

## AUTOIGNITION OF ETHANOL: ANALYSIS AND EXPERIMENT OF ETHANOL IGNITION IN SHOCK TUBE

**Leonel Rincón Cancino, leonel@labcet.ufsc.br**

Laboratorio de Combustão e Engenharia de Sistemas Térmicos – LABCET  
Universidade Federal de Santa Catarina, Brazil

**Mustapha Fikri, mustapha.fikri@uni-due.de**

Institut für Verbrennung und Gasdynamik – IVG  
Universität Duisburg Essen, Germany.

**Amir A M Oliveira, amir@emc.ufsc.br**

Laboratorio de Combustão e Engenharia de Sistemas Térmicos – LABCET  
Universidade Federal de Santa Catarina, Brazil

**Christof Schulz, christof.schulz@uni-due.de**

Institut für Verbrennung und Gasdynamik – IVG  
Universität Duisburg Essen, Germany.

**Abstract.** *The present work proposes a detailed kinetic model for the thermal oxidation of ethanol-air blends at high and intermediates temperatures. The kinetic model is the result of a blending of different models available in the literature including an upgrading of data for a few key reactions obtained from computational chemistry. Values of ignition delay time in shock tube are calculated and compared to measurements for a stoichiometric mixture at 10, 30 and 50 bar from 650 K to 1220 K. The measurements present the typical fall-off regime for lower temperatures and a lower sensitivity to pressure for the higher pressures. Although the simulations are able to predict the general trend with temperature and pressure, they do not predict any fall-off regime. This is believed to be caused by a lack of adequate data for the reaction parameters of a group of reactions in the low temperature regime. To find out what data needs to be systematically improved, a sensitivity analysis of the effect of each reaction on temperature, OH, H<sub>2</sub>O<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>OH concentrations, for the combustion in a perfectly stirred reactor, using stoichiometric composition, pressures of 10, 30 and 50 bar and temperatures of 1100 K and 950 K, is performed. The sensitivity analysis identified the set of important reactions. The kinetic parameters for these reactions must be optimized to improve the predictability of the model.*

**Keywords:** *Ethanol Oxidation, Detailed Kinetic Model, Perfectly Stirred Reactor, Shock Tube, Sensitivity analysis.*

### 1. INTRODUCTION

The rapid increase of energy costs and the global warming issue have led to increased interest in alternative fuels. In this context, ethanol plays a major role as a promising alternative fuel due to its clean combustion and high availability as an automotive and transportation fuel. In this scenario, there are several motivations to investigate and learn about the combustion process of ethanol: a) need of alternatives to conventional hydrocarbon fuels, b) fuels to reduce pollutant emissions in combustion process, c) additives which can replace undesirable lead alkyls to control engine knock. These three reasons rest on economic and environmental considerations. Ethanol (C<sub>2</sub>H<sub>5</sub>OH) and methyl tert-butyl ether (MTBE C<sub>4</sub>H<sub>9</sub>OCH<sub>3</sub>) are the most widely employed oxygenated fuels in the transportation sector, used both as an additive and as a neat fuel. Since 2004, ethanol is rapidly raising its market share because of new technologies involving multi-fuel car engines developed by all major car manufacturers. Multi-fuel engines are mostly designed to work with gasoline, alcohol or any mixture of both fuels. Additionally, ethanol and MTBE have been used as an octane number enhancer and oxygen source to reduce carbon monoxide emissions. Ethanol can be synthesized from biomass, while MTBE is obtained from isobutene, which in turn is obtained from the refining of gasoline. This renders ethanol a basically renewable resource.

