

## ANALYSIS AND COMPARISON OF TWO DETAILED KINETIC MODELS FOR THE THERMAL OXIDATION OF ETHANOL-OXYGEN MIXTURES IN HIGH TEMPERATURES

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*Abstract.* This work shows the comparison of two kinetic models, highly recognized in the literature for the thermal oxidation of hydrocarbons. One, the Marinov's mechanism, was developed specifically for the ethanol, an oxygenate hydrocarbon, and this mechanism was tested numerically and was compared with results of several experimental setups, obtaining good results Marinov (1998). The Konnov's mechanism, was developed for hydrocarbons with up to three carbons in the molecular structure, this mechanism also was validated for several hydrocarbons with different experimental setups Konnov (2002 b). The Konnov's mechanism has not been validated for oxygenate hydrocarbons, however, with an accurate kinetic database for the ethanol, it can reproduce the experimental results satisfactorily Konnov (2005).

The Marinov's mechanism is composed of four chemical elements, 57 chemical species and 383 elementary reactions, this mechanism does not have the kinetics for the nitrogen oxidation. The Konnov's mechanism is composed of five chemical elements, 127 chemical species and 1207 elementary reactions, this mechanism has a full kinetic database for the nitrogen oxidation. In this work, the kinetic database for the nitrogen oxidation in the Konnov's mechanism was eliminated, this fact to permit simplify and reduce the number of variables in the data post-processing. The Konnov's mechanism without the database for the nitrogen oxidation is composed of five chemical elements, 93 chemical species and 777 elementary reactions.

Preliminary results show that the Konnov's mechanism indicates a small induction period in relation to the Marinov's mechanism.

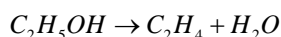
**Keywords.** Ethanol, Detailed Kinetic Mechanism. Thermal Oxidation.

### 1. Introduction

Ethanol ( $C_2H_5OH$ ) is a very important energy carrier that can be produced from renewable energy resources. It can be used as a fuel extender, octane enhancer and oxygen-additive in, or as alternative, neat fuel to replace reformulated gasoline. Ethanol also has potential as a hydrogen carrier for fuel cell applications. Figueroa (2006) has been developed a numerical model for the steam reforming of ethanol, and Figueroa and Oliveira (2005) has reported a thermodynamic analysis of the steam reforming of ethanol for fuel cell applications.

### 2. High temperature ethanol oxidation.

A small quantity of works in the thermal oxidation of ethanol is actually reported in the literature. The work of Marinov (1998) is one of these works. His work emphasized the high sensitivity of experimentally measured ignition delay during shock induced decomposition of rich ethanol-oxygen mixtures to the rate constants of ethanol decomposition reactions. Marinov considers the two major ways of branching of ethanol oxidation: Molecular dissociation and H-Abstraction. Li (2004) was reported a numerical and experimental study of the decomposition of ethanol, Li encountered that several parameters in the Marinov's mechanism are underestimating one of the channels in the molecular dissociation of ethanol. The channel of dissociation described for the reaction:



producing  $C_2H_4$  and  $H_2O$  is pointed for Li (2004) as the major channel in the thermal decomposition of ethanol. The target in this work is to validate numerically the performance of the Konnov's mechanism for the thermal oxidation of mixtures of ethanol-oxygen. The Konnov's mechanism has a full kinetic database for high temperature oxidation

for hydrocarbons with up tree carbons, this kinetic database is including several reactions for the thermal oxidation of ethanol, and consider the two principals decomposition routes described for Marinov (1998) and Li (2004). The Figure 1 compare the number of reactions involved in the two detailed models analyzed in this work for the thermal oxidation.

