

# Comparative Investigation of Ethanol and Butanol Combustion Profiles in an Internal Combustion Engine

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## Abstract

In this work, a systematic study aiming to compare the combustion profiles of butanol and ethanol was performed. Mechanisms for ethanol and butanol combustion processes have been analyzed at high and low temperature conditions. Ignition delay times decrease from 1.5 to 0.04 ms, for both ethanol and butanol, in the temperature range from 1200 to 1500 K. The behavior of these fuels in an internal engine machine has been assessed in two processes of the Otto cycle: the adiabatic compression and the isochoric combustion. Moreover, implications to the atmospheric chemistry and pollutants generation are also discussed. This work suggests that both fuels have similar characteristics of combustion, and the substitution of ethanol by butanol can be feasible, with slight modifications related to ignition.

## Introduction

Attempts to avoid the dependence on fossil fuels and the search for sustainable and renewable energy sources are issues of great importance, worldwide [1]. Ethanol is, up to date, the most used biofuel, despite some disadvantages as high hygroscopicity, corrosivity and vapor pressure [2]. An alternative fuel is butanol, which can be produced from the biomass through a fermentative process [3]. The energetic content of butanol is significant higher than that of ethanol, approaching the value found for gasoline [4]. Since butanol has an increased molecular chain with respect to ethanol, the stoichiometric combustion requires more oxygen and, consequently, a higher air/fuel ratio. Butanol vapor pressure is lower than ethanol vapor pressure, and the evaporative loss of the former is significantly decreased [5]. The vaporization enthalpy is approximately equal to that of gasoline and lower than that of ethanol, allowing the efficient ignition in internal combustion engines, even in cold days or scenarios [5]. The octane number is close to the gasoline octane number, and lower than the corresponding value of ethanol [5]. Moreover, butanol is less corrosive and hygroscopic than ethanol [5,6].

Despite the advantages of butanol over ethanol, a systematic and comparative study of the combustion profiles is needed. Moreover, and prior to its implementation in light vehicles, the investigation of the atmospheric implications of the adoption of butanol as a light vehicle fuel, is recommended [7,8].

The main goal of this work is the investigation of the combustion kinetics of ethanol and butanol and the assessment of the possible adoption of butanol as an alternative fuel. Risk analysis of the atmospheric implications and pollution impact is foreseen. In order to reach these goals, modified chemical models for combustion of ethanol and butanol have been adopted and the concentration profiles of the most important *species* in these mechanisms are analyzed.

## Computational Methods

The kinetic models proposed by Marinov [9] and Dunphy [10] and Mounaim-Rousselle [11], for ethanol and butanol combustion, respectively, slightly modified to account for the NO<sub>x</sub> formation, have been used to simulate the combustion profiles of these biofuels, assessed at both high and low initial temperatures. The simulations at high temperatures were performed at constant volume. The simulation at low temperatures was performed in order to analyze the behavior of these fuels in two processes of the Otto cycle, the adiabatic compression and isochoric combustion. This is a first approach to evaluate, from a theoretical method, the operation of an internal combustion engine. The Kintecus® software [12] has been adopted, using the numerical method DVODE to integrate the coupled ordinary differential equations.

## Results and Discussion

The simulations at high temperatures were performed with initial pressure of 1 atm, constant volume, initial temperature varying from 1000 K to 1500 K and equivalence ratio equal to 1 (*i.e.* stoichiometric mixture), where the oxygen comes from a mixture of 21% of O<sub>2</sub> and 79% of N<sub>2</sub>. At these conditions the combustion ignition is spontaneously observed, without the need of a physical or chemical induction.

In order to quantify the ignition delay time, this instant was assumed as the maximum point in the curve representing the first derivative of the system temperature in relation to the time, as shown in Figure 1. This derivative was numerically evaluated from the central finite difference method.

This procedure for the determination of the ignition delay time has been applied after the simulation of the combustion of butanol and ethanol at high temperatures, aiming to compare the results of both of them.

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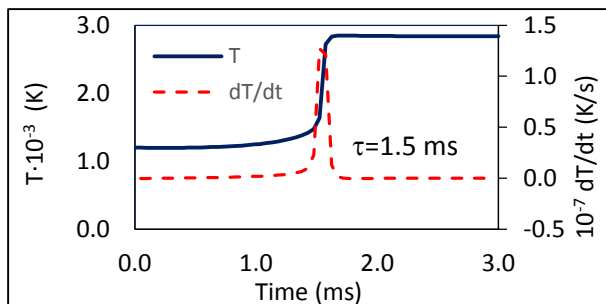


Figure 1: Determination of the ignition delay time,  $\tau$ .

