COBEM 2023 27TH INTERNATIONAL CONGRESS OF MECHANICAL ENGENEERING

ABCM Brazilian Society of Mechanical Sciences and Engineering
27th ABCM International Congress of Mechanical Engineering
December 04-08, 2023, Florianópolis-SC, Brazil

COB-2023-0058
VALIDATION OF AN ETHANOL-REDUCED CHEMICAL KINETIC MECHANISM AT SUPERCRITICAL CONDITIONS USING REAL GAS STATE EQUATION

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Abstract.
Several studies have been conducted to find an effective system to reduce particulate emissions from vehicle exhaust gas, which have become a primary source of air pollution in large cities. A promising system uses supercritical combustion, directly injecting fuel over its critical temperature and pressure. Supercritical fluids have a lower viscosity and surface tension than liquids and high diffusion rates, which promotes a uniform mixture distribution, improving thermal efficiency and reducing particulate emissions. This study focuses on supercritical Ethanol as a biofuel option to propose a reduced kinetic mechanism composed of 71 species and 684 reactions obtained by directed relation graph error propagation (DRGEP) and sensitivity analysis for simulating its combustion. This mechanism was validated using Cantera with a cubic Redlich-Kwong (RK) and an ideal (I) equation of state (EoS) through 0D constant-volume auto-ignition delay times (IDT) and an ideal EoS for laminar flame speed (LFS) simulations for pure Ethanol. The IDT results are consistent with experimental data at 10, 30, 50, 75, and 80 atm, in a temperature range of 700 - 1250 K, showing a satisfactory agreement with LFS experiments at 380 - 400 K, 1 - 4 atm and (ϕ) of 0.6 - 1.4.

Keywords: *Chemical Kinetic Mechanism, Supercritical Combustion, Ethanol Mechanism, Ignition Delay Time, Redlich-Kwog.*

1. INTRODUCTION

In recent human history, vehicle logistics, and fossil fuel consumption has rapidly grown due to social development, especially in large metropolises. International attention has been focused on minimizing the impacts of air pollution and vehicle emissions on climate change and population health (Li *et al.*, 2016). Therefore, gas emission and fuel efficiency regulations require clean and highly efficient combustion systems. Improving internal combustion engines' fuel economy, combustion, and emission performance has been vital.

Although an elective technology system to improve the efficiency of gasoline engines is the direct injection of gasoline (GDI) Binder *et al.* (2015), it has a shorter time to mix fuel and air, this can lead to partial uneven mixing, and severe PM emissions problems Mohr *et al.* (2000). Therefore, the main problem is reducing the PM emissions in parallel with improving the thermal efficiency of GDI engines. Zong *et al.* (2004); Piock *et al.* (2011).

Given the low thermal efficiency of GDI engines and particulate problems, a method to achieve a high temperature and pressure environment in the combustion chamber during engine operation is called the fuel's supercritical environment Mayer *et al.* (2000). A fluid or a mixture of fuels is defined as being in the supercritical state if the pressure and temperature exceed all fuel species' critical values.

Supercritical fluids (SCFs) are attractive media for chemical reactions because of their unique properties. According to Liu *et al.* (2017), supercritical fluids exhibit lower viscosities and surface tension than liquids; at the same time, supercritical fluids also present high diffusion rates. Because of those properties, the uniform mixture distribution of fuel and air can effectively improve thermal efficiency and reduce the particulate emissions of the engine when supercritical fuel is injected into a cylinder in a supercritical environment (Song *et al.*, 2020).

Another way to control emissions is to use biofuels in the mixture. In this way, Lee *et al.* (2009) and Szybist *et al.*

(2011) investigated the beneficial use of ethanol as an alternative fuel to control particulate emissions from GDIs, mainly when used in high concentrations. The main finding of their study is that the use of E85 results in 1-2 orders of magnitude reduction in particle emissions relative to GDI fueling with gasoline and E20.

With that in mind, there are many reasons why someone might want to look into the combustion of ethanol. For one, there is a growing need for alternative fuel sources that are renewable and sustainable Heufer *et al.* (2012). Additionally, there is a push to reduce carbon emissions and other pollutants from traditional energy and power sources (hydrocarbon fuels). Finally, there is a need for additives that can help control engine knock Konnov (2009). These needs are rooted in a desire to be more economically and environmentally conscious.

In the literature, several kinetic models provide a comprehensive description of the reaction mechanism of ethanol oxidation. Marinov's mechanism (Marinov, 1999) was one of the earliest detailed models of ethanol oxidation. More recent kinetic models, some derived from Marinov's mechanism, have been published. These models, such as those found in references (Cancino *et al.*, 2010), Lee *et al.* (2012), (Konnov, 2009; Konnov *et al.*, 2011), (Cai and Pitsch, 2015), and (Roy and Askari, 2020), have significantly improved the description of ethanol combustion chemistry. Our study focuses on only a few available kinetic models in the literature. However, as they interest us, we will briefly discuss two recent ones in references (Cancino *et al.*, 2010) and Heufer *et al.* (2012).

