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VALIDATION OF A REDUCED CHEMICAL KINETIC MECHANISM FOR SUPERCRITICAL COMBUSTION OF GASOLINE/ETHANOL BLENDS

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Abstract.
Gas emission and fuel efficiency regulations require clean and highly efficient combustion systems. A promising system is the direct injection of gasoline under ultra-high pressure and temperature above the critical point of fuel species (called supercritical). Supercritical combustion is a clean and efficient combustion technology that reduces particulate emissions of engines. This study proposes a kinetic mechanism for the combustion of supercritical gasoline/ethanol blends. Reduced gasoline surrogate and ethanol kinetic mechanisms were obtained by applying Directed Relation Graph error propagation and sensibility analysis to the gasoline mechanism of Andrae (159 species and 734 reactions, composed of n-heptane, isooctane, toluene, and Diisobutylene (TRF/DIB)), and to the ethanol mechanism of Cancino (136 species and 1349 elementary reactions). A TRF/DIB skeletal model (118 species and 580 reactions) and a reduced model for ethanol (28 species and 193 reactions) were obtained. These two models were combined into a gasoline/ethanol mechanism (124 species and 703 reactions), which was validated using 0D constant-volume auto-ignition delay times (IDT) simulations and available experimental results under supercritical conditions. The simulation results are consistent with the experimental data, and the merged kinetic mechanism can predict the IDT under high-pressure ranges (30, 50, and 70 atm) and temperatures between 690-1200 K.

Keywords: *Chemical Kinetic mechanism, Supercritical Combustion, Gasoline mechanism, Ethanol mechanism*

1. INTRODUCTION

Ambient air pollution, caused by the largest logistics and consumption of fossil fuel in recent human history, and its impact on climate changes and population health are significant issues around the World (Li *et al.*, 2016). In recent years, vehicle emissions have become a primary anthropogenic air pollution source worldwide, especially in large metropolises. According to do Clima (2020), in Brazil in 2019, the energy sector represented 19% of the gas emission by using fossil fuels, whereas transport was responsible for 47% of all emissions from the energy sector. However, engine technology, such as gasoline direct injection (GDI), is one of the main factors that affect gasoline-fueled vehicle emissions.

The GDI technology provides lower CO_2 emissions while providing fuel economy because it can more accurately control the fuel volume and injection timing (Maricq *et al.*, 2012). De Boer *et al.* (2010) studied the pollutant emission of supercritical and subcritical gasoline GDI injectors at different engine operating conditions. Their results indicated that supercritical gasoline presents a higher NO_x emission than subcritical gasoline, but supercritical gasoline's soot emission is low. In subsequent research, Boer *et al.* (2013) developed a study about supercritical combustion using a single-cylinder gasoline spark-ignition engine with GDI over a wide range of engine speed and load conditions. Their results showed a particulate mass reduction above 50% in measured and particle count reduction of more than 90% concerning the literature results.

Supercritical combustion is supercritical fluid combustion in a supercritical environment. A fluid (mixture) is defined as being in the supercritical state if the pressure and temperature are above the critical values. Critical properties, such as critical temperature and pressure, are shown in Table 1 for selected hydrocarbon and alcohol fluids.

Table 1: Critical properties of selected fluids (Poling *et al.*, 2001)

Formula	Name	Tc $[K]$	Pc $[atm]$
C_8H_{18}	Iso-octane	543.9	25.70
C_8H_{16}	Diisobutylene	559.9	25.85
C_7H_{16}	n-Heptane	540.2	27.40
C_7H_8	Toluene	591.7	41.08
C_2H_6O	Ethanol	513.9	61.48

Supercritical fluids (SCFs) are attractive media for chemical reactions because of their unique properties. At supercritical conditions, the state of the species is often referred to simply as fluid. This is because changes in temperature at fixed supercritical pressure do not result in phase change. The fluid becomes less dense as the temperature increases. According to Liu *et al.* (2017), supercritical fluids exhibit significantly lower viscosities and surface tension than liquids (typically an order of magnitude), which provides favorable flow properties. However, they also present high diffusion rates (typically an order of magnitude higher than those of liquids). Because of those properties, the uniform mixture distribution can effectively improve the thermal efficiency and reduce the particulate emissions of the engine when supercritical gasoline is injected into a cylinder in a supercritical environment.

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 use of E85 results in 1-2 orders of magnitude reduction in particle emissions relative to GDI fueling with gasoline and E20. Furthermore, GDI particle emissions with E85 are similar to port fuel injection (PFI) fueling gasoline.

In contrast, the knowledge of the ignition and combustion process of ethanol and gasoline mixtures at very high pressure requires a detailed study of chemical kinetics and its properties in this condition, and most of the kinetics products are validated for only one fuel at ambient pressure. They do not consider fuel mixtures at high pressures.