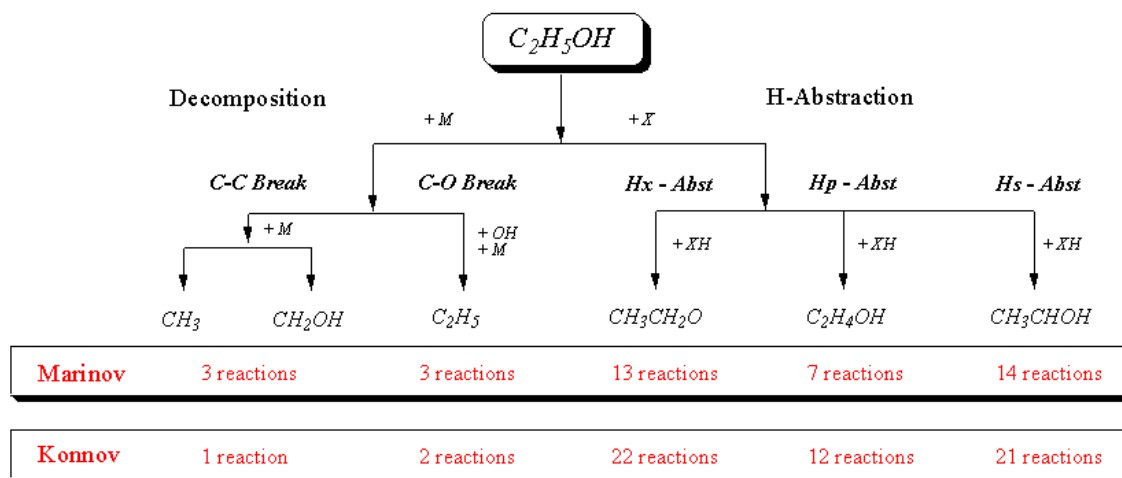


Figure 1 Main ethanol high-temperature oxidation routes.

The response of temperature for the two kinetics models is showed in the Figure 2

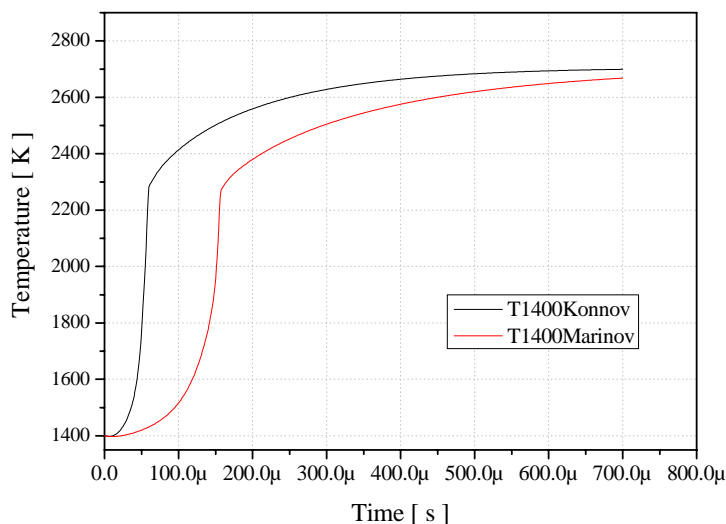
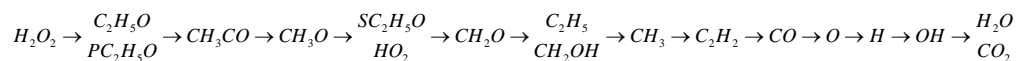


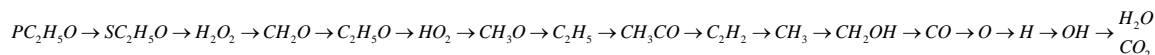
Figure 2 Temperature evolution for the two detailed models for the ethanol-oxygen mixture.

The Figure 2 shows that the prediction for the induction period for the thermal ignition in the two models is different. The Konnov’s mechanism have a kinetics advanced in the time (100 μs Approx.) in relation to Marinov’s mechanism, for the same initial temperature, the prediction for the final temperature is equal in the two kinetics models, this fact indicate that the thermodynamic database is consistent in the two mechanisms.

