The values that were originally published by SEABRA *et al.*, (2011) were deduced from the fossil usage for ethanol transportation and distribution to account to the same base of MACEDO; SEABRA; SILVA, (2008) when necessary, which reported a “seed-to-factory gate” approach. The electricity produced with vinasse biogas injected on the grid replaces the electricity that is otherwise produced by natural-gas-fuelled power plants with an emission factor of 579 t CO_{2eq}/GWh for 2005 and 560 t CO_{2eq}/GWh for 2020 (MACEDO; SEABRA; SILVA, 2008). For the evaluation of 2008, an emission factor was calculated based on the data presented by SEABRA *et al.*, (2011) as 626 t CO_{2eq}/GWh.

For GHG emissions, the value form IPCC of the natural gas direct emissions of 56.1 gCO_{2eq}/MJ was used; for natural gas indirect emissions, the value of 16.1 gCO_2eq/MJ was considered, as presented by the Joint Research Centre of the European Community for Natural Gas transported for 4000 km via pipelines, which is similar in distance to the Bolivia-Brazil pipeline of 3150 km. The diesel direct and indirect GHG emissions were considered as 74.1 gCO_{2eq}/MJ and 14.5 gCO_{2eq}/MJ (EDWARDS et al., 2014; GÓMEZ et al., 2006).

Process trains

Electricity production: The vinasse generated in the distillery is sent to a high-rate covered anaerobic lagoon-type digester. After digestion, vinasse is sent to the fertirrigation. Sulfur rich biogas is sent to a biological desulfurization system based on the biotrickling technology. The low-sulfur biogas is cooled to remove excessive moisture and compressed to the recommended level for the gas intake train of high-efficiency Otto cycle biogas gensets. The electricity generated by the gensets has its voltage increased and is subsequently connected to the electricity distribution grid. A schematic arrangement for electricity production from the biogas from vinasse is shown in Figure 4-1.

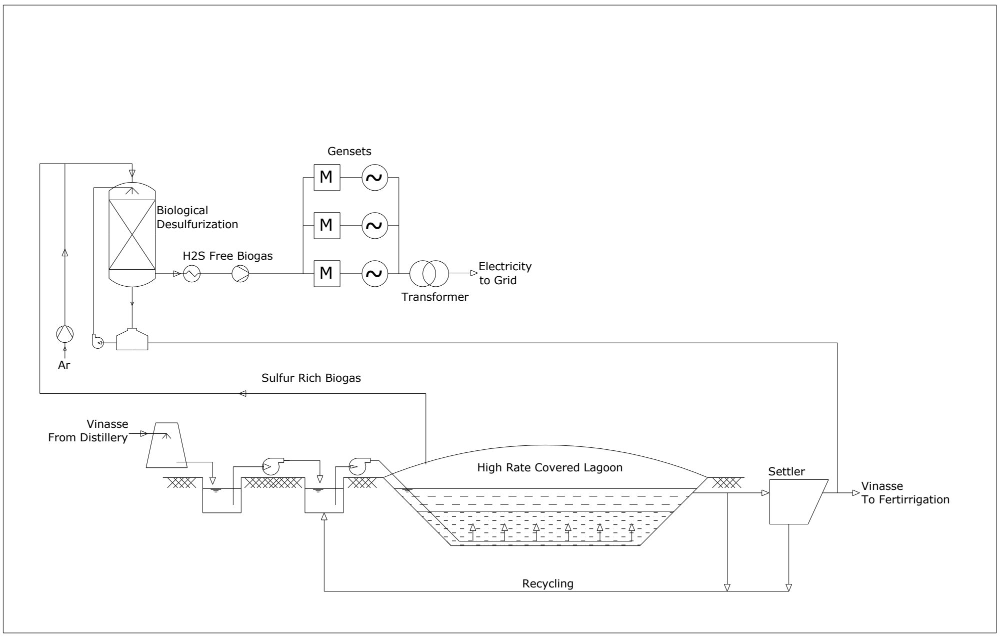


Figure 4-1: Process arrangements for electricity production from biogas obtained from sugarcane ethanol vinasse’s anaerobic digestion

Biomethane: Biogas is produced as previously described. The sulfur-rich biogas goes through a water scrubbing unit. After the CO_2 and H_2S removal, the gas is sent to a PSA unit for water removal. The offgas from the water scrubbing unit is sent to a biological desulfurization unit, as presented in the previous section, to prevent the H_2S emissions to the atmosphere.

For the natural gas grid injection, the biomethane should be odorized, which is presumably done by the gas distribution company. In addition, the biomethane pressure that leaves the upgrading unit should be sufficiently high to be injected in a distribution pipeline, in the range of 6 to 8 Bar. For vehicle use, biomethane should receive further compression to achieve 220-250 Bar. A type of biomethane storage and vehicle feeding should also be present. A schematic process arrangement for the biomethane production from biogas from vinasse is shown in Figure 4-2.

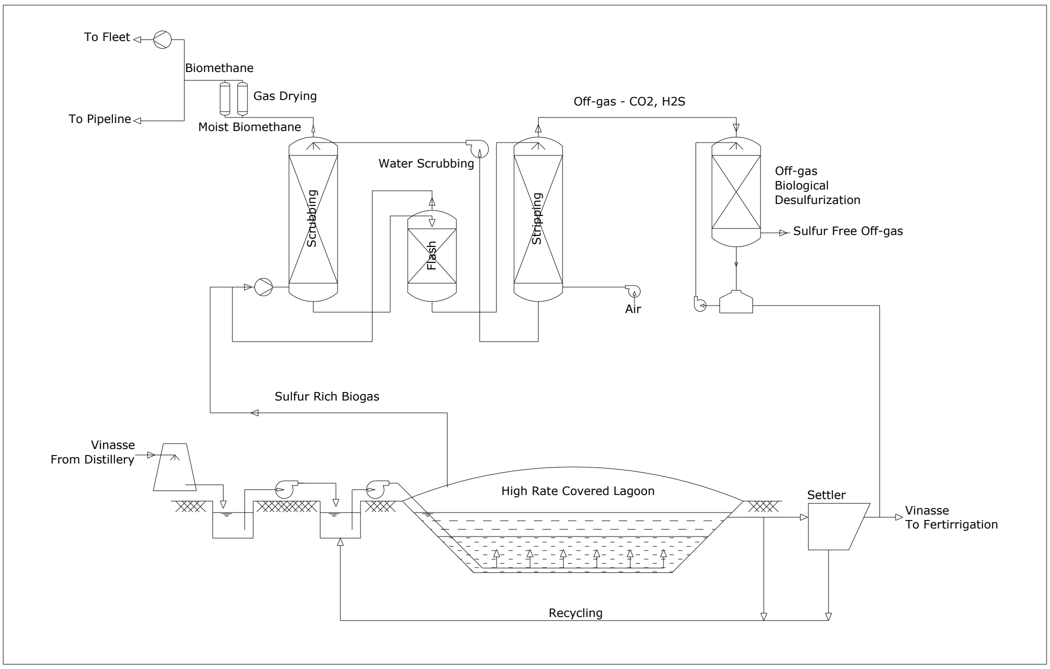


Figure 4-2: Process arrangements for biomethane production from biogas obtained from sugarcane ethanol vinasse’s anaerobic digestion

4.3 Results

EB and GHGEA of Ethanol with biogas for electricity production. For the electricity production with vinasse biogas, it is considered a gross electrical efficiency of 40% over methane LHV and 2.5% of electricity are used in the biogas production, desulfurization and electricity production processes. No leakages of biogas to the atmosphere were considered, and the energy consumption for plant construction was not considered. The energy output and emissions avoided by vinasse biogas producing electricity are shown in Table 4-5.

Table 4-5: Vinasse’s biogas producing Electricity: energy and emissions aspects

Parameter	*Value*	*Unit*
*Ethanol Yield**	*86.6*	*Litres/ton cane*
Vinasse Yield	*11.5*	*litres/litres*
COD	*31.5*	*kgO2/m³*
Methane Yield	*0.225*	*Nm^3CH_4/kgO2*
Methane LHV	*35.818*	*MJ/Nm^3 CH_4*
Gross Energy from Biogas	*252.7*	*MJ/TC*
Electrical Efficiency	*40%*	*% over LHV*
Electricity Generated	*28.1*	*kWhe/TC*
Electrical Internal Consumption (2.5%)	*0.7*	*kWhe/TC*
Electricity Net Output	*27.4*	*kWhe/TC*
	98.6	*MJ/TC*
*Grid Emission Factor**	*588.49*	*$kgCO_2eq/MWh$*
Emissions Avoided	*16.1*	*$kgCO_2eq/TC$*
	186.1	*$kgCO_2eq/m^3$ Ethanol*
** Average from Macedo (2008) and Seabra (2011)*		

With the additional electricity production from the vinasse biogas, new EB can be calculated for the sugarcane ethanol, as shown in Table 4-6.

Table 4-6: Energy balance of Ethanol production including by-products and electricity produced from Vinasse's biogas (MJ/tc)

	2005/2006(1)	2008(2)	Projection 2020(1)
Fossil input			
a. Total Fossil Input	233.8	273.6	262.0
Renewable Output			
b. Ethanol	1,926.4	1,811.7	2,060.3
c. Bagasse Surplus	176.0	59.8	-
d. Electricity from Bagasse Power Plant	82.8	108.7	972.0
e. (=b+c+d) Total Current Renewable Output	2,185.2	1,980.2	3,032.3
f. Electricity surplus from Biogas	98.3	92.3	105.1
g. (=e+f) Current Renewable output + electricity from biogas	2,283.5	2,072.6	3,137.4
Renewable output/fossil input			
h. (=e/a) Current EB	9.3	7.2	11.6
i. (=g/a) EB including electricity from Biogas	9.8	7.6	12.0
j.(=1-i/h) Increase in EB with electricity from biogas	4.5%	4.7%	3.5%
(1) MACEDO, I. C. et al. (2008); (2) SEABRA, J. E. et al. (2011)			

The electricity generated by the vinasse biogas will avoid GHG based on the national grid emission factor shown in the methodology section, which give us the values in Table 4-7 in terms of GHGEA from sugarcane ethanol.

Table 4-7: Net Avoided Emissions of Ethanol with the contribution of Vinasse's Biogas Electricity (kg CO_2 eq/m^3 anhydrous ethanol)

Year	2005/2006(1)	2008(2)	Projection 2020(1)
GHG emissions from Ethanol production and Sugarcane Farming			
a. Total emissions	436	579	345
GHG emissions avoided from ethanol and sugarcane by-products use			
b. Use of ethanol	2,111	2,066	2,111
c. Use of biomass surplus	150	60	-
d. Electricity surplus	62	83	819
e. (=b+c+d) Total avoided emissions from current products	2,323	2,209	2,930
f. (=e-a) Net Avoided Emissions from current products	1,887	1,631	2,585
g. Emissions Avoided by Electricity from Vinasse's Biogas	183.1	198.1	177.1
h. (=f+g) Net Avoided Emissions Including Vinasse's Biogas	2,070	1,829	2,762
i. (=h/f-1) Contribution of Biogas electricity to GHGEA	9.7%	12.1%	6.9%
(1) MACEDO, I. C. et al. (2008); (2) SEABRA, J. E. et al. (2011)			

EB and GHGEA of Ethanol with biogas for the production of Biomethane to Natural Gas Grid. The present evaluation assumes that the biogas production and purification processes require 0.40 kWh of electricity per Nm^3 of biomethane produced at 8 Bar of pressure, as presented by Bauer (2013) (BAUER et al., 2013b), and no further compression is required for the gas distribution grid injection. The energy required is generated with biogas produced in the plant at 40% electrical efficiency over LHV of methane on Otto cycle gensets. Then, 0.5% methane slip in off-gas is assumed from the purification process, which will not receive any further treatment. The energy output and emissions avoided by the vinasse biogas that replaces natural gas are shown in Table 4-8.

Table 4-8: Vinasse's biomethane replacing Natural Gas: energy and emissions aspects

Parameter	Value	Unit
Ethanol Yield*	86.6	Litres/TC
Vinasse Yield	11.5	litres/litres
COD	31.5	$kgO2/m^3$
Methane Yield	0.225	$Nm^3CH_4/kgO2$
Gross Methane Production	7.058	$Nm^3\ CH_4/TC$
Methane Internal Consumption	0.709	$Nm^3\ CH_4/TC$
Methane Slip (0,5%)	0.035	$Nm^3\ CH_4/TC$
Methane % in ANP Biomethane	96.5%	%
Net Biomethane Production	6.543	Nm^3Biomethane/TC
Biomethane LHV	34,564	kJ/Nm^3 Biomethane
Net Energy from Biomethane	226	**MJ/TC**
Natural Gas LHV	39,515	kJ/Nm^3 Natural Gas
Natural Gas replaced by Biomethane	5.723	Nm^3Natural Gas/TC
Emission factor Natural Gas	72.2	gCO_2eq/MJ
Gross Emission Avoided by Biomethane Replacing Natural Gas	16.3	$kgCO_2eq/TC$
Direct emissions from methane slip	0.7	$kgCO_2eq/TC$
Net GHGEA by Biomethane Replacing Natural Gas	**15.6**	**$kgCO_2eq/TC$**
	180.4	**$kgCO_2eq/m^3$ Ethanol**
* Average from MACEDO, I. C. et al. (2008) and SEABRA, J. E. et al. (2011)		

Table 4-9 shows the results in terms of EB of ethanol in a mill that produces and injects biomethane in the natural gas grid to replace this fossil fuel.

Table 4-9: Energy balance of Ethanol production including by-products and Biomethane from Vinasse injected in natural gas grid (MJ/TC)

	2005/ 2006(a)	2008(b)	Projection 2020(a)
Fossil input			
a. Total Fossil Input	233.8	273.6	262.0
Renewable Output			
b. Renewable output regular products	2,185.2	1,980.2	3,032.3
c. Net Biomethane Production	225.4	211.8	241.0
d. (=b+c) Renewable output regular products + biomethane	2,410.6	2,192.0	3,273.3
Renewable output/fossil input			
e. (=b/a) Regular Products	9.3	7.2	11.6
f. (=d/a) Regular Products + biomethane from vinasse	10.3	8.0	12.5
g.(=f/e-1) Increase in energy ratio with biomethane from vinasse	10.3%	10.7%	7.9%
(a) MACEDO, I. C. et al. (2008); (b) SEABRA, J. E. et al. (2011)			

The GHGEA of ethanol can be calculated considering the avoided emissions of biomethane injected on the grid to replace fossil natural gas, as shown in Table 4-10.

Table 4-10: Net Avoided Emissions of Ethanol with the contribution of Vinasse's Biomethane Injected in Natural Gas Grid (kg CO_2 eq/m^3 anhydrous ethanol)

Year	*2005/ 2006(a)*	*2008(b)*	*Projection 2020(a)*
GHG emissions			
a. Total Emissions Ethanol Production	*436*	*579*	*345*
b. Direct Emissions CH_4 Slip	*8.2*	*8.2*	*8.2*
GHG avoided emissions			
c. Total Avoided Emissions Ethanol Production and Use	*2,323*	*2,209*	*2,930*
d. (=c-a) Net Avoided Emissions from current products	*1,887*	*1,631*	*2,585*
e. Emissions Avoided by Vinasse's Biomethane replacing Natural Gas	*188.5*	*188.5*	*188.5*
f. (=d-b+e) Net Avoided Emissions Including Vinasse's Biomethane	*2,067*	*1,811*	*2,765*
g. (=f/d-1) Contribution of Vinasse's Biomethane to GHG balance	*9.6%*	*11.1%*	*7.0%*
(a) MACEDO, I. C. et al. (2008); (b) SEABRA, J. E. et al. (2011)			

EB and GHGEA of Ethanol with biogas vinasse to produce biomethane to replace Diesel. The conversion of sugarcane transportation trucks to dual-fuel diesel-gas engines was considered for 2005 and 2008 at an Energy Substitution Rate (ESR) of 40%. Harvesters, which are the highest individual consumer of diesel oil in sugarcane operations, were also considered to be converted at 60% ESR for 2020 when the trucks have ESR increased to 45%, considering some improvements of the technology. Only a fraction of the biomethane potential will be used as diesel replacement because of the limits of dual-fuel ESR. This fact limits the EB and GHGEA that biomethane has theoretical potential as a diesel replacement fuel. The remaining biomethane from the diesel replacement is injected into the natural gas grid. The energy required for biomethane production is considered identical to that in the previous section with further energy requirement for gas compression to 220 Bar at additional 0.20 kWh/Nm^3 of biomethane for the dual fuel. Table 4-11 shows the diesel replacement by biomethane in each scenario.

Table 4-11: Calculated Diesel consumption in sugarcane harvesting and transportation and projections for fuel consumption with Dual-Fuel Diesel-Gas (l/TC for Diesel, Nm^3Biomethane/TC for Biomethane)

		Estimated Diesel Consumption			*Projected Consumption Dual-Fuel*		
		2005/2006(a)	*2008(b)*	*Projection 2020(a)*	*2005/2006(a)*	*2008(b)*	*Projection 2020(a)*
Harvesting	*Diesel (l/tc)*	*1.05*	*1.00*	*0.99*	*1.05*	*1.00*	*0.40*
	Methane (Nm^3/tc)	*-*	*-*	*-*	*-*	*-*	*0.60*
Cane transportation	*Diesel (l/tc)*	*1.04*	*0.97*	*1.26*	*0.63*	*0.59*	*0.71*
	Methane (Nm^3/tc)	*-*	*-*	*-*	*0.42*	*0.40*	*0.58*
(a) MACEDO, I. C. et al. (2008); (b) SEABRA, J. E. et al. (2011)							

The EB of ethanol with biomethane that replaces diesel oil in dual-fuel diesel-gas cane transport trucks and harvesters with surplus gas injected into the natural gas grid is presented in Table 4-12.

Table 4-12: Energy balance of Ethanol production including by-products and Biomethane from Vinasse replacing Diesel and injected in natural gas grid (MJ/tc)

	2005/ 2006[a]	2008[b]	Projection 2020[a]
Fossil input			
a. Total Fossil Input	*233.8*	*273.6*	*262.0*
b. Biomethane Replacing Diesel	*- 15.2*	*- 14.2*	*- 42.4*
c. (=a+b) Total fossil input with Biomethane replacing diesel	*218.6*	*259.4*	*219.6*
Renewable Output			
d. Renewable output regular products	*2,185.2*	*1,980.2*	*3,032.3*
e. Biomethane Exported to Natural Gas Grid	*209.4*	*196.9*	*196.4*
f. (d+e) Renewable output regular products + biomethane to grid	*2,394.6*	*2,177.1*	*3,228.7*
Renewable output/fossil input			
g. (=d/a) Regular Procucts	*9.3*	*7.2*	*11.6*
h. (=f/c) Regular Products + biomethane	*10.95*	*8.39*	*14.70*
j. (=h/g-1) Increase in energy ratio with biomethane from vinasse	*17.2%*	*16.0%*	*27.0%*
(a) MACEDO, I. C. et al. (2008); (b) SEABRA, J. E. et al. (2011)			

A new GHGEA of ethanol in distilleries using biomethane for the partial substitution of diesel in sugarcane transportation and harvesting and exceeding the gas being injected into the natural gas grid is presented in Table 4-13.

Table 4-13: Net Avoided Emissions of Ethanol with the contribution of Vinasse's Biomethane replacing Diesel and Injected in Natural Gas Grid (kg CO_2 eq/m³ anhydrous ethanol)

Year	2005/ 2006[a]	2008[b]	Projection 2020[a]
GHG emissions			
a. Total Emissions Ethanol Production	*436*	*579*	*345*
b. Direct Emissions CH_4 Slip	*8.2*	*8.2*	*8.2*
GHG avoided emissions			
c. Total Avoided Emissions Ethanol Production and Use	*2,323*	*2,209*	*2,930*
d. (=c-a) Net Avoided Emissions Ethanol Production and Use	*1,887*	*1,631*	*2,585*
e. Emissions Avoided Biomethane replacing Diesel Oil	*15*	*15*	*39*
f. Emissions Avoided Biomethane replacing Natural Gas	*176*	*176*	*155*
g. (=d+e+f-b) Net Avoided Emissions Including Vinasse's Biomethane	*2,070*	*1,814*	*2,770*
h. (=g/d-1) Contribution of Vinasse's Biomethane to GHG balance	*9.7%*	*11.2%*	*7.2%*
(a) MACEDO, I. C. et al. (2008); (b) SEABRA, J. E. et al. (2011)			

4.4 Discussion

4.4.1 Biogas for electricity production

The GHGEA of the ethanol of a typical Brazilian distillery can be improved by up to 12.1% using vinasse biogas for electricity production compared with a distillery that does not adopt this practice. In terms of EB, the production of electricity with biogas from vinasse can improved the ethanol performance by up to 4.7% compared to the mills with current production practices and by 3.5% for the projections of more efficient mills, where larger amounts of electricity from bagasse are expected.

The connection to the grid should not be a problem for relatively low power biogas projects, since the electrical distribution network is well established in sugarcane production areas. The electricity from vinasse biogas brings benefits of the distributed generation, and its production should occur in the low rainfall period of the year for most hydro power plants in Brazil, which may complement this source of energy in a non-intermittent, base-load fashion. In addition, this electricity should partially prevent the natural gas power plants from being dispatched with high CO_2 emission factor at the operating margin, which was 0.5890 tCO_2/MWh in 2017 on average and consistent with the values in the present evaluation (MCTIC, 2018).

