UNIVERSIDADE ESTADUAL DE CAMPINAS
Faculdade de Engenharia Mecânica

WAGNER ROBERTO DA SILVA TRINDADE

n-Butanol as biofuel: characteristics and evaluation of its application in internal combustion engines through 1D simulation

n-Butanol como biocombustível: características e avaliação de sua aplicação em motores de combustão interna através de simulação 1D

CAMPINAS
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Orientador: Prof. Dr. Rogério Gonçalves dos Santos

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Resumo

Neste trabalho, foi feita uma revisão onde se apresentaram as características e propriedades do butanol sob o ponto de vista geral de um álcool produzido industrialmente e também do ponto de vista específico de um biocombustível. Uma visão geral sobre os meios de produção atuais desse álcool (via síntese química ou via fermentação) foram apresentadas bem como estudos atuais para melhorar o processo acetona-butanol-etanol (ABE), que é o mais difundido para a produção do biobutanol. Alguns tópicos de trabalhos de outros autores focados na cinética química de butanol foram brevemente introduzidos e, a partir destas análises, estudou-se o n-butanol dando ênfase na sua aplicação como biocombustível automotivo. Verificou-se que existe pouca informação sobre o desempenho de motores trabalhando com este álcool, dificultando a avaliação de suas vantagens em relação a outros combustíveis. Essa dificuldade foi contornada com o uso de simulação numérica, em especial modelos 1D, para representar todo o motor e visualizar o seu desempenho sob diferentes condições de operação e funcionando com diferentes combustíveis. Um motor, abastecido com mistura n-butanol-gasolina, foi modelado usando GT-Power, um código 1D para simulação de motores de combustão interna. Foram usadas medições feitas nesse motor para calibrar os resultados e ajustar a propriedades do combustível. Comparando o desempenho do motor abastecido com uma mistura BU40 (40% de butanol e 60% de gasolina), observou-se que ele apresenta níveis de potência e torque inferiores ao motor abastecido com etanol, porém similares ao motor abastecido com a mistura gasolina mais etanol e superiores ao motor abastecido com gasolina pura. O motor com BU40 também apresenta menores níveis de pressão de combustão, o que representa um menor carregamento mecânico nos componentes do motor. Em termos de eficiência, o motor com BU40 se apresenta no mesmo nível do motor rodando com mistura gasolina etanol e inferior ao motor com etanol.

Palavras-chave: butanol, biocombustivel, motores de combustão interna, simulação.

Abstract

In this work, a review is done presenting the characteristics and properties of butanol from the general point of view of an industrially produced alcohol and also from the specific point of view of a biofuel. An overview about the current production process of this alcohol (via chemical synthesis or by fermentation) was presented, as well as some current studies aiming to improve the acetone-butanol-ethanol (ABE) process, which is the most widely used for the production of biobutanol. Some topics from articles of other authors focused on the chemical kinetics of butanol were briefly introduced and starting from these analyzes, n-butanol was studied with emphasis on its application as automotive biofuel. It was realized that there is little information about the performance of engines working with this alcohol, complicating the assessment of their advantages over other fuels. This difficulty was bypassed by the use of numerical simulation, in particular 1D models, to represent the entire engine and evaluate its performance under different operating conditions and working with different fuels. An engine fueled with mixture of n-butanol-gasoline was modeled using GT-Power, a 1D code for simulation of internal combustion engines. Measurements performed in this engine were used to calibrate the results and to adjust the fuel properties used. Comparing the performance of the engine fueled with BU40 blend (40% butanol and 60% gasoline), it was observed that it presents levels of power and torque lower than the same engine fueled with ethanol, but similar levels when the engine is fueled with the blend of gasoline plus ethanol and higher than the engine fueled with pure gasoline. The engine with BU40 also presents lower levels of combustion pressure, which represents lower mechanical load to the engine components. In terms of efficiency, the engine fueled with BU40 is at the same level of the engine running on gasoline – ethanol blend, but in a lower level in relation to the engine with ethanol only.

Keywords: butanol, biofuel, internal combustion engines, simulation.

SUMMARY

SUMMARY **9**

1 Introduction **11**

2 Review on the characteristics of butanol, its production and use as fuel in internal combustion engines **13**

2.1 Introduction . . . 13
2.2 Properties, advantages and disadvantages of n-butanol . . . 14
2.3 The production of n-butanol: a general overview . . . 19
2.4 Use of alcohols as fuels . . . 23
2.5 Alcohols as fuels in the transportation industry . . . 27
2.5.1 n-Butanol applied to spark ignited (SI) engines . . . 29
2.5.2 n-Butanol applied to compression ignited (CI) engines . . . 31
2.6 Conclusions . . . 33

3 Combustion modeling applied to engines using a 1D simulation code **35**

3.1 Introduction . . . 35
3.2 Available 1D codes for SI engines simulation . . . 36
3.3 Predictive vs. non-predictive combustion models . . . 38
3.4 Non-predictive combustion models . . . 40
3.4.1 Imposed combustion profile . . . 40
3.4.2 Spark-ignition Wiebe model . . . 40
3.5 Predictive combustion models . . . 42
3.5.1 Spark-ignition turbulent flame model . . . 42
3.5.2 Homogeneous charge compression ignition model . . . 44
3.6 Results obtained with the combustion models . . . 46
3.6.1 SI-Wiebe . . . 46
3.6.2 SI turbulent flame . . . 49
3.6.3 Homogeneous charge compression ignition (HCCI) model . . . 51
3.7 Conclusions . . . 53

4 1D model of SI engine using n-butanol as fuel: comparison between measurements and simulation results **55**

4.1 Introduction . . . 55

4.2 Potentials and limitations of n-butanol as automotive fuel 56
4.3 Modeling of internal combustion engines and adjusting numerical to experimental results 59
4.4 General flow solution 61
4.5 Experimental engine 64
4.6 Setting up and running the 1D engine model 66
4.6.1 Engine performance using BU40 as fuel 70
4.6.2 Potential application of BU40 in a commercial SI engine 76
4.7 Conclusions 87

5 Conclusions **89**

References **93**

1 Introduction

This dissertation, presented in an alternative format, consists of a sequence of three articles with information on n-butanol alcohol, modeling of 1D engines and application of n-butanol in the automotive industry. The aim of this work was to study the use of n-butanol as biofuel in internal combustion engines, using 1D numerical simulation.

The first article titled "Review on the characteristics of n-butanol, its production and use of fuel in internal combustion engines" represents the Chapter 2 of this dissertation and was submitted to the journal *Renewable and Sustainable Energy Reviews* (under review by editors). This is a review article, where the chemical characteristics of n-butanol were presented. Their properties have been shown from the general point of view of an alcohol produced industrially and also from the more specific point of view of a biofuel. An overview of the production of petro-butanol as well as biobutanol was presented to discuss its characteristics in the context of the chemical and/or transportation industries. A brief review was made about new and growing studies to improve the Acetone-Butanol-Ethanol (ABE) process, the main routes of production of renewable n-butanol, showing novelties focused on new strains of bacteria and the use of new raw materials for fermentation, in the search for a better yield of the process. A brief presentation of studies of other authors focused on the chemical kinetics of n-butanol was made and it was useful to start a debate about the great potential of this alcohol – or its mixture with gasoline or diesel – as a new and environmentally interesting biofuel. The purpose of this first article was to present in an organized and accessible way the potential and disadvantages of n-butanol, allowing to explore the approach of using it in the automotive industry.

Within this context, two routes could be taken to verify the application of n-butanol as biofuel: by measurements in engine tests or by numerical simulation of internal combustion engines. In this work we have chosen for the second approach and, for the best understanding, a study on computational modeling of engines was done, generating a new article. This second article titled "Combustion modeling applied to engines using a 1D simulation code" is presented as Chapter 3 of this dissertation and was entered in the SAE Brazil 2016 Congress (already approved for publication). This article begins with an explanation about the current state of the modeling of internal combustion engines. It is perceived that this is a multidisciplinary activity, which is constantly growing and is increasingly present during the development phase of an engine, especially today, when the time for production and sale of products is reduced. It has been seen that there are different levels of complexity when thinking about engine modeling, from the highest level of detail of 3D models to a simpler approach of 1D models. It can be said that in commercial applications, the 1D model is best suited to analyze the entire engine system

with multiple components together, looking at its performance. In this article, some possibilities of 1D modeling were presented, a brief explanation about some terms and definitions used in the combustion study was made and these topics were placed from the point of view of using a 1D code for modeling of internal combustion engines . After that, some combustion models present in this code were studied and finally applied in the construction of 1D models of motors to verify their results, advantages and disadvantages of each combustion model. The objective was to establish best practices in the construction of 1D models in general and the models that were used in the development of the present work in particular.

During the development of this work it has been observed that there are still no commercially produced engines running on n-butanol or with its blend with gasoline or diesel. With this, little or no literature dealing with commercial engines fueled with n-butanol is available. In order to verify the characteristics of n-butanol as fuel, it was necessary to construct numerical simulation models with 1D codes and to simulate the behavior of these engines when fueled with n-butanol. With the fundamental knowledge about n-butanol presented in the first article and the applied knowledge on modeling and simulation 1D of internal combustion engines of the second, a third article was written. This article composes Chapter 4 of this dissertation and should be presented to *Applied Energy* journal for publication. This third article was intended to merge the first two works, adding knowledge from other articles dealing with performance measurements of engines fueled with n-butanol. Some properties of n-butanol from the combustion point of view were raised by adjustments of simulation models and, finally, it was shown how the use of n-butanol can be viable in commercial motors, presenting comparative performance, advantages and the disadvantages of n-butanol to existing fuels.

2 Review on the characteristics of butanol, its production and use as fuel in internal combustion engines

2.1 Introduction

Biofuels are today a reality and are receiving more and more attention from the society, industry and academy. Several factors contribute to this, but the most relevant are related to the uncertainty of fossil fuels price and the search for lower emissions of greenhouse gases as well as for different options of energy generation. For the transportation industry, namely the automotive, a variety biofuels have been researched. All those biofuels can be derived from renewable feedstock and not from fossil feedstock, as in the case of gasoline or diesel fuels.

The alcohols are widely used as fuels. Ethanol and methanol are the most commonly used alternative fuels in internal combustion engines. The first one is a biomass-based renewable fuel that can be produced by alcoholic fermentation of sugar from vegetable materials, being sugar cane the most popular raw material, followed by corn starch. One of its big advantages when looking for the environment protection is that ethanol enables a closed carbon cycle, it means, a part of the CO_2 generated during its production and combustion is reabsorbed by the plants (Yao *et al.*, 2010a).

Ethanol is already established as alternative fuel in many countries presenting several advantages in relation to gasoline, mainly concerning engine performance and efficiency (Brassat *et al.*, 2011; Schwaderlapp *et al.*, 2012). It is known that the share of biofuels in the automotive market is expected to grow in the next decade. The EPA-RFS2 (Environment Protection Agency - Renewable Fuel Standard version 2) drives the definitions for the American automotive market and requires that 21 billion gallons (79.5 billion liter) of renewable fuel should be available in the US market by 2022 (Schnepf and Yacobucci, 2013). Ethanol consumption grew from 8 percent by volume in 2009 to nearly 10 percent in 2011 and in the first eight months of 2012 (U.S. market). In Brazil, ethanol is fully available and already commonly used.

Butanol is another promising, although not very well known, renewable fuel for use in internal combustion engines that presents several advantages. It may also be a biomass-based renewable fuel that can be produced by the fermentation of biomass feedstock (Bankar *et al.*, 2013; Jin *et al.*, 2011; Chen *et al.*, 2009). 1-butanol (or n-butanol), iso-butanol and tert-butanol can be used as gasoline additives, but n-butanol is the most promising since it can be easily mixed with gasoline. It could also be a future option for blending with diesel since it has more

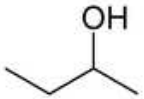
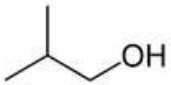
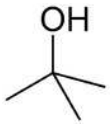
oxygen content compared with biodiesel, potentially leading to reduction of emissions, mainly soot (Jin *et al.*, 2011). Butanol presents higher heat of evaporation than ethanol which is beneficial for reducing the combustion temperature (Dernotte *et al.*, 2010) and possibly leading to the reduction of formation of NO_x. Therefore, n-butanol may present some additional advantages as biofuel than other bioalcohols, ethanol for instance. Although promising, butanol and its isomers present the disadvantage of its quite low production. Compared butanol and isomers fermentation to ethanol fermentation process, ethanol process has a 10 to 30 times higher production rate (Chen *et al.*, 2009).

In this review, some basic knowledge about the properties of butanol are presented and compared with those of the conventional gasoline, ethanol, gasohol (blend of gasoline and ethanol) and diesel. Following, the description of butanol production is reviewed, as it started and as it is today. Next, a brief summary about its chemical kinetics is presented, showing what the researchers and institutes are studying on this field. Finally, the application of n-butanol as a liquid fuel and its main combustion parameters are summarized from the point of view of its usage in internal combustion engines. All those points together serve as a good start to open the discussion for future research in the use of n-butanol as liquid fuel in the transportation industry, mainly in automotive applications.

2.2 Properties, advantages and disadvantages of n-butanol

The main characteristic of the alcohols, from the chemical point of view, is the presence of a hydroxyl group (–OH) attached to one of the carbons atoms of the molecule. Butanol and its isomers present 4-carbon structure and may present straight-chain or branched structures. The differences in the structures, as well as the position of the –OH, normally lead to different properties and serve to classify the butanol isomers (Solomons and Fryhle, 2009). A general overview on the physical properties of butanol and its isomers can be seen in Table 2.1 (Jin *et al.*, 2011; Liu *et al.*, 2013).

Table 2.1: Butanol isomers: structures and applications (Jin *et al.*, 2011; Liu *et al.*, 2013).

Butanol isomer	Molecular structure	Main Applications	Specific characteristic
1-butanol (n-butanol)		Solvents (paint industry) Plasticizers (plastics industry) Hydraulic brake fluid Cosmetics	Gasoline additive Potential gasoline alternative
2-butanol		Solvent (several industries) Domestic cleaning agent Industrial cleaner and paint remover	Perfumes and artificial flavors
iso-butanol		Solvent and additive (paint industry) Industrial cleaner and paint remover Ink ingredient	Gasoline additive
tert-butanol		Solvent Industrial cleaner and paint remover Intermediate for MTBE, ETBE, TBHP	Gasoline additive and octane booster Denaturant for ethanol

Although the properties of the various butanol isomers are different, the main applications are similar. Another interesting point is that all these butanol isomers can be produced from fossil fuels as well as from biomass. 1-butanol, better known as n-butanol, has a straight-chain structure with the –OH at the terminal carbon and presents the best characteristics to be used as liquid fuel or additive to other fuels.

Some of the main physical and chemical properties of gasoline, diesel, ethanol and n-butanol are listed in Table 2.2. From the analysis of these properties is possible to verify that n-butanol has some interesting features that indicate that it has the potential to overcome some disadvantages brought by other lower-carbon alcohols used as fuel or fuel additives like ignition problems in cold weather, higher fuel consumption, low lubricity and corrosion. Those potentials of n-butanol are (Brassat *et al.*, 2011; Jin *et al.*, 2011; Sarathy *et al.*, 2014):

- Higher heating value. Normally, the low heating value of alcohol rises with increased carbon content. n-Butanol is a four carbon alcohol, the double in relation to ethanol and containing 50% more energy density in volume. In practice, it means that an engine running on n-butanol is expected to present a lower fuel consumption and a better mileage when compared with ethanol.

- Less ignition problems. One engine running on n-butanol is expected to has less problems of cold start than the same engine running on ethanol (considering the same air to fuel relation). It happens because the heat of vaporization of n-butanol is less than half of that of ethanol.

- Intersolubility. Higher carbon numbered alcohols are easier to be blended into gasoline and n-butanol with its four carbons has very good intersolubility with gasoline. Lower carbon numbered alcohols are more polar and more soluble in water than non-polar hydrocarbons. It may be a challenge since introduces some more difficulties in their distribution which must prevent water contamination. Also, it lowers the upper limit of blending in petroleum fuels without the use of a co-solvent. n-Butanol and higher carbon alcohols are increasingly less polar due to their longer non-polar hydrocarbon chains. They are thus easier to blend with non-polar hydrocarbons and have lower affinity for water.

- Higher viscosity and lubricity. The viscosity of alcohols increases as the number of the carbons in the molecule grows. Then, it may potentially protect against wear problems some components of the engine that have direct contact with fuel (like fuel pumps, fuel rails, injectors).

- Safer. The saturation pressure of alcohols decreases with the increase of carbon content.

It means that n-butanol will have lower vapor pressure. In addition, it has higher flash point in relation to ethanol and then is safer when considering transportation and use in high temperatures.

Table 2.2: Properties of some alcohols and conventional fossil fuels (Bankar *et al.*, 2013; Jin *et al.*, 2011).

	Gasoline	Diesel	Methanol	Ethanol	n-Butanol
Molecular formula	$C_4 - C_{12}$	$C_{12} - C_{25}$	CH_3OH	C_2H_5OH	C_4H_9OH
Molecular weight	111.19	198.4	32.04	46.06	74.11
Cetane number	0 – 10	40 – 55	3	8	25
Octane number	80 – 99	20 – 30	111	108	96
RON	88 – 98	0	109	109	98
MON	80 – 88	0	89	90	85
Oxygen content (% weight)	–	–	50	34.8	21.6
Density (g/mL) at 20°C	0.72 – 0.78	0.82 – 0.86	0.796	0.79	0.808
Autoignition temperature (°C)	300	210	470	434	385
Flash point (°C) at closed cup	-45 to -38	65 – 88	12	8	35
Lower heating value (MJ/kg)	42.7	42.5	19.9	26.8	33.1
Boiling point (°C)	25 – 215	180 – 370	64.5	78.4	117.7
Stoichiometric ratio	14.7	14.3	6.49	9.02	11.21
Latent heating (kJ/kg) at 25°C	380 – 500	270	1109	904	582
Flammability limits (%vol.)	0.6 – 8	1.5 – 7.6	6.0 – 36.5	4.3 – 19	1.4 – 11.2
Saturation pressure (kPa) at 38°C	31.01	1.86	31.69	13.8	2.27
Viscosity (mm^2/s) at 40°C	0.4 – 0.8	1.9 – 4.1	0.59	1.08	2.63
Energy density (MJ/L)	32	35.86	16	19.6	29.2

As already observed in the previous section, butanol can be produced from biomass just like ethanol. Considering this similarity – the production from biomass – it has several analogies with ethanol mainly that butanol may be produced from the same agricultural feedstock as ethanol (i.e. sugar cane, corn, wheat, sugar beet and others). Also, the existing ethanol plants can be cost-effectively adapted to butanol production with just some minor changes in fermentation and distillation processes. Details of the production of butanol are described in the Section 2.3.

From those discussed points, it is possible to consider that n-butanol has some interesting advantages and benefits in relation to the low-carbon alcohols as an engine fuel or fuel additive. However, there are still some potential issues with the direct use of n-butanol in the engine. These possible issues are (Merola *et al.*, 2012; Rakopoulos *et al.*, 2010; Sarathy *et al.*, 2014):

- Limitations to reach engine performance. Since n-butanol has lower heating value than gasoline, it may occur engine operation conditions where an engine burning n-butanol will have lower performance than the same engine burning gasoline.
- Higher fuel consumption. The use of n-butanol fuel as a substitute for gasoline demands more fuel injected by cycle and then higher fuel consumption in relation to gasoline (engines running under the same conditions). Butanol has higher energy density than ethanol, but its heating value is still lower than the conventional gasoline fuel.
- While butanol has higher energy density than ethanol, it has lower octane number, forcing the engine to work with lower compression ratios and then lower efficiency. Higher combustion engine efficiency (as found in ethanol) has to be pursuit since it enables less greenhouse gas emissions per unit motive energy extracted. Ethanol has high research octane number (RON) and have long been used to improve the octane number of SI engine fuels. Butanol isomers have octane ratings similar to that of conventional gasoline and are thus suitable for SI engines although not presenting the same advantage as presented by ethanol.
- n-Butanol has lower cetane number compared with diesel or biodiesel fuels, reducing autoignition and potentiality harming the control of the combustion.

2.3 The production of n-butanol: a general overview

There are basically two big lines of production of butanol: from biomass (as "biobutanol") and from fossil fuels (as "petro-butanol"), but biobutanol and petro-butanol have the

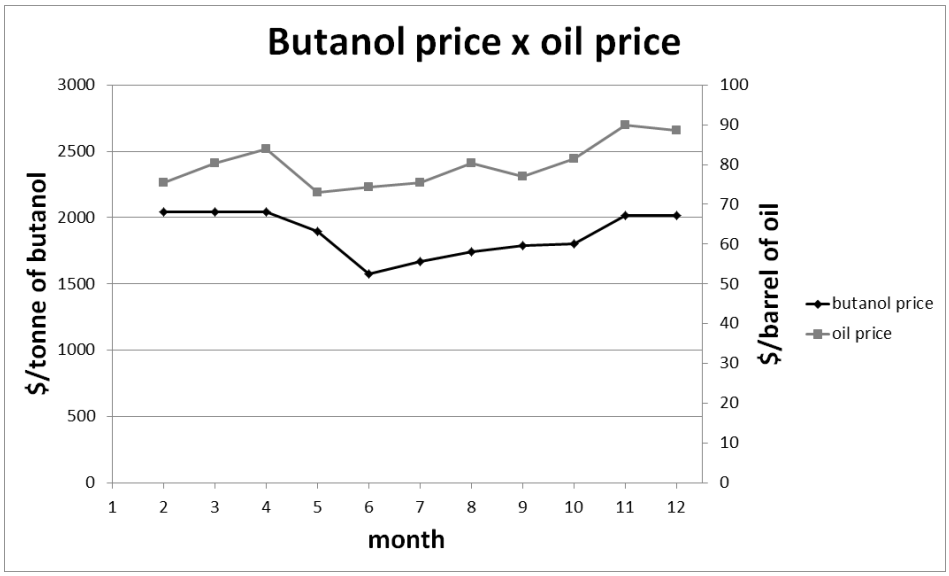


Figure 2.1: Relation between crude oil price and synthetic butanol price in China (2010) (Green, 2011).

same chemical properties. Most of butanol produced today is synthetic (petro-butanol), derived from a petrochemical reaction. Currently, the biggest producers of synthetic butanol are Dow, Basf, Celanes and Eastman followed by Sasol in South Africa and KH Neochem in Japan (Nejame, 2010), all of them working in industry scale production. Only a few biobutanol plants are operating in China in a pilot scale production and in Brazil (Brotas-SP), there is a demonstration plant that converts sugarcane bagasse and other non-food feedstock into biobutanol (Lane, 2013).

Petro-butanol is obtained by the propylene hydroformylation, well known as oxo route (Heaton, 1994; Nejame, 2010). Although common, this scenario is not the most interesting since synthetic butanol production costs are linked to the propylene market that are strongly linked to the price of crude oil, as can be seen in Figure 2.1 (Green, 2011). Also, as previously discussed, since the society is searching for diversity of solutions that are independent of petroleum derivatives, this is not the best path to be followed and at the same time not as environmentally friendly as desired.

Renewable n-butanol can be produced from the fermentation of carbohydrates in a process better known as ABE fermentation since its major chemical products are acetone, butanol and ethanol. The fermentation occurs in two stages; the first is a growth stage in which acetic and butyric acids are produced and the second stage is characterized by acid re-assimilation into acetone, butanol and ethanol. The fermentation also produces carbon dioxide and hydrogen (Jones and Woods, 1986). First registers of butanol production from ABE process are from 1912, in

UK. However, fermentation process fell out in 1950s when synthetic equivalents evolved in production and presented better prices (Pometto *et al.*, 2005). China is one of the few countries which maintained the fermentative acetone-butanol-ethanol (ABE) production for several decades. Because of the international prices of the synthetic butanol, advantageous compared to the biobutanol, some plants were closed in the 1990's. Today, China leads efforts to produce butanol by the ABE fermentation process. Huge investments are being done and there are basically six major plants producing butanol using corn starch as feedstock. Due to the current concern about renewable energy sources, pollution and emissions regulation, new opportunities have emerged for the traditional ABE fermentation industry since it could again be potentially competitive with chemical synthesis. From 2006, several ABE fermentation plants in China have restarted their production and today the total solvent (acetone, butanol and ethanol) production capacity from ten plants reached 210,000 tons with an optimistic scenario of growing for the coming years (Ni and Sun, 2009).

