

NUMERICAL ANALYSIS OF DETAILED KINETICS MODELS FOR ETHANOL OXIDATION

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Abstract. *In this work three recently published detailed kinetics models for ethanol oxidation are revised. Numerical simulations by using the detailed kinetics models under conditions similar to those found in internal combustion engines were performed. The numerical results are then compared to experimental values of ignition delay times in shock tubes at pressures of 3.3, 3.4 and 3.5 bar for equivalence ratio 0.5, 2.0 and 1.0 respectively to temperature from 1100 K to 1500 K. Also, the results are compared for pressures 10, 30 and 50 bar for temperatures ranging from 800 K to 1200 K and stoichiometric compositions available in the literature. One of the aims of this work is to understand the recent developments of detailed kinetics models for ethanol thermal oxidation and to identify the major advantages and flaws when used for ethanol-air combustion under engine-like conditions. The final purpose of this work is to prepare a well-validated detailed kinetics model for ethanol oxidation, in order to be used as a starting point to the development of a reduced kinetics model suitable to be used in computational fluid dynamics simulations.*

Keywords: *Ethanol, Detailed kinetics model, Internal combustion engines, Numerical simulation.*

1. Introduction

The expected shortage in fossil energy resources and the growing need for transportation fuels is continuously increasing the interest in biomass-derived fuels. Fuel blends containing ethanol have become a reality in many countries. Especially in countries like Brazil, fuels with very high ethanol concentrations are on the market. The fundamental understanding of the combustion chemistry of ethanol and ethanol-containing fuels, however, has not yet reached the required level. Detailed kinetics models for ethanol oxidation have been reported since the eighties, Natarajan and Bhaskaran (1981) reported the first detailed kinetics model for high-temperature oxidation of ethanol with 56 elementary reactions. Marinov (1998) reported a detailed model involving 383 elementary reactions among 57 chemical species. Marinov's model included the three paths of hydrogen abstraction to form the three isomers of C₂H₅O. Saxena and Williams (2007) reported a detailed kinetics model with 288 elementary reactions among 57 chemical species where the 53 steps among 14 species needed to attend to NO_x chemistry and 43 steps and 7 species to address formation of compounds involving three carbon atoms. Haas et al. (2009) presented a kinetics model composed by 39 chemical species and 238 elementary reactions. Recently, Cancino et al. (2009a) reported a detailed kinetics model, based on the previous works of Marinov (1998) and Konnov (2009) and composed by 1349 elementary reactions among 136 chemical species.

In this work, the more recent detailed kinetics model reported at literature, Cancino et al. (2009a), Haas et al. (2009) and Saxena and Williams (2007) are used in the present analysis of ethanol thermal oxidation under engine-like conditions.

All the models considered in this work are analyzed at low pressures, 3.3, 3.4 and 3.5 bar, temperatures ranging from 1100 K to 1500 K with equivalence ratio 0.5, 2.0 and 1.0, in oxygen, respectively, and at high pressures, 10, 30 and 50 bar, temperatures ranging from 800 K to 1200 K using stoichiometric composition in air.

Profiles of temporal evolution of temperature and concentration show that the Cancino's model usually reach first the ignition point when compared to the other models analyzed in this work. The parameter used to determine the onset of ignition was the maximum O-atoms radical concentration.

Temperature distributions show that the mechanisms of Haas et al. and Saxena and Williams have low reactivity in the beginning, also for low pressures and high temperatures the mechanisms are strongly affected by endothermic reactions in the beginning of the oxidation process, decreasing the temperature of the mixture.

Comparisons to experimental results of ignition delay times (IDTs) shows that the detailed kinetics model from Cancino et al (2009a) is the mechanism with the best agreement, both for low as for high pressures; although for pressures of 3.4 and 10 bars some discrepancy is found. The mechanisms of Haas and Saxena can represent the data of IDT for low pressures with relatively good approximation, although low temperature results deviate from experimental data. Similar to the mechanism of Cancino to 3.4 bar, the mechanisms do not provide good results. For high pressure the mechanism of Haas and Saxena's model can not cope with the change in the behavior profile of IDT and are overestimating the experimental data.

2. Principals characteristics of mechanisms.

For the characterization of fuels the ignition delay time - IDT is a critical parameter for internal combustion (IC) engines. The IDT influences the performance of both compression-ignition (CI) and spark-ignition (SI) engines. In CI and homogeneous-charge compression-ignition (HCCI) engines, the combustion process is initiated by auto ignition. Therefore, it is crucial to know “when” ignition will occur. In SI engines, auto ignition causes knock which limits the accessibility of the most efficient engine operation regimes, Cancino et al. (2009b).

The detailed kinetics mechanisms were analyzed by using the CHEMKIN-PRO[®] computational tool. The mechanisms of Saxena and Williams, Haas et al. and Cancino et al. were compared against experimental results available in the literature, covering different ranges of pressure, temperature and equivalence ratio.

Table 1 shows the major characteristics of the detailed kinetics models considered in this work. The table includes the key characteristics such as number of chemical species, elementary reactions and validation against experimental parameters.

Table 1 Detailed kinetics models analyzed in this work.