According to the research paper by Cancino *et al.* (2010), their kinetic model involves 136 species and 1349 elementary reactions. They combined the mechanisms from Marinov (1999) and the C3 hydrocarbon model from Konnov (2009) to form their model. Additionally, the model incorporates up-to-date rate data for ethanol consumption reactions. It is worth noting that the Cancino et al. model exhibits remarkable conformity with high-pressure shock tube data (10, 30, and 50 bar) for stoichiometric and lean ethanol-air mixtures, which is particularly interesting as an initial start to analyze Ultra-High pressure combustion (supercritical combustion).

Also came an interesting research article by Heufer *et al.* (2012) on the Kinetic Modeling of n-Pentanol Oxidation. The author developed a detailed model of 599 species and 3248 reactions, validated against ignition delay times, speciation data, and laminar flame velocity measurements. The study concludes that the model agrees well with the experiments and allows for a detailed discussion of the differences between alcohols and alkanes.

Also, understanding the speed at which flames burn is essential for ensuring safe and efficient combustion. This is especially crucial when working with fuels like Ethanol (Dirrenberger *et al.*, 2014; Broustail *et al.*, 2011; Bradley *et al.*, 2009; Monteiro *et al.*, 2015) and mixtures that include Ethanol. Researchers have conducted several studies to measure these fuels and mixtures' Laminar flame speed (LFS) using flame front imaging and pressure rise measurements. Some of these studies have focused on pure Ethanol, while others have looked at mixtures with Methane, biogas (Hinton *et al.*, 2018), or n-butanol (Alviso *et al.*, 2022). By analyzing the parameters of flame speed, researchers can better understand how different fuels and blends will burn and optimize combustion for safety and efficiency.

In contrast, knowing fuel's ignition and combustion process at supercritical conditions requires a detailed study of chemical kinetics and its properties in this condition. Beyond that, simulation and analysis of high-pressure combustion, where significant species experience transcritical and supercritical states, must incorporate non-idealities in thermodynamic and chemical kinetic properties. Critical properties, such as critical temperature and pressure, are shown in Table 1 for the alcohol fuel (Ethanol), oxygen, and nitrogen.

Table 1: Critical properties of selected alcohol fuel, oxygen, and nitrogen (Poling *et al.*, 2001)

Formula	Name	Tc $[K]$	Pc $[bar]$
C_2H_6O (C_2H_5OH)	ethanol	513.9	61.48
O_2	oxygen	154.6	50.43
N_2	nitrogen	126.2	33.98

Experimental ignition delay studies must be improved to validate the kinetic models used in high-pressure combustion simulations. In most cases, the kinetic treatments of high-pressure reacting mixtures assume ideal gas behavior. In this way, Kogekar *et al.* (2018) studied the real gas effects (i.e., a multi-component R–K formulation) on high-pressure combustion by comparing simulated and experimentally measured ignition delay time (IDT) from shock tube for n-dodecane/O_2 /N_2 mixtures, using a chemical mechanism with 100 species and 432 reactions, developed by Wang *et al.* (2014). Their results demonstrate that non-ideal behavior can affect predicted IDTs by as much as 50–100 μs in the NTC region.

The present paper focuses on a new reduced mechanism that contains ethanol (oxygenated hydrocarbon) for calculating the oxidation of supercritical ethanol. The final ethanol kinetic mechanism comprised 71 species and 684 reactions. The simulation used a 0D constant-volume auto-ignition delay times IDT, calculated by Cantera version 2.5.1 (Goodwin *et al.*, 2021). The validation was done using available experimental results under supercritical conditions of ignition delay times (IDT) at shock tube (ST) under stoichiometric equivalence ratios (ϕ), high-pressure range (10-75 atm), and temperatures between 700-1200 K. And Laminar flame speed (LFS) at 1 - 4 atm and 380 - 450 K using the ideal EoS. All the IDT simulations used the cubic Redlich-Kwong (RK) and the ideal (I) equation of states (EoS). The critical properties

of each species in the merged mechanism necessary to obtain the parameters using the cubic R-K equation of state were obtained by applying Joback's Group Method Poling *et al.* (2001); Thomson *et al.* (2008).

2. METHODOLOGY

2.1 Reduction process

The reduced mechanisms are developed using a mechanism reduction approach, which is the combination of the Directed relation graph with error propagation (DRGEP) (Pepiot-Desjardins and Pitsch, 2008) and the sensitivity analysis (SA) (Rabitz *et al.*, 1983; Turányi, 1990). All these features are available in Pymars code, version 1.1.0, developed by Mestas *et al.* (2019).