The chemical kinetics of the combustion of ethanol is more complex than the kinetics of methanol (Gardiner, 2000). While methanol has been studied, both experimentally and theoretically, e.g., Warnatz (1999) analyzed the spark ignition of methanol using a 2D-LIF (Laser Induced Fluorescence) system; few studies have been devoted to the homogeneous combustion of ethanol. Glassman (1996) presented a discussion of the oxidation of oxygenated hydrocarbons and explained that since the C-CH<sub>3</sub> bond is weaker than the C-OH bond, the thermal decomposition initiates with the methyl group abstraction, instead of the hydroxyl group abstraction. Within the few studies dedicated to the development of chemical reaction mechanisms, Marinov (1998) proposed a detailed kinetic model for high temperature ethanol oxidation and tested it predicting measurements for shock tubes, burning velocities in freely propagating flames and flow reactors. In shock tube experiments Marinov's numerical results of IDT – Ignition Delay Time – were validated against experimental results of Dunphy and Simmie (1991) and Natarajan and Bhaskaran (1981)

at pressures of 1.0, 2.0, 3.3, 3.4 and 3.5 bar and temperature range of  $1600\text{ K} > T > 1200\text{ K}$ . Laminar flame speeds were compared with experimental results of Gulder (1982) and Egolfopoulos et al (1992) for temperatures of 300 K, and 453 K, pressure of 1 atm and 2 atm, and equivalence ratio of  $1.4 > \Phi > 0.6$ . In flow reactor species concentration, Marinov validated against experimental data of Norton and Dryer (1992) at 1100 K, equivalence ratio  $1.24 > \Phi > 0.6$ . Marinov model never was validated against experimental data at higher pressures and intermediates temperatures, the figure 1 shows experimental and numerical results using the Marinov model for prediction of IDT in shock tube at pressure of 30 bar,  $1200\text{ K} > T > 690\text{ K}$  of ethanol – air blend at stoichiometric composition.

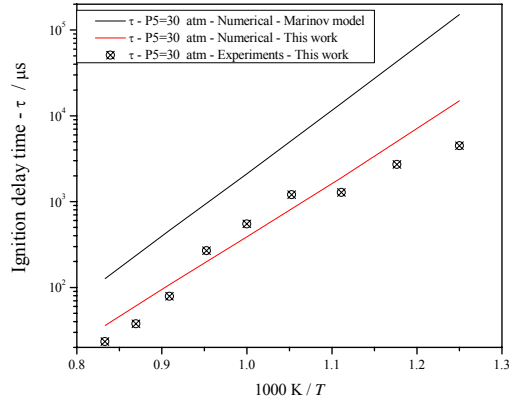


Figure 1. IDT predictions for ethanol-air blend at stoichiometric composition using the Marinov model.

Table 1. Works involving ethanol.

Author	Study	Fuel	Oxider	Parameters analyzed	phi	T [K]	P [bar]	Experimental Setup	Numerical model	Year
Gulder	Experimental	Methanol Ethanol Isooctane	Air	L. B. V	0.7 - 1.4	300	1	Constant pressure bomb	***	1982
Dunphy and Simmie	Experimental	Ethanol	O <sub>2</sub>	I. D. T	0.25 - 2.0	1080 - 1660	1.8 - 4.6	Shock tube	***	1991
Dunphy et al	Numerical	Ethanol	O <sub>2</sub>	I. D. T	0.25 - 2.0	1080 - 1660	1.8 - 4.6	***	RXR	1991
Egolfopoulos et al	Experimental and Numerical	Ethanol	Air / O <sub>2</sub>	L. B. V Chem Spec IDT	0.6 - 1.8 0.81 - 1.0	298 - 453 1090 1300 - 1600	1	C. F. Tw-F Flow Reactor Shock tube	CHEMKIN	1992
Curran et al	Experimental and Numerical	Ethanol isobutylene MTBE	O <sub>2</sub>	I. D. T	0.25 - 1.5 0.1 - 4.0 0.15 - 2.4	1100 - 1900	2.3 3.5 4.5	Shock tube	HCT	1992
Marinov	Experimental and Numerical	Ethanol	Air / O <sub>2</sub>	L. F. S I. D. T Chem Spec	0.6 - 1.4 0.5 - 2.0 0.2 - 2.0	298 - 453 1300 - 1700 1000 - 1200	1 - 2 1 - 3.4 1	C. F. Tw-F Shock tube Jet-stirred R	CHEMKIN	1998
Cancino and Oliveira	Numerical	Ethanol	Air	I. D. T	0.55 - 3.3	1200	1.0 - 5.0	***	CHEMKIN CANTERA	2005
Cancino and Oliveira	Numerical	Ethanol	Air	Ethanol Kinetics	1.0	1400	1	***	CHEMKIN CANTERA	2006
Li et al	Experimental and Numerical	Ethanol	Air	Chem Spec	0.3 - 1.4	800 - 950	3.0 - 12	Flow Reactor	***	2007
Kohse-Höinghaus	Experimental	Ethanol	O <sub>2</sub>	Flame structure	1.0 - 2.57	298	0.05	Flat flame	***	2007
Saxena and Williams	Experimental and Numerical	Ethanol	Air / O <sub>2</sub>	I. D. T L. B. V	0.5 - 2.0 0.6 - 1.7	1300 - 1700 298 - 453	1.0 - 4.6 1	Shock tube C. F. Tw-F	CHEMKIN FlameMaster	2007
Cancino et al	Experimental and Numerical	Ethanol	Air	I. D. T	1.0	690 - 1200	30	Shock tube	CHEMKIN	2007

