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THE AVAILABLE DETAILED KINETICS MODELS FOR ETHANOL - A NUMERICAL ASSESSMENT ON IGNITION DELAY TIMES, LAMINAR FLAME SPEED AND SPECIATION.

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Abstract. *Ethanol is a renewable fuel increasingly recognized for its potential to reduce greenhouse gas emissions in transportation. To fully leverage its benefits as a biofuel for internal combustion engines (ICEs), a comprehensive understanding of its combustion kinetics is essential. Accurate and reliable kinetics mechanisms for ethanol combustion are critical for optimizing engine performance, reducing emissions, and improving fuel efficiency. Kinetics modeling also helps to identify key reactions controlling combustion, guiding the development of innovative combustion technologies. The aim of this work was to evaluate the performance of chemical kinetics mechanisms available in the literature to predict the characteristics of ethanol combustion. The simulations were carried out using the Cantera open-source code for reactive flow and then compared to experimental data of ignition delay times, laminar flame speed and species concentration profiles. Therefore, five kinetics models, including Aramco v3.0 (ARAMCO), CRECK, LLNL, San Diego, and PCRL, were analyzed regarding their ability to reproduce the key combustion features of ethanol oxidation. In addition, a brute-force sensitivity analysis using the PCRL kinetics model was conducted, focusing on the most important reactions. Through analysis and comparison with experimental data, this study confirms the reliability of the examined mechanisms in simulating the combustion of ethanol under SI engine-relevant conditions. The AramcoMech v3.0, CRECK, and PCRL mechanisms were found to be the most accurate in predicting ignition delay times, while the PCRL and LLNL mechanisms performed well in predicting laminar flame speeds. The PCRL and CRECK mechanism showed the best agreement with experimental data for species concentration profiles. Overall, this study contributes to the understanding of the fundamental chemical processes involved in ethanol combustion, with significant information for the field of engine design and optimization.*

Keywords: *Ethanol, Ignition delay times, Laminar flame speed, Detailed chemical kinetics, Cantera open-source code for reactive flow*

1. INTRODUCTION

Modern transportation heavily relies on internal combustion engines (ICEs), which serve as the primary means of propulsion for vehicles (Sinigaglia *et al.*, 2022). These engines operate by converting the heat generated from combustion into mechanical work and have traditionally been powered by gasoline and diesel fuels (Bae and Kim, 2017). However, fossil fuel combustion emits a greater quantity of greenhouse gases (GHGs) when compared to biofuels, thus making a substantial contribution to climate change. Considering the current rates of consumption, global CO_2 emissions from energy use will increase by 29% by 2035, resulting in nearly double the amount of emissions seen in 1990 (Mofijur *et al.*, 2015). Hence, there is a necessity to develop advanced technologies which use CO_2-neutral renewable fuels to reduce the GHG emissions, as well as to reduce the transport sector's fossil fuel dependency (Yadav *et al.*, 2023). One promising solution is ethanol. According to Mendiburu *et al.* (2022), ethanol is an alcohol that is mainly used as a transportation fuel in spark ignition engines (SIEs), either in pure form or as an additive to gasoline. Due to the ever-growing demand for energy, there is a continuous need to study and improve biofuels like ethanol (Roy and Askari, 2020). Therefore, an understanding of the combustion of ethanol is highly necessary for simulating processes associated with its use, as well as for optimization and development of combustion systems (Sarathy *et al.*, 2014). As a result, many researchers had investigated the combustion properties of ethanol and developed several detailed kinetic mechanisms.

Early studies by Natarajan and Bhaskaran (1981) and Dunphy and Simmie (1991) focused on ignition characteristics of ethanol-oxygen mixtures. They developed numerical models with 56 and 97 elementary reactions, respectively. Subsequently, Marinov (1999) from the Lawrence Livermore National Laboratory (LLNL) expanded the aforementioned ethanol studies. He introduced a kinetics model for ethanol oxidation, developed to calculate laminar flame speeds, ethanol oxidation profiles from jet-stirred reactors, and turbulent flow reactors. The compiled mechanism consisted of 56 species and 351 reversible reactions. Overall, since the mechanism was based on high-temperature conditions, it was not able to predict low-temperature conditions accurately. Marinov's model was later updated by Li *et al.* (2007) and Saxena and Williams (2007) to improve predictions and minimize uncertainties, and the updated mechanisms yielded reasonable predictions for various combustion parameters. Over time, the development of this combustion mechanisms for ethanol progressed, and numerous detailed mechanisms have emerged, including the Aramco-Mech v3.0 (Zhou *et al.*, 2018), developed to characterize the kinetics of a large number of C_1-C_4 based hydrocarbon and oxygenated fuels; CRECK (Ranzi *et al.*, 2012), which includes the chemistry of small and larger hydrocarbons, alcohols, and soot formation kinetics; LLNL (Marinov, 1999), that is based on high-temperature conditions; San Diego mechanism (Williams, 2016), which is comparatively a very small, yet detailed mechanism widely used in research works; and PCRL-Mech1 (Roy and Askari, 2020). Cancino *et al.* (2010) reported a detailed kinetics model for ethanol autoignition, with no option for laminar flame speed calculations. These advanced mechanisms, rigorously validated against experimental data, offer a comprehensive understanding of ethanol combustion. Therefore, in this study, is compared and analyzed these mechanisms to assess their accuracy in representing key combustion features of ethanol oxidation, in order to enhance the understanding of the strengths and limitations of each kinetics model. Form the literature review, five detailed kinetics models where then selected to be used in this work, those kinetics models are then chronologically summarized in the Table 1.