The present work achieved the ethanol-reduced model by reducing the Cancino *et al.* (2010) (136 species and 1349 reactions). Concerning that the Cancino *et al.* (2010) ethanol mechanism was validated using only IDT experimental results obtained in an ST at 10, 30, and 50 bar, no 1D freely propagating flames were considered in Cancino et al. work. So, before the reduced process, we tried to run it in Cantera using an LFS approach. But it does not run because it presents three duplicate reactions '$C_2H_5OH + HO_2 <=> SC_2H_5O + H_2O_2$', in which one of them exhibits the largest pre-exponential factor of the mechanism that is equal to 10^{129}, which struggles to reach convergence. However, when we decrease the pre-exponential factor one step by time, the simulation of LFS starts to run when the pre-exponential factor equals 10^{100}. Besides, the resulting original mechanism with the highest pre-exponential factor 10^{100} is referred to as the "Original mechanism" (Original M.). The true original ethanol Cancino *et al.* (2010) mechanism with the highest pre-exponential factor 10^{129} is referred as "Original* mechanism" (Original* M.).

The ethanol model reduction was performed based on operating conditions for 0D constant-volume IDT for two equivalence ratios, corresponding to a lean (ϕ = 0.50) and a stoichiometric mixture (ϕ = 1.0), and the temperature range of 700 $\leq$ T $\leq$ 1280 K at pressures of about 10, 30, 50 and 70 atm. The interactive remotion of reactions and species in the DRGEP reduction occurs until a defined threshold of 1% error in IDT, computed overall conditions of interest. DRGEP targets included species OH, CO, and the hydroperoxy radical (HO_2), acetaldehyde (CH_3HCO = C_2H_4O), hydrogen peroxide (H_2O_2), and 1-hydroxyethyl radical CH_3CHOH (named "SC2H5O" in Cancino *et al.* (2010)) to the Ethanol reduction process due to their highest sensitivity pressure. In the reduction process, the target combustion products were CO_2 and H_2O. After all these processes, the reduced kinetic model of Ethanol consists of 71 species and 684 reactions.

All the mechanisms used in the reduced process are summarized in Tab. 2.

Table 2: Ethanol mechanisms

Name	Species	Reaction	Type	Reference
Ethanol OM	136	1349	Detailed	Cancino *et al.* (2010)
Ethanol RM	71	684	Reduced	-

OM, Original mechanism; RM, Reduced mechanism;

2.2 Real Equations of state: properties

Although the ideal (I) equation of states (EoS) was used until here, to understand better the magnitude of the real gas effects on reflected shock tube IDTs at high-pressure combustion, it is necessary consideration of an accurate gas equation of state at the simulations. This goal is supported using the cubic multi-component Redlich-Kwong equation of state in CANTERA Goodwin *et al.* (2021). This R–K EoS implementation gives qualitatively accurate results across a range of non-ideal states, and its accuracy suffers in the liquid-vapor equilibrium region. The present study uses a multi-component, mixture-averaged form of the R–K EoS to predict real gas behavior.

For a pure species, The R–K EoS is:

$$P = \frac{RT}{V-b} - \frac{a}{T^{1/2}V(V+b)}; \tag{1}$$

$$a = 0.42748\frac{R^2T_c^{5/2}}{P_c}; \tag{2}$$

$$b = 0.08664\frac{RT_c}{P_c} \tag{3}$$

Here, the influence of molecular interactions is given by the species-specific Van der Waals attraction parameter (a) and repulsive volume correction parameter (b). Where P is the pressure (Pa); V is the molar volume ($m^3\,mol^{-1}$); R is

the gas constant (8.314 $J\,mol^{-1}K^{-1}$); T is the absolute temperature (K); P_c is the critical pressure for the component of interest (Pa); T_c is the critical temperature for the component of interest (K);

For mixtures, Eq. 1 assume the following form:

$$P = \frac{RT}{V - b_{mix}} - \frac{a_{mix}}{T^{1/2}V(V + b_{mix})} \tag{4}$$

where the coefficients a_{mix}, and b_{mix} are dependent on species i and j, as indicated in Eqs. 5, and 6.

$$a_{mix} = \sum_i \sum_j X_i X_j a_{i,j} = \sum_i \sum_j X_i X_j \sqrt{a_i a_j} \tag{5}$$

$$b_{mix} = \sum_i X_i b_i \tag{6}$$

The (a) and (b) parameters in R–K EoS (Eq. 1) must be known or estimated for each species in the reaction mechanism. These parameters depend on a species' critical temperature and pressure, readily available for most stable species but not for the many intermediate species and radicals in most chemical mechanisms (including the present mechanism). The present study uses the group contribution Joback method Joback (1984) to estimate critical temperature (T_c), critical pressure (P_c), and boiling point (T_b).

The Joback method combines basic structural properties for each chemical group within an individual species. The properties of a compound are functions of structurally dependent parameters and are determined by summing the frequency of each group in the molecule multiplied by its contribution. The method assumes that group interactions are negligible and valid for polar and non-polar species.

Owczarek and Blazej tabulated critical temperatures for a range of gases using multiple approaches Owczarek and Blazej (2003, 2004). The Joback method limited errors to less than 5.0% for branched and unbranched hydrocarbons.