An effective way to analyze the combustion characteristics of gasoline is to replace it with surrogates with similar physical and chemical properties. Tanaka *et al.* (2003) developed a simplified mechanism with 32 species and 55 elementary reactions to study the influences of composition, molecular structure, and additives on primary reference fuel (PRF), which comprises iso-octane and n-heptane, in a rapid compression machine.

As toluene is the most abundant aromatic hydrocarbon in the gasoline fuel, a surrogate for gasoline composed of a mixture of iso-octane, n-heptane, and toluene was developed (called a toluene reference fuel (TRF)). Different researchers have proposed many TRF mechanisms. Andrae (2008) developed a detailed mechanism model with 1121 species and 4961 reactions for describing the auto-ignition of gasoline using the Pera and Knop (2012) TRF mechanism, and the Diisobutylene (DIB) mechanism of Metcalfe *et al.* (2007). The DIB is an olefin, an important component of real gasoline. Andrae (2008) results showed the same tendency as the experimental data of IDT on an ST from Fikri *et al.* (2008) for various stoichiometric mixtures of two multi-component model fuels. The chemical proportions by liquid volume of the components were: n-heptane (18%)/isooctane (62%)/ethanol (20%) with RON 95 and MON 89 (called Fuel B), and n-heptane (20%)/toluene (45%)/isooctane (25%)/diisobutylene (10%) with RON 94 and MON 85 (called Fuel C).

Andrae and Head (2009); Andrae and Kovács (2016) developed a new semi-detailed mechanism that showed good agreement with the experimental ST data of Fikri *et al.* (2008) and Gauthier *et al.* (2004). Andrae and Kovács (2016) model was also validated against the experimental data of Kukkadapu *et al.* (2012) for IDT of the research gasoline RD387 obtained in a rapid compression machine under low-to-intermediate temperature conditions. The composition used in the model fuel were n-heptane (18%)/toluene (26.4%)/isooctane (51%)/diisobutylene (4.6%) with RON 90.6 and MON 83.7. Fuel/air equivalence ratios of (ϕ = 0.3, 0.5, and 1) are investigated at two different pressures (P_c = 20 and 40 bar). The RD387 (Kukkadapu *et al.*, 2012) were composed (Liq. Volume %) by iso-alkenes(42.3%)/n-alkanes(9.5%)/cyclo-alkanes(16%)/aromatics(26.4%)/Olefins(4.7%) with MON 82.7 and RON (91). More information about the Research RD387 gasoline can be found in Chaos *et al.* (2007) and Gauthier *et al.* (2004).

A new detailed mechanism consisting of iso-octane, n-heptane, toluene, diisobutylene, and ethanol was developed by Cancino *et al.* (2011) with 1130 species and 5242 reactions. Their ethanol component of the mechanism was obtained by combining the ethanol mechanism of Marinov (1999), and Konnov (2009) resulting in Cancino *et al.* (2010). The iso-octane and n-heptane base kinetics were taken from Curran *et al.* (1998), the toluene mechanism from Andrae *et al.* (2007); Maurice (1996), and the DIB kinetics from Metcalfe *et al.* (2007). Cancino validated results showed good agreement with the IDT of the ST for mixtures without ethanol but underestimated IDTs for pure ethanol, binary, ternary and quaternary mixtures containing ethanol.

Research on the gasoline kinetic mechanisms mainly focuses on sub-critical conditions. In contrast, the present paper focuses on a new reduced mechanism that contains TRF/ÐIB (Aromatic, iso-paraffin, n-paraffin, olefin) and ethanol (oxygenated hydrocarbon) for calculating IDT of supercritical gasoline/ethanol blends. A gasoline/ethanol kinetic mechanism was developed, consisting of 124 species and 703 reactions. The simulation was done using a 0D constant-volume auto

IDT, calculated by Cantera version 2.5.1 (Goodwin *et al.*, 2021). The validation was done using available experimental results under supercritical conditions of IDT at ST under different equivalence ratios, high-pressure range (30, 50, 70 atm), and temperatures between 690-1200 K. The resulting combined reduced mechanism for gasoline/ethanol combustion is referred to as the TRFE/DIB mechanism in the present study.

2. METHODOLOGY

2.1 Reduction of gasoline and ethanol mechanisms

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).

In the present work, the reduction of the chemical kinetic model of Andrae and Kovács (2016) (159 species and 734 reactions) was carried out to obtain a skeletal kinetic model that contains TRF/DIB as gasoline surrogates. This skeletal model was combined with the reduced chemical kinetic ethanol model of Cancino *et al.* (2010) (136 species and 1349 reactions). The Cancino's ethanol mechanism was initially validated using experimental results of IDT obtained in an ST under conditions with equivalence ratio (ϕ) between 0.3 and 1.0, pressure range of 10, 30, and 50 atm, and a temperature range between 650 K until 1220 K. These conditions will be used as a target to the TRFE/DIB reduced chemical kinetic mechanism developed in this work. After this reduction, a TRF/DIB skeletal mechanism (118 species and 580 reactions) and a reduced mechanism of ethanol (28 species and 193 reactions) were obtained. All the mechanisms used in the reduced process are summarized in Tab. 2.

