

ASYMPTOTIC ANALYSIS FOR COUPLED HYDROGEN, CARBON MONOXIDE, METHANOL AND ETHANOL REDUCED KINETIC MECHANISMS

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Abstract— Based on a mechanism composed by 372 reversible chemical reactions among 56 reactive species for the oxidation of ethanol, we propose a reduction strategy to obtain a six-step kinetic mechanism for the methanol and a seven-step mechanism for the ethanol. A three-step kinetic mechanism results for the carbon monoxide and two-step for the hydrogen. The reduction strategy consists of four steps: 1) estimate the order of magnitude of the rates of chemical reaction, 2) define the main chain, 3) apply the steady-state and partial equilibrium assumptions and 4) justify the assumptions by asymptotic analysis. The main advantage of the obtained reduced mechanisms is the decrease of the work needed to solve the system of chemical equations. Such decrease is proportional to the order of the number of elementary reactions present in the complete mechanism.

Keywords— Hydrogen, carbon monoxide, methanol, ethanol, reduced mechanisms.

I. INTRODUCTION

Methanol is commonly used in biodiesel production for its reactivity, and can be employed as one possible replacement for conventional motor fuels (Demirbas, 2007). Methanol has advantages over traditional hydrocarbon fuels derived from mineral oil, because it can be produced from biological sources.

Ethanol can be used as an oxygen additive fuel extender, octane enhancer, or as an alternative fuel to replace reformulated gasoline. Although most ethanol is currently generated by fermentation, recent developments suggest that the ethanol fuel can be derived more efficiently from other types of biomass, thus offering the potential to reduce dependence on fossil-fuel energy resources (Li *et al.*, 2004).

Some mechanisms were obtained and published in the mid-1980s for premixed and nonpremixed flames (Peters and Rogg, 1993). For the oxidation of the

hydrogen it is used about 10 chemical species and 20 elementary reactions while for the oxidation of the ethanol it is used about 350 elementary reactions among 50 chemical species (Marinov, 1999).

The computational simulations with detailed mechanisms turn complicated by the existence of highly reactive radicals which induces significant stiffness to the governing equations. Consequently, there exists the need to develop reduced mechanisms of fewer variables and moderate stiffness, while maintaining the accuracy of the detailed mechanism (Lu and Law, 2006).

Kinetic mechanisms for methanol combustion were proposed by Westbrook and Dryer (1980), Dove and Warnatz (1983), Norton and Dryer (1990) and a reduced mechanism based on these works was derived by Paczko *et al.* (1988). The chemical kinetics of ethanol combustion has been studied by Marinov (1999), Li *et al.* (2004), Saxena and Williams (2007), Seiser *et al.* (2007), among others.

Hydrogen is an important intermediate species in the principal path of oxidation of methanol (Seiser *et al.*, 2007). The principal species in the oxidation of methanol (Yalamanchili *et al.*, 2005) and of ethanol are H_2O , CO_2 , CO , H_2 , O_2 and CH_2O .

In what follows, we propose a strategy to obtain reduced kinetic mechanisms using the hypotheses of partial equilibrium and of steady-state; we check the reduced mechanisms using an asymptotic analysis and compare some numerical values with data found in the literature.

II. STRATEGY TO OBTAIN REDUCED KINETIC MECHANISMS

The reduction strategy proposed here is to:

- Estimate the order of magnitude for rates of reaction;
- Define the main chain;
- Apply the assumptions of steady-state and of partial equilibrium;
- Justify the assumptions by asymptotic analysis.

The specific velocity k of each elementary reaction is obtained by the relation

$$k_{\kappa} = AT^{\beta} \exp\left(-\frac{E}{RT}\right) \quad (1)$$

where A is the frequency factor, T the temperature, β the temperature exponent, E the activation energy, and R the gas constant. With these values, it is estimated the magnitude of the rates of reaction and it is defined a main chain for the combustion process.