Table 1: Detailed kinetics models for ethanol combustion used in this work

Mechanism	**Year**	**Number of elements**	**Number of Species**	**Number of Reactions**	**References**
LLNL	2004	4	57	383	Marinov (1999)
CRECK	2012	6	339	9781	Ranzi *et al.* (2012)
San Diego	2016	6	58	270	Williams (2016)
Aramco v3.0	2018	6	581	3037	Zhou *et al.* (2018)
PCRL	2020	14	67	1016	Roy and Askari (2020)

2. METHODOLOGY

For the development of this study, three kinds of simulations of reactive systems where performed: (i) ignition delay time simulation on homogeneous adiabatic constant volume reactor, (ii) laminar free propagating flame speed, and (iii) species concentration profiles in a jet-stirred reactor (JSR). Therefore, from the literature, a complete collection of experimental results was extracted to validate the simulation results. Table 2 summarizes the experimental conditions used for comparison in this work.

Table 2: Experimental data of ethanol combustion reported in the literature used in this work

Experimental Conditions							
Author	***T*** [K]	***p*** [atm]	ϕ	**Author**	***T*** [K]	***p*** [atm]	ϕ
IDT				LFS			
Mathieu *et al.* (2019)	990-1125	25±1.5	1.0	Konnov *et al.* (2011)	298, 318	1.0	0.65-1.55
	945-1085	51±2.5	1.0		338, 358	1.0	0.65-1.55
	900-1223	9.5±1.3	1.0	Veloo *et al.* (2010)	343	1.0	0.70-1.50
Cancino *et al.* (2010)	789-1197	30±1.2.0	1.0	Species Concentration			
	841-1234	49.3±2.0	1.0	Leplat *et al.* (2011)	890-1250	1.0	1.0
	912-1183	32.4±2.5	0.3				

All the simulations were carried out on a Windows operating system with 8GB RAM and a Core-i5 processor, utilizing the Cantera-Python interface (Goodwin *et al.*, 2021). The in-house simulation code was developed by the Combustion Research Group at LABMCI/UFSC.

3. RESULTS AND DISCUSSION

3.1 Ignition delay times (IDT)

Experimental data of IDT are compared with the simulations performed in the software Cantera using the five mechanisms. The predicted ignition delay times for C_2H_5OH as a function of temperature is indicated in Figure 1 for different pressures and equivalence ratios.

