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# A SIMPLIFIED MODEL FOR COMPRESSION-IGNITION INTERNAL COMBUSTION ENGINES ANALYSIS BY USING DETAILED CHEMICAL KINETICS

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*Abstract. Compression-ignition internal combustion engines are widely used in the transportation and agricultural industry sectors. However, it is known that they are responsible for much of the environmental and urban pollution. Also, since fossil fuels come from limited sources, there is a need to look for new sources, more viable and less polluting. In this way, many studies have been done, attempting to new techniques to improve the combustion and utilization of fuels from renewable sources that may cause less environmental impacts, such as ethanol. This work aims to numerically study a simplified compression ignition engine, using diesel / ethanol blends as fuel. A diesel fuel surrogate was chosen to represent the diesel oil, the ethanol content was varied in 7 different percentages (from 0.0% to 15.0% ethanol vol.% with $\Delta 2.5\%$), and varying the engine speed (from 2500 to 4000 rpm with $\Delta 100$ rpm). In order to understand the effect of the multiple injection technique, three injection strategies where defined. Numerical simulation was performed using a detailed kinetics mechanism using an in-house-code over Python / CANTERA platform. After results, analysis of the expansion power and emissions of formaldehyde, carbon monoxide and nitrogen monoxide were performed. The analyses were made based on some simplifying hypotheses, so improvements can still be made in order to obtain more accurate results.*

*Keywords: Diesel surrogate, Ethanol, Compression-ignition internal combustion engines, Detailed chemical kinetics, CANTERA.*

## 1. INTRODUCTION

Since the development of ethanol as renewable fuel source, going through the Proálcool period in Brazil, ethanol studies for use and optimization in internal combustion engines (ICE) have been deepened in order to apply it as an efficient and economically viable alternative fuel source. Its bias, in addition to economic, aims to minimize the emissions effects, since ethanol is an alternative to fossil fuels, which are related to the emission of carbon dioxide ($CO_2$), the main substance that contributes to the greenhouse effect. It is also known that oil is a limited source and the use of ethanol helps to extend its useful life (Leite and Leal, 2007). Studies on the use of ethanol in compression ignition internal combustion engines (CI-ICE) have been discussed in recent decades, and some techniques are already developed and can be divided into three categories: ethanol fumigation, double injection system and mixtures of ethanol and diesel. However, the use of ethanol has some limitations, such as an increase in the chemical ignition delay, which prevents that the fuel/air mixture burns easily, resulting in a negative impact on the performance of CI-ICEs (Şahin and Durgun, 2009). On the other hand, it is also known that ethanol has a high octane index and can resist high compression rates, which is good for CI-ICEs that operate at high rates (Brunetti, 2012). Compression ignition combustion is a very complex process that depends on several factors: (a) the fuel physical and chemical characteristics, (b) the combustion chamber geometry/design, (c) the fuel injection system as well as the spray behavior, among others. The most relevant factor in energy conversion efficiency is fuel feeding process, which must be fast enough and at the most suitable crankshaft angle, and for that, an efficient injection system is needed, which injects an appropriate amount of fuel mass at high speed and pressure, among other characteristics (Heywood, 1988). In order to improve this process, many researchers have been studying injection strategies, including the main ones: variation in injection pressure, injection rate shaping, injection timing and multiple injections (Mohan *et al.*, 2013). Thus, given the limitations to the use of ethanol in relation to its physical and chemical properties, it can be seen that there are already many strategies that can mitigate these limiting factors. CI-ICEs, also called "diesel engines", are still in improvement process in order to improve thermal efficiency with the use of ethanol, however, the growing demand to use fuels from renewable and less polluting sources should lead the automotive sector to invest

more and more in adaptations and improvements geared towards to ethanol use. In view of all the reasons mentioned, the present work sought to numerically analyze the operation of a simplified CI-ICEs, using a mixture of diesel and ethanol, also applying the multiple injection technique, in order to better understand the potential benefits as well as the limitations of the use of ethanol in this type of engines. A mixture of three chemical species was used as "diesel surrogate" and ethanol was then added in order to understand its effect in the engine operation. For that, a script native to CANTERA (Goodwin *et al.*, 2018) was adapted for the purposes of this work. Thereby, numerical simulations of a simplified CI-ICE involving detailed chemical kinetics were made, aiming in this way to direct the study more focused on the chemical kinetics interaction between diesel and ethanol when both fuels are present in the engine cylinder. In results, the analysis of the ignition delay of mixtures, expansion power, and emission of the chemical species formaldehyde, carbon monoxide, and nitrogen monoxide are presented.