Table 2: Comparison of TRF/DIB and Ethanol mechanisms

Name	Species	Reaction	Type	Reference
Cancino's ethanol mechanism	136	1349	Detailed	Cancino *et al.* (2010)
Andrae's mechanism (TRF/DIB)	159	734	Detailed	Andrae and Kovács (2016)
Ethanol reduced mechanism	28	193	Reduced	-
TRF/DIB reduced mechanism	118	580	Reduced	-
TRFE/DIB	124	703	Reduced	-

2.1.1 Reduced gasoline and ethanol mechanisms

The TRF/DIB and ethanol models reduction was performed based on operating conditions for 0D constant-volume to auto-ignition in different equivalence ratios ($\phi = 0.50$ and $= 1.0$), the temperature range of 690 $\leq$ T $\leq$ 1280 K at pressures of about 10, 30, and 55 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 and CO, and combustion products CO_2 and H_2O. After all these processes, the final skeletal kinetic model of TRF/DIB consists of 118 species and 580 reactions, and the final reduced ethanol kinetic model consists of 28 species and 193 reactions.

IDT as a function of temperature for equivalence ratio (ϕ) of the mixture of gasoline surrogates (TRF/DIB) and the air is selected to be 1, representing stoichiometric combustion condition, and pressures of 25 and 55 atm and initial temperatures in the range between 900 and 1140 K, is presented in Fig. 1. This figure shows the comparison of the detailed and the reduced TRF/DIB kinetic mechanism model under the same conditions. The calculation was done using open source code Cantera version 2.5.1 (Goodwin *et al.*, 2021). The "OH" species was used as a reference species to compute the ignition delay time.

Figure 1 shows that the TRF/DIB reduced gasoline mechanism agrees well with the original detailed mechanism in all the selected conditions. Figure 1 can also be observed in agreement with experimental data of IDT as a function of the temperature (as an Arrhenius plot) to surrogate B obtained from Gauthier *et al.* (2004) for the stoichiometric mixture at a pressure of 55 atm. The experimental data can be fitted to an equation of the form τ = A exp(B/T)p^{-x}, where x is the pressure exponent. Multiple linear regression analyses using ln(τ) as the dependent variable and $(1/T)$ and ln(p) as independent variables identified the value of x = 0.96 using the data available in Gauthier *et al.* (2004) for ϕ = 1.0. The experimental pressure was scaling through an expression of $\tau = \tau_{55}(55/p \text{ atm})^{-0.96}$ as shown in Fig. 1. The surrogate B consists of mixtures of isooctane, toluene, and n-heptane in proportion: surrogate B (69%,14%,17%) by liquid volume or surrogate B (63%,20%,17%) by mole fraction. The highest difference of IDT between Andrae and Kovács (2016) and TRD/DIB reduced mechanism was 1.0%.

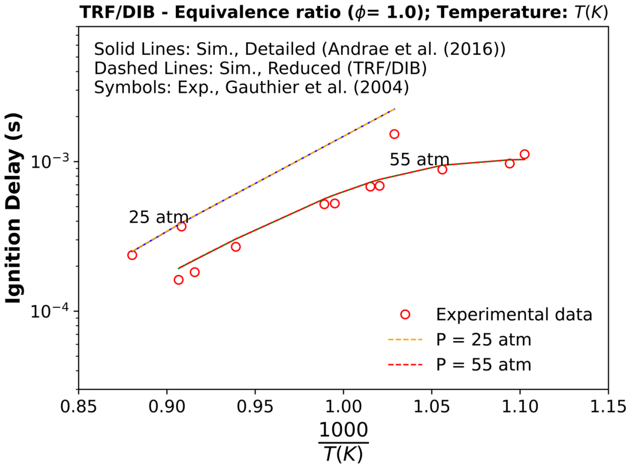
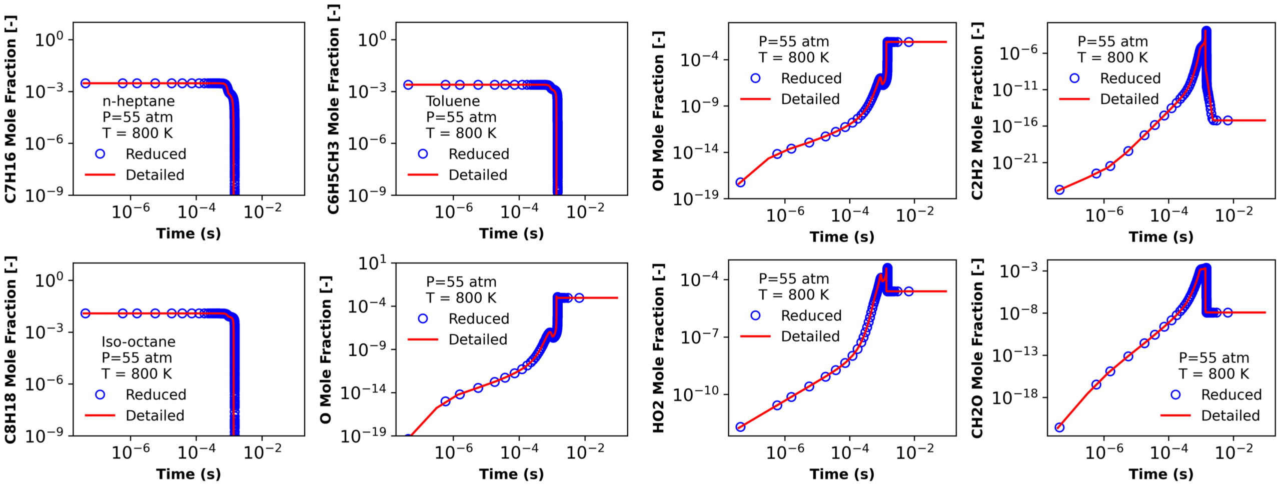