Instead of building a biogas plant, mill operators can increase the electricity production in their Cogeneration Plants using tops and leaves (commonly left on the field) as additional fuel or using higher-fiber-content sugarcane (or energy cane varieties) (GRASSI; PEREIRA, 2019; LEAL; WALTER; SEABRA, 2013), which would not require major capital expenditures in retrofitting the cogeneration plant to operate at higher temperature and pressure. Two main points should be considered, which favour vinasse biogas: the higher electrical efficiency of Otto cycle engines in biogas plants against Rankine cycle in the mills and the associated cost of collecting the biomass, which can be substantial. In addition, the collection of tops and leaves may cause negative implications to the current agronomic and industrial operations of the mills (HASSUANI; LEAL; MACEDO, 2005), and the higher fiber content in sugarcane may affect the milling and extraction process (GRASSI; PEREIRA, 2019). The bagasse, tops and leaves may also soon become feedstock for the second-generation ethanol, but the electricity from biogas implies an entire new plant to be built at relevant investments.

4.4.2 Biomethane production for the natural gas grid injection

Unlike electricity, which has been traded by independent power producers in Brazil since the early 1990s, biomethane production is a developing and less common activity, even in countries where biogas production is a well-established practice. The biomethane specification regulation in Brazil was published in 2015 by ANP, but there is no obligation of mixing renewable fuel with fossil natural gas, as it occurs with gasoline and diesel. There are pending regulations for the use of transportation pipelines, and the exchange or swap of the gas among different distribution companies remains not entirely defined. In addition, comparing to electricity, the natural gas distribution and transport pipelines have much lower extension, so the connection of biomethane plants to natural gas pipelines tends to be more expensive or difficult. Only 60 ethanol mills in São Paulo State among 159 existing mills are in a 20-km range from natural gas pipelines, and several of those are near the transport gas pipes, which would require a much higher pressure to inject the produced biomethane.

To date, there is no single “independent connection” of biomethane (and even natural gas) to the transport pipeline, and the natural gas transport company in the central-southern region of Brazil declares that there is no spare capacity for additional contracts, which limits the possibility of delivering biomethane to distribution pipelines and further reduces the number of mills at practical distance from the pipeline to perform connection.

The biomethane injected on the natural gas grid will directly replace its fossil counterpart, which avoids fossil direct and indirect emissions independently of its final use. The projected result for a mill injecting biomethane on the grid is an improvement of 10.7% and 7.9% in EB for mills with current production practices and future projections, respectively. Concerning GHGEA, the biomethane injected on the grid can represent 11.1% and 7.0% improvements compared with current practices and future projections, respectively.

Biomethane production should have mainly water and electricity as the operation supplies, and significantly fewer moving parts are subject to friction and wear compared with the electricity production. In addition, biomethane production should be composed of only one purification unit instead of multiple gensets, which favours the reduction in acquisition and maintenance costs due to the scale of the projects. Unlike the electricity generation, the biomethane production should have higher internal energy consumption due to the compression of biogas in the purification process. This energy can be obtained from the biogas or bagasse power plant. This second possibility will depend on the available surplus of electricity of the power plant and be constrained by commercial conditions and contracts of bagasse and electricity sales that the mill may have.

4.4.3 Biomethane replacing Diesel

The results for GHGEA of distilleries with dual-fuel diesel-gas trucks and harvesters will be affected by a larger emission factor from diesel oil (88.6 gCO_2/MJ (EDWARDS et al., 2014)) than natural gas (72.2 gCO_2/MJ (EDWARDS et al., 2014; GÓMEZ et al., 2006)), but as previously mentioned, this effect is limited by the number of consumers that can use such technology and by the higher energy use resulted from the biomethane compression to 200-250 Bar for Dual-Fuel use.

The biomethane used as a diesel replacement directly affects the fossil consumption of sugarcane production instead of provoking GHG and fossil energy abatement elsewhere. Note that the production of biomethane from vinasse geographically and seasonally coincides with most diesel consumption of sugar mills, which introduces commercial and logistics advantages for diesel replacement with biomethane.

The use of dual-fuel diesel-gas technology to replace diesel appears logical because of its flexibility to operate only with diesel in the off-season period, when no gas is available for most mills, but the incomplete replacement of diesel limits the amount of fossil energy that can be avoided. In addition, the cost associated with the consumer conversion to dual-fuel may limit the technology to few operations with intense diesel consumption, such as cane transportation and harvesting. Because a limited amount of biomethane can practically replace diesel in dual-fuel trucks and harvesters, a large amount of biogas is available for further biomethane production or electricity generation.

Since the scale plays an important role in the acquisition and operation costs of biomethane plants, and the quality of biomethane for the grid injection or diesel replacement is the same (except for the pressure), it appears logical to produce biomethane from all available biogas to increase the size and gain scale in the purification unit, which directs the product for dual-fuel consumers and the remaining flows to grid injection, but this possibility is also constrained by the existence of natural gas grids near the mill, as discussed.

Surplus biogas from the biomethane production for dual-fuel consumers can be directed to electricity production, but a different process train should be designed with higher specific costs for the biomethane production, although this arrangement is applicable for most mills.

The compression of biomethane adds a fair amount of energy consumption to the overall process, which diminishes the effect of replacing a more carbon-intense fuel (diesel) than the biomethane injection on the natural gas grid option. In terms of GHG emissions, the unburnt methane in dual-fuel exhaust gases should receive attention, which can eliminate any benefits of replacing fossil diesel by the renewable biomethane.

Biomethane used on the mill fleet directly reduces the fossil diesel use and results in a much more favourable EB. The calculated improvements in EB of the biomethane replacement are 16.0% for current operations and 27.0% when the harvesters are included. In terms of GHGEA, the biomethane replacement results in biomethane injection on the grid activity and causes 11.2% and 7.2% better GHGEA balances compared to a mill without such biomethane energetic use. The results are shown in Figure 4-3.

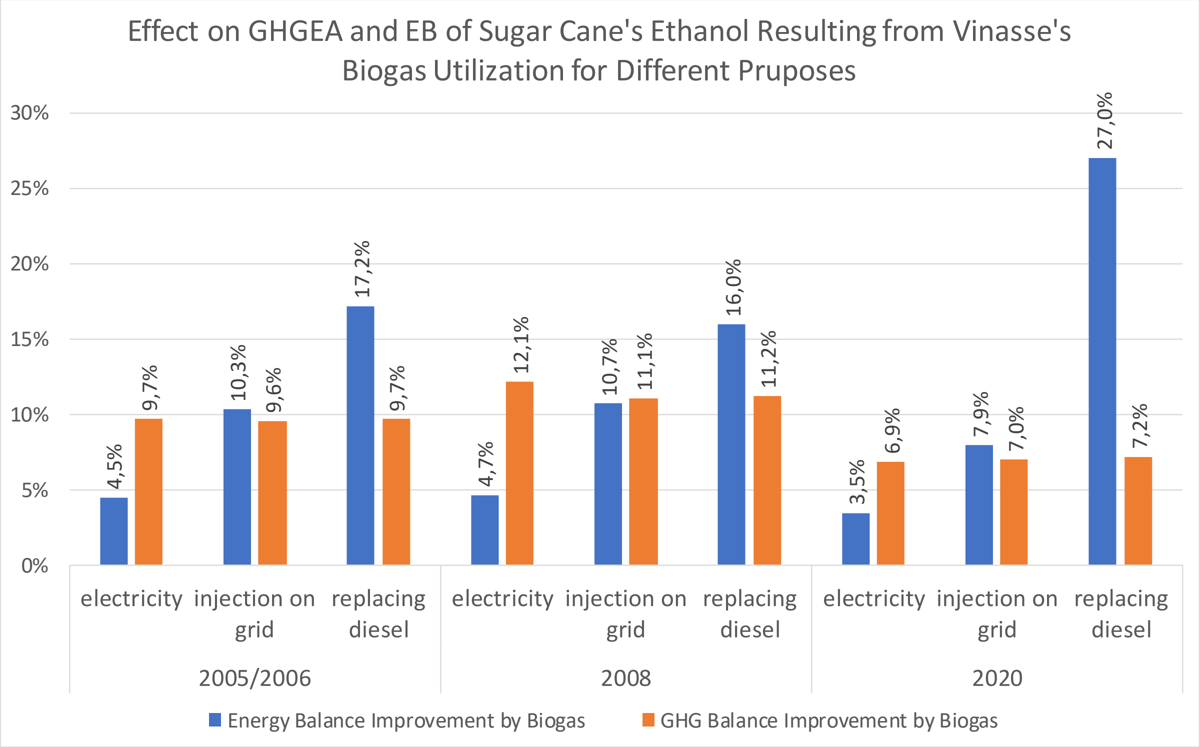


Figure 4-3: Energy and GHG Balances of Ethanol Production in Existing Practices and Future Scenario with Potential Biogas Benefits

4.5 Conclusions

The production and use of biogas from vinasse have considerable energetic and GHGEA potential, that, if allocated to sugarcane ethanol, can improve the environmental and energetic performance of this important renewable fuel.

Commercial technologies are available to produce biogas from vinasse and biogas processing to electricity, biomethane and there are many examples of successful similar projects in other industries and countries. However, this is not a common practice in Brazil, although the seasonal operation and high-sulfur level in the biogas from vinasse impose some penalties for these projects.

When considering the production of vinasse biogas and its use to produce electricity or biomethane (injected in a natural gas pipeline or replacing fossil diesel in mill operations), the indicators of sustainability such as GHGEA and EB can be improved by as much as 27.0% in GHGEA by using biomethane to replace diesel in the future scenario. In the worst case, there is a 3.5% improvement in EB for future scenario with biogas for electricity generation.

The technological, energetic, environmental, economic and logistics aspects must be considered when evaluating the production of electricity or biomethane from vinasse, but because of the biogas versatility, there is a range of possibilities for different arrangements and conditions of specific projects.

The proposed activities introduce other benefits: small-scale, geographically distributed, technologically intensive, near-end-user, high-skilled-labor-demanding biogas projects, which may be implemented in the sugarcane industry in Brazil.

The establishment of mandates to mix biomethane into natural gas with premium price for the renewable gas and benefits for mills with better GHGEA and EB are discussions in course by the Brazilian government and can motivate this possibility. Policy makers should be diligent in understanding the peculiarities of these projects to stablish rules that can help the development of this practice, which can induce several benefits to Brazilian society and the biofuel industry.

5 Article 3 - Potential impacts of vinasse biogas replacing fossil oil for power generation, natural gas, and increasing sugarcane energy in Brazil[7]

Abstract

This paper presents the potential of biogas from anaerobic digestion of vinasse and its impact in different contexts. The use of vinasse biogas (VBG) for power generation is evaluated and the potential of this energy source is compared with fossil oil power plants in terms of energy, costs and greenhouse gases (GHG) emissions in Brazil, suggesting a program where the most expensive oil power plants are replaced by biogas plants with benefits in all aspects. Secondly, the use of vinasse biomethane (VBM) to replace natural gas (NG) in the state of São Paulo is examined, presenting an incentive program that could make this alternative fuel feasible even in smaller scale plants with minimal impact on NG costs in this state, while providing considerable emission reduction. The impact of VBG considering the increase in ethanol production over the next ten years is also evaluated, showing that substantial additional energy can be obtained and larger amounts of fossil fuels can be replaced. By crossing vinasse biogas potential with selected fossil fuels demand, the article brings insights to help the transition to a low-carbon society in a novel approach. The conclusions are that VBG and VBM can provide great benefits, such as USD 1 billion/year cost reductions and 6.7 million tons CO_{2e}/year emissions avoided by replacing fossil oil by biogas in power generation in Brazil and 3.2 million tons CO_{2e}/year avoided with biomethane replacing natural gas in the state of São Paulo, which, with specific programs and policies, could be achieved.

Highlights:

- Vinasse biogas could replace fossil oil and natural gas in Brazil
- Electricity from vinasse biogas avoid GHG emissions at lower costs than oil plants
- Vinasse biomethane can replace natural gas in São Paulo with minimal cost increase
- Vinasse biogas can substitute more fossil fuels with increased ethanol production

---

[7] This chapter is an *ipsis litteris* reproduction of the paper accepted by the Journal *Renewable & Sustainable Energy Reviews* in August 2020.

Silva Neto, J.V., Gallo, W.L.R., 2020. Potential impacts of vinasse biogas replacing fossil oil for power generation, natural gas, and increasing sugarcane energy in Brazil. Renewable and Sustainable Energy Reviews. In Press. https://doi.org/10.1016/j.rser.2020.110281

5.1 Introduction

Brazil is the second largest ethanol producer in the world, with 27.8 billion liters in 2018 (UNICA, 2019b). Each liter of ethanol produces an average of 11.5 liters of vinasse, a liquid with high pollution potential (ELAIUY et al., 2018; ELIA NETO; SOUZA, 2016; JANKE et al., 2015; WILKIE; RIEDESEL; OWENS, 2000). When submitted to anaerobic digestion, vinasse generates biogas, which is composed of methane (CH_4), carbon dioxide (CO_2) and hydrogen sulfide (H_2S), and can account for a substantial increase in energy output from sugarcane crops. After the removal of H_2S, this gas can be used to generate electricity, and by removing H_2S, CO_2 and water it acquires similar characteristics to natural gas (NG) (ANP, 2015) and can be injected in NG pipelines or replace diesel in sugarcane agricultural operations. In most Brazilian mills, the vinasse is applied in the crop fields (process called fertirrigation), with the objective of recycling the nutrients contained in the vinasse (Nitrogen, Phosphorous and Potassium). After anaerobic digestion, vinasse can be also used for fertirrigation, maintaining its original properties as fertilizer (CHRISTOFOLETTI et al., 2013).

Considered as an ethanol byproduct, vinasse biogas (VBG) can improve energy and greenhouse gases (GHG) emissions balances of ethanol itself, result of better transformation of sugarcane biomass into renewable energy (DA SILVA NETO; GALLO; NOUR, 2020). Considered as an “independent” biofuel (dissociated from the ethanol that originated the vinasse from which it was produced), it would produce energy with a carbon footprint up to 96% lower than the fossil counterpart (MATSUURA et al., 2018).

Although there are 355 ethanol distilleries in Brazil (ANP, 2019a), only ten projects using vinasse to produce biogas have been developed in the past 38 years, and most of them are no longer in operation (ELIA NETO; SOUZA, 2016).

Biogas is produced worldwide. Europe leads the biogas industry with 10.4GW of installed capacity, followed by the United States with 2.4GW. In Europe, Germany leads in number of plants and energy production, followed by the UK and Italy in energy production (SCARLAT; DALLEMAND; FAHL, 2018). Since the Renewable Energy Sources Act in 2000, Germany has experienced exponential growth; in 2016 it had 8,300 biogas plants with 4.5GW of installed capacity and 196 biomethane plants, although recent changes in incentive schemes have slowed down this expansion (DANIEL-GROMKE et al., 2018). Thailand leads among developing countries with 500MW of biogas installed capacity (IRENA, 2019).

Possible explanations for the timid adoption of vinasse biogas as an energy source in Brazil may be the competition against cheaper, better established electricity sources (e.g. photovoltaic, wind, and hydro), lack of incentive policies, restricted technical information and perceived risks of this new activity (JENDE et al., 2016; KPMG, 2015; QUADROS et al., 2015).

Most of the electricity in Brazil is generated by renewable sources (EPE, 2018a), but, due to the strong dependency on hydro power plants, unfavorable rain regimes lead to the dispatch of fossil oil and gas power plants, as happened in the past years. VBG power could help to reduce the dispatch of fossil oil plants in Brazil if adequate conditions are created.

NG is responsible for 12.9% of internal energy supply in Brazil (EPE, 2018a), but unlike other fuels, such as gasoline and diesel, which are mixed with ethanol and biodiesel respectively, it does not have a renewable blending mandate. The state of São Paulo is the largest NG consumer and ethanol producer in Brazil, where would be possible to partially substitute NG by purified vinasse biogas (vinasse biomethane - VBM), if a mandate is established and incentives are created to this new biofuel.

The Brazilian Energy Research Office (EPE) forecasts up to 83% increase in ethanol production for next ten years in the country (EPE, 2018c). Total energy output from sugarcane could be amplified if vinasse biogas is also considered, resulting in further substitution of fossil fuels and improved sustainability of the ethanol.

This article presents costs and GHG emissions of the fossil oil electricity generation nationwide, as well the consumption of NG in the state of São Paulo and compares this information with the potential of VBG and VBM in the same regions, showing potential reductions in cost and GHG emissions that could result from the substitution of fossil fuels by renewable VBG and VBM. By making these comparisons direct and objectively, this article presents valuable information in a novel approach which may serve as a tool for policymakers, who may have not realized practical possibilities of VBG and VBM and the benefits these renewable fuels can bring to energy sector in Brazil.

The objective of this article is to present and discuss a program to replace fossil oil power plants by VBG in Brazil, considering potential power replacement, indicative prices for VBG electricity and the program’s economic and emissions reduction benefits. Indicative prices and premium to be paid for VBM will be also be presented, evaluating the effects on the cost of NG in the state of São Paulo and benefits in terms of emissions with the replacement of NG by renewable VBM. The article also shows the additional energy that can be obtained from VBG considering the expected ethanol production expansion in the country in the coming years.

5.2 Potential benefits of vinasse biogas

5.2.1 Electricity production

Biogas is not a common energy source in Brazil. Only 38 biogas projects are registered in the ANEEL database (April 2019), with a total capacity of 156MW. Among them, 90% are landfill sites and none have sold energy in national electricity auctions (MINISTRY OF FOREIGN AFFAIRS OF DENMARK, 2018; QUADROS et al., 2015). Among biogas projects in Brazil from other sources, only one was contracted through a national electricity auction, a large VBG project (20.9MW) by a major ethanol producer (MERCOSUR AD HOC GROUP ON BIOFUELS, 2017; MINISTRY OF FOREIGN AFFAIRS OF DENMARK, 2018). Investments required to VBG production and desulfurization are high, so in competition against other sources of energy in auctions, and also because of restricted technical information about biogas, VBG is in disadvantage.

The Brazilian Energy Operation Plan for 2018/2022 recognizes that the increasing volume of electricity from solar and wind power generation and the falling reserve capacity of hydro power in Brazil, alongside recurring unfavorable climatic conditions, leads to the increased dispatch of fossil power plants.

Most fossil power plants in Brazil are powered by diesel, fuel oil and NG, dispatched when the rainfall regime is unfavorable, which occurred frequently in the past five years, especially in 2014 and 2015 (CCEE, 2018).

Figure 5-1 shows the share of selected sources of the electricity sources in Brazil in last decade.

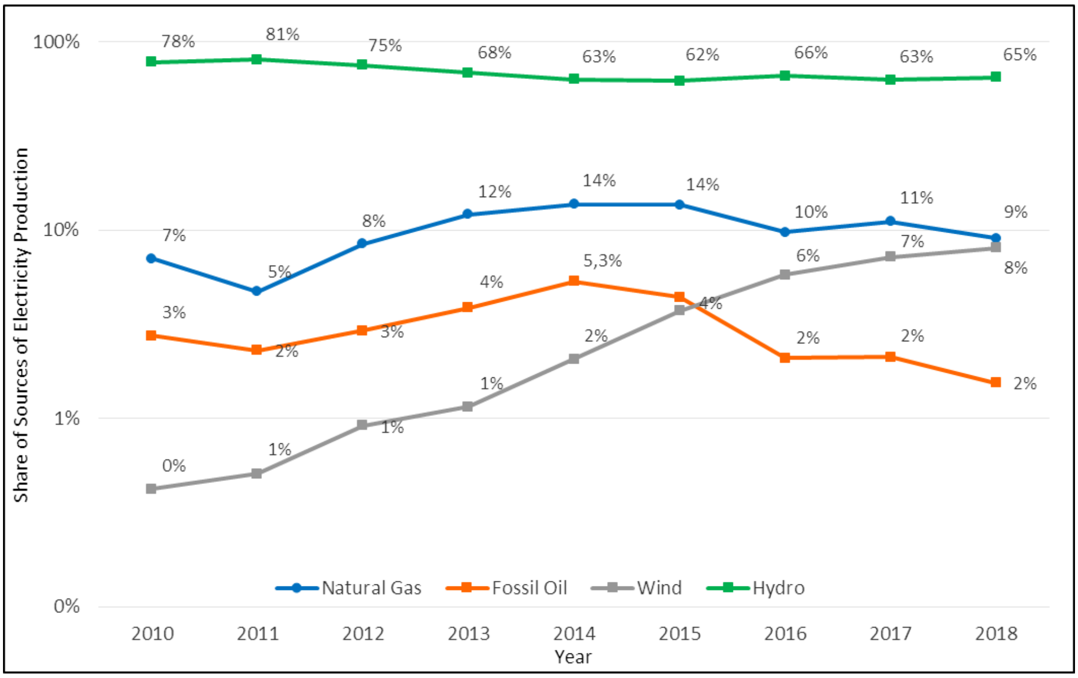


Figure 5-1: Share of selected sources of electricity generation in Brazil in the last decade. Sources: EPE (2017), EPE (2018).