Concerning the process of production of biobutanol, most plants operate in a semi-continuous way with each fermentation lasting up to 21 days. The plants typically house several trains of big tanks (up to 400m^3). Fresh feedstock, together with periodic additions of seed culture, flows through the fermentors in a process that provides sufficient residence time for re-assimilation of the acids to solvents. Final product is then distilled to recover acetone, butanol and ethanol in a proportion of 3:6:1 by mass, meaning, 3 parts of acetone, 6 parts of butanol and 1 part of ethanol (Green, 2011; Ni and Sun, 2009; Pometto *et al.*, 2005).

Brazil has used sugarcane as raw material for the large scale production of ethanol since the 70's. The current and widely installed model of production is based on the so called first-generations plants. In those plants, sugars from the sugarcane juice are converted to ethanol and sugar and the sugarcane bagasse (biggest sub-product) is burnt to generate steam and power. Ethanol production is very well established and, in this context, the biobutanol would then be produced from the conversion of ethanol. This process is know as Guerbet reaction, converting a primary aliphatic alcohol into its β-alkylated dimer alcohol with loss of one equivalent of water. This reaction requires a catalyst and elevated temperatures (Jones and Woods, 1986; Nexant, 2009; Rodrigues, 2011).

In Brazil, half of the annual demand of about 60×10^3 tonnes of butanol is produced internally (ABIQUIM-Associação Brasileira da Indústria Química, 2013). The automotive market is not the focus of the refineries since there is no penetration of n-butanol as transportation fuel. However, as a strategy, the refineries are focusing in the chemical market, since it provides larger profitability, and at the same time several developments are being done to reduce pro-

duction costs to reach more competitive levels, possibly allowing to go to the biofuels market in the near future. Because of this, research on butanol production has been intensified during the last decade and important advances have been achieved mainly in microbial strain development, processing of low-cost biomass residues and fermentation technology (Green, 2011; Naik *et al.*, 2010). The continuous search for better performance in the ABE process is intense and involves the use of bacteria from the genus *Clostridium* in order to maximize the production of hydrogen, butyric acid and its conversion to butanol in a two stage fermentation.

Although largely used and studied, the ABE process for butanol production still has some limitations that should be considered, as follows (Green, 2011):

- high feedstock cost that significantly increase operating costs,
- low performance of the ABE process that leads to low butanol titres, increasing recovery costs, reducing sugar loadings and increasing water usage,
- low butanol production yield increases feedstock usage and then the final costs,
- low volumetric solvent productivity increases capital and operating costs,
- butanol recovery using conventional distillation is energy intensive and expensive,
- higher waste-water footprint in relation to ethanol production is not sustainable and increases the cost of effluent treatment (ethanol plant:10.7L of stillage per liter of ethanol produced; butanol plant: 87L of stillage/L butanol (Mariano *et al.*, 2013))

Reach profitability is a difficulty for n-butanol production as a bioalcohol. Table 2.3 shows prices of ethanol, butanol and sugar in the international market (Mariano *et al.*, 2013), serving for comparison and to start some discussions. The commercialization of n-butanol in the chemical market – that presents higher price – may reach revenues slightly higher than those of an integrated first and second generation ethanol production sugarcane biorefinery (with no n-butanol production). However, if butanol is considered to be sold in the fuel market, earnings show that the process is not attractive for the investor (Mariano *et al.*, 2013; Pereira *et al.*, 2014). In other words, the biobutanol is very interesting from the economical point of view for the chemical industry, not for the fuel market.

Looking specifically for the transportation industry, it is necessary to gain scale with the chemical market and then, when a competitive price is reached, go to the automotive fuel market. More research is necessary to improve the production of n-butanol to bring it to a commer-

Table 2.3: Ethanol, n-butanol and sugar prices.

Product	Price [a]
Sugarcane price	US$27.26/tonne
Sugar price	US$0.48/kg
Ethanol price	US$0.66/L
n-Butanol (chemical) price	US$1.34/L
n-Butanol (biofuel) price	US$0.83/L

[a] 2011 international prices

cial scale and in this way butanol would show its possibilities, allowing it to penetrate the fuel market and to compete against gasoline and ethanol.

2.4 Use of alcohols as fuels

Most of the energy used in the world is based on fossil-fuels. However, the concern of the governments and the society with emissions of greenhouse gases is growing. Emissions from the combustion of fossil-fuels have been associated with the strong deterioration of air quality due to the formation of pollutants like nitrogen oxides (NO_x), carbon monoxide (CO), particulate matter (PM) and other gaseous products from incomplete combustion. Because of this, clean combustion processes are still an important research topic. There are several possibilities to improve the combustion systems, they are always being reviewed and one of the most considered options is the use of alcohols as alternative fuels or fuel additives (Farkade and Pathre, 2012).

The biofuel production and its use (especially ethanol) in internal combustion engines is a relatively well known matter and has been studied and reviewed for several research groups. However, an overview and summary of research on alcohol combustion chemistry is still lacking, mainly for n-butanol. The following section gives a comprehensive overview of the use of alcohol fuel and its combustion, with special comments focused on butanol isomers, trying to complement this article with this advanced topic.

Moss (Moss *et al.*, 2008) present in their article a study about the oxidation of the four isomers of butanol. They studied the autoignition of n-butanol and isomers at high temperatures in a shock tube. With this, a kinetics mechanism for description of the oxidation of butanol isomers at high-temperature was developed. This mechanism provided a good correlation with the experiments in terms of reactivity of the four isomers. Some uncertainties in the mechanism

still remains but it was possible to conclude that tert-butanol and 2-butanol are less reactive. For the continuity of the work, additional data in shock tubes at higher pressures would be of interest, giving more information on falloff effects. The analysis of the obtained products would also be helpful to evaluate the mechanism.

Sarathy *et al.* (2009) discuss the proposal of n-butanol as an alternative fuel to gasoline and diesel. To better understand the combustion characteristics of n-butanol, they present experimental data obtained for n-butanol in different experimental conditions. The results are focused in species concentration profiles in jet stirred reactor (JSR) under atmospheric conditions and a range of equivalence ratios. The laminar flame speed is obtained in a n-butanol premixed laminar flame as well as species concentration profiles for n-butanol in an opposed-flow diffusion flame. This study gives a better understanding of n-butanol combustion and the product species distribution.

Mohamed (2009) obtained the burning velocities of mixtures of air with ethanol and butanol. The results were retrieved from measurements of flame speed and flame temperature, using tube method. Different fuel-air equivalence ratios were tested (ϕ=0.7-1.4) during the pre pressure period of combustion, employing a detailed density correction scheme by using a thermocouple technique. Mohamed considers the laminar burning velocity as one of the most essential parameters for analysis and performance predictions of various combustion engines. He defines it as the velocity, relative to the unburned gas, with which a plane, one-dimensional flame front travels along the normal to its surface. It is a required information for the majority of turbulent combustion models. In the study, Mohamed shows that for ethanol and butanol-air flames, the burning velocity (S_u) increases with increasing ϕ for the fuel-lean region, while S_u decreases with increasing ϕ for the fuel-rich region. Ethanol presents higher burning velocities in relation to butanol for stoichiometric and rich mixtures, and lower rates for lean mixtures. Table 2.4 presents a summary of results for flame speed (S_f), flame temperature (T_b), burning velocity (S_u), initial mixture temperature (T_i) and initial mixture pressure (P_i).

Table 2.4: Maximum values of flame speed, flame temperature and burning velocity for butanol and ethanol fuels (Mohamed, 2009; Takashi and Kimitoshi, 2006).

Fuel	S_f (m/s)	T_b (K)	S_u (m/s)	T_i (K)	P_i (kPa)	Reference
Ethanol	3.6	2310	0.49	301	101	(Mohamed, 2009)
Butanol	3.5	2340	0.46	301	101	(Mohamed, 2009)
Gasoline	3.5	2330	0.46	300	100	(Takashi and Kimitoshi, 2006)

Black *et al.* (2010) present a series of measurements of autoignition delay at different equivalent ratios for butanol (0.5, 1 and 2) with reflected shock pressures of 1, 2.6 and 8 atm

in the temperature range from 1100 to 1800 K. From this, a detailed chemical kinetics model is developed and used to simulate butanol ignitions. The model was built and tested against measurements in a jet stirred reactor, presenting good correlation of results.

Veloo *et al.* (2010) participate in a larger experimental and modeling effort on the fundamental combustion characteristics of alcohols as biofuels. Several combustion parameters as laminar flame speeds and extinction strain rates of premixed methanol, ethanol and n-butanol flames were measured in the counterflow configuration at atmospheric pressure and elevated unburned mixture temperatures. For both propagation and extinction experiments, the flow velocities were determined using digital imaging methods. Laminar flame speeds were based on direct numerical simulations of the experiments. Two recently developed detailed kinetics models of n-butanol oxidation were also used to simulate the experiments. The results from those numerical simulation of n-butanol/air freely propagating flames revealed discrepancies between these two kinetics models regarding the consumption pathways of n-butanol and its intermediates. The study shows that for propagation and extinction, that are typical high-temperature flame phenomena, the effect of hydroxyl radical in the fuel molecule strongly decreases as the number of carbons in the molecule increases. It is an important observation to be studied when thinking about the development of fuels whit larger carbon chains.

Grana *et al.* (2010) developed a model to describe the combustion of butanol and its isomers. They applied a method that starts from lower molecular weight compounds of the isomers family and proceeds to higher molecular weight compounds. The study is done with pyrolysis and oxidation mechanisms of butanol isomers being similar to those for hydrocarbon fuels. Beside of this, the development of the complete set of the primary propagation reactions for butanol isomers proceeds from the extension of the kinetics parameters for similar reactions already studied and recently revised for other alcohols like ethanol. The model is validated by comparing predictions made using their kinetics model with previous and new experimental data on counterflow non-premixed flames of n-butanol and iso-butanol. Final comparisons for these two isomers were satisfactory.

Weber *et al.* (2011) also looked at problems related to butanol autoignition doing several experiments using a heated rapid compression machine at compressed pressures of 15 and 30 bar, in the temperature range of 675–925 K, and for equivalence ratios of 0.5, 1.0, and 2.0. Under these conditions, it was observed that the ignition delay decreases monotonically as temperature increases and the autoignition response exhibits single-stage characteristics, it means, a constant step of fixed pressure in a range of time (ignition delay). In his article, Weber also compared experimentally measured ignition delays to simulations, but no satisfactory correlation was ob-

tained. It is suspected that the modeled fuel decomposition reactions are not correct and play a major role in the process, leading to the poor agreement. Further experimental investigations of the fuel decomposition are required.

Frassoldati *et al.* (2012) cite the importance of butanol as a potential replacement or additive to fossil fuels in the automotive industry and then uses it as motivation to detail a route for butanol combustion chemistry. He shows that the structure of fuel molecules can be of crucial importance in this process when evaluating the nature and amount of potential pollutants. Based on other studies in this area, Frassoldati is motivated to further develop a detailed and comprehensive chemical kinetics model that complements the previous models. He focus his work in the major differences in the overall chemical pathways especially with respect to the formation of undesired emissions.

Merola *et al.* (2012) discuss the use of fuel blends of n-butanol and gasoline as liquid fuels, aiming to increase the fuel octane number as well as the engine performance. The criterion of evaluation was basically direct comparison of measured indicated mean effective pressure (IMEP) and curves of combustion pressure. In their work, several experiments were conduced and to evaluate the influence of n-butanol addition to gasoline, a port fuel injection (PFI), spark-ignition (SI) engine, with an external boosting device was used. The effect on the spark ignition and combustion process of 20% and 40% in volume of n-butanol blended with pure gasoline was investigated through cycle-resolved visualization. After several experimental observations, like flame luminosity and pressure signals, they concluded that n-butanol blends allow the engine to work in more advanced spark timing without knocking occurrence. BU40 (blend of gasoline plus 40% butanol) delivered the same level of performance – from the point of view of IMEP – than the one running with pure gasoline and changes in the injection system granted reduction of emissions.

Wu and Law (2013) studied the laminar flame speeds for the four butanol isomers at pressures from 1 to 5 atm. Results at all pressures show that n-butanol presents the highest flame speeds, followed by s-butanol and i-butanol, and then t-butanol. Computation and flame chemistry analysis were done and comparison shows results from satisfactory to less satisfactory agreements between results, depending on the model used. They found that the primary reason for the lowered flame speed of s-butanol, i-butanol and t-butanol is that they crack into more branched intermediate species which are relatively stable. This indicates that the general rule that fuel branching reduces flame speed for hydrocarbons can also be applied to alcohols, and that the fundamental reason for this generality is that, in alcohols, the O–C bond has similar bond energy to the C–C bond while O–H has similar bond energy to the C–H bond.

Beeckmann *et al.* (2014) also consider that the laminar burning velocity is one key parameter for the characterization of fuels also serving as an important quantity to validate chemical kinetics models. They observe that burning velocity depends only on the mixture composition, temperature and pressure, and serves as a fundamental property of a fuel. In his work, Beeckmann studies several alcohols, including n-butanol, and those alcohols have their laminar burning velocities measured in an experiment conducted in a spherical combustion vessel at an unburnt temperature of 373 K and a pressure of 10 bar. He measured burning velocities and compared the results from his study and from the published literature to those of numerical simulation data from published chemical mechanisms. He concluded that the models tend to under predict the experimentally measured values. However, a sensitivity analysis suggests further investigation of the pressure dependence for the fuel specific reactions with hydrogen and hydroxyl radicals.

2.5 Alcohols as fuels in the transportation industry

Alcohols are used as fuels since the beginning of the automotive industry. For the Brazilian market, the fleet suffered a deep change in its structures because of the introduction of the so called Flex Fuel engines, in 2003. These engines can basically burn type C gasoline (that is a mixture of gasoline A resulting from oil refining processes with anhydrous ethanol in some established proportions (ANP-Agência Nacional do Petróleo, Gás Natural e Biocombustíveis, 2013)), ethanol or a mixture of these two fuels, in any proportion. The introduction of this type of vehicle in the Brazilian fleet was quite successful from commercial point of view, leading to significant increase in its production over the years, reaching about 80% of the total fleet in 2008 and present in 95% of new cars built today in the country (ANFAVEA-Associação Nacional dos Fabricantes de Veículos Automotores, 2014).

In addition to Brazil, countries like the United States of America, Sweden and Canada also use bi-fuel vehicles, but in a different way: vehicles run on gasoline with ethanol addition to the fixed volumetric blend of 85% anhydrous ethanol and 15% gasoline, known as E85, whose availability at service stations is expanding (Rodrigues, 2012). Table 2.5 shows a summary of the blends of gasoline-ethanol currently used in the World.

The alternation of fuels in the Brazilian flex fuel vehicles is possible basically due to the use of electronic technology to control the fuel injection and ignition point. In the flex fuel engine, there is a sensor that detects the proportion of alcohol-gasoline mixture that is being used and informs the control center of the vehicle – known as electronic injection system.

Table 2.5: Regulated gasoline-ethanol blends in the World.

Country	Fuel blend	Proportion [a]
Brazil	ethanol + gasoline	from 72.5% G + 27.5% E to 82% G + 18% E or 100% E
USA Canada Europe [b]	ethanol + gasoline	15% G + 85% E

[a] G: gasoline; E: ethanol.
[b] Sweden and Finland.

With this information, the central adjusts the engine operation following several maps that were previously recorded during the engine development phase known as calibration. Based on these maps, the vehicle systems operate by changing the ignition timing, the fuel injection timing, the air-to-fuel ratio, the opening and closing of the valves – when the engine hardware permits - among other parameters (Yu *et al.*, 2010). The use of this technology allows any fuel ratio to be used and not only the fixed ratio of E85 used in the United States of America (de Lemos Alves and Brandao, 2007).

The Brazilian market presents today an automotive fleet that works with a regulated mixture from about 72.5% of gasoline and 27.5% of ethanol to 82% of gasoline and 18% of ethanol (ABNT-Associação Brasileira de Normas Técnicas, 1997; ANP-Agência Nacional do Petróleo, Gás Natural e Biocombustíveis, 2013; BRASIL, 2014), known as gasohol. Vehicles can also run on pure ethanol or using a mixture in any proportion of gasoline and ethanol. Because of this big fleet already burning alternative fuels, when we think about biobutanol as a new option of fuel, there are some points of interest that are readily asked. Those main points are related to the application of this fuel in the currently available engines, engine performance, emissions and fuel consumption. To address those points is necessary to know the demands of the modern engines in relation to fuels.

Fuel property requirements for SI engine are dictated by ASTM D4814, Standard Specification for Automotive Spark-Ignition Engine Fuels (ASTM International, 2014). From the properties of n-butanol seen in Section 2.2 and ASTM specification, it is reasonable to say that n-butanol has good potential as an alternative fuel, possibly avoiding the disadvantages brought by low-carbon alcohols like ethanol (ignition problems in cold weather, corrosion, low lubricity and higher fuel consumption). Several researchers are studying n-butanol from the point of view of alternative fuel to fossil fuels, more efficient combustion and lower emissions, being n-butanol used pure in the engines as well as blended with gasoline in different proportions.

Some considerations from those works are presented in Section 2.5.1.

From the point of view of compression ignition engines there also some possibilities that have been studied along the years looking for lowering emissions, increasing performance and establishing an option to diesel fuel. Biodiesel, which has many similar properties to diesel fuel and can theoretically be blended with diesel in any proportion, has been intensively studied and widely used in diesel engines (DNV Research and Innovation, 2010). Lower carbon alcohols, mainly ethanol, have also been considered as alternative fuels for diesel engines but presenting disadvantages that have to be considered (Waterland *et al.*, 2003): increased risks of fire and explosion compared to diesel fuel due to the lower vapor pressure and flammability limits of ethanol, decreased maximum power, increased incidence of fuel pump vapor lock, reduced fuel pump and fuel injector life due to decrease lubricity of ethanol and necessity of use of co-solvents due to problems with phase separation between ethanol and diesel. n-Butanol can be a future option for blending with diesel and can overcome some of these drawbacks of ethanol, like is discussed in Section 2.5.2.

2.5.1 n-Butanol applied to spark ignited (SI) engines

Concerning the use of n-butanol in the existing gasoline engines, as shown in Alasfour (1997), the knocking tendency of n-butanol is similar to that of RON 87 gasoline as well as the engine behavior and sensitivity to spark timing and compression ratio. Combustion duration for pure n-butanol and n-butanol blends with gasoline are similar to those for gasoline alone. n-Butanol blends with gasoline reduce the ignition delay (0–10% of mass fraction burn - MFB) and advance the crank angle degree (CAD) of 50% MFB when compared with gasoline alone. Maximum break torque is obtained when the spark ignition timing is retarded for the engine running on n-butanol blends probably because of their faster combustion. There is not sensible changes in combustion stability for the pure n-butanol or butanol blend as inferred by measurements of indicated mean effective pressure (IMEP).

Regarding fuel properties and performance, the energy density of gasoline is about 32 MJ/L, well compared to butanol that delivers 29.2 MJ/L while ethanol and methanol have only 19.6 MJ/L and 16 MJ/L, respectively (Jin *et al.*, 2011). From this point of view n-butanol is very similar to gasoline, allowing its direct replacement in the engine in terms of energy, maintaining all other engines characteristics constant. Looking for fuel consumption, butanol contains about 25% more energy than ethanol. It directly affects the engine fuel consumption with advantages for butanol.

Like ethanol, butanol can be mixed with gasoline and this blend can be used as liquid fuel for SI engines. In fact, it can be considered the scenario of the engine burning pure butanol without any modification since the octane number of gasoline and butanol overlap in some range, as can be seen in Table 2.2. However, the engine efficiency burning n-butanol will probably be lower than the efficiency of the same engine running ethanol because of the higher octane number of the last. To overcome this issue the engine calibration has to be changed, mainly in relation to the advance of the spark timing. Blends of butanol-gasoline up to 40% butanol allowed working in more advanced spark timing without negative effects on performance (Merola *et al.*, 2012).

Alasfour (1997); Jin *et al.* (2011) and Kim *et al.* (2011) showed that the engine power can be maintained the same as with gasoline without almost no modifications of the engine when butanol content in the blend butanol-gasoline is below 20% by volume, while the maximum engine power drops as the blending ratio of butanol approaches 30% by volume. n-Butanol blend with gasoline has lower specific fuel consumption (SFC) than ethanol-gasoline blend due to its higher heating value (see Table 2.2). Increasing the content of n-butanol in the blends, the SFC will increase since n-butanol has lower energy density when compared with gasoline. However, the penalty for the SFC is small when n-butanol content is below 20%, while the change in SFC is within 10% of that of pure gasoline for stoichiometric mixture when n-butanol content goes up to 40% in the blend (Dernotte *et al.*, 2010; Kim *et al.*, 2011). Another study from Dernotte *et al.* shows that the slight increase in SFC with butanol addition is related to butanol-gasoline blend reduced combustion enthalpy in relation to gasoline. They show that B40 has a 10% lower combustion enthalpy than gasoline, increasing SFC by 10% for stoichiometric and slightly lean mixtures (Dernotte *et al.*, 2010).

The CO, HC, and NO_x emissions depend on the kind of engine being tested as well as on its operating conditions and blending ratios. In general, n-butanol blends with gasoline have higher unburned alcohol emission rates than gasoline, and the unburned alcohol emission rates increases as the content of n-butanol is higher. Research activities (Dernotte *et al.*, 2010) demonstrated that concentrations of 20% to 40% butanol in gasoline enabled the engine to be run at a leaner mixture than gasoline for a fixed performance. Also, these blends offered HC emissions similar to gasoline, occurring the increment on emissions only at higher butanol concentrations.

On the other hand, the blends decreased the NO_x emissions to a level lower that one with pure gasoline at its leanest mixture (Dernotte *et al.*, 2010). Another study on emissions of a spark-ignited engine fueled with n-butanol-gasoline blends combined with EGR up to concentrations of 30% shows that HC, CO and NO_x emissions on an engine fueled with gasoline and

n-butanol blends are lower than those of gasoline. More than this, pure n-butanol increases the specific HC and CO emissions while decreases the specific NO_x emissions compared to those of gasoline. And also, n-butanol addition can decrease particle emissions compared with that of gasoline (Gu *et al.*, 2012).

In Wallner *et al.* (2010), is possible to verify that blends of gasoline and iso-butanol increase both acetaldehyde and formaldehyde emissions, while ethanol-gasoline blends increase acetaldehyde emissions, but not significantly formaldehyde. Aldehyde emissions are eliminated in an active (warm) three-way catalyst, pointing that an improved cold-start engine operation with high-alcohol fuels (including iso-butanol blends) is critical for meeting emissions targets.

Table 2.6 brings a summary of the reviews, showing some engine parameters compared between gasoline-n-butanol blends in relation to pure gasoline.

Table 2.6: Gasoline-n-butanol blends vs. gasoline in SI engines.

Parameter	Comparison to pure gasoline
Knocking resistance	Similar to gasoline
Combustion duration	Similar to gasoline
Ignition delay	Lower than gasoline
Ignition advance	Similar to gasoline
Combustion stability	No observable variation
Fuel consumption	Slightly higher than gasoline
IMEP (up tp BU40)[a]	Higher than gasoline
IMEP (above BU40)[a]	Equal to lower than gasoline
Air-to-fuel ratio	Leaner than gasoline
HC emissions	Similar to gasoline
NO_x emissions	Lower than gasoline

[a] BU40: blend of 60% gasoline + 40% n-butanol.

2.5.2 n-Butanol applied to compression ignited (CI) engines

In comparison to the fuel blends based on diesel and ethanol, the use of butanol can solve some problems of phase separation because of higher miscibility of n-butanol in diesel fuel. More than that, the blends of diesel and n-butanol present properties close to pure diesel. Low fraction n-butanol blends (up to 5 vol.%) appear to be a good alternative for compression ignition engines utilization without cetane booster additive, delivering nearly the same specific fuel consumption. There is also the additional advantage of lower carbon build up in injectors and pistons (Chotwichien *et al.*, 2009).

In their study, Liu and Lee (2010) compared an engine running on butanol-diesel blend with and engine running on pure diesel. The autoignition is slightly retarded and the premixed combustion peak is higher for butanol-diesel blends with low butanol content (<20 vol.%), without significant change in the maximum pressure. The autoignition delay when using neat n-butanol is longer with the decrease of oxygen concentrations.

With the increment of butanol in the blends, an increase in break specific fuel consumption (BSFC) of about 2% is observed, slightly higher brake thermal efficiency (1–2%) is obtained and lower exhaust temperatures are reached when compared to neat diesel fuel (Yao *et al.*, 2010b).