Model	Species	Elementary reactions	NOx Chemistry	Ethanol reactions in:		Validated against			
				Reactants	Products	<i>p</i> [bar]	<i>T</i> [K]	ϕ	
Saxena and Williams (2007)	57	288	Yes	17	0	IDT in Shock tube	1 - 4.6	1300 - 1700	0.5, 1.0, 2.0
						Laminar flame speed	1	298 - 453	0.7, 0.9, 1.0
						Chemical species	C ₂ H ₅ OH, N ₂ , O ₂ , H ₂ O, CO, CO ₂ , H ₂ , CH ₄ , C ₂ H ₂ + C ₂ H ₄ , C ₂ H ₆		
Haas et al. (2009)	39	238	No	17	0	Flow reactor	12.5	498 - 903	0.43 - 0.91
						Chemical species	C ₂ H ₅ OH, H ₂ O, CO, CO ₂ , O ₂ , CH ₄ , CH ₃ CHO, CH ₂ O, C ₂ H ₄		
Cancino et al. (2010)	136	1349	Yes	33	7	IDT in Shock tube	10, 30, 50	700 - 1600	0.3, 1.0

IDT = Ignition Delay Time

Figure 1 shows the principal routes of primary degradation of ethanol proposed of Marinov (1998) and Natarajan and Bhaskaran (1981), also, it can be observed that the model from Cancino et al. allows more reactions involving hydrogen abstraction, when compared to the Haas and Saxena models.

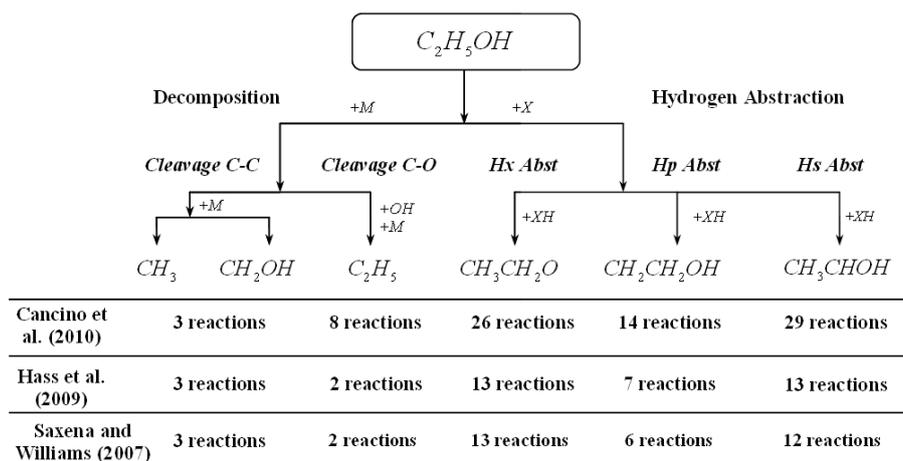


Figure 1: Number of reactions involving the thermal decomposition of ethanol relating the five possible routes of bound cleavage in the mechanisms of Cancino, Hass and Saxena.

3. Analysis of mechanisms.

The detailed kinetic mechanisms for the ethanol oxidation studied here were analyzed from various aspects such as temporal distribution of temperature, time distribution of concentration of O radical and thermal ignition delays time.

The analysis was divided into two groups; low pressure oxidation and high pressure oxidation. The group of low pressure allows pressures of 3.3, 3.4 and 3.5 bar with equivalence ratio 0.5, 2.0 and 1.0 respectively, and temperatures ranging from 1100 K to 1500 K. For this group, the numerical results of ignition delay time were compared with experimental data from Dunphy and Simmie (1991). The group of high pressure, gather the pressures of 10, 30 and 50 bar, temperatures ranging from 800 K to 1200 K and stoichiometric composition. The numerical results of ignition delay at high pressures were compared with experimental data from Cancino et al (2009a).

3.1. Temporal distribution of temperature at low pressures.

The analysis of temporal distribution of temperature were performed using the module Closed Homogeneous Batch Reactor (CHBR) available in CHEMKIN PRO[®]. The module CHBR, as its name suggest, is a closed Perfectly Stirred Reactor (PSR), ie there is no mass flow acrossing the borders of the reactor. The reactor is considered adiabatic and the pressure kept constant.

To the situation with $\phi = 0.5$ and pressure of 3.3 bar, were analyzed 25 different data of temperature, ranging from 1132 K to 1476 K, the same temperature points of the experimental data from Dunphy and Simmie. Considering the case for $\phi = 1.0$ and pressure of 3.5 bar were used 17 points, with temperatures between 1150 K to 1530 K. For the equivalence ratio $\phi = 2.0$, pressure of 3.4 bar and temperatures ranging from 1124 K to 1492 K, were considered and 17 temperature points.

Two results from simulations, one for each given pressure will be presented here, one for low temperature and one for high temperature. Figure 2 shows the results for the temperature distribution in the cases analyzed. The selected points correspond to the temperature extremes of the experimental condition $\phi = 0.5$ and pressure of 3.3 bar .

For pressure of 3.3 bar and equivalence ratio $\phi = 0.5$, the temperatures selected were 1132 K and 1476 K. Observing Figure 2, it is possible to observe that the mechanism of Cancino et al., primarily reaches the ignition point, followed by Saxena and Williams and finally the mechanism from Haas et al.

It can be observed for the temperature of 1132 K that the elementary reactions of the mechanisms of Haas et al. and Saxena and Williams show less reactivity. This is observed in the left side of Figure 2, where the Saxena and Haas models do not show a considerable increase on temperature when compared to the Cancino model.