## 2. THEORETICAL BACKGROUND

### 2.1 The operation of CI-ICE and use of diesel and bio-diesel

Compression ignition internal combustion engines, also known as diesel cycle engines, are classified as alternative engines, they are used in vehicles that require high torque, normally applied in road transport vehicles, such as trucks and buses. The goal of a good diesel fuel, in function of its physic-chemical properties, is to promote the autoignition as fast as possible with high compression rates in order to achieve high thermal efficiency and low as possible pollutant emissions. The engine always operates at maximum volumetric efficiency, thus, what is controlled is the amount of fuel mass injected, that the bigger it is, the bigger the torque will be. However, the mass is restricted in view of a lean fuel/air mixture for maximum combustion efficiency, avoiding unburned fuel (Heywood, 1988). The diesel engine can run in a two- or four-stroke cycle. Details and a very complete explanation about the strokes for each system can be found in literature (Heywood (1988); Martins (2013); Brunetti (2012); Merker *et al.* (2012) and references therein). The fuel injection is done with control, in such a way that the exact amount is introduced, and also at the most appropriate angle, so that high combustion efficiency is achieved, high utilization of the work generated, smooth combustion to reduce noise, among other reasons. The quality of fuel ignition is a determining factor for compression ignition engines, which require easy ignition. It is measured by the cetane number – (CN), the property of a fuel that determines its capacity to ignite. Physically, the CN is related to the time between the start of fuel injection and the start of combustion and is called "diesel ignition delay time" (Diesel-IDT). In cases of high CN, the ignition delay is less than for fuel with low CN. The delay implies a shorter firing period, increasing the proportion of incomplete firing and, consequently, a higher specific consumption. This condition is also undesirable because it favors emissions of pollutants such as carbon monoxide (CO) and nitrogen oxides ($NO_x$), whose formation increases at high temperatures. Larger and more linear carbon chains, as in the case of alkanes and alkenes, have a higher CN because they are more susceptible to fragmentation by temperature, facilitating auto-ignition at lower temperatures (Brunetti, 2012; Heywood, 1988).

### 2.2 Combustion models and Detailed chemical kinetics

For numerical simulation of combustion several models can be used, each one with its specific characteristics and detailed approach to the combustion process. Their differences also result in data processing capacity, which means using them for different response time needs. The zero-dimensional (or simplified thermodynamic) model is the simplest, it simplifies the combustion chamber as being ideally mixed at each point in time and is based on empirical approaches to the rate of combustion. Heywood (1988) describes a simplified engine using a zero-dimensional model for the combustion process. The quasi-dimensional (or phenomenological) model is capable of spatially subdividing the combustion space into zones of temperature and composition. It differs from the thermodynamic model in that, in addition to combustion, it is able to calculate the formation of pollutants, depending on important physical and chemical phenomena such as spray dispersion, mixture formation and reaction kinetics. The third and most complex model is the multi-dimensional that uses Computational Reactive Fluid Dynamics (CRFD) in order to fully solve all the transport properties including turbulence. In this model, it is possible to obtain more detailed results, since in its calculation processes the most diverse phenomena are considered, such as flow in the cylinder, exhaust gas recirculation, charge change, internal flow of the nozzle, among others (Merker *et al.*, 2012). Independently of the combustion model used for engine simulation, it should be necessary any kind of approach for the reaction rate (or energy release). Simple approaches focus on chemical equilibrium or other less complex methods, advanced approaches involve chemical kinetics with global, reduced or detailed kinetics models, in this last case containing thousand elementary reactions among hundred chemical species (Cancino, 2009). The difference between the mechanisms is due to the number of simplifications assumed in the set of reactions. The description by means of detailed mechanisms is much more complex in relation to global mechanisms. Detailed kinetics models provide more in-depth information into the time and spatial evolution of the concentration of chemical species in a combustion system. A well structured detailed kinetics model must be able to describe all the stages of the kinetics process, beginning with the pyrolysis / thermal decomposition of the fuel, followed by the total or partial depletion of the fuel, formation

and consumption of intermediate species and finally describing the formation of saturated combustion products (Cancino, 2009). In order to achieve the objective of this work, the use of a detailed kinetics mechanism is seen as a viable and more efficient way of obtaining valuable results. The detailed kinetics mechanism of pyrolysis, partial oxidation and combustion of hydrocarbons and oxygenated fuels developed by The CRECK Modeling Group, which has a total of 484 species among 19341 reactions (Ranzi *et al.*, 2012) was used in this work.

## 2.3 Diesel surrogates and Detailed kinetics model used in this work

For more than 50 years, computational models have been developed and improved rapidly over the years. For chemical kinetics models, this accelerated growth is relevant due to the complexity and quantity of chemical species present in fuels (real or surrogate fuels) (Westbrook *et al.*, 2005; Cancino *et al.*, 2011). Fuels are composed by hundreds of hydrocarbon and its kinetics is difficult to characterize through kinetics mechanisms, which is not possible due to current computational resources and software limitations. Because of this, surrogate fuels have been developed, with few species to facilitate the study of combustion behavior, which are able to imitate the general behavior of real fuels (Cancino *et al.*, 2020; RANZI *et al.*, 2014; [da Silva Jr.] *et al.*, 2019). To be a good fuel surrogate, the mixture of chemical species needs to represent the chemical and physical characteristics of the fuel. Chemical characteristics include ignition behavior, molecular structures, C / H / O content among others. Physical characteristics include parameters of volatility, density, viscosity, and diffusion coefficients among others. These properties are necessary to adequately predict the spray, evaporation and transport of species that determine the temperature of the reaction mixture and the species concentration fields. The main chemical classes of the petroleum-based diesel fuel components are *n*-alkanes, *i*-alkanes, cyclo-alkanes and aromatics. The carbon numbers of the components vary approximately from C10 and C22 (Pitz and Mueller, 2011). The detailed kinetics model used for all simulations in this work was proposed by Ranzi *et al.* (2012). For its validation, they have developed and validated some works to reach the current version. In two previous studies ((Faravelli *et al.*, 2003) and (Frassoldati *et al.*, 2003)) the basis of the mechanism was developed and tested to investigate the interactions between nitrogen oxide (NO) and hydrocarbons during thermal oxidation, at low and high temperatures respectively. The model was validated by comparison with experimental measurements from different research groups, referring to various hydrocarbon fuels under different operating conditions. According to the authors, the model shows good agreement across the investigated range of conditions, confirming the validity of the kinetics assumptions and their reliability. Later on, Cuoci *et al.* (2009) continued to improve the mechanism by investigating unstable effects on the formation of soot and nitrogen oxides ($NO_x$), imposing harmonic oscillations in the deformation rate of various counterflow diffusion flames fed with propane. For the validation of the mechanism in the 2012 version, Ranzi *et al.* (2012) experimentally collected, reviewed and consolidated a large amount of experimental data on laminar flame speeds of hydrocarbons and oxygenated fuels that were reported from 1990 to 2011, reproduced and analyzed them using the mechanism and, thus, were able to evaluate additional points of improvement.