In a homogeneous system, the assumption of steady-state is valid for those intermediate species that are produced by slow reactions and are consumed by fast reactions, so that their concentrations remain small (Turns, 2000). The partial equilibrium hypothesis is justified when the specific velocities of forward and backward reactions are much larger than all the other reaction specific velocities of the mechanism (Peters, 1988).

A. Reduced Kinetic Mechanisms for Hydrogen and Carbon Monoxide

Wang *et al.* (1993) presented a reduced mechanism of three-step for wet CO flames that gave reasonable agreement with predictions compared to the mechanism composed by 67 elementary steps among 12 reacting species.

In this work we reproduce the reduced mechanism obtained by Wang *et al.* (1993) for carbon monoxide, but based on the detailed kinetic mechanism for the oxidation of ethanol presented by Marinov (1999). We note that, like those for the hydrocarbons, the kinetic models for the oxygenated fuels have a logical hierarchy, where the kinetic mechanism of any fuel has, as a subset, the same skeletal mechanism of all fuel smaller molecules (Westbrook *et al.*, 2005).

Consider the reactions 1-20 (hydrogen-oxygen sub-mechanism), 111-114 (HCO consumption) and 126 (CO consumption) presented by Marinov (1999), according to the Table 1. They were chosen based on the order of magnitude of the reaction rates and to establish the main chain. Based on the calculation of specific velocities of each elementary reaction, with $T = 800 K$, we determine the main chain for the carbon monoxide, shown below the dashed line (Fig. 1).

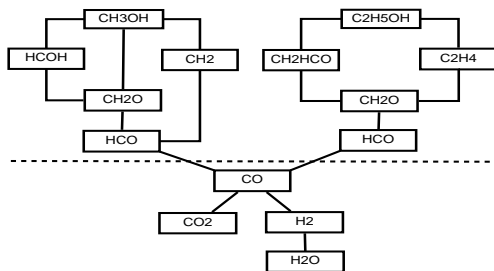
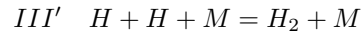
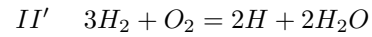
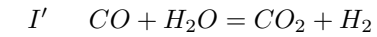


Figure 1: Diagram of the main chain for hydrogen, carbon monoxide, methanol and ethanol.

Table 1: Carbon monoxide mechanism rate coefficients (units are mol, cm^3, s, K and cal/mol).

Reaction	A	β	E
1. $OH + H_2 = H + H_2O$	2.14E+08	1.52	3449
1b. $H + H_2O = OH + H_2$	5.09E+09	1.30	18588
2. $O + OH = O_2 + H$	2.02E+14	-0.40	0
3. $O + H_2 = OH + H$	5.06E+04	2.67	6290
4. $H + O_2 + M = HO_2 + M$	4.52E+13	0.00	0
5. $OH + HO_2 = H_2O + O_2$	2.13E+28	-4.83	3500
6. $H + HO_2 = OH + OH$	1.50E+14	0.00	1000
7. $H + HO_2 = H_2 + O_2$	6.63E+13	0.00	2126
8. $H + HO_2 = O + H_2O$	3.01E+13	0.00	1721
9. $O + HO_2 = O_2 + OH$	3.25E+13	0.00	0
10. $2OH = O + H_2O$	3.57E+04	2.40	-2112
11. $H + H + M = H_2 + M$	1.00E+18	-1.00	0
12. $H + OH + M = H_2O + M$	2.21E+22	-2.00	0
13. $H + O + M = OH + M$	4.71E+18	-1.00	0
14. $O + O + M = O_2 + M$	1.89E+13	0.00	-1788
15. $HO_2 + HO_2 = H_2O_2 + O_2$	4.20E+14	0.00	11982
16. $OH + OH + M = H_2O_2 + M$	1.24E+14	-0.37	0
17. $H_2O_2 + H = HO_2 + H_2$	1.98E+06	2.00	2435
18. $H_2O_2 + H = OH + H_2O$	3.07E+13	0.00	4217
19. $H_2O_2 + O = OH + HO_2$	9.55E+06	2.00	3970
20. $H_2O_2 + OH = H_2O + HO_2$	2.40E+00	4.04	-2162
111. $HCO + O_2 = HO_2 + CO$	7.58E+12	0.00	410
112. $HCO + M = H + CO + M$	1.86E+17	-1.00	17000
113. $HCO + OH = H_2O + CO$	1.00E+14	0.00	0
114. $HCO + H = CO + H_2$	1.19E+13	0.25	0
126. $CO + OH = CO_2 + H$	9.42E+03	2.25	-2351