The right side of Figure 2 shows the temperature distribution for initial temperature of $T = 1476$ K. It is observed in the region highlighted that the mechanisms of Saxena and Williams and Haas et al., show a decreasing of the temperature at the beginning of the process, and this decrease of temperature is more intense for the Haas mechanism. A possible explanation for this behavior is that in both, Saxena and Haas mechanism, and at the beginnig of the thermal oxidation process, the chemistry is strongly affected for the endothermic reactions included in these mechanisms. This behavior was observed in all the numerical results of this work and it effect increase as the initial temperature of the system increases.

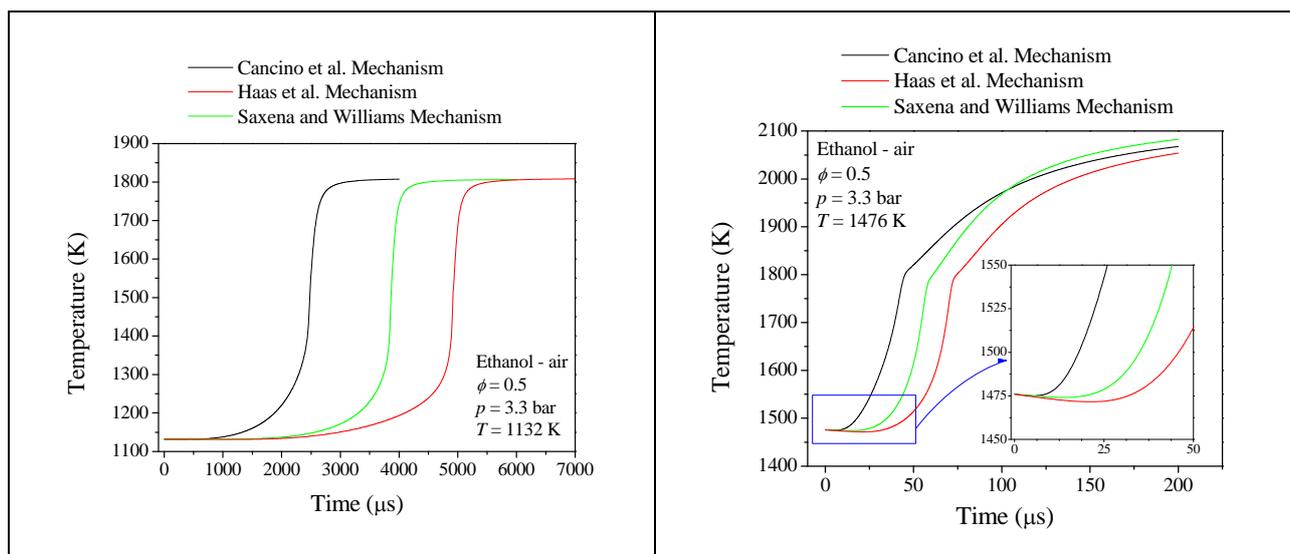


Figure 2: Temperature evolution for $\phi = 0.5$ and $p = 3.3$ bar.

For pressure of 3.4 bar and equivalence ratio $\phi = 2.0$, the temperatures selected were 1124 K and 1492 K, and the results for these two temperature values are shown in Figure 3 below. For this case considering fuel-rich mixtures, the mechanisms show different behaviours, in relation of temperatutre distribution. For the same temperature, the shape of the curve of one mechanism when compared with other mechanism is different.

The right side of Figure 3, as shown in Figure 2, the mechanism of Saxena and Williams and the mechanism of Haas et al. show the temperature drop at the beginning of the process and this being more pronounced for the mechanism of Haas et al.. This decrease in the temperature hovers around 10K for the mechanism of Haas et al. and 5 K for the mechanism of Saxena and Williams. For the mechanism of Cancino et al. this temperature drop is also observed, (the maximum value observed was 2 K). It is noteworthy that the temperature drop is accentuated as the initial temperature of the system increases.