## 3. METHODOLOGY

### 3.1 The in-house computational tool for analysis

As stated above, a Python script native to CANTERA (Goodwin *et al.*, 2018) was adapted for the research purposes of this work. The adapted script simulates an HCCI 4-stroke compression ignition engine and modifications were made in order to adapt it to the needs and objectives of the present study, such as, for example, the characteristic of multiple injections as well as the piston speed. This program has been improved by the Vehicular Systems Energy Efficiency Research Group, of the Internal Combustion Engines Laboratory - LABMCI / CTJ / UFSC in a collaborative effort by different users and researchers of the group. The program (Python script) executes the following logical-for-solution steps: (a) kinetics model database interpreter, (b) input parameter, (c) engine solution and, (d) data writing for data post processing. As input data, it was necessary to define parameters and geometric relationships normally used to characterize the engine operation. Formulas to obtain piston speed were added instead of those used by the native file on CANTERA. The entire theoretical basis and nomenclatures adopted were based on Heywood (1988). The cylinder in the CI-ICE is interpreted as an adiabatic - variable volume chemical reactor, compression ratio is defined as the ratio between the maximum and minimum volume of the cylinder, represented by the equation $r_c = \frac{V_d + V_c}{V_c}$ and, rearranging this equation, the clearance volume ($V_c$) is found. The stroke ($L$) was defined by $L = \frac{V_d}{A_p}$, with $A_p$ being the piston crown surface area. The cylinder volume ($V$) at any crankshaft position is defined by Equation (1) as follows:

$$V = V_c + \frac{\pi B^2}{4}(l + a - s),  \tag{1}$$

where $s$ is the distance between the crank axis and the piston pin axis given by Equation (2)

$$s = a \cos\theta + (l^2 - a^2 \sin^2\theta)^{1/2}.  \tag{2}$$

The crank angle ($\theta$) is defined by the equation $\theta = 2\pi N$, as a function of the engine rotation, since the crank rotational speed is $N = rpm/60$. For the calculation of the instantaneous piston velocity ($S_p$), equation $S_p = \frac{d_s}{d_t}$ was applied with the differentiation of Eq. (2), as Heywood (1988) shows, and it was multiplied by the average piston speed, given by $\bar{S}_p = 2LN$, resulting in the Equation (3):

$$S_p = \bar{S}_p \frac{\pi}{2} \sin\theta [1 + \frac{\cos\theta}{(R^2 - \sin^2\theta)^{1/2}}] \qquad (3)$$

For the solver, two important initial parameters that program presents are the number of revolutions and time steps, which were defined as 8 and 100000, respectively. The value of revolutions means that a total of 4 cycles of a 4-stroke internal combustion engine will be simulated and the time step represents the refinement of simulation, that is, the number of calculations made over time so that results have more real values and continuous behavior. When the simulation starts, the program starts all programmed calculations and combustion processes using chemical kinetics reaction mechanisms. The program understands the mechanism as an "object" in gas phase. To load it, its initial and final states, such as temperature and pressure, are defined. The states of connection devices are also defined, which are: injectors, valves, piston and cylinder. The injectors are modeled as mass flow controllers that act separately by injecting fuel into the gas phase, the piston is modeled as a movable wall and cylinder as an ideal gas reactor. In addition, the valve is a flow device with a mass flow rate that is in function of pressure drop across it. To simulate combustion, the program has a function that creates a network of reactors (the engine cylinder) so that they move forward on time, for each time step and computing the chemical state depending on the new thermodynamic condition imposed by Equations (1,2 and 3), of this form, the engine combustion model in the script is a simplified form of a closed system thermodynamic model, with the following simplifications: (a) Regarding energy conservation, the energy loss to walls, loss of pressure generated by the looseness of piston rings (or *blow-by*) and energy consumed by the vaporization of fuel are not considered. (b) Regarding mass conservation, the mass loss by *blow-by* is not considered, and the mass of fuel is completely evaporated. (c) Regarding the spray, the in-house code does not calculate any spray or fuel atomization/vaporization process, instead, the fuel is injected into the cylinder in gas phase. Also, as the liquid fuel injection process does not exist, no physical effects that may occur are considered, such as nozzle cavitation. Another consideration is that head losses are not considered, only the friction coefficient of valves was used, however, with a value too low to represent negligible friction losses. These simplifications are made because the program does not consider energy transfer across system surfaces, that is, it is an adiabatic system. The chemical solver of CANTERA (Goodwin *et al.*, 2018) internally pursues solution tolerance parameters, related to absolute (atol) and relative (rtol) tolerances that are used when integrating chemical reactor equations. In this work, the values of $1\text{x}10^{-16}$ and $1\text{x}10^{-12}$, respectively were used. As the simulation progresses, the program performs calculations at each defined time step (which also represents an angular position of crankshaft) and, if there is any value outside established tolerances, it understands that it must refine the time step, making results remain within limits. At the end of simulation, the output data is recorded and reports are generated with the programmed parameter values. Despite the strong phenomenological simplifications made along the engine model, the authors consider that tendencies as well as the main characteristics related to kinetics process and engine performance are relatively well captured.