Among all sources of electricity in Brazil, fossil oil is the most expensive (ONS, 2018) and, although responsible for less than 5.3% of power generation in the country between 2014 and 2018, it is responsible for as much as 23.4% of greenhouse gases emissions associated to electrical sector of the country (SISTEMA DE ESTIMATIVA DE EMISSÕES DE GASES DE EFEITO ESTUFA - SEEG, 2019).

Oil power plants in Brazil were mostly contracted in auctions between 2005 and 2008, predicted to start operating 3 to 5 years after the auction and usually with a contract term of 15 years, which means that most of these contracts are approaching their expiration.

VBG electricity is a non-intermittent source, which can be produced night and day during the sugarcane crop season (April to November in Brazil Center-South region), which is the low rainfall period of the year for most of the hydro power plants in the country.

VBG electricity could be used in a preventive fashion, balancing the gaps of intermittency of wind and solar and preserving water in the reservoirs of hydro power, thus, instead of dispatch oil power plants when critical situations are forecasted, VBG could be dispatched as baseload of the electrical system to avoid future critical situations. VBG electricity may be an alternative to replace fossil oil power plants, bringing economic and emissions benefits to Brazil. Fossil oil power plants dispatch could be avoided if a program focusing on their replacement by VBG power plants were put in place.

5.2.2 VBM replacing NG

In 2015 the National Agency of Oil, Natural Gas and Biofuels (ANP) issued Resolution 8/2015 establishing specifications, sources and uses of biomethane as a substitute for NG. According to this regulation, purified biogas that achieves the specifications can be blended with NG in any proportion. Since then, 8 biomethane projects have been commissioned in Brazil, and only one has had the gas injected in the pipeline, which shows the early development stage of this market.

São Paulo State Decree 58659/2012 created the Biogas Program to establish a blending mandate of biomethane in NG in the state (SÃO PAULO, 2012). Although the program is not yet in force, indicative values of biomethane percentage to be mixed into NG have been unofficially announced (ABEGAS, 2018). São Paulo has three NG distribution concession areas, each one with different sales volumes and different VBG production potential. According to this unofficial announcement, each NG distribution company in the state will have a different blending mandate and the distribution company with larger volume of NG sales does not have significant VBG potential.

São Paulo is the largest consumer of NG and the largest producer of ethanol in the country. In addition, most of its landfill gas is committed to electricity generation (MINISTRY OF FOREIGN AFFAIRS OF DENMARK, 2018; PNUD, 2010), and therefore VBG represents the biggest potential for biomethane production in the state.

VBM is a new biofuel in Brazil. The knowledge, engineering capabilities, operating experience and equipment supply required for its full establishment are still being developed, which implies higher costs of VBM projects. As it is a new biofuel, higher risks are perceived by operators, project developers and mill owners, and thus increased rates of return are demanded from VBM projects. It is natural that some sort of price benefit may be required for its production on a large scale. As an example, after 13 years of blending mandate with fossil diesel and a 10% share of the diesel volume, biodiesel in Brazil is still more expensive than fossil diesel (ANP, 2019b; EPE, 2018a).

The RenovaBio program (BRASIL, 2017) establishes Brazil’s decarbonization goals for the fuel energy mix and creates decarbonization credits (CBIOS) to be issued by biofuel producers proportionally to their efficiency and production and acquired by fuel distribution companies according to their individual targets (MME, 2017). Theoretically, NG distribution companies should also have decarbonization targets, since they are fuel distribution companies.

CBIO has the merit of allowing more credits for more efficient biofuels in terms of avoided emissions, which is the case of VBM. On the other hand, CBIO value fluctuations in face of international oil prices (MME, 2017) may bring satisfactory results for well-established biofuels but have arguable benefits to new products entering the market, such as VBM.

Alternative incentive schemes could be adopted. For example, the state of São Paulo encourages NG distribution companies to extend their area of operation by allowing regions that are not yet served by the NG feeding pipeline to receive compressed gas transported by trucks, which then feed a low-pressure distribution network inside the cities. The state regulator allows the costs associated with gas compression and transportation to be paid by all consumers in the concession area rather than only the consumers in the region served by the compressed, road transported gas. This arrangement allows the development of new consumers without an excessive increase in fuel price, since it is limited to a small fraction of the distribution companies' costs (ARSESP, 2011).

A similar concept could be adopted to allow NG distribution companies to buy VBM at a premium price over fossil NG, limited to a pre-established value and term, in order to make these projects viable in the dawn of this new market.

5.2.3 Vinasse biogas implications face of increased ethanol production

The increase in ethanol demand forecasted to 2030 would require the additional production of 24.6 billion liters of ethanol. In this increased production forecast, vinasse biogas could account for additional energy, which could contribute even further to the reduction of fossil fuel consumption. Alternatively, if VBM is capable of providing the same energy service as ethanol (e.g., light Otto cycle vehicles fuel), less area would be required to meet the estimated increase in energy demand, since more energy could be obtained from the same amount of biomass when vinasse is anaerobically digested.

In any case, higher efficiency in energy transformation of sugarcane biomass would be achieved, resulting in a higher renewable to fossil energy ratio and greater emission reductions of the whole sugarcane industry (DA SILVA NETO; GALLO; NOUR, 2020).

5.3 Methodology

5.3.1 Electricity from vinasse biogas

The top-level approach of the methodology of this work can be summarized as follows:

1 – Calculate, based on Brazilian ethanol production, vinasse quantitative and qualitative aspects and transformation coefficients (from vinasse COD to methane and from methane to electricity), the potential electricity that can be produced from VBG.

2 – Calculate, based on average operating hours per year of ethanol plants, the average power of VBG plants.

3 – Calculate, based on actual electricity production between 2014 and 2018 and on installed power, the average capacity factor of fossil oil power plants in Brazil.

4 – Calculate, based on average power of oil fossil plants and average power of VBG plants, how much of the capacity of fossil oil plants can be replaced by VBG plants.

5 – Based on the calculated fossil oil plants substitution by VBG plants and on GHG emissions factor and generation costs of the two kinds of plants, benefits of VBG can be calculated.

It is worth noting that, although VBG power is here calculated as an overall sum, there should be one VBG plant annex to each of the 355 ethanol plants – if all potential is used, so the totality of power produced would be divided in 355 small scale and short construction cycle VBG plants distributed over the country. Total VBG power potential is calculated based on Brazilian ethanol production, the average of Brazilian vinasse yield and Chemical Oxygen Demand (COD), Methane Conversion Factor (MCF) found in literature, methane Lower Heating Value (LHV), electrical efficiency of biogas gensets of major suppliers in the market (CATERPILLAR ENERGY SOLUTIONS GMBH, 2017; INNIO, 2019; SIEMENS ENERGY INC., 2018) and estimated operating hours per year of ethanol distilleries in Brazil, according to Equation 5-1, with the result given in kW:

$$E.Power_{VBG} = \frac{\left(Production_{etho-BR}\ X\ Yield_{vinasse}\ X\ COD_{vinasse}\ X\ MCF\ X\ LHV_{methane}\ X\ EE_{genset}\right)}{\left(3{,}600\ X\ Operating\ Hours_{year}\right)} \qquad \text{Equation 5-1}$$

Where:

$Production_{etho\text{-}BR}$: Ethanol produced per year [m^3_{etoh}]

$Yield_{vinasse}$: Litres of vinasse produced by liter of ethanol [m^3/m^3]

$COD_{vinasse}$: Chemical Oxygen Demand of vinasse [kgO_2/m^3]

MCF: Methane Conversion Factor, i.e.: amount of methane that is produced per kg of COD of vinasse submitted to anaerobic digestion [$Nm^3CH_4/kgCOD$]

$LHV_{methane}$: Lower Heating Value of methane [kJ/Nm^{3}CH$_4$]

EE_{genset}: Electrical Efficiency of gensets, i.e.: Percentage of biogas energy, measured by its lower heating value (LHV), that is converted into electricity in Otto cycle biogas gensets [%]

$Operating\ Hours_{year}$ – Number of operating hours of a typical distillery per year in Brazil [hours/year]

3,600 – Conversion factor from kJ/h to kW

Otto cycle biogas gensets were chosen for calculation since they present higher electrical efficiency compared to gas or steam turbines (ENERGY AND ENVIRONMENTAL ANALYSIS INC;; EASTERN RESEARCH GROUP (ERG);, 2007) and because they are standard power generation equipment used in biogas plants (DANIEL-GROMKE et al., 2018; VAN FOREEST, 2012).

The VBG power plant annual capacity factor is the result of the division of Brazilian distilleries' operating hours per year by total hours in a year (Equation 5-2).

$$Capacity\ Factor_{VBG} = \frac{Operating\ Hours_{year}}{8{,}760} \qquad \text{Equation 5-2}$$

Where:

$Operating\ Hours_{year}$: Number of operating hours of a typical distillery per year in Brazil [h]

8,760: Number of hours per year

The average VBG plant power is calculated by multiplying VBG power plant capacity by the capacity factor (Equation 5-3):

$$Average\ Power_{VBG} = E.Power_{VBG}\ X\ Capacity\ Factor_{VBG} \qquad \text{Equation 5-3}$$

The average power dispatched in kW by fossil oil power plants is calculated based on the actual electricity generated by each individual power plant "j" in each month "i" (CCEE, 2018), divided by the number of hours of each month divided by the number of months in the period of January 2014 to December 2018 (Equation 5-4):

$$Average\ Power_{oil\ plant\ j\ (2014-2018)} = \frac{\sum_{i=1}^{60}\left(\frac{Electricity\ Generated_{month\ i, oil\ plant\ j}}{Month\ Hours_i}\right)}{60} \qquad \text{Equation 5-4}$$

Where:

60: Number of months in the period of January 2014 to December 2018.

$Electricity\ Generated_{month\ i,\ oil\ plant\ j}$: Electricity generated by oil power plant "j" in the month "i" [kWh]

$Month\ Hours_i$: Number of hours in month "i" [h]

The average power dispatched by fossil oil power plants between January 2014 and December 2018 is the sum of the average power of each individual fossil oil power plant in the period (Equation 5-5).

$$Average\ Power_{oil\ plants\ (2014-2018)} = \sum_{j=1}^{n} Average\ Power_{oil\ plant\ j\ (2014-2018)} \qquad \text{Equation 5-5}$$

The capacity factor of fossil oil power plants is calculated as an average for all oil fossil plants by dividing the average fossil oil power between 2014 and 2018 by the total installed capacity (CCEE, 2018) (Equation 5-6).

$$Capacity\ Factor_{oil\ plants\ (2014-2018)} = \frac{Average\ Power_{oil\ plants\ (2014-2018)}}{Installed\ Power_{oil\ plants}} \qquad \text{Equation 5-6}$$

Where:

$Installed\ Power_{oil\ plants}$: Total installed power of oil plants considered in the study [kW]

The installed capacity of fossil oil power plants that can be replaced by VBG power plants is calculated based on the theoretical power of VBG plants and their estimated capacity factor and on the installed capacity of fossil oil plants and their average capacity factor (Equation 5-7):

$$Installed\ Capacity_{oil\ plants\ replaced} = \frac{E.Power_{VBG}\ X\ Capacity\ Factor_{VBG}}{Capacity\ Factor_{oil\ plants\ (2014-2018)}} \qquad \text{Equation 5-7}$$

The cost of fossil oil dispatch is the sum of the variable costs plus the fixed costs per year of each plant. The variable cost for each plant is the product of the energy generated by each individual power plant in MWh (CCEE, 2018) multiplied by its VUC in USD/MWh. VUC is presented by ONS (2019). The yearly fixed cost is calculated by multiplying the installed capacity of oil power plants by the average yearly fixed costs declared by oil plant operators in auctions, according to (MURCIA NETO, 2016), and adjusted for inflation by the IPCA index between 2015 and 2019, corresponding to USD195,370/$MW_{installed}$/year.

The replacement of fossil oil power plants by VBG power plants is suggested to happen in stages. In each year a block of fossil oil plants is replaced by a block of vinasse plants. That way, in a 5-year program, all energy generated by VBG plants will replace fossil oil plant energy.

For each year under the program, new fixed and variable costs of fossil oil plants are calculated, based on the remaining oil plant power and projected electricity generated by remaining plants, assuming the average capacity factor of these plants in the past 5 years is maintained during the course of projections.

The variable cost of each block of fossil oil plants is calculated by the weighted average power of individual plants and their VUC. Only oil power plants with VUC above USD135/MWh were considered to be replaced.

The variable cost of VBG plants is assumed as the maximum reference value for biogas electricity in distributed generation as per Ministry of Mines and Energy Ordinance n. 65/2018 (MME, 2018) of USD108/MWh and is considered to be high enough to make these projects viable.

GHG emission from fossil oil dispatch is considered as 781 tCO_{2e} per GWh generated (VAHL; FILHO, 2015). GHG emission from VBG electricity is calculated based on VBG Carbon Intensity (CI) $3.7gCO_{2e}/MJ$ (MATSUURA et al., 2018) and 40% electrical efficiency as $33.3tCO_{2e}/GWh$. Main parameters of VBG and oil electricity are shown in Table 5-1.

Table 5-1: Comparison of the basic economic assumptions for VBG and oil plants

	VBG Electricity	*Fossil Oil Electricity*	*Unit*
Unit Cost	*108*	*135-288*	*USD/MWh*
Fixed Cost	*0*	*195,370*	*$USD/MW_{installed}/Year$*
Emission Factor	*33.3*	*781*	*tCO_{2e}/GWh*
Sources: (a): MME (2018); (b): ONS (2019); (c): Murcia Neto (2016); (d): Vahl FP, Filho NC. (2015).			

5.3.2 Vinasse Biomethane

To evaluate the volume of NG that could be replaced by VBM in the state of São Paulo, the study considered the NG sales of each distribution company (excluding thermoelectricity consumption) published in the Ministry of Mines and Energy (MME) NG Industry Monthly Bulletin (MME, 2019).

The number of ethanol mills in the state of São Paulo is considered according to ANP (2019a). Ethanol production in the state of São Paulo is considered according to UNICA (2019) and the volume of ethanol of each mill is considered as the average value between ethanol production and the number of ethanol mills in each area of concession and in the entire state.

Potential VBM production in Nm^3 (Equation 5-8):

$$Biomethane_{SP} = \frac{(Production_{etho-SP} \times Yield_{vinasse} \times COD_{vinasse} \times MCF)}{0.965} \quad \text{Equation 5-8}$$

Where:

$Production_{etho-SP}$: Ethanol produced per year in state of São Paulo [m^3]

0.965: assumed molar fraction of methane in VBM

The average VBM production per day is calculated considering the sugarcane season of 210 days per year with continuous VBM production over this period.

The volume in m³ of NG replaced by VBM is calculated based on the Higher Heating Value (HHV) ratios at 20ºC, 1 Atm, reference condition for NG billing in São Paulo (ARSESP, 2018a) (Equation 5-9).

$$NG_{replaced} = \frac{Biomethane \times HHV_{VBM}}{HHV_{NG}} \quad \text{Equation 5-9}$$

Where:

HHV_{NG}: Higher Heating Value of natural gas at 20ºC and 1 atm [kJ/m³]

HHV_{VBM}: Higher Heating Value of vinasse biomethane at 20ºC and 1 atm [kJ/m³]

To investigate the price of VBM, the NG acquisition and transport costs of distribution companies were taken as reference, based on historical data of the MME NG Industry Monthly Bulletins between August 2011 and January 2019 for domestic and imported gas, converted from USD/MMBTU to R$/m³ assuming 26.81m³ of NG per MMBTU and exchange rates presented in the same bulletins; the values were adjusted for inflation by the IGP-M index (MME, 2019) and then converted back to US Dollar at the present exchange rate of R$3.7/USD.

To investigate possible price incentives for VBM, the NG costs (acquisition and transport) of distribution companies were obtained from ARSESP Resolution n. 793/2018 (ARSESP, 2018b) and the CBIO value was adopted from Renovabio Explanatory Note (MME, 2017).

VBM carbon intensity was calculated with RenovaCalc, assuming the electricity needed for its production obtained from biogas at 40% electrical efficiency, biomethane transported by pipelines and no additional transport of vinasse.

GHG emissions avoided in tons of CO_{2e} (tCO_{e2}) by VBM under the Renovabio framework are calculated with equation 5-10:

$$Emissions\ Avoided_{VBM} = \frac{\left(CI_{reference} - CI_{VBM}\right) \times LHV_{VBM} \times Vol_{VBM}}{10^6} \quad \text{Equation 5-10}$$

Where:

CI_{ref}: Carbon Intensity of reference fossil fuel, considered an average of gasoline, diesel and NG [gCO_{2e}/MJ]

CI_{VBM}: Carbon Intensity of VBM [gCO_{2e}/MJ]

LHV_{VBM}: Lower Heating Value of VBM at 0ºC and 1 atm [kJ/Nm³]

VOL_{VBM}: Volume of VBM produced at 0ºC and 1 atm [kJ/Nm³]

5.3.3 Vinasse biogas and increased sugarcane planted area and ethanol production

The gross energy produced from vinasse biogas based on ethanol production is calculated with the aid of equation 5-11:

$$Gross\ Energy_{VBG} = Production_{etoh}\ X\ Yield_{vinasse}\ X\ COD_{vinasse}\ X\ MCF\ X\ LHV_{methane} \quad \text{Equation 5-11}$$

The gross energy produced from ethanol can be calculated with the aid of equation 12:

$$Gross\ Energy_{Ethanol} = Production_{etoh}\ X\ LHV_{Ethanol} \quad \text{Equation 5-12}$$

Where:

$LHV_{Ethanol}$: Lower Heating Value of ethanol - average of anhydrous and hydrated [MJ/m³]

The main parameters used in the calculations are shown in Table 5-2:

Table 5-2: Main parameters used on calculations.

Parameter	*Value*	*Unit*	*Symbol*	*Reference*
Vinasse Yield	*11.5*	$m^3_{vinasse}/m^3_{etanol}$	$Yield_{Vinasse}$	*(ELAIUY et al., 2018; ELIA NETO; SOUZA, 2016; JANKE et al., 2015; WILKIE; RIEDESEL; OWENS, 2000)*
Vinasse COD	*31.5*	$kgO_2/m^3_{vinasse}$	$COD_{vinasse}$	
Methane Conversion Factor	*0.225*	$Nm^3CH_4/kgCOD$	MCF	*(DA SILVA NETO; GALLO; NOUR, 2020),*
Methane Lower Heating Value	*35,818 (at 0ºC, 1Atm)*	kJ/Nm^3CH_4	$LHV_{methane}$	*(ABNT, 2008)*
Biomethane Lower Heating Value	*34,564 (at 0ºC, 1 Atm)*	kJ/Nm^3	LHV_{VBM}	
Biomethane Higher Heating Value	*35,747 (at 20ºC, 1 Atm)*	kJ/m^3	HHV_{VBM}	
NG Higher Heating Value	*39,348 (at 20ºC, 1 Atm)*	kJ/m^3	HHV_{NG}	*(ARSESP, 2018a)*
Biomethane CI	*3.7*	gCO_{2e}/MJ	CI_{VBM}	*(MATSUURA et al., 2018)*
Fossil of Reference CI (mix of gasoline, diesel, and NG)	*86.7*	gCO_{2e}/MJ	CI_{ref}	
Ethanol Lower Heating Value (average of anhydrous and hydrated)	*21,832*	MJ/m^3	$LHV_{ethanol}$	*(EPE, 2018b)*

5.4 Results & Discussion

5.4.1 Vinasse Biogas replacing fossil oil in power generation

From 2014 to 2018 the variable operating costs of fossil oil power plants accounted for USD12BI, calculated at the present unit and fixed costs of each plant (CCEE, 2018; ONS, 2019). Total electricity generated from oil power plants was more than 69TWh in this period, produced by an installed capacity of 5.32GW with average power of 1.58GW (CCEE, 2018), a capacity factor of 29.7% (Equation 5-6).

The potential power that could be produced if all vinasse were anaerobically digested is 1.79GW (Equation 5-1). VBG power plants are considered to operate at a capacity factor of 57.5%, (Equation 5-2) considering the sugarcane crop season, resulting in an average VBG potential power of 1.03GW. Considering the oil power plants with a VUC higher than USD135/MWh, their capacity factor is equal to 29.3%, thus VBG power would be able to displace 1.03GW of the average capacity of oil power plants (Equation 5-7) or 3.51GW of installed capacity. Dividing the oil power plants into 5 blocks with approximately 200MW (average power) each, the weighted average VUC of each block is shown in Table 5-3 and Figure 5-2.