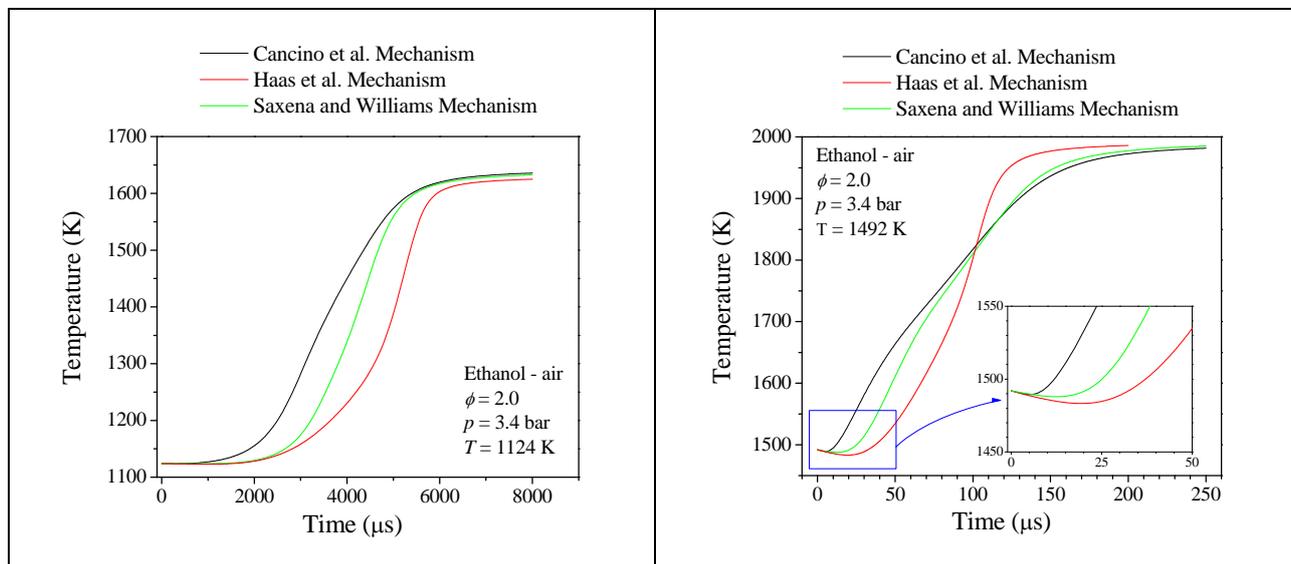


Figure 3: Temperature distribution for $\phi = 2.0$ and $p = 3.4$ bar.

Figure 4 presents the results for temperatures of 1153 K and 1530 K for stoichiometric mixtures ($\phi = 1.0$). For the values of the temperatures analyzed, the curves have similar shapes. In the right side figure, about 1830 K, there is a change in behavior of the curves. This change comes about after the ignition point of the system. This same behavior also was observed for fuel-lean mixtures ($\phi = 0.5$).

Increasing the initial temperature of the process, also is observed the same effect of temperature drop as in the last cases showed in figures 2 and 3.

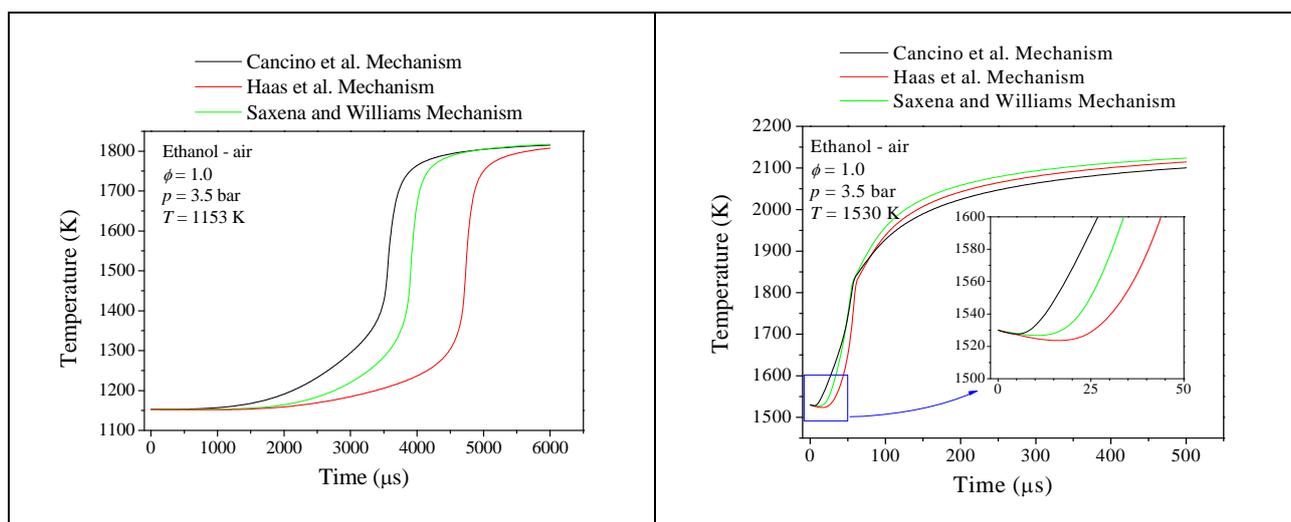


Figure 4: Temperature distribution for $\phi = 1.0$ and $p = 3.5$ bar.

3.2. Temporal distribution of temperature at high pressures.

Figure 5 below shows the temperature distributions considered when high pressures (10, 30 and 50 bar). These pressures were analyzed only for stoichiometric mixtures ($\phi = 1.0$).