I. D. T. = Ignition delay time  
C. F. Tw-F = Counterflow Twin flame  
L. F. S = Laminar Flame Speed  
L. B. S = Laminar Burning Speed

Marinov detailed kinetic model is over predicting the IDT at high pressure and intermediates temperatures, the validation against our experimental data allows elucidate the flaws of the mechanism in order to further improvements. Marinov (1998) rightly identified the main hydrogen abstraction reaction paths. Then, besides the data already available in the literature for specific reactions, he also used computational chemistry to calculate the reaction constants for reactions not studied before. Although he did an extensive testing of the kinetic model, a more extensive set of

experimental comparisons are necessary in order to validate and improve his detailed model, for example, IDT at high pressures and intermediate temperatures (this work), laminar flame speed at lower and higher than atmospheric pressure, temperature measurements in shock tube, flow reactor, laminar flame. Gardiner (2000) compiles information about ethanol kinetics showing the complexity and suggesting several decomposition routes. Table 1 summarizes the different works involving ethanol.

The main focus of this paper is to report ignition delay time data for ethanol – air system in shock tube at high pressure and intermediate temperatures, which are not available in the literature, and validate our proposed detailed kinetic model for ethanol oxidation in the same conditions. The ignition delay times are obtained in shock-tube at temperatures ranging between 650 K and 1250 K, pressures of 10, 30 and 50 bar at stoichiometric conditions.

## 2. ETHANOL OXIDATION

Formal studies and publications regarding the development of ethanol combustion kinetics began in the fifties. The result of the efforts in the last sixty years is a discrete amount of experimental and numerical investigations involving different experimental setup and numerical models.

In one of the earlier studies, Barnard and Hughes (1960) showed that the pyrolysis of ethanol at temperatures between 849 K and 897 K is a first order reaction in the ethanol concentration. Marinov (1998) emphasized the high sensitivity of experimentally measured ignition delay during shock induced decomposition of rich ethanol-oxygen mixtures to the rate constants of ethanol decompositions reactions. Marinov considered the two major ways of branching of ethanol oxidation, molecular dissociation and *H*-Abstraction.

Lin (2002, 2003, 2004) employed computational chemistry to analyze several possible routes of ethanol oxidation, involving molecular dissociation, *H*-Abstraction and reactions involving active radicals whit ethanol molecule. Li (2004) found that several parameters in the Marinov's mechanism are underestimating one of channels in the molecular dissociation of ethanol.

The figure 2 summarizes the different routes studied by Marinov, Li and Lin:

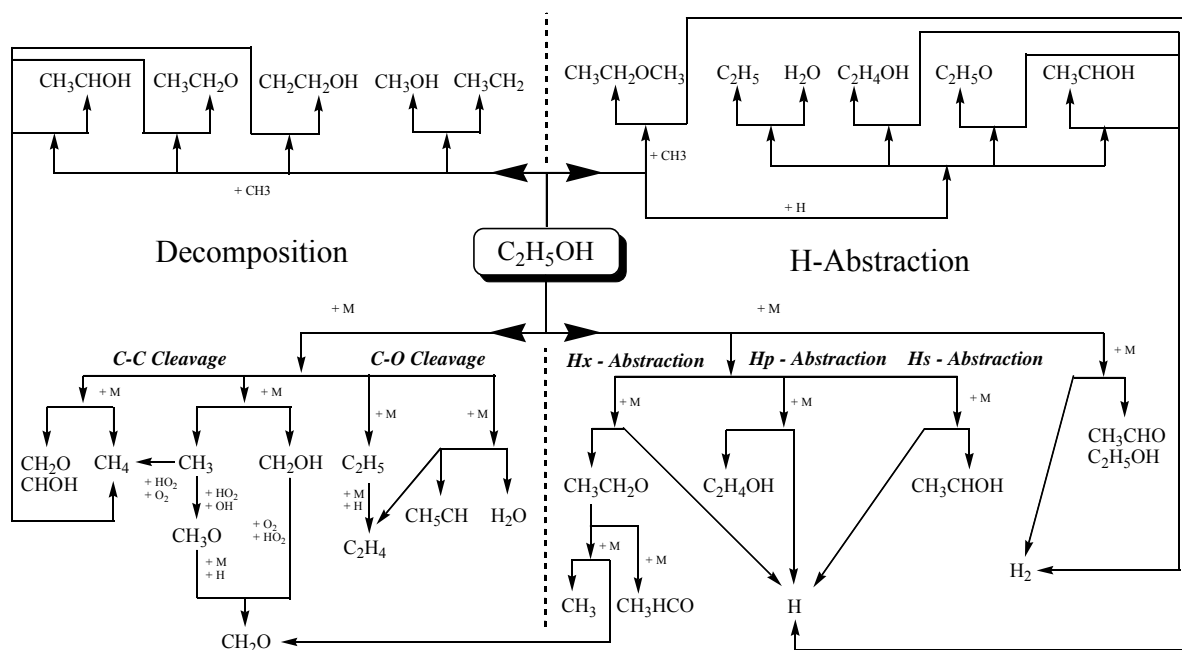


Figure 2. Routes for the ethanol oxidation

The figure 2 allows all routes for the ethanol oxidation, involving *H*-Abstraction by molecular decomposition and for direct action of radicals (+*CH3* and +*H*). The left side of the figure shows the decomposition routes (molecular decomposition and decomposition by action of methyl radical).

Gardiner (2000) denotes the reaction of *C-C* cleavage yield methyl (*CH3*) and hydroxymethyl radical (*CH2OH*) like the fastest initiation reaction. Other special features of the ethanol combustion include the secondary reactions of

the  $C_2$  radicals with active species and oxygen the main product of these reactions is acetaldehyde ( $CH_3CHO$ ), this aspect demand the inclusion of the sub-mechanisms of  $CH_3CHO$  as a part of the ethanol kinetic model.

Other chemical species like methane, mono-atomic and molecular hydrogen and methanol are presents like sub products. Is observed that the oxidation process start with the cleavage of the bonds  $C-O$  and  $C-C$  and the molecular  $H$ -Abstraction (lower part of the figure 2), whose process yield the first concentrations of methyl and hydrogen radicals that are necessary to the starting the propagation reactions (upper part of the figure 2).

### 3. EXPERIMENTAL

The experiments were carried out in high-pressure shock tube with an internal diameter of 90 mm. It is divided by an aluminum diaphragm into a driver section of 6.1 m and a driven section of 6.4 m in length. The driven section was pumped down to pressures below 10–2 mbar. Gas mixtures were prepared by injection of liquid ethanol and subsequent complete evaporation in a stainless-steel mixing vessel.

The total amount of fuel and air was controlled manometrically in order to ensure the desired equivalence ratio. The shock tube was heated to 50°C. The shock speed was measured over two intervals using three piezo-electric pressure gauges. The data were recorded with a time resolution of 0.1  $\mu$ s.

