

COMPARISON BETWEEN N-BUTANOL AND ETHANOL COMBUSTION KINETIC MODELS THROUGH ONE-DIMENSIONAL PREMIXED FLAME SIMULATIONS

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Abstract. The alcohol *n*-Butanol is an organic substance being proposed as an alternative fuel for internal combustion engines. Improvements in its production as a biofuel, through fermentation processes, and its combustion characteristics, close to those of gasoline and diesel, grow attention to its viability as a renewable and economically interesting substitute to petrol-based fuels. However, few is known about its combustion characteristics, thus motivating research in that area. Ethanol is a biofuel widely used in commercial engines, specially in Brazil and the United States, and is a proposed blending agent for *n*-butanol. The present study compares chemical kinetic models for *n*-butanol, ethanol and their mixtures through numerical simulation in order to generate information for a future experiment, to be developed in a counter-flow laminar burner. In this equipment a mixture of fuel and air is injected through an axi-symmetric convergent burner against either the same mixture or a methane/air mixture. Hot gases are located between two flame fronts parallel to the stagnation plane. The flame front structure depends on the equivalence ratio and the strain rate. Strain rate can be changed by varying the injection velocities. In the present study, 1-D freely-propagating flame formulation is employed to describe the premixed flame configuration. Following this work, further analysis in 1-D counter-flow configuration shall be done. The system is modeled by considering detailed chemical kinetics and multi-component transport properties.

Keywords: *n*-butanol, ethanol, combustion, kinetic modeling, premixed flame burning

1. INTRODUCTION

The use of biofuels, specially in transportation and industrial processes, is seen as one of the most promising energy solutions for the future. Attention to this field is driven by uncertainties related to oil prices, greenhouse gases and pollutant emissions, as well as the need for lower dependence from petrofuel producers and higher diversity in sources (Jin *et al.*, 2011).

According to the *Key World Energy Statistics 2014* (IEA, 2014), 81.7% of the world primary energy supply comes from fossil fuels, being 31.4% of the total amount represented by oil. Biofuels and waste, including firewood - one of the main energy sources in developing nations - account for only 10%. This is a critical situation, not only because of the dependence from fossil fuel producers but also because of the huge amount of pollutants and greenhouse gases emitted in the atmosphere. In order to limit global average temperature increase to 2°C, emissions must be reduced in 32%, compared to 2012 figures. Therefore, alternative energy sources must be explored.

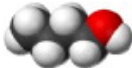
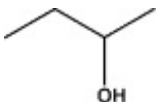
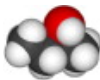
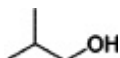
Biofuels are defined as a wide range of fuels in some way derived from biomass (Jin *et al.*, 2011). In this category, alcohols produced in fermentation processes, such as bioethanol and biobutanol, are considered as some of the most suitable for transportation purposes, due to their liquid form in environment temperatures, their relatively easy production and, like petrofuels, their high energy density (Bergthorson and Thomson, 2015). Alcohols have also high octane numbers, which make them suitable for spark ignition engines. Some countries already consume bioethanol as a fuel in large scale. Brazil and the United States are the most important examples, using it pure or blended with gasoline in different

proportions (Agarwal, 2007). In Brazil, most commercial cars operate with flex-fuel engines, which are able to consume any mixture of ethanol and gasoline. Both countries also have legislations that stipulate a mandatory minimum percentage of ethanol in gasoline to be distributed to the market.

Apart from alcohols, another group of biofuels being extensively studied, and also beginning to be used in commercial levels is the biodiesel class (Agarwal, 2007). Depending on the country legislation, biodiesel can be considered as any kind of fuel derived from biomass used in compression ignition engines, but the word is more commonly used to refer to fuels containing fatty acid methyl esters (FAME), which can substitute or be blended with diesel. In Brazil, like with bioethanol, the addition of a certain percentage of biodiesel in petrol-based diesel is mandatory, although the proportions are much lower than in the previous case.