The boiling-point temperature may be evaluated using the Joback method (J-M):

$$T_b(K) = 198 + \sum_j N_j C_{T_b,j} \tag{7}$$

Subsequently, the critical temperature (T_c) and pressure (P_c) are estimated as:

$$\frac{T_c}{T_b} = \left[0.584 + 0.965\left\{\sum_j N_j C_{T_c,j}\right\} - \left\{\sum_j N_j C_{T_c,j}\right\}^2\right]^{-1} \tag{8}$$

$$P_c(bar) = \left[0.113 + 0.0032 N_{atoms} - \sum_j N_j C_{p_c,j}\right]^{-2} \tag{9}$$

In these expressions, the index j indicates the group type and N_j the total number of j groups in the interest species. Each group type j has a contribution to the critical temperature ($C_{T_c,j}$), the boiling-point temperature ($C_{T_b,j}$), and the critical pressure ($C_{p_c,j}$). In Equation 9, N_{atoms} indicates the number of atoms in the interest species. In the present study, all group contributions ($C_{T_c,j}$, $C_{T_b,j}$, $C_{p_c,j}$) are taken from Poling *et al.* (2001). A comparison between Literature Ethanol (Poling *et al.*, 2001) and Joback's estimated properties is presented in Fig. 1.

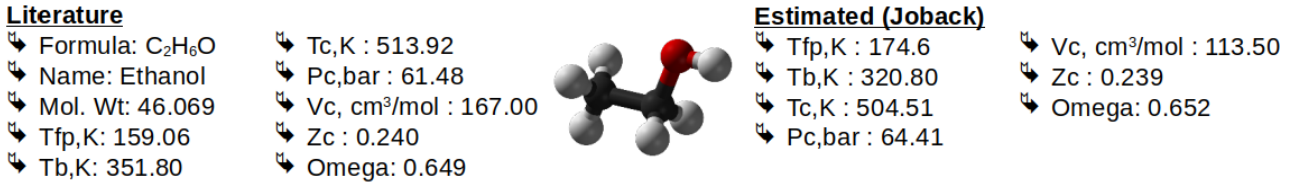


Figure 1: Literature Ethanol properties (Poling *et al.*, 2001) versus Ethanol Joback's estimated properties. $(Mol.Wt)$ is the molecular weight of the Ethanol molecule, T_c is the critical Temperature, P_c is the critical Pressure, (Tfp, K) is the Temperature freezing point in Kelvin, (ω) is the acentric factor, V_c is the critical Volume, and Zc is the Compressibility factor.

It is necessary to highlight that Group contribution parameters for short-lived species and radicals are generally unavailable. However, they may be estimated as equal to analogous stable species Kogekar *et al.* (2018).

After this process, the parameters (a) and (b) from R–K EoS were implemented in the Ethanol reduced chemical kinetic mechanism file developed here. Its format is '.yaml' in Cantera version 2.6.

3. RESULTS AND DISCUSSIONS

As discussed in subsection 2.1, the Ethanol original* mechanism of Cancino *et al.* (2010) presents the highest pre-exponential factor 10^{129} in duplicate reaction '$C_2H_5OH + HO_2 <=> SC_2H_5O + H_2O_2$', resulting in a minor IDT at intermediate-lower temperatures when compared with the "Ethanol Original mechanism" with the highest pre-exponential factor 10^{100}. However, no 1D freely propagating flames were considered in Cancino et al. work.

As a comparison between the Ethanol reduced M. and the Ethanol original M. (100^{100}), an laminar flame speed (LFS) run was performed in Cantera using an initial temperature of 380 K, Pressure equal to 2 atm, and equivalence ratios range (ϕ = 0.7 to 1.4), as demonstrated in Fig. 2(a). This LFS simulation exhibits an excellent agreement between the reduced and the original ethanol mechanism. However, it presents a considerable deviation from the experimental data of Hinton *et al.* (2018), mainly in lean and stoichiometric equivalence ratios.

A laminar flame speed(LFS) sensitivity was performed to improve the Ethanol reduced mechanism LFS simulations regarding the conditions of the Hinton *et al.* (2018) experimental data, and a straightforward approach consisted of modifying the most critical reactions pre-exponential factor (A) of Arrhenius equation at the target conditions, as performed for IDT in the study of Song *et al.* (2019) for a gasoline surrogate mixture mechanism.

Figure. 2(b) shows LFS simulation at the same operating conditions of Hinton *et al.* (2018), but after modifying the pre-exponential factor of some main reactions. It is possible to notice better accordance between the Ethanol reduced M. and the LFS experimental data at all ranges of equivalence ratios.