After applying the hypothesis of partial equilibrium for those reactions with high specific forward and backward velocities, it remains the reactions 1, 3, 11, 12, 13, 14 and 126. Considering the steady-state assumption for the species OH , it results the following three-step mechanism among six species for carbon monoxide



where M is an inert needed to remove the bond energy that is liberated during recombination (Peters, 1992).

In this mechanism, the step I' is the overall CO consumption step, which neither creates nor destroys reaction intermediaries. The step II' represents an overall recombination step, and the step III' an overall radical-production, oxygen-consumption step. The reactions II' and III' constitute the two-step mechanism for the hydrogen.

The reduced mechanism obtained for carbon monoxide can be justified by asymptotic analysis. For the set of elementary reactions presented in the Table 1, the balance equations for the carbon monoxide can be written as

$$L(C_{H_2}) = -w_1 + w_{1b} - w_3 + w_7 + w_{11} + w_{17} + w_{114}$$

$$L(C_H) = +w_1 - w_{1b} + w_2 + w_3 - w_4 - w_6 - w_7 - w_8 - 2w_{11} - w_{12} - w_{13} - w_{17} - w_{18} + w_{112} - w_{114} + w_{126}$$

$$L(C_{O_2}) = +w_2 - w_4 + w_5 + w_7 + w_9 + w_{14} + w_{15} - w_{111}$$

$$L(C_O) = -w_2 - w_3 + w_8 - w_9 + w_{10} - w_{13} - 2w_{14} - w_{19}$$

$$L(C_{H_2O}) = +w_1 - w_{1b} + w_5 + w_8 + w_{10} + w_{12} + w_{18} + w_{20} + w_{113}$$

$$L(C_{OH}) = -w_1 + w_{1b} - w_2 + w_3 - w_5 + 2w_6 + w_9 - 2w_{10} - w_{12} + w_{13} - 2w_{16}$$

$$\begin{aligned}
& +w_{18} + w_{19} - w_{20} - w_{113} - w_{126} \\
L(C_{HO_2}) & = +w_4 - w_5 - w_6 - w_7 - w_8 - w_9 \\
& -2w_{15} + w_{17} + w_{19} + w_{20} + w_{111} \\
L(C_{H_2O_2}) & = +w_{15} + w_{16} - w_{17} - w_{18} - w_{19} \\
& -w_{20} \\
L(C_{CO}) & = +w_{111} + w_{112} + w_{113} + w_{114} - w_{126} \\
L(C_{CO_2}) & = +w_{126} \\
L(C_{HCO}) & = -w_{111} - w_{112} - w_{113} - w_{114}
\end{aligned}$$

where $L(C_i)$ denotes a linear differential operator applied to the concentration of the species i and w_κ represents the reaction rate of the reaction κ . The plus sign refers to species that appear on the right side of an elementary reaction, while the minus sign refers to species on the left. For example, in the reaction 1. $OH + H_2 = H + H_2O$, $L(C_{OH}) = -w_1$ and $L(C_H) = +w_1$, repeating this procedure for all other species and reactions of the mechanism.