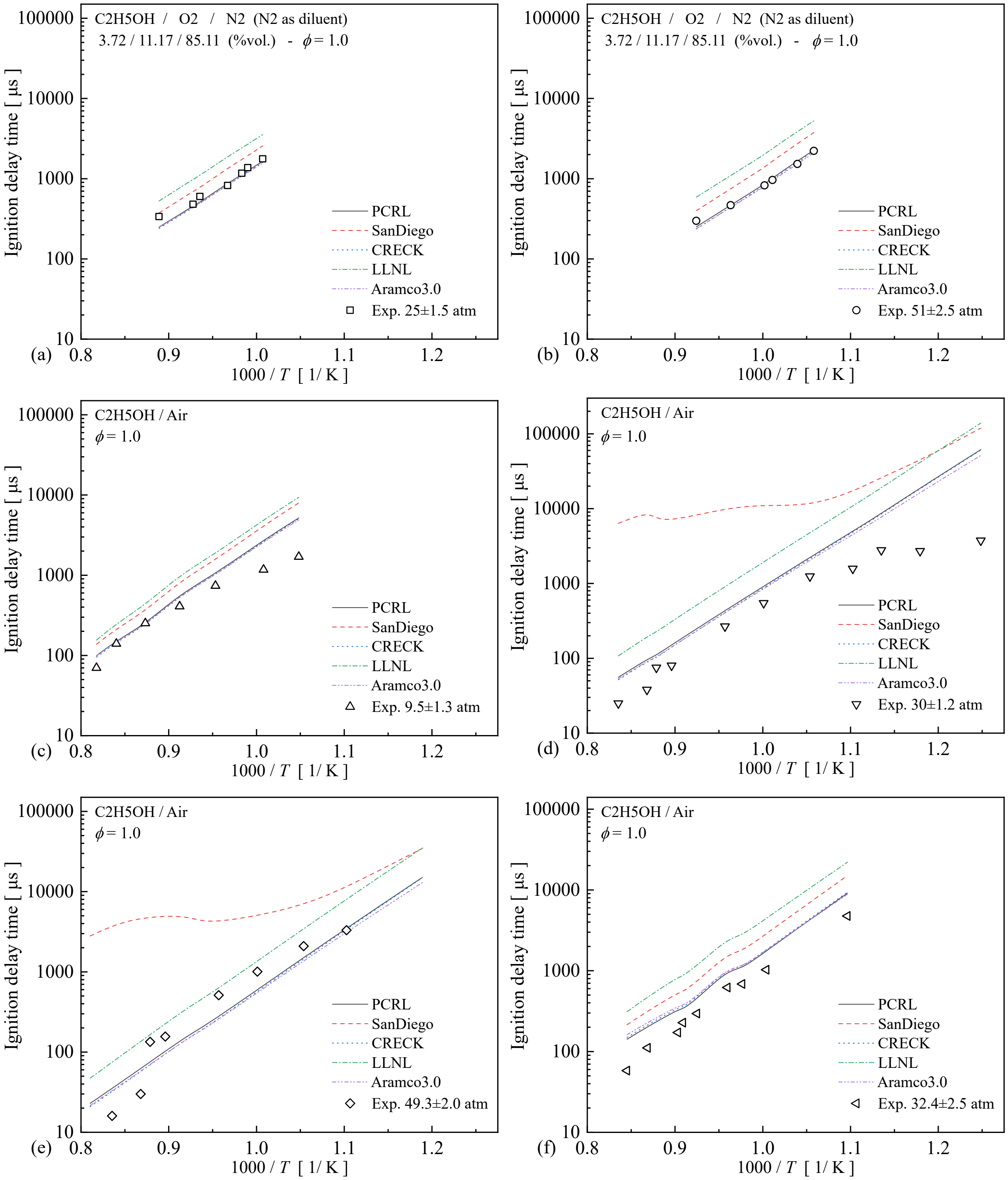


Figure 1: Comparison of ethanol ignition delay time for different mechanisms. (a) and (b), the symbols represent the experimental results of Mathieu *et al.* (2019). (c) to (f), the symbols represent the experiments of Cancino *et al.* (2010) (see Table 2 for details)

Firstly, it is evident that by increasing temperature, ignition delay times decrease in all conditions evaluated. At higher temperatures, the reactivity increases, resulting in shorter ignition delays. This trend was consistently observed in all kinetics models evaluated during this study. Among the kinetics models assessed during this study, the CRECK, Aramco v3.0, and PCRL demonstrated superior performance in predicting ignition delay times in shock tube experiments. These models accurately represented the experimental data obtained by Mathieu *et al.* (2019), as depicted in Figure 1(a) and (b). However, some deviations were found when comparing the mechanisms to the experiments of Cancino *et al.* (2010). Specifically, at a pressure of 9.5±1.3 atm, as shown in Figure 1(c), all kinetics models overpredict IDT at temperatures higher than 1096 K. In addition, at lower temperatures, the mechanisms exhibited higher divergence from the experimental results. This discrepancy may be attributed to the limited knowledge of lower-temperature chemical kinetics, with some coefficients and pathways yet to be well-characterized. Experimental data showed a highly nonlinear reactivity increase at lower temperatures, whereas the models predicted a much lower IDT, displaying clear exponential behavior on the log scale. Furthermore, it should be noticed from Figure 1(d) and (e), at ϕ = 1.0 and pressures higher than 30 atm, that the calculated IDT from the San Diego mechanism oscillated within the experimental range. However, this trend was not observed at ϕ = 0.3, as shown in Figure 1(f). Notably, at $p \sim 30$ atm, all mechanisms overpredict the experimental data of Cancino *et al.* (2010), whereas at $p \sim 50$ atm, the IDT was underestimated, as indicated in Figure 1(e), and the LLNL model demonstrated a better fit to the data.

3.1.1 Brute-force sensitivity analysis on IDT

To investigate the key reactions responsible for discrepancies in ignition delay times, sensitivity analyses were then conducted by using the brute force technique. The simulations were performed using the PCRL mechanism, at temperatures of 800 K and 1200 K, and a pressure of 30 atm. Figure 2 highlight the key reactions with the greatest influence on the PCRL model, based on a threshold of 0.5% and 2.0% change (absolute) in IDT.