Yao *et al.* (2010a) showed that the soot is significantly reduced when using butanol-diesel blends especially at high to full load. NO_x emissions are slightly reduced with the use of butanol-diesel blends compared with the neat diesel fuel, when butanol blend ratio is below 40%. Since butanol-diesel blend fuel allows higher EGR rates without increasing soot emissions, there is even more potential to decrease NO_x emissions. The CO emissions were reduced, but the hydrocarbons (HC) emissions were not affected or slightly increased compared with the neat diesel fuel at a low volumetric blend ratio (<24%). However, the HC and CO emissions increase at the urban drive cycle while they are not significantly impacted at the highway drive cycle at the 40% butanol blend.

Siwale *et al.* (2012) reported a high load, light duty, turbo-charged diesel engine running on several different blends of n-butanol-diesel (5%, 10% and 20%, or BU5, BU10 and BU20). The objective was to compared the effects of these different contents of n-butanol on the diesel engine performance, combustion characteristics and emissions. All the n-butanol blends presented reduction in the emissions of soot and CO, but increments in the emissions of NO_x and HC. Combustion presented itself more stable for any of the blends in relation to pure diesel.

Zhang and Balasubramanian (2014) studied the influence of n-butanol-diesel blends (BU5, BU10, BU15 and BU20) concerning the emission of particulate. It was observed that BU15 and BU20 (15% and 20% of n-butanol) blends presented significant reduction in the emissions, mainly particulate and elemental carbon (EC).

The combustion and emissions of an diesel engine running on BU40 (blend of diesel plus 40% of n-butanol) were studied by Chen *et al.* (2014). Their article explains that the diesel engine running on BU40 presents better results in terms of performance than the same engine running on pure diesel. The engine presents higher cylinder pressure, longer ignition delay and

faster burning rate. As seen in other studies, the engine emissions reduced in terms of soot but increased in terms of NO_x. Combination of BU40 and EGR may potentially lead to lower NO_x emissions, low soot emissions and higher efficiency in relation to BU00.

Table 2.7 brings a summary of the reviews, showing some engine parameters compared between diesel-n-butanol blends in relation to pure diesel fuel.

Table 2.7: Diesel-n-butanol blends vs. diesel in CI engines.

Parameter	Comparison to pure diesel
Fuel consumption [a]	About 2% higher
Efficiency [a]	About 1 to 2% more efficient
Soot emissions	Lower than pure diesel
NO_x emissions	Lower than pure diesel
CO emissions	Lower than pure diesel
HC emissions	Not affected or slightly increased

[a] Up to 5% of mixed n-butanol.

2.6 Conclusions

Due to its characteristics, n-butanol appears as an interesting renewable fuel for replacing gasoline or to form mixtures with gasoline presenting better properties than ethanol-gasoline blends in terms of engine performance and reduction of emissions. Chemical structure and similar energy content, characteristics of n-butanol, allow to employ it directly in a gasoline engine with small or even no modification in the current engine designs.

For SI engines, performance of an engine burning n-butanol is similar to the same engine burning gasoline. For some blends of n-butanol and gasoline, the fuel consumption is about the same or even lower than the same engine burning ethanol. However, pure n-butanol engines have higher specific fuel consumption in relation to engines burning gasoline, but lower than burning pure ethanol. Engines burning gasoline-n-butanol blends presented CO, HC, and NO_x levels similar or lower than the same engine burning pure gasoline with the extra advantage of running in a leaner mixture for the same performance. In the case of CI engines, the advantages are shown basically when one refers to emissions, potentially lower when burning n-butanol-diesel blends, and as a good substitute for ethanol-diesel blends from the point of view of security, intersolubility and components durability. Research on n-butanol application as liquid fuel is being done and is continuously growing.

Concerning its production, the biobutanol seems to be the focus for the future and some plants have recently resumed their processes in China and one started in Brazil. The focus is in the chemical industry. From the point of view of fuel industry, the big challenge for biobutanol is that its production is not as efficient as the production of ethanol. The fermentation of biobutanol is not economically feasible on the basis of the current market needs and scenario. Use of cheaper agricultural wastes (lignocellulosic materials) and other industrial wastes may be suitable to establish an economical ABE fermentation. Besides, it is necessary to develop more efficient fermentation processes based on different strains or feedstock or both. Although promising, production of biobutanol on dedicated refineries implies high investments that requires a deep economical assessment to assure its implementation.

3 Combustion modeling applied to engines using a 1D simulation code

3.1 Introduction

The modeling of internal combustion (IC) engines is an area of engineering that involves several disciplines. The modeling of an engine can follows different levels of approximation and is always trying to predict its performance. Current models can be built from simple air standard cycles reaching complex 3D models that may include turbulence, chemical reactions, spray dynamics and lots of other physics. There are several approaches available, but as López and Nigro (2000) presented in their work, IC engine simulation can be basically classified in four categories: zero-dimensional single zone, 0D/1D single zone models, quasi-dimensional multi-zone models and multidimensional models, being the first the least complex and the last the most complex from the point of view of required details.

If a high level of detail in the models is required, it is necessary to use more complex 3D computational fluid dynamics (CFD) models. However, due to the high computational cost of these models, they are more suitable to analyze the components of the system individually (López and Nigro, 2000). To set a 1D model, a lower level of detail is required, the models are easier to implement and faster to run. So, this kind of model is adequate to analyze the whole engine system with multiple components together. There are several codes available today like GT-Power, AVL BOOST, Ricardo Wave as well as different academic codes based on research done in Universities (López and Nigro, 2000; Alqahtani *et al.*, 2015; Barros, 2003; Coble *et al.*, 2011). In all of them, the 1D engine model is represented as an arrangement of pipes and volumes interconnected among them with templates that simulate different parts of the engine (valves, cylinders, pipe junctions, etc.). One-dimensional CFD models are used for pipes and thermodynamic models for the above mentioned templates (López and Nigro, 2000; Barros, 2003).

The most common type of application for the 1D codes is engine performance calculation. It is a very generic term, but for engines development it is related to the calculation of torque, volumetric efficiency, fuel consumption, valve timing optimization and peak cylinder pressure (PCP). Advanced topics like combustion and emission can also be addressed and, again, the codes currently available present some combustion models that allow these calculations.

The aim of this article is to bring a general overview about engine modeling, but with

specific comments on 1D engine modeling and combustion. To study these topics, GT-Power, a code applied in the development of engines was used (Gamma Technologies, 2015a). The description of details and application of some of the different spark ignited (SI) combustion models available in the package is done, as well as one combustion model for compressed ignited (CI) engine. Finally, simulation results comparing some of the different combustion models present in the code library are presented, giving some orientation on which of these models to be selected, depending on the problem to be solved.

3.2 Available 1D codes for SI engines simulation

With the advances in computational hardware, that is faster and more cost competitive day by day, is possible to develop codes for almost any application. The same occurs for the engine development and some companies and Universities have developed their own codes to support this necessity along the past decades.

López and Nigro (2000) presented in their work a code for computational simulation of internal combustion engines. The project was focused on a single cylinder four stroke SI engine. Their article presents a brief description of the mathematical models and the numerical methods that they used. The mathematical model was based on a thermodynamic model for the cylinder and a one-dimensional gas dynamics description of the intake and exhaust systems. Then, they wrote a code in language Python language in order to take advantage of the object oriented programming, also looking for the possibility of integration with other different codes. Several test cases were run and compared with measurements to validate the results. The produced code allows solving spark- and compression-ignition, two- and four-stroke IC engines. It is still a simple code, based on non-predictive Wiebe functions (Heywood, 1988) and as future work they propose to use this code as a generator of boundary conditions for CFD-3D codes.

Barros (2003) also presented in his thesis an internal combustion engine modeling study. He used object oriented analysis to develop the model and to encapsulate all data and methods related to the engine, becoming a complete independent model. He starts from an algebraic model of the engine and writes his code based on conservation equations on a two zone model, using combustion wave equations. Some empirical relations are used for the combustion turbulence factor. Because of this, the model has to be carefully verified when changing the engine to be studied since the empirical relations obtained for the base engine may not work for other engines. The simulation results are retrieved for a one cylinder engine only, using pure gasoline and a mixture of gasoline/ethanol. The model presented is able to predict the basic engine per-

formance parameters (power and torque) as well as to estimate knocking and pressure in the oil sump.

Kodah *et al.* (2000) did a study to validate a thermodynamic model of the combustion process in a SI engine. To calculate the quantity of fuel burned, they used a pre-defined curve of fuel consumption in relation to the propagation of the flame front and the angle of the crankshaft, enabling the determination of energy delivery rate to the system. Gas properties were obtained by an algorithm that calculates the fraction of each component present in the chamber as a function of temperature. The combustion chamber was divided into three basic areas:

- Front flame: region where the burning reaction occurs
- Unburned mixture or fresh mixture: region downstream of the flame front, where the temperature rises due to heat transfer
- Burnt gases: region of the products of combustion, which is located upstream of the flame front.

During the combustion process, the flame front propagates and consumes the fuel-air mixture located in the unburned region. The speed of the flame front is calculated using empirical correlations related to the speed of the front, dynamic viscosity of the gas, average gas temperature and internal energy. The propagation of the flame front is assumed as spherical and the size of this sphere is based on the velocity of the front. Thus, the surface of the flame front is defined by the format of the combustion chamber and the location of the spark plug, allowing the calculation of the propagation rate of the flame front. The power transferred to the cylinder wall was also found through the empirical correlation for the heat transfer coefficient. The theoretical results were close to experimental in terms of pressure profile, temperature or heat exchange, and the differences found are attributed to the imprecision of the spark advance information. The model run for just one case study and the adaption to other engines was not tested.

Ricardo WAVE (2016) is a 1D engine and gas dynamics simulation package. It is produced by Ricardo Software and is used by the industry for passenger car, motorcycle, truck, locomotive, motor sport, marine and power generation applications. WAVE enables engine performance simulations, with prediction and optimization of the engine behavior. It also has combustion and emissions models as well as allows the prediction of component temperatures. It may be used for both diesel and gasoline engines, including models to study direct injection. Finally, it also allows detailed chemical kinetic simulation. As occurs in other codes, it presents

combustion models for compression ignited (CI) and spark ignited (SI) engines. In this latest type, SI Wiebe non-predictive combustion and SI turbulent flame predictive combustion are available.

AVL BOOST (2016) is another code with 1D models for predicting engine performance. It supports the engine development retrieving results on torque and power in combination with emissions and fuel consumption. In a general overview, it is very similar to Ricardo WAVE in the model setup, combustion models and obtained results. It also relies on non-predictive Wiebe model, predictive combustion modeling and also allows that the users input their own combustion models.

GT-SUITE, from Gamma Technologies (2015a), is another software package for modeling and simulation of systems in automotive and transportation industry. It also allows the assessment of engine performance including some combustion models. The module of GT-SUITE responsible for the engine modeling is GT-Power.

For the development of this article, it was necessary to install and use a 1D code in order to better understand some of the characteristics of 1D modeling. GT-SUITE package was chosen and its engine modeling module was used along this work to build the engine models and to obtain the results presented. So, all the references to simulation software, explanations about engine modeling, combustion models and engine results along the text should be understood as related and/or obtained from GT-Power.

3.3 Predictive vs. non-predictive combustion models

When simulating any kind of engine, spark ignited (SI) or compressed ignited (CI), it is important to apply the correct and appropriate combustion model. The first decision to be done inside the code, when available, is to choose if the combustion model will be predictive or non-predictive and it is strictly related to the objective of the modeling in question.

A non-predictive combustion model simply imposes a burn rate as a function of crank angle. This prescribed burn rate will be followed regardless of the conditions in the cylinder and the only restriction is that there is enough fuel in the cylinder to maintain the burn rate (Gamma Technologies, 2015d). In this way, the burn rate will not be affected by engine factors like injection timing or spark time. This is the model to be used if the variable in study has small influence of the burn rate, for example: the influence of intake manifold runner length

Table 3.1: Comparison of non-predictive combustion models and predictive combustion model (Gamma Technologies, 2015d).

Non-Predictive Models	Predictive Models
Burn rate prescribed/imposed explicitly by the user	No measurements/tests required (except for initial model correlation)
Requires experimental combustion data at each operating conditions for best accuracy	Self-adjusting for transient conditions
Not affected by operating conditions (i.e. speed, load, A/F)	Spatial resolution gives more detailed output (i.e. NO_x, knock, heat transfer)
Fast computation	
Imposed combustion burn rate removes an unknown from simulation	

on volumetric efficiency, the volume of the air box of an air filter or the acoustic performance of different muffler designs. In any of these cases, the studied variable is not influenced by the burn rate.

On the other hand, a non-predictive model is not a good choice when the studied variable presents significant changes due to the burn rate. In this case, a predictive combustion model is a more appropriate choice. Examples are: a model aiming to verify the influence of injection timing and injection rate, study of the effects of EGR or spark timing on engine performance or NO_x emissions. The burn rate strongly affects in any of these cases and then the predictive model is necessary.

In predictive combustion the burn rate is predicted from the appropriate inputs (pressure, temperature, equivalence ratio, residual fraction, etc.) and then applied in the simulation (Gamma Technologies, 2015d). In theory, predictive combustion models are appropriate and may be used in any kind of simulation. One of the points that should be considered when selecting a model is related to the computational time. Predictive models, due to their complexity, may run substantially slower. Another issue related to predictive models concerns a required calibration to measurement data in order to provide accurate results. Keeping it in mind, a logical strategy would be to implement non-predictive models always when is possible and to implement predictive models only when necessary.

Table 3.1 brings a summary of the characteristics of predictive and non-predictive models. In the following section is presented the specific characteristics of some of the non-predictive and predictive combustion models available in GT-Power.

3.4 Non-predictive combustion models

3.4.1 Imposed combustion profile

Imposing a burn rate is the simplest method and can be used with any type of fuel or injection. It is particularly interesting if there are measured cylinder pressure curves to adjust the model. Normally, the burn rate is an input for the calculation and the cylinder pressure is the output. In this approach, the amount of fuel that is transferred from the unburned to the burned zone is iterated within each time step until the calculated cylinder pressure matches the measured cylinder pressure (Gamma Technologies, 2015d; Ricardo WAVE, 2016). Imposed combustion profile is simple and the best approach to use if the cylinder pressure curves are available from engine measurements. The limitation is that in some preliminary calculations, cylinder pressure curve is not available and then this method may not be applied.

3.4.2 Spark-ignition Wiebe model

The burn rate and performance of internal combustion engines can also be calculated using continuous functions. These functions are normally based on normal distribution of a continuous random variable. In the study of internal combustion engines and combustion calculation, the best known function to do that is the Wiebe function (Ghojel, 2010), that can be used to predict the burn fraction and burn rate in internal combustion engines operating with different combustion systems and fuels. A general form of the Wiebe function to represent the mass fraction burned in relation to the crank angle can be seen in Heywood (1988):

$$x_b = 1 - \exp\left[- a\left(\frac{\theta - \theta_0}{\Delta\theta} \right)^{m+1} \right], \tag{3.1}$$

where θ is the crank angle, θ_0 is the start of combustion, $\Delta\theta$ is the total combustion duration ($x_b = 0$ to $x_b = 1$) and a and m are adjustable parameters.

In numerical simulation software using this approach, the burn rate for spark-ignition engines can be imposed using a Wiebe function, approximating the shape of an SI engine burn rate.

Wiebe equations, as used in simulation codes, are given for example as follows (Gamma Technologies, 2015a):

Necessary inputs

- AA = Anchor angle, in crank angle degree (CAD)
- D = Duration, in CAD
- E = Wiebe exponent
- CE = Fraction of fuel burned (may be seen as "combustion efficiency")
- BM = Burned fuel percentage at anchor angle
- BS = Burned fuel percentage at duration start
- BE = Burned fuel percentage at duration end

Constants calculation

$$BMC = -\ln(1 - BM), \tag{3.2}$$

$$BSC = -\ln(1 - BS), \tag{3.3}$$

$$BEC = -\ln(1 - BE), \tag{3.4}$$

$$WC = \left[\frac{D}{BEC^{1/(E+1)} - BSC^{1/(E+1)}}\right]^{-E+1}, \tag{3.5}$$

$$SOC = AA - \frac{(D)(BMC)^{1/(E+1)}}{BEC^{1/(E+1)} - BSC^{1/(E+1)}}, \tag{3.6}$$

where:
BMC = Burned midpoint constant
BSC = Burned start constant
BEC = Burned end constant
WC = Wiebe constant
SOC = Start of combustion

Output: burn rate calculation

θ = Instantaneous crank angle

$$Combustion(\theta) = CE\Big\{1 - \exp\big[-WC(\theta - SOC)^{E+1}\big]\Big\}. \tag{3.7}$$

The anchor angle (AA) is the number of crank angle degrees between top death center (TDC) and the 50% combustion point of the Wiebe curve. The duration of the combustion (D) relates to the angle excluding the first 10% and last 10% of the total combustion duration. Wiebe exponent (E) is an adjustable parameter typically varying from 1 to 3 (Ghojel, 2010; Gamma Technologies, 2015b). Equation 3.7 represents the cumulative burn rate normalized to 1.0. The physical meaning is that the combustion starts at 0 crank angle (0.0% burned), progressing until 100% or any other pre-defined fraction.

This model is particularly interesting for the situations where the pressure curve is not available due to difficulties for measurement or when the engine does not exist because is in the development phase.

3.5 Predictive combustion models

3.5.1 Spark-ignition turbulent flame model

This model predicts the burn rate for homogeneous charge and spark-ignition engines. Its formulation is based on the work of Blizard and Keck (1974), Hires *et al.* (1978) and Morel *et al.* (1988). To proceed with this model, is necessary to have a previous knowledge about the geometry of the cylinder (bore, stroke, top death center clearance, connecting rod length), spark

locations and timing, air motion and fuel properties. The mass entrainment rate into the flame front and the burn rate are governed by the following three equations (Blizard and Keck, 1974; Hires *et al.*, 1978):

$$\frac{dM_e}{dt} = \rho_u A_e (S_T + S_L), \tag{3.8}$$

$$\frac{dM_b}{dt} = \frac{M_e - M_b}{\tau}, \tag{3.9}$$

$$\tau = \frac{\lambda}{S_L}, \tag{3.10}$$

where:
M_e = entrained mass of the unburned mixture
t = time
ρ_u = unburned density
A_e = entrainment surface area at the edge of the flame front
S_T = turbulent flame speed
S_L = laminar flame speed
M_b = burned mass
τ = time constant
λ = Taylor microscale length

Equation 3.8 establishes that the unburned mixture of fuel and air is carried (entrained) into the flame front through the flame area at a rate proportional to the sum of the turbulent and laminar flame speeds. The burn rate is proportional to the amount of unburned mixture behind the flame front, (M_e-M_b), divided by a time constant, τ, as seen in Equation 3.9. Finally, Equation 3.10, defines the time constant that is calculated by dividing the Taylor microscale, λ, by the laminar flame speed. Taylor length scale or turbulent length scale is the size used to characterize a turbulent flow (Tennekes, H. and Lumley, J.L., 1972). The Taylor microscale is the intermediate length scale at which fluid viscosity significantly affects the dynamics of turbulent eddies in the flow.

Spark-ignition turbulent flame model requires the turbulence intensity and length scale.

In this way, the in-cylinder flow dynamics is necessary and should be described. These data, as well as turbulent flame speed (S_T) and laminar flame speed (S_L) are difficult to be obtained and aren't easily available in the literature. A calibration of the model with experiments is normally necessary and it can be done setting the effects of turbulence intensity and length scale on the calculation of turbulent flame speed and the Taylor micro-scale length. It can be done adjusting the parameters of the combustion inside the simulation software (Gamma Technologies, 2015c). It is normally done manually in a trial and error basis, comparing the numerical results with the measurements until some level of agreement is obtained. A previous knowledge about the shape of the combustion chamber is also necessary since it directly affects the in-cylinder flow dynamics.

The initialization of this model is a simple Wiebe combustion model to be used for the first several engine cycles. In this way, the airflow can converge to nearly steady state before the predictive combustion model starts. The final results obtained from this model on engine performance may be more accurate than from the other previously discussed models. However, it demands several engine parameters and combustion settings that may be difficult to obtain without measurements.

3.5.2 Homogeneous charge compression ignition model

This is a predictive, single-zone, combustion model that is used to represent homogeneous charge compression ignition (HCCI) combustion. In this model, the user can directly input the fuel chemical kinetics which is used to predict the combustion rate. As the name implies, this model assumes that the mixture is completely homogeneous. The reactions can be directly input or alternatively the user can point to a standard CHEMKIN II format text file (Kee *et al.*, 1989).

One of the advantages of this modeling approach is the possibility of estimate emissions more accurately. The emissions products are based on the reactions specified by the CHEMKIN file. The number of reactions used improves the accuracy of the results. However, it is necessary to know that a more complex model solution (i.e. more reactions) is more computationally expensive (slower running). For instance, a model with few reactions, like 20, will run much faster than the same model with 200 reactions.

The engine model can be set to run the reactions for the entire 720 crank angle degrees, it means, considering the four strokes of the engine (admission, compression, expansion and exhaust). However, for most applications, combustion specified slightly before the intake valve

closes and slightly after the exhaust valve opens should be sufficient. It is also very helpful to save computational efforts.

Concerning the chemical reactions, in the simulation code used, the production rate of a reaction is the product of a rate constant and a concentration based expression. The rate constant is assumed to obey the modified Arrhenius' law shown in Equation 3.11. Thus, HCCI combustion model supports chemical reactions of the following general type:

$$K = A \exp\left(\frac{-Ea}{T}\right) f(T) g(P), \tag{3.11}$$

where:
K = overall rate
A = pre-exponent multiplier
T = temperature
Ea = activation temperature
f(T) = function of temperature
g(P) = function of pressure

A difficulty to work with this predictive combustion model is the amount of information needed to define it. As in the other models, all the information related to the engine is necessary to build the model. The following point is a list that maps species in the chemical reaction. Next, a thermodynamic data file that contains thermodynamic parameters for all species presented in the reaction system has also to be supplied. It must be NASA POLYNOMIALS format file as in GRI mechanism (Smith *et al.*, 2015b,a). Gas phase chemistry file may also be used in the modeling. It is a file that may consists of dozens of species and hundreds of reactions. There is also a limitation of 2000 reactions.

It is important to notice that chemical kinetic models for fuels, although not simple are known and continuously studied. Researchers have already developed chemical kinetic models for different fuels, like ethanol and diesel. Many others are available, but some explanation can be found in the studies of Saxena and Williams (2007) that developed a new detailed chemical kinetic mechanism for ethanol based on previous hydrogen, carbon monoxide, methane, ethane, ethylene, acetylene, propane, propene, propyne, allene and methanol mechanisms, Niemeyer *et al.* (2010) that developed a comprehensive diesel kinetic mechanism that showed good agreement with experimental data, Leplat *et al.* (2011) that built a new chemical kinetic mechanism

for ethanol after detailed literature review and Chang *et al.* (2013) that studied auto-ignition of diesel/air mixtures in a heated high pressure shock tube.

3.6 Results obtained with the combustion models

Given the introductory information from the previous sections, in order to obtain some comparative results, 1D models were setup in GT-Power and run, namely SI-Wiebe (non-predictive) and SI Turbulent Flame (predictive). The models were evaluated, their results were compared and some of their advantages and limitations detailed in the following sections. As a complement, a model considering chemical reactions was run using the HCCI model. This last one considers a compressed ignited engine system and then cannot be directly compared with the two previous models, since they are related to spark ignited models.

3.6.1 SI-Wiebe

In the 1D code, a basic engine model was built. It is a mono-cylinder engine with geometric characteristics as presented in Table 3.2. Those dimensions are similar to an example model present in the library of the software and that was adapted to reproduce a mono-cylinder engine used to perform measurements. Schematic of the power cell is shown in Figure 3.1.

Table 3.2: Dimensions of the power cell used in the calculation with SI-Wiebe.

Attribute	Object value
Bore	79.0 mm
Stroke	81.3 mm
Connecting rod length	143.0 mm
Compression ratio	10:1
TDC clearance height	1.0 mm
Intake valve diameter	45.0 mm
Intake valve lift	10.0 mm
Exhaust valve diameter	37.5 mm
Exhaust valve lift	10.0 mm
Air-to-fuel ratio	14.5:1
Engine speed	3600 rpm

The fuel used in this simulation is gasoline and its properties are those from the software fuel library. Air is set as a mixture of N_2 (76.7% in volume) and O_2 (23.3% in volume) entering the engine at 1 bar and 300 K; operating condition is fixed at engine speed of 3600 rpm.