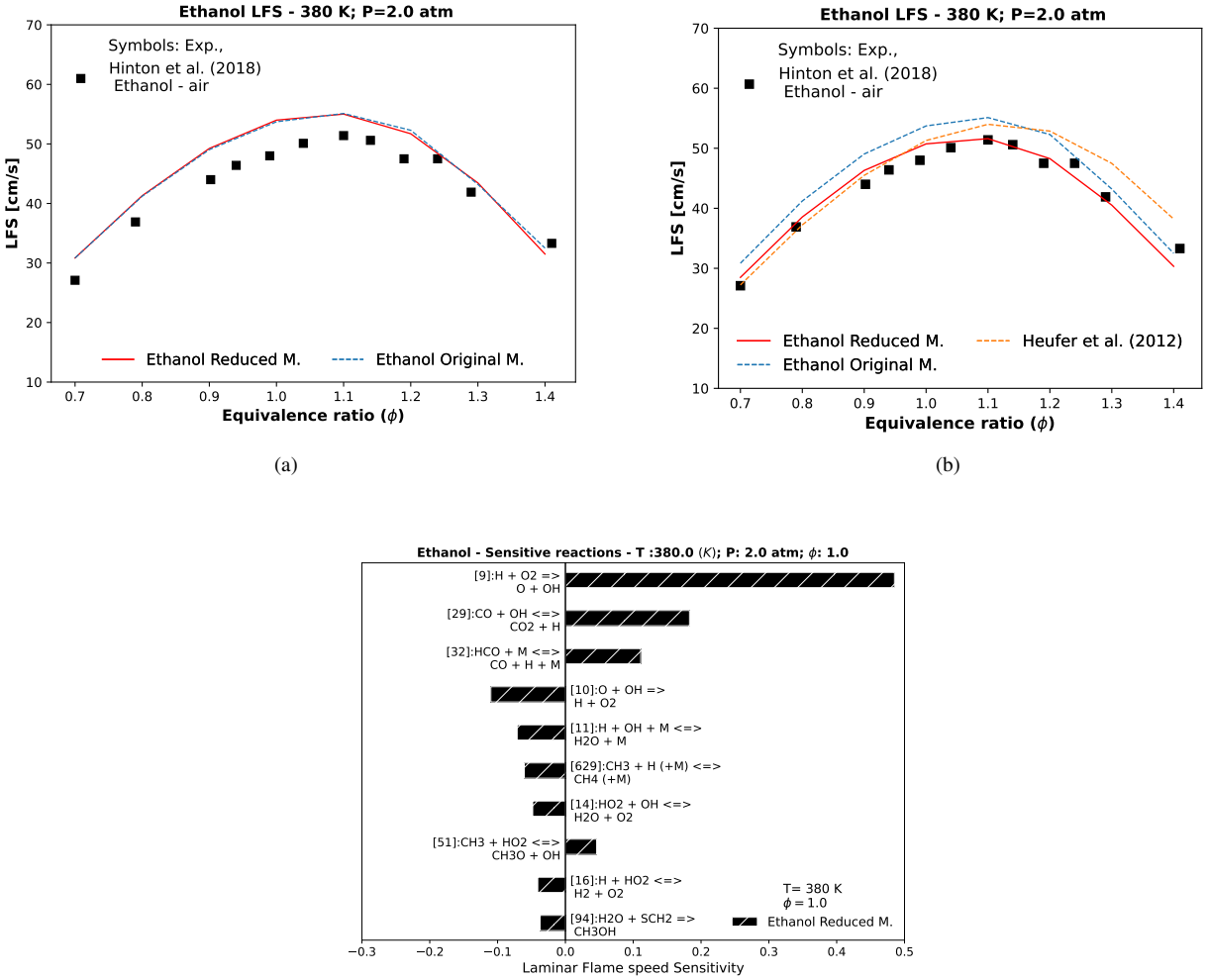


Figure 2: Numerical stoichiometric LFS simulation at different pressure considering the Ethanol reduced mechanism versus (a) the original mechanism with the highest pre-exponential factor 10^{100} before modifying the pre-exponential factor (A) of main reactions, and (b) after modifying (A) use ideal EoS, c) represents the Laminar flame speed sensitivity to select the main reactions at target conditions.

Concerning the modifying pre-exponential factor approach, Figure. 2(c) shows the ten most sensitive reactions from the Hinton et al. experimental selected conditions for Stoichiometric Ethanol laminar flame speed.

All the modifications of the pre-exponential factor of the first three reactions numbered [9], [29], [32] are according to the previous Hydrogen, and Ethanol literature from GALWAY Database (Zhang *et al.*, 2017; Heufer *et al.*, 2012; Mittal *et al.*, 2014; Zhang *et al.*, 2018). Furthermore, the mechanism from Heufer *et al.* (2012) is a detailed Pentanol mechanism containing Ethanol (EM) and presents 599 species and 3248 reactions, which is much more species and reactions than the ethanol-reduced mechanism with 71 species and 684 reactions presented here.