Figure 1: Comparison of IDT for stoichiometric TRF/air (surrogate B) IDT for different values of equivalence ratio and pressures of 25 and 55 atm using the kinetic detailed mechanism of Andrae and Kovács (2016) and the developed reduced TRF/DIB kinetic model (118 species and 580 reactions).

In addition, a detailed validation is conducted by comparing the predicted instantaneous mole fractions of major species during the homogeneous auto-ignition process. A constant-volume auto-ignition of a stoichiometric mixture of gasoline surrogates (surrogate B) and the air was simulated using reduced and detailed mechanisms. The initial temperature for the auto-ignition process is 800 K, and the initial pressure is 55 atm.

The mole fraction of each species, including the surrogate species (TRF) and important intermediate species, i.e., O, OH, HO_2, CH_2O, and C_2H_2, as a function of time, agrees with the values predicted by the detailed mechanism as shown in Fig. 2. This agreement in the instantaneous mole fraction of species proves that the TRF/ĐIB reduced mechanism can adequately reproduce the key reaction pathways of the detailed mechanism in the simulation of low-temperature homogeneous auto-ignition.



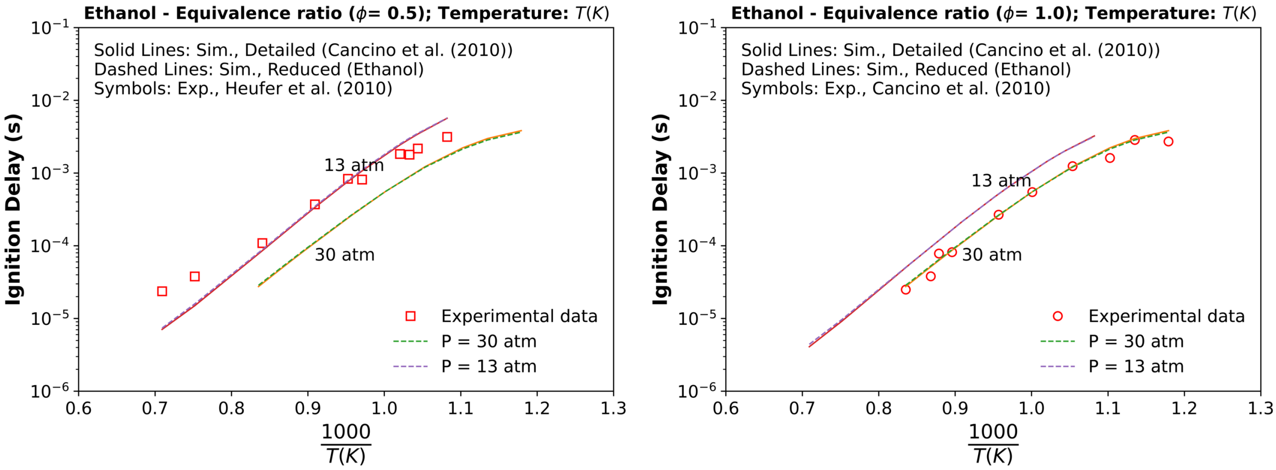
(a)

(b)

Figure 2: Comparison of the instantaneous molar fraction of (a) gasoline surrogates B and (b) key intermediate species during the homogeneous IDT process at T= 800 K and Pressure = 55 atm using the kinetic detailed mechanism of Andrae and Kovács (2016) and the developed reduced TRF/DIB kinetic model (118 species and 580 reactions).

Figure 3 shows the experimental results for ethanol IDT as a function of the temperature (as an Arrhenius plot) for different pressures (13 and 30 atm). The experimental ethanol data can also be fitted to an equation of the form τ = A exp(B/T)p^{-x}, where x is the pressure exponent. Multiple linear regression analyses using ln(τ) as the dependent variable and ($1/T$) and ln(p) as independent variables identified the value of x = 0.88 using the data available in Cancino *et al.*

(2010) for ϕ = 1.0. The experimental pressure was scaling through an expression of $\tau = \tau_{30}(30/p \text{ atm})^{-0.88}$ as presented in Fig. 3b. In Figure 3a the experimental pressure was scaling through an expression of $\tau = \tau_{13}(13/p \text{ atm})^{-0.77}$, which is based on data available in Heufer and Olivier (2010).