As can be seen from Table 1, the models suggest indistinguishable profiles of the ignition delay time for temperatures above 1200K, the ignition delay time for butanol being slightly greater than that for ethanol at lower temperatures. For temperature values below 1000 K, an ignition time smaller than  $10^{-2}$  s was not observed, suggesting that, at this temperature range, the combustion reaction should be induced.

Table 1: Ignition delay times (in ms) for butanol and ethanol combustion at high temperature values.

T (K)	Ignition time (ms)	
	Butanol	Ethanol
1000	60	27
1100	8.0	5.3
1200	1.5	1.2
1300	0.38	0.31
1400	0.11	0.11
1500	0.040	0.047

For the simulation of the combustion of butanol and ethanol in an internal combustion engine, we have first assumed that the piston was filled with air (21%  $O_2$  and 79%  $N_2$ ) and the biofuel with equivalence ratio equal to 1, pressure of 1 atm and temperature of 298 K. Then the compression was assessed for six compression rate values, varying between 7:1 and 12:1. The ideal gas model and adiabatic, reversible and isentropic compression conditions were assumed. In the standard thermodynamic equation for such compression process, the specific heat at constant volume ( $c_v$ ) values for the air-butanol and air-ethanol mixtures ( $26.1 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  and  $25.9 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ , respectively) were used. The results of the compression are listed in Table 2, the final states of both mixtures being almost the same, due to the similarity of their  $c_v$  values.

After compression, the temperature is still below the necessary for the combustion to occur spontaneously (1000 K), even though the pressure has been enhanced. In light vehicles, the ignition is done by a spark. Considering a theoretical approach for such induction, it was assumed that the main consequence of the spark is the dissociation of the  $O_2$  to oxygen atoms.

Table 2: Final temperature (K) and pressure (atm) values, after the adiabatic and reversible compression, as a function of the compression rate (CR).

CR	Butanol		Ethanol	
	T (K)	P (atm)	T (K)	P (atm)
7	553.7	13.0	556.7	13.1
8	577.7	15.5	581.1	15.6
9	599.8	18.1	603.6	18.2
10	620.3	20.8	624.3	21.0
11	639.4	23.6	643.7	23.8
12	657.3	26.5	662.0	26.7

Therefore, in order to simulate the isochoric combustion, after the adiabatic compression, an initial value for the O atoms was set in the chemical models, resulting from the dissociation of 5% of the  $O_2$  in the air-ethanol mixture, and 5% and 6% of the  $O_2$  in the air-butanol mixture. Then the operational parameters, ignition delay time, final temperature and pressure in the system, as well as the formation of nitrogen oxides ( $NO$ ,  $N_2O$ ,  $NO_2$ ,  $NO_3$  and  $N_2O_3$ ), aldehydes and the ratio between carbon monoxide and carbon dioxide (which are important parameters for the Atmospheric chemistry and pollution) could be analyzed.

As can be seen from Figure 2, the increase of the compression rate causes a drastic reduction in the ignition delay time. This is in good agreement with the expected behavior, since at higher compression rates the temperature and pressure are also higher, favoring most reactions in the combustion model. Moreover, there is a large discrepancy in the ignition delay times for butanol and ethanol with 5% of  $O_2$  dissociated, being the ignition time of butanol higher than that of ethanol. This is, at least qualitatively, in agreement with the results obtained at high temperatures for 1000K and 1100 K. It can be also seen from Figure 2 that the mechanism for the combustion of butanol is highly sensitive to the initial concentration of oxygen radicals, since the increase of the percentage of dissociated molecules from 5% to 6% has caused a significant decrease in the ignition delay time. With 6% of the initial  $O_2$  content dissociated, the ignition times of butanol approaches the ignition times of ethanol, considering 5% of the initial  $O_2$  content dissociated. Therefore, these different fractions of dissociated  $O_2$  molecules were assumed for each combustion model. According to these preliminary results, it can be inferred that the replacement of ethanol by butanol in an internal combustion engine may be feasible with slight modifications related to ignition.

Regarding the increase of the temperature in the system, as can be seen from Figure 3 that as the compression rate increases, the final temperature resulting from the combustion of butanol and ethanol tend to the same value. Even though the combustion of butanol ignited by dissociation of 6% of  $O_2$  showed temperature values higher than the ethanol combustion, the difference does not exceed 0.63% of the ethanol

combustion final temperature, suggesting a negligible difference.