### 3.2 Fuel surrogates used in this work

For this simulation, the kinetic mechanism to represent combustion was defined, which makes calculations from a certain number of chemical species (surrogates) that represent as closely as possible the physical, chemical, combustion and emissions properties of a given real fuel. Thus, when looking for validation of a surrogate, tests of some properties are made to verify the correlation between them. Currently, the main properties measured to validate surrogate fuels are ignition delay time (IDT), species concentration and laminar flame speed. To validate kinetic mechanism models, these properties are simulated to compare with experimental tests and to identify the proximity of values between them. Also, is very important the experimental test of surrogates combustion and comparison with reference fuel, being able to analyze their behavior in general.

Table 1. Diesel Surrogates

| Species | Author/year |
|---|---|
| 70% *n*-decane / 30% 1-methylnaphthalene | Ramirez L. *et al.* (2010) |
| 41.3% *n*-hexadecane / 36.8% *iso*-cetane / 21.9% 1-methylnaphthalene | Bai *et al.* (2020) |
| 85% *n*-heptane / 15% toluene<br>81% *n*-heptane / 14% toluene / 5% *c*-hexane<br>80% *n*-heptane / 20% toluene<br>81% *n*-dodecane / 14% toluene / 5% *c*-hexane | Liu *et al.* (2017) |
| 41.3% *n*-cetane / 36.8% 2,2,4,4,6,8,8-heptamethylnonane / 21.9% 1–methylnaphthalene | Yu *et al.* (2019) |

Table 1 shows four studies that used diesel surrogates. His studies sought to validate the properties mentioned above. All have had their results relevant and satisfactory compared to experiments. However, surrogates indicated by Liu *et al.* (2017) were chosen due to the fact that they were used in an engine, comparing the experimental tests with the numerical simulations and obtaining good results from the comparison between these tests, among which authors pointed out *n*-dodecane (81%), toluene (14%) and cyclohexane (5%) as the most appropriate diesel surrogates fuels. Table 2 shows the properties of chosen diesel and ethanol surrogates. Vaporization heat and auto-ignition temperature of diesel surrogates were not mentioned by authors, however, in the work of Elzahaby *et al.* (2018) the values of these properties were presented as 0.27 MJ/kg and 254°C, respectively, (as well as all properties for ethanol) therefore, they were considered as a reference for adopted surrogates.

Table 2. Surrogates Properties

| Properties | Diesel: $C_{12}H_{26}(81\%)$; $C_7H_8(14\%)$; $C_6H_{12}(5\%)$ | Ethanol: $C_2H_5OH$ |
|---|---|---|
| Cetane Number | 44.3 | 11 |
| Density (kg/m$^3$) | 718 | 790 |
| Lower heating value (MJ/kg) | 44.3 | 28.86 |
| Heat of vaporization (MJ/kg) | 0.27 | 1.11 |
| Autoignition temperature (°C) | 254 | 357 |

### 3.3 Engine parameters analysed

Engine performance parameters as expansion power and emissions were then analyzed in this work in function of ethanol content in the fuel as well as in function of injection parameters. In order to do it, seven ethanol percentages combined to three injection methods were numerically implemented. Injection parameters have been modified using the multiple injection method, which consists of up to three injections. Pre-injection (PI) was established in the injection period between 335° and 345° of a cycle, with 25% of the total injected mass. The main post-injection (MPI) was between 395° and 415°, with 15% of the total mass. The main injection (MI) occurred in the period between 350° and 365° with the rest of the mass injected. Many studies have already been published regarding the effects of this technique, which can be improved by adjusting parameters such as time and start of injections. In their review, (Mohan *et al.*, 2013) showed some techniques adopted by several authors, and among them is the multiple injection. The total fuel mass per cycle was defined as $11.5 \times 10^{-5}$kg. In order to analyze the influence of ethanol on combustion, the simulations were divided into two groups of displaced volume ($V_d$) equal to 400 and 500 cm$^3$ and both were programmed for 1, 2 and 3 steps of injection. The percentage of ethanol in each injection is different. In simulations with 1 injection, the total mass was injected into the MI. In simulations with 2 injections, PI and MI were programmed. For simulations with 3 injections, MPI was 15% of the mass, PI 25% and MI 60%. The ethanol mass was varied in a total of 7 different percentages (from 0.0% to 15.0% ethanol with a 2.5% step), and each percentage have had a variation of the rotation (from 2500rpm to 4000rpm with a step of 100rpm), in a total of 16 different engine speeds. Therefore, a total of 336 simulations were performed for each displaced volume and 672 simulations in total, resulting in a total computational time of 25 days - full time (Computation performed in a personal computer Intel Core i7-5500U CPU @2.40 GHz). Geometrical engine parameters as bore ($B$) = 0.10m, stroke ($l$) = 0.15m and compression ratio $r_c$ = 25 were kept constant for all simulations.

### 4. RESULTS AND DISCUSSION

### 4.1 The impact of the ethanol percentage in terms of ignition delay time

In order to analyze the effect of ethanol on IDT, numerical simulations assuming combustion in a constant volume homogeneous reactor for three fuel/air equivalence ratios ($\phi$ = 0.7 ; 1.0 ; 1.3) were performed. Figure 1, shows the results. The graphs show the IDT as a function of temperature, ranging from 800K to 1200K with $\Delta$50K, for different percentages of ethanol ranging from 0.0% (100% diesel surrogates) to 15.0% (85% diesel surrogates, 15% ethanol) with $\Delta$2.5%. The reactor pressure was set to 20 bar.