(a) (b)

Figure 3: Comparison of IDT for (a) lean and (b) stoichiometric ethanol/air IDT for different values of equivalence ratio, at 13 and 30 atm, using the detailed mechanism of Cancino *et al.* (2010) and the reduced ethanol kinetic model (28 species and 193 reactions) in comparison with (a) Heufer and Olivier (2010) and (b) Cancino *et al.* (2010) experimental data.

2.2 Merging the reduced mechanisms

This section describes merging the reduced chemical kinetic models of TRF/DIB and ethanol, consisting of 118 species and 580 reactions and 28 species and 193 reactions, respectively, into a single intermediate multi-component chemical mechanism. The individual fuel components' combustion mechanisms are independent, although they contain a relevant number of common species and reactions. At the same time, those reactions generally have different Arrhenius parameters and thermochemical and species transport properties across the selected kinetic models. Nonetheless, the main issue is to decide which rates, coefficients, and properties to choose when duplicated reactions or species are present during the mixing process. The reduced ethanol and gasoline surrogates kinetic models had 17 species and 54 reactions in common. The reduced mechanisms were mixed in two ways to find the most accurate intermediate kinetic model for IDT, as followed in the methodology of Alviso *et al.* (2020).

The first one consisted of choosing the reduced TRF/DIB model as the base mechanism, in which Arrhenius parameters, thermochemical properties, and transport properties remain in the composition of the generated intermediate kinetic mechanism. At the same time, concerning the reduced ethanol model as a complement: only species and reactions that were not present in the base mechanism were added into the intermediate kinetic mechanism and ignored the rest of the species or duplicate reactions.

The second option is to treat reduced ethanol as the base mechanism and the TRF/DIB model as a model complement, so the process is repeated.

Both merging options generated an intermediate mechanism with 124 species and 703 elementary reactions. Their restricted differences are in the Arrhenius parameters, thermochemical, and transport properties from duplicate reactions and duplicated species. New IDT simulations were compared to the experimental data from Cancino *et al.* (2010); Lee *et al.* (2012). The intermediate model with the reduced TRD/DIB model as a base presented better accuracy in the experimental data. In the next section is provided the comparison.

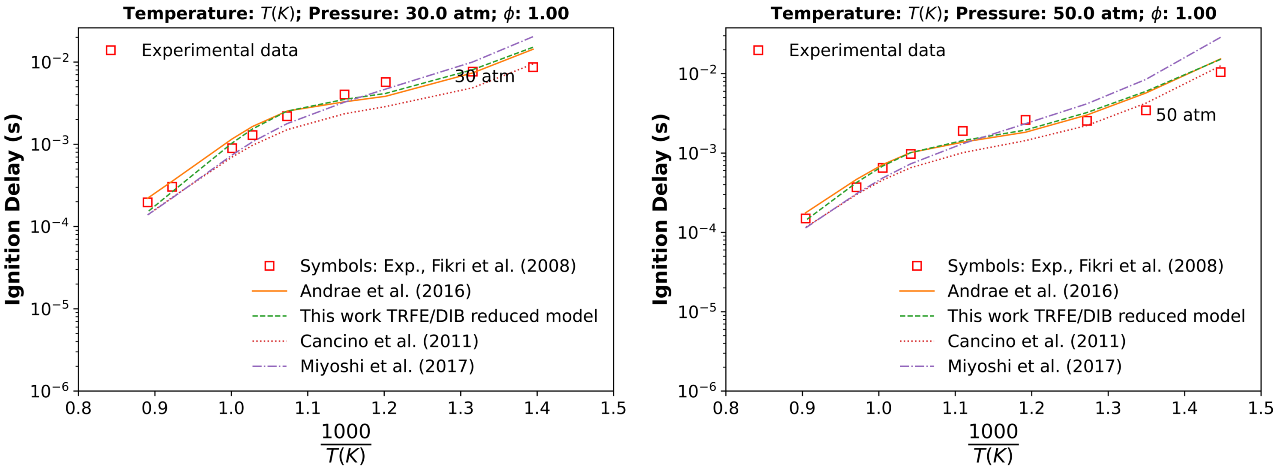
3. MECHANISM VALIDATION AND DISCUSSION

3.1 Auto-ignition results

The final mechanism (TRFE/DIB) is validated against experimental results of IDT from Cancino *et al.* (2010) and Lee *et al.* (2012) to ethanol and against experimental results of IDT from Fikri *et al.* (2008) to gasoline surrogate C (TRF/DIB). Moreover, the mechanism is compared with other available mechanisms in the literature. Three detailed mechanisms of gasoline surrogates (Andrae and Kovács, 2016; Cancino *et al.*, 2011; Miyoshi and Sakai, 2017) are considered for the comparison.