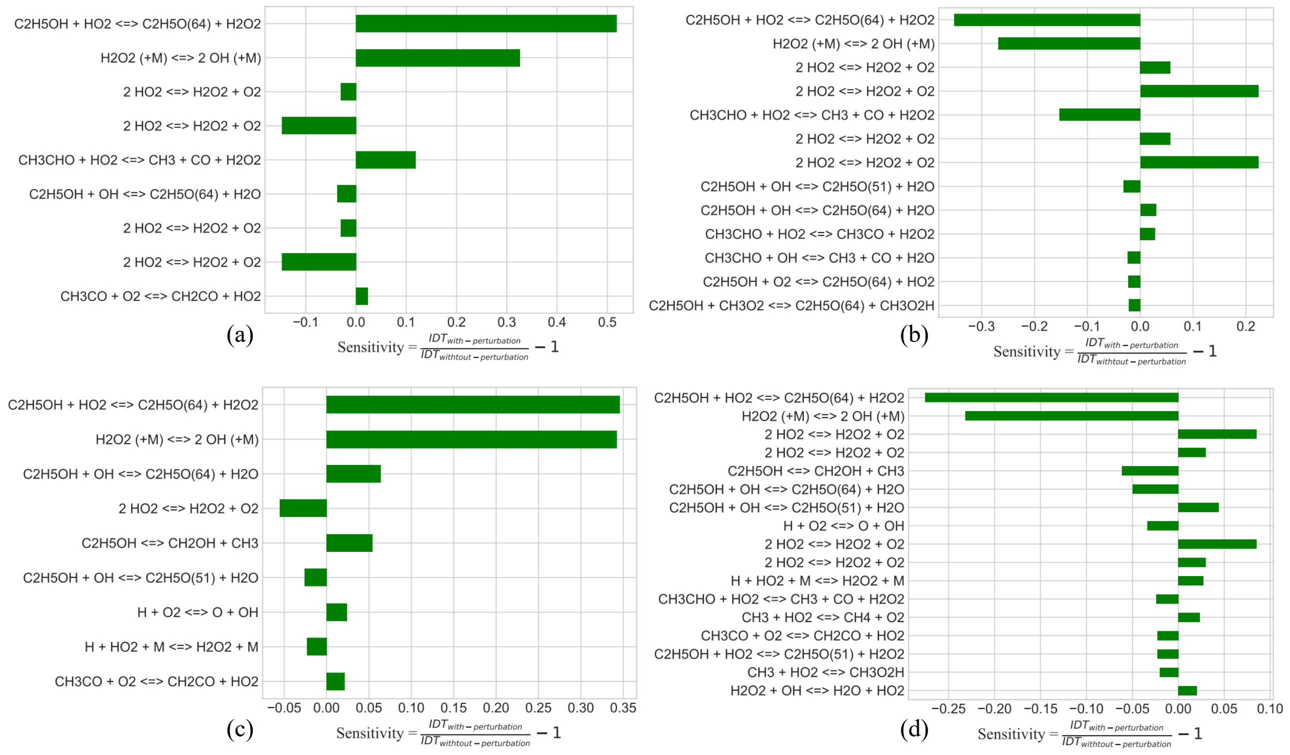


Figure 2: Brute force sensitivity results for ethanol / air (ϕ = 1.0) ignition delay. (a) k x 0.5, T = 800 K, (b) k x 2.0, T = 800 K, (c) k x 0.5, T = 1200 K, (c) k x 2.0, T = 1200 K

The sensitivity analysis reveals that the abstraction reaction $C_2H_5OH + HO_2 \rightarrow C_2H_5O(64) + H_2O_2$ significantly influences the consumption of ethanol across all the evaluated conditions. As a result, it can be considered a major factor contributing to the observed discrepancies. This particular reaction exhibits a positive impact on the ignition delay times (IDT), specially at a temperature of 800 K and k x 0.5. Consequently, it may be responsible for the increase in the ignition delay. As depicted in Figure 1d), the largest discrepancies indeed occur within the low-temperature range. It is important to note that the species $C_2H_5O(64)$ is the ethanol (C_2H_5OH) we've know, with well-established and calculable thermochemistry. The designation "(64)" indicates that this species is the sixty-fourth compound with more than one atom, generated by the Reaction Mechanism Generator (RMG).

Another crucial reaction for chain branching is the methyl abstraction of acetaldehyde $CH_3CHO + HO_2 \rightarrow CH_3 + CO + H_2O_2$. This reaction yields three highly reactive radicals: methyl, carbon monoxide, and hydrogen peroxide, making it significantly impactful in accelerating the combustion process. It plays a more pronounced role in influencing the ignition delay times (IDT) at 800 K but exhibits lower significance in the sensitive hierarchy at 1200 K. This suggests its greater importance in branching the ethanol decomposition at lower temperatures, where it consumes the primary byproduct of ethanol's hydrogen abstraction: $H + C_2H_5OH \rightarrow CH_3CHOH + H_2$. Additionally, a concurrent reaction is the acetyl abstraction: $CH_3CHO + HO_2 \rightarrow CH_3CO + H_2O_2$, which competes with the methyl abstraction and reduces the low-temperature reactivity of ethanol decomposition since the oxidation of acetyl is a slower process $CH_3CO + O_2 \rightarrow CH_2CO + HO_2$. Another notable reaction affecting the reactivity of the system is the chain branching reaction $H_2O_2(+M) \rightarrow 2OH(+M)$. This reaction has well-defined Arrhenius parameters established by various research groups. However, it's worth noting that the LLNL mechanism used in this study, last updated in 2004, might not accurately capture this reaction due to the older experimental data it relies on. Consequently, this may lead to lower accuracy values in predicting the IDT. Furthermore, as noted by Roy and Askari (2020), this reaction exhibits high sensitivity under high-pressure conditions. This characteristic also contributes to the disparities between experimental measurements and model predictions. Overall, the sensitivity analysis sheds light on the specific reactions that significantly influence the discrepancies observed in the simulation results of ignition delay times. Additionally, it also highlights the strengths and weaknesses of the different mechanisms in capturing these reactions accurately.

3.2 Laminar Flame Speed (LFS)

The mechanisms are now compared in terms of laminar flame speed (S_L) experiments. Figure 3 depicts the results obtained at pressure of 1 atm and different temperatures. As shown, there are some notable relative differences between the simulations and the experimental data. The San Diego mechanism tends to overestimate laminar flame speeds at low equivalence ratios, across all temperatures evaluated. Similar trends are also observed in the works of Raida *et al.* (2021) and Katoch *et al.* (2018). Firstly, it is essential to note the influence of the initial temperature on LFS results. In this case, laminar flame speed increases with increasing temperature. According to the findings in Lu *et al.* (2023), at high temperatures, the system generates H or OH radicals, which are the key factors contributing to the increase in laminar flame speed. Additionally, when compared to the experimental results of Konnov *et al.* (2011), both the Aramco v3.0 and CRECK mechanisms also tend to overestimate laminar flame speeds at low equivalence ratios, while demonstrating reasonable agreement at high equivalence ratios, as seen in Figure 3(a), (b), (c), and (e). Nevertheless, they overpredict LFS results at the fuel-rich side when compared to the results of Veloo *et al.* (2010), as seen in Figure 3(d). In contrast, the PCRL mechanism show accurate representation of the experimental data, although it also tend to overestimate the LFS results of Veloo *et al.* (2010) at the rich side. Conversely, the LLNL mechanism exhibits a reasonable match with experimental data, especially the results of Veloo *et al.* (2010). However, regarding the experimental results of Konnov *et al.* (2011), both mechanisms overestimate LFS at the fuel-lean side and underestimate it at the fuel-rich side. Therefore, based on the results obtained, both the PCRL and LLNL mechanisms demonstrate a more accurate representation of the laminar flame speed of ethanol/air flames within the evaluated temperatures, with an average deviation of 6.27% and 11%, respectively.