As can be seen, graphs (a), (b) and (c) show similar behavior in their curves. It can be seen that the IDT, in the temperature range, has a maximum point just after 1000K for 100% diesel substitute fuel, it decreases with increasing temperature, decreases for lower temperatures but has a minimum point just after the 850K temperature, where it increases again for lower temperatures. This is the well-known Negative Temperature Coefficient (NTC) behavior present in these results because of the high content of normal paraffin (*n*-dodecane, 81%) in the fuel mixture. For CI-ICE the main important information that can be taken from Figure 1 is that the IDT increases with the addition of ethanol to the mixture for the entire temperature range, in the 3 equivalence ratios. Its maximum point moves up to 950K with an increase in the ethanol percentage. This is because ethanol has a low cetane number, and the addition of it decreases the
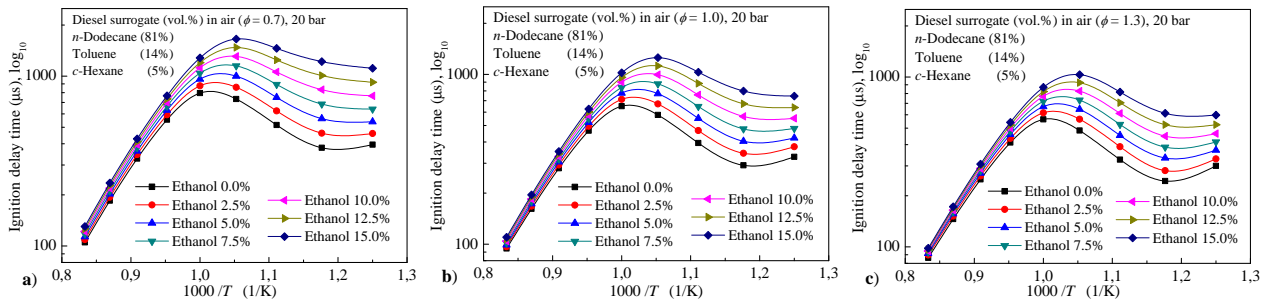
Figure 1. Ignition delay as a function of temperature for different equivalence ratios: a) $\phi = 0.7$, b) $\phi = 1.0$ and c) $\phi = 1.3$.

CN of the mixture and, consequently, increases the IDT. Like the aromatic hydrocarbon group, alcohols have low ignition quality, being one of the reasons for the difficulty of their use in compression ignition engines (Heywood, 1988).

### 4.2 Expansion power

In this subsection the effect on ethanol percentage on expansion power (EP) for two displaced volumes ($V_d$) is discussed. Figure 2 shows the EP graphs for $V_d = 400$ cm$^3$, ($V_d$400) for the 3 fuel injection conditions studied.
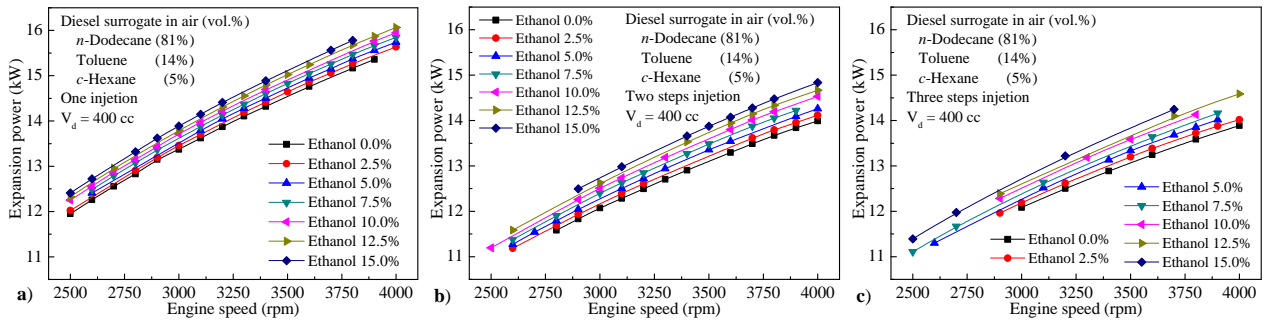


Figure 2. Expansion power $V_d = 400$ cm$^3$: a) 1 injection, b) 2 injections and c) 3 injections.