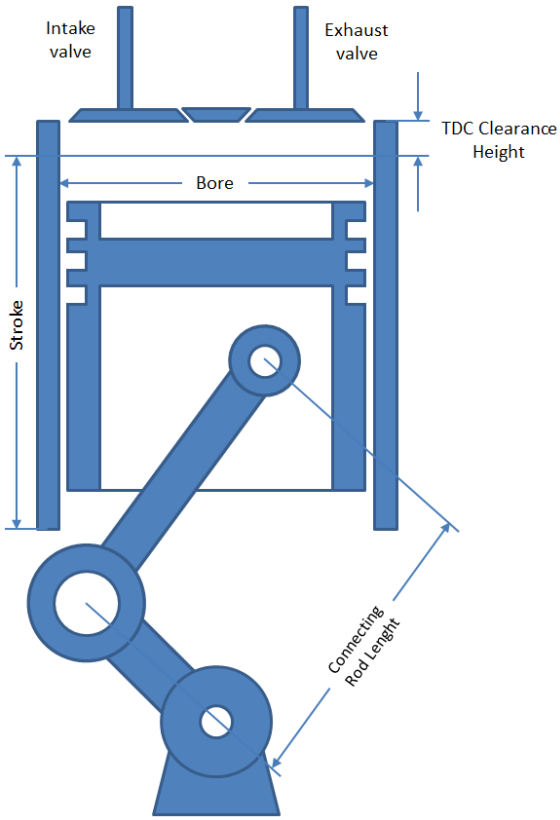


Figure 3.1: Schematic of the power cell used in the calculation with SI-Wiebe.

Concerning the combustion profile, some parameters have to be set. Wiebe curve is related ("anchored") to the top death center (TDC) of the engine cycle. This parameter is specified as an angle and is the number of crank angle degrees between TDC and the 50% combustion point of the Wiebe curve. Typical values for anchor angles in SI engines are 5 to 12 degrees after TDC (Gamma Technologies, 2015b) and in this simulation this value was set as 8 degrees. The duration of the combustion is another important parameter. Basically, it relates to angle excluding the first 10% and last 10% of the total combustion duration. Optionally, the burn points where the duration is measured can be set. Typical values are 25 to 35 degrees (Gamma Technologies, 2015b) and in this simulation was set as 25 degrees. Finally, Wiebe curve exponent should be defined. Typical value for SI engines is 2 (Gamma Technologies, 2015b) and was used. A summary of the used attributes is presented in Table 3.3.

Table 3.3: Attributes used to define burn rate in SI-Wiebe (Gamma Technologies, 2015c).

Attribute	Object value
Anchor angle	8°
Duration	25°
Wiebe exponent	2

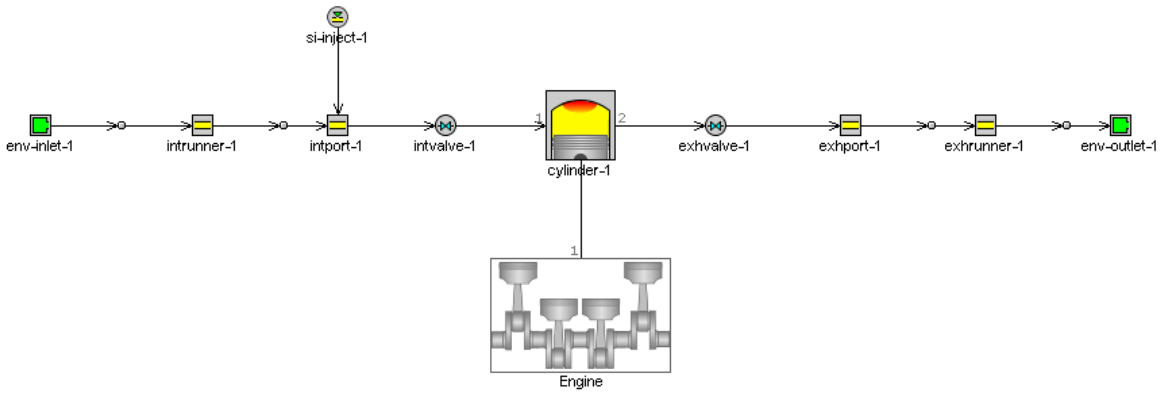


Figure 3.2: 1D model built in GT-Power to run SI-Wiebe combustion model.

From those geometrical data, burn rate model definitions, fuel parameters and operating condition point is possible to build a 1D model using the templates available in the 1D code. The model developed is presented in Figure 3.2.

Results retrieved from this model are related to engine performance. Many other results are available but in this article the focus will be maintained at indicated mean effective pressure (IMEP), combustion pressure and torque. A summary of results is presented in Table 3.4. The column "Calculated" brings the result retrieved from the 1D simulation. "Measured (average)" is the average result obtained from measurements of an engine similar to the modeled. A mono-cylinder engine was setup in a dynamometer and this engine was instrumented with a pressure transducer flush installed at the engine overhead. During the engine run, 100 measurements of IMEP, engine torque and pressure are done and at the end of the run an average value from those 100 measurements is used for comparison. "%Diff" column brings the difference between calculation and measurement.

Table 3.4: Results retrieved from SI-Wiebe combustion model and from engine measurements.

Parameter	Calculated	Measured (average)	% Diff.
IMEP	12.8 bar	12.9 bar	-0.77%
Pressure	58.9 bar	64 bar	-8%
Torque	44.29 N-m	45 N-m	-1.6%

Results obtained with SI-Wiebe are close to those measured in the experimental engine, being the peak cylinder pressure (PCP) the variable that presents more difference in relation to the engine (8%). It probably occurs because this combustion model does not take in to account some physical behavior of the combustion, mainly the burn rate, since it is imposed in this model. SI-Wiebe is a simple to implement, non-predictive way to define combustion. It runs

very fast, but the attributes necessary to define it are related to each operating condition, so it will be necessary to change the attributes for different conditions consuming more time to prepare the model, especially if many speeds are simulated. With SI-Wiebe is also possible to model engine knock, NO_X emissions and CO emissions (not covered in this article). However, several parameters like correct knocking formulation, flame geometry, kinetics of burned zone and others need to be known. Those are normally information difficult to obtain and calibration with measurements are usually necessary, otherwise the results may not be accurate.

3.6.2 SI turbulent flame

The same engine model presented in Section 3.6.1 was simulated here. Again, it is a mono-cylinder engine with geometric characteristics as presented in Table 3.2. Schematic of the power cell is shown in Figure 3.1 and the GT-Power model represented in Figure 3.2. The fuel used in this simulation is again gasoline with default data from the software library; air is set as a mixture of N_2 (76.7% in volume) and O_2 (23.3% in volume) entering the engine at 1 bar and 300 K; operating condition is maintained at engine speed of 3600 rpm.

Concerning the combustion profile, SI turbulent flame is used to model combustion in a homogeneous charge SI engine. It is a predictive model and then demands some more information about the engine in relation to the non-predictive models. Besides the necessary information already described in the Section 3.6.1, this combustion model also needs to be input with cylinder temperature and pressure, in-cylinder composition, spark timing, spark position, fuel properties, flame and wall interaction and in-cylinder flow.

When using a turbulent flame model, experimental data have to be used to calibrate the model. Inside the simulation software is possible to set factors of adjust that should be modified in order to obtain the correct effect. Since model start can be difficult, it is useful to impose a simple Wiebe model to be used for initial cycles before the turbulent flame calculations begin. So, the flow solution in most of the system will be almost steady state before the detailed combustion calculations begin. In other words, the initial Wiebe calculation will generate the initialization values for the turbulent flame model.

Also necessary, is the description of the in-cylinder geometry for the flame and wall interaction. They are related to the spark position, defined by a X ,Y ,Z coordinate, the location of the cylinder head top (or dome) center in X, Y coordinates, the diameter of the dome, the dome height in the Z coordinate, the location of the piston combustion bowl (or cup) center in X, Y

coordinates, the diameter of the cup and the cup depth in the Z coordinate. Finally, is necessary to define the value of the spark timing of this engine. It is defined as an input variable and for this calculation it was assigned the value –15 degrees before TDC.

Table 3.5 presents a summary of the input parameters and values applied to this model additionally to those previously shown in Table 3.2, that were also used here. To start the model, a simple Wiebe with the parameters shown in Table 3.3 was run to initialize the SI turbulent flame model.

Table 3.5: Parameters for the flame in SI Turbulent Flame combustion model (Gamma Technologies, 2015c).

Attribute	Object value
Cylinder temperature	420 K
Spark location	[0,0,3] mm
Dome location	[0,0]
Dome diameter	80 mm
Dome height	5 mm
Cup location	[0,0] mm
Cup diameter	80 mm
Cup depth	5 mm
Spark timing	–15°

Results retrieved from this model are again related to engine performance. The focus was maintained at IMEP, combustion pressure and torque. A summary of results is presented in Table 3.6, being the columns "Calculated" the result retrieved from the simulation, "Measured(average)" the average result obtained from measurements of engines similar to the modeled (as explained in 3.6.1) and %Diff the difference between calculation and measurement.

Table 3.6: Results retrieved from SI Turbulent Flame combustion model and from engine measurements.

Parameter	Calculated	Measured (average)	% Diff.
IMEP	12.93 bar	12.9 bar	0.23%
Pressure	64.31 bar	64 bar	0.48%
Torque	44.48 N-m	45 N-m	-1.15%

SI turbulent flame presents calculated results closer to the measured than SI-Wiebe. It possibly occurs because in this model the combustion is better represented since it considers all the geometry of the combustion chamber, spark plug position and spark timing, as well as several other parameters related to the engine flow and combustion. However, it is not uncommon the situation where not all these information is available. Lack of input data occurs and may

potentially leads to not accurate results. Geometry of the combustion chamber is sometimes difficult to be obtained since it is proprietary information of the engine block manufacturer or engine producer. Also, when using the turbulent flame model, it is necessary to calibrate the model with experimental results. As explained in the Section 3.5.1, values of turbulent flame speed and laminar flame speed are not easily available. The calibration of the model is normally accomplished by adjusting the values related to laminar and turbulent speed (e.g. maximum laminar speed, fuel dilution effects, maximum turbulent flame speed, flame kernel growth, Taylor length scale). It will probably demand measurements in specific conditions that may lead to a bigger time and cost to development of this engine. Finally, the time to solution may be higher than in non-predictive models due to the more detailed nature of the predictive model. As a comparison basis, using a Windows 7 machine, with 1 processor Xeon 2.7 GHz and 4 GB dedicated to the 1D solver, the engine model considering SI-Wiebe as combustion model runs 6% faster than the same model using SI turbulent flame speed as combustion model.

3.6.3 Homogeneous charge compression ignition (HCCI) model

Another basic engine model was built to study the HCCI model. It is a different model from the engine model presented in the previous sections. Compression ratio in this case is higher (16.0 vs. 9.5) since it is a compressed ignited (CI) engine. It is still a mono-cylinder engine with general geometric characteristics as presented in Table 3.7. Schematic of the power cell follows the same general idea already presented in Figure 3.1 for the SI models but now the engine has 4 valves (two intake valves and two exhaust valves) while the previous model had just 1 intake valve and 1 exhaust valve. This model also includes a fraction of 20% of exhaust gas recirculation (EGR).

The fuel used in this simulation is n-heptane C_7H_{16} and its properties are extracted from the software library. Air-to-fuel ratio is 20:1 and injector fuel delivery is set as 7 g/s. Just one injector is considered, using default definitions of the software and adopting a fraction of evaporated fuel – the fraction of fuel that will evaporate immediately after the injection – of 30%. Cylinder temperature was set to 420 K, engine head temperature to 490 K and piston to 510 K. Heat transfer is also enabled and uses classical Woschni correlation without swirl (Heywood, 1988).

Air is set as a mixture of N_2 (76.7% in volume) and O_2 (23.3% in volume) entering the engine at 1bar and 300K; operating condition is fixed at engine speed of 3000 rpm. It is necessary to ensure that the fuel used in this model is represented by files containing its chemical

Table 3.7: Definitions of the power cell used in the calculation with HCCI model (Gamma Technologies, 2015c).

Attribute	Object value
Bore	86.0 mm
Stroke	86.07 mm
Connecting rod length	175 mm
Compression ratio	16:1
TDC clearance height	1.0 mm
Intake valve diameter	34.5 mm
Intake valve lift	10.2 mm
Exhaust valve diameter	31.0 mm
Exhaust valve lift	10.2 mm
Air-to-fuel ratio	20:1
Engine speed	3000 rpm
EGR	20%

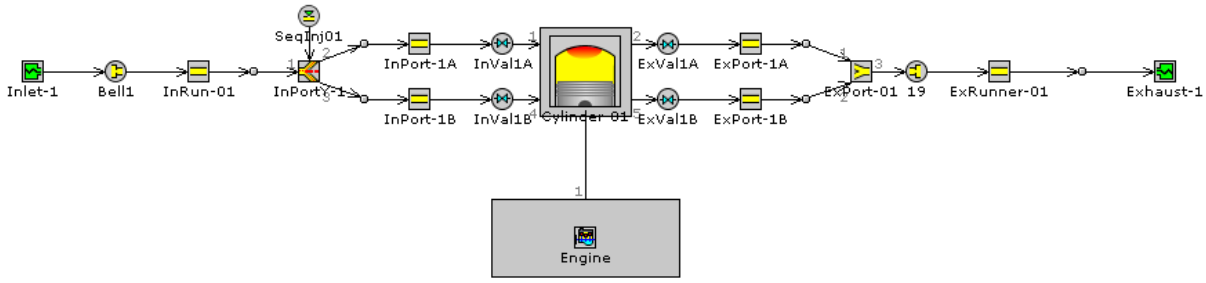


Figure 3.3: 1D model built in GT-Power to run HCCI combustion model.

mechanism. Chemical mechanism for a particular type of combustion has to be defined from external calculation. Those mechanisms can also be downloaded from some internet repositories like the website of Lawrence Livermore National Laboratory (2015). The chemical reactions used for n-heptane follows the CHEMKIN II formatted thermodynamic and chemistry input format. These information are input in two different files, one for the thermodynamic data and another for the gas phase chemistry data, both the files from the software library.

Start of combustion and end of combustion values have also to be set and in this case were used the values of –90 and 100 crank angle degrees (CAD), respectively. To start the model, a simple Wiebe with the parameters shown in Table 3.3 was run to initialize the HCCI combustion model. From those geometrical data, chemical reactions, fuel parameters and operating condition point is possible to build a 1D model using the templates available in GT-Power. The model developed is presented in Figure 3.3.

Results retrieved from this model are again related to engine performance. In this case the model does not represent an existent engine and was not compared with any measured data. This model was used in this article just to present how to setup a HCCI combustion model and how to input chemical reactions. Results related to IMEP, combustion pressure and torque were retrieved. A summary of results is presented in 3.8.

Table 3.8: Results retrieved from HCCI combustion model.

Parameter	Calculated
IMEP	12.85 bar
Pressure	58.9 bar
Torque	44.29 N-m

HCCI is a much more complex, predictive way to define combustion. It is expected that this model presents better correlation with measurements since more physical information of the engine is used. It also allows to study knocking and emissions with much more details than those presented by non-predictive models. On the other hand, HCCI model takes more time to run, especially if the number of reactions defined for the model is high. As a comparison, this model took the double of the time to run in relation to a model set with Wiebe combustion model (using a Windows 7 machine, with 1 processor Xeon 2.7GHz and 4GB dedicated to the 1D solver). It demands the knowledge of several engine parameters, like occurred in the SI turbulent flame and for most of the situations those attributes are not available, mainly specific engine operation conditions (injection timing, injected volume, temperature of the fuel) and the chemical kinetics for different fuels. Files containing the reactions are available in literature but a good knowledge about the engine is necessary to correct apply the fuel. Calibration with measurements are usually necessary.

3.7 Conclusions

Engine modeling is more and more present in the industry. The virtual development of engines is an important subject and simulation codes are available to build these models. 1D codes are the most interesting option when modeling the whole engine due to its simplicity, also allowing the study of more advanced topics, like combustion.

Non-predictive models are the easiest way to calculate combustion. They are simple to implement and run very fast. However, it is necessary to have engine parameters for each operation condition and it may be difficult to obtain, mainly in an engine in the design/development phase.

Predictive models are more precise than non-predictive models and may potentially better calculate the engine performance. However, they demand more information to accomplish their preparation. Predictive models allow to study knocking and emissions with more details than those presented by non-predictive models, mainly if the predictive model used considers chemical reactions as input. On the other hand, they need more time to run and also good calibration with experimental results is necessary.

In the SI-Wiebe approach, the engine model simulated presented good correlation with the measurements with error differences of less than 1% for IMEP, 1.6% for torque and 8% for pressure. Time to solution is very fast, just 30 seconds for each operating condition. With the SI turbulent flame approach, the engine model simulated presented better correlation with the measurements than SI-Wiebe. The error differences were below 0.23% for IMEP, 0.48% for cylinder pressure and 1.15% for torque. Time to solution is about 6% higher than SI-Wiebe, so it is still manageable. HCCI may potentially presents the best results in terms of performance and emissions, but also needs more accurate and specific data related to the fuel chemical kinetics. This last combustion model is also the most computationally expensive since it lasts about twice the time that SI-Wiebe needs to run the same model.

4 1D model of SI engine using n-butanol as fuel: comparison between measurements and simulation results

4.1 Introduction

Biofuels are today a reality and are receiving more and more attention from the society, industry and academy. Several factors contribute to this, but the most relevant are related to the uncertainty of fossil fuels price and the search for lower emissions as well as for different options of energy generation. For the transportation industry, namely the automotive, different biofuels have been researched and all those biofuels can be derived from renewable feedstock and not from fossil feedstock as in the case of gasoline or diesel fuels. In this scenario, the alcohols are already used as alternative fuels, being ethanol and methanol the most commonly used in internal combustion engines. Ethanol is already established as alternative biofuel in some countries presenting several advantages in relation to gasoline, mainly concerning engine performance and efficiency (Brassat *et al.*, 2011; Schwaderlapp *et al.*, 2012).

Another bioalcohol that has been considered for the automotive applications is butanol. Although not very well known, this renewable fuel for use in internal combustion engines presents advantages in relation to the already known methanol and ethanol. It may also be produced by the fermentation of biomass feedstock (Bankar *et al.*, 2013; Jin *et al.*, 2011; Chen *et al.*, 2009). 1-butanol (or n-butanol), iso-butanol and tert-butanol can be used as gasoline additives, but n-butanol is the most promising since it can be easily mixed with gasoline (Nejame, 2010). It also could be a future option for blending with diesel since it has more oxygen content compared with biodiesel, potentially leading to reduction of emissions, mainly soot (Jin *et al.*, 2011).

The potential use of n-butanol as automotive fuel is relatively recent. There is still no commercial application of an engine running with n-butanol or its blend with gasoline, but there are significant number of academic literature reporting the effects of n-butanol on the engine performance (Farkade and Pathre, 2012; Hall *et al.*, 2012; Tornatore *et al.*, 2012), exhaust emissions (Kim *et al.*, 2011; Rakopoulos *et al.*, 2010; Siwale *et al.*, 2012; Gu *et al.*, 2012), fuel consumption (Liu *et al.*, 2013) and combustion (Black *et al.*, 2010; Beeckmann *et al.*, 2014; Frassoldati *et al.*, 2012; Yao *et al.*, 2010a). One of the most interesting features of n-butanol is the possibility of its use as fuel in a direct replacement of gasoline and this stimulates the development of applications using this fuel in the automotive industry.

From the point of view of the transportation industry, the use of ethanol as fuel for spark ignited (SI) engines has been widely investigated since many years. Its properties are well known and it is possible to setup numerical models to propose new developments. On the other hand, only a few studies based on engine tests have been performed on n-butanol-gasoline blends. The almost totality of studies about engines running with n-butanol-gasoline blends consisted in the evaluation of engine performance and exhaust gas emissions for different engine operating conditions. This situation is similar on the field of numerical simulation, where modeling of internal combustion engines fueled with n-butanol is almost unknown.

Modeling of internal combustion engines is a multidisciplinary activity that is continuously growing and is more and more present during the development phase of an engine, mostly today when the time to production is reduced. Literature presents three dimensional (3D), computational fluid dynamics (CFD) engine models or one dimensional (1D) engine models focused on the study and development of engines fueled with ethanol or ethanol-gasoline blends (Yeliana, 2010; Hall *et al.*, 2012; Iliev, 2015). As already explained, the situation related to n-butanol is totally different. The main difficulty to setup one of these models is to obtain the necessary data to be input in the engine model, mainly the n-butanol properties demanded by the combustion models. After modeling and running the numerical simulation is also difficult to obtain correctly measured data from engines to validate the simulation results.

The objectives of this article are to present an overview of the characteristics of n-butanol as biofuel, as well as a brief discussion about numerical modeling of engines. In the sequence, a 1D engine model was built and – with the help of engine test measurements extracted from the literature – simulate, adjust and validate some combustion parameters of n-butanol. Finally, these parameters were applied in subsequent simulations to compare in a virtual model the performance of an engine fueled with n-butanol in relation to the same engine fueled with other fuels.

4.2 Potentials and limitations of n-butanol as automotive fuel

n-Butanol has some interesting features and the potential to overcome some disadvantages brought by other lower-carbon alcohols used as fuel or fuel additives, like ignition problems in cold weather, higher fuel consumption, low lubricity and corrosion. Those potentials of n-butanol are well discussed by Brassat *et al.* (2011), Dernotte *et al.* (2010), Jin *et al.* (2011) and Sarathy *et al.* (2014) in their studies and are summarized as follows:

- Higher heating value. Normally, the low heating value of alcohol rises with increased carbon content. n-Butanol is a four carbon alcohol, the double in relation to ethanol and containing 50% more energy density by volume. In practice, it means that an engine running with n-butanol is expected to present lower fuel consumption and better mileage when compared with ethanol.

- Less ignition problems. One engine fueled with n-butanol is expected to have less problems of cold start than the same engine fueled with ethanol (considering the same air to fuel ratio). It happens because the heat of vaporization of n-butanol is less than half of that of ethanol.

- Intersolubility. Higher carbon numbered alcohols are easier to be blended into gasoline and n-butanol with its four carbons has very good intersolubility with gasoline. Lower carbon numbered alcohols are more polar and more soluble in water than non-polar hydrocarbons. It introduces some more difficulties in their distribution which must prevent water contamination. Also, it lowers the upper limit of blending in petroleum fuels without the use of a co-solvent. n-Butanol and higher carbon alcohols are increasingly less polar due to their longer non-polar hydrocarbon chains. They are thus easier to blend with non-polar hydrocarbons and have lower affinity for water.

- Higher viscosity and lubricity. The viscosity of alcohols increases as the number of the carbons in the molecule grows. Then, n-butanol may potentially protect against wear problems some components of the engine that have direct contact with fuel (like fuel pumps, fuel rails, injectors).

- Safer. The saturation pressure of alcohols decreases with the increase of carbon content. It means that n-butanol will have lower vapor pressure. In addition, it has higher flash point in relation to ethanol and then is safer when considering transportation and use in high temperatures.

However, there are still some potential issues with the direct use of n-butanol in the engine. These topics are discussed in Rakopoulos *et al.* (2010) and Sarathy *et al.* (2014) and are summarized as follows:

- Limitations to reach engine performance. n-Butanol has lower heating value than gasoline. It is possible to have engine operation conditions where an engine fueled with n-butanol will have lower performance than the same engine burning gasoline.

- Higher fuel consumption. The utilization of n-butanol fuel as a substitute for gasoline demands more fuel injected by cycle and then higher fuel consumption in relation to gasoline (engines running under the same conditions). n-Butanol has higher energy density than ethanol, but its heating value is still lower than the conventional gasoline fuel.

- While n-butanol has higher energy density than ethanol, it has lower octane number, forcing the engine to work with lower compression ratios and then lower efficiency. Higher combustion engine efficiency (as found in ethanol) has to be pursued since it enables less greenhouse gas emissions per unit motive energy extracted. Ethanol has high research octane number (RON) and has long been used to improve the octane number of SI engine fuels. n-Butanol isomers have octane ratings similar to that of conventional gasoline and are thus suitable for SI engines although not presenting the same advantage in efficiency as presented by ethanol.