Butanol is the common name of a group of substances that present the chemical formula C_4H_9OH . Its four isomers are the n-butanol (or 1-butanol), the iso-butanol, the sec-butanol (or 2-butanol) and the tert-butanol (Niemistö *et al.*, 2013). Tab. 1 shows the molecular structure and the main applications of these isomers.

Table 1. Molecular structure and main application of butanol isomers (Jin *et al.*, 2011).

Butanol isomers	Molecular structure and sketch map	Main application
1-Butanol	 	Solvents - for paints, resins, dyes, etc. Plasticizers - improve a plastic material processes Chemical intermediate - for butyl esters or butyl ethers, etc. Cosmetics - including eye makeup, lipsticks, etc. Gasoline additive
2-Butanol	 	Solvent Chemical intermediate - for butanone, etc. Industrial cleaners - paint removers Perfumes or in artificial flavors
iso-Butanol	 	Solvent and additive for paint Gasoline additive Industrial cleaners - paint removers Ink ingredient
tert-Butanol	 	Solvent Denaturant for ethanol Industrial cleaners - paint removers Gasoline additive for octane booster and oxygenate Intermediate for MTBE, ETBE, TBHP, etc.

Studies show that n-butanol and iso-butanol, like ethanol, can easily blend with gasoline (Jin *et al.*, 2011). The work of He *et al.* (2015) is an example of research on mixtures of butanol and gasoline. In spark ignition engines, its relatively high octane number and higher energy density, much closer to that of gasoline than to ethanol's, grow interest on this application. Butanol can also be a future option for blending with diesel, considering its relatively high cetane number as a desirable characteristic, as well as its greater oxygen content that can lead to further reduction of soot and its higher heat of evaporation, resulting in lower combustion temperature and reduced NOx emissions. (Jin *et al.*, 2011). Tab. 2 shows some characteristics of butanol isomers.

Table 2. Comparison of butanol isomers (Wallner *et al.*, 2009)

	1-butanol	2-butanol	Tert-butanol	Iso-butanol
Density (kg/m ³)	809.8	806.3	788.7	801.8
Research octane number	96	101	105	113
Motor octane number	78	32	89	94
Boiling temperature (°C)	117.7	99.5	82.4	108
Enthalpy of vaporization (kJ/kg) at T _{boil}	582	551	527	566
Self-ignition temperature (°C)	343	406.1	477.8	415.6
Flammability limits vol. %	1.4-11.2	1.7-9.8	2.4-8	1.2-10.9
Viscosity (mPa · s) at 25 °C	2.544	3.096	-	4.312

From the point of view of butanol production, improvements on biomass-fed processes have also been attracting attention to the fuel. One of the most important methods is the ABE process, which involves fermentation of organic

matter by bacteria from the *Clostridium* gender, specially the *Clostridium acetobutylicum*, generating a mixture of acetone, butanol and ethanol in different proportions. Depending on the yeast, the bacteria can consume either food-related feedstock, like potato starch and sugar cane juice, or lignocellulosis, available in organic waste (Niemistö *et al.*, 2013). Other processes, like the one described by Dias *et al.* (2014), use ethanol as feedstock for butanol production. Despite recent improvements in the renewable processes, it is known that most butanol produced in the world comes from oxo synthesis, a chemical process that uses petrol, being therefore not interesting from the point of view of renewability.

In this sense, it is important to study the combustion of butanol, not only pure but with different proportions of ethanol. Bioethanol, as previously stated, is also a by-product in some production process and is considered harder than acetone to be separated from the final mixture. It is also involved in other production processes, as a feedstock Dias *et al.* (2014) or as a by-product. Therefore, it is interesting to analyse how both fuels influence each other, in terms of flame speed, pollutants and temperature profile, foreseeing the usage of these mixtures in a commercial level, focusing on spark ignition internal combustion engines.