Table 3: Modifying the pre-exponential factor of Ethanol

Reaction	Previous (A)	Modified (A)	Reference (GALWAY Database)
R. [9] H + O_2 => O + OH	9.75e+13	1.04e+14	Zhang *et al.* (2017), Zhang *et al.* (2018)
R. [29] CO + OH <=> CO_2 + H	1.17e+07	5.76e+12	Heufer *et al.* (2012), Zhang *et al.* (2018)
Duplicate Reaction	-	7.01e+04	Zhang *et al.* (2018), Mittal *et al.* (2014)
R. [32] HCO + M <=> CO + H + M	1.56e+14	5.70E+11	Zhang *et al.* (2018), Mittal *et al.* (2014)
R. [16] H + HO_2 <=> H_2 + O_2	4.28e+13	1.140e+10	Zhang *et al.* (2017), Mittal *et al.* (2014)

After all this process with LFS, and as described in the methodology section, the IDT simulations of the mixture Ethanol/air as a function of temperature for stoichiometric combustion conditions (ϕ = 1), pressures of 1, 10, 50, and 100 atm, and initial temperatures in the range between 700 and 1250 K are presented in Fig. 3(a). Besides, the resulting original mechanism with the highest pre-exponential factor 10^{100} (Original M.) at higher-intermediate temperature conditions agrees well with The genuine original ethanol Cancino *et al.* (2010) mechanism with the highest pre-exponential factor 10^{129} ("Original* M.) although present a higher deviation at lower intermediate temperature conditions.

Figure 3(b) shows that the Ethanol reduced mechanism agrees well with its Ethanol original mechanism in all the selected conditions (1, 10, 50, and 100 atm) and the highest difference of IDT simulation results between reduced mechanisms and the original Ethanol were 1.0%.

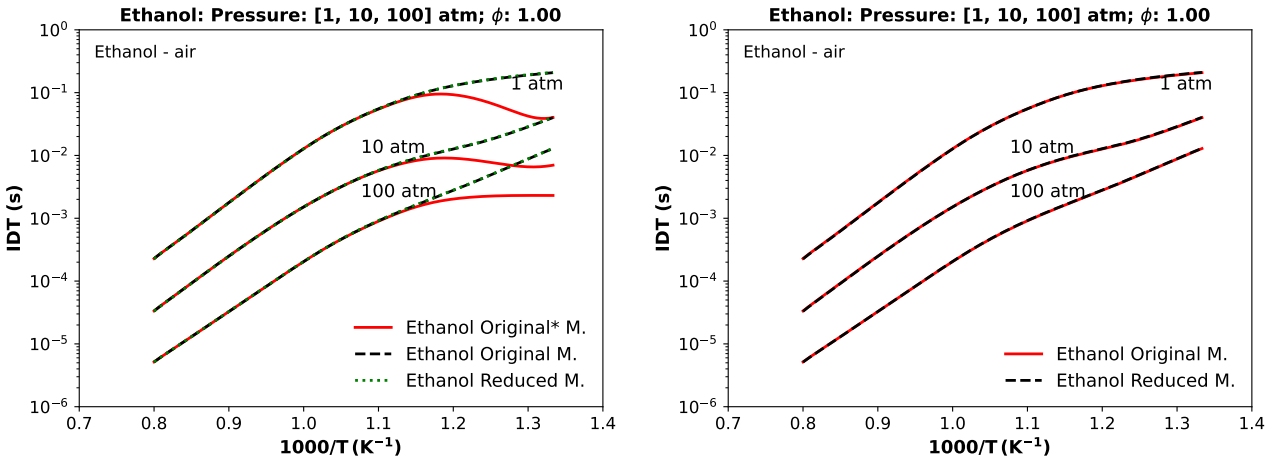
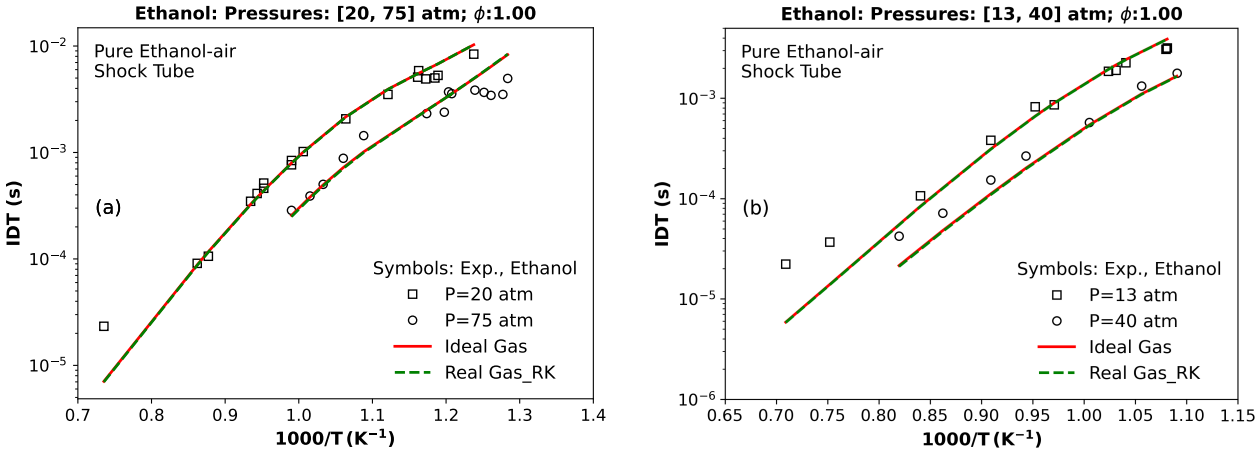


Figure 3: Numerical stoichiometric IDT at different pressure considering the Ethanol reduced mechanism against (a) the original mechanism with the highest pre-exponential factor 10^{100}, versus the Ethanol original* mechanism of Cancino *et al.* (2010) with the highest pre-exponential 10^{129} (1, 10, 100 atm) and (b) versus the first one. Both simulations use ideal EoS.