- n-Butanol has lower cetane number compared with diesel or biodiesel fuels, increasing autoignition and potentiality harming the control of the combustion.

n-Butanol also presents difficulties to be introduced in the automotive industry, but now from the economical point of view. Reach profitability is a challenge for n-butanol production as a bioalcohol using the current fermentation process. Renewable n-butanol can be produced from the fermentation of carbohydrates in a process better known as the ABE fermentation since its major chemical products are acetone, butanol and ethanol (Jones and Woods, 1986; Green, 2011). The fermentation occurs in two stages; the first is a growth stage in which acetic and butyric acids are produced and the second stage is characterized by acid re-assimilation into acetone, butanol and ethanol. The fermentation also produces carbon dioxide and hidrogen. This process is not as yield as the ethanol fermentation, produces more residuals and also consumes more water (Green, 2011). The commercialization of n-butanol in the chemical market is profitable when thinking about the petro-butanol (butanol produced from a chemical route). However, if butanol is considered to be sold in the fuel market as a biofuel (from ABE process), earnings show that the process is not attractive for the investor (Mariano *et al.*, 2013; Pereira *et al.*, 2014). In other words, the biobutanol is very interesting from the economical point of view for the chemical industry, but not for the automotive fuel market where ethanol production by fermentation is more efficient and more profitable.

4.3 Modeling of internal combustion engines and adjusting numerical to experimental results

The modeling of internal combustion (IC) engines is an area of engineering that involves several disciplines. The modeling of an engine can follows different levels of approximation and is normally trying to predict its performance. Current models can be built from simple air standard cycles reaching complex 3D models that may include turbulence, chemical reactions, spray dynamics and lots of other physics. There are several approaches available but IC engine simulation can be basically classified in four categories, as described in López and Nigro (2000): zero-dimensional single zone, 0D/1D single zone models, quasi-dimensional multi-zone models and multidimensional models, being the first the least complex and the last the most complex from the point of view of required details.

If a high level of detail in the models is required, it is necessary to use more complex 3D computational fluid dynamics (CFD) models. However, due to the high computational cost of these models (time to solution), they are more suitable to analyze the components of the system individually. To set a 1D model, a lower level of detail is required, the models are easier to implement and faster to run. So, this kind of model is adequate to analyze the whole engine system with multiple components together. There are several codes available today and in all of them the 1D engine model is represented as an arrangement of pipes and volumes interconnected among them with templates that simulate different parts of the engine (valves, cylinders, pipe junctions, etc.). One-dimensional CFD models are used for pipes and thermodynamic models for the above mentioned templates (López and Nigro, 2000; Barros, 2003).

The most common type of application for the 1D codes is performance calculation. It is a very generic term, but for engines development the issues typically involved are the calculation of torque, volumetric efficiency, fuel consumption and peak cylinder pressure (PCP). Advanced topics like combustion and emission can also be addressed and, again, the simulation codes currently available presents some combustion models to enable those calculations. Combustion models may present very basic results like pressure curves to very sophisticated like prevision of emissions, knocking and others. But as in the comparison with the three-dimensional CFD, the more detailed the model is, more time consuming and more details are necessary to setup the simulation.

After modeling the engine, it is necessary that the results obtained from the simulation are adherent with the real engine. Results like fuel consumption, torque, power and so on need to be similar in behavior and magnitude. A correct setup of numerical model, including all the

input data, normally guarantee that the numerical results will be similar to the test results . Unfortunately, in most of the cases, some input data are not available and have to be adopted in order to run the numerical model. Adopting correct values may be a difficult task and a technique commonly used is to adjust the adopted values based on test results.

This technique basically consists in modeling a well-known, similar engine, so called baseline. Some of the input data necessary to build the numerical model, but sometimes not available, are estimated and adjusted in such a way that the results from baseline simulation are comparable with the results from engine test measurements. After that, the same parameters used in the baseline model are used in other models (e.g., of an in-development engine) that was not yet measured or, in some cases, even does not exist. Since the input data is well adjusted, it is expected that the results from the numerical model of the in-development engine will be correct and will agree with future measurements. Several authors used this approach in their works to obtain a well correlated numerical model with the experimental results.

Grill *et al.* (2006) proposed a quasi-dimensional combustion model for homogeneous spark ignition combustion processes with variable valve timing. With this model is possible to calculate a complete engine map in advance and it can be quickly calibrated. Methods for model adjustment with measurements as well as the implementation in the 1D flow simulation used int their work were shown.

Boretti *et al.* (2008) presented experimental and computational results obtained on an in-line, six cylinder, naturally aspirated, gasoline engine. Steady state measurements collected in several operation conditions were used to validate a simulation model performed by using an engine thermo-fluid model. The model presented good accuracy and demonstrated the ability of the approach to produce fairly accurate steady state maps of BMEP and BSFC.

Harrison *et al.* (2014) used 1D simulation to study a variable displacement vane pump used in engines. The analysis of pumps is needed to ensure that the component design meets the demands of the oil circuit. By employing 1D flow simulation, it was possible to verify the most important issues related to the pumps. The paper showcases the prediction of several performance quantities of a variable displacement vane pump and a good correlation from numerical results to measurement data. From this correlation, a predictive friction model for vane pumps is proposed and shows good agreement with experiment.

Schiffmann *et al.* (2014) performed high-speed particle image velocimetry (PIV) and large-eddy simulation (LES) for a two-valve research engine. The aim of the work was to

quantify, understand and ultimately to predict and control cycle-to-cycle variations (CCV) in flow and combustion. Initial quantitative comparisons between experiment and simulation are made for motored cycles. One-dimensional engine simulation tool, has been used to develop a detailed flow model for the research engine, which has been extensively validated with experimental data. After the validation, this model has been used to prescribe boundary conditions for the LES.

Mirzaeian *et al.* (2016) coupled a turbulence model to a predictive turbulent combustion model using a 1D code. They adopted a procedure to calibrate the turbulent combustion model parameters based on design of experiments (DOE) in order to predict the burn rate at various engine operating points. Finally, using an extensive experimental data set, they performed a validation process, looking to the burn rates and the in-cylinder pressure traces for several engine operating points, achieving good agreement and thus confirming the reliability of the used approach.

4.4 General flow solution

To obtain the results presented in this work, 1D engine modeling was used. The focus of this article is not to discuss about the numerical procedures involved in 1D gas flow calculation, but use a simulation code to obtain the engine performance results. GT-Power, a well known 1D engine simulation code was used in order to model the internal combustion engines presented along this article. To have a general understanding on how GT-Power works, a brief summary on its solver is presented, based on the description of the code developer (Gamma Technologies, 2015d).

GT-Power flow model involves the solution of the Navier-Stokes equations, namely the solution of the equations of conservation of continuity (Equation 4.1), momentum (Equation 4.2) and energy (Equation 4.3). These equations are solved in one dimension. In other words, all quantities are averaged across the flow direction.

$$\frac{dm}{dt} = \sum_{\text{boundaries}} \dot{m}, \tag{4.1}$$

$$\frac{d\dot{m}}{dt} = \frac{dpA + \sum_{\text{boundaries}} (\dot{m}u) - 4C_f \frac{\rho u|u|}{2} \frac{dxA}{D} - C_p(\frac{1}{2}\rho u|u|)A}{dx}, \tag{4.2}$$

$$\frac{d(me)}{dt} = -p\frac{dV}{dt} + \sum_{\text{boundaries}} (\dot{m}H) - hA_s(T_{fluid} - T_{wall}), \tag{4.3}$$

where:
$\dot{m}$: boundary mass flux into volume,
$\dot{m} = \rho A u$
m: mass of the volume
V: volume
p: pressure
ρ: density
A: cross-sectional flow area
A_s: heat transfer surface area
e: total specific internal energy (internal energy plus kinetic energy per unit mass)
H: total specific enthalpy, h=e+$\frac{p}{\rho}$
h: heat transfer coefficient
T_{fluid}: fluid temperature
T_{wall}: wall temperature
u: velocity at the boundary
C_f: skin friction coefficient
C_p: pressure loss coefficient
D: equivalent diameter
dx: length of mass element in the flow direction (discretization length)
dp: pressure differential acting across dx

The whole system is discretized into volumes and these volumes are connected to each other by boundaries. Scalar variables like pressure, temperature, density, internal energy, enthalpy and species concentrations are assumed to be uniform inside each volume. The vector variables like mass flux, velocity and mass fraction fluxes are calculated for each boundary. Explicit method is used for time integration.

The discretization of the parts in smaller parts is done to improve the accuracy of the result. The engine components are break in sets of smaller pipes and volumes and the calculation

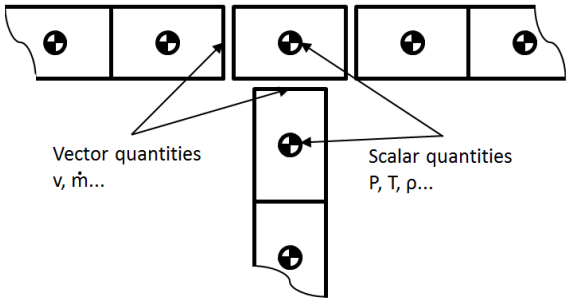


Figure 4.1: Schematic of grid approach: scalars calculated at centroid, vector quantities at boundaries.

proceeds in these smaller parts. Highly discretized components will lead to more accurate results with the penalty of higher times to solution. Coarser discretization results in faster solution, but sometimes at the expense of the accuracy. There is a limit where decreasing the size of the pipes does not lead to better results, only in higher computation times. The ideal discretization size is the one that leads to the best accuracy with reasonable time to solution.

The primary solution variables in the explicit method are mass flow rate, density and internal energy, calculated based on the conservation equations. In the explicit method, the right hand side of the Equations 4.1, 4.2, and 4.3 is calculated based on values from initialization. The calculation is done and results on the derivative of the primary variables are obtained. The values of the new step are calculated by the integration of these derivatives at the new time step and applied to the next iteration. Stability is ensured using restricted time steps that satisfy the Courant condition (Anderson, 1995), as in Equation 4.4:

$$\frac{\Delta t}{\Delta x}(|u| + c) \leq 0.8 \cdot m, \tag{4.4}$$

where:
Δt: time step (s)
u: fluid velocity (m/s)
m: time step multiplier (user specified)
Δx: minimum discretized element length (m)
c: speed of sound (m/s)

This method uses small time steps making it not adequate for simulations that are relatively long. Due to its small time step it produces high resolution results and accurate predictions of pressure pulsations that occur in engine air flows and fuel injection systems. In this way, the

explicit method is recommended for the large majority of 1D gas flow simulations.

4.5 Experimental engine

To develop this study, enabling the construction of a 1D engine model fueled with n-butanol, it was necessary to select an engine previously instrumented and measured to be modeled. The engine used in the experiments is presented in the work of Merola *et al.* (2012) and Tornatore *et al.* (2012). It was an optically accessible single cylinder, port fuel injection (PFI), spark ignited (SI) engine. It was equipped with the cylinder head of a commercial SI turbocharged engine with the same geometrical specifications (bore, stroke, compression ratio). Further details on the engine are reported in Table 4.1.

Table 4.1: Specifications of the single cylinder PFI boosted SI engine. (Tornatore *et al.*, 2012)

Parameter	Value
Displaced volume	399 cc
Stroke	81.3 mm
Bore	79 mm
Connecting rod	143 mm
Compression ratio	10:1
Number of valves	4
Exhaust valve open	153 CAD[a]ATDC[b]
Exhaust valve close	360 CAD ATDC
Inlet valve open	357 CAD ATDC
Inlet valve close	144 CAD BTDC[c]

[a] CAD: crank angle degree
[b] ATDC: after top death center
[c] BTDC: before top death center

The cylinder head had four valves and a centrally positioned spark plug. The injection system was the same as the baseline engine. Intake air pressure and temperature were controlled by an external device, in a range of 1000-2000 mbar and 290-340 K, respectively. A quartz pressure transducer was flush installed in the region between intake-exhaust valves at the side of the spark plug. The transducer allowed to perform in-cylinder pressure measurements in real-time. An elongated engine piston was used, it was flat and its upper part was transparent being made of fused silica.

Combustion tests were carried out using two fuels. Baseline fuel was gasoline and comparison fuel was BU40, a blend of 60% of gasoline and 40% of n-butanol (by volume). The main properties of gasoline and n-butanol are reported in Table 4.2.

Table 4.2: Fuel specifications. (Tornatore *et al.*, 2012)

	Gasoline	n-Butanol
Low heating value (MJ/kg)	43.5	32.01
Latent heat of vaporization (kJ/L)	223	474
A/F stoichiometric	14.6	11.1
Density (kg/m^3)	720-775	813
Oxygen (% weight)	< 2.7	21.6
RON	95	113
Adiabatic flame temperature (K)	2370	2340

All the tests were carried out at engine speed of 2000 rpm and wide open throttle (WOT). Absolute intake air pressure and temperature were fixed at 1.4 bar and 338 K, respectively. The start of injection (SOI) for each fuel was fixed at 130 CAD ATDC and 300 CAD BTDC in order to inject the fuel in two different configurations: at closed intake valves (CV) and open intake valves (OV), respectively. The spark timing was changed in order to obtain the maximum brake torque. The duration of injection (DOI) was changed in order to set λ=1.0 as measured by a lambda sensor installed in the engine. All these configurations of fuel injection timing are summarized in Table 4.3. GAS_OV is the engine fueled with gasoline, injected with open intake valve; GAS_CV is the engine fueled with gasoline, injected with closed intake valve; BU40_OV is the engine fueled with BU40, injected with open intake valve and BU40_CV is the engine fueled with BU40, injected with closed intake valve.

Table 4.3: Summary: fuel injection timing. (Tornatore *et al.*, 2012)

Label	Fuel	SOI[a]	DOI[b]
GAS_OV	Gasoline	300 CAD BTDC	133 CAD
GAS_CV	Gasoline	130 CAD ATDC	148 CAD
BU40_OV	BU40	300 CAD BTDC	153 CAD
BU40_CV	BU40	130 CAD ATDC	165 CAD

[a] SOI: start of injection
[b] DOI: duration of injection

Accordingly Tornatore, there is a difference in the injection duration between gasoline and BU40. It happens because, as occurs with any alcohol, gasoline-butanol blends have lower stoichiometric air-fuel ratio. To ensure the same air-to-fuel ratio for BU40 in relation to pure gasoline, fuel flow must be increased. About the spark timing, Tornatore observed that for gasoline, the knocking limit was evaluated around 16 CAD BTDC for both fuel injection conditions. For BU40, the knocking limit was changed to about 20 CAD BTDC. BU40 allows the engine to work with more advanced spark timing without harming the combustion. It collaborates to the increment of the engine efficiency, represented by an increment of indicated mean effective

pressure (IMEP). In Tornatore's article, results obtained at fixed 14 CAD BTDC spark timing were defined as reference, in order to evaluate the effect of selected fuels on the normal combustion process at comparable IMEP with satisfactory engine stability.

4.6 Setting up and running the 1D engine model

Using all the geometrical and experimental data presented in Section 4.5, it was possible to build a 1D model in order to simulate the combustion process observed in Tornatore's study. GT-Power, a 1D simulation code used in the development of engines, was used to build this 1D model.

GT-Power solver follows the solution of flow as presented in section 4.4. The code presents some alternatives to model engine combustion like non-predictive models, where the combustion is imposed following a measured pressure curve and predictive models, where the combustion is calculated using fuel characteristics, injection data and engine geometry (Gamma Technologies, 2015d). There were a lot of data available about the engine from Tornatore's article. With all these information, a detailed model could be done and thus a predictive, spark-ignition, turbulent flame combustion model was selected. This model predicts the burn rate for homogeneous charge and spark-ignition engines. Its formulation is based on the work of Blizard and Keck (1974), Hires *et al.* (1978) and Morel *et al.* (1988). To proceed with this model, is necessary to have a previous knowledge about the geometry of the cylinder, spark locations and timing, air motion and fuel properties.

This model also requires the turbulence intensity and length scale. In this way, the in-cylinder flow dynamics is necessary and should be described. A calibration of the model with experiments is normally necessary and it can be done adjusting the effects of turbulence intensity and length scale on the calculation of turbulent flame speed and the Taylor micro-scale length. It is normally done manually in a trial and error basis, comparing the numerical results with the measurements until some level of agreement is obtained. A previous knowledge about the shape of the combustion chamber is also necessary since it directly affects the in-cylinder flow dynamics.

Also necessary, is the description of the in-cylinder geometry for the flame and wall interaction. They are related to the spark position, defined by a X, Y, Z coordinate, the location of the cylinder head top (or dome) center in X, Y coordinates, the diameter of the dome, the dome height in the Z coordinate, the location of the piston combustion bowl (or cup) center in X, Y

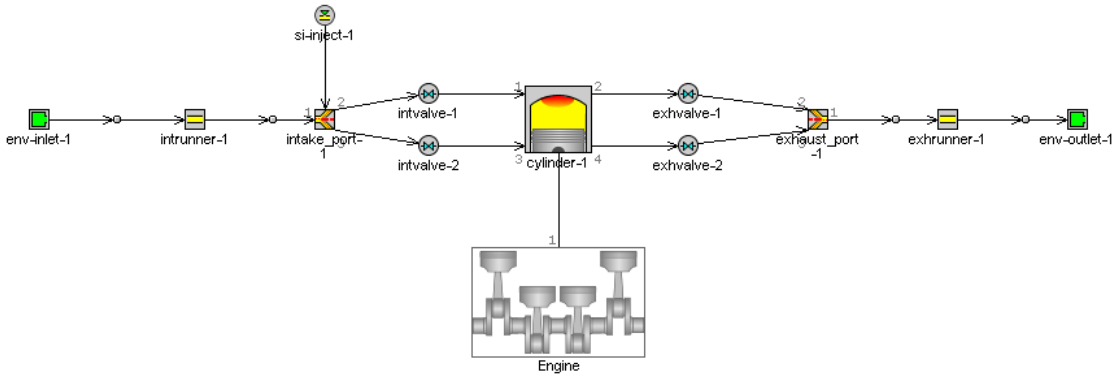


Figure 4.2: 1D model built in GT-Power to represent Tornatore's engine model.

coordinates, the diameter of the cup and the cup depth in the Z coordinate. Finally, is necessary to define the value of the spark timing of the engine.

Table 4.4 presents a summary of the input parameters and values applied to this model.

Table 4.4: Geometrical parameters for the flame in SI Turbulent Flame combustion model.

Attribute	Object value
Spark location	[0,0,3] mm
Dome location	[0,0]
Dome diameter	79 mm
Dome height	0 mm (flat top)
Cup location	[0,0]mm
Cup diameter	80 mm
Cup depth	0 mm (flat top)
Spark timming	–14 BTDC

General overview of the 1D model built for this study is shown in Figure 4.2. It is a mono-cylinder engine with geometric characteristics as presented in Table 4.1. Schematic of the power cell is shown in Figure 4.3.

Fuel injection timing followed the same strategy as described in Table 4.3, it means, four models were setup considering two fuels (gasoline and BU40) and two injection schemes (with open valve and with closed valve). Model was setup to run under stoichiometric condition, it means, λ=1. Maintaining the start of combustion (SOI) fixed as an input data, the fuel delivery was changed for each engine model in order to reach the values of duration of combustion (DOI) used in the test. In this way, 2.565 g/s of fuel were injected for GAS_OV configuration, 2.296 g/s for GAS_CV , 2.478 g/s for BU40_OV and 2.297 g/s for BU40_CV.

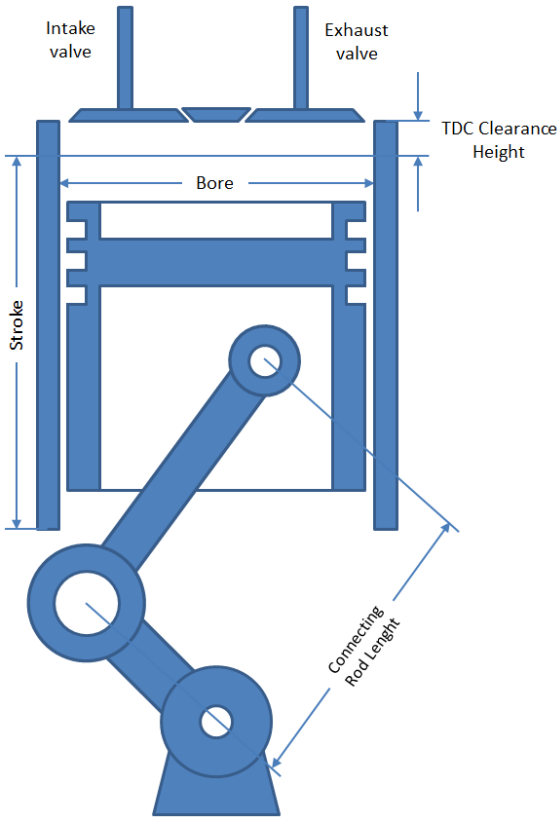


Figure 4.3: Schematic of the power cell used in the calculation.

Engine simulation was run considering 2000 rpm of engine speed and wide open throttle (WOT), the same condition used during the measurements of the engine. The intake air temperature was set at 338K. Absolute intake air pressure in the 1D model was set at 1.1bar, lower than the intake pressure of 1.4bar used in the engine. A lower pressure was used in the simulation model because the real engine presents localized pressure losses that are not present in simulation. So, the mathematical model has to be set with a lower intake air pressure to reach the same performance of the measured engine, otherwise the engine simulation would deliver higher performance.

Fuel properties are also necessary to run the 1D model. In the simulation code is necessary to define two fluids to characterize a fuel: liquid part and gaseous part. Liquid definitions are used to describe the properties of incompressible liquids (Gamma Technologies, 2015d). It is only intended to be used in circuits which are primarily composed of gases (i.e. engine circuits), where the mass fraction of the liquid in the liquid/gas mixture is very small. In this case the effect of the compressibility of the liquid may be negligible and can be ignored. Gaseous definitions are used to describe the properties of gases and/or vapors. In engine simulation, the composition of all combustible gases (even for non-fuels) must be entered so that their impact on combustion and emissions can be determined.

Advanced properties for combustion modeling are also required as input data of this model. These properties are normally obtained from measurements or from previous similar works. Since most of the fuel properties characteristics are not available in the literature, the values used on the modeling were based on the recommended values from the 1D code.

Maximum laminar speed is the maximum value of speed of a laminar flame propagating through the air - fuel mixture at 1.01325 bar and 300 K. Usual values for this speed occurs between 1 and 1.2 m/s and in this model 1.1 m/s was used. Laminar speed roll-off is a parameter used to describe how the flame speed decay from its maximum value as a function of fuel/air equivalence ratio. In this model, -0.549 m/s was used.

Equivalence ratio at maximum speed is the fuel/air equivalence ratio at the maximum laminar flame speed. Recommended value used was 1.1. Flame kernel growth multiplier is an adjusting factor used to scale the calculated value of the growth rate of the flame kernel. This scaling is applied depending on results from measurements and it influences the ignition delay. Larger numbers shorten the delay, advancing the transition from laminar combustion to turbulent combustion. The recommended value is 1.0.

Turbulent flame speed multiplier is also an adjusting factor. It is used to scale the calculated turbulent flame speed and this variable influences the overall duration of combustion: larger numbers increase speed of combustion, lower values decrease. Recommended value used was 1.0.

Taylor length scale multiplier was used to scale the calculated value of the Taylor microscale of turbulence. Taylor length scale or turbulent length scale is the size used to characterize a turbulent flow (Tennekes, H. and Lumley, J.L., 1972). The Taylor microscale is the intermediate length scale at which fluid viscosity significantly affects the dynamics of turbulent eddies in the flow. The Taylor microscale modifies the time constant of combustion of fuel/air mixture entrained into the flame zone by changing the thickness of the plume. This multiplier mostly influences the tail part of the combustion and is relatively insensitive. Recommended value used was 1.0.

Some iterations using Wiebe model (Heywood, 1988) were run to initialize the SI turbulent flame model. Wiebe curve is related ("anchored") to the top death center (TDC) of the engine cycle. This parameter is specified as an angle and is the number of crank angle degrees between TDC and the 50% combustion point of the Wiebe curve. Typical values for anchor angles in SI engines are 5 to 12 degrees after TDC (Heywood, 1988; Gamma Technologies,

2015d). In this simulation this value was set as an average of 8 degrees, just to have values for initialization. The duration of the combustion is another important parameter. Basically, it relates to angle excluding the first 10% and last 10% of the total combustion duration. Optionally, the burn points where the duration is measured can be set. Typical values for SI engines are 25 to 35 degrees(Heywood, 1988; Gamma Technologies, 2015d) and in this simulation it was set as 25 degrees as recommended in the references. Finally, Wiebe curve exponent should be defined. Typical value for SI engines is 2 and was used, again as recommended in references (Heywood, 1988; Gamma Technologies, 2015d).