The temperature and pressure behind the reflected shock wave were computed from the measured incident shock speed and the speed attenuation using a one-dimensional shock-tube model (shock-tube code of the CHEMKIN package). The estimated uncertainty in reflected shock temperature is less than  $\pm 25$  K in the temperature and time range of our measurements. The experiments were carried out in synthetic air containing 79.5%  $N_2$  and 20.5%  $O_2$ .

The ignition was observed by measuring pressure profiles with a piezo-electric gauge (PCB HM 112 A03) located 15 mm upstream of the end flange. Also, the  $CH^*$  emission at 431.5 nm was selected by a narrow band pass filter (5 nm HWHM) and measured with a photomultiplier. All ignition delay times shown in this work were determined by extrapolating the steepest increase of the emission signal to its zero level on the time axis.

The driver gas was mixed in-situ by using two high-pressure mass-flow controllers (Bronkhorst Hi-Tec flow meter F-136AI-FZD-55-V and F-123MI-FZD-55-V), see Figure 3. Helium was used as the main component and Argon was added to match the acoustic impedance of the test gas.

The required driver gas composition was calculated by a spreadsheet analysis prior to the experiments using equations by Oertel (1966) and Palmer and Knox (1961). Concentrations of 5 to 20%  $Ar$  in  $He$  were required to generate tailored shock waves.

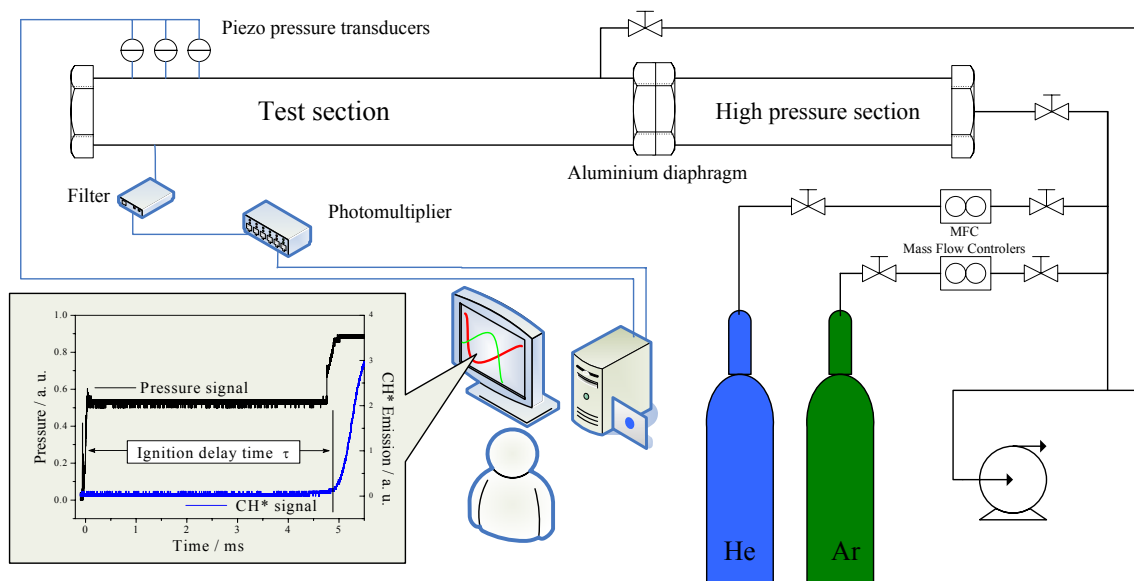


Figure 3 Experimental Setup

## 4. RESULTS AND DISCUSSION

### 4.1. Ignition delay time measurements.

Experiments were conducted for stoichiometric mixtures ( $\phi = 1.0$ ) of ethanol-air at 10, 30 and 50 bar covering a temperature range of  $690 \text{ K} \leq T \leq 1200 \text{ K}$ . All ignition delay times are summarized in an Arrhenius representation in figure 3.