As shown, in Figure 4a and Figure 4b, the TRFE/DIB reduced mechanism presents a relatively well agreement prediction compared to the experimental data of Fikri *et al.* (2008) for the IDT of stoichiometric mixture of surrogate C, composed by n-heptane (20%)/toluene (45%)/isooctane (25%)/diisobutylene (10%) in liquid volume, with RON 94 and MON 85, at two different scaled pressures 30 and 50 atm.

Multiple linear regression analyses identifies the pressure exponent, x, to be 0.65 for TRF/DIB experimental data of Fikri *et al.* (2008) in Fig. 4a and Fig. 4b.

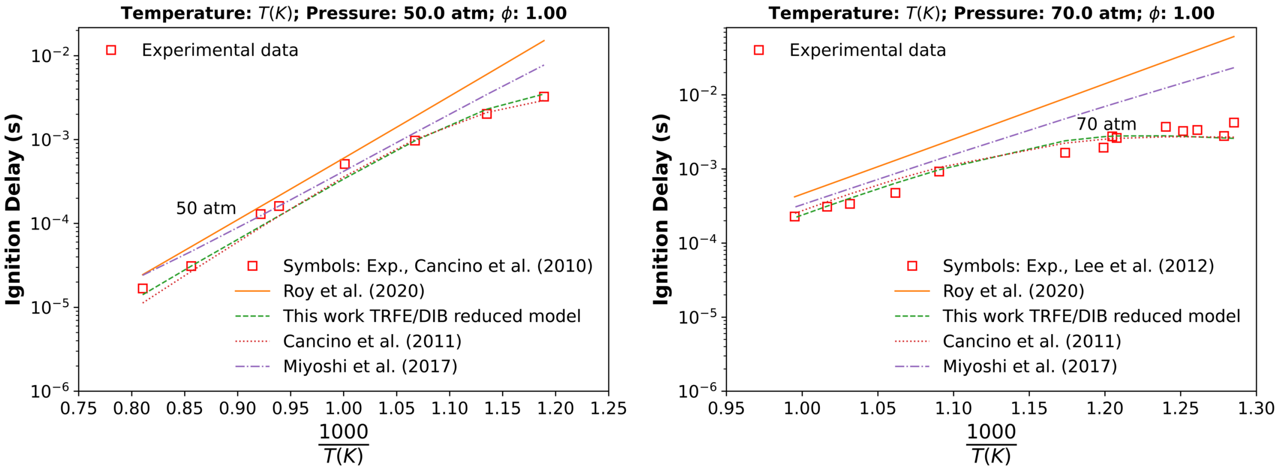


(a) (b)

Figure 4: Comparison of IDT for stoichiometric (surrogate C) TRF/DIB/air at pressure of 30 atm (a) and 50 atm (b), using the fuel C experimental data of Fikri *et al.* (2008), the detailed mechanisms of Andrae and Kovács (2016); Cancino *et al.* (2011); Miyoshi and Sakai (2017) and the developed reduced TRFE/DIB kinetic model (124 species and 703 reactions).

The TRFE/DIB mechanism also has a good agreement prediction with the experimental data of IDT for pure ethanol/air stoichiometric mixture ($\phi = 1$) at 50 atm (Cancino *et al.*, 2010) and at 70 atm (Lee *et al.*, 2012). Multiple linear regression analyses identifies the pressure exponent, x, to be 0.88 for ethanol experimental data of Cancino *et al.* (2010) in Figure 5a and x, to be 1.803 for ethanol experimental data of Lee *et al.* (2012) in Fig. 5b.

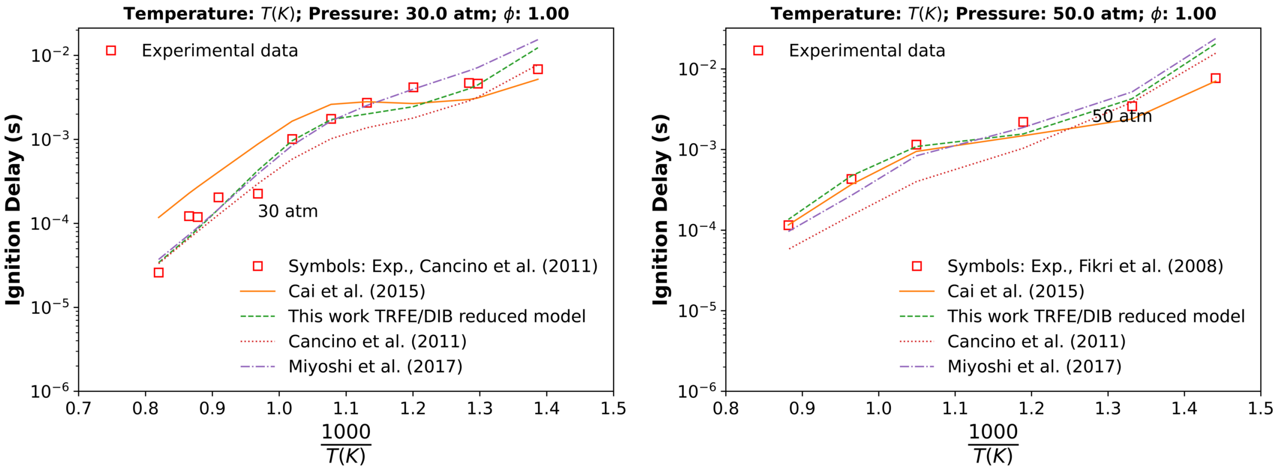
The ethanol mechanisms by Cancino *et al.* (2010); Roy and Askari (2020); Miyoshi and Sakai (2017) were also considered for comparison with TRFE/DIB mechanisms.