The present work involves the numerical analysis of the combustion of n-butanol, ethanol and their blends, through the package REGATH, developed in the CentraleSupélec, in Paris, France. One-dimensional laminar premixed flame in steady state approach was used in order to generate information on laminar flame speed, maximum temperature, flame thickness, pollutant formation, among other information. Chemical kinetics available in the literature were used in the simulations, and experimental data were used to compare the results. N-butanol was the chosen isomer, due to the extensive number of experimental and numerical studies available on the subject.

In the future, blends between ethanol and n-butanol are intended to be studied in an experimental approach, in a laminar counterflow burner, in order to generate data on the issue, as well as to validate the numerical approach. The work of Alviso *et al.* (2015), on methyldecanoate, is a good example of the next steps to be taken.

2. METHODOLOGY

Chemical kinetics is the name given to the study of the elementary reactions and their rates, belonging to the field of physical chemistry. For many applications, the global reaction, the equation in which reactants and final products are solely described, is enough to generate information. However, it is known that the oxidation of combustibles involves a series of intermediate reactions, generating thousands of species, and resulting in, sometimes, very different outcomes. Not less important is to take account of the thermodynamics and the transport properties of the involved elements. To understand all these issues is fundamental to the comprehension of pollutant formation, burning profiles and flame speed for different values of pressure, injection temperature, and any complex burning conditions (Turns, 2012).

2.1 Chemical model

As previously mentioned, the full chemical kinetics of a fuel combustion contains thousands of reactions and species. However, it is impossible to know the exact amount of reactions and substances, and even if it were possible, the computational time required to run numerical analysis would be tremendously high, making it impracticable. Therefore, simplified chemical models are required in order to understand the phenomenon and make simulations.

For bimolecular reactions, reactions that involve two reactants, the collision theory is applied. In general, elementary reactions are bimolecular, with the only addition of an inactive catalyst, that create termolecular reactions with a similar formulation. An arbitrary bimolecular reaction, between reactants A and B, can be expressed as



The rate at which the reaction happens, that means the rate the species A is consumed, is proportional to the concentration of the species, as in Eq. (2):

$$\frac{d[A]}{dt} = -k_{bimolec}[A][B] \quad (2)$$

The value of $k_{bimolec}$ depends on the temperature and experimental values. This can be expressed by the Arrhenius equation:

$$k(T) = AT^b \exp\left(-\frac{E_a}{R_u T}\right) \quad (3)$$

In which T is the temperature, R_u is the universal gas constant and A , b and E_a are empirical values, and can be organized in tables. The REGATH package uses these tables in order to generate data on the species' formation, among other information.

2.2 Thermodynamic approach

Another set of information required to the simulation involves thermodynamic properties. For example, in order to generate data on the temperatures, it is necessary to know the enthalpy of the mixture well. Considering a complex situation, in which thousands of species are mixed, the sum of the values of the enthalpy of each element is the desired number.

In order to generate the properties values for each species, approximations must be done. The work of Darabiha *et al.* (2006) cites the use of a process in which 14 constants are applied into fourth order polynoms, generating values for C_{pk} , the molar heat capacity, H_{pk} , the molar enthalpy and S_{pk} , the molar entropy, as a function of T_{inf} , the temperature in the environment, T_{sup} , the highest temperature, T_{med} , the average temperature and the constants $a_{1k...14k}$ for each element.

These constants are contained in tables, which are read by the package REGATH in order to evaluate temperatures, among other factors, during the simulation.

2.3 Transport properties

The last data to be used in the numerical analysis are the transport properties. In order to simulate the actual conditions of the combustion it is necessary to take into account some characteristics (Darabiha *et al.*, 2006). They are explained next:

1. If the molecule has a mono-atomic, linear or non-linear geometry. In REGATH files, the values 0, 1 and 2 are attributed to them, respectively.
2. The Lennard-Jones potential, $\frac{\epsilon}{k_b}$ [K], a model that approximates the interaction between a pair of neutral atoms or molecules.
3. The Lennard-Jones collision diameter, σ [Å], the finite distance at which the inter-particle potential is zero.
4. The dipole moment, μ [Debye].
5. The polarizability, α [Å³].
6. The rotational relaxation collision number, Z_{rot} , at 298 K.