Assuming the steady-state hypothesis for the species O , OH , HO_2 , H_2O_2 and HCO , their differential operators L are set equal to zero, which leads to five algebraic equations among the reaction rates w_κ : $w_6 = +w_4 - w_5 - w_7 - w_8 - w_9 - w_{15} + w_{16} - w_{18} + w_{111}$, $w_{12} = -w_1 + w_{1b} - 2w_2 + 2w_4 - 3w_5 - 2w_7 - w_8 - 2w_9 - w_{10} - 2w_{14} - 3w_{15} - w_{16} + w_{17} + w_{19} + 2w_{111} - w_{126}$, $w_{13} = -w_2 - w_3 + w_8 - w_9 + w_{10} - 2w_{14} - w_{19}$, $w_{20} = +w_{15} + w_{16} - w_{17} - w_{18} - w_{19}$ and $w_{113} = -w_{111} - w_{112} - w_{114}$.

Making the rates $w_{I'}$, $w_{II'}$ and $w_{III'}$ equal to $w_{I'}$ = w_{126} , $w_{II'}$ = $-w_2 + w_4 - w_5 - w_7 - w_9 - w_{14} - w_{15} + w_{111}$ and $w_{III'}$ = $-w_1 + w_{1b} - 3w_2 - w_3 + 3w_4 - 3w_5 - 2w_7 - 3w_9 + w_{11} - 3w_{14} - 3w_{15} + w_{17} + 3w_{111} + w_{114} - w_{126}$, one obtains the following linear combinations

$$\begin{aligned}
L(C_{H_2}) & = +w_{I'} - 3w_{II'} + w_{III'} \\
L(C_H) & = +2w_{II'} - 2w_{III'} \\
L(C_{O_2}) & = -w_{II'} \\
L(C_{H_2O}) & = -w_{I'} + 2w_{II'} \\
L(C_{CO}) & = -w_{I'} \\
L(C_{CO_2}) & = +w_{I'}
\end{aligned}$$

The stoichiometry of these balance equations corresponds to the global mechanism of three-step for the carbon monoxide (I' , II' , III'), which includes the two-step mechanism for the hydrogen (reactions II' and III' given before).

B. Reduced Kinetic Mechanisms for Methanol and Ethanol

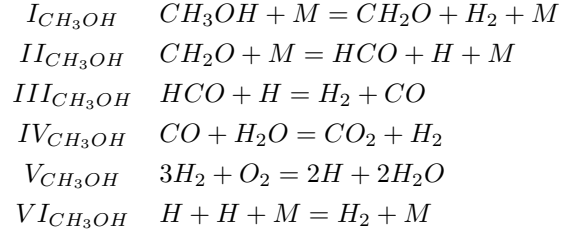
For the methanol, we use the first 129 reversible reactions among 23 species listed by Marinov (1999). Based on the specific velocities of each elementary reaction, with $T = 800 K$, we determine the main chain for methanol, shown in the Fig. 1.

We apply the hypothesis of partial equilibrium for those reactions with high specific forward and backward velocities; it remains the reactions 1, 3, 7, 11, 12, 13, 14, 43, 109, 111 and 126 (see the tables 1 and

Table 2: Methanol mechanism rate coefficients (units are mol, cm^3, s, K and cal/mol).

Reaction	A	β	E
7. $H + HO_2 = H_2 + O_2$	6.63E+13	0.00	2126
26. $CH_4 + HO_2 = CH_3 + H_2O_2$	1.12E+13	0.00	24640
30. $CH_3 + O_2 = CH_3O + O$	1.45E+13	0.00	29209
31. $CH_3 + O_2 = CH_2O + OH$	2.51E+11	0.00	14640
38. $CH_3 + M = CH + H_2 + M$	6.90E+14	0.00	82469
39. $CH_3 + M = CH_2 + H + M$	1.90E+16	0.00	91411
40. $CH_3 + OH + M = CH_3OH + M$	8.70E+13	0.10	0
41. $CH_3OH + M = CH_2 + H_2O + M$	2.84E+10	1.00	83871
42. $CH_3OH + M = HCOH + H_2 + M$	4.20E+09	1.12	85604
43. $CH_3OH + M = CH_2O + H_2 + M$	2.03E+09	1.00	91443
49. $CH_3OH + CH_3 = CH_2OH + CH_4$	3.19E+01	3.17	7171
50. $CH_3OH + CH_3 = CH_3O + CH_4$	1.45E+01	3.10	6935
51. $CH_3OH + HO_2 = CH_2OH + H_2O_2$	9.64E+10	0.00	12578
68. $HCOH = CH_2O$	2.10E+19	-3.07	31700
109. $CH_2O + M = HCO + H + M$	3.31E+16	0.00	81000
111. $HCO + O_2 = HO_2 + CO$	7.58E+12	0.00	410
112. $HCO + M = H + CO + M$	1.86E+17	-1.00	17000
117. $HCOOH + M = CO + H_2O + M$	2.09E+14	0.00	40400
118. $HCOOH + M = CO_2 + H_2 + M$	1.35E+15	0.00	60600
124. $HCOOH + HO_2 = CO + H_2O_2 + OH$	2.40E+19	-2.20	14030
128. $CO + O_2 = CO_2 + O$	2.53E+12	0.00	47688
129. $CO + HO_2 = CO_2 + OH$	5.80E+13	0.00	22934