We have observed a difference in the species evolution predicted in the two mechanisms for the oxidation of ethanol in stoichiometric conditions. The formation and posterior destruction of chemical species in the Konnov’s mechanism is



in the Marinov’s mechanism is



This chemical species are selected as the major relevance in the chemical process. The Konnov's mechanism is starting the formation/destruction with the hydrogen peroxide ( $H_2O_2$ ), and the Marinov's mechanism is starting the formation/destruction with an anion ( $HOC_2H_4O_2$ ) followed by  $PC_2H_5O$ . Last studies of thermal oxidation in hydrocarbons show that the hydrogen peroxide is the first chemical specie in starting the process of formation/destruction, Cancino (2004), Cancino and Oliveira (2004, 2005, 2005b). The sequence of formation/destruction is the same from carbon monoxide to water and carbon dioxide. The Marinov's mechanism is starting with the isomers  $PC_2H_5O$  and  $SC_2H_5O$  followed by hydrogen peroxide. We have encountered that the production of hydroxyl radical is equal from the two kinetics models. The Konnov's mechanism overestimate the production of acetylene, underestimate the production of hydrogen peroxide, overestimate the production of hydroperoxy radical ( $HO_2$ ) and overestimate the production of ethyl radical ( $C_2H_5$ ). Two important aspects, the fact of overestimate the production of acetylene and ethyl radical is influencing in the induction period, the kinetic of the oxidation of the acetylene is quick in relation to other hydrocarbons, and this effect is yield for the influence of the in saturation of atoms of hydrogen in the molecular structure of acetylene, Cancino and Oliveira (2005). The overestimation in the production of ethyl radical also can to agree a contribution to the global effect of overestimate the induction period, this radical have a great capacity of oxidation, in relation to methyl and others radicals. Great easy oxidations in the chemical species involved in the process reflect an overestimation in the induction period for the thermal ignition.

### 2.1. Sensitivity Analysis.

Sensitivity analysis of a problem solution allows quantitative understanding of how the solutions depend on the various parameters contained in the model. A first order sensitivity analysis was applied in the two detailed models used in this work. The software Chemkin 3.7.1 was used for this proposes. We are selected two parameters to obtain the sensitivity analysis, Temperature and Hydroxyl radical  $OH$ . We believe that these two parameters can explain the difference in the induction period for the two models.

The Figure 3 show the sensitivity coefficients of temperature for the major, or representative, elementary reactions in the Konnov's mechanism, and the figure 4 show the sensitivity coefficients for the hydroxyl radical.