Figure 2 shows that EP increases for higher ethanol percentages. This can be explained by the fact that, because ethanol has a lower CN than the diesel substitute (Tab. 2), the ignition delay increases with the increase in ethanol mass (discussed in subsection 4.1). According to Brunetti (2012), it is known that with the longest ignition delay, the fuel takes longer to start combustion, accumulating more mass that is then burned and generates a high peak of pressure and temperature. This high pressure makes EP higher for all ethanol percentages. Analyzing the graphs (b) and (c) in Fig. 2, EP is approximately 10% lower for 2 and 3 injections compared to combustion with 1 injection. Injections in different stages do not accumulate as much fuel to be burned at once and, consequently, there are lower EP values. Making the comparison now for the EP with $V_d = 400$ cm$^3$, the graphs in Fig. 3 were made for $V_d = 500$ cm$^3$.
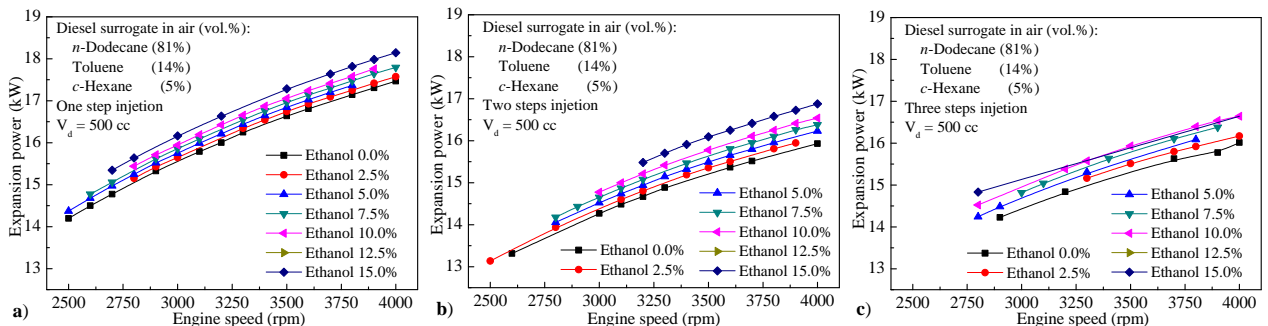


Figure 3. Expansion power $V_d = 500$ cm$^3$: a) 1 injection, b) 2 injections and c) 3 injections.

It can be seen that both Figures 2 and 3 have the same behavior, EP also increases for higher ethanol percentages, and for 2 and 3 injections the EP is less than for 1 injection. Also, for $V_d = 500$ cm$^3$, EP increased in relation to $V_d = 400$ cm$^3$ for all speeds, from a maximum value close to 16.5kW in $V_d = 400$ cm$^3$ to approximately 18.5kW in $V_d = 500$ cm$^3$. Additionally, it can be observed that EP increases as engine speed increases for all cases. Knowing that the fuel mass injected was the same for both the displaced volumes ($11.5 \times 10^{-5}$kg), it is understood that the defined mass has generated a highly rich mixture for $V_d = 400$ cm$^3$, and in $V_d = 500$ cm$^3$ this mixture has decreased from very rich

to closer to the stoichiometric, since in $V_d = 500$ cm$^3$ more air is admitted, leading to more complete combustion and generating greater EP. To confirm this analysis, the equivalence ratio of $V_d = 400$ cm$^3$ (estimated after air was admitted from the closing of the intake valve) was calculated, which presented values between $3.4 < \phi < 1.2$ from lowest to the highest rotation, respectively (portion of air mass admitted with the vacuum that piston generates when going from top-dead-center (TDC) to bottom-dead-center (BDC) is greater with increasing rotation). Therefore, the increase in EP with rotation is due to the combustion closer to the stoichiometric, and the increase in EP to $V_d = 500$ cm$^3$ is also due to more complete combustion for admitting more air to be mixed with the fuel mass. It was considered $11.5 \times 10^{-5}$ kg of fuel because the simulation did not converge to smaller values, and the non-convergence can be explained by the fact that the adopted kinetics mechanism has approximately 20000 reactions and almost 500 chemical species, thus having many degrees of freedom that can influence the convergence. Thus, by varying $V_d$, it was also possible to have an idea of the necessary mass for combustion to occur closer to the stoichiometric, since the program does not automatically adjust fuel mass for different revolutions. Still, there is one more analysis in relation to ethanol. It can be observed that, for both displaced volumes, the expansion power has increased by increasing the percentage of ethanol, which at first may go against common sense, since the energetic power of ethanol (per unit mass) is lower when compared to diesel. In addition to the possible reasons mentioned above, there are others that can support this type of behavior. The fuel mass was kept constant for all simulations ($11.5 \times 10^{-5}$ kg of mixture) as well as the injection angle (or the injection angles in the case of simulations with multiple injections). This can generate the following hypothesis: the engine injection point (numerically) was not at the injection point that generates the maximum torque. When ethanol was added, it began to postpone the start of combustion, bringing the peak pressure closer to maximum torque point, which leads the system to have greater EP. The relevance of ethanol CN in fuel mixture is observed here, since it has a CN of 11, causing the system to ignite a little later, increasing ethanol content and approaching maximum torque point. To confirm this hypothesis, the graph in Fig. 4 was generated with pressure data as a function of the crankshaft angle, from the simulation data with $V_d = 400$ cm$^3$, main injection and 3000 rpm.
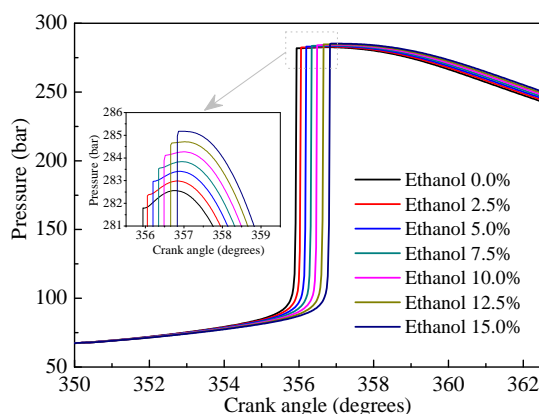


Figure 4. Pressure as a function of crankshaft angle for different percentages of ethanol.