2). The additional application of the steady-state assumption for the species HO_2 and OH , results in the following mechanism



For the asymptotic analysis, consider the reactions with specific velocities less than 5.07×10^9 in addition to the reactions 7 and 111, according to Table 2. Their corresponding balance equations can be written as

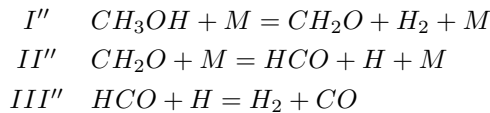
$$\begin{aligned}
L(C_{H_2}) & = +w_7 + w_{38} + w_{42} + w_{43} + w_{118} \\
L(C_H) & = -w_7 + w_{39} + w_{109} + w_{112} \\
L(C_{O_2}) & = +w_7 - w_{30} - w_{31} - w_{111} - w_{128} \\
L(C_O) & = +w_{30} + w_{128} \\
L(C_{H_2O}) & = +w_{41} + w_{117} \\
L(C_{OH}) & = +w_{31} + w_{124} + w_{129} \\
L(C_{HO_2}) & = -w_7 - w_{26} - w_{51} + w_{111} - w_{124} - w_{129} \\
L(C_{H_2O_2}) & = +w_{26} + w_{51} + w_{124} \\
L(C_{CO}) & = +w_{111} + w_{112} + w_{117} + w_{124} - w_{128} \\
& \quad -w_{129} \\
L(C_{CO_2}) & = +w_{118} + w_{128} + w_{129} \\
L(C_{CH_4}) & = -w_{26} + w_{49} + w_{50} \\
L(C_{CH_3}) & = +w_{26} - w_{30} - w_{31} - w_{38} - w_{39} - w_{49} \\
& \quad -w_{50} \\
L(C_{CH_2}) & = +w_{39} + w_{41} \\
L(C_{CH}) & = +w_{38} \\
L(C_{CH_3O}) & = +w_{30} + w_{50} \\
L(C_{CH_3OH}) & = -w_{41} - w_{42} - w_{43} - w_{49} - w_{50} - w_{51} \\
L(C_{CH_2O}) & = +w_{31} + w_{43} + w_{68} - w_{109} \\
L(C_{CH_2OH}) & = +w_{49} + w_{51} \\
L(C_{HCO}) & = +w_{109} - w_{111} - w_{112} \\
L(C_{HCOH}) & = +w_{42} - w_{68} \\
L(C_{HCOOH}) & = -w_{117} - w_{118} - w_{124}
\end{aligned}$$

The species O_2 , O , H_2O , OH , HO_2 , H_2O_2 , CO_2 , CH_2OH , CH_3O , CH_4 , CH_3 , CH_2 , CH , $HCOOH$ and $HCOH$ are assumed to be in steady-state and their corresponding L -operators are set equal to zero, what leads to 15 algebraic equations among the reaction rates w_κ : $w_7 = w_{111} + w_{112}$, $w_{26} = -w_{51}$, $w_{30} = w_{38} = w_{50} = w_{124} = w_{128} = 0$, $w_{31} = w_{41} = w_{118} = w_{112}$, $w_{39} = w_{117} = w_{129} = -w_{112}$, $w_{49} = -w_{51}$, $w_{68} = +w_{42}$.