3.2.1 Brute-force sensitivity analysis on LFS

In order to better understand the reduced ability of the PCRL mechanism to predict the laminar flame speeds, a brute force sensitivity analysis on LFS was performed. Simulations were performed at a temperature of 358 K, at ϕ = 0.7 and ϕ = 1.55, and a pressure of 1 atm. Figure 4 shows the most sensitive reactions in laminar flame speed calculations.

As expected, hydrogen oxidation reactions are the most sensitive in LFS calculations. The reaction $H + O_2 <=> O + OH$ is positively sensitive for k x 2.0, specially at ϕ = 1.55. Another important reaction is the propagation reaction between carbon monoxide and the hydroxyl radical $CO + OH \rightarrow CO_2 + H$, which produces an H atom. This reaction is extremely sensitive at fuel-lean mixtures. On the other hand, at fuel-rich mixtures, the second most sensitive reaction is the bimolecular reaction involving methyl radicals $(CH3)$ and hydrogen atoms (H) in the presence of a third body $CH_3 + H(+M) <=> CH_4(+M)$. This reaction is a key step in methane formation, and therefore it affects the overall reactivity, having a notable impact in flame propagation. This reaction is also defined as a three-body reaction due to the collision of an unspecified collision partner M that carries away excess energy to stabilize the reactants. Some chemical models define a collision efficiency coefficient for the possible M species but they vary according to the source. It's noted that for this reaction PCRL and CRECK mechanism give almost the same coefficients. While San Diego mechanism give much greater efficient for water molecules and twice the efficiency for methane molecules and also brings fewer coefficients values. In the same note LLNL mechanism decrease the number of molecules with coefficients even further, although its coefficient values are similar to the PCRL and CRECK values. It's known that for numerically generated mechanism like the PCRL these coefficients are thermodynamically generated with a collision model build in together with thermodynamic and kinetics calculations. This approach may give greater consistency for the three-body reactions.