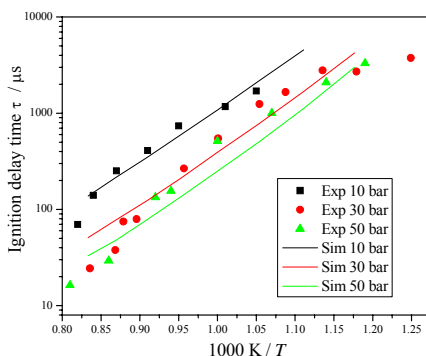
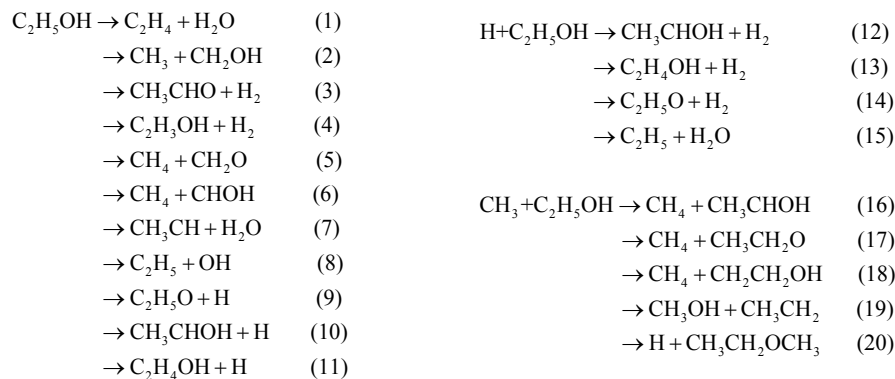


Figure 3 Simulation and experimental results of ignition delay time, ethanol – air system,  $\phi = 1.0$ , pressures of 10, 30 and 50 bar

The measurement indicates that for ethanol-air system, the IDT is not pressure-dependent at higher pressures, 30 and 50 bar. Below  $\sim 950 \text{ K}$  no ignition occurs, within the measurement time (15 ms), in the mixture for the experiments at pressure of 10 bar.

### 4.2. Kinetic model for ethanol oxidation.

In this work is proposed a detailed kinetic model for ethanol oxidation. This model is the result of a blending process of several sub-structures for ethanol and small hydrocarbons (up C3 atoms: hydrogen, methane, ethylene, ethane and propane). The model contain the Konnov (2000) mechanism like central kinetic structure and was added the detailed chemistry of ethanol from Marinov (1998) and the last results and reactions of Lin (2002, 2003 and 2004), summarizing, the model allows the follows specific reactions for ethanol decomposition (oxidation routes):



These oxidation routes lead ultimately to the production of methane, formaldehyde and other oxygenated hydrocarbons, see figure 2, whose kinetics are well treated by other detailed mechanisms (methane, etc.). Lin (2002) found that at pressures below 10 bar, the unimolecular decomposition of ethanol occurs primarily by the dehydration reaction producing  $\text{C}_2\text{H}_4 + \text{H}_2\text{O}$ , reaction (1). At high pressure limit and over 1500 K the production of  $\text{CH}_3$  and  $\text{CH}_2\text{OH}$  becomes dominant, reaction (2). The  $\text{H}_2$ -molecular elimination process, reactions (3) and (4) are not important through out the temperature range investigated (700 – 2500 K).

Concerning the propagation reactions by H atom (12-15) the reaction of dehydration (15) has a high energy barrier and the possibility to proceed is very low. In this group of reactions, the reaction (14) represent about 10% of the total reaction rate, in the temperature range analyzed by Lin (2003) and of this form, reactions (12) and (13) remain like the most important.

In the  $CH_3$  – propagation reactions, the reactions (19) and (20) have high energy barrier and of this form rules out its feasibility kinetically. The other reactions forming methane by  $H$ -abstraction (16), (17) and (18) remain like more important but at higher temperatures,  $T > \sim 1200$  K the reaction (18) becomes predominant.

In the proposed detailed kinetic model were selected and placed the most important reactions for the ethanol oxidation, leaving account the energy barriers limitations denoted by the different authors. The final proposed detailed kinetic model is composed by 103 chemical species and 921 elementary reactions.