These values are used to solve the mass, momentum, energy and chemical species balances, in this case, for a 1-D set of equations.

3. RESULTS AND DISCUSSION

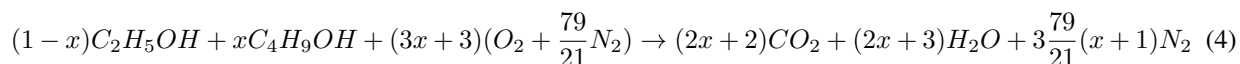
In this study, several chemical kinetic models available in the literature were compared, for simulations with ethanol, n-butanol and their blends, in the following fuel volume proportions: 100% n-butanol (B100); 75% n-butanol, 25% ethanol (B75); 50% n-butanol, 50% ethanol (B50); 25% n-butanol, 75% ethanol (B25); 100% ethanol (E100). The fuel-air equivalence ratio, ϕ , was also varied, for values from 0.4 to 1.7 in some cases.

For pure n-butanol, both schemes from the same first author, Sarathy *et al.* (2009) and Sarathy *et al.* (2012), which are extensively studied and cited in the literature, were used. The scheme presented in Sarathy *et al.* (2012) was validated for the four butanol isomers. This scheme also contains ethanol, therefore, it was chosen not only for pure n-butanol, but also for the mixtures. For laminar flame speed for different equivalent ratios, experimental data from the works of Sarathy *et al.* (2009) and Liu *et al.* (2011) were used for comparison. Maximum temperature and flame thickness were compared only between models. Initial temperature was set to 353 K for pure n-butanol, and to 298 K for the blends. Pressure was 1 atm for both cases. Experimental data for blends are not available in the literature, therefore, further experiments will be run to validate the tested model.

For pure ethanol, schemes due to Marinov (1999) and Konnov *et al.* (2011) were used and compared to the one in Sarathy *et al.* (2012). Apart from the model of Sarathy *et al.* (2012), the other works were validated with experiments cited in their articles. For laminar flame speed for different ϕ values, experimental data from Konnov *et al.* (2011) and an empirical formula proposed by Liao *et al.* (2007) were also used for comparison. Maximum temperature and flame thickness were compared only for the models. Initial temperature was set to 298 K, and the pressure, to 1 atm.

3.1 Input values

For the 1-D premixed calculation, mass fractions of each reactant in the fresh mixture are given as input, in order to evaluate the desired reaction. A global reaction for the combustion on air of the ethanol/butanol mixture, considering x the molar fraction of butanol in the resulting fuel, can be presented as follows:



Through this equation, it is possible to generate the mass proportions for each component in the fuel/air mixture in

stoichiometric conditions. Further calculations based in the reaction lead to proportions for different fuel-air equivalence ratios.

3.2 Results

Calculations using the REGATH package generated information on the laminar flame speed, the flame thickness and the maximum temperature for each value of ϕ , for each evaluated chemical scheme. From these data, the graphics below could be plotted.