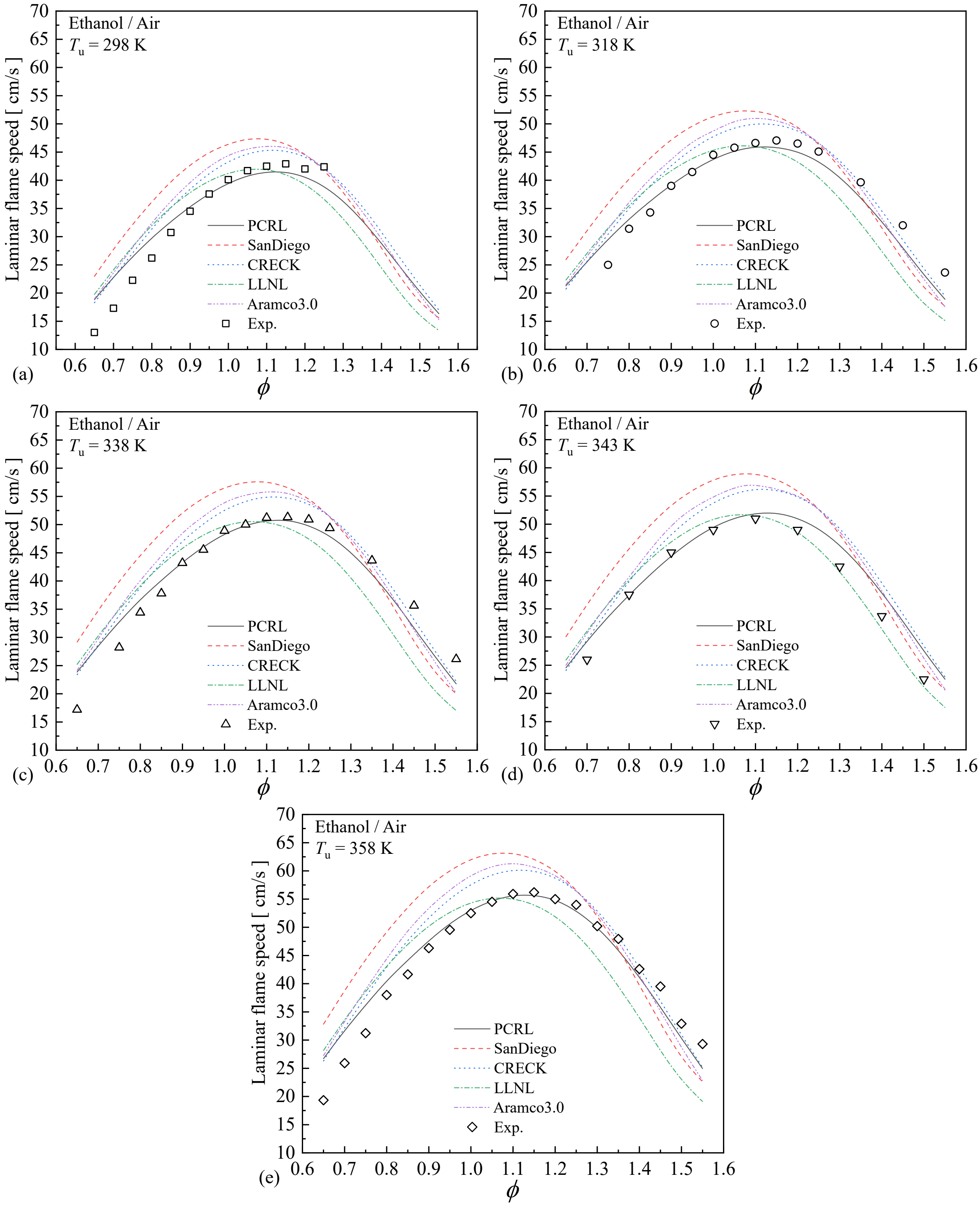
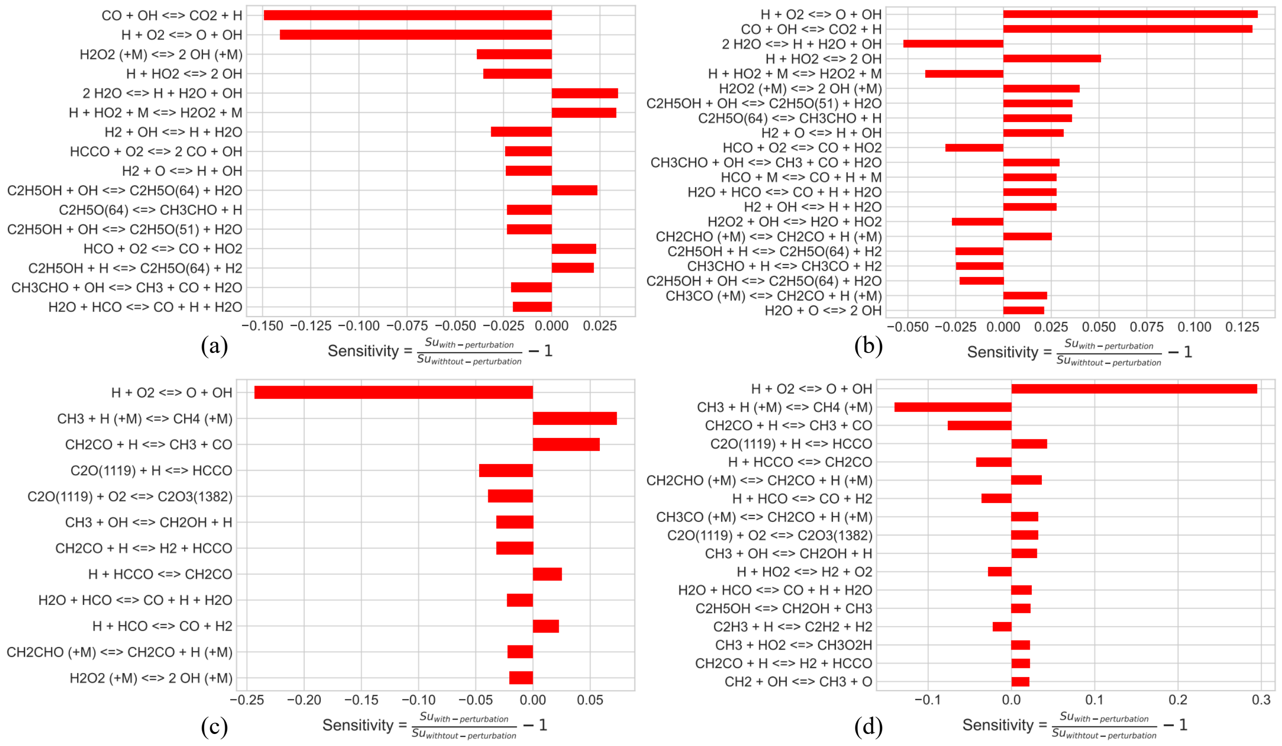


Figure 3: Comparison of ethanol laminar flame speeds for different mechanisms. (a), (b), (c) and (e) symbols represent the experimental results of Konnov *et al.* (2011). (d) symbols represent the experimental results of Veloo *et al.* (2010)

3.3 Species Concentration Profiles

Lastly, the simulation results of mole fraction calculation from a jet-stirred reactor as a function of temperature are evaluated. Figure 5 shows the comparison of the mole fraction of ethanol oxidation compared with the results reported by Leplat *et al.* (2011).