The numeric model does not show a good agreement of ignition delay time in the temperature range between 1100 – 950 K and is not clearly identified a negative temperature coefficient region. A new set of experiments is in progress for range of temperature, and for lowers temperatures in order of identify, if present, the negative temperature coefficient. No experimental results are available of ethanol at high pressures and lowers temperatures. Lack of experimental data in the literature make not possible the comparison with others experimental results.

Sensitivity analyses were performed in order to identify the more important reactions for Temperature,  $OH$  radical,  $H_2O_2$  and  $C_2H_5OH$ . Were taken six points Temperature-pressure, in a Perfectly Stirred Reactor, for the sensitivity analysis, table 2 summarizes the results.

Table 2. Sensitivity analysis for ethanol-air system in six points of temperature-pressure.

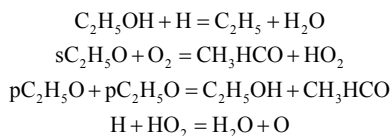
Sensitivity Analysis -- Ethanol-air system	50 bar - 1100 K	50 bar - 950 K	30 bar - 1100 K	30 bar - 950 K	10 bar - 1100 K	10 bar - 950 K
	Temperature	Temperature	Temperature	Temperature	Temperature	Temperature
	Reaction (+)	Reaction (+)	Reaction (+)	Reaction (+)	Reaction (+)	Reaction (+)
	$C_2H_5OH+H = C_2H_5+H_2O$	$C_2H_5OH+H = C_2H_5+H_2O$	$C_2H_5OH+H = C_2H_5+H_2O$	$C_2H_5OH+H = C_2H_5+H_2O$	$C_2H_5OH+H = C_2H_5+H_2O$	$C_2H_5OH+H = C_2H_5+H_2O$
	Reaction (-)	Reaction (-)	Reaction (-)	Reaction (-)	Reaction (-)	Reaction (-)
	$SC_2H_5O+O_2 = CH_3HCO+HO_2$	$SC_2H_5O+O_2 = CH_3HCO+HO_2$	$SC_2H_5O+O_2 = CH_3HCO+HO_2$	$SC_2H_5O+O_2 = CH_3HCO+HO_2$	$SC_2H_5O+O_2 = CH_3HCO+HO_2$	$SC_2H_5O+O_2 = CH_3HCO+HO_2$
	<b>OH</b>	<b>OH</b>	<b>OH</b>	<b>OH</b>	<b>OH</b>	<b>OH</b>
	Reaction (+)	Reaction (+)	Reaction (+)	Reaction (+)	Reaction (+)	Reaction (+)
	$C_2H_5OH+H = C_2H_5+H_2O$	$C_2H_5OH+H = C_2H_5+H_2O$	$C_2H_5OH+H = C_2H_5+H_2O$	$C_2H_5OH+H = C_2H_5+H_2O$	$C_2H_5OH+H = C_2H_5+H_2O$	$C_2H_5OH+H = C_2H_5+H_2O$
	Reaction (-)	Reaction (-)	Reaction (-)	Reaction (-)	Reaction (-)	Reaction (-)
	$PC_2H_5O+PC_2H_5O = C_2H_5OH+CH_3HCO$	$SC_2H_5O+O_2 = CH_3HCO+HO_2$	$PC_2H_5O+PC_2H_5O = C_2H_5OH+CH_3HCO$	$SC_2H_5O+O_2 = CH_3HCO+HO_2$	$PC_2H_5O+PC_2H_5O = C_2H_5OH+CH_3HCO$	$SC_2H_5O+O_2 = CH_3HCO+HO_2$
	<b>H<sub>2</sub>O<sub>2</sub></b>	<b>H<sub>2</sub>O<sub>2</sub></b>	<b>H<sub>2</sub>O<sub>2</sub></b>	<b>H<sub>2</sub>O<sub>2</sub></b>	<b>H<sub>2</sub>O<sub>2</sub></b>	<b>H<sub>2</sub>O<sub>2</sub></b>
	Reaction (+)	Reaction (+)	Reaction (+)	Reaction (+)	Reaction (+)	Reaction (+)
	$C_2H_5OH+H = C_2H_5+H_2O$	$C_2H_5OH+H = C_2H_5+H_2O$	$C_2H_5OH+H = C_2H_5+H_2O$	$C_2H_5OH+H = C_2H_5+H_2O$	$C_2H_5OH+H = C_2H_5+H_2O$	$C_2H_5OH+H = C_2H_5+H_2O$
	Reaction (-)	Reaction (-)	Reaction (-)	Reaction (-)	Reaction (-)	Reaction (-)
	$SC_2H_5O+O_2 = CH_3HCO+HO_2$	$SC_2H_5O+O_2 = CH_3HCO+HO_2$	$SC_2H_5O+O_2 = CH_3HCO+HO_2$	$SC_2H_5O+O_2 = CH_3HCO+HO_2$	$SC_2H_5O+O_2 = CH_3HCO+HO_2$ $H+HO_2=H_2O+O$	$SC_2H_5O+O_2 = CH_3HCO+HO_2$
	<b>C<sub>2</sub>H<sub>5</sub>OH</b>	<b>C<sub>2</sub>H<sub>5</sub>OH</b>	<b>C<sub>2</sub>H<sub>5</sub>OH</b>	<b>C<sub>2</sub>H<sub>5</sub>OH</b>	<b>C<sub>2</sub>H<sub>5</sub>OH</b>	<b>C<sub>2</sub>H<sub>5</sub>OH</b>
	Reaction (+)	Reaction (+)	Reaction (+)	Reaction (+)	Reaction (+)	Reaction (+)
$SC_2H_5O+O_2 = CH_3HCO+HO_2$	$SC_2H_5O+O_2 = CH_3HCO+HO_2$	$SC_2H_5O+O_2 = CH_3HCO+HO_2$	$SC_2H_5O+O_2 = CH_3HCO+HO_2$	$PC_2H_5O+PC_2H_5O=C_2H_5OH+CH_3HCO$	$SC_2H_5O+O_2 = CH_3HCO+HO_2$	
Reaction (-)	Reaction (-)	Reaction (-)	Reaction (-)	Reaction (-)	Reaction (-)	
$C_2H_5OH+H = C_2H_5+H_2O$	$C_2H_5OH+H = C_2H_5+H_2O$	$C_2H_5OH+H = C_2H_5+H_2O$	$C_2H_5OH+H = C_2H_5+H_2O$	$C_2H_5OH+H = C_2H_5+H_2O$	$C_2H_5OH+H = C_2H_5+H_2O$	