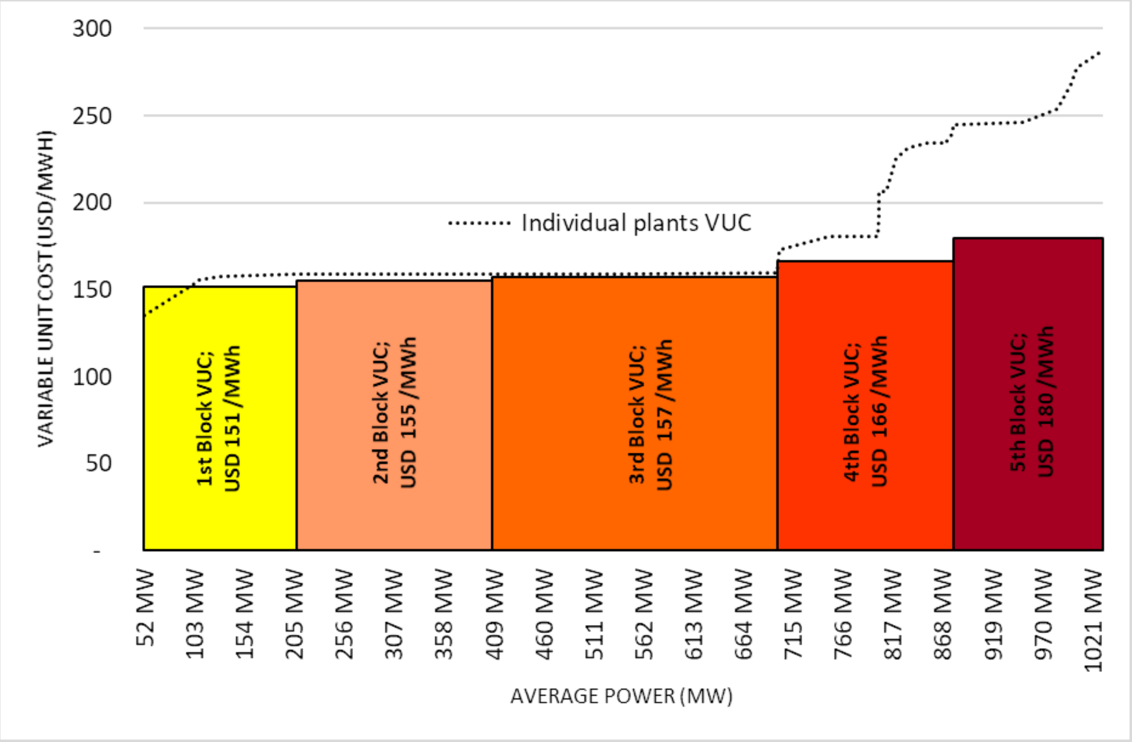


Figure 5-2: Oil power plants VUC - per block and individual. For plants with VUC>USD 135/MWh. Based on dispatch from 2014 to 2018 Source: ONS (2019)

Table 5-3: Heavy fuel and diesel oil power plants with VUC higher than USD135/MWh with VUC of plants and block of plants

<table>
<tr><th>Oil Power Plants VUC > USD135/MWh (a)</th><th>Average Power 2014-2018 (MW_{avg})(a)</th><th>VUC (USD/MWh)(b)</th><th>Accumulated Average Power 2014-2018 (MW_{avg})</th><th colspan="5">Block Average VUC (USDMWh)</th></tr>
<tr><td>PERNAMBUCO_III</td><td>52.4</td><td>135</td><td>52</td><td rowspan="5">USD151</td><td rowspan="8">USD155</td><td rowspan="11">USD157</td><td rowspan="34">USD166</td><td rowspan="40">USD180</td></tr>
<tr><td>MARACANAUI</td><td>51.5</td><td>154</td><td>104</td></tr>
<tr><td>MAUA$_4$</td><td>3.3</td><td>155</td><td>107</td></tr>
<tr><td>TERMOCABO</td><td>22.4</td><td>157</td><td>130</td></tr>
<tr><td>TERMONORDESTE</td><td>79.5</td><td>159</td><td>209</td></tr>
<tr><td>TERMOPARAIBA</td><td>78.9</td><td>159</td><td>288</td><td rowspan="35"></td></tr>
<tr><td>GERAMAR_I</td><td>60.5</td><td>159</td><td>348</td></tr>
<tr><td>GERAMAR_II</td><td>59.9</td><td>159</td><td>408</td></tr>
<tr><td>VIANA</td><td>72.5</td><td>159</td><td>481</td><td rowspan="32"></td></tr>
<tr><td>CAMPINA_GRANDE</td><td>51.2</td><td>159</td><td>532</td></tr>
<tr><td>SUAPE_II</td><td>167.9</td><td>160</td><td>700</td></tr>
<tr><td>SANTANA_I</td><td>1.2</td><td>173</td><td>701</td><td rowspan="29"></td></tr>
<tr><td>GLOBAL_I</td><td>49.1</td><td>181</td><td>750</td></tr>
<tr><td>GLOBA_LII</td><td>51.8</td><td>181</td><td>802</td></tr>
<tr><td>MAUA_5</td><td>1.0</td><td>192</td><td>803</td></tr>
<tr><td>ALTOS</td><td>0.8</td><td>207</td><td>804</td></tr>
<tr><td>ARACATI</td><td>0.6</td><td>207</td><td>805</td></tr>
<tr><td>BATURITE</td><td>0.7</td><td>207</td><td>805</td></tr>
<tr><td>CAMPO_MAIOR</td><td>0.7</td><td>207</td><td>806</td></tr>
<tr><td>CAUCAIA</td><td>1.0</td><td>207</td><td>807</td></tr>
<tr><td>CRATO</td><td>0.5</td><td>207</td><td>807</td></tr>
<tr><td>ENGUIA_PECEM</td><td>0.9</td><td>207</td><td>808</td></tr>
<tr><td>IGUATU</td><td>0.8</td><td>207</td><td>809</td></tr>
<tr><td>JUAZEIRO_DO_NORTE</td><td>1.1</td><td>207</td><td>810</td></tr>
<tr><td>MARAMBAIA</td><td>0.5</td><td>207</td><td>811</td></tr>
<tr><td>NAZARIA</td><td>0.6</td><td>207</td><td>811</td></tr>
<tr><td>SÃO_JOSE</td><td>9.7</td><td>225</td><td>821</td></tr>
<tr><td>IRANDUBA</td><td>12.4</td><td>231</td><td>833</td></tr>
<tr><td>FLORES</td><td>15.8</td><td>235</td><td>853</td></tr>
<tr><td>FLORES</td><td>20.0</td><td>235</td><td>873</td></tr>
<tr><td>ELECTRON</td><td>0.1</td><td>236</td><td>873</td></tr>
<tr><td>DAIA</td><td>5.2</td><td>239</td><td>879</td></tr>
<tr><td>SANTANAII</td><td>0.7</td><td>243</td><td>879</td></tr>
<tr><td>APARECIDA</td><td>0.1</td><td>245</td><td>879</td></tr>
<tr><td>TERMONORTE_II</td><td>70.3</td><td>246</td><td>950</td><td rowspan="6"></td></tr>
<tr><td>GOIANIA_II</td><td>13.9</td><td>249</td><td>964</td></tr>
<tr><td>IGARAPE</td><td>22.3</td><td>254</td><td>986</td></tr>
<tr><td>BAHIA_I</td><td>13.8</td><td>268</td><td>1000</td></tr>
<tr><td>ARAGUAIA</td><td>5.4</td><td>278</td><td>1005</td></tr>
<tr><td>PALMEIRAS_DE_GOIAS</td><td>27.4</td><td>288</td><td>1033</td></tr>
<tr><td colspan="9">Sources: (a) Brazilian Electric Energy Commercialization Chamber - CCEE (2018) (CCEE, 2018); (b) ONS (2019) (ONS, 2019)</td></tr>
</table>

A five-year program for contracting approximately 20% of potential VBG plants per year, with the VBG electricity selling price at USD108/MWh, (maximum reference value for biogas electricity in distributed generation as per Ministry of Mines and Energy Ordinance n. 65/2018 (MME, 2018)), could result in total savings of USD7.6 billion in ten years, as Table 5-4 shows, assuming the oil plants' capacity factor of 29% is maintained over the projection period. These savings include oil plant fixed costs avoided after the contracts have expired. The values for power, electricity and costs are shown in Table 5-4. The actual order of replacement of oil plants by VBG shall be according to contract expiration but using the VUC as a ranking parameter is a good approximation and favors conservativeness.

The suggested price of USD108/MWh for VBG electricity should be sufficiently high to motivate ethanol mill owners and also possibly investors in BOT[8] schemes to participate in such auctions, which would generate firm energy for the Brazilian interconnected electrical system during the period of low rainfall.

Table 5-4: Suggested oil plants substitution schedule, depicting power, energy and costs in each stage

	Year 1	Year 2	Year 3	Year 4	Year 5	Year 6 -> 10
Installed Power Oil (MW)	3,506	2,665	1,831	1,106	603	-
Average Power Oil (MW_{med})	1,028	819	620	329	153	-
Installed Power VBG (MW)	-	363	710	1,217	1,521	1,788
Average Power VBG (MW_{med})	-	209	408	700	875	1,028
Oil Generation (MWh/year)	9,009,559	7,177,781	5,432,835	2,878,112	1,342,512	-
VBG Generation (MWh/year)	-	1,831,778	3,576,724	6,131,447	7,667,048	9,009,559
Fixed Cost Oil (1,000 USD/MW/year) (a)	195					
VUC Oil (USD/MWh) (b)	151	155	157	166	180	180
Fixed Cost VBG (1,000 USD/MW/year)	–					
VUC VBG (USD/MWh) (c)	108					
Fixed Cost Oil (USD million)	685	521	358	216	118	-
Variable Cost Oil (USD million)	1,365	1,114	853	477	241	-
Total Cost Oil (USD million)	2,050	1,635	1,211	694	359	-
Total VBG Cost (USD million)	-	198	387	663	829	974
Total Generation Costs of Proposed Program (USD million)	2,050	1,833	1,598	1,356	1,188	974
Total Generation Cost keeping Current Condition (USD million)	2,050	2,050	2,050	2,050	2,050	2,050
Savings (USD million)	-	217	452	693	862	1,076
Savings in 10 years (USD million)	7,604					
Sources: (a) Murcia Neto E. (2016); (b) ONS (2019); (C) MME (2018)						

The proposed program could reduce CO_2 emissions from fossil oil combustion. The emission factor from VBG electricity was calculated, based on VBG CI, as 33.3tonCO_{2e}/GWh of electricity generated, which, compared to 781 tonCO_{2e}/GWh of oil power plants, would avoid the emission of 6.7 MI ton of CO_{2e} per year after the program is fully operational, which

---

[8] BOT is a business arrangement where a third-party company invests in a plant associated with an existing facility, operates it and transfers the asset to the host company after an established contract term.

accounts for 16.1% of emissions associated with power generation in Brazil in the period analyzed (SISTEMA DE ESTIMATIVA DE EMISSÕES DE GASES DE EFEITO ESTUFA - SEEG, 2019). The yearly CO_{2e} emissions avoided are shown in Table 5-5. Total emissions avoided would reach 48MI ton CO_{2e} in ten years. Figure 5-3 shows the projected results.

Table 5-5: Emissions Avoided by VBG replacing oil in power generation.

	Year 1	*Year 2*	*Year 3*	*Year 4*	*Year 5*	*Year 6 -> 10*
Emissions Reduction ($tonCO_{2e}$)	-	*1,369,620*	*2,674,316*	*4,584,483*	*5,732,651*	*6,736,447*

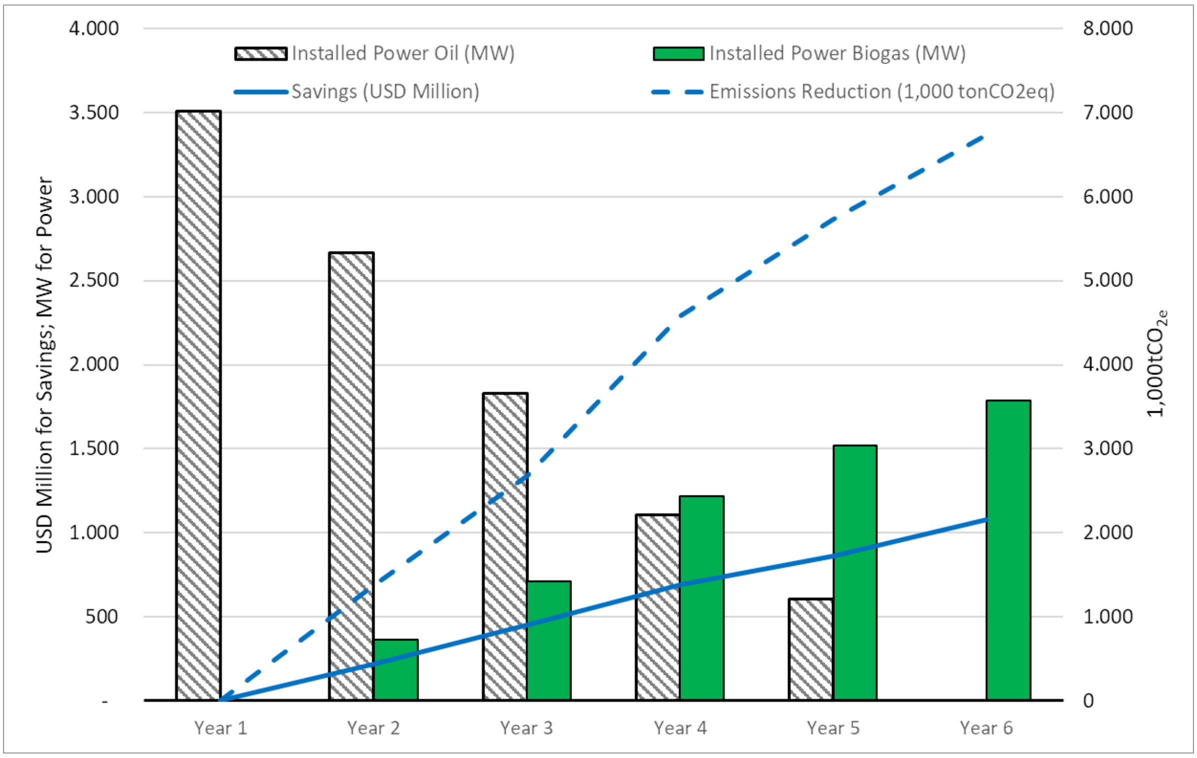


Figure 5-3: Vinasse Biogas replacing oil power plants: Program projected results

It is worth noting that the Brazilian Association of Thermo Power Generators had suggested that oil power plants should be replaced by NG plants in the Northeast region of Brazil (THYMOS, 2018) and the Brazilian Association of Electricity Distribution Companies had suggested the early termination of oil power plant contracts to reduce costs (POLITO, 2018). The characteristics of VBG plants such as proximity to points of consumption, firm (not intermittent) energy generation in the low rainfall season, potential GHG emissions avoidance and better use of sugarcane biomass (thus better competitiveness of this industry) favor the adoption of VBG plants over other energy sources.

Balancing Period: Until recently in Brazil, wind power auctions allowed projects based on this source to calculate generation balances on annual and quadrennial basis, with eventual deficits paid back to energy buyers in monthly instalments after the balancing period. This could be applied to VBG electricity auctions, so that the possible underperformance of VBG plants could be overcome by technical adjustments or additional investments in subsequent periods, reducing investor exposure to perceived risks and enabling lower hurdle rates, thus increasing the possibility of developing VBG projects. This feature would be especially important for biogas power plants, which could improve their performance as experience is gained in individual plants (MARIANI, 2018).

Achieving the target: To achieve the target substitution of fossil oil power plants by VBG plants, policymakers could create a program of a series of specific auctions for VBG. Each auction in the program should be designed and prepared to substitute the fossil oil power plants whose contracts are closer to expiration, until the sum of 200MW average capacity of these plants in each auction. After results of the first auction and by accompanying the construction schedule of the contracted plants, the following auctions could be adjusted in terms ceiling energy price to be bought, schedule for entering in operation and fossil oil power to be substitute. The short construction schedule of VBG plants, most of them in scale smaller than 5MW, will help the implementation of the program. The existence of a program of auctions will create a perspective of market expansion, based on what VBG's projects participants (engineering design and consultancy companies, equipment suppliers, financing agents, ethanol mill owners and operators, energy investors) can develop themselves to participate of this new market, which may lead to lower the costs of VBG plants.

5.4.2 Vinasse Biomethane in São Paulo State

Table 5-6 shows NG sales, number of ethanol mills and potential VBM in each NG distribution company area in the state of São Paulo (excluding power plants). The potential for VBM production in the Gasbrasiliano area is 3.5 times the company's NG sales volume. On the other hand, in the Comgas area, all VBM could replace only 5.3% of NG sales. Gas Natural SP Sul has more similar indicators to state averages. The total VBM potential is equal to 21.5% of the total NG consumed in the state of São Paulo.

Table 5-6: VBM potential in each area of NG distribution in São Paulo

Area	*NG Sales (power plants excl.) (2018) (Ml m^3/day)[(a)]*	*Number of ethanol mills[(b)]*	*Ethanol Production (1.000m^3)[(c)]*	*VBM Potential Average Year (Ml m^3/day)*	*VBM potential x NG Sales*
Comgas	*12.45*	*19*	*1,653*	*0.38*	*3.1%*
Gasbrasiliano	*0.71*	*123*	*10,700*	*2.48*	*347.3%*
Gas Natural SP Sul	*1.10*	*10*	*870*	*0.20*	*18.3%*
Total SP	*14.26*	*152*	*13,223*	*3.06*	*21.5%*
Sources: (a) MME (2019); (b) ANP (2019); (c) UNICA (2019).					

The indicative targets for the replacement of NG by biomethane used as reference are shown in Table 5-7, based on HHV of both NG and VBM. To achieve the blending mandate with VBM in the first period of commitment, 17.91% of vinasse generated in the Comgas concession area should be anaerobically digested. In the opposite direction, in the Gasbrasiliano area, only 0.32% of the vinasse generated in the area would produce enough VBM to meet the blending target. In the second period of commitment, the renewable blending percentage is doubled. If the ratio between ethanol and NG production remains the same, in the Comgas area more than 35% of vinasse would be needed to produce the required volume of VBM to meet the blending targets.

The indicative blending mandate of biomethane in NG in São Paulo is timid: only 1.13% of NG replaced by biomethane in volume, compared to other blending mandates in Brazil (27.5% of ethanol in gasoline, 10% of biodiesel in diesel). VBM potential is sufficient to meet blending targets in the state, although there is a strong imbalance between potential VBM supply and demand in each concession area. Also, if all VBM is used to replace NG in the state of São Paulo, GHG emissions avoided can be calculated as 3.2 million tCO_{2e}/year. With the full application of this hypothetical blending mandate, by the end of the second commitment period, with 1.13% of NG replaced by VBM, emissions avoided would total only 185,271 tCO_{2e}/year.

Table 5-7: Indicative Decree 58659/2012 biomethane blending mandate

Area	*First period (years 1 to 4)*			*Second period (years 5 to 8)*		
	Mandate % of NG in volume	*VBM to meet mandate Ml m^3/day*	*VBM Mandate x potential*	*Mandate % of NG in volume*	*VBM to meet mandate Ml m^3/day*	*VBM Mandate x potential*
Comgas	*0.5%*	*0.069*	*17.91%*	*1.0%*	*0.137*	*35.82%*
Gasbrasiliano	*1.0%*	*0.008*	*0.32%*	*2.0%*	*0.016*	*0.63%*
Gas Natural SP Sul	*1.0%*	*0.012*	*6.03%*	*2.0%*	*0.024*	*12.06%*
Average SP	*0.56%*	*0.088*	*2.89%*	*1.13%*	*0.177*	*5.78%*

Figure 5-4 depicts the imbalance between potential VBM production (as a proportion of ethanol mills) and NG sales in each area of NG concession in the state of São Paulo.

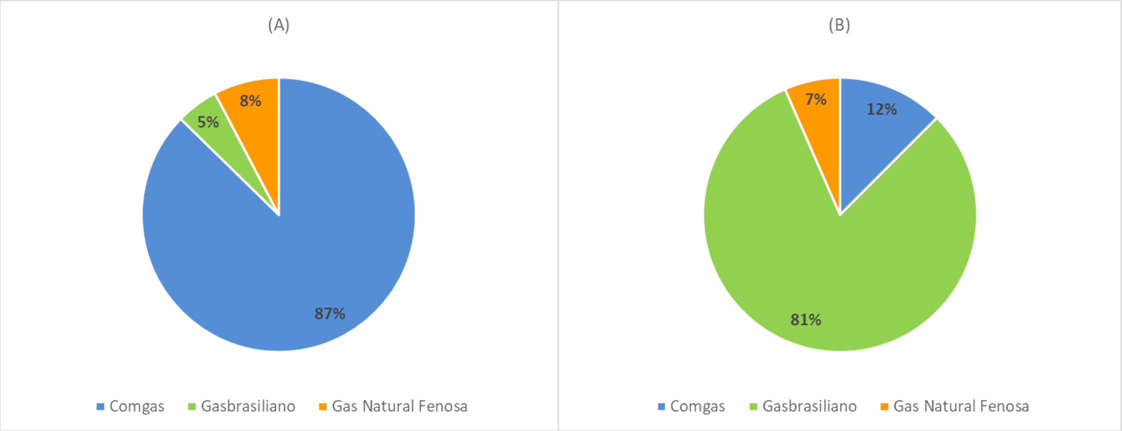


Figure 5-4: (A) NG Demand by Concession Area in the state of São Paulo (excluding thermo power), (B) Ethanol Mills in each NG Concession Area in the state of São Paulo. Sources: NG Demand: MME (2019); Ethanol Mills: ANP (2019).