From Fig. 4 is possible to identify how the maximum pressure moves closer to the TDC (360°) with the increase in ethanol percentage. This implies that combustion will do more expansion work, from gases to the piston, when the piston is moving from the TDC to BDC. Considering the inverse, decreasing the percentage of ethanol, the peak pressure moves away from the TDC, and in this case, combustion performs less expansion work, from the gases to the piston, when the piston is moving from TDC to BDC.

## 4.3 Emissions

Formaldehyde is a toxic pollutant that must be controlled due to adverse effects on health and the environmental. Here, its formation is analysed, thus, comprehensive information about its negative effects can be found in Cogliano *et al.* (2005) and Salthammer *et al.* (2010). Figure 5 presents the results of the simulation for $CH_2O$ with $V_d = 400$ cm$^3$.

Figures 5 (a) and (b) with 1 and 2 injections, respectively, show similar behaviors, since the increase in ethanol percentage decreases the formation of formaldehyde, however, the increase in rotation increases emissions. This can be explained by the fact that ethanol increases the pressure and temperature due to the longer ignition delay accumulating fuel to burn (Brunetti, 2012), thus understanding that the pollutant forms more under lower temperature and pressure conditions. With the increase in rotation, there is less time to develop combustion, with greater incomplete burning (which also depends on fuel reactivity, as well as the temperature and pressure level reached in the cylinder), but with little emission difference between rotations. Figure 5 (c), on the other hand, shows the opposite behavior of emissions in relation to ethanol percentages, since emissions are higher with increase of ethanol. Still, the ethanol ranges, from 2.5% to 15.0%, point to emissions much higher than for 1 and 2 injections. In this case, the start of the third injection
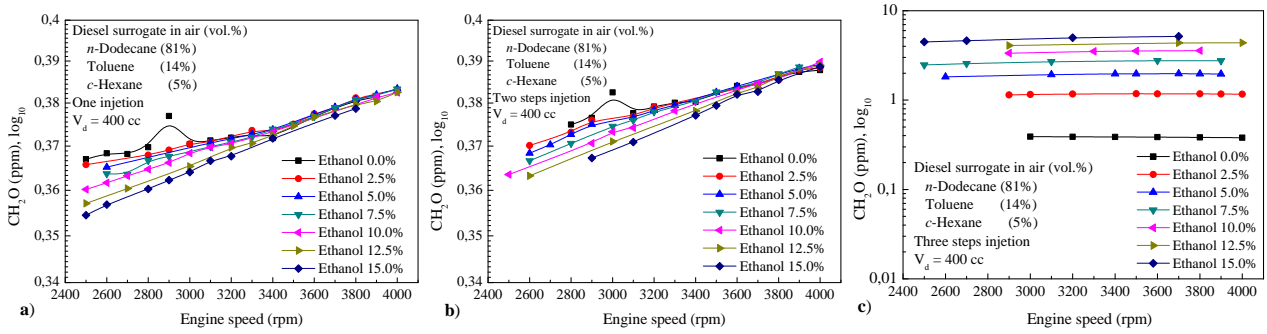
Figure 5. Formaldehyde formation: a) 1 injection, b) 2 injections and c) 3 injections.

is after the TDC and combustion of this late mixture occur more at the end of combustion period, which results in much more incomplete burning than by the increase in rotation, influenced even by greater resistance (higher IDT) of ethanol in mixture. It is understood, therefore, that the pollutant formation in an incomplete burning condition is strongly influenced by ethanol, with the hydroxyl of the ethanol molecule as the greatest influence on the pollutant formation. Also, the total injected mass is divided between the 3 injections, making the average temperature lower in this case than for the conditions of 1 and 2 injections. Thus, it can be seen that the strategy of multiple injections with an injection period after TDC using ethanol can be a limiting factor in terms of emissions, as they are much greater than combustion with pure diesel substitute. The greater presence of ethanol in incomplete combustion and in conditions of lower temperature and pressure favors and has a greater influence on the formation of formaldehyde. Figure 6, bellow, shows the simulations for the 3 fuel injection conditions, in different percentages of ethanol, analyzing CO emissions with $V_d = 400$ cm$^3$.
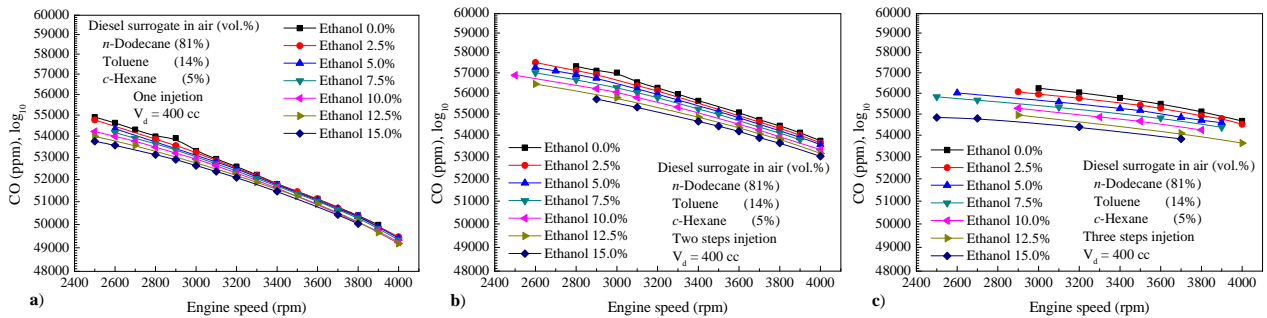


Figure 6. Carbon monoxide formation: a) 1 injection, b) 2 injections and c) 3 injections.