3.1 Ethanol IDT

After the reduction, various experimental conditions of shock tube (ST) data are collected to compare the Ethanol-reduced mechanism at more comprehensive pressure and temperature conditions. Shock tube (ST) data for Ethanol from (Cancino *et al.*, 2009; Heufer and Olivier, 2010; Heufer *et al.*, 2011; Zyada and Samimi-Abianeh, 2019).

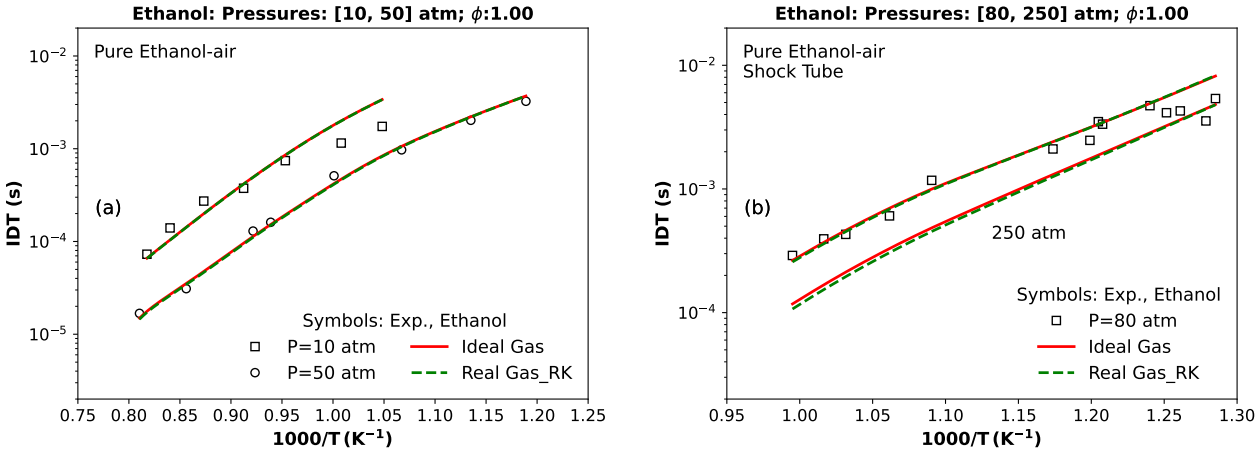
Figure 4(a) shows the reasonable agreement of the ethanol-reduced mechanism with the experimental ethanol data of ignition delay time (IDT) at different pressures using a sub-critical shock tube at 20 atm and a supercritical shock tube (ST) at 75 atm pressure (Heufer and Olivier, 2010). Also, Figure 4(b) shows a sub-critical experimental data at 13 and 40 atm pressure (Heufer *et al.*, 2011; Zyada and Samimi-Abianeh, 2019).



(a) (b)

Figure 4: IDT simulations against (a) a sub-critical shock tube (ST) data at 20 atm and a supercritical (ST) data at 75 atm (Heufer *et al.*, 2011); and (b) a sub-critical data at 13, and at 40 atm (Heufer *et al.*, 2011; Zyada and Samimi-Abianeh, 2019) using a stoichiometric mixture composition of Ethanol, O_2, and N_2; Symbols represent experiments; solid and dashed lines are the Ethanol reduced mechanism, respectively, using the ideal (I) and the real gas Redlich-Kwong (RK) EoS.

Figure 5(a) shows the numerical IDT of ethanol/air against the experimental data from Cancino *et al.* (2010), respectively, at 10 (sub-critical) and 50 atm (supercritical). At 10 atm pressure conditions, a relatively large deviation is observed at intermediate-lower temperatures for this ethanol-reduced mechanism, whereas improved agreement can be observed at intermediate-higher temperatures.