To avoid the imbalance shown in Figure 5-4, it would be interesting to allow each company to receive in its pipeline the VBM produced in its area of concession. Renewable fuel certificates could be traded among companies to compensate possible deficits of their biomethane blending targets. This suggestion would relieve the pressure of producing the renewable gas where potential is lower and demand is higher, allowing the production of VBM in areas where potential is higher and costs are possibly lower.

The São Paulo biogas program, if well-coordinated with Renovabio, could set specific concession mandates and rely on the decarbonization credits market to allow each NG distribution company to fulfill their quota.

Pricing VBM: In principle, the price of VBM could be linked to NG prices, but even though NG in Brazil is expensive compared to other parts of the world, it is unlikely that VBM projects could be viable at NG prices, especially in smaller scale projects. NG acquisition and transport costs of distribution companies are shown in Figure 5-5. The volatility of NG prices poses risks that may be unacceptable for investors in VBM projects. Also, assuming VBM price fluctuations according to NG prices seems to overlook important merits of VBM and biofuels in general, which are their relatively constant prices over time and the minimized exposure to fossil fuel price volatility (MADLENER; MYLES, 2000).

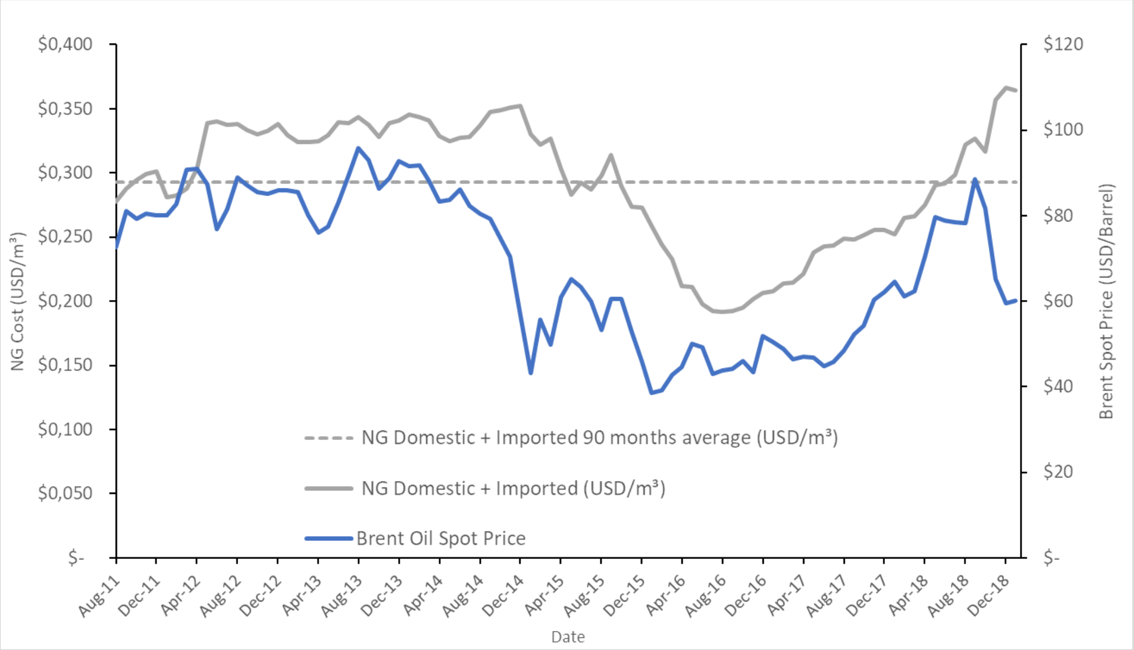


Figure 5-5: NG Prices for Distribution Companies, Brazil Center-South Market, Values excluding taxes. Brent Spot Prices, converted to USD at date exchange rate, adjusted by inflation and reconverted to USD at present exchange rate. Sources: NG costs: MME (2019); Brent Spot Price: DOE-IEA (2019).

Comparing the average NG cost of distribution companies of USD0.2926/Nm³ to the VBM selling price presented by Leme and Seabra (2017), which is USD0.3005/Nm³ for an autonomous distillery with a 2 million tons sugarcane crushing capacity, and USD0.4185/Nm³ for an autonomous distillery with a 1 million ton sugarcane crushing capacity, it is clear that setting the VBM price at the average historical price of NG does not seem to be high enough to motivate the widespread adoption of VBM. At first glance, the VBM produced at larger mills seems competitive, if sold at NG historical average prices. Possibly the perceived risks of new activity may require higher returns and, in this case, the historical value of NG as reference for purchasing value for VBM may not be high enough. In the other hand, if VBM is sold at spot NG price, volatility may bring uncertainties to investors' returns that won't pay-off the risk. An incentive scheme could improve returns of VBM projects and promote attractiveness.

Value of Incentives: The NG compression and transportation costs for feeding remote local grids presented by ARSESP are assumed as an acceptable value reference for incentives in the São Paulo NG industry. The impact of an incentive scheme can be estimated by using the average price of NG (Figure 5-5), the blending mandates of Decree 58659/2012 and the costs of NG acquisition and transport for distribution companies (ARSESP, 2018b), and defining a premium of 20% above the average NG price. A 20% premium paid to VBM, after the full application of the blending mandate program, would account for only 0.39% of the total cost of acquisition and transport of NG in the state of São Paulo and should not have a significant impact on NG demand (Table 5-8). This premium could motivate larger mills to produce VBM, but even so it is not high enough to make smaller VBM plants viable. An increased premium paid to VBM of 39.2% would make a 1MI ton sugarcane autonomous distillery viable to produce VBM (USD0.4185/Nm³) and cause an increase in NG cost of 0.83% after the full application of the blending mandate program. An additional future blending mandate of 5% of NG sales in São Paulo with VBM sold with a premium of 20% would increase the cost of NG by 1.71%. In this situation, 25.6% of vinasse in the state of São Paulo should be used to produce VBM.

Table 5-8: Impact of possible VBM incentive scheme in overall cost of NG in São Paulo

	first blending period	*second blending period*	*second period - higher premium*	*future blending target*	*Unit*
Blending Mandate - São Paulo % of NG sales in volume	*0.56%*	*1.13%*	*1.13%*	*5.00%*	*%*
VBM volume to achieve mandate	*0.088*	*0.177*	*0.177*	*0.785*	*MI Nm³/day*
90 months Average NG Price	*0.2926*				*USD/Nm³*
Premium paid to VBM above historical NG price in USD	*0.0585*	*0.0585*	*0.1141*	*0.0585*	*USD/Nm³*
Premium paid to VBM above historical NG price in %	*(20%)*	*(20%)*	*(39%)*	*(20%)*	*%*
Annual cost of VBM premium (USD/year)	*1,890,212*	*3,780,425*	*8,137,428*	*16,767,407*	*USD/year*
Total NG acquisition and transport cost - São Paulo (2018)	*981,765,019*				*USD/year*
VBM Premium as % of total NG acquisition and transport cost	*0.19%*	*0.39%*	*0.83%*	*1.71%*	*%*

Value of CBIO for Vinasse Biomethane: Using VBM and NG CI in Equation 9, a total of 348.7Nm³ of VBM is required to avoid one ton of CO_{2e} emissions (one CBIO). Considering the projected values for CBIO as a function of the petroleum price and the decarbonization target of the fuel matrix (MME 2017), the contribution of CBIO to the VBM price is shown in Table 5-9, assuming an exchange rate of R$3.70/USD:

Table 5-9: Contribution of CBIO to VBM price

	CBIO Value (USD) [(a)]	*Contribution to VBM Price*
Decarbonization Target 10%, Petroleum USD60/bbl	*USD 11.00/CBIO*	*USD 0.0324/Nm³*
Decarbonization Target 10%, Petroleum USD80/bbl	*USD 0.00/CBIO*	*USD 0.00/Nm³*
Source: (a) MME (2017)		

It is worth mentioning that in case of the oil prices are kept low (e.g. USD60/bbl in this study), the CBIO price can represent more than 10% price increase for VBM, which would be a significant income to producers. In the other hand, if oil prices go higher than USD 80/bbl, the value of CBIO for VBM producer would be zero.

Fixed Price for CBIO: For well-established biofuels such as ethanol and biodiesel, this fluctuating value of CBIO is acceptable, for if international oil prices increase, the biofuel price can increase as well, and even if the CBIO value is lower, the return on investment of the biofuel producer is protected.

For a new entrant on the market, however, especially when dealing with new technologies, predictability of return on investment helps mitigate risk. VBM is likely to be sold in long term contracts in local currency, adjusted by a national inflation index. This would ensure predictable returns on VBM projects for investors and ethanol mill operators, who already perceive too many risks in biogas projects other than product price risk. Having VBM contracted in local currency could be an advantage for NG distribution companies when dealing with potential clients that are risk-averse to energy costs, especially in the face of recent fuel price fluctuations in Brazil. If CBIO of VBM projects has a fixed price for carbon emissions avoided, this would greatly contribute to mitigating risk and leveraging VBM projects.

To accommodate this condition VBM projects should be allowed to emit certificates at fixed prices, proportional to the actual emissions avoided, that could be exchanged to CBIOs (being convertible to certificates to other fuel distribution companies), giving this new certificate a liquid market at fixed value. VBM projects certificate prices could be established when each project is contracted, reflecting current NG prices conditions, i.e.: if VBM price is high, the certificate has a lower value. This emission scheme could be valid for a predefined term, after which VBM projects should emit CBIOs as any other biofuel.

A fixed price of CBIO for VBM projects helps achieve the Renovabio objective of promoting the expansion of renewable fuels. This proposition is similar to a feed-in tariff, widely used as a renewable energy incentive in various countries (VAN MEIJL; SMEETS; ZILBERMAN, 2015). It creates a fuel with predictable future costs which may increase renewable fuel consumption, providing GHG emission reductions. The proposed pricing for CBIO could be combined with state mandates, in a more elaborate construction, and the CBIO value could trigger the payment of a premium to VBM if the former falls below a certain value. In any case, the costs associated with the introduction of VBM in the market can be known beforehand, assuring cost predictability for end users.

Developing VBM market: Policymakers in São Paulo could establish a blending mandate of biomethane to NG relying on VBM potential. A program of "call for projects" to buy VBM could be promoted, allowing a premium price for the renewable fuel. In each stage of the program, a determined amount of VBM should be contracted to meet blending targets. Blending target should increase as the program evolves. The sell price of VBM could be set at the average historical cost of NG (acquisition + transport) to distribution companies, added of a premium set as a percentage of the sell price. Resources for paying this premium could be financed with a slight increase in NG cost for all consumers in the state, defined by specific rules. These rules should include maximum price increase to NG users due to premium paid to VBM and period for premium payment. Blending target could be set individually for each distribution company, but projects could be implemented outside of the distribution company area of concession to take advantage of different VBM potential in each area. VBM volume contracted, project's schedule and volume of production in the initial stages of the program will be essential tools for price and quantity discovery (IRENA, 2015) to further adjustments of the program.

5.4.3 Contribution of vinasse biogas in future energy scenarios

The Brazilian Ethanol Supply Scenarios and Otto Cycle Demand for 2018-2030 (EPE, 2018c) forecasts an increase in ethanol demand from 29.4 billion litres in 2017 to 54.0 billion litres in 2030 in the high growth scenario. This increase in ethanol production will come with an increase in sugarcane cultivation area of 1.7 million hectares (18.9% more area), together with a 25% increase in sugarcane productivity (adding 309 million tons of sugarcane to Brazilian production) and combined with a 30% increase in ethanol production per ton of cane (from changes in ethanol/sugar mix). This increase in ethanol production represents gross energy of 537 TJ. Energy from vinasse could add 157TJ or 29.4% more energy to the Brazilian energy mix compared to the estimated ethanol energy increase (Table 5-10).

Table 5-10: Energy expected from VBG production

	Reference	*Scenario without Biogas*	*Scenario with Biogas*
Parameter	*2017*	*2030*	*2030*
Sugarcane Harvested Area (ha)	*8,772,414*(a)	*10,430,464*(a)	*10,430,464*
Ethanol Production (1.000 m^3)	*29,400*(a)	*54,000*(a)	*54,000*
Ethanol Energy (TJ)	*642*	*1,179*	*1,179*
Methane Energy (TJ)			*157*
Total Energy (Methane + Ethanol)	*642*	*1,179*	*1,336*
Source: (a) EPE (2018)			

VBM could replace gasoline in CNG Otto cycle light vehicles or replace diesel in dual-fuel diesel-gas or heavy-duty Otto cycle vehicles in sugarcane operations or elsewhere, such as public transportation, which often receives subsidies. Vehicles to use VBM (and NG as well) should be adapted to gaseous fuels, which, together with VBM distribution, is a challenge to be overcome. When considering the use of VBM in Otto cycle heavy-duty applications, lower energy efficiency of this equipment should be accounted.

In the strictly energetic sense, as a matter of comparison, future potential biogas production from vinasse can represent 33.8% of diesel oil estimated to be imported by the country in 2027. In commercial terms, this volume of diesel would represent USD1.9 billion in 2017 values (ANP, 2018).

Today's potential VBM production represents approximately 95% of Liquified NG imported in 2018 or USD 879 million FOB (MME, 2019). By replacing imported fossil fuels, VBG and VBM also reduce the exposure of end users to the volatility of international energy prices and exchange rates.

Alternatively, in a scenario where expansion of sugarcane becomes an environmental concern and assuming methane and ethanol can provide the same energy service (e.g. light Otto cycles vehicle fuel), the energy from VBM can represent a decrease in the expansion of planted area of 1.23 million hectares, since 139TJ out of 537TJ expected to come from ethanol could come from VBM, which could account for USD2.4 billion savings[9] in new sugarcane plantations. In this case, a more detailed evaluation should be performed, since reducing the sugarcane planted area, the ethanol production and sales, with all the benefits associated to it, will be also reduced. The reallocation of investments from new sugarcane planted areas to VBG and/or VBM plants, in such a way that the gross energy output increase from sugarcane as a whole is maintained, should be compared in economic, environmental and energy terms.

---

[9] At the BNDES maximum financeable value of sugarcane plantation of USD1.986/ha (R$7,350/ha) (BNDES, 2019)

5.5 Conclusion

VBG can represent a considerable source of energy in Brazil. VBG electricity can be produced in enough quantity to replace around 65% of fossil oil power plants in the country, resulting in lower energy prices and reduced GHG emissions. Electricity produced by VBG is seasonal, but during the sugarcane harvest season it is a non-intermittent energy source, produced night and day. Since the sugarcane harvest season is in the low rainfall period of the year, VBG electricity helps preserve water in hydropower reservoirs while avoiding the dispatch of fossil power plants. VBG electricity would be produced close to high electricity consumption areas, and should bring benefits of distributed generation, such as improved quality and reliability of electricity supply, reduced grid losses, postponed investments in distribution and transmission capacity (PEPERMANS et al., 2005), which should be valued accordingly when establishing prices for VBG electricity.

VBM is an alternative to NG blending mandates in the state of São Paulo. Monetary benefits to facilitate the large scale adoption of VBM can come in the form of incentives paid by users, which would account for a small cost increase for NG users but could promote a fuel whose price is largely dissociated from external influences of fossil fuel prices or exchange rates. Additional energy costs arising from VBM incentive schemes should be compared to benefits such as job creation, collected taxes, avoided fuel imports and others. Since VBM is a biofuel that can be produced locally, with little connection to fossil fuel prices or exchange rates, decarbonization credits, as proposed by Renovabio, could be set at a fixed price, similar to feed-in tariffs around the world, but with a biofuel instead of renewable electricity.

Considering the increased ethanol production for next years, gross energy produced from VBG or VBM could add 29.4% more energy than the ethanol alone to the Brazilian energy mix and could replace fossil fuels even further.

In the GHG emissions perspective, VBG electricity replacing fossil oil can avoid 6.7MI tonCO_{2e}/year, and if vinasse in the state of São Paulo State were used to replace NG, 3.2 million tonCO_{2e}/year could be avoided. Other emissions would also be avoided from the anaerobically digested vinasse applied in sugarcane fields, which are lower than *in natura* vinasse (MORAES et al., 2017).

The main objective of any program for contracting VBG or VBM production should be creating a clear perspective of market expansion, based on which engineering design and consultancy companies, equipment suppliers, financing agents and ethanol mill owners and operators, as well as energy investors, can plan ahead, training people, creating the necessary skills and investing in innovation, building a virtuous system that tends to decrease costs with experience, as observed in the ethanol industry as a whole (GOLDEMBERG et al., 2004; VAN DEN WALL BAKE et al., 2009; WALTER et al., 2015). Incentive schemes for VBG or VBM could be a temporary development tool while this important experience is built.

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

The authors thank Espaço da Escrita – Pró-Reitoria de Pesquisa – UNICAMP - for the language services provided.

6 General Conclusions

Vinasse is a sugarcane by-product resulted from ethanol distillation. It has high COD, high sulfate concentration, low pH and is seasonally produced. Vinasse biogas production projects should be done with special attention in planning, design and operation. Although not a widespread practice in the Brazilian sugarcane industry, biogas from vinasse has considerable energy potential.

Given the existing technology and accumulated experience in anaerobic digestion, biogas desulphurization, purification, and biogas power generation in other industries and countries, it can be concluded that there should not be any relevant technological barrier to further diffusion of vinasse biogas energy projects, but the seasonal operation imposes financial penalties and the high level of sulfur in vinasse biogas tends to increase investments in projects of this nature.

The gross production potential of biogas from vinasse can represent more than 13% of additional energy in distilleries compared to the gross energy of the ethanol, meaning that sugarcane biomass can be more efficiently used. Biogas can be used for electricity generation and biomethane production, representing an additional supply of renewable energy that can replace fossil fuels.

Anaerobic digestion of vinasse can represent a relevant source of renewable energy and can be produced without any additional biomass. This possibility is in line with the recent change in concept of biofuel production plants from simple distilleries to biorefineries, with more efficient and integrated processes and a wider range of products, leading to better use of biomass.

This work shows a practical demonstration of an anaerobic digestion mathematical model based on ADM1 in large-scale anaerobic reactor processing ethanol vinasse, which presents potential optimisation and operation improvement of anaerobic digestion of vinasse, reducing expenditure, risk, and time.

The modelled higher solids retention time (SRT) optimised reactor showed higher biogas production and methane per volume of reactor and reduced hydraulic retention time (HRT) from 15 to 7 days. By adding an external settler with sludge return, substantial savings in materials and services associated with a lagoon-type digestor construction and operation costs can be obtained. Moreover, methane yield, methane concentration and biogas production can be higher when SRT is higher.

The predictions of H_2S levels in biogas by the modified ADM1, based on sulfate and COD content, is a useful tool to assess biogas composition, especially for projects where the gas is not yet under production, but wastewater composition is available.

The quality of predictions of the model allows practitioners and designers of vinasse-to-energy projects to anticipate with reasonable accuracy the H_2S levels in biogas and plan ahead appropriate biogas downstream processing and technology to convert biogas into clean renewable bioenergy.

The H_2S model presented small differences between the averages of modelled results and large-scale reactor measured data. The model can be qualified as medium accuracy based on relative absolute errors (rAE), although the majority of calculated values were within a +/-10% error range. The model also improves the accuracy in prediction of energetic value of biogas by reducing errors in biogas flow and CH_4 content compared to previous models.

Vinasse-to-biogas projects may have its risks minimized if special attention is given to mathematical models such as ADM1 for evaluation, optimisation, and design of existing and planned biogas plants.

Vinasse biogas can be used to produce electricity or biomethane (injected in a natural gas pipeline or replacing fossil diesel in mill operations). This work shows that the production and use of biogas from vinasse has considerable energetic potential and can avoid substantial emissions of greenhouse gases. If these benefits are allocated to sugarcane ethanol, they can improve the environmental and energetic performance of this important renewable fuel.

These improvements are more intense when biomethane is used as a substitute for diesel oil in sugarcane transport trucks and harvesters. In this case, ethanol’s GHGEA can be improved by as much as 27.0%. In the worst case evaluated, there is a 3.5% improvement in EB with biogas used for electricity generation.

Furthermore, this work shows that vinasse biogas can represent a considerable source of energy in Brazil. Vinasse biogas (VBG) electricity can be produced in quantity enough to substitute around 65% of fossil oil power plants in the country, resulting in lower energy prices and GHG emissions reduction.

The electricity produced by VBG is seasonal, but not intermittent. During the sugarcane season (the low rainfall period of the year in most of the country), is a firm, flat energy, produced night and day, so it helps keeping water in the hydropower reservoirs while avoid the dispatch of fossil power plants.

At same time, vinasse biogas electricity is generated near to consumption areas, bringing the benefits of distributed generation, such as improved quality and reliability of electricity supply, reduced grid losses, postpone investments in distribution and transmission capacity. These benefits should be valued accordingly when establishing prices for VBG electricity.

Biomethane from vinasse can make possible a natural gas blending mandate in São Paulo State. Monetary benefits to make economically viable the large adoption of vinasse biomethane would account for minor cost increase for natural gas users. Furthermore, VBM is a fuel whose price is, to a large extent, disassociated from external influences such as fossil fuel prices and exchange rates. VBM also brings benefits such as job creation, taxes collected, fuel importation avoided and others.