As it can be seen, the concentration of H_2O steadily rises in the temperature range of 950 to 1150 K, indicating the prevalence of high-temperature chemistry. In contrast, the O_2 concentration decreases slightly between 900 and 1100 K. All the kinetics models can adequately represent the ethanol (C_2H_5OH) mass fraction (depletion) along the temperature



(a) (b) (c) (d)

Figure 4: Brute force sensitivity results for ethanol / air laminar flame speed at T = 358 K. (a) k x 0.5, ϕ = 0.70, (b) k x 2.0, ϕ = 0.70, (c) k x 0.5, ϕ = 1.55 (c) k x 2.0, ϕ = 1.55

range evaluated. However, it can be noticed that, according to Figure 5(a), the LLNL mechanism underestimates the ethanol reaction rate within the temperature range of approximately 980 K to 1080 K, while the San Diego Mech exhibits a similar issue within the temperature range of approximately 960 K to 1150 K, as demonstrated in Figure 5(b). The Aramco3.0, CRECK and PCRL models, on the other hand, are nicely fit to the ethanol mass fractions (depletion) experimental data from Leplat *et al.* (2011). In addition, the five mechanisms consistently show an overestimation of O_2 mass fractions, with PCRL Mech demonstrating a relatively lower deviation, as seen in Figure 5(a). However, PCRL Mech tends to underestimate the mass fractions of O_2 within the temperature range of approximately 1040 to 1075 K, whereas the CRECK, LLNL, and Aramco v3.0 mechanism overestimate the results at the same range. Similarly, according to Figure 5(b), San Diego mechanism also underestimates the mass fractions over a slightly wider range, from around 1040 K to approximately 1155 K. It is important to note that, in all cases, the mechanisms tend to converge toward the experimental results as the temperature increases (> 1200 K). Unfortunately, there is a lack of sufficient experimental data above this temperature for further comparison.

The mole fractions of CO, however, show deviations from experimental results as the temperature increases, especially above 1150 K. At temperatures lower than this threshold, the LLNL mechanism exhibits a better fit to the experimental results, as observed in Figure 5(d), while CRECK and Aramco v3.0 (Figure 5(c) and (d), respectively) show a slight deviation at around 1100-1150 K. On the other hand, the PCRL Mech tends to slightly overestimate the mole fractions at all evaluated temperatures in this study, as shown in Figure 5(a). Further, among the five mechanisms evaluated, the San Diego mechanism exhibits a more significant overestimation of CO mole fractions when compared to the other mechanisms. Following, below 1150 K, all five mechanisms displayed accurate predictions of CO_2 mole fractions. However, at higher temperatures, the simulated mole fractions were consistently overestimated across all cases. Among them, the LLNL and Aramco v3.0 mechanisms exhibited only a minimal deviation.

Lastly, regarding H_2O mole fractions, the PCRL and CRECK mechanisms demonstrated better agreement with the results of Leplat *et al.* (2011), although slight deviations are still present. The San Diego mechanism tended to overestimate the mass fractions at temperatures higher than 975 K, whereas the LLNL and Aramco v3.0 underestimated it. Overall, despite the deviations found, all mechanisms showed reasonable agreement with the experimental results.

4. CONCLUSIONS

In this study, five kinetic mechanisms, namely Aramco v3.0, CRECK, LLNL, PCRL, and San Diego were evaluated to assess their accuracy in predicting key combustion features of ethanol oxidation. Three kinds of simulations of reactive systems were performed: ignition delay time simulation on homogeneous adiabatic constant volume reactor, laminar