The difference of the pressure values at the end and at the beginning of the combustion tends to increase with the enhancement of the compression rate for both biofuels, as shown in Figure 4. Furthermore, the pressure difference caused by the combustion of butanol was not sensible to the initial concentration of O atoms, and almost the same values are found for the ethanol combustion, which can be a good indicative that a spark ignition engine using butanol should have the same power of a similar engine using ethanol.

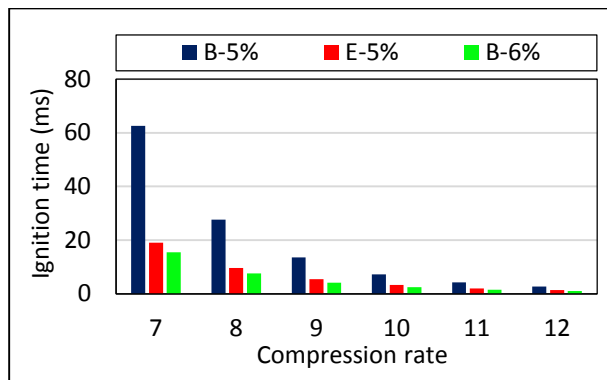


Figure 2: Ignition delay times (ms) for Butanol (B) and Ethanol (E) combustion, as a function of the compression rate.

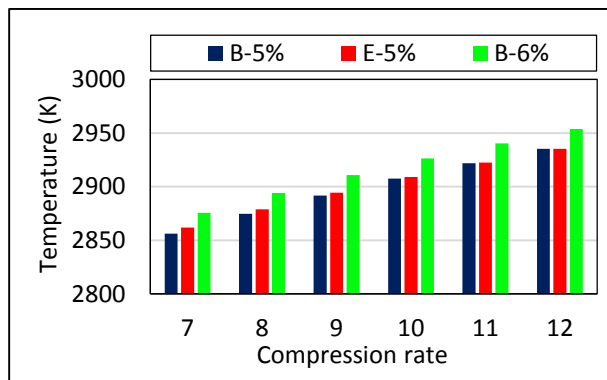


Figure 3: Final temperature values after the combustion of Butanol (B) and Ethanol (E), as a function of the compression rate.

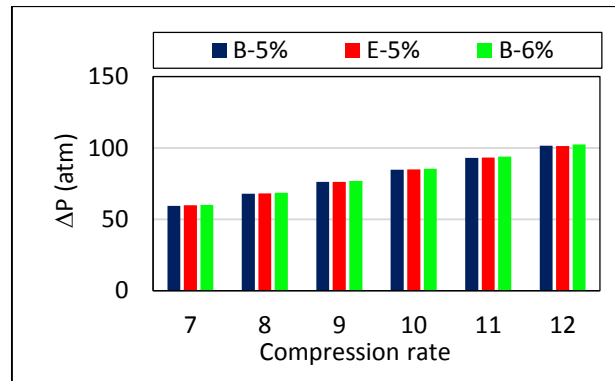


Figure 4: Differences of pressure values at the instants immediately after the ignition delay time and after the adiabatic compression, for Butanol (B) and Ethanol (E) combustion models, as a function of the compression rate.

As can be seen in Figure 5, the ratio between carbon monoxide and carbon dioxide concentrations was shown independent of the compression rate. However, higher values were found for the ethanol combustion suggesting that butanol should show an environmental advantage over ethanol, as a fuel.

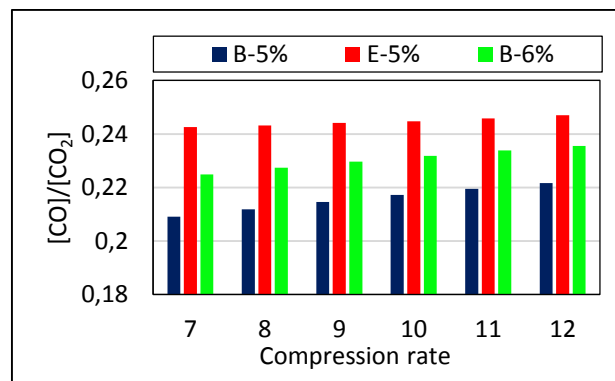


Figure 5: Ratio between the concentrations of carbon monoxide and carbon dioxide after the combustion of Butanol (B) and Ethanol (E), as a function of the compression rate.