Since VBM is a biofuel that can be produced locally, with little connection to fossil fuel prices or exchange rates, decarbonization credits, as proposed by Renovabio, could be set at fixed price, as example to what happens to feed in tariffs around the world, but here with a biofuel instead of renewable electricity. As example of what carbon credits did to biogas projects in South-East Asia and other places (SUZUKI; KEHDY; JAIN, 2010), CBIOs can play an important role in the development of vinasse biogas projects in Brazil.

EPE forecasts an increase in ethanol demand of 83.7% in the 2017-2030 period in Brazil (EPE, 2018d). Since VBG increases the energy yield from sugarcane crops, in the strict energetic perspective, gross energy produced from the anaerobic digestion of vinasse originated from the ethanol could increase renewable fuel production by 29.4% comparing to ethanol alone.

The potential biogas from vinasse could represent 17.8% of the imported diesel oil by the country in 2017, representing a cost of USD 1 billion (ANP, 2018), or approximately 90% of Liquified NG imported in 2018 at cost of USD833 Million FOB (MME, 2019).

In the GHG emissions perspective, VBG producing electricity replacing fossil oil can avoid 6.7MI tonCO_2e/year and if vinasse in São Paulo State would be used to replace natural gas, 3.2MI tonCO_2e/year could be avoided.

Biomass electricity has been commercialized by independent energy producers in Brazil since the early 1990s, but biomethane is a noticeably young and less usual activity, even in countries where biogas production is in practice for many years or decades. Price incentive mechanisms and blending mandates (such as ethanol and biodiesel) could accelerate biomethane insertion into the national energy matrix.

Many technological, energetic, environmental, economic and logistical considerations must be taken into account when evaluating the possibility of producing electricity or biomethane from vinasse biogas. Thanks to biogas versatility, there is a range of technical possibilities and arrangements that allows developers to find adequate solutions for virtually any specific project condition.

The production and use of vinasse biogas can bring environmental, social and energy benefits, resulting from small scale, geographically distributed, technologically intensive projects which are near to end users, require skilled labor and may be implemented in the sugarcane industry in Brazil.

Electricity or fuel (as biomethane) produced from vinasse biogas are not subject of any premium price or incentives, and treatment of ethanol vinasse is not compulsory for mills in Brazil. The establishment of mandates to mix biomethane into natural gas with premium price for the renewable gas and benefits for mills with better GHGEA and energy balances (EB) are discussions in course by the Brazilian government and can motivate this possibility.

Policy makers should be diligent in understanding the peculiarities of these projects, in order to establish rules that can help the development of this practice, given the many benefits they can bring to the Brazilian society and to the biofuels industry.

Future Developments:

In terms of Anaerobic Digestion Models, future developments could cover the addition to the model of recirculation of digestate being mixed with substrate to be introduced into the reactor, to reflect a common practice in industry which could help in predict the pumping capacity and operational pH of biogas plants. Better calibrated anaerobic bacteria and archaea constants (biomass production, half saturation, growth rate) could also improve accuracy of the model, especially after the sulfur reactions introduction to the model.

There are some possible implications of vinasse anaerobic digestion that could bring other benefits to the mills. Reduced pollution potential and higher pH of digested vinasse may allow larger quantities of vinasse applied is crop fields, which could reduce mill’s fertirrigation costs. The further investigation and demonstration of this aspect may be relevant.

Also, if a reduction of GHG emissions from fertirrigation of digested vinasse in comparison to *in natura* vinasse is clearly demonstrated, additional benefits may arise to mill owners and operators and this could be an interesting future development of works associated with anaerobic digestion of vinasse.

The volume reduction of vinasse (mainly concentration by evaporation) is a practice that many mills are adopting or evaluating in order to reduce the cost of fertirrigation. The anaerobic digestion of vinasse may decrease capital and operational costs of vinasse concentration by the use of less sophisticated construction materials and reduction of equipment cleaning efforts. These aspects can be also subject of in-depth evaluation.

Vinasse from other types of ethanol (e.g. second-generation/cellulosic ethanol and corn ethanol) are also interesting research subjects. The second-generation ethanol may use sugarcane bagasse as feedstock, reducing the electricity production potential of mills, which vinasse biogas could increase back again.

Corn ethanol (an emerging and promising practice in Brazil) cannot rely on bagasse as energy source as traditional Brazilian sugarcane ethanol does. The anaerobic digestion of thin or whole stillage could supply energy for mill’s operation, but would bring impact in production cost and sale value of DDG/DDGS (Distillers Dried Grains/ Distillers Dried Grains with Solubles), this trade-off could be better evaluated.

These new (in Brazilian perspective) types of ethanol (corn and second generation) may also bring effects to seasonality of ethanol production, which could be investigated in terms of its impact on the vinasse biogas production as well.

Other by-products from sugarcane ethanol production, such as filter cake (press mud) and sugarcane tops and leaves, left on the crop fields, are attractive biogas production substrates with relevant potential. Evaluations of availability and costs for collecting tops and leaves and potential impacts on seasonality, production and other aspects of biogas plants as well costs and benefits of digestate disposal are very interesting research subjects. Also, possible cost increase for the mills of filter cake digestate handling and disposal could be better evaluated.

The use of dedicated energy crops (e.g. sorghum, corn, energy cane) as biogas substrate, closing the offseason gap of vinasse biogas, is an interesting research topic.

7 References

ABATZOGLOU, N.; BOIVIN, S. A review of biogas purification process. **Biofuels, Bioprod. Bioref.**, n. 3, p. 42–71, 2008.

ABBASI, T.; TAUSEEF, S. M.; ABBASI, S. A. **Biogas Energy**. London: Springer Science & Business Media, 2011.

ABEGAS. **SP define percentual mínimo de biometano na rede de gás**. Disponível em: <https://www.abegas.org.br/arquivos/69270>. Acesso em: 20 abr. 2019.

ABNT. NBR 15213:2008 - Calculation of calorific values, density, relative density and Wobbe index of combustible gases from composition. 2008.

ADLER, P.; BILLIG, E.; BROSOWSKI, A.; DANIEL-GROMKE, J.; FALKE, I.; et al. **Leitfaden Biogasaufbereitung und -einspeisung**. [s.l: s.n.].

AHN, Y.; MIN, K.; SPEECE, R. E. Full Scale UASB Reactor Performance in the Brewery Industry. **Environmental Technology**, v. 22, n. 4, p. 463–476, 2001.

ALLEGUE, L. B.; HINGE, J. Biogas and bio-syngas upgrading. **DTI - Danish Technological Institute.**, p. 97, 2012.

ALLEGUE, L. B.; HINGE, J. Biogas upgrading Evaluation of methods for H2S removal. **DTI - Danish Technological Institute.**, p. 31, 2014.

ALVALÁ, P. C.; KIRCHHHOFF, V. W. J. H.; PAVÃO, H. G. Metano na atmosfera. **Biotecnologia Ciências & Desenvolvimento**, p. 40–43, 1995.

ALVES, H. B.; MOCHIDA, G. A.; DUMA, M.; GOMES, C. S. Precipitação química e cloração para combate a maus odores em estações de tratamento de esgoto anaeróbias. **Sanare. Revista Técnica da Sanepar**, v. 21, n. 21, p. 19–32, 2004.

ANP. RESOLUÇÃO ANP Nº 8, DE 30.1.2015 - Especificação do Biometano. . 2015.

ANP. Oil, Natural Gas and Biofuels Statistical Yearbook 2018. 2018.

ANP. **Autorizações Etanol ANP**. Disponível em: <http://www.anp.gov.br/producao-de-biocombustiveis/autorizacao-para-producao-de-biocombustiveis>. Acesso em: 10 mar. 2019a.

ANP. Summary of Biodiesel Auctions Results - Jan/Mar 2019. 2019b.

APHA. **Standard methods for the examination of water and wastewater**. 21st. ed. Washington - DC, USA: American Public Health Association, 2005.

APPELS, L.; BAEYENS, J.; DEGRÈVE, J.; DEWIL, R. Principles and potential of the anaerobic digestion of waste-activated sludge. **Progress in Energy and Combustion Science**, v. 34, n. 6, p. 755–781, 2008.

AQUINO, S. F. DE; CHERNICHARO, C. A. L. Acúmulo de ácidos graxos voláteis (AGVs) em reatores anaeróbios sob estresse: causas e estratégias de controle. **Engenharia Sanitaria e Ambiental**, v. 10, n. 2, p. 152–161, 2005.

ARNOLD, M. **Reduction and monitoring of biogas trace compounds**. Espoo: VTT - Research Notes, 2009.

ARSESP. Deliberação n. 211 de 3 de Março de 2011. n. D, p. 6, 2011.

ARSESP. Deliberação n. 842 de 07 de Dezembro de 2018. p. 1–11, 2018a.

ARSESP. Deliberação n. 793 de 07 de Maio de 2018. p. 2, 2018b.

ATKINS; CENEX. **Low Carbon Truck and Refuelling Infrastructure Demonstration Trial Evaluation**. UK: [s.n.].

BANCHI, A.; LOPES, J.; FERREIRA, A.; MARTINS, J. Análise de índices técnicos da colheita mecanizada de cana de açúcar na safra 2011/2012. **Revista AgriMotor**, p. 6–9, 2012.

BARBELI, M. C. **Análise do uso e das possibilidades do gas metano fossil e de biodigestão nas fortas de veículos**. [s.l.] UNICAMP, 1998.

BARBOSA CORTEZ, L. A.; CRUZ, C. H. DE B.; SOUZA, G. M.; CANTARELLA, H.; SLUYS, M.-A. VAN; et al. **ProÁlcool 40 anos - Universidades e empresas: 40 anos de ciência e tecnologia para o etanol brasileiro**. [s.l: s.n.].

BARRERA, E. L.; SPANJERS, H.; DEWULF, J.; ROMERO, O.; ROSA, E. The sulfur chain in biogas production from sulfate-rich liquid substrates: a review on dynamic modeling with vinasse as model substrate. **Journal of Chemical Technology & Biotechnology**, v. 88, n. 8, p. 1405–1420, 2013.

BARRERA, E. L.; SPANJERS, H.; SOLON, K.; AMERLINCK, Y.; NOPENS, I.; et al. Modeling the anaerobic digestion of cane-molasses vinasse: Extension of the Anaerobic Digestion Model No.1 (ADM1) with sulfate reduction for a very high strength and sulfate rich wastewater. **Water Research**, v. 71, n. 1, p. 42–54, 2015.

BARROS, V. G. DE; DUDA, R. M.; OLIVEIRA, R. A. DE. Biomethane production from vinasse in upflow anaerobic sludge blanket reactors inoculated with granular sludge. **Brazilian Journal of Microbiology**, v. 47, n. 3, p. 628–639, jul. 2016.

BATSTONE, D. J.; KELLER, J.; ANGELIDAKI, I.; KALYUZHNYI, S. V.; PAVLOSTATHIS, S. G.; et al. **Anaerobic digestion model no. 1 (ADM1), IWA task group**

for mathematical modelling of anaerobic digestion processesIWA Publishing, London, , 2002a.

BATSTONE, D. J.; KELLER, J.; ANGELIDAKI, I.; KALYUZHNYI, S. V.; PAVLOSTATHIS, S. G.; et al. The IWA Anaerobic Digestion Model No 1 (ADM1). **Water Science & Technology**, v. 45, n. 10, p. 65–73, maio 2002b.

BATSTONE, D. J. Mathematical modelling of anaerobic reactors treating domestic wastewater: Rational criteria for model use. **Reviews in Environmental Science and Biotechnology**, v. 5, n. 1, p. 57–71, 2006.

BATSTONE, D. J.; KELLER, J.; STEYER, J. P. A review of ADM1 extensions, applications, and analysis: 2002-2005. **Water Science & Technology**, v. 54, n. February, p. 2002–2005, 2006.

BAUER, F.; HULTEBERG, C.; PERSSON, T.; TAMM, D. **Biogas upgrading – Review of commercial technologies**. Malmo: [s.n.].

BAUER, F.; PERSSON, T.; HULTEBERG, C.; TAMM, D. Biogas upgrading - technology overview, comparison and perspectives for the future. **Biofuels, Bioproducts and Biorefining**, v. 7, n. 5, p. 499–511, set. 2013b.

BEIL, M.; HOFFSTEDE, U.; HAHN, H. Guidelines for the implementation and operation of biogas upgrading systems. **Biogasmax**, p. 29, 2010.

BENKE, M. B.; MERMUT, A. R.; CHATSON, B. Carbon-13 CP/MAS NMR and DR-FTIR spectroscopic studies of sugarcane distillery waste. **Canadian Journal of Soil Science**, p. 227–236, 1997.

BIEL, M.; BEYRICH, W.; HOLZHAMMER, U.; KRAUSE, T. Biomethane. **FNR**, v. 15, n. 2, p. 1–2, 2013.

BLASZCZYK, R.; GARDNER, D.; KOSARIC, N. Response and recovery of anaerobic granules from shock loading. **Water Research**, v. 28, n. 3, p. 675–680, 1994.

BNDES. **BNDES Prorenova**. Disponível em: <https://www.bndes.gov.br/wps/portal/site/home/financiamento/produto/bndes-prorenova>. Acesso em: 6 mar. 2019.

BOEHM, A. M. Sludge Gas Utilization: A Discussion. **Sewage Works Journal**, v. 19, n. 2, p. 174–177, 1947.

BORZACCONI, L.; LÓPEZ, I.; PASSEGGI, M.; ETCHEBEHERE, C.; BARCIA, R. Sludge deterioration in a full scale UASB reactor after a pH drop working under low loading conditions. **Water Science & Technology**, v. 57, n. 5, p. 797–802, 2008.

BP. BP Statistical Review of World Energy - Renewable energy. 2017.

BP. BP Statistical Review of World Energy - 67 th edition. p. 1–56, 2018.

BRASIL. Decreto n. 19.717 de 20 de Fevereiro de 1931 - aquisição obrigatória de álcool. p. 8–10, 1931.

BRASIL. Lei 13.576, de 26 de Dezembro de 2017 - Política Nacional de Biocombustíveis (RenovaBio). p. 1–32, 2017.

CABRAL, C. B. G. **Tecnologias de digestão anaeróbia com relevância para o brasil substratos, digestores e uso de biogás - Probiogás**. Brasília: Ministério das Cidades, 2015.

CAMPOS, J. R. Tratamento de esgotos sanitários por processo anaeróbio e disposição controlada no solo. **Prosab**, p. 464, 1999.

CATERPILLAR ENERGY SOLUTIONS GMBH. CHP reciprocating engine TCG 2020 Datasheet. p. 5, 2017.

CCEE. **InfoMercado - Dados Individuais - 2014-2018**. Disponível em: <https://www.ccee.org.br/portal/faces/pages_publico/o-que-fazemos/infomercado>. Acesso em: 5 mar. 2019.

CETESB. Norma Técnica CETESB P 4.231 – Vinhaça – Critérios e procedimentos para aplicação no solo agrícola. p. 1–14, 2015.

CHAMY, R.; PIZARRO, C.; VIVANCO, E.; SCHIAPPACASSE, M. C.; JEISON, D.; et al. Selected experiences in Chile for the application of UASB technology for vinasse treatment. **Water Science & Technology**, v. 2, p. 39–48, 2007.

CHERNICHARO, C. A. DE L. **Anaerobic Reactors**. Belo Horizonte: UFMG, 2007a.

CHERNICHARO, C. A. DE L. **Reatores Anaeróbios - Volume 5**. Belo Horizonte: Editora UFMG, 2007b.

CHERNICHARO, C. A. DE L.; STUETZ, R. M.; SOUZA, C. L.; MELO, G. C. B. DE. Alternativas para o controle de emissões odorantes em reatores anaeróbios tratando esgoto doméstico. **Engenharia Sanitaria e Ambiental**, v. 15, n. 3, p. 229–236, 2011.

CHOU, H. S. J. **Hydrogen sulfide: Human health aspects.** Geneva: World Health Organization, 2003.

CHRISTOFOLETTI, C. A.; ESCHER, J. P.; CORREIA, J. E.; MARINHO, J. F. U.; FONTANETTI, C. S. Sugarcane vinasse: Environmental implications of its use. **Waste Management**, v. 33, n. 12, p. 2752–2761, 2013.

CHUM, H. L.; WARNER, E.; SEABRA, J. E. A.; MACEDO, I. C. A comparison of commercial ethanol production systems from Brazilian sugarcane and US corn. **Biofuels, Bioproducts and Biorefining**, v. 8, n. 2, p. 205–223, mar. 2014.

CIRNE, D. G.; VAN DER ZEE, F. P.; FERNANDEZ-POLANCO, M.; FERNANDEZ-POLANCO, F. Control of sulphide during anaerobic treatment of S-containing wastewaters by adding limited amounts of oxygen or nitrate. **Reviews in Environmental Science and Biotechnology**, v. 7, p. 93–105, 2008.

COLTURATO, L. F. DE D. B. **Dessulfuração de biogás da metanização da vinhaça: uma nova abordagem para remoção de altas concentrações de H2S**. [s.l.] UFMG, 2015.

CORAZZA, R. I.; SALLES-FILHO, S. L. M. Opções produtivas mais limpas: uma perspectiva evolucionista a partir de um estudo de trajetória tecnológica na agroindústria canavieira. **XXI SIMPÓSIO DE GESTÃO DA INOVAÇÃO TECNOLÓGICA**, 2000.

CORTES PIRES, J. R.; NOUR, E. A. A.; BARBOSA, P. S. F.; ALMEIDA, P. C.; LOPES, L. R. O. **Geração de Eletricidade a Partir da Biodigestão da Vinhaça e o Potencial para o Brasil (Electricity Generation from Vinasse Biodigestion and the Potential for Brazil)**. VIII CITENEL. **Anais**...2015

CRAVEIRO, A. M.; SOARES, H. M.; SCHMIDELL, W. Technical aspects and cost systems treating vinasse and brewery/soft drink wastewaters. **Water Science & Technology**, v. 18, n. 12, p. 123–134, 1986.

DA SILVA NETO, J. V.; GALLO, W. L. R.; NOUR, E. A. A. Production and use of biogas from vinasse: Implications for the energy balance and GHG emissions of sugar cane ethanol in the brazilian context. **Environmental Progress & Sustainable Energy**, v. 39, n. 1, p. 13226, 4 jan. 2020.

DANIEL-GROMKE, J.; RENSBERG, N.; DENYSENKO, V.; STINNER, W.; SCHMALFUSS, T.; et al. Current Developments in Production and Utilization of Biogas and Biomethane in Germany. **Chemie-Ingenieur-Technik**, v. 90, n. 1–2, p. 17–35, 2018.

DERELI, R. K.; ERSAHIN, M. E.; OZGUN, H.; OZTURK, I.; JEISON, D.; et al. Potentials of anaerobic membrane bioreactors to overcome treatment limitations induced by industrial wastewaters. **Bioresource Technology**, v. 122, p. 160–170, 2012.

DERELI, R. K. Modeling long-term performance of full-scale anaerobic expanded granular sludge bed reactor treating confectionery industry wastewater. **Environmental Science and Pollution Research**, 27 jun. 2019.

DEUBLEIN, D.; STEINHAUSER, A. **Biogas from Waste and Renewable Resources**. Weinheim: WILEY-VCH Verlag GmbH & Co., 2011.

DOELSCH, E.; MASION, A.; CAZEVIEILLE, P.; CONDOM, N. Spectroscopic characterization of organic matter of a soil and vinasse mixture during aerobic or anaerobic incubation. **Waste Management**, v. 29, n. 6, p. 1929–1935, 2009.

DONOSO-BRAVO, A.; MAILIER, J.; MARTIN, C.; RODRÍGUEZ, J.; ACEVES-LARA, C. A.; et al. Model selection, identification and validation in anaerobic digestion: A review. **Water Research**, v. 45, n. 17, p. 5347–5364, 2011.

DRIESSEN, W. J. B. M.; TIELBAARD, M. H.; VEREIJKEN, T. L. F. M. Experience on anaerobic treatment of distillery effluent with the UASB process. **Water Science & Technology**, v. 30, n. 12, p. 193–201, 1994.

EDWARDS, R.; LARIVE, J.-F.; RICKEARD, D.; WEINDORF, W. **Well-to-Wheels analysis of future automotive fuels and powertrains in the European context. WELL-TO-TANK (WTT) Appendix 2. Version 4a.** Ispra - Italy: EC - JRC- Institute for Energy and Transport, 2014.

ELAIUY, M. L. C. **Biodigestão anaeróbia da vinhaça de cana-de-açúcar: abordagem do modelo adm1 e eficiência de biodegradação no solo**. [s.l.] UNICAMP, 2016.

ELAIUY, M. L. C.; BORRION, A. L.; POGGIO, D.; STEGEMANN, J. A.; NOUR, E. A. A. ADM1 modelling of large-scale Cigar treating sugarcane vinasse. **Water Science & Technology**, v. 77, n. 5, p. 1397–1409, 2018.