Gasoline properties used in the model, like heat of vaporization, density, absolute entropy, enthalpy, dynamic viscosity, thermal conductivity, molecular weight, carbon atoms per molecule, hydrogen atoms per molecule, lower heating value, critical temperature and critical pressure were extracted from articles (Linstrom, 2016) and books (Moran *et al.*, 2014; Stephan, 2013) that deal with gasoline fuel properties. Pure n-butanol general properties are widely available but those specifically related to combustion like critical temperature, critical pressure, laminar flame speed, turbulent flame speed, are available in dedicated references only (Gu *et al.*, 2011; Wu and Law, 2013). However, the 1D model built in the 1D code needs to be input with the properties of BU40, properties of liquid fuel and its vapor. Those data are not readily available and represent the biggest difficulty to correctly setup this model.

To by-pass this limitation, a new fuel was defined in GT-Power as being 60% of gasoline plus 40% of n-butanol (by volume). Initial properties of n-butanol fraction were defined based on the literature. GT-Power takes care to do the mixing, weighting the properties of gasoline and n-butanol in relation to the fraction of fuels, 0.6 and 0.4, respectively. It basically uses the fractions of the fuels (0.6 and 0.4) as weights to calculate the final properties of the fuel (Gamma Technologies, 2015d).

4.6.1 Engine performance using BU40 as fuel

n-Butanol values were initially assumed and the 1D models were run several cycles, changing the values of the fuel properties cycle after cycle and retrieving results. After running those cycles, simulation results of indicated mean effective pressure (IMEP), pressure curve, rate of heat release (ROHR)curve and flame radius curve were retrieved and compared with results of the engine measurements from Tornatore's study. In a trial and error basis, the final properties of BU40 were those properties included in the 1D model, which allowed that the engine performance results of this virtual engine were close to those measured in the test (lowest

percentual difference).

First result obtained is IMEP. The measurements were characterized by nearly the same IMEP (12.2 bar $\pm$ 0.5%). Simulated values of IMEP follow the same characteristic and are all near to 12.2 bar: 12.11 bar for GAS_OV, 12.10 bar for GAS_CV, 12.15 bar for BU40_OV and 12.14 bar for BU40_CV. So, for any fuel, the values of IMEP are similar to the measurements in a difference lower than 0.1 bar. IMEP results obtained from simulation, using the adjusted properties of BU40, present good approximation to the values of IMEP measured in the engine.

Cylinder pressure results are presented in Figure 4.4. The red lines are the measured pressure curves and the black lines are the simulated pressure curves. In all the cases, the curve shapes are similar. As presented in Table 4.5, there are differences lower than 8% in the peak cylinder pressure (PCP) when comparing the measurements and simulation using BU40. The peak value of the curves is higher in simulation probably because some pressure losses that occur in the engine are not considered in the 1D model. This leads to a better volumetric efficiency in the 1D model and, as a consequence, to higher PCP's. Again, results obtained from simulation, using the adjusted properties of BU40, present good approximation to the values measured in the engine.

Table 4.5: Comparison of values of PCP: simulation vs. measurements.

Peak Cylinder Pressure			
Fuel	Simulation	Measurement[a]	%Diff
BU40_CV	58.93	55.61	5.6%
GAS_CV	58.47	55.15	5.7%
BU40_OV	59.13	54.44	7.9%
GAS_OV	58.78	54.12	7.9%

[a] Ref: (Merola *et al.*, 2012; Tornatore *et al.*, 2012)

Figure 4.5 presents the comparisons in terms of ROHR. The general shape of the curves – measured (Merola *et al.*, 2012; Tornatore *et al.*, 2012) and simulated – are similar but there are some differences that should be observed. The flat parts of the curves from simulation (–40 CAD to about 0 CAD and about 27 CAD to 80 CAD) are smoother than in the curves from measurements. There is no explanation in Tornatore *et al.* (2012) to this behavior but it is possibly happening due to noise in measurements or incorrect data treatment. Also, the region from –40 CAD to about 0 CAD presents values of ROHR below zero. It is not an expected behavior since values of ROHR are normally positive. There is also no explanation about it in the reference article but it may be occuring due to the heat exchange between gases and cylinder wall that is not correctly modeled in the 1D engine. Again, there are differences in the peak values but they are below 6.9%, as presented in Table 4.6.

Table 4.6: Comparison of values of ROHR: simulation vs. measurements.

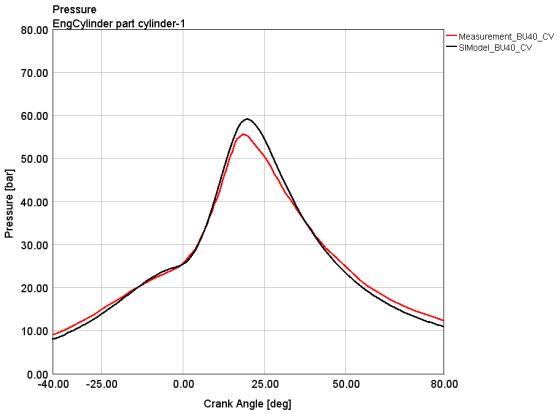
	Rate of Heat Realease – ROHR		
Fuel	Simulation	Measurement[a]	%Diff
BU40_CV	177.98	186.67	-4.9%
GAS_CV	175.08	181.34	-3.6%
BU40_OV	170.94	159.17	6.9%
GAS_OV	172.50	170.00	1.4%

[a] Ref: (Merola *et al.*, 2012; Tornatore *et al.*, 2012)

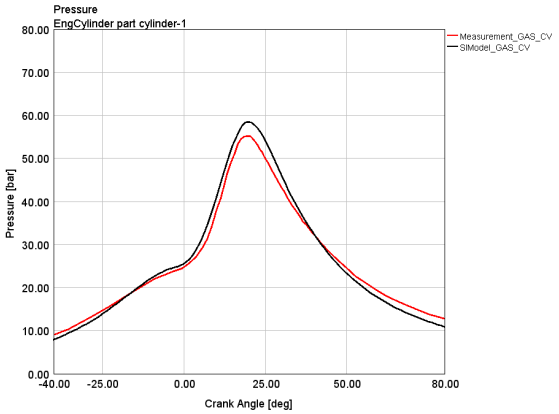
The comparisons related to flame radius are presented in Figure 4.6. The superposition of the curves – simulated and measured – is visible, mainly for BU40 (Figures 4.6a and 4.6c). In spite of the good approximation, the shape of the curves in some regions is different (mainly for gasoline, Figures 4.6b and 4.6d). The possible explanation is that, in the simulation, the flame front is modeled as perfectly round and expanding from the centered spark plug, growing symmetrically until it reaches the cylinder wall. In the engine, a different behavior was observed.

Images in Tornatore's work show the combustion process from the spark plug until the flame front reaches the cylinder wall. The flame front starts from the spark plug and then it expands with almost radial shape for around 10 CAD. After this time, the flame front starts to present an asymmetry and the flame reaches first the exhaust side of the cylinder. Tornatore explains that this asymmetry was induced by fuel film deposited on the intake valves and combustion chamber surfaces. It should be noted that the asymmetry was less evident for BU40, which showed a more regular evolution. In this way, the simulation better represented the engine setup fueled with BU40.

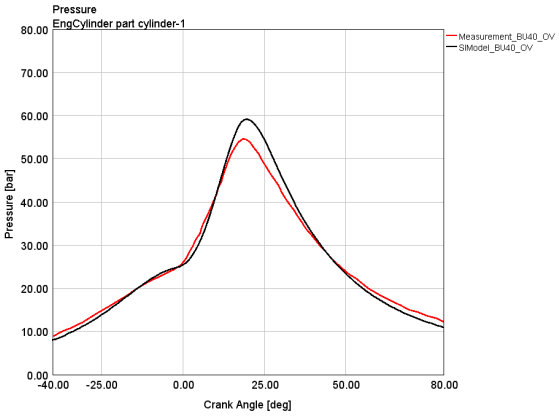
The performance indicators, starting with IMEP, after PCP and finally ROHR, presented good correlation between measurements and simulation. In the case of flame radius, the same general behavior between engine measurement and modeling was observed, although the engine showed a slightly different result due to simplification in the injection modeling used in the simulation. Since the results from measurements are similar to those retrieved from the virtual engine, it is possible to say that the adjusted properties of BU40 are close enough to the real properties of the fuel. As an important result, these properties may be used in future numerical models where the study of BU40 is required or to initialize a model with more realistic initial values. Table 4.7 brings a summary of the adjusted properties and their final values.



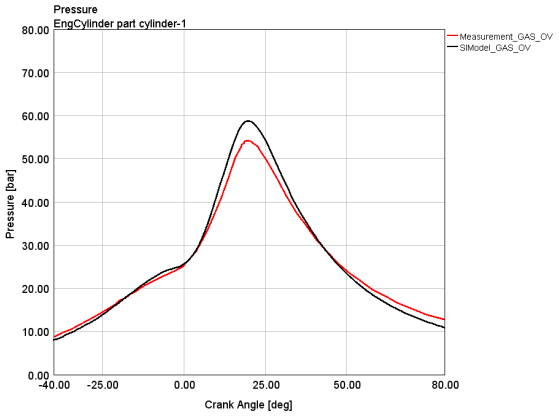
(a) Cylinder pressure in bar, BU40, closed valve.



(b) Cylinder pressure in bar, gasoline, closed valve.

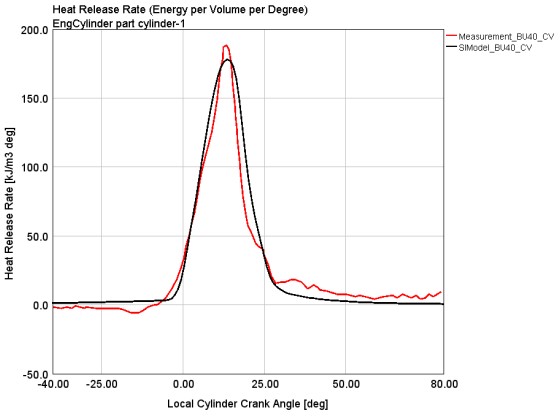


(c) Cylinder pressure in bar, BU40, open valve.

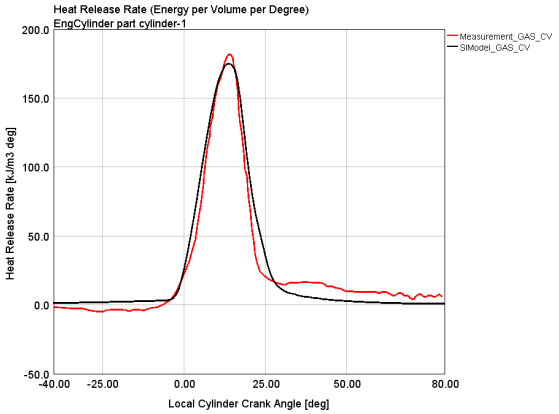


(d) Cylinder pressure in bar, gasoline, open valve.

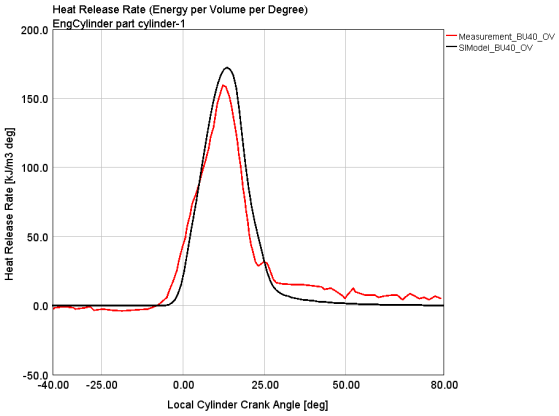
Figure 4.4: Comparison of results - cylinder pressure curve: experimental vs. 1D simulation.



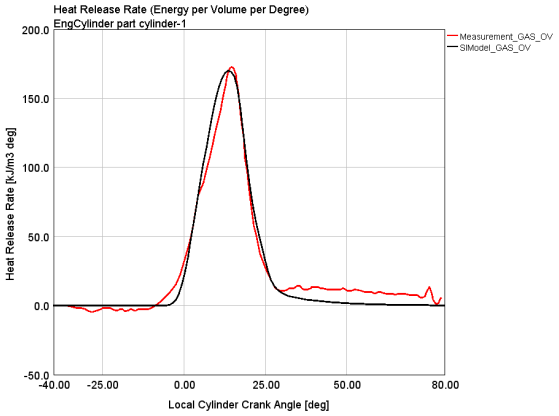
(a) ROHR in KJ/m^{3}deg, BU40, closed valve.



(b) ROHR in KJ/m^{3}deg, gasoline, closed valve.

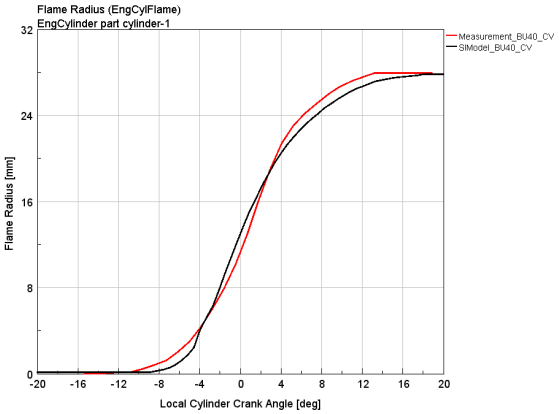


(c) ROHR in KJ/m^{3}deg, BU40, open valve.

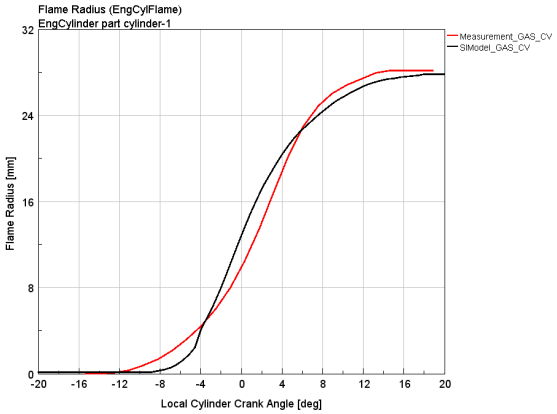


(d) ROHR in KJ/m^{3}deg, gasoline, open valve.

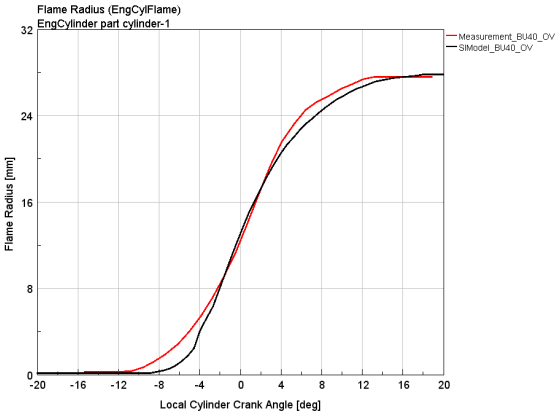
Figure 4.5: Comparison of results - ROHR: experimental vs. 1D simulation.



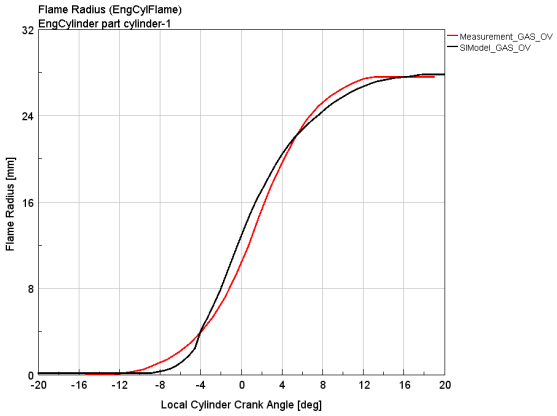
(a) Flame radius in mm, BU40, closed valve.



(b) Flame radius in mm, gasoline, closed valve.



(c) Flame radius in mm, BU40, open valve.



(d) Flame radius in mm, gasoline, open valve.

Figure 4.6: Comparison of results - flame radius: experimental vs. 1D simulation.

Table 4.7: Fuel specifications applied to simulation model.

Property	n-butanol
Liquid fuel heat of vaporiz. @ 298 K (kJ/kg)	583
Density (kg/m^3)	813
Liquid fuel abs. entropy @ 298 K (J/kg-K)	3015.78
Liquid fuel enthalpy coeff. a_1	2074
Liquid fuel enthalpy coeff. a_2	-0.17129
Liquid fuel enthalpy coeff. a_3	$7.6231e^{-4}$
Critical temperature (K)	563
Critical pressure (MPa)	4.5
Gaseous fuel abs. entropy @ 298K (J/kg-K)	4723.79
Gaseous fuel enthalpy coeff. a_1	1566.5
Gaseous fuel enthalpy coeff. a_2	1.4344
Gaseous fuel enthalpy coeff. a_3	-4.1495^{-4}
Gaseous fuel enthalpy coeff. a_4	6.0823^{-8}
Gaseous fuel enthalpy coeff. a_5	-3.4985^{-12}

4.6.2 Potential application of BU40 in a commercial SI engine

To verify the advantages and limitations of BU40 as biofuel in a commercial application, a comparison of performance of one engine fueled with BU40 was done against the same engine using other fuels like E25 (75% gasoline plus 25% ethanol, by volume), E100 (100% ethanol) and E0 (100% gasoline). Results of engine tests with BU40 are not available and simulation was used to do the comparison. To proceed with this, a typical engine of the Brazilian market was considered and a new 1D model was built. It was a four cylinder, port fuel injection (PFI), spark ignited (SI), aspirated engine. The cylinder head had four valves and a centrally positioned spark plug. Intake air pressure and temperature were set at 1000 mbar (average) and 296 K (average), respectively. Engine speed went from 700 to 6200 rpm and the engine was set at wide open throttle (WOT) condition. Further details on the engine are presented in Table 4.8.

Combustion simulation was carried out using four fuels: E25 (75% gasoline plus 25% ethanol, by volume), E100 (100% ethanol), E0 (100% gasoline) and BU40 (60% gasoline plus 40% butanol, by volume). The main properties of the pure fuels were reported in Table 4.9, additional properties of gasoline and ethanol used in the model, like heat of vaporization, density, absolute entropy, enthalpy, dynamic viscosity, thermal conductivity, molecular weight, carbon atoms per molecule, hydrogen atoms per molecule, lower heating value, critical temperature and critical pressure were based on the software database, extracted from articles (Linstrom, 2016) and books (Moran *et al.*, 2014; Stephan, 2013) that deal with gasoline fuel properties. Additional properties of n-butanol, mainly those related to combustion, were based on the results

Table 4.8: Specifications of the four cylinder PFI aspirated SI engine.

Parameter	Value
Displaced volume	1400 cc
Stroke	73.4 mm
Bore	77.6 mm
Connecting rod	137.3 mm
Compression ratio	12.4:1
Number of valves	4
Exhaust valve open	111 CAD[a]ATDC[b]
Exhaust valve close	360 CAD ATDC
Inlet valve open	357 CAD ATDC
Inlet valve close	110 CAD BTDC[c]

[a] CAD: crank angle degree
[b] ATDC: after top death center
[c] BTDC: before top death center

Table 4.9: Fuel specifications. (Bankar *et al.*, 2013; Jin *et al.*, 2011; Tornatore *et al.*, 2012)

	Gasoline	n-Butanol	Ethanol
Molecular formula	$C_4 - C_{12}$	C_4H_9OH	C_2H_5OH
Low heating value (MJ/kg)	43.5	32.01	26.8
Latent heat vaporiz. (kJ/L)	223	474	714
A/F stoichiometric	14.6	11.1	9.0
Density (kg/m^3)	720-775	813	790
Oxygen (% weight)	< 2.7	21.6	34.8
RON	95	98-113	109-125
Adiabatic flame temp. (K)	2370	2340	2308

obtained in the Section 4.6 and also on the summary presented in Table 4.7.

Table 4.10 brings a summary of additional input parameters and values applied to the model. General overview of the 1D model scheme is shown in Figure 4.7.

For E100, E25 and E0, fuel injection followed the engine manufacturer recommendations to use defined air-to-fuel ratio. Small fluctuations can occurs due to engine test conditions, but in general the stoichiometric condition of λ=1 was pursued. Values of fuel injection for BU40 were not available. The engine virtual model was run using assumed values of fuel injection. The simulation was run several times, with different values of injection and, by a trial and error process, the condition of λ=1 was reached. The value of fuel injection that enables λ=1 was then adopted. Table 4.11 shows the employed values, accordingly to the fuel and engine speed.

Table 4.10: Geometrical parameters for the flame in SI Turbulent Flame combustion model.

Attribute	Object value
Spark location	[0,0,3]mm
Dome location	[0,0]
Dome diameter	77mm
Dome height	0mm (flat top)
Cup location	[0,0]mm
Cup diameter	77.6mm
Cup depth	0mm (flat top)

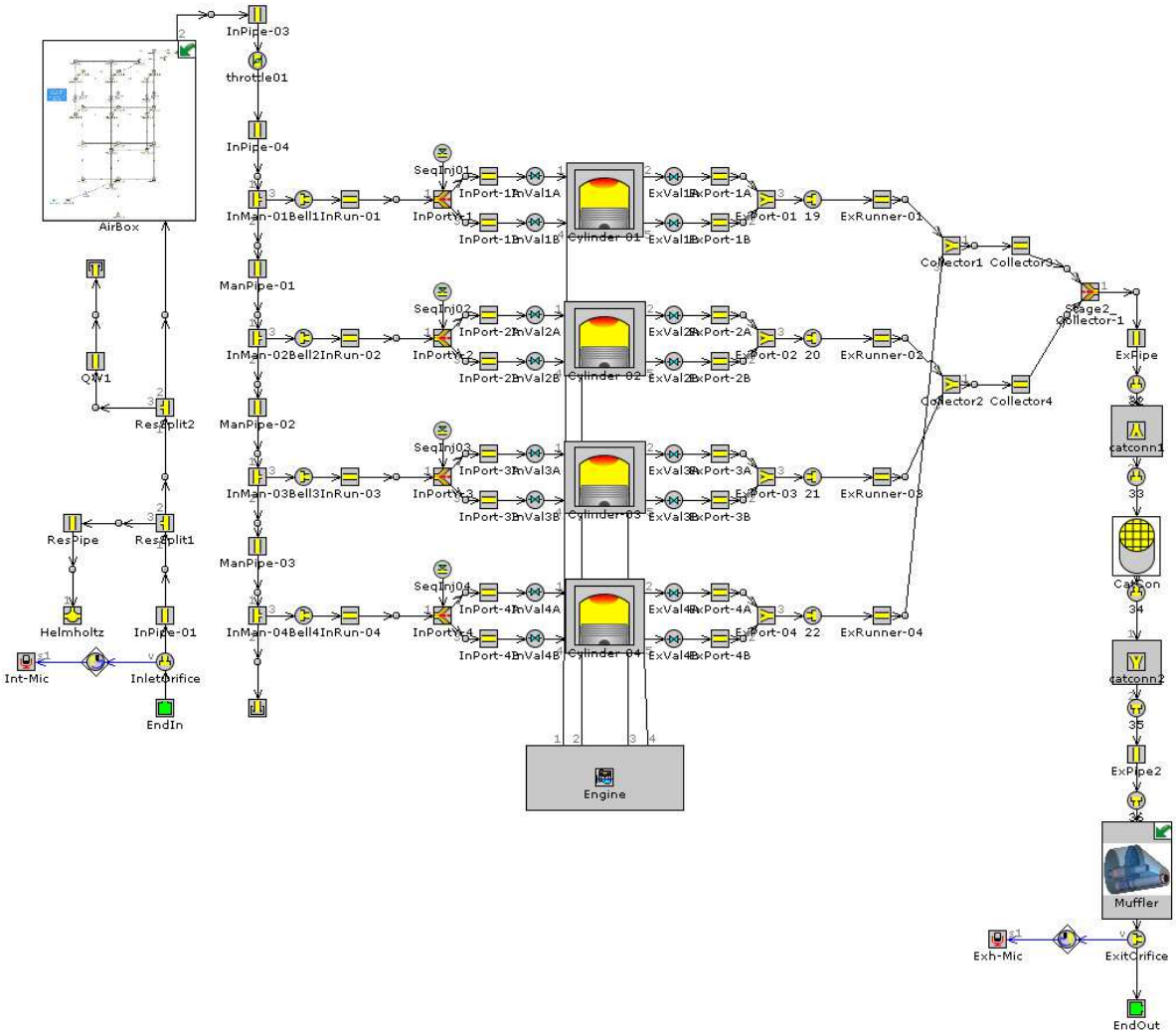


Figure 4.7: 1D model built in GT-Power to represent a four cylinder engine model.

Table 4.11: Air-to-fuel ratio accordingly the fuel, engine speed from 3200 to 6200 rpm.