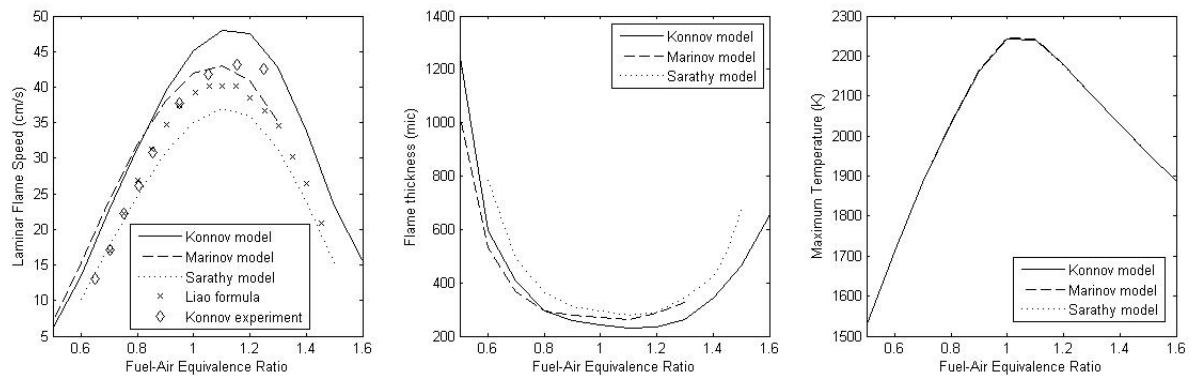


Figure 1. Laminar flame speed, flame thickness and maximum temperature for ethanol-air equivalence ratio

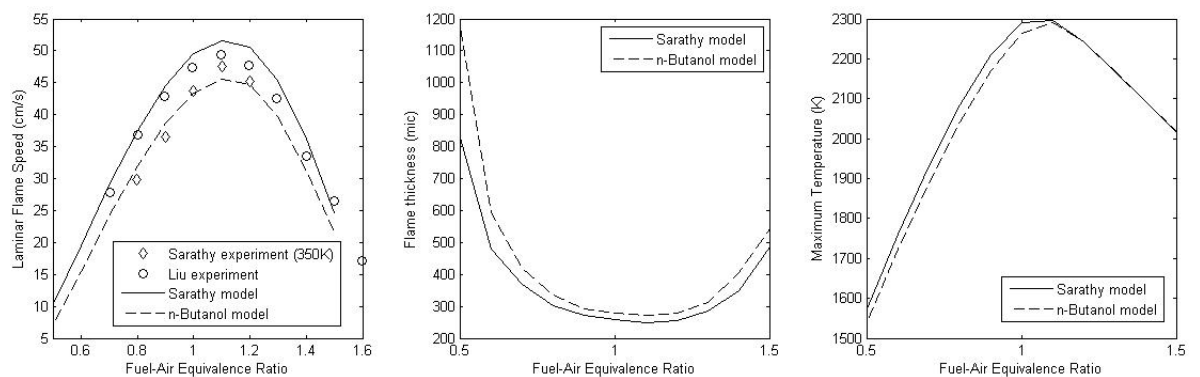


Figure 2. Laminar flame speed, flame thickness and maximum temperature for butanol-air equivalence ratio

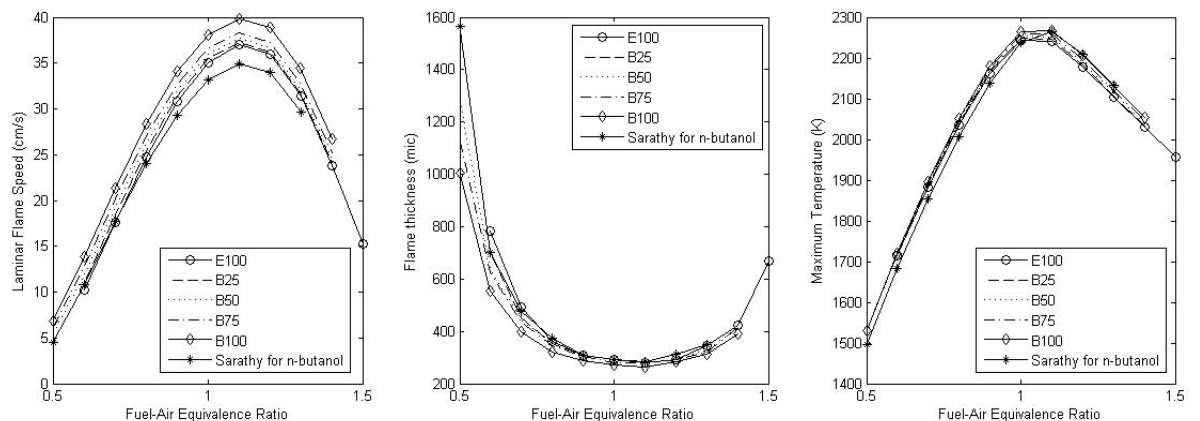


Figure 3. Laminar flame speed, flame thickness and maximum temperature for fuel-air equivalence ratio