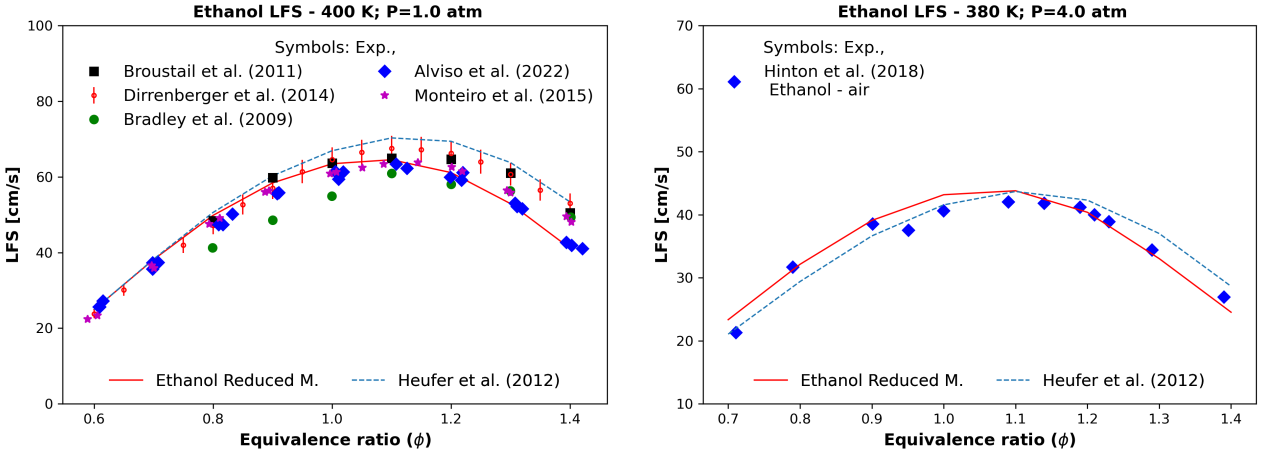
(a) (b)

Figure 5: IDT simulations against (a) a sub-critical shock tube (ST) data at 10 and 50 atm (Cancino *et al.*, 2010); and (b) a supercritical shock tube (ST) data at 80 (Lee *et al.*, 2012), and also a supercritical simulation at 250 atm using a stoichiometric mixture composition of Ethanol, O_2, and N_2; Symbols represent experiments; solid and dashed lines are the Ethanol reduced mechanism, respectively, using the ideal (I) and the real gas Redlich-Kwong (RK) EoS.

In Figure 5(b), the same pure Ethanol/air mixture is validated against supercritical shock tube experimental data of Lee *et al.* (2012) at 80 atm; Also, in Figure 5(b) is possible to notice an increase in pressure (80 to 250 atm) promotes 9% the deviation between simulations using the ideal gas (I) and real gas (RK) equation of states.

3.2 Ethanol LFS

To validate the mechanism for a broader range, different temperature and pressure conditions are considered in sub-critical conditions. No Laminar flame speed (LFS) experimental data is available at supercritical conditions in the literature.



(a) (b)

Figure 6: Ethanol LFS reduced model results compared to the LFS experimental data of a) Broustail *et al.* (2011), Dirrenberger *et al.* (2014), Bradley *et al.* (2009), Alviso *et al.* (2022), and Monteiro *et al.* (2015) at 400 K and 1 atm, b) Hinton *et al.* (2018) at 380 K and 4 atm. Dotted lines are the literature mechanism (Heufer *et al.*, 2012). All FLS simulations using the ideal (I) EoS.

The results at atmospheric pressure and 400 K, in Fig. 6(a), are in excellent agreement with most of the recent experimental data found in literature (Alviso *et al.*, 2022), which shows the resulting Ethanol-reduced mechanism gives reliable results at atmospheric pressure. Beyond that, it is found that the Ethanol reduced model agrees well with the experiment at 380 K and 4 atm conditions, as shown in Fig. 6(b) for 1D Laminar flame speed simulations. Based on Figures 6(a) and 6(b), the Ethanol Reduced M. gives reliable results even when compared with more extensive detailed literature kinetic models, which is the case of (Heufer *et al.*, 2012) comprising 599 species and more than 3000 reactions.

4. CONCLUSIONS

This work obtained a reduced model for simulating supercritical Ethanol; the model comprises 71 species and 684 reactions.

This new mechanism was validated using sub-critical and supercritical experimental data of ignition delay times (IDT) for pure ethanol as a function of temperature and pressure. Under the operating conditions studied here, incorporating non-idealities decreases the predicted ignition times by approximately 3% between R–K and ideal gas EoS simulations at 80 atm. Although the non-ideal effects are moderate at 75 atm, they increase in significance at elevated operating pressures. At 250 atm, the relative difference between ideal and real gas EoS predicted ignition delay times is roughly 9% in higher temperature regions for Ethanol.

Based on the available experimental data for ethanol combustion, the Ethanol reduced mechanism does a pretty good job of reproducing the results of IDT at both sub-critical and supercritical conditions. Although there are some discrepancies between the model's predictions and the actual experimental results, the subcritical predictions for the flame species are reasonably accurate, especially when considering the uncertainties that arise from changes in the pre-exponential factor. Overall, this mechanism performs well across various temperature and pressure conditions.

5. ACKNOWLEDGEMENTS

The support of Fundação de Desenvolvimento da Pesquisa – Fundep, Rota 2030 - Linha V to the first author in the form of a Ph.D. Program Scholarship is gratefully acknowledged.

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