The chooses of the six points of temperature-pressure were taken in function of the more visible discrepancies of IDT – Ignition delay time ( $\tau$ ) between numerical and experimental results:

- For  $T > 1100$  K,  $\tau_{exp} < \tau_{num}$  at pressures of 30 bar and 50 bar
- For  $1100$  K  $> T > 950$  K  $\tau_{exp} > \tau_{num}$  at pressures of 30 bar and 50 bar

Table 2 list the major reaction with a positive effect (**Reaction (+)** - positive value of sensitivity coefficient) and negative effect (**Reaction (-)** - negative value of sensitivity coefficient) in each parameter analyzed in the sensitivity analysis; Temperature, *OH* radical, *H2O2* and *C2H5OH*.

One can see that there are a small set of elementary reactions is the responsible by the increasing or decreasing of the four parameters, for all temperature-pressure points, analyzed in this study:



The chemical species *sC2H5O* and *pC2H5O* are sub-products of the ethanol decomposition by *H*-abstraction observed at the down right part of figure 2. The reaction involving ethyl radical (*C2H5*) and water (*H2O*) in products is one of the channels of decomposition by *H* radical contemplated at the upper right part of figure 2.

The reactions placed in table 2 are the reactions with higher sensitivity coefficients values; however, other more complete set of reactions, also important, is in study for further improvements in the proposed detailed kinetic model. A complementary Rate of Production Analysis is in progress in order to improving the performance of the kinetic model.

#### 4. ACKNOWLEDGEMENTS

The authors gratefully acknowledge the Conselho Nacional de Desenvolvimento Científico e Tecnológico – CNPq – Brazil and Deutscher Akademischer Austausch Dienst – DAAD - Germany, for the support given in the development of this work.

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