(a) (b)

Figure 5: Comparison of IDT for stoichiometric pure ethanol/air at pressures of 50 atm (a) and 70 atm (b), using the ethanol experimental data of Cancino *et al.* (2010); Lee *et al.* (2012), the detailed mechanisms of (Roy and Askari, 2020; Cancino *et al.*, 2010; Miyoshi and Sakai, 2017) and the reduced TRFE/DIB kinetic model (124 species and 703 reactions).

On the other hand, in Figure 6a and Figure 6b, the TRFE/DIB reduced mechanism (proposal model) agrees well with the experimental results, capturing absolute values of IDT, and deviates from the experimental data of Cancino *et al.* (2011) and Fikri *et al.* (2008) just in lower temperatures range (T < 750 K), respectively, for the IDT of stoichiometric quinary mixture composed by iso-octane (30%)/toluene(25%)/n-heptane(22%)/diisobutylene(13%)/ ethanol(10%) in liquid volume, and for the IDT of stoichiometric ternary mixture composed by n-heptane(18%)/iso-octane(62%)/ethanol(20%), at two different scaled pressures 30 and 50 atm. In both Figures, the agreement is precise in the high-temperature range for the results at 30 and 50 atm, respectively, when considering the quinary mixture in Figure 6a and ternary mixture in Figure 6b.



(a) (b)

Figure 6: Comparison of IDT, respectively, for experimental data of (a) Cancino *et al.* (2011) stoichiometric quinary mixture (TRFE/DIB-air) at pressure of 30 atm and (b) Fikri *et al.* (2008) ternary mixture at 50 atm, with the detailed mechanisms of Cai and Pitsch (2015); Cancino *et al.* (2011); Miyoshi and Sakai (2017) and the developed reduced TRFE/DIB kinetic model (124 species and 703 reactions).

In order to quantify how close they typically are to one another, we have calculated the Room mean Square error (RMSE) of different kinetic models relative to experimental data available in the literature using the Eq (1):

$$RMSE = \sqrt{\frac{1}{n}\sum_{j=1}^{n}(y_j - \bar{y}_j)^2}, \tag{1}$$

where y_j and $\bar{y}_j$, are the experimental IDT and calculated values, respectively, and n is the number of points (1000/T(K)).

The results given in Table 3 show that the TRFE/DIB reduced model (124 species and 703 reactions) proposal in this work is grated accurate over the range of available ethanol experimental data of Lee *et al.* (2012). Comparison between the reaction mechanism developed in this work and the experimental data of Fikri *et al.* (2008) reveals that Cancino *et al.* (2011) detailed kinetic model is slightly closer to the experimental data than the TRFE/DIB one. The RMSE of IDT presented in the two last rows of the Table 3, respectively, to Cancino *et al.* (2011) quinary and Fikri *et al.* (2008) ternary gasoline surrogates/ethanol mixtures experimental data highlight that Cai and Pitsch (2015) kinetic model is closer to the experimental data than the others mechanisms. Otherwise, the Miyoshi and Sakai (2017) model and the TRFE/DIB model predicted very well the IDT to high-temperature points but struggled to capture the experimental data of IDT to correspond to temperature values less than 750 K. Although, the combined (TRFE/DIB) kinetic model predicts extremely accurate ethanol (E100%) experimental IDT data Cancino *et al.* (2010), giving the lowest standard deviation RMSE of all kinetic models compared to all experiments.

Table 3: Standard deviations RMSE of IDT for different kinetic models compared to the gasoline surrogates C, ethanol E100%, and gasoline surrogates/ethanol blends experimental data.