ELIA NETO, A.; SHINTAKU, A.; PIO, A. A. B.; CONDE, A. J.; GIANETTI, F.; et al. **Manual de conservação e reuso de água na agroindustria sucroenergetica (Water conservation and reuse manual in sugar-energy agroindustry)**. Brasília: ANA, FIESP, UNICA, CTC, 2009.

ELIA NETO, A.; SOUZA, Z. **Panorama do Biogás no Brasil – Setor SucroalcooleiroOficina Biogas e Biometano - Renovabio**. [s.l: s.n.].

ENERGY AND ENVIRONMENTAL ANALYSIS INC;; EASTERN RESEARCH GROUP (ERG); Biomass Combined Heat and Power Catalog of Technologies. n. September, p. 122, 2007.

EPA. **Principles of Design and Operations of Wastewater Treatment Pond Systems for Plant Operators, Engineers, and Managers**. Cincinnati, Ohio: U.S. Environmental Protection Agency, 2011.

EPE. Balanço Energético Nacional 2018 - Ano Base 2017/Brazilian Energy Balance 2018 - year 2017. 2018a.

EPE. Brazilian Energy Balance 2018 Summary Report - year 2017. 2018b.

EPE. Ethanol Supply Scenarios and Otto Cycle Demand 2018-2030. p. 2, 2018c.

EPE. Cenários de oferta de etanol e demanda de ciclo otto 2018-2030. p. 41, 2018d.

FEDOROVICH, V.; LENS, P.; KALYUZHNYI, S. Extension of Anaerobic Digestion Model No . 1. **Applied biochemistry and biotechnology**, v. 109, p. 33–45, 2003.

FELDMAN, H.; ALSINA, X. F.; KJELLBERG, K.; JEPPSSON, U.; BATSTONE, D. J.; et al. Model - based analysis and optimization of a full - scale industrial high - rate anaerobic bioreactor. **Biotechnology and Bioengineering**, v. 115, p. 2726–2739, 2018.

FERMENTEC. **Economia de milhões de reais**. Disponível em: <http://fermentecnews.com.br/2015/10/01/economia-de-milhoes-de-reais/>. Acesso em: 2 fev. 2016.

FERRAZ JÚNIOR, A. D. N.; KOYAMA, M. H.; DE ARAÚJO JÚNIOR, M. M.; ZAIAT, M. Thermophilic anaerobic digestion of raw sugarcane vinasse. **Renewable Energy**, v. 89, p. 245–252, 2016.

FRARE, L. M.; VIEIRA, M. G. A.; SILVA, M. G. C.; PEREIRA, N. C.; GIMENES, M. L. Hydrogen Sulfide Removal from Biogas Using Fe/EDTA Solution: Gas/Liquid Contacting and Sulfur Formation. **Environmental Progress & Sustainable Energy**, v. 29, n. 1, p. 34–41, 2010.

FUESS, L. T.; ZAIAT, M. Economics of anaerobic digestion for processing sugarcane vinasse: Applying sensitivity analysis to increase process profitability in diversified biogas applications. **Process Safety and Environmental Protection**, v. 115, p. 27–37, abr. 2018.

GOLDEMBERG, J.; COELHO, S. T.; NASTARI, P. M.; LUCON, O. Ethanol learning curve - The Brazilian experience. **Biomass and Bioenergy**, v. 26, n. 3, p. 301–304, 2004.

GOLDEWIJK, K. K. Three centuries of global population growth: A spatial referenced population (density) database for 1700-2000. **Population and Environment**, v. 26, n. 4, p. 343–367, 2005.

GÓMEZ, D. R.; WATTERSON, J. D.; AMERICANOHIA, B. B.; HA, C.; MARLAND, G.; et al. IPCC Guidelines for National Greenhouse Gas Inventories. Volume 2: Energy. Chapter 2: Stationary Combustion. 2006.

GONÇALVES, D. A. **Análise logística e ambiental no sistema de corte, carregamento e transporte da cana-de-açúcar**. [s.l.] UNESP, 2012.

GORDINHO, M. C. From Alcohol to Ethanol: a Winning Trajectory. p. 144, 2010.

GOULD, R. H. Present Status of Sludge Gas Utilization. **Sewage Works Journal**, v. 19, n. 2, p. 170–174, 1947.

GRANDE, C. A. Biogas Upgrading by Pressure Swing Adsorption. **Biofuel's Engineering Process Technology**, 2011.

GRASSI, M. C. B.; PEREIRA, G. A. G. Energy-cane and RenovaBio: Brazilian vectors to boost the development of Biofuels. **Industrial Crops and Products**, v. 129, n. December 2018, p. 201–205, mar. 2019.

HASSUANI, S.; LEAL, M.; MACEDO, I. **Biomass Power Generation, Sugarcane Bagasse and TrashBiomass power generation: Sugar cane bagasse and trash**. Piracicaba: [s.n.].

HORIKAWA, M. S.; ROSSI, F.; GIMENES, M. L.; COSTA, C. M. M.; DA SILVA, M. G. C. **Chemical absorption of H2S for biogas purificationBrazilian Journal of Chemical Engineering**. [s.l: s.n.].

HOYER, K.; HULTEBERG, C.; SVENSSON, M.; JERNBERG, J.; NORREGARD, O. **Biogas up-grading: technical review**. [s.l: s.n.].

IEA. Key world energy statistics - 2018. 2018.

INNIO. Jenbacher Type 3. p. 2, 2019.

INTERNATIONAL SUSTAINABILITY & CARBON CERTIFICATION. **ISCC 201-1 Waste and Residues - Version 3.0**. Disponível em: <https://www.iscc-system.org/wp-content/uploads/2017/02/ISCC_201-1_Waste_and_Residues_3.0.pdf>. Acesso em: 5 dez. 2017.

IPCC. **Climate change 2014. Synthesis report.** [s.l: s.n.].

IRENA. RENEWABLE ENERGY AUCTIONS - A GUIDE TO DESIGN. 2015.

IRENA. **Biogas for Road Vehicles**. [s.l: s.n.].

IRENA. **Renewable capacity statistics - 2019**. Abu Dhabi: International Renewable Energy Agency (IRENA), 2019.

JANKE, L.; LEITE, A.; NIKOLAUSZ, M.; SCHMIDT, T.; LIEBETRAU, J. Biogas Production from Sugarcane Waste : Assessment on Kinetic Challenges for Process Designing. **International Journal of Molecular Sciences**, v. 16, p. 20685–20703, 2015.

JANKE, L.; LEITE, A. F.; BATISTA, K.; SILVA, W.; NIKOLAUSZ, M.; et al. Enhancing biogas production from vinasse in sugarcane biorefineries: Effects of urea and trace elements supplementation on process performance and stability. **Bioresource Technology**, v. 217, p. 10–20, 2016.

JENDE, O.; ROSENFELDT, S.; COLTURATO, L. F. DE D. B.; GOMES, F. C. DE S. P.; HOFFMANN, H.; et al. **Barreiras e Propostas de Soluções para o Mercado de Biogás no Brasil - Probiogás**. Brasília: Ministério das Cidades, 2016.

KAZADI MBAMBA, C.; FLORES-ALSINA, X.; JOHN BATSTONE, D.; TAIT, S. Validation of a plant-wide phosphorus modelling approach with minerals precipitation in a full-scale WWTP. **Water Research**, v. 100, n. May, p. 169–183, 2016.

KHANAL, S. K. **Anaerobic Biotechnology for Bioenergy Production: Principles and Applications**. Ames - USA: Wiley- Blackwell, 2008.

KHANAL, S. K.; HUANG, J. C. ORP-based oxygenation for sulfide control in anaerobic treatment of high-sulfate wastewater. **Water Research**, v. 37, n. 9, p. 2053–2062, 2003.

KLEEREBEZEM, R.; LOOSDRECHT, M. C. M. Critical analysis of some concepts proposed in ADM1. **Water Science & Technology**, v. 54, n. 4, p. 51–57, 2006.

KNOBEL, A. N.; LEWIS, A. E. A mathematical model of a high sulphate wastewater anaerobic treatment system. **Water Research**, v. 36, n. 1, p. 257–265, 2002.

KOBAYASHI, T.; XU, K.; CHIKU, H. Release of Extracellular Polymeric Substance and Disintegration of Anaerobic Granular Sludge under Reduced Sulfur Compounds-Rich Conditions. **Energies**, v. 8, p. 7968–7985, 2015.

KORENS, N.; SIMBECK, D. R.; WILHELM, D. J. **Process Screening Analysis of Alternative Gas Treating and Sulfur Removal for Gasification**. Mountain View: [s.n.].

KPMG. **Taxes and incentives for renewable energyKPMG International**. [s.l: s.n.]. Disponível em: <https://assets.kpmg.com/content/dam/kpmg/pdf/2015/09/taxes-and-incentives-2015-web-v2.pdf>.

LEAL, M. R. L. V.; WALTER, A. S.; SEABRA, J. E. A. Sugarcane as an energy source. **Biomass Conversion and Biorefinery**, v. 3, n. 1, p. 17–26, 12 mar. 2013.

LEITÃO, R. C.; VAN HAANDEL, A. C.; ZEEMAN, G.; LETTINGA, G. The effects of operational and environmental variations on anaerobic wastewater treatment systems: A review. **Bioresource Technology**, v. 97, n. 9, p. 1105–1118, 2006.

LEME, R. M.; SEABRA, J. E. A. Technical-economic assessment of different biogas upgrading routes from vinasse anaerobic digestion in the Brazilian bioethanol industry. **Energy**, v. 119, p. 754–766, jan. 2017.

LÓPEZ-LÓPEZ, A.; LEÓN-BECERRIL, E.; ROSALES-CONTRERAS, M. E.; VILLEGAS-GARCÍA, E. Influence of alkalinity and VFAs on the performance of an UASB reactor with recirculation for the treatment of Tequila vinasses. **Environmental Technology**, v. 36, n. 19, p. 2468–2476, 2 out. 2015.

LOW, E. W.; CHASE, H. A. The effect of maintenance energy requirements on biomass production during wastewater treatment. **Water Research**, v. 33, n. 3, p. 847–853, 1999.

MACARIE, H.; ESQUIVEL, M.; LAGUNA, A.; BARON, O.; EL MAMOUNI, R.; et al.

Strategy to identify the causes and to solve a sludge granulation problem in methanogenic reactors: application to a full-scale plant treating cheese wastewater. **Environmental Science and Pollution Research**, v. 25, n. 22, p. 21318–21331, 26 ago. 2018.

MACEDO, I. C.; SEABRA, J. E. A.; SILVA, J. E. A. R. Green house gases emissions in the production and use of ethanol from sugarcane in Brazil: The 2005/2006 averages and a prediction for 2020. **Biomass and Bioenergy**, v. 32, n. 7, p. 582–595, 2008.

MACEDO, I. DE C.; LEAL, M. R. L. V.; SILVA, J. E. A. R. DA. **Assessment of greenhouse gas emissions in the production and use of fuel ethanol in Brazil**. São Paulo: [s.n.].

MADLENER, R.; MYLES, H. Modelling socio-economic aspects of bioenergy systems: a survey prepared for IEA Bioenergy Task 29. **IEA Bioenergy Task**, n. July, 2000.

MAHONY, T. **Feasibility study for centralised anaerobic digestion for treatment of various wastes and wastewaters in sensitive catchment areas : final project report** /. [s.l.] EPA - Ireland, 2002.

MAPA. **Sistema de Acompanhamento da Produção Canavieira - Base cadastral completa de instituições**. Disponível em: <http://sistemasweb.agricultura.gov.br/sapcana/downloadBaseCompletaInstituicao>. Acesso em: 12 abr. 2018.

MAPA. **Sistema de Acompanhamento da Produção Canavieira - Base cadastral completa de instituições**. Disponível em: <http://sistemasweb.agricultura.gov.br/sapcana/downloadBaseCompletaInstituicao>. Acesso em: 7 mar. 2019.

MARIANI, L. **Levantamento de unidades de produção de biogás no Brasil para fins energéticos ou Mecanismo de Desenvolvimento Limpo (MDL)**. [s.l: s.n.].

MARIANI, L. **Biogás: diagnóstico e propostas de ações para incentivar seu uso no Brasil**. [s.l.] UNICAMP, 2018.

MATSUURA, M. I. S. F.; SCACHETTI, M. T.; CHAGAS, M. F.; SEABRA, J. E. A.; MOREIRA, M. M. R.; et al. **RenovaCalc CP10-2018 - Ferramenta de cálculo de emissões de Gases de Efeito Estufa (GEE) de biocombustíveis**, 2018.

MCCARTY, P. L. The development of anaerobic treatment and its future. **Water Science & Technology**, v. 44, n. 8, p. 149–156, 2001.

MCTIC. **Método da análise de despacho.** Disponível em: <http://www.mctic.gov.br/mctic/opencms/ciencia/SEPED/clima/textogeral/emissao_despacho.html.>. Acesso em: 25 jun. 2018.

MERCADO, Á. G. **Remoção de sulfeto de hidrogênio de biogás em instalação piloto com óxido de ferro**. [s.l.] UFSC, 2010.

MERCOSUR AD HOC GROUP ON BIOFUELS. **Mercosur Biogas and Biomethane Report**. Foz do Iguaçu: [s.n.].

MINISTRY OF FOREIGN AFFAIRS OF DENMARK. The Biogas Sector in Brazil. 2018.

MME. Nota Explicativa sobre a Proposta de Criação da Política Nacional de Biocombustíveis. p. 138, 2017.

MME. Portaria MME 65 de 27 de Feveiro de 2018. . 2018.

MME. Boletim mensal de acompanhamento da indústria de gás natural. n. 143, p. 38, 2019.

MONTEGGIA, L. O.; LADEMIR, L. B.; LUCA, S. J. DE. **Requerimento de alcalinidade em processos biológicos anaeróbios**Porto AlegreInstituto de Pesquisas Hidráulicas, , 1985.

MORAES, B. S.; PETERSEN, S. O.; ZAIAT, M.; SOMMER, S. G.; TRIOLO, J. M. Reduction in greenhouse gas emissions from vinasse through anaerobic digestion. **Applied Energy**, v. 189, n. 2017, p. 21–30, 2017.

MORAES, B. S.; ZAIAT, M.; BONOMI, A. Anaerobic digestion of vinasse from sugarcane ethanol production in Brazil: Challenges and perspectives. **Renewable and Sustainable Energy Reviews**, v. 44, p. 888–903, abr. 2015.

MUÑOZ, R.; MEIER, L.; DIAZ, I.; JEISON, D. A review on the state-of-the-art of physical/chemical and biological technologies for biogas upgrading. **Reviews in Environmental Science and Biotechnology**, v. 14, n. 4, p. 727–759, 2015.

MURCIA NETO, E. **Contratos por disponibilidade de usinas termelétricas: uma análise dos resultados econômicos de operação**. [s.l.] Universidade de São Paulo, 2016.

NANDY, T.; SHASTRY, S.; KAUL, S. N. Wastewater management in a cane molasses distillery involving bioresource recovery. **Journal of Environmental Management**, v. 65, n. 1, p. 25–38, 2002.

NOVACANA. **Custos de produção de cana e etanol e as novas tecnologias das usinas**. Disponível em: <https://www.novacana.com/usina/evolucao-setor-melhorias-proporcionadas-pela-pd/>. Acesso em: 26 fev. 2017.

ONG, M. D.; WILLIANS, R. B.; KAFFKA, S. R. **Comparative Assessment of Technology Options for Biogas Clean-up**: Task 8. California: [s.n.].

ONS. **Plano da Operação Energética 2018-2022Pen 2018**. [s.l: s.n.].

ONS. **Sumário do Programa Mensal de Operação - Janeiro 2019**. Disponível em: <http://ons.org.br/AcervoDigitalDocumentosEPublicacoes/SUMARIOEXECUTIVO_PMO_201901_RV3.pdf>. Acesso em: 7 fev. 2019.

OSWALD, W. J.; GREEN, F. B.; LUNGDIST, T. J. Performance of methane fermentation pits in advanced integrated watewater pond systems. **Water Science & Technology**, v. 30, n. 12, p. 287–295, 1994.

OZKAN-YUCEL, U. G.; GÖKÇAY, C. F. Application of ADM1 model to a full-scale anaerobic digester under dynamic organic loading conditions. **Environmental Technology**, v. 31, n. 6, p. 633–640, 2010.

PANTOJA FILHO, J. L. R. **Avaliação da utilização de diferentes materiais suporte na biofiltração de sulfeto de hidrogênio.** [s.l.] USP, 2008.

PARNAUDEAU, V.; CONDOM, N.; OLIVER, R.; CAZEVIEILLE, P.; RECOUS, S. Vinasse organic matter quality and mineralization potential, as influenced by raw material, fermentation and concentration processes. **Bioresource Technology**, v. 99, n. 6, p. 1553–1562, 2008.

PELL FRISCHMANN. Enhancement and treatment of digestates from anaerobic digestion. **Waste and Resources Action Programme**, p. 122, 2012.

PENATTI, C. P. **Vinhaça e seus efeitos no solo e na planta**. Workshop tecnológico vinhaça. **Anais**...Jaboticabal: 2007

PEPERMANS, G.; DRIESEN, J.; HAESELDONCKX, D.; BELMANS, R.; D'HAESELEER, W. Distributed generation: Definition, benefits and issues. **Energy Policy**, v. 33, n. 6, p. 787–798, 2005.

PERSSON, M. **Evaluation of upgrading techniques for biogas**. [s.l: s.n.]. Disponível em: <www.sgc.se/rapporter/resources/SGC142.pdf>.

PETERSSON, A.; WELLINGER, A. **Biogas upgrading technologies – developements and innovations**. [s.l: s.n.].

PINTO, C. P. **Tecnologia da digestão anaeróbia da Vinhaça e desenvolvimento sustentável**. [s.l.] UNICAMP, 1999.

PINTO, M. J. A. Investimentos diretos estrangeiros no setor sucroenergético. p. 174, 2011.

PNUD. Estudo sobre o Potencial de Geração de Energia a partir de Resíduos de Saneamento. **Arcadis Tetraplan**, p. 56, 2010.

POLITO, R. Distribuidoras querem fim de contratos com térmicas a óleo. **Jornal Valor Econômico**, 15 ago. 2018.

PRESSURE WORX. **Rotary Vane Compressors**, 2018.

PRIESTLEY, J. **Experiments and Observations on Different Kinds of Air**. London: [s.n.].

QUADROS, R.; TAVARES, A. N.; SANTOS, G. V. DOS; BAJAY, S. V. **Industrial and Energy Policies for Biogas-Based Electricity from Municipal Solid Waste in Brazil**. 30 th International Conference on Solid Waste Technology and Management. **Anais**...Philadelphia: 2015

RAMÍREZ TRIANA, C. A. Energetics of Brazilian ethanol: Comparison between assessment approaches. **Energy Policy**, v. 39, n. 8, p. 4605–4613, 2011.

RAMOS, C. R. G. **Desempenho operacional da colheita mecanizada de cana-de-açúcar (saccharum spp.) em função da velocidade de deslocamento e rotação do motor da colhedora**. [s.l.] UNESP, 2013.

REICHERT, P. **Concepts underlying a Computer Program for the Identification and Simulation of Aquatic Systems**. Dübendorf (Switzerland): [s.n.].

RIBAS, M. M. F. **Tratamento de vinhaça em reator anaeróbio operado em batelada seqüencial contendo biomassa imobilizada sob condições termofílicas e mesofílicas**. [s.l.] USP, 2006.

RIZZO, A. C. .; LEITE, S. G. . Produção de Sulfeto em Reator do tipo UASB e sua Potencial Aplicação na Remoção de Metais Pesados. p. 109, 2004.

ROSEN, C.; JEPPSSON, U. Aspects on ADM1 implementation within the BSM2 framework. **Technical report**, v. TEIE-7224, p. 1–35, 2006.

RUIZ, L. M.; ARÉVALO, J.; PARADA, J.; GONZÁLEZ, D.; MORENO, B.; et al. Respirometric assays of two different MBR (microfiltration and ultrafiltration) to obtain kinetic and stoichiometric parameters. **Water Science & Technology**, v. 63, n. 11, p. 2478–2485, 2011.

SALIHU, A.; ALAM, Z. Upgrading strategies for effective utilization of Biogas. **Environmental Progress & Sustainable Energy**, v. 34, n. 5, 2015.

SANDER, R. Compilation of Henry’s law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry (Version 3.0). 1999.

SÃO PAULO. Decreto nº 58.659, de 4 de dezembro de 2012. Institui o Programa Paulista de Biogás e dá providências correlatas. v. 1, p. 2, 2012.

SCARLAT, N.; DALLEMAND, J. F.; FAHL, F. Biogas: Developments and Perspectives in Europe. **Renewable Energy**, v. 129, p. 457–472, 2018.

SCHEIDL, H. A.; SIMON, A. T.; PACAGNELLA JUNIOR, A. C.; SALGADO JÚNIOR, A. P. Environmental Impacts of Mechanization in Brazil’s Sugar and Ethanol Industry: The Cutting, Loading, and Transportation Process Case. **Environmental Progress & Sustainable Energy**, v. 34, p. 1748–1755, 2015.