Making the rates $w_{I''}$, $w_{II''}$ and $w_{III''}$ equal to $w_{I''} = w_{42} + w_{43} + w_{112}$, $w_{II''} = w_{109}$ and $w_{III''} = w_{111} + w_{112}$, one obtains the following linear combinations

$$\begin{aligned} L(CH_2) &= +w_{I''} + w_{III''} \\ L(CH) &= +w_{II''} - w_{III''} \\ L(CO) &= +w_{III''} \\ L(CCH_3OH) &= -w_{I''} \\ L(CCH_2O) &= +w_{I''} - w_{II''} \\ L(CHCO) &= +w_{II''} - w_{III''} \end{aligned}$$

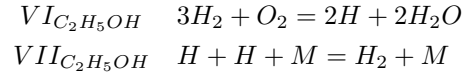
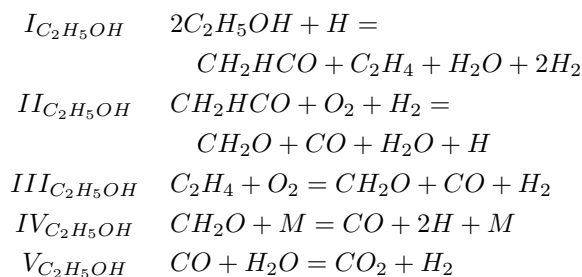
The stoichiometry of these balance equations corresponds to the reactions



As the carbon monoxide is an important intermediate species in the principal path of oxidation of methanol, we obtain the six-step mechanism for the methanol (I_{CH_3OH} , II_{CH_3OH} , III_{CH_3OH} , IV_{CH_3OH} , V_{CH_3OH} , VI_{CH_3OH} given before), whose reaction rates are given by $w_{I_{CH_3OH}} = w_{42} + w_{43} + w_{112}$, $w_{II_{CH_3OH}} = w_{109}$, $w_{III_{CH_3OH}} = w_{111} + w_{112}$, $w_{IV_{CH_3OH}} = w_{126}$, $w_{V_{CH_3OH}} = -w_2 + w_4 - w_5 - w_7 - w_9 - w_{14} - w_{15} + w_{111}$ and $w_{VI_{CH_3OH}} = -w_1 + w_{1b} - 3w_2 - w_3 + 3w_4 - 3w_5 - 2w_7 - 3w_9 + w_{11} - 3w_{14} - 3w_{15} + w_{17} + 3w_{111} + w_{114} - w_{126}$.

For the ethanol we consider the 372 elementary reactions among 56 reactive species listed by Marinov (1999). We apply the hypothesis of partial equilibrium for the reactions with high specific forward and backward velocities; it remains the reactions 1, 2, 3, 11, 12, 13, 14, 17, 29, 109, 112, 126, 132, 133, 174, 180, 208 and 224 (see the Tables 1 and 3).

The application of the steady-state assumption for the species CH_3HCO , C_2H_2 , CH_3 , O , HCO , H_2O_2 and OH , results in the following mechanism



For the asymptotic analysis, consider the reactions with specific velocity less than 4.0×10^{-5} in addition to the reactions 1, 2b, 17, 29, 112, 174, 180 and 224, according to the Table 3. The corresponding balance equations can be written as