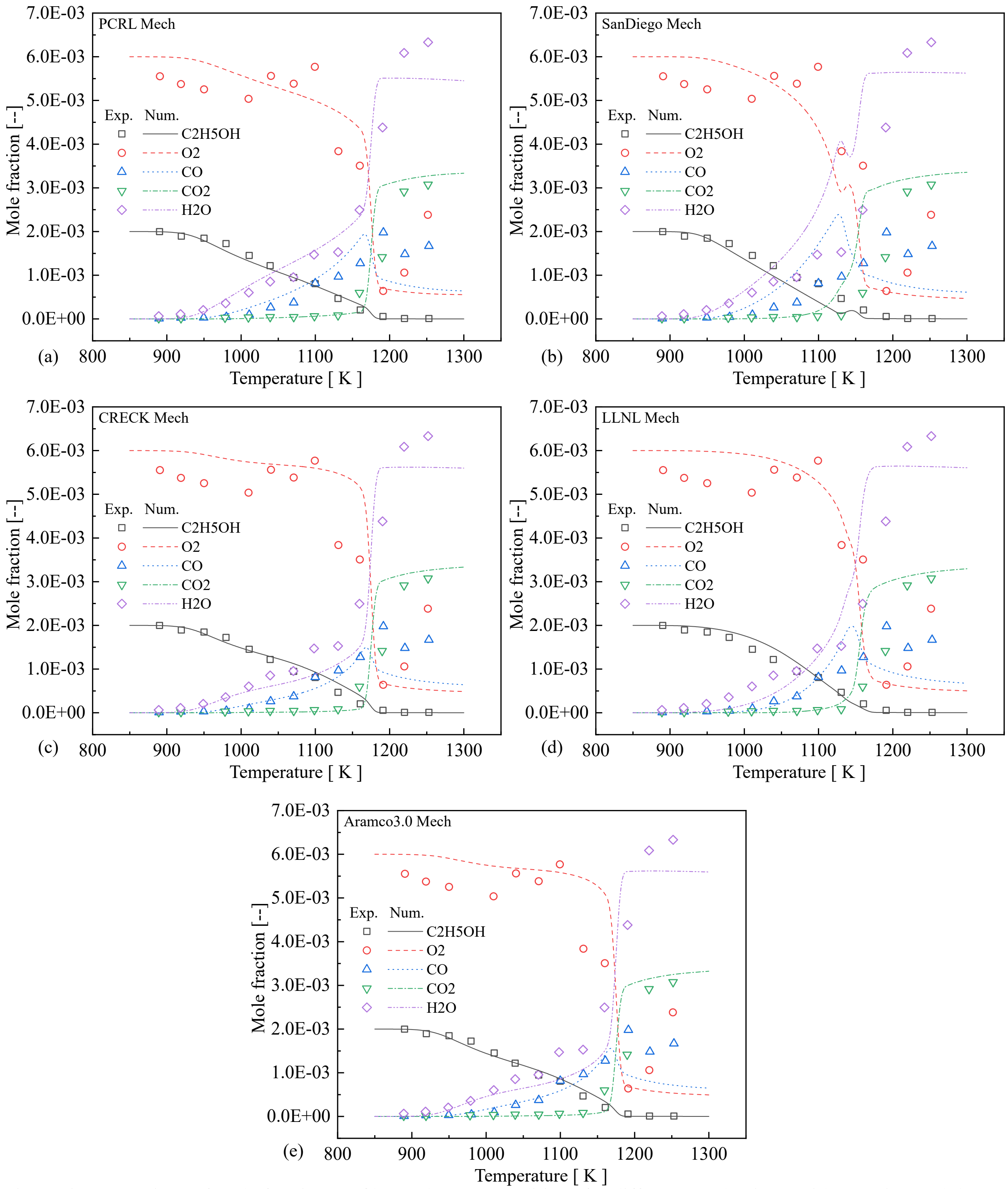


Figure 5: Comparison of mole fraction profiles under JSR conditions for different mechanisms with experimental data at pressure of 1 atm and equivalence ratio of 1.0. Symbols represent the experimental results of Leplat *et al.* (2011)

free propagating flame speed, and species concentration profiles in a jet-stirred reactor (JSR). A brute-force sensitivity analysis was also conducted to identify the reactions that most influenced the discrepancies observed in the IDT and LFS simulations, specifically. The main conclusions of this work can be itemized as follow:

- The simulations revealed that CRECK, Aramco, and PCRL performed exceptionally well in predicting ignition delay times, while San Diego and LLNL tended to overestimate the results. However, at high pressures, LLNL showed better agreement with experimental data.

- The sensitivity analysis on IDT revealed that the primary sources of discrepancies in the PCRL model's ignition delay time calculations were found to be the abstraction reaction $C_2H_5OH + HO_2 \rightarrow C_2H_5O(64) + H_2O_2$, that has a significant influence in ignition delay times at 800 K and k x 0.5; the methyl abstraction of acetaldehyde $CH_3CHO + HO_2 \rightarrow CH_3 + CO + H_2O_2$, which played a crucial role in impacting ethanol decomposition at lower temperatures; the chain branching reaction $H_2O_2(+M) \rightarrow 2OH(+M)$ that is extremely sensitivity under high-pressure conditions, and the acetyl abstraction $CH_3CHO + HO_2 \rightarrow CH_3CO + H_2O_2$, a concurrent reaction that competes with the methyl abstraction and reduces the low-temperature reactivity of ethanol decomposition.

- Regarding laminar flame speeds, the PCRL and LLNL mechanisms provided the most accurate representation of the experimental data. In addition, sensitivity analysis highlighted the reactions $H + O_2 \rightarrow O + OH$ (especially at k x 2.0) and $CO + OH \rightarrow CO_2 + H$ as the major sources of discrepancies in the PCRL model's predictions for laminar flame speeds at fuel-lean mixtures. On the other hand, at fuel-rich mixtures, the bimolecular reaction rate $CH_3 + H(+M) \rightarrow CH_4(+M)$ also played a notable role in flame propagation dynamics.

- An analysis of species concentration profiles reveals that Aramco v3.0, CRECK, and PCRL models effectively represent the ethanol (C_2H_5OH) mass fractions. However, for the O_2 mass fraction, the PCRL model shows better agreement. On the other hand, when it comes to the production of CO, the CRECK and Aramco models demonstrate a closer fit to the data, while the LLNL and Aramco models exhibit only minimal deviation in calculating CO_2 mass fractions. Lastly, concerning the H_2O mass fractions, both the PCRL and CRECK mechanisms show better agreement.

- The superior performance of Aramco v3.0 and CRECK can be attributed to their larger number of chemical species and reactions, allowing a more accurate representation of the complex chemical reactions involved in the combustion of ethanol. Consequently, the discrepancies observed with the LLNL and San Diego mechanisms may be attributed to their limited number of species and reactions.

- Notably, the PCRL has the most accurate predictions, even despite being a mechanism with a significantly smaller number of chemical species and reactions compared to CRECK and Aramco. It is also the only model that combines thermodynamically generated coefficients seamlessly integrated with a collision model, alongside comprehensive thermodynamic and kinetics calculations. This approach potentially enhances the consistency of three-body reactions, thereby potentially contributing to the accuracy of the model's predictions.

Overall, among the five mechanisms evaluated in this study, the PCRL mechanism emerged as a more accurate representation of ethanol combustion characteristics within the evaluated experimental data. Not only did it demonstrate similar or better predictions than Aramco v3.0 and CRECK, but it also exhibited computational efficiency, with significantly lower computational time. In summary, the findings of this work contribute to a deeper understanding of the complex chemical processes involved in ethanol combustion and provide valuable insights for refining these kinetic models, particularly in predicting the key combustion features of ethanol oxidation.

5. ACKNOWLEDGEMENTS

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