SEABRA, J. E. A.; MACEDO, I. C.; CHUM, H. L.; FARONI, C. E.; SARTO, C. A. Life cycle assessment of Brazilian sugarcane products: GHG emissions and energy use. **Biofuels, Bioproducts and Biorefining**, v. 5, n. 5, p. 519–532, set. 2011.

SEADI, T. AL; RUTZ, D.; PRASSL, H.; KOTTNER, M.; FINSTERWALDER, T.; et al. **Biogas Handbook**. Esbjerg: University of Southern Denmark Esbjerg, 2008.

SIEMENS ENERGY INC. SGE-H series gas engines and gen-sets Biogas 1,200/1,500/1,800 rpm. p. 4, 2018.

SISTEMA DE ESTIMATIVA DE EMISSÕES DE GASES DE EFEITO ESTUFA - SEEG. **Geração de eletricidade e emissões de GEE**. Disponível em: <http://monitoreletrico.seeg.eco.br/>. Acesso em: 5 mar. 2019.

SMIL, V. **Energy transitions: history, requirements, prospects.** [s.l.] ABC Clio, 2010.

SOARES, L. H. DE B.; ALVES, B. J. R.; URQUIAGA, S.; BODDEY, R. M. Mitigação das emissões de gases de efeito estufa. **Agroanalysis**, 2009.

SOLON, K. IWA Anaerobic Digestion Model No. 1 extended with Phosphorus and Sulfur Literature Review. **Industrial Electrical Engineering and Automation - Lund University**, p. 16, 2015.

SOREANU, G.; AL-JAMAL, M.; BÉLAND, M. Biogas treatment using an anaerobic biosystem. **3rd Canadian Organic Residuals and Biosolids Management Conference, Calgary, AB**, p. 502–513, 2005.

SOUZA, M. E.; FUZARO, G.; POLEGATO, A. R. Thermophilic anaerobic digestion of vinasse in pilot plant UASB reactor. **Water Science & Technology**, v. 25, n. 7, p. 213–222, 1992.

SPANJERS, H. **Anaerobic Fermentation - Environmental FactorsBiogas Compact Workshop**OldensburgLettinga Associates Foundation, , 2011.

STAMBASKY, J. Biomethane Production Routes An Overview. **GIE-ERGaR-CEDEC Biomethane Workshop**, n. April, 2017.

STETTLER, M. E. J.; MIDGLEY, W. J. B.; SWANSON, J. J. .; CEBON, D.; BOIES, A. M. Greenhouse Gas and Noxious Emissions from Dual Fuel Diesel and Natural Gas Heavy Goods Vehicles. **Environmental Science and Technology**, v. 50, p. 2018–2026, 2016.

SUZUKI, M.; KEHDY, B. O.; JAIN, S. Identifying barriers for the implementation and the operation of biogas power generation projects in South- east Asia : An analysis of clean Development Mecha- nism projects in Thailand. n. December, 2010.

SYED, M.; SOREANU, G.; FALLETTA, P.; BÉLAND, M. Removal of hydrogen sulfide from gas streams using biological processes - A review. **CANADIAN BIOSYSTEMS ENGINEERING**, v. 48, p. 14, 2006.

TAUSEEF, S. M.; ABBASI, T.; ABBASI, S. A. Energy recovery from wastewaters with high-rate anaerobic digesters. **Renewable and Sustainable Energy Reviews**, v. 19, p. 704–741, mar. 2013.

TEWARI, P. K.; BATRA, V. S.; BALAKRISHNAN, M. Water management initiatives in sugarcane molasses based distilleries in India. **Resources, Conservation and Recycling**, v. 52, n. 2, p. 351–367, 2007.

THYMOS. **Estudo da Thymos Energia avalia benefícios de usina térmica a gás no nordeste**. Disponível em: <http://thymosenergia.com.br/home/>. Acesso em: 3 fev. 2019.

TOMORY, L. Let it Burn: Distinguishing Inflammable Airs 1766–1790. **Ambix**, v. 56, n. 3, p. 253–272, 2009.

TUROVSKIY, I. S.; MATHAI, P. K. **Wastewater Sludge Processing**. Hoboken: John Wiley & Sons, 2006.

UNESP. **Termo de referência para o workshop tecnológico vinhaça**. Workshop tecnológico vinhaça. **Anais**...Jaboticabal: 2007

UNICA. **Boletim UNICA - A bioeletricidade da cana em números - Abril 2018**. Disponível em: <http://www.unica.com.br/documentos/>. Acesso em: 7 jan. 2018a.

UNICA. **Unicadata - Histórico de produção e moagem**. Disponível em: <www.unicadata.com.br/>. Acesso em: 15 maio. 2018b.

UNICA. **Unicadata - Histórico de produção e moagem**. Disponível em: <www.unicadata.com.br>. Acesso em: 15 abr. 2019a.

UNICA. **UNICA - Moagem de cana-de-açúcar e produção de açúcar e etanol - safra 2017/2018**. Disponível em: <http://www.unicadata.com.br/>. Acesso em: 17 abr. 2019b.

UNSW-CRC. **Treatment of abattoir wastewater using covered anaerobic lagoon - 1998**Meat & Livestock Australia, , 1998.

VAHL, F. P.; FILHO, N. C. Energy transition and path creation for natural gas in the Brazilian electricity mix. **Journal of Cleaner Production**, v. 86, p. 221–229, 2015.

VAN DEN WALL BAKE, J. D.; JUNGINGER, M.; FAAIJ, A.; POOT, T.; WALTER, A. Explaining the experience curve: Cost reductions of Brazilian ethanol from sugarcane. **Biomass and Bioenergy**, v. 33, n. 4, p. 644–658, 2009.

VAN FOREEST, F. Perspectives for biogas in Europe. **Oxford Institute for Energy Studies**,

n. December, p. 54, 2012.

VAN HAANDEL, A. C.; VAN DER LUBBE, J. G. Handbook of biological wastewater treatment: design and optimisation of activated sludge systems. p. 377–380, 2012.

VAN LIER, J. B.; MAHMOUD, N.; ZEEMAN, G. Anaerobic Wastewater Treatment. In: **Biological Wastewater Treatment: Principles, Modelling and Design**. London: IWA Publishing, 2008. p. 401–442.

VAN MEIJL, H.; SMEETS, E.; ZILBERMAN, D. Bioenergy Economics and Policies. In: SOUZA, G. M. et al. (Eds.). . **Bioenergy & Sustainability: bridging the gaps**. [s.l: s.n.]. p. 27.

VIEIRA, M. C. A.; LIMA, J. F.; BRAGA, N. M. Setor Sucroalcooleiro Brasileiro: Evolução e Perspectivas. **BNDES**, p. 209–245, 2007.

VLISSIDIS, A.; ZOUBOULIS, A. I. Thermophilic anaerobic digestion of alcohol distillery wastewaters. **Bioresource Technology**, v. 43, p. 131–140, 1993.

WALL, G.; HAMMOND, B.; DONLON, P.; JOHNSON, N. D.; SMITH, J. C. **Commissioning and operation of high rate anaerobic lagoon (HRAL) reactors**. 63rd Annual Water Industry Engineers and Operators' Conference. **Anais**...Warrnambool: 2000

WALTER, A.; GALDOS, M. V.; SCARPARE, F. V.; LEAL, M. R. L. V.; SEABRA, J. E. A.; et al. Brazilian Sugarcane Ethanol: Developments so far and Challenges for the Future. **Wiley Interdisciplinary Reviews: Energy and Environment**, v. 3, n. February, p. 70–92, 2015.

WEILAND, P. Biogas production: current state and perspectives. **Appl Microbiol Biotechnol**, v. 85, p. 849–860, 2010.

WELLINGER, A.; ANNA, L. Biogas Upgrading and Utilisation. **Task 24: Energy from biological conversion of organic waste**, 1999.

WILKIE, A. C.; RIEDESEL, K. J.; OWENS, J. M. Stillage characterization and anaerobic treatment of ethanol stillage from conventional and cellulosic feedstocks. **Biomass and Bioenergy**, v. 19, n. 2, p. 63–102, ago. 2000.

YAMADA, M.; HARADA, H.; YAMAUCHI, M.; YAMAGUSHI, T.; AHASHI, A. Reduction of Alkali Supplement in a Pilot-Scale Thermophilic Multi-Staged UASB Reactor Treating Alcohol Distillery Wastewater. **Int. J. Environ. Res.**, v. 7, n. 4, p. 823–830, 2013.

YASAR, A.; ALI, A.; TABINDA, A. B.; TAHIR, A. Waste to energy analysis of shakarganj sugar mills; biogas production from the spent wash for electricity generation. **Renewable and Sustainable Energy Reviews**, v. 43, p. 126–132, mar. 2015.

ZAHER, U.; RODRÍGUEZ, J.; FRANCO, A.; VANROLLEGHEM, P. A. **Application of the**

IWA ADM1 model to simulate anaerobic digester dynamics using a concise set of practical measurements. IWA Conference on Environmental Biotechnology. Advancement on Water and Wastewater Applications in the Tropics. **Anais**...2003

ZICARI, S. M. **Removal of Hydrogen Sulfide from Biogas using Dry Desulfurization Systems**. [s.l.] Cornell University, 2003.

A. Appendix 1: Mathematical modeling of anaerobic digestion

In 2001 the IWA (International Water Association) presented the “ADM1 - Anaerobic Digestion Model no. 1”, a general model of the anaerobic digestion process that includes 19 biochemical processes (disintegration, extracellular hydrolysis, acidogenesis, acetogenesis and methanogenesis from acetate and H_2/CO_2) and 9 physicochemical processes (association and dissociation of ions and liquid to gas phase transfer process) in a set of 24-variable differential and algebraic equations related to soluble compounds and particulate matter, kinetic and stoichiometric parameters, and inhibitory processes (BATSTONE et al., 2002a; REICHERT, 1994).

The ADM1 model was developed motivated by the benefits of anaerobic digestion, including net energy production through biogas, and the need for a mathematical model of the anaerobic digestion process that would provide 1) the application for design, operation and optimization of large-scale biogas plants; 2) further development of process optimization and control, aiming at the implementation in large-scale plants; 3) a common basis for future model developments and validations, obtaining comparable and compatible results and 4) assist in technology transfer from research to industry (BATSTONE et al., 2002a). ADM1 is currently considered the most realistic and general model for describing the anaerobic digestion process (ELAIUY et al., 2018).

The implementation of the ADM1 model suggested by Batstone (2002) consists of a liquid phase complete stirred tank reactor (CSTR), with an influent inlet and an effluent outlet and a “headspace”, a gas phase to which the gases are released, also with a gas outlet, as shown in Figure A-1.

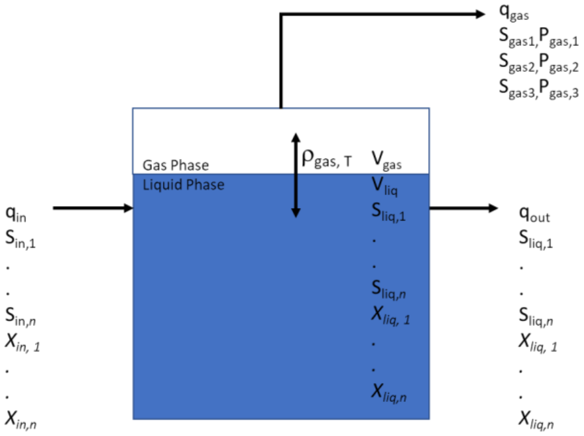


Figure A-1: Schematic diagram of an anaerobic digestion model configured as a CSTR reactor. Source: Adapted from (BATSTONE et al., 2002a).

For each component of the reactor liquid phase the mass balance is given (Equation A-1):

$$\frac{\mathrm{d}S_{\mathrm{liq},i}}{\mathrm{d}t} = \frac{q_{\mathrm{in}}S_{\mathrm{in},i}}{V_{\mathrm{liq}}} - \frac{S_{\mathrm{liq},i}q_{\mathrm{out}}}{V_{\mathrm{liq}}} + \sum_{j=1-19} \rho_j \nu_{i,j} \qquad \text{Equation A-1}$$

Where:

$$\sum_{j=1-m} \rho_j \times \nu_{i,j}$$

is the sum of the kinetic rate of each process multiplied by the stoichiometric coefficient that describes the influence of the process on each component.

The model can be described by a Peterson matrix (Tables A-1 and A-2, including sulfur-related reactions). Each process (presented in the matrix lines) is subject to a kinetic rate "ρ" (shown in the far left column Table A-2), which, multiplied by the matrix coefficient associated with each component, calculates the generation or consumption of the corresponding component of that column. This rate is in turn multiplied by the inhibition coefficients (not shown) that are calculated for each operating condition and is added or subtracted from the amount of the component that is loaded or removed from the reactor.

The original implementation of ADM1 does not include in its modeling the reactions involving sulfur, whose metabolization produces hydrogen sulfide. In the case of vinasse the presence of sulfate is significantly high, which implies in high levels of hydrogen sulfide in biogas, besides the possibility of bacteria inhibition. Also, the ADM1 provides a complete mixing reactor without bacterial biomass retention, effect that can result in better operating conditions of anaerobic reactors.

Elauiy (2018) presents a mathematical model of anaerobic digestion based on the operation of the anaerobic reactor built at the Ester Plant using 2012 and 2014 crop seasons data for model calibration and validation. The model was implemented following the ADM1 methodology using the Aquasim 2.1 software as a constant volume two-chamber reactor, one containing liquid and the other configured as headspace. Aquasim simultaneously solves, for each component and under each condition, in continuous or variable feeding regime, Equation A-1, as well as calculates diffusion of biogas products from liquid to gas phase as a function of their solubilities and transfer coefficients, resulting in the calculation of biogas production and composition. In this present work, the model described by Elauiy (2018) was improved by the inclusion of reactions involving sulfur as well as the introduction of a settler in the reactor outlet that provides anaerobic sludge retention, enabling its return to the reactor.

With the addition of sulfur reactions to the ADM1 and with operation data of the sulfate concentration in vinasse and hydrogen sulfide concentration in the biogas, a new model was calibrated and validated to predict the production of H_2S in biogas as well as the its effect on methane production (competition from sulfate-reducing bacteria for methane precursors) and inhibition of undissociated H_2S on the reactor liquid phase. This is, as far as we know, the first anaerobic digestion model including sulfur, calibrated and validated with real operating data of a large-scale reactor using vinasse as substrate, thus is a very useful tool in the development of vinasse biogas projects. The tool is even more relevant when considering that among biogas production and recovery processes, the generation of H_2S in biogas is possibly the least studied aspect (LEME; SEABRA, 2017).

The implementation of a settler in the reactor outlet can improve its performance, promoting the decoupling of the hydraulic residence time from the cell retention time, allowing a higher concentration of microorganisms inside the reactor and lower substrate to microorganisms ratio, which should result in lower biomass and higher methane production (APPELS et al., 2008; LOW; CHASE, 1999; RUIZ et al., 2011; TUROVSKIY; MATHAI, 2006). From data obtained from a small settler (flow rate of $2m^3/h$) installed at Ester biogas project, it was possible to obtain the solids retention efficiency of this type of device operating with digested vinasse. Based on this data, solid (anaerobic biomass) retention and recycle features were implemented in ADM1 to ascertain the potential for process improvement and possible cost savings in the construction and operation of high-rate pond-based anaerobic reactors.

The model presented by Elauiy (2018) considers that the reactor feed substrate is already solubilized, such as proteins, carbohydrates and fats, so that the disintegration stage was disregarded in the original model (ELAIUY et al., 2018). This assumption is valid for vinasse, however, when large amounts of bacterial biomass are introduced by the use of a settler, the disintegration stage takes more important contours, so the disintegration process in the proposed implementation was considered in the model. The hydrolysis rate considered were those originally suggested by ADM1, whose values are adequate for activated sludge digestion, a product also largely characterized as bacterial biomass (ELAIUY, 2016).

Table A-1: Peterson Matrix of anaerobic digestion process including sulfur - soluble material

Component i → / Process j ↓		1	2	3	4	5	6	7	8	9	S1	S2
		S_{su}	S_{aa}	S_{fa}	S_{va}	S_{bu}	S_{pro}	S_{ac}	S_{h2}	S_{ch4}	Sh_2so_4	S_{H2S}
1	Disintegration											
2	Hydrolysis Carbohydrates	1										
3	Hydrolysis of Proteins		1									
4	Hydrolysis of Lipids	=1-f_FA_LI		=f_FA_LI								
5	Uptake of Sugars	-1				=(1-Y_su)*f_BU_SU	=(1-Y_su)*f_PRO_SU	=(1-Y_su)*f_AC_SU	=(1-Y_su)*f_H2_SU			
6	Uptake of Amino Acids		-1		=(1-Y_aa)*f_VA_AA	=(1-Y_aa)*f_BU_AA	=(1-Y_aa)*f_PRO_AA	=(1-Y_aa)*f_AC_AA	=(1-Y_aa)*f_H2_AA			
7	Uptake of LCFA			-1				=(1-Y_fa)*0.7	=(1-Y_fa)*0.3			
8	Uptake of Valerate				-1		=(1-Y_c4)*0.54	=(1-Y_c4)*0.31	=(1-Y_c4)*0.15			
9	Uptake of Butyrate					-1		=(1-Y_c4)*0.8	=(1-Y_c4)*0.2			
10	Uptake of Propionate						-1	=(1-Y_pro)*0.57	=(1-Y_pro)*0.43			
11	Uptake of Acetate							-1		=(1-Y_ac)		
12	Uptake of Hydrogen								-1	=(1-Y_h2)		
S1	Uptake of Propionate by pSRB						-1	=(1-Y_pSRB)*f_ac_pSRB			=-(1-Y_pSRB)*f_SO4_pSRB/64	=(1-Y_pSRB)*(1-f_ac_pSRB)
S2	Uptake of Acetate by aSRB							-1			=-(1-Y_aSRB)/64	=(1-Y_aSRB)
S3	Uptake of Hydrogen by hSRB								-1		=-(1-Y_hSRB)/64	=(1-Y_hSRB)

Table A-2: Peterson Matrix of anaerobic digestion process including sulfur - particulate material

Component i → / Process j ↓		13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	Rates (ρ)
		X_c	X_{ch}	X_{pr}	X_{li}	X_{su}	X_{aa}	X_{fa}	X_{c4}	X_{pro}	X_{ac}	X_{h2}	X_I	X_{pSRB}	X_{aSRB}	X_{hSRB}	
1	Disintegration	-1	=f_CH_XC	=f_PR_XC	=f_LI_XC								=f_XI_XC				=kdis*Xc_r
2	Hydrolysis Carbohydrates		-1														=khyd_ch*Xch_r
3	Hydrolysis of Proteins			-1													=khyd_pr*Xpr_r
4	Hydrolysis of Lipids				-1												=khyd_li*Xli_r
5	Uptake of Sugars					=Y_su											=km_su*Xsu_r*Ssu_r/(Ssu_r+Ks_su)
6	Uptake of Amino Acids						=Y_aa										=km_aa*Xaa_r*Saa_r/(Saa_r+Ks_aa)
7	Uptake of LCFA							=Y_fa									=km_fa*Xfa_r*Sfa_r/(Sfa_r+Ks_fa)
8	Uptake of Valerate								=Y_c4								=km_c4*Xc4_r*Sva_r/(Sva_r+Ks_c4)*1/(1+Sbu_r/Sva_r)
9	Uptake of Butyrate								=Y_c4								=km_c4*Xc4_r*Sbu_r/(Sbu_r+Ks_c4)*1/(1+Sva_r/Sbu_r)
10	Uptake of Propionate									=Y_pro							=km_pro*Xpro_r*Spro_r/(Spro_r+Ks_pro)
11	Uptake of Acetate										=Y_ac						=km_ac*Xac_r*Sac_r/(Sac_r+Ks_ac)
12	Uptake of Hydrogen											=Y_h2					=km_h2*Xh2_r*Sh2_r/(Sh2_r+Ks_h2)
S1	Uptake of Propionate by pSRB													=Y_pSRB			=km_pSRB*Spro/(Ks_pro+Spro)*Sso4/(Ks_so4_pSRB+Sso4)
S2	Uptake of Acetate by aSRB														=Y_aSRB		=km_aSRB*Sac/(Ks_ac+Sac)*Sso4/(Ks_so4_aSRB+Sso4)
S3	Uptake of Hydrogen by hSRB															=Y_hSRB	=km_hSRB*Sh2/(Ks_h2+Sh2)*Sso4/(Ks_so4_hSRB+Sh2)
13	Decay of X_{su}	1				-1											=kdec_xsu*Xsu_r
14	Decay of X_{aa}	1					-1										=kdec_xaa*Xaa_r
15	Decay of X_{fa}	1						-1									=kdec_xfa*Xfa_r
16	Decay of X_{C4}	1							-1								=kdec_xc4*Xc4_r
17	Decay of X_{pro}	1								-1							=kdec_xpro*Xpro_r
18	Decay of X_{ac}	1									-1						=kdec_xac*Xac_r
19	Decay of X_{h2}	1										-1					=kdec_xh2*Xh2_r
S4	Decay of X_{pSRB}	1												-1			=kdec_xpSRB*XpSRB
S5	Decay of X_{aSBR}	1													-1		=kdec_xaSRB*XaSRB
S6	Decay of X_{hSBR}	1														-1	=kdec_xhSRB*XhSRB