In Fig. 1, calculations were done using the Konnov model (Konnov *et al.*, 2011), the Marinov model (Marinov, 1999), the Sarathy model (Sarathy *et al.*, 2012), the Liao formula (Liao *et al.*, 2007) and the Konnov experiment (Konnov *et al.*, 2011) generated the values. In Fig. 2, data from the Sarathy experiment at 350 K (Sarathy *et al.*, 2009) and the Liu experiment (Liu *et al.*, 2011) were used to validate results obtained with schemes from the Sarathy model (Sarathy *et al.*, 2012) and the n-Butanol model (Sarathy *et al.*, 2009). In Fig.3, all the blends were evaluated through the Sarathy scheme (Sarathy *et al.*, 2012), and B100 in the Sarathy for n-butanol scheme (Sarathy *et al.*, 2009).

Between the models, first of all, maximum temperatures for all models seem very similar. For ethanol simulations, the maximum difference between the values was of only 0.1%, while for pure butanol, only 2%. However, flame thickness varies a lot for butanol in extremely low ϕ values - 0.5 and 0.6 -, as much as 42%, but keeps an average of 15%; for ethanol this difference is more critical: an average of 26% between the models of Konnov *et al.* (2011) and Sarathy *et al.* (2012). Finally, for the laminar flame speed, differences between the models are also very sensitive: for butanol at extremely low ϕ values - 0.5 and 0.6 - differences can be as high as 30%, however, they are only 15% on average; for ethanol, values differ from an average of 25% between the models of Konnov *et al.* (2011) and Sarathy *et al.* (2012).

For the laminar flame speed, by comparing experimental data with the models, other differences are noted. For butanol, the model of Sarathy *et al.* (2012) has an average difference of 16% from the experimental data in Sarathy *et al.* (2009), while the previous model (Sarathy *et al.*, 2009) presents an average difference of 4%; comparing with the experiment of Liu *et al.* (2011), the model of Sarathy *et al.* (2012) shows an average difference of 5%, while for the previous model, 11%. For ethanol, the average difference between the model of Marinov (1999) and the experiment of Konnov *et al.* (2011) is of 17%, while for the model of Konnov *et al.* (2011), 15%, and for the model of Sarathy *et al.* (2012), 11%; comparing with the experiment of Liao *et al.* (2007), the differences are of 13% for Marinov (1999), 22% for Konnov *et al.* (2011) and 8% for Sarathy *et al.* (2012).

4. CONCLUSION

In the present work, chemical kinetics models could be evaluated, and their usage in calculations for multiple fuels led to interesting results.

First of all, the models for ethanol/air combustion showed very different values from each other, both in terms of flame thickness and laminar flame speed, and also compared to experimental data. The model of Sarathy *et al.* (2012), used for evaluating the blends, presented a significant discrepancy when compared to the experimental data, which means that the model is not very suitable for ethanol. On the other hand, models for n-butanol did not present these differences, therefore, it can be concluded that they are both suitable for n-butanol simulations. This means that, for the blends tested, values may differ from the reality.

For future works, a new scheme should be developed, by combining the scheme of Sarathy *et al.* (2009) and that of Marinov (1999) or Konnov *et al.* (2011). Also, counter-flow flame simulations should be done, in order to generate results in a configuration closer to that of the real burner to be used in the experimental part of the research.

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