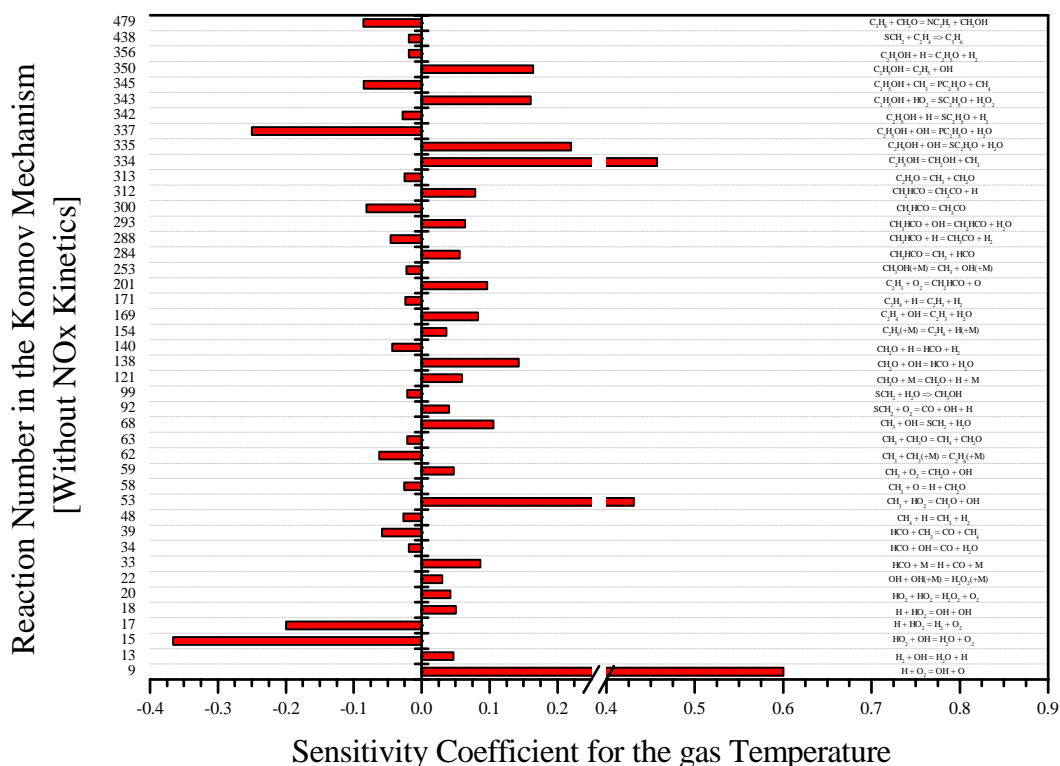


Figure 3 Sensitivity Coefficient for the gas temperature in the Konnov's Mechanism.

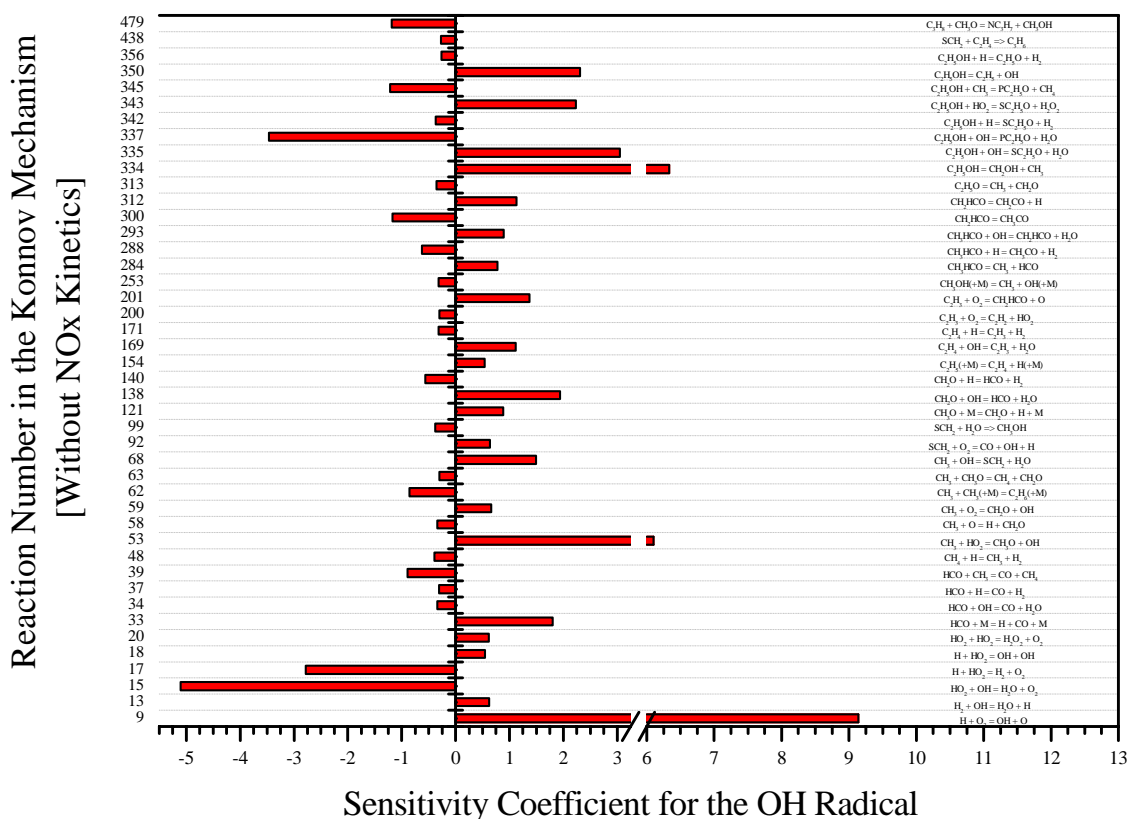
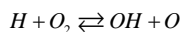