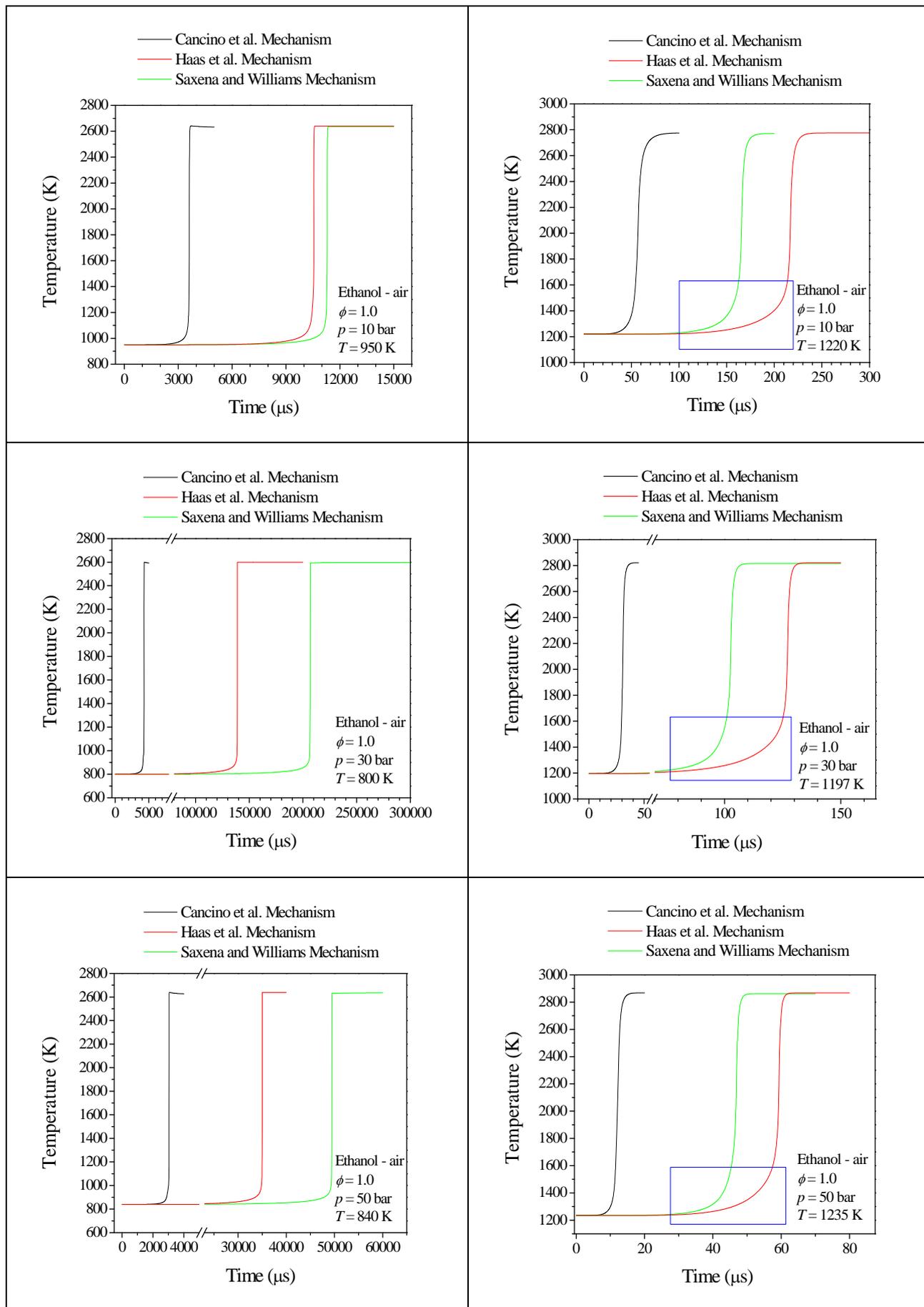


Figure 5: Temperature distribution for $\phi = 1.0$ and pressures of 10, 30 and 50 bar.

For the pressure of 10 bar, seven temperature points were analyzed, for temperatures between 950 K to 1220 K, these data coincide with the experimental data of Cancino et al.(2009a) For the pressure of 30 bar, eleven points of temperature were considered, from 800 K to 1200 K. For pressure of 50 bar the temperature range was from 840 K to 1235 K, and eight temperature points were analyzed.

In figure 5, it can be observed that all the curves exhibit similar behavior. All mechanisms reach nearly the same maximum temperature.

The mechanism developed by Cancino et al. (2009a) reach the ignition temperature before the Saxena and Haas mechanism. It is worth noting that for low temperatures the mechanism of Haas et al. reaches the ignition point first than the mechanism of Saxena and Williams, as observed in the left-side of Figure 5, however when the temperature increases the mechanism of Saxena and Wiliams reaches the ignition point first than the mechanism of Haas et al., as observed in the right-side of Figure 5.

Also, for higger temperatures (right-side figures on figure 5) is observed low reactivity behaviour on the Saxena and Haas mechanisms. Note that, also, for higger temperatures is more strong the effect of endothermic reactions in these mechanisms (Saxena and Haas) “consuming” energy and retarding the ignition event in the system. This low reactivity is more significant for the mechanism of Haas.

3.3. Time-evolution of O-atoms radical.

In this work, the parameter used to locate the start of ignition point was the maximum concentration of oxygen atoms. The figures of the O-atoms distribution are presented by using adimensional scale, dividing the concentration for a given time (t) the largest concentration observed over the time spectrum.

Figures 6 and 7 show the distribution O-atoms radical concentration of the low and high pressures analyses As expected from the last results, it can be observed that the model that first reaches the ignition point is the mechanism Cancino.