	RPM	6200	6000	5800	5600	5400	5200	4800	4400	4000	3600	3200
Fuel							A-F					
E0		12.98	13.15	13.04	13.66	13.68	13.71	13.77	13.93	14.26	14.02	14.15
E25		10.81	10.96	10.87	11.38	11.40	11.42	11.48	11.61	11.89	11.69	11.79
E100		8.19	8.30	8.23	8.62	8.63	8.65	8.69	8.79	9.00	8.85	8.93
BU40		10.81	10.96	10.87	11.38	11.40	11.42	11.48	11.61	11.89	11.69	11.79

Table 4.12: Air-to-fuel ratio accordingly the fuel, engine speed from 3000 to 700 rpm.

	RPM	3000	2800	2600	2400	2000	1600	1200	1000	900	800	700
Fuel							A-F					
E0		14.39	14.48	14.43	13.94	14.10	14.69	14.93	15.12	15.15	15.26	15.03
E25		11.99	12.07	12.02	11.62	11.75	12.24	12.44	12.60	12.63	12.72	12.53
E100		9.08	9.14	9.11	8.80	8.90	9.27	9.42	9.54	9.56	9.64	9.49
BU40		11.99	12.07	12.02	11.62	11.75	12.24	12.44	12.60	12.63	12.72	12.53

Since the physical engine was available, it was installed in a dynamometer to measure its performance. The equipment used is produced by AVL, an eddy current dynamometer with power up to 700 kW, with measuring capabilities for power, torque, temperature, pressure, smoke, fuel and oil consumption. The engine was tested with three different fuels: E0, E25 and E100 under imposed engine speeds from 1100rpm to 6200rpm. The basic procedure to obtain the measurements is: when the engine was stable at a defined speed, a batch of measurements of performance was done. At least 100 measurements are done for each parameter and then the speed is changed for the next value, repeating the procedure. At the end, an average of the measurements is done and a curve is generated for each measured performance item.

1D simulation model was set to run under the same conditions and the results – power, torque, BSFC and engine efficiency – from simulation were compared with the average measured results, as presented in Figures 4.8, 4.9 and 4.10. E0 result from simulation for torque (Figure 4.8a) is very similar to the results from measurements, for the whole range of speeds. Some minor differences can be seen at about 3000rpm and 4500rpm, where results from simulation for torque are higher than the values from test results. The same can be observed for power (Figure 4.8b). In both the cases, the percentual difference between measurement and simulation is 4% or lower (Figure 4.8c).

E100 result from simulation for torque (Figure 4.9a) is also similar to the results from measurements, presenting very close shapes for torque curves. Some differences can be seen in speeds below 2000rpm and above 4500rpm, where the results of tests present higher values of torque in relation to the simulation. The percentual difference between measurement and simulation is again 4% or lower (Figure 4.9c).

E25 result from simulation for torque (Figure 4.10a) is in general close to the results from measurements, but the curve shape is something different from measurements to simulation. Differences can be seen at 2500rpm, 4000rpm, 4250rpm – where results from simulation are higher than those from tests – and 4750rpm, where the result from test shows higher values of torque in relation to the simulation. However, the percentual difference between measurement and simulation is lower in relation to the other fuels: 3% or lower (Figure 4.10c).

Experimental measurements with BU40 were not performed. The 1D model used in this section was run considering BU40 as fuel and the results from the numerical simulation were compared with those from simulation using E0, E25 and E100 as fuel. Two points were taken in consideration to compare BU40 with the other fuels in terms of virtual engine performance. First, the same model used to simulate the engine burning E0, E25 and E100 was used to sim-

ulate the engine burning BU40. For the three first fuels, the results were close to the measurements and then we can assume that the general behavior of the engine is well modeled. Second point, in the Section 4.6.1, 1D model was run using BU40 as fuel and the results from simulation showed good correlation with the measurements. We can also assume that the fuel properties obtained are well adjusted and will provide well correlated results. In this way, with good adjusted engine model and good adjusted fuel properties, it was possible to compare the results obtained for E0, E100 and E25 against a virtual engine running BU40. The focus of the comparisons were from the point of view of engine performance, varying the fuels used in the engines.

Figure 4.11a shows that the torque values delivered by the engine until 1500 rpm, independently of the fuel, are almost the same. After this speed, the engine running with E100 always delivers more torque than the same engine running with other fuels. This behavior is strongly related to the spark timing since ethanol, with its higher RON, can run with more advance in relation to the other fuels without harming the combustion stability or presenting issues with knocking. In these simulations, the engine model running with E100 was –21 crank angle degrees before top dead center (CAD BTDC) advanced, E25 was –14 CAD BTDC advanced, E0 was –12 CAD BTDC advanced (all those data supplied by the engine manufacturer) and BU40 was –16 CAD BTDC advanced, adapted from Merola *et al.* (2012). BU40 presents higher values of torque in relation to E25 and E0 in the range of 2250 to 3000 rpm and above 4250 rpm due to the advance it uses.

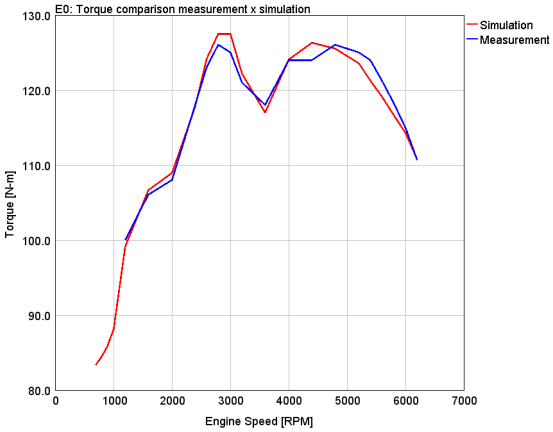
Figure 4.11b shows that the values of power in kW delivered by this engine, for all fuels, are very similar one to each other until about 3000 rpm. Above this engine speed, E100 delivers more power. Again, the better performance of the engine running with ethanol is related to the advance applied to the engine, as already explained.

E100 presents advantages in terms of power and torque in relation to the other studied fuels. On the other hand, E100 presents some disadvantages in relation to fuel consumption and consequently vehicle autonomy. Figure 4.11c shows the brake specific fuel consumption (BSFC) of this engine running with different fuels. For the condition of λ=1 used in all the models, ethanol presents the highest BSFC for any speed and E0 presents the lowest BSFC. It is related to the energy content of the fuels, being the pure gasoline the one with more energy content – leading to the lowest fuel consumption – and ethanol the one with the lower energy content – leading to the highest fuel consumption. Interesting to notice that BU40 and E25 have almost the same behavior, it means, both present similar BSFC. In terms of vehicle usage, E0, E25 and BU40 present better mileage in relation to ethanol.

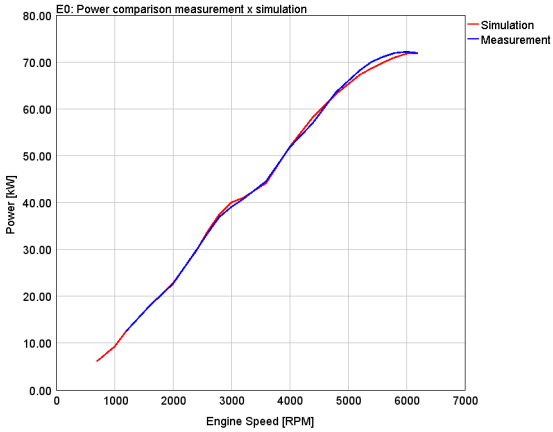
However, since we are using the same engine with different fuels, the direct comparison of BSFC may not be fair with E100, due to its lower energy content. A better parameter to verify the engine behavior when using different fuels is to compare the engine efficiency. Figure 4.11d shows the efficiency of the four simulated engines compared one to each other. The engine fueled with ethanol presents the highest efficiency for the whole range of engine speeds (peak of 30% at 2600 rpm). It occurs mainly because ethanol can support higher compression ratios due to its higher RON. This engine presents compression ratio of 12.4:1, more suitable for ethanol, delivering more efficiency. E0 presents the worst efficiency (peak of 33% at 2800 rpm). Since the compression ratio is high for gasoline (recommended values for this fuel are around 10:1), the engine advance has to be reduced to avoid knocking and then the combustion does not occurs in its best point. Also, to protect the engine, the electronic injection delivers more fuel than necessary per cycle, lowering the engine efficiency even more. BU40 and E25 present almost the same efficiency, with advantage for E25 (peak of 35.77% at 2600 rpm for E25, peak of 35.4% at 2800 rpm for BU40). Both are higher than E0 due to the addition of an alcohol (n-butanol) to the mixture (increment of RON). However, the efficiency of the engine running on BU40 may still be improved, working on the engine advance and optimizing injection strategy for this fuel.

Besides performance requirements, cylinder pressure is another characteristic to be verified in the engine from the point of view of resistance of the engine components. Pistons, bearings, connecting rods and piston rings are submitted to cylinder pressure as mechanical load and it is used during the design phase of these components. Higher cylinder pressures may potentially lead to mechanical failures (cracks) and to avoid this, without reducing the engine load, the components have to be more robust or need to use more resistant and expensive raw materials.

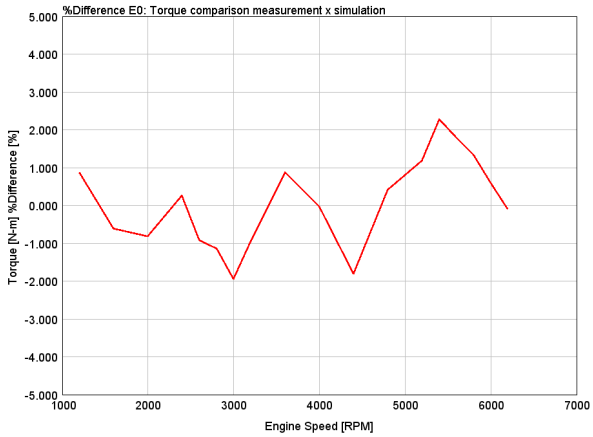
Figure 4.11e shows the pressure curves of cylinder number one of this engine. The engine running with E100 will present higher peak cylinder pressure than the other engines (65 bar). The mechanical load that the engine components need to support is directly related to cylinder pressure and higher PCP's mean higher mechanical load. It is also related to the spark advance: if the end of the combustion process occurs earlier by advancing the spark timing the peak cylinder pressure occurs earlier in the expansion stroke and is increased in magnitude. Due to the higher PCP, engines running on ethanol may potentially present components with structural problems like cracks, requiring stiffer and more expensive components. Just as comparison, ethanol is followed by BU40 that presents PCP of 60 bar, E25 (56.1 bar) and E0 (56.1 bar). On this way, using BU40, E25 or E0 may lead to light weight, optimized components in relation to those used under E100.



(a) Engine torque in Nm, E0.

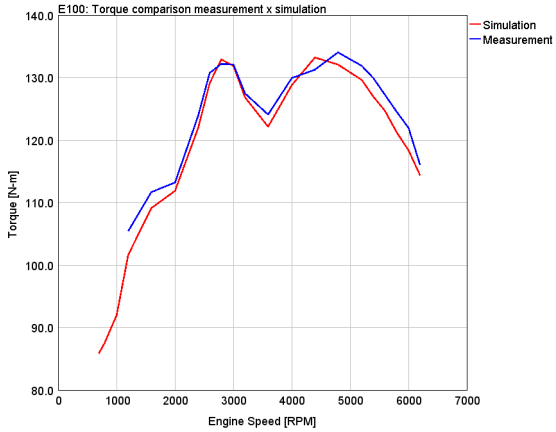


(b) Engine power in kW, E0.

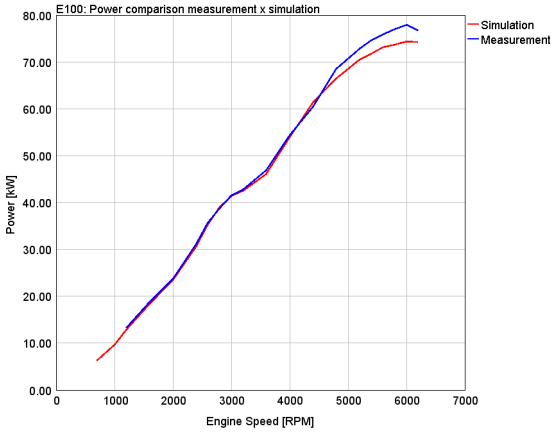


(c) Error difference - engine torque.

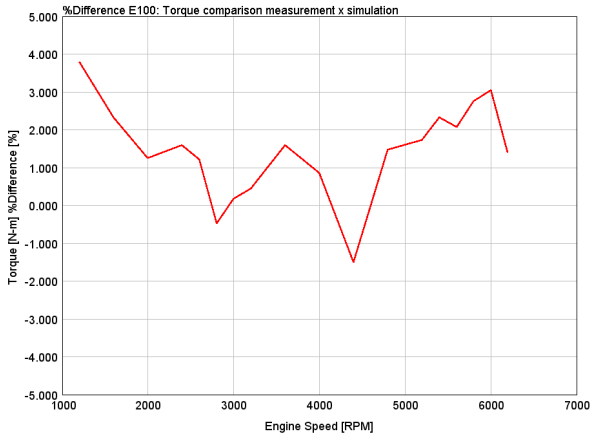
Figure 4.8: Comparison of results - performance: experimental vs. 1D simulation. Fuel E0, four cylinder engine, aspirated, injection data from Tables 4.11 and 4.12



(a) Engine torque in Nm, E100.

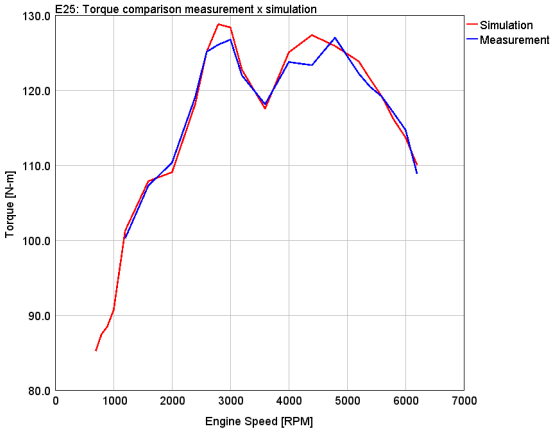


(b) Engine power in kW, E100.

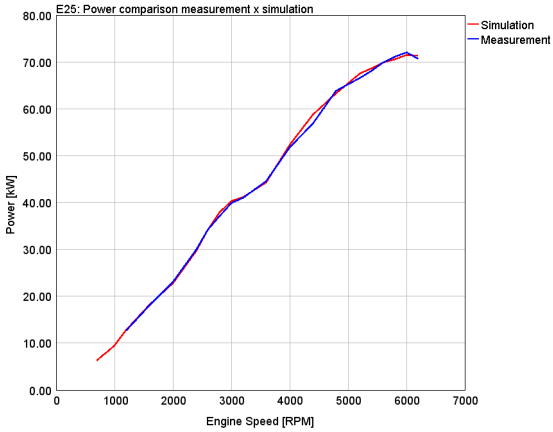


(c) Error difference - engine torque.

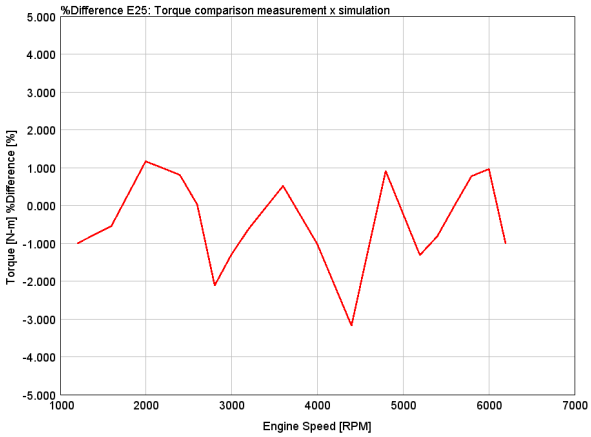
Figure 4.9: Comparison of results - performance: experimental vs. 1D simulation.Fuel E100, four cylinder engine, aspirated, injection data from Tables 4.11 and 4.12



(a) Engine torque in Nm, E25.

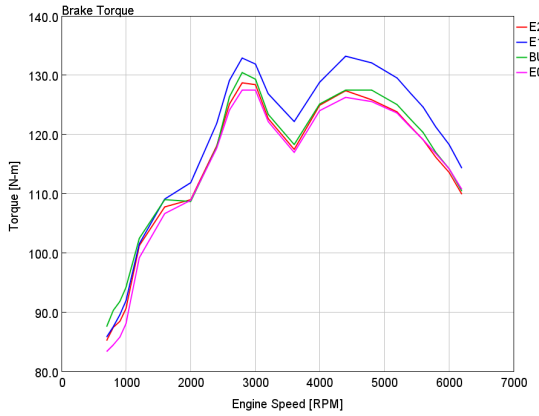


(b) Engine power in kW, E25.

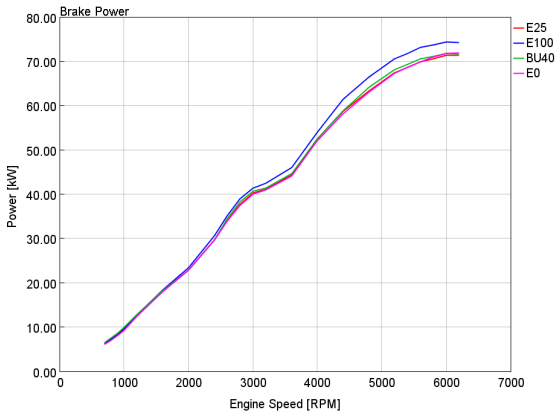


(c) Error difference - engine torque.

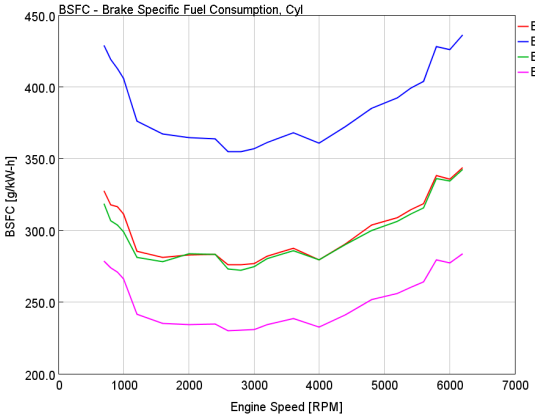
Figure 4.10: Comparison of results - performance: experimental vs. 1D simulation. Fuel E25, four cylinder engine, aspirated, injection data from Tables 4.11 and 4.12



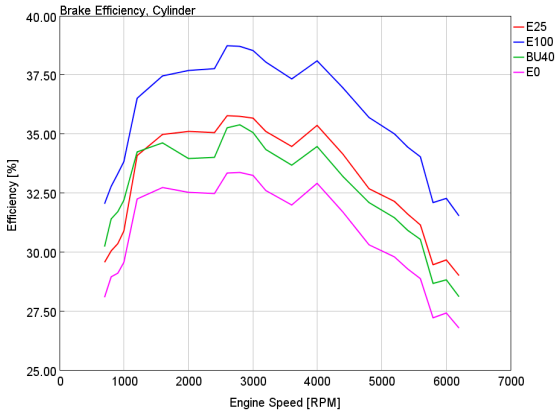
(a) Engine power in kW, comparison: different fuels.



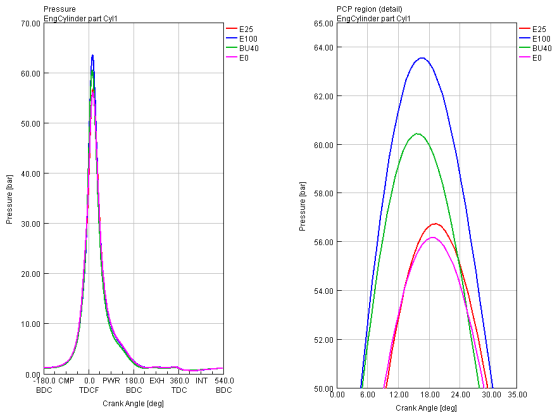
(b) Engine torque in Nm, comparison: different fuels.



(c) Engine BSFC in g/kW-h, comparison: different fuels.



(d) Engine efficiency in %, comparison: different fuels.



(e) Cylinder pressure in bar, comparison: different fuels.

Figure 4.11: Comparison of results - performance for different fuels. E0, E25, E100 and BU40, four cylinder engine, aspirated, injection data from Tables 4.11 and 4.12

4.7 Conclusions

Due to its characteristics, n-butanol appears as an interesting renewable fuel for replacing gasoline or to form mixtures with gasoline, potentially presenting better properties than ethanol-gasoline blends in terms of engine performance and reductions emissions, maintaining a good engine efficiency. There are just a few studies showing measurements related to these statements in literature and there is no commercial engine available to validate this affirmation. A good approach to overcome this difficulty is to use numerical simulation. With an engine model is possible to evaluate different fuels, compare results and select the better engine setup. However, is also difficult to obtain input data necessary to build these numerical engine models for simulation, mainly from the point of view of n-butanol fuel properties.

To surpass this difficulty, an engine found in literature running BU40 was modeled in a 1D software. Input data related to combustion of BU40 were adjusted in the model until the performance of the simulation model was close to the engine. The performance of BU40 against other fuels was compared by means of simulation. For that, a commercial engine running on E100, E25 and E0 was also modeled in the 1D code, but now its performance results (power, torque and BSFC) were validated with measurements in a dynamometer. The virtual model of this commercial engine running on BU40 was simulated and its results compared with those from E100, E25 and E0.

In this comparison, using simulation results, we noted that an commercial engine running with BU40 presented overall performance (power and torque) similar to the same engine running with E25, worse performance in relation to E100 (it means, lower power and torque) and better in relation to E0 (meaning, higher power and torque). Engine efficiency of the engine fueled with E100 was the highest and the engines with E25 and BU40 presented similar efficiency. The engine burning BU40 presented lower peak cylinder pressure (PCP) in relation to the same engine using E100. It was, however, higher than the PCP of the engine running with E25 and E0.

5 Conclusions

Due to its energetic characteristics (similar to gasoline), with interesting properties in relation to ethanol (lower specific fuel consumption, less problems with cold start and better lubricity, among others), n-butanol appears as a renewable fuel and is interesting for replacement of gasoline or to form blends with gasoline, presenting better properties than ethanol-gasoline blends in terms of engine performance and emission reduction. An important conclusion is that, due to its structure and energy characteristics, n-butanol can be used directly in a gasoline engine with little or no modification of that engine.

To verify such behavior of the engine, two techniques could be used: direct measurements in engine tests or with the use of numerical simulation. Engine modeling is increasingly present in the industry. The virtual development of engines is an important subject and simulation codes are available to build these models. 1D codes are the most interesting in modeling a complete engine, allowing you to check from simple components to more advanced topics such as combustion. The codes on the market have several different models for defining engine combustion. Non-predictive models are the easiest way to define combustion. They are simple to build and run very fast. However, it is necessary to have engine parameters for each operating condition, which can be difficult to obtain, especially for engines at the design/development stage. Predictive models are more accurate and can potentially better represent engine performance. However, they require much more information to carry out their preparation. In addition, when using models such as the turbulent flame model, calibration with experimental results becomes necessary. With the use of 1D modeling and information about the engine being studied, it is possible to build a complete model of the engine and check its performance when fueled with n-butanol – or n-butanol-gasoline mixture – compared to other fuels .

However, for correct modeling of n-butanol, it is necessary to use measurements or literature information in order to obtain the properties of this fuel required for the 1D model. Despite their potential, there are only a few studies that show measurements on engines using n-butanol as fuel. They occur only in engines used in academic studies and there is no commercial application available to validate the possible gains promoted by n-butanol. Knowing some characteristics of n-butanol and with an overview on 1D engine modeling, a good approach to overcome this difficulty is the use of numerical simulation. However, it is also difficult to obtain input data needed to construct these numerical models for simulation, especially from the point of view of fuel properties. The approach adopted to solve this question was, using a well-known engine and performance measurements presented in the literature, construct a 1D model of engine fueled with n-butanol-gasoline mixture (BU40). With this model, several performance

parameters were calculated and used to estimate the best properties for n-butanol, especially the combustion characteristics used in the 1D model.