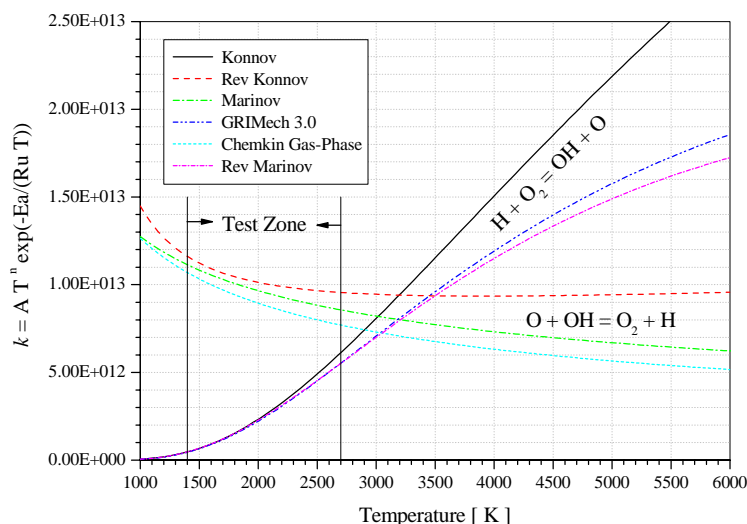
Figure 4 Sensitivity Coefficient for the Hydroxyl radical in the Konnov's Mechanism.

The sensitivity analysis indicates several elementary reactions as being representatives in the kinetic structure for the temperature response. These same sets of reactions are pointed for the sensitivity analysis as being the principals for the hydroxyl radical. This set of reactions is formed of several elementary reactions of the  $H_2 - O_2$  system and all reactions involving the primary degradation of the ethanol in the thermal oxidation, in other words, the reactions of molecular dissociation and the H-Abstraction of ethanol. A similar methodology applied to Marinov's mechanism yield a set of elementary reactions with the same characteristics.

Salvi (1975) indicates that the most important reaction in the  $H_2 - O_2$  system in high temperatures is:



We compare this principal reaction of the  $H_2 - O_2$  system in the two models, this reaction is written in the two models, but in the Marinov's Mechanism this reaction is written in the back form. The Chemkin program compute the forward reactions rates with the Arrhenius parameters listed in the mechanism, and the back rates is calculated from chemical equilibrium. The CHEMRev program of Rolland and Simmie (2004) was used for calculate the reverse Arrhenius of the reaction to compare the reaction rates in two mechanisms. The Figure 5 shows the comparison.