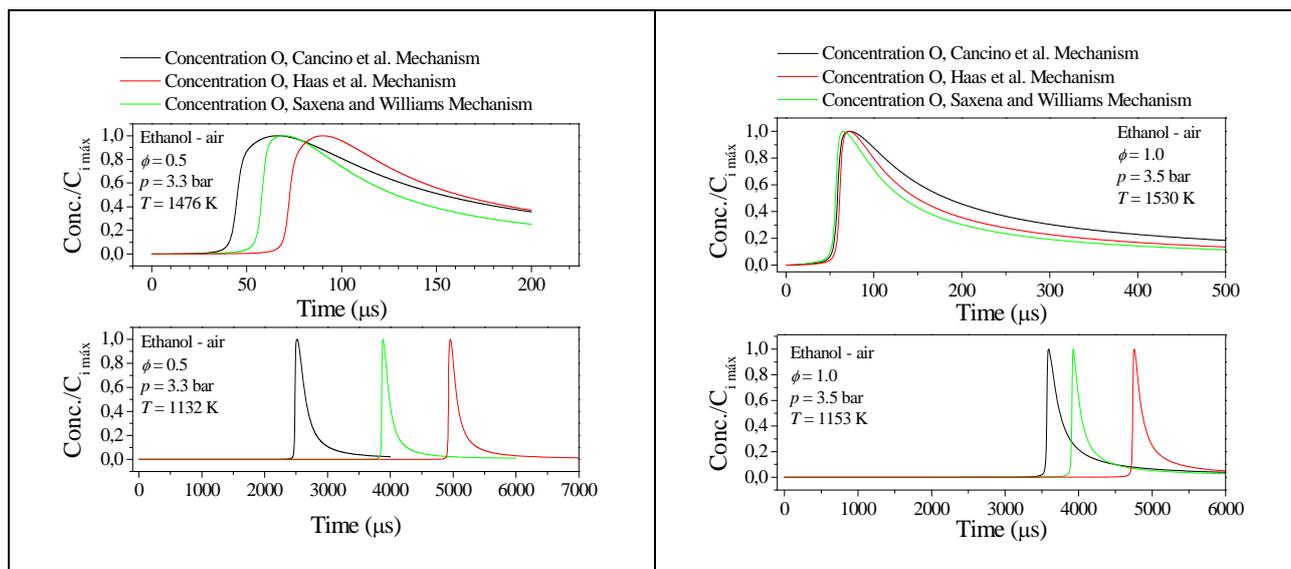


Figure 6: Distribution of oxygen-atoms concentration for low pressures.

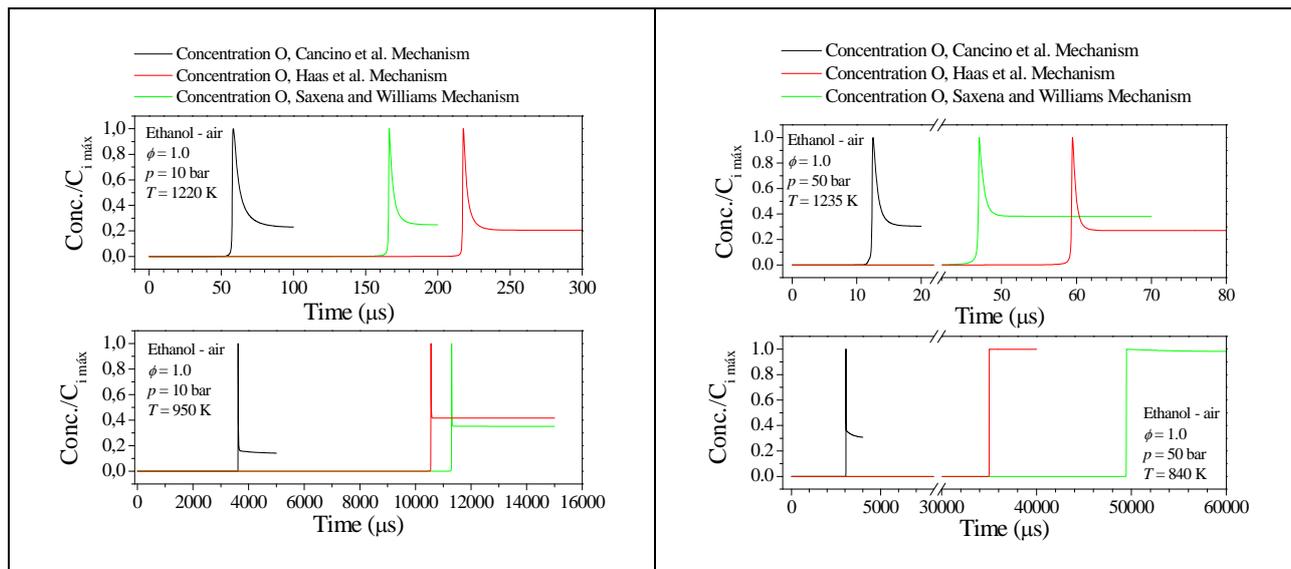


Figure 7: Distribution of oxygen-atoms concentration for high pressures.

For high temperatures, the depletion of oxygen-atoms radical is slower when compared to the low temperature regime. At low temperatures, after the ignition temperature of radical oxygen concentration drops to very low values.

The Figure 7 shows the distribution of concentration of radical oxygen at high pressures. It can be observed the change in the behavior of the concentration of radical oxygen in the Haas and Saxena mechanisms. At low temperatures the mechanism of Haas et al. ignites first than Saxena's model, however, for high temperatures the mechanism of Saxena initiates the ignition first than Haas mechanism.

3.4. Ignition delay time.

The numerical results of ignition delay time (IDT) for low pressures (3.3, 3.4 and 3.5 bar) were compared with experimental data of Dunphy and Simmie (1991), while for high pressures (10, 30 and 50 bar) the results were compared with the experimental data of Cancino et al. (2009a).

For pressures of 3.3 and 3.4 bar the results are shown in Figure 8. For the pressure of 3.3 bar and $\phi = 0.5$ (left side of Figure 8) the mechanism that best represents the experimental data of Dunphy and Simmie is the mechanism of Cancino et al. The Cancino's model represents well the whole temperature range studied, only for few points of low temperature the numerical data deviate slightly from experimental data. The mechanism of Saxena and Williams is the best reproduces the experimental data after Cancino's model.