The three graphs in Fig. 6 show similar behavior for CO emission, since the increase in ethanol percentage decreases emissions due to the decrease in mass of diesel substitute, which has a greater number of carbon atoms and thus has a greater influence on pollutant formation. The influence of different injection configurations can be seen in the emissions amount, since for 2 and 3 injections emissions are greater than for one step fuel injection. Analyzing the graphs (a) and (b) in Fig. 6 it can be seen that emissions increase when injection steps increase and the difference in emissions between the lowest and highest rotation decrease. The peak pressure and temperature are higher when injecting fuel in one step, thus, it is seen that the formation of CO is greater under lower temperature and pressure conditions. However, among the three graphs, it is seen that the most favorable condition for greater CO formation is for the lowest rotation in the configuration of 2 steps injection. Therefore, it is understood that there is a more favorable pressure and temperature condition for CO formation since in this configuration the conditions are intermediate. Thus, for CO emissions, the strategy of multiple injections had no greater benefit due to easing pressure and temperature and favoring the pollutant formation. Figure 7 shows simulations for the 3 fuel injection conditions, in different ethanol percentages, analyzing NO emissions.

Analyzing Fig. 7 (a) with one injection, emissions are higher with the percentage of ethanol up to approximately 3000 rpm, after which mixtures with ethanol have lower values. In this case, only with the main injection, we see that ethanol can be used to reduce NO emissions in rotation operations above 3100 rpm. Compression ignition engines operate normally at low speeds, so we see that engines that operate at high speeds and have only the main injection can have lower NO emissions when adding ethanol to the fuel mixture. Looking now at Figure 7 (b) and (c), it can be seen that strategies of 2 and 3 fuel injections do not show a decrease in NO with the use of ethanol, for any engine speed. However, for the entire speed range, the average emissions are lower in both cases compared to combustion with one fuel injection. It is understood, therefore, that NO forms more under conditions of higher pressure and temperature since in 2 and 3 injections the total mass is divided and attenuates these conditions. Thus, the strategy of using pre and post-injection can be used for lower NO emissions, on average. Among the 3 cases, Fig. 7 (b) with pre-injection and main injection shows the lowest
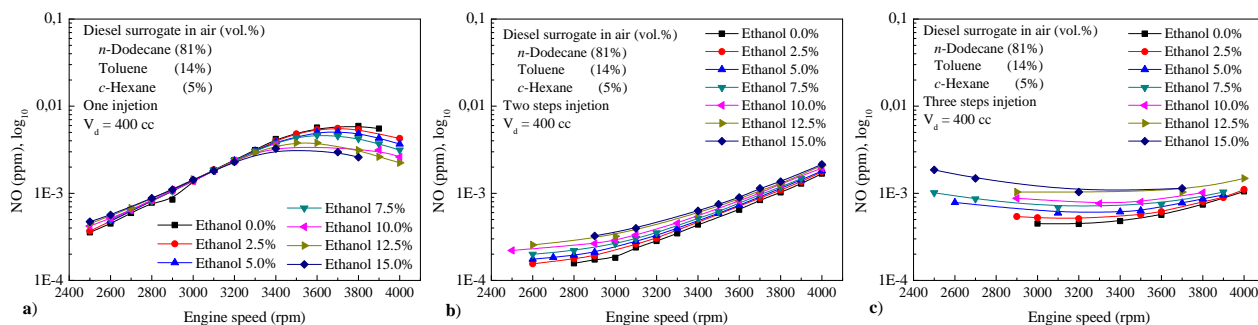
Figure 7. Nitrogen monoxide formation: a) 1 injection, b) 2 injections and c) 3 injections.

average, being below $1\mathrm{x}10^{-3}$ ppm. The higher NO emission values achieved by ethanol mixtures can be explained by the fact that ethanol has increased the pressure and temperature in the cylinder due to the longer ignition delay. Mixtures with a higher IDT lead to a sudden increase in pressure due to the accumulation of fuel (Brunetti, 2012), consequently an increase in temperature.

## 5. CONCLUSSION

In this work, it has been possible to numerically analyze a simplified CI-ICE using detailed chemical kinetics. Mixtures of diesel oil and ethanol surrogates as fuel were used and tendencies on engine operation in terms of engine performance and emissions were obtained. It was seen that ethanol has increased ignition delay generating a higher pressure peak with increase of its percentage in the mixture, and that it increased the expansion power. It was analyzed that the strategy of multiple injections after the TDC can be a limiting in terms of formaldehyde emissions when using ethanol in this late mixture. It was understood that there is a more favorable pressure and temperature condition for CO formation and that multiple injections did not help to decrease it. Also, engines that operate at high speeds and have only the main injection, may have lower NO emissions when adding ethanol to mixture. However, there are some considerations to do due to the simplifying assumptions adopted in this simulation. The $V_d = 400$ cm$^3$ equivalence ratio has shown values between 3.4 $< \phi <$1.2 for the adopted speed range, which represents mixtures rich in fuel well above the standard, thus, it is known that the emission values of the chemical species analyzed are being strongly influenced by the highly rich mixture, which generates much more incomplete burning. Still, all the simplifying assumptions adopted make a big difference compared to real results. For example, it is known that ethanol has greater heat of vaporization than the diesel surrogates, thus, the average combustion temperature could be lower and NO emissions would be lower when using ethanol, however, according to the simplifying hypotheses, there is no vaporization process in the simulations. In this way, the analyses were made taking into account all the simplifications, analyzing only the results generated by the simulation of this work.

## 6. ACKNOWLEDGEMENTS

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