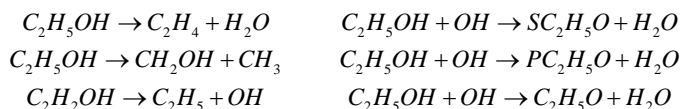


**Figure 5 Comparison of the several reference data of the reaction  $H + O_2 \Rightarrow OH + O$**

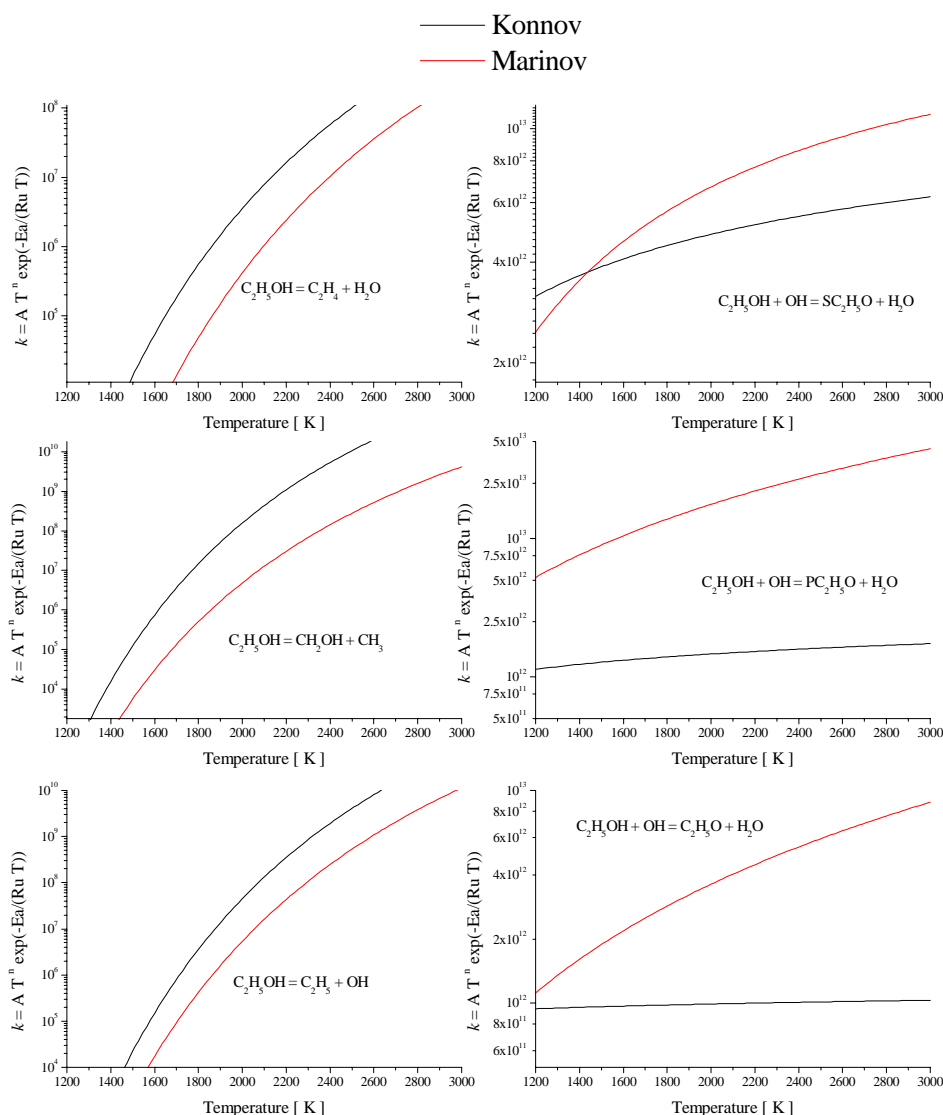
The Figure 5 presents a relative coherence in the several set of parameters for the reaction rates, forward and backward for the reaction  $H + O_2 \Rightarrow OH + O$  in the test zone. This test zone is the range of numerical application in this work.

The Figure 5 indicate that the kernel kinetic of the system  $H_2 - O_2$  in the Konnov's and Marinov's mechanisms are consistent.

The other part of the set of reactions indicates for the sensitivity analysis is the set of reactions relating the starting of the degradation of the ethanol. We have encountered several differences in the Arrhenius parameters in the two mechanisms for these reactions. A set of six reactions are reported for several authors in the literature, Marinov (1998), Li (2004). Three reactions involving the break of the C-C and C-O chemical bond in the molecular structure of ethanol, and three reactions involving abstractions of atoms of hydrogen of the molecular structure, see Figure 1. The reactions are:



The figure 6 show the comparison of the reaction rate in the test zone for these six reactions.



**Figure 6 Comparison of the reaction rates of the major elementary reactions for the primary degradation of the ethanol, in the two kinetics models**

The Figure 6 show that the Konnov’s mechanism is underestimating the break of bonds C-C and C-O and is overestimate the H-abstraction channels in relation to Marinov’s mechanism.

Li (2004) indicates that the methodology of calculation, employed for Marinov, in the determination of Arrhenius parameters of reactions of C-C and C-O break (Molecular Dissociation), is not adequate. The fact of separate the two channels in independents calculations can allow errors in the results for the reaction rates.