From numerical simulation it was possible to verify that a commercial engine fueled with BU40 has some advantages over the same engine fueled with E0, E25 or E100. The engine running on BU40 has lower peak cylinder pressure than the same engine using E100. This represents lower mechanical loads applied to the engine components. It is noted that the engine configurations required to run the model using BU40 are almost the same as those used for E25 and E0. In practice, this may mean that an engine running on E25 or E0 can run directly with BU40 with little or no modification. At this point, it is important to say that the E25 is the most widely used fuel in SI engines in Brazil which opens up a huge potential for using the BU40 in existing engines. The overall performance (power and torque) of the engine fueled with BU40 is similar to the same engine fueled with E25, worse than E100 and better than E0. This is mainly related to the engine advance. The E100 supports more advance and with this, one can extract more power and torque from the engine. The BU40 can also work with more advance compared to pure gasoline, but its limit is lower than ethanol. Finally, for mixtures of n-butanol and gasoline, engine efficiency is similar to or slightly below the efficiency of the same engine when fueled with E25, but still has the potential to improve this condition for n-butanol through changes in injection.

The major disadvantage of n-butanol lies in its production. Biobutanol seems to be the focus for the future with some plants resuming its processes in China and one starting in Brazil. From the point of view of the fuel industry, the big challenge for biobutanol is that its production is not as efficient as the production of ethanol. The fermentation of biobutanol is not economically feasible due to the needs of the current market. The use of cheaper agricultural waste (lignocellulosic materials) and other industrial waste may be appropriate to establish a more economical ABE fermentation. But in addition, it is necessary to develop more effective fermentation processes based on different strains of bacteria or feedstock, or both. While promising, the production of biobutanol in dedicated refineries entails high investments that require a thorough economic assessment to ensure their implementation.

Future works

There are some work possibilities to be addressed in the topic n-butanol as a new biofuel. All the results obtained in the final part of the work were obtained from numerical simulation exclusively. It is interesting to run a commercial motor with n-butanol and verify its behavior, if it is adherent to the one obtained in simulation and if the parameters used for combustion in

the model are those that occur in practice.

The parameters obtained in the simulation, although coherent, were obtained only by adjusting the results to measurements. It would be interesting to conduct chemical kinetics studies of n-butanol, gasoline, ethanol and all mixtures thereof. Thus, it would be possible to apply to the models effectively measured values. It could be established if the adopted values in the work are in good approximation or in what form they could be improved. There is also the possibility of applying chemical kinetics models directly to 1D engine models.

It was not evaluated in this study, but since n-butanol RON is higher than that of gasoline it is expected that an engine working with BU40 will be more tolerant to detonation than the same engine running on gasoline. However, in the topic of detonation, ethanol still presents itself as the most tolerant of all fuels studied, presenting the best results. 1D detonation modeling is still a relatively new topic and deserves a deeper study in itself.

The characteristics of n-butanol with respect to emission reduction were also discussed in the articles. There is the possibility of modeling engine emissions, but it is also a very specific topic and can be resumed in a future work.

References

ABIQUIM-ASSOCIAÇÃO BRASILEIRA DA INDÚSTRIA QUÍMICA. **Anuário da Indústria Química Brasileira**. ABIQUIM, 2013.

ABNT-ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. Gasolina automotiva - determinação do teor de álcool etílico anidro combustível (AEAC). 1997.

ALASFOUR, F. Butanol, a single cylinder engine study: availability analysis. **Appl Therm Eng**, v. 17, 537–549, 1997.

ALQAHTANI, A.; SHOKROLLAHIHASSANBAROUGH, F. and WYSZYNSKI, M.L. Thermodynamic simulation comparison of AVL BOOST and Ricardo WAVE for HCCI and SI engines optimisation. **Combustion Engines**, v. 161, n. 2, 68–72, 2015.

ANDERSON, J.D. **Computational Fluid Dynamics**. McGraw-Hill Education, 1 ed., 1995.

ANFAVEA-ASSOCIAÇÃO NACIONAL DOS FABRICANTES DE VEÍCULOS AUTOMOTORES. **Anuário da indústria automotiva brasileira**. ANFAVEA, 2014.

ANP-AGÊNCIA NACIONAL DO PETRÓLEO, GÁS NATURAL E BIOCOMBUSTÍVEIS. Resolução ANP no. 40: Política nacional do petróleo, gás natural e biocombustíveis. 2013.

ASTM INTERNATIONAL. ASTM D4814-14a, Standard specification for automotive spark-ignition engine fuel. ASTM International, 2014.

AVL BOOST. Virtual engine simulation. 2016. Acessed on 04 April 2016.
URL: *https://www.avl.com/boost*

BANKAR, S.B.; SURVASE, S.A.; OJAMO, H. and GRANSTRÖM, T. Biobutanol: the outlook of an academic and industrialist. **RSC Advances**, v. 3, 24734–24757, 2013.

BARROS, José Eduardo Mautone. **Estudo de Motores de Combustão Interna Aplicando Análise Orientada a Objetos**. Fevereiro 2003. Dissertation (Master). Universidade Federal de Minas Gerais.

BEECKMANN, J.; CAI, L. and PITSCH, H. Experimental investigation of the laminar burning velocities of methanol, ethanol, n-propanol, and n-butanol at high pressure. **Fuel**, v. 117, 340–350, 2014.

BLACK, G.; CURRAN, H.; PICHON, S.; SIMMIE, J. and ZHUKOV, V. Bio-butanol: Combustion properties and detailed chemical kinetic model. **Combustion and Flame**, v. 157, 363–373, 2010.

BLIZARD, N.C. and KECK, J.C. Experimental and theoretical investigation of turbulent burning model for internal combustion engine. In **SAE International Congress**. SAE - Society of Automotive Engineering, 1974. SAE740191.

BORETTI, A.A.; LODI, F.; WATSON, H.C.; BREAR, M.J.; DINGLI, R.; JIN, S.H.; VOICE, G. and WILL, F. Experimental and numerical analysis of engine gas exchange, combustion and heat transfer during warm-up. In **SAE International Congress**. SAE - Society of Automotive Engineering, 2008. 2008-01-1653.

BRASIL. Lei nº 13.033, de 24 Setembro de 2014. 2014. Ethanol addition to automotive fuel.

BRASSAT, A.; THEWES, M.; MÜTHER, M. and PISCHINGER, S. Tailor-made fuels from biomass for gasoline combustion engines. **MTZ - Motortechnische Zeitschrift**, v. 72, n. 12, 56–63, 2011.

CHANG, Y.; JIA, M.; LIU, Y.; LI, Y. and XIE, M. Development of a new skeletal mechanism for n-decane oxidation under engine-relevant conditions based on a decoupling methodology. **Combustion and Flame**, v. 160, 1315–1332, 2013.

CHEN, C.; FAWCET, A.; POSNER, A. and RAVIV, T. Butanol by two stage fermentation. Technical report, University of Pennsylvania, April 2009.

CHEN, Z.; WUA, Z.; LIU, J. and LEE, C. Combustion and emissions characteristics of high n-butanol-diesel ratio blend in a heavy-duty diesel engine and EGR impact. **Energy Conversion and Management**, v. 78, 787–795, 2014.

CHOTWICHIEN, A.; LUENGNARUEMITCHAI, A. and JAI-IN, S. Utilization of palm oil alkyl esters as an additive in ethanol-diesel and butanol-diesel blends. **Fuel**, v. 88, 1618–1624, 2009.

COBLE, A.R.; SMALLBONE, A.; BHAVE, A.; MOSBACH, S.; KRAFT, M.; NIVEN, P. and AMPHLET, S. Implementing detailed chemistry and in-cylinder stratification into 0/1-D IC engine cycle sSimulation tools. In **SAE International Congress**. SAE - Society of Automotive Engineering, 2011. 2011-01-0849.

DE LEMOS ALVES, M. and BRANDAO, L.E.T. Automóvel flex fuel: Quanto vale a opção de escolher o combustível? In **XXXI Encontro da ANPAD**. September 2007.

DERNOTTE, J.; MOUNAIM-ROUSSELLE, C.; HALTER, F. and SEERS, P. Evaluation of butanol-gasoline blends in a port fuel-injection, spark-ignition engine. **International Journal of Energy and Environmental Engineering**, v. 65, 345–351, 2010.

DNV RESEARCH AND INNOVATION. Biofuels 2020: A policy driven logistics and business challenge. February 2010.

FARKADE, H.S. and PATHRE, A.P. Experimental investigation of methanol, ethanol and butanol blends with gasoline on SI engine. **International Journal of Emerging Technology and Advanced Engineering**, v. 2, n. 4, 205–215, April 2012.

FRASSOLDATI, A.; GRANA, R.; FARAVELLI, T.; RANZI, E.; OßWALD, P. and KOHSE-HÖINGHAUS, K. Detailed kinetic modeling of the combustion of the four butanol isomers in premixed low-pressure flames. **Combustion and Flame**, v. 159, 2295–2311, 2012.

GAMMA TECHNOLOGIES. **GT-SUITE: Engine Performance Application Manual**. Gamma Technologies, 2015a. Version 7.5.

GAMMA TECHNOLOGIES. **GT-SUITE: Engine Performance Help Manual**. Gamma Technologies, 2015b. Version 7.5.

GAMMA TECHNOLOGIES. **GT-SUITE: Engine Performance Tutorials**. Gamma Technologies, 2015c. Version 7.5.

GAMMA TECHNOLOGIES. **GT-SUITE: Flow Theory Manual**. Gamma Technologies, 2015d. Version 7.5.

GHOJEL, J.I. Review of the development and applications of the wiebe function: a tribute to the contribution of Ivan Wiebe to engine research. **International Journal of Engine Research**, v. 11, 297–312, May 2010.

GRANA, R.; FRASSOLDATI, A.; FARAVELLI, T.; NIEMANN, U.; RANZI, E.; SEISER, R.; CATTOLICA, R. and SESHADRI, K. An experimental and kinetic modeling study of combustion of isomers of butanol. **Combustion and Flame**, v. 157, 2137–2154, 2010.

GREEN, E. Fermentative production of butanol - the industrial perspective. **Current Opinion in Biotechnology**, v. 22, 1–7, 2011.

GRILL, M.; BILLINGER, T.; and BARGENDE, M. Quasi-dimensional modeling of spark ignition engine combustion with variable valve train. In **SAE International Congress**. SAE - Society of Automotive Engineering, 2006. 2006-01-1107.

GU, X.; HUANG, Z.; CAI, J.; GONG, J.; WUA, X. and FON LEE, C. Emission characteristics of a spark-ignition engine fuelled with gasoline-n-butanol blends in combination with EGR. **Fuel**, v. 93, 611–617, 2012.

GU, X.; LI, Q.; HUANG, Z. and ZHANG, N. Measurement of laminar flame speeds and flame stability analysis of tert-butanol?air mixtures at elevated pressures. **Energy Conversion and Management**, v. 52, n. 10, 3137–3146, September 2011.

HALL, C.M.; SHAVER, G.M.; CHAUVIN, J. and PETIT, N. Combustion phasing model for control of a gasoline-ethanol fueled si engine with variable valve timing. In **2012 American**

Control Conference. June 2012.

HARRISON, J.; AIHARA, R.; ESHRAGHI, M. and DMITRIEVA, I. Modeling engine oil variable displacement vane pumps in 1d to predict performance, pulsations, and friction. In **SAE International Congress**. SAE - Society of Automotive Engineering, 2014. 2014-01-1086.

HEATON, C. **The Chemical Industry**. Springer Science & Business Media, 1994.

HEYWOOD, J.B. **Internal combustion engines fundamental**. McGraw-Hill, Inc., 1988.

HIRES, S.D.; TABACZYNSKI, R.J. and NOVAK, J.M. The prediction of ignition delay and combustion intervals for a homogeneous charge, spark ignition engine. In **SAE International Congress**. SAE - Society of Automotive Engineering, 1978. SAE780232.

ILIEV, S. A comparison of ethanol and methanol blending with gasoline using a 1-d engine model. **Procedia Engineering**, v. 100, 1013–1022, 2015.

JIN, C.; YAO, M.; LIUC, H.; FON F. LEE, C. and JI, J. Progress in the production and application of n-butanol as a biofuel. **Renewable and Sustainable Energy Reviews**, v. 15, 4080–4106, 2011.

JONES, D. and WOODS, D. Acetone-butanol fermentation revisited. **Microbiological Review**, v. 50, 484–524, 1986.

KEE, R.; RUPLEY, F. and MILLER, J. Chemkin-II: A Fortran chemical kinetics package for the analysis of gas-phase chemical kinetics. Technical report, Sandia Report SAND89-8009, 1989.

KIM, D.H.; LEE, J.M.; PARK, E.H.; SONG, J.H. and PARK, S.I. Engine performance and toxic gas analysis of biobutanol-blended gasoline as a vehicle fuel. **International Journal of Automotive Technology**, v. 12, n. 3, 409–416, December 2011.

KODAH, Z.H.; SOLIMAN, H.S. and QUDAIS, M.A. Combustion in a spark-ignition engine. **Applied Energy**, v. 66, 237–250, Jul 2000.

LANE, J. Granbio and Rhodia ink pact for biobased n-butanol, in Brazil, from bagasse. Biofuels Digest:http://www.biofuelsdigest.com, August 2013. Acessed: 2015-09-16.

LAWRENCE LIVERMORE NATIONAL LABORATORY. Mechanisms. Combustion Mechanisms, October 2015. https://combustion.llnl.gov/mechanisms. Accessed 19 October 2015.

LEPLAT, N.; DAGAUT, P.; TOGBÉ, C. and VANDOOREN, J. Numerical and experimental study of ethanol combustion and oxidation in laminar premixed flames and in jet-stirred reactor. **Combustion and Flame**, v. 158, 705–725, 2011.

LINSTROM, P. NIST chemistry webbook. NIST Standard Reference Database, July 2016. http://webbook.nist.gov/chemistry. Accessed 28 July 2016.

LIU, H.; WANG, G. and ZHANG, J. **The Promising Fuel: Biobutanol**, chapter 6, pp. 175–198. INTECH, 2013.

LIU, H.F. and LEE, C.F. Spray and combustion in a constant volume combustion chamber with some biofuels. In **Graduate automotive technology education (GATE) seminar: automotive bio-energy, September 29. 2010**. September 2010.

LÓPEZ, E.J. and NIGRO, N.M. Validation of a 0D/1D computational code for the design of several kind of internal combustion engines. Technical report, Centro Internacional de Métodos Computacionales en Ingeniería, Instituto de Desarrollo Tecnológico para la Industria Química, 2000.

MARIANO, A.P.; DIAS, M.O.S.; JUNQUEIRA, T.L.; CUNHA, M.P.; BONOMI, A. and FILHO, R.M. Butanol production in a first-generation brazilian sugarcane biorefinery: Technical aspects and economics of greenfield projects. **Bioresource Technology**, v. 135, 316–323, 2013.

MEROLA, S.; TORNATORE, C.; MARCHITTO, L.; VALENTINO, G. and CORCIONE, F. Experimental investigations of butanol-gasoline blends effects on the combustion process in a SI engine. **International Journal of Energy and Environmental Engineering**, v. 3, 6–20, 2012.

MIRZAEIAN, M.; MILLO, F. and ROLANDO, L. Assessment of the predictive capabilities of a combustion model for a modern downsized turbocharged si engine. In **SAE International Congress**. SAE - Society of Automotive Engineering, 2016. 2016-01-0557.

MOHAMED, E.M. Burning velocities and flame temperatures of ethanol and butanol-air mixtures. 2009. Technical Institut - Babylon.

MORAN, M.J.; SHAPIRO, H.N.; BOETTNER, D.D. and BAILEY, M.B. **Fundamentals of Engineering Thermodynamics**. Wiley, 8 ed., 2014.

MOREL, T.; RACKMIL, C.I.; KERIBAR, R. and JENNINGS, M.J. Model for heat transfer and combustion in spark-ignited engine and its comparison with experiments. In **SAE International Congress**. SAE - Society of Automotive Engineering, 1988. SAE880198.

MOSS, J.T.; BERKOWITZ, A.M.; OEHLSCHLAEGER, M.A.; BIET, J.; WARTH, V.; GLAUDE, P.A. and BATTIN-LECLERC, F. An experimental and kinetic modeling study of the oxidation of the four isomers of butanol. **The Journal of Physical Chemistry A**, v. 112, 10843–10855, August 2008.

NAIK, S.; GOUD, V.V.; ROUT, P.K. and DALAI, A.K. Production of first and second generation biofuels: A comprehensive review. **Renewable and Sustainable Energy Reviews**, v. 14, 578–597, 2010.

NEJAME, S. Butanol as a fuel - view from the field. Technical report, NREL-National Renewable Energy Laboratory, 2010.

NEXANT. Biobutanol: The next big biofuel - a techno-economic and market evaluation. Technical report, Nexant, 2009.

NI, Y. and SUN, Z. Recent progress on industrial fermentative production of acetone-butanol-ethanol by Clostridium acetobutylicum in China. **Applied Microbiology and Biotechnology**, v. 83, 415–423, May 2009.

NIEMEYER, K.; SUNG, C. and RAJU, M. Skeletal mechanism generation for surrogate fuels

using directed relation graph with error propagation and sensitivity analysis. **Combustion and Flame**, v. 157, 1760–1770, 2010.

PEREIRA, L.G.; DIAS, M.O.; JUNQUEIRA, T.L.; PAVANELLO, L.G.; CAVALETT, M.F.C.O.; FILHO, R.M. and BONOMI, A. Butanol production in a sugarcane biorefinery using ethanol as feedstock. Part II: Integration to a second generation sugarcane distillery. **Chemical Engineering Research and Design**, v. 92, 1452–1462, 2014.

POMETTO, A.; SHETTY, K.; PALIYATH, G. and LEVIN, R. **Food Biotechnology**. CRC Press, 2 ed., 2005.

RAKOPOULOS, D.C.; RAKOPOULOS, C.D.; GIAKOUMIS, E.; DIMARATOS, A.M. and KYRITSIS, D.C. Effects of butanol-diesel fuel blends on the performance and emissions of a high-speed DI diesel engine. **Energy Conversion and Management**, v. 51, 1989–1997, 2010.

RICARDO WAVE. Engine performance using Ricardo WAVE. 2016. Acessed on 04 April 2016.
URL: *http://www.ricardo.com/en-GB/What-we-do/Software/Products/WAVE/*

RODRIGUES, Bruna Rocha. **Estoques reguladores de etanol combustível frente à introdução dos veículos flex fuel na frota nacional**. March 2012. Dissertation (Master). COPPE - UFRJ.

RODRIGUES, J.A.R. Do engenho à biorrefinaria. a usina de açúcar como empreendimento industrial para a geração de produtos bioquímicos e biocombustíveis. **Revista Química Nova**, v. 34, n. 7, 1245–1254, May 2011.

SARATHY, S.M.; OßWALD, P.; HANSEN, N. and KOHSE-HÖINGHAUS, K. Alcohol combustion chemistry. **Progress in Energy and Combustion Science**, v. 44, 40–102, June 2014.

SARATHY, S.M.; THOMSON, M.J.; TOGBE, C.; DAGAUT, P.; HALTER, F. and MOUNAIM-ROUSSELLE, C. An experimental and kinetic modeling study of n-butanol combustion. **Combustion and Flame**, v. 156, 852–864, 2009.

SAXENA, P. and WILLIAMS, F. Numerical and experimental studies of ethanol flames. **Proceedings of the Combustion Institute**, v. 31, 1149–1156, 2007.

SCHIFFMANN, P.; PALTRINIERI, S.; SHEKHAWAT, Y.; REUSS, D.; SICK, V.; FONTANESI, S. and HAWORTH, D. An integrated experimental and simulation study of cycle-to-cycle variations in a homogeneous-charge spark-ignition engine. In **International Multidimensional Engine Modeling Meeting**. SAE - Society of Automotive Engineering, 2014.

SCHNEPF, R. and YACOBUCCI, B.D. Renewable fuel standard (RFS): Overview and issues. Technical report, Congressional Research Service, USA, 2013.

SCHWADERLAPP, M.; ADOMEIT, P.; KOLBECK, A. and THEWES, M. Ethanol and its pottential for downsized engine concepts. **MTZ - Motortechnische Zeitschrift**, v. 73, 24–29, 2012.

SIWALE, L.; KRISTÓF, L.; ADAM, T.; BERECZKY, A.; MBARAWA, M.; PENNINGER, A. and KOLESNIKOV, A. Combustion and emission characteristics of n-butanol/diesel fuel blend in a turbo-charged compression ignition engine. **Fuel**, v. 107, 409–418, November 2012.

SMITH, G.P.; GOLDEN, D.M.; FRENKLACH, M.; MORIARTY, N.W.; EITENEER, B.; GOLDENBERG, M.; BOWMAN, C.T.; HANSON, R.K.; SONG, S.; GARDINER, W.C.; JR.; LISSIANSKI, V.V. and QIN, Z. NASA polynomials format: CHEMKIN. GRI-Mech: Gas Research Institute, March 2015a. http://www.me.berkeley.edu/gri-mech/data/k_form.html. Acessed on 08 October 2015.

SMITH, G.P.; GOLDEN, D.M.; FRENKLACH, M.; MORIARTY, N.W.; EITENEER, B.; GOLDENBERG, M.; BOWMAN, C.T.; HANSON, R.K.; SONG, S.; GARDINER, W.C.; JR.; LISSIANSKI, V.V. and QIN, Z. NASA polynomials format: polynomials. GRI-Mech: Gas Research Institute, March 2015b. http://www.me.berkeley.edu/gri-mech/data/nasa_plnm.html. Accessed on 08 October 2015.

SOLOMONS, T.W.G. and FRYHLE, C.B. **Organic Chemistry**. Wiley, USA, 10 ed., 2009.

STEPHAN, P. **VDI-Wärmeatlas**. Springer Vieweg, 11 ed., 2013.

TAKASHI, H. and KIMITOSHI, T. Laminar flame speeds of ethanol, n-heptane, iso-octane air mixtures. In **FISITA 2006**. International Federation of Automotive Engineering Societies, 06 2006.

TENNEKES, H. AND LUMLEY, J.L. **A First Course in Turbulence**. MIT Press, 1972. ISBN 0-262-20019-8.

TORNATORE, C.; MARCHITTO, L.; VALENTINO, G.; CORCIONE, F.E. and MEROLA, S.S. Optical diagnostics of the combustion process in a pfi si boosted engine fueled with butanol-gasoline blend. **Energy**, v. 45, n. 1, 277–287, 09 2012.

VELOO, P.S.; WANG, Y.L. and WESTBROOK, F.N.E.C.K. A comparative experimental and computational study of methanol, ethanol, and n-butanol flames. **Combustion and Flame**, v. 157, 1989–2004, 2010.

WALLNER, T.; SHIDORE, N. and ICKES, A. Impact of ethanol and butanol as oxygenates on SIDI engine efficiency and emissions using steady-state and transient test procedures. In **16th Directions in Engine-Efficiency and Emissions Research (DEER) Conference**. 2010.

WATERLAND, L.R.; VENKATESH, S. and UNNASCH, S. Safety and performance assessment of ethanol/diesel blends (E-Diesel). Technical report NREL/SR-540-34817, National Renewable Energy Laboratory., 2003.

WEBER, B.W.; KUMAR, K.; ZHANG, Y. and SUNG, C.J. Autoignition of n-butanol at elevated pressure and low-to-intermediate temperature. **Combustion and Flame**, v. 158, 809–819, 2011.

WU, F. and LAW, C.K. An experimental and mechanistic study on the laminar flame speed, Markstein length and flame chemistry of the butanol isomers. **Combustion and Flame**, v. 160, 2744–2756, 2013.

YAO, M.F.; ZHANG, Q.C.; LIU, H.F.; ZHENG, Z.Q.; ZHANG, P. and LIN, Z.Q. Diesel engine combustion control: medium or heavy EGR. **SAE**, 2010a. 2010-01-1125.

YAO, M.F.; ZHANG, Q.C.; LIU, H.F.; ZHENG, Z.Q.; ZHANG, P. and LIN, Z.Q. Experimental study of n-butanol additive and multi-injection on HD diesel engine performance and emissions. **Fuel**, v. 89, 2191–2201, 2010b.

YELIANA**Parametric combustion modeling for ethanol-gasoline fueled spark ignition engines**. March 2010. Thesis (PhD). Michigan Technological University.

YU, A.S.O.; NASCIMENTO, P.; NIGRO, F.E.B.; FREDERICK, B.W.B.; VARANDAS, A.; VIEIRA, S.F.A. and ROCHA, R.L. The evolution of flex-fuel technology in Brazil: the BOSCH case. In **PICMET 2010**. July 2010.

ZHANG, Z.H. and BALASUBRAMANIAN, R. Influence of butanol-diesel blends on particulate emissions of a non-road diesel engine. **Fuel**, v. 118, 130–136, 2014.