For pressures of 3.4 bar and $\phi = 2.0$ (right side of Figure 8), it is difficult to say what is the mechanism that best represents the experimental data. The models from Cancino and Haas underpredicts the ignition delay time on the whole temperature range of experimental results, and the Saxena model overpredicts the IDT in the region of high temperatures and underpredicts the IDT in the low temperature region.

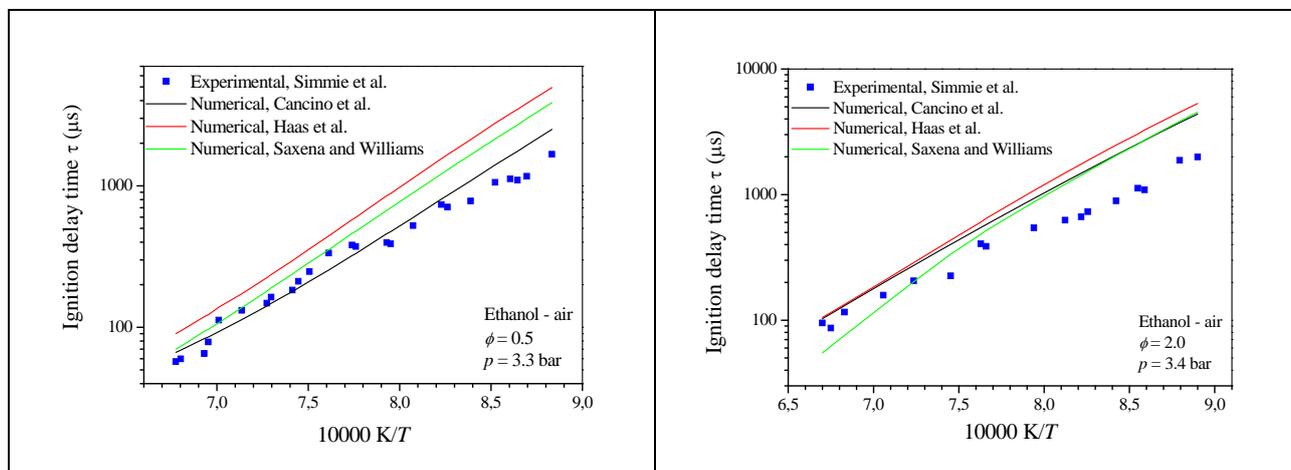


Figure 8: Comparison of experimental and numerical simulation for IDT, $p=3.3$ bar (left) and $p=3.4$ bar (right).

The Figure 9 below shows data for the conditions of 3.5 bar (left) and 10 bar (right). Analyzing the left side of Figure 9, it can be observed that for high temperatures all the mechanisms are in good agreement with the experimental data. However, when temperature decreases, the numerical results from all models underpredicts the IDT.

The right side of Figure 9 gathers the data for equivalence ratio $\phi = 1.0$ and pressure of 10 bar. The mechanism that best represents the experimental data at 10 bar is the mechanism of Cancino et al., although the numerical data are still rather far from the experimental data. The mechanisms of Haas et al. and Saxena and Williams underpredicts the IDT when compared to experimental data. These mechanisms can not reproduce the change in the slope of the IDT behaviour.

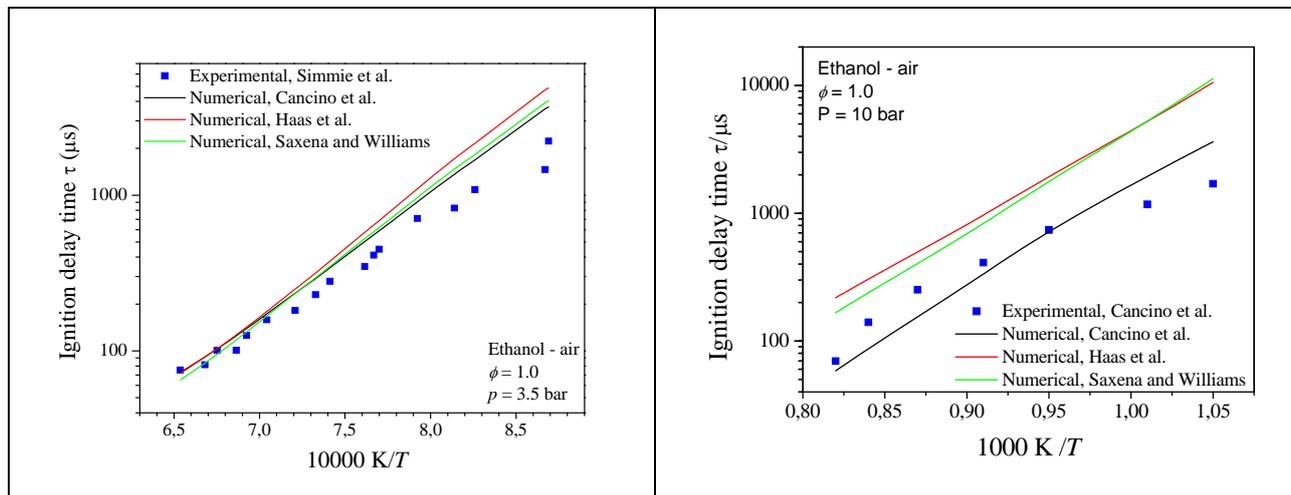


Figure 9: Comparison of experimental and numerical simulation for IDT, $p=3.5$ bar (left) and $p=10$ bar (right).