So as the carbon monoxide and carbon dioxide concentration ratios, the formation of nitrogen oxides ( $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_2$ ,  $\text{NO}_3$  and  $\text{N}_2\text{O}_3$ , globally abbreviated as  $\text{NO}_x$ ) was also independent of the compression rate, as shown in Figure 6. The combustion of ethanol has yielded the lowest  $\text{NO}_x$  concentration values. Moreover, in the mechanism for butanol combustion, the  $\text{NO}_x$  concentration values have not demonstrated any sensitivity with respect the initial O atoms concentration.

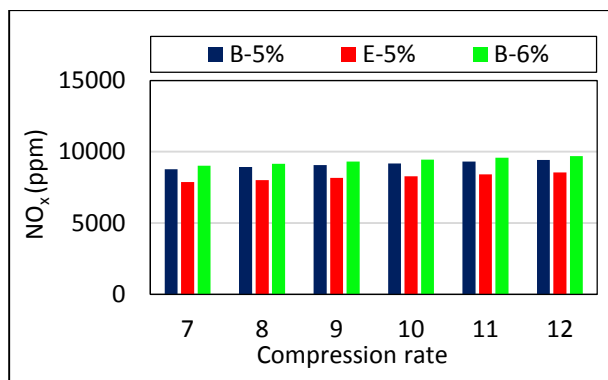


Figure 6: Final concentrations of NO<sub>x</sub> (in parts per million, ppm), after the combustion of Butanol (B) and Ethanol (E), as a function of the compression rate.

The formation of aldehydes (formaldehyde, acetaldehyde and propionaldehyde, the latter only present in the butanol combustion model) slightly increases with the increase of the compression rate for both fuels, as can be seen from Figure 7. The highest concentration values of these pollutants have been observed in the ethanol combustion. The mechanism for the combustion of butanol has showed to be slightly dependent on the initial concentration of O atoms.

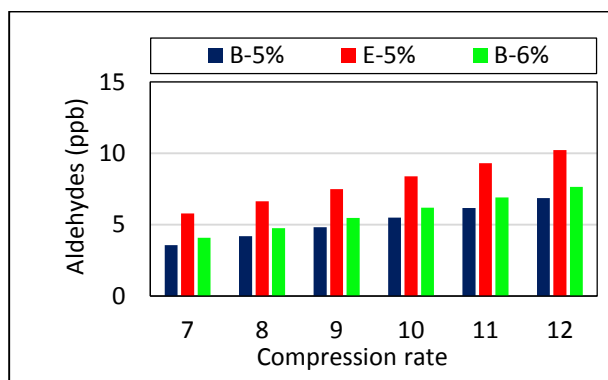


Figure 7: Final concentration values of aldehydes (in parts per billion, ppb) after the combustion of Butanol (B) and Ethanol (E), as a function of the compression rate.

## Conclusions

Ethanol shows some disadvantages as a biofuel, such as hygroscopicity, low flash point, high vapor pressure and corrosivity and the substitution by butanol is under discussion. In this work, a systematic study aiming to compare the combustion profiles and efficiency of butanol and ethanol was performed. Mechanisms for ethanol and butanol combustion processes have been analyzed at high and low temperature conditions. A high temperature values (1000 and 1100 K) the ignition delay times of butanol were slightly higher than that of ethanol, whereas for temperature values in the range from 1200 to 1500K, both fuels have shown indistinguishable profiles.

At low temperature values, the behavior of these fuels in an internal engine machine has been assessed in two processes of the Otto cycle: the adiabatic compression and the isochoric combustion. After the adiabatic

compression, both fuels showed very similar final conditions of pressure and temperature. In order to simulate the combustion, a percentage of the initial O<sub>2</sub> content have been considered dissociated, as a consequence of the spark in a spark ignition engine. The results of the ignition delay time at low temperatures have demonstrated that the mechanism for the combustion of butanol is highly dependent on the initial concentration of the dissociated O<sub>2</sub> molecules. The final pressure and temperature have found to be very similar for both fuels. Regarding the environmental issues, butanol has shown to be less pollutant in relation to the aldehyde formation and the ratio between carbon monoxide and dioxide. However, the formation of nitrogen oxides from the butanol combustion was slightly higher than from the combustion of ethanol. This work finally suggests that both fuels have similar characteristics of combustion, and the substitution of ethanol by butanol can be feasible, with slight modifications related to ignition.

## Acknowledgements

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