Standard deviations RMSE of gasoline surrogates IDT (s)					
Exp/model	Pressure	Andrae and Kovács (2016)	Cancino et al. (2011)	Miyoshi and Sakai (2017)	This work TRFE/DIB
Fikri et al. (2008)	30 atm	1.991e-03	1.490e-03	5.661e-03	2.216e-03
Fikri et al. (2008)	50 atm	1.829e-03	9.120e-04	6.341e-03	1.817e-03
Standard deviations RMSE of ethanol (E100%) IDT (s)					
Exp/model	Pressure	Cancino et al. (2010)	Roy and Askari (2020)	Miyoshi et al. (2017)	This work TRFE/DIB
Cancino et al. (2010)	50 atm	1.460e-04	4.327e-03	1.607e-03	1.286e-04
Lee et al. (2012)	70 atm	6.060e-04	2.539e-02	8.875e-03	6.311e-04
Standard deviations RMSE of gasoline surrogates/ethanol IDT (s)					
Exp/model	Pressure	Cai and Pitsch (2015)	Cancino et al. (2011)	Miyoshi and Sakai (2017)	This work TRFE/DIB
Cancino et al. (2011) (Quinary Mixture)	30 atm	9.98e-4	1.098e-3	2.631e-3	1.686e-3
Fikri et al. (2008) (Ternary Mixture)	50 atm	5.91e-4	3.292e-3	6.607e-3	5.194e-3

3.2 Pressure relevance

As available in the literature and observed in Figure 1, 3, 4, 5, 6 and 7, temperature and pressure definitely have an effect on the ignition delay time (IDT). Increasing the temperature and pressure of the initial mixture leads to quicker combustion. The reduction in the ignition delay is exponential, and the autoignition is more sensitive to temperature.

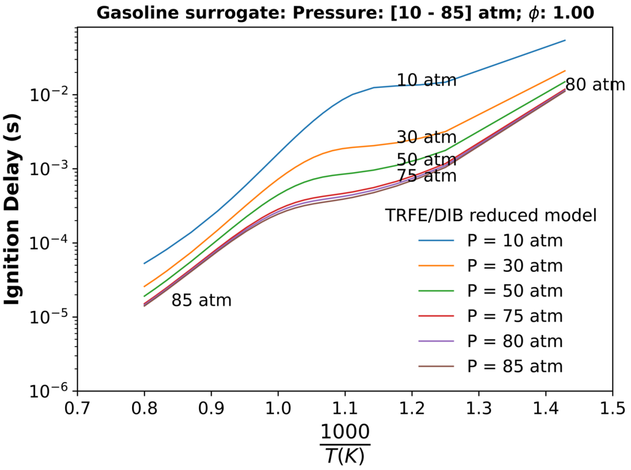


Figure 7: Comparison of IDT for stoichiometric Cancino *et al.* (2011) TRFE/DIB quinary surrogate at different values of pressures (10 to 85 atm) using the developed reduced TRFE/DIB kinetic model (124 species and 703 reactions).

Concerning the supercritical conditions, by raising the pressure, the properties of the fuel and oxidizer vary; In addition, as available in Poling *et al.* (2001); Anikeev and Fan (2013); Sarkar (2015), no surface tension is presented in a supercritical fluid, so there is no liquid/gas phase boundary. Due to this, at the critical point, any fluid's liquid and gas phases become a single supercritical phase. So changing the pressure and temperature of the fluid, the properties can be "tuned" to be more liquid-like or gas-like. Therefore, we inferred from Figure 7 concerning the critical properties from Table 1, that far from the critical point, the ignition delay time decreases with an increase in pressure, similarly to in subcritical conditions. Furthermore, the decrease in ignition delay becomes smaller and smaller as observed in Figure 7 to the pressures 75, 80, and 85 atm.

4. CONCLUSIONS

This paper has presented numerical studies of gasoline surrogates/ethanol blends combustion in 0D constant-volume auto-ignition delay. Several chemical kinetics models exist in the literature for gasoline surrogates mixtures among n-heptane/toluene/iso-octane/Diisobutylene and ethanol under sub-critical conditions. However, to our knowledge, none of them describe the combustion of these components as a blend in supercritical conditions. In this work, a TRF/DIB detailed model and a detailed ethanol model were selected and reduced using the DRGEP method and sensibility analysis considering supercritical conditions. The resulting skeletal models were merged into an intermediate reduced mechanism called TRFE/DIB. Gasoline surrogates and ethanol auto-ignition delays were calculated using the original individuals' combustion mechanisms (Andrae and Kovács, 2016; Cancino *et al.*, 2010) and the merged reduced kinetic model (TRFE/DIB). The validation of this new mechanism was done using experimental data of ignition delay times for mixtures of TRF/DIB concerning Fuel B Gauthier *et al.* (2004), (Heufer and Olivier, 2010), Fuel C (Fikri *et al.*, 2008), a quinary gasoline surrogate/ethanol blend Cancino *et al.* (2011), and pure ethanol (Cancino *et al.*, 2010; Lee *et al.*, 2012) as a function of equivalence ratio, pressure, and temperature. In conclusion, it was shown that the new mechanism reproduces the IDT observed experimentally for TRF/DIB and ethanol, whereas for ethanol, it reproduces the experimental results of Cancino *et al.* (2010), at 50 atm, with the lowest standard deviation in this validation.

5. ACKNOWLEDGEMENTS

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