The results for pressures of 30 bar and 50 bar are depicted in Figure 10. It can be observed that the mechanism of Cancino et al (2009a) is in good agreement with the experimental results and also the model can keep up the slope change observed in the experimental results. The mechanism of Haas and Saxena’s model does not represent a good approximation the experimental data, mainly to the region of low temperatures, when occurs a change in the slope of the IDT. A similar behavior can be observed for the pressure of 50 bar (right-side figure 10).

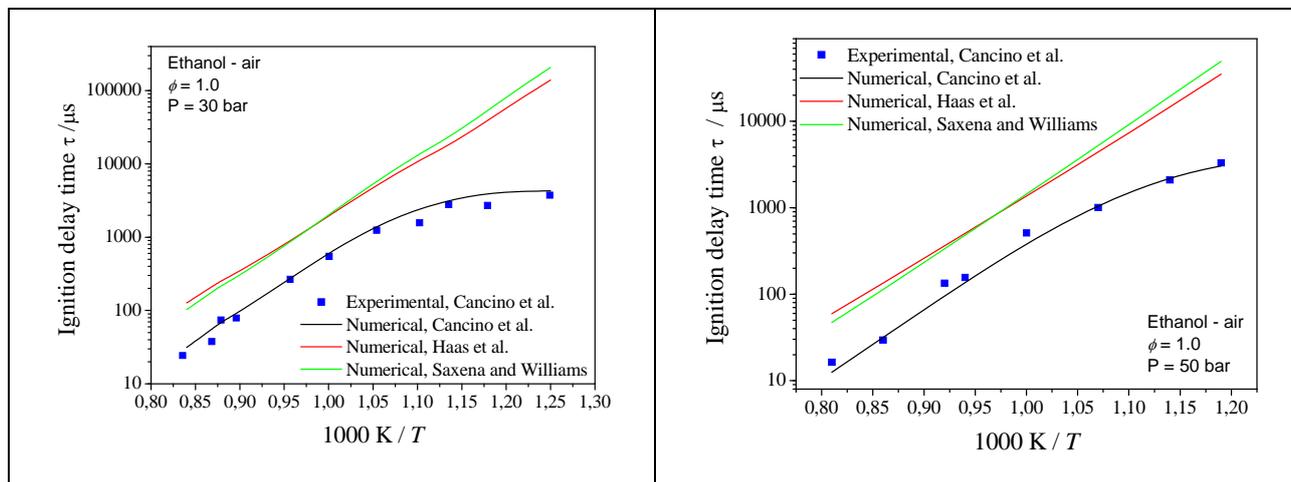


Figure 10: Comparison of experimental and numerical simulation for IDT, $P=30$ bar (left) and $P=50$ bar (right).

The Table 2 shows the maximum and minimum difference in IDT between the kinetic mechanisms and the experimental results from the literature. Looking at the maximum and minimum values, see that the best results are obtained from the mechanism of Cancino et al. For high pressures the mechanism of Saxena and Williams shows values of maximum difference quite large reaching values of over 5000% difference. For low pressures, the mechanism of Saxena best represents the experimental data than the mechanism of Haas.

Table 2 Maximum and minimal difference between in IDT for models analyzed in this work.

Model	Difference (%)	$p = 3.3$ bar $\phi = 0.5$	$p = 3.4$ bar $\phi = 2.0$	$p = 3.5$ bar $\phi = 1.0$	$p = 10$ bar $\phi = 1.0$	$p = 30$ bar $\phi = 1.0$	$p = 50$ bar $\phi = 1.0$
Cancino et al. (2010)	Minimum	2,35	8,26	2,09	0,20	5,54	7,69
	Maximum	65,89	148,21	145,48	113,28	54,60	28,77
Haas et al. (2009)	Minimum	23,47	11,05	2,39	97,44	246,81	167,86
	Maximum	227,81	199,32	225,06	522,16	3604,10	959,93

4. Conclusions

In this work, three detailed kinetics models for ethanol oxidation were analyzed. Numerical simulations by using computational tools were performed for several conditions of temperature, pressure and stoichiometry. The numerical results were then compared to experimental results available in the literature. From this comparison, it can be observed that the Cancino et al. (2009a) model reproduce more closely the IDT in the experimental conditions simulated in this work, however, the model presents considerable discrepancies for fuel-rich ($\phi = 2.0$) composition, as observed in the right-side of figure 8.

For low pressures it can be observed that the mechanism from Haas and Saxena's represent a good approximation the experimental data, especially for high temperatures. For low pressures the mechanism of Saxena produces better results for IDT than the mechanism from Haas. Also, it can be observed that, the detailed kinetics models from Haas et al. and Saxena overpredicts the ignition delay time in the whole experimental conditions studied here and especially at low temperatures.

By analysis of temperature distribution, (right-side figures on figure 5), is observed low reactivity behaviour on the Saxena and Haas mechanisms. Note that, also, for higher temperatures is more strong the effect of endothermic reactions in these mechanisms (Saxena and Haas) "consuming" energy and retarding the ignition event in the system. This low reactivity is more significant for the mechanism of Haas.

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