Li (2004) suggest others Arrhenius parameters for two of tree channels of dissociation for a pressure of 1 atm:

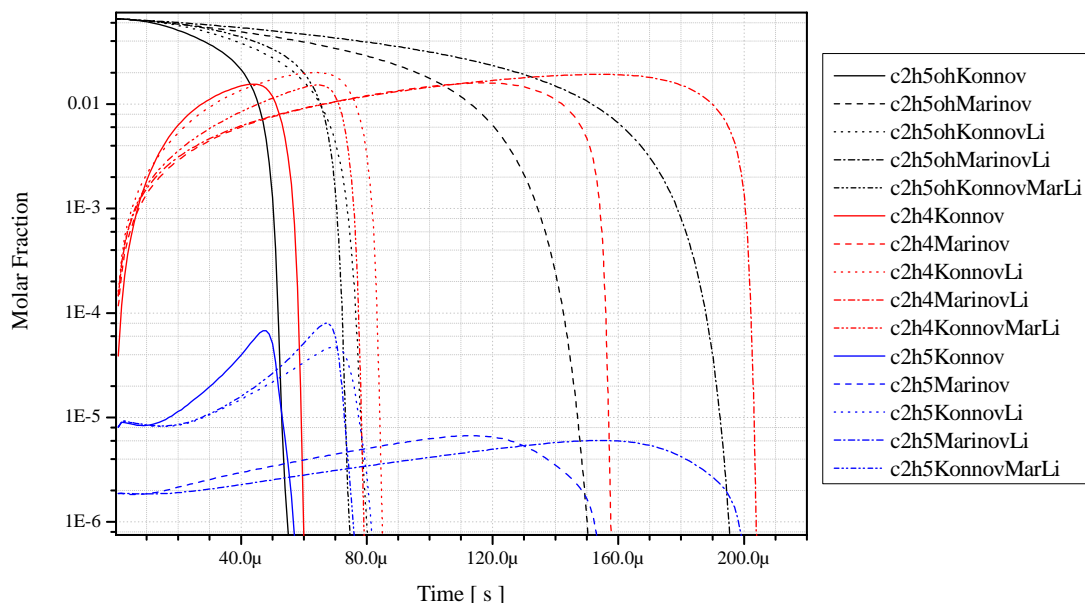
$$C_2H_5OH \rightarrow C_2H_4 + H_2O$$

$$A_o = 8.80 \cdot 10^{25} \quad n = -3.68 \quad E_a = 70798.0$$

$$C_2H_5OH \rightarrow CH_2OH + CH_3$$

$$A_o = 1.26 \cdot 10^{51} \quad n = -10.59 \quad E_a = 100868.28$$

We have taken these parameters and replaced in the Marinov's mechanism and also in the Konnov's mechanism. We have taken the Arrhenius parameters of the *H*-Abstraction routes of the Marinov's mechanism and replaced in the Konnov's mechanism. The Figure 7 shows the results of these different alterations in the two detailed models.



**Figure 7 Time-evolution of ethanol, ethylene and ethyl radical in the kinetics models with the alterations in the Arrhenius parameters.**

The Figure 7 shows that the fact of including the Arrhenius parameters suggested for Li (2004), the consumption rate of ethanol is diminished for all combinations of alteration of parameters. In the Konnov's mechanism, the two set of parameters for the molecular dissociation of ethanol yield a great amount of ethylene, and diminish the amount of ethyl radical, but, increase the permanence time of these two species, adding the set of parameters for the *H*-abstraction of Marinov, in junction with the Li parameters, the productions of ethylene and ethyl radical is the same in relation to original Konnov's mechanism, also increase the permanence time of these two species.

In the Marinov's mechanism the inclusion of the set of Arrhenius parameters of Li (2004), cause a strongly variation in the permanence time of ethylene and the ethyl radical.

## 2.2. Conclusions

Two kinetics models was analyzed for the thermal oxidation of ethanol, the Konnov's mechanism, and the Marinov's mechanism. We have tested the two models with an initial temperature of 1400 K and 1 atm, in stoichiometric compositions for the reactants.

The Konnov model is a good and widely know kinetic model for several hydrocarbons, but is not reported experimental validations for oxygenate hydrocarbons, however, this kinetics mechanism shows a good performance and it is able to reproduce qualitatively the primary degradation of ethanol. The kinetics of the Konnov's mechanism is defaced in the time, but, is able to reproduce the same final temperature of the Marinov's mechanism.

The Li (2004) set of parameters for the molecular dissociation of ethanol produce a variation of in the prediction of the induction period for the thermal ignition of ethanol in the two kinetic models.

## 3. Acknowledgements

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