$$\begin{aligned} L(CH_2) &= -w_1 + w_{17} + w_{38} + w_{42} + w_{43} + w_{133} \\ & \quad + w_{208} + w_{294} \\ L(CH) &= +w_1 - w_{2b} - w_{17} + w_{29} + w_{39} + w_{109} \\ & \quad + w_{112} + w_{231} \\ L(CO_2) &= -w_{2b} - w_{180} \\ L(CO) &= +w_{2b} - w_{29} \\ L(COH) &= -w_1 + w_{2b} + w_{131} + w_{180} - w_{224} \\ L(CH_2O) &= +w_1 + w_{41} + w_{132} \\ L(CHO_2) &= +w_{17} - w_{174} \\ L(CH_2O_2) &= -w_{17} + w_{174} \\ L(CCO) &= +w_{112} + w_{180} + w_{224} + w_{248} \\ L(CCH_4) &= +w_{293} \\ L(CCH_3) &= -w_{29} - w_{38} - w_{39} + w_{130} + w_{224} \\ & \quad + w_{266} \\ L(CCH_2) &= +w_{39} + w_{41} + w_{248} \\ L(CCH) &= +w_{38} \\ L(CCH_3OH) &= -w_{41} - w_{42} - w_{43} \\ L(CCH_3HCO) &= +w_{133} - w_{174} \\ L(CCH_2O) &= +w_{29} + w_{43} - w_{109} + w_{180} \\ L(CCH_2OH) &= +w_{130} \\ L(CCH_2HCO) &= +w_{174} - w_{180} \\ L(CCH_2CO) &= -w_{248} \\ L(CHCOH) &= +w_{42} \\ L(CHCO) &= +w_{109} - w_{112} \\ L(CH_2CCCH_2) &= +w_{294} \\ L(CC_2H_5OH) &= -w_{130} - w_{131} - w_{132} - w_{133} \\ L(CC_2H_5) &= +w_{131} + w_{266} \\ L(CC_2H_4) &= +w_{132} - w_{208} \\ L(CC_2H_2) &= +w_{208} - w_{224} - w_{231} + w_{293} \\ L(CC_2H) &= +w_{231} \\ L(CC_3H_8) &= -w_{266} \\ L(CC_3H_6) &= -w_{293} - w_{294} \end{aligned}$$

The species O , OH , HO_2 , H_2O_2 , CH_4 , CH_3 , CH_2 , CH , $HCOH$, HCO , H_2CCCH_2 , CH_2OH , CH_3OH , CH_3HCO , CH_2CO , C_2H_5 , C_2H_2 , C_2H , C_3H_8 and C_3H_6 are assumed to be in steady-state and their corresponding L -operators are set equal to zero, what leads to 19 algebraic equations among the reaction rates w_κ : $w_1 = +w_{180} + w_{208}$, $w_{2b} = -w_{43} + w_{208}$, $w_{17} = +w_{133}$, $w_{29} = -w_{43} + w_{208}$, $w_{38} = 0$, $w_{39} = +w_{43}$, $w_{41} = -w_{43}$, $w_{42} = w_{43} = 0$, $w_{112} = +w_{109}$, $w_{130} = w_{131} = 0$, $w_{174} = +w_{133}$, $w_{224} = +w_{208}$, $w_{231} = w_{248} = w_{266} = w_{293} = w_{294} = 0$.

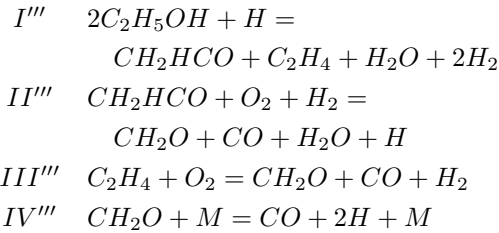
Table 3: Ethanol mechanism rate coefficients (units are $\text{mol}, \text{cm}^3, \text{s}, \text{K}$ and cal/mol).

Reaction	A	β	E
2b. $\text{O}_2 + \text{H} = \text{O} + \text{OH}$	2.00E+14	0.00	70
17. $\text{H}_2\text{O}_2 + \text{H} = \text{HO}_2 + \text{H}_2$	1.98E+06	2.00	2435
29. $\text{C}_2\text{H}_3 + \text{O} = \text{CH}_2\text{O} + \text{H}$	8.00E+13	0.00	0
38. $\text{CH}_3 + \text{M} = \text{CH} + \text{H}_2 + \text{M}$	6.90E+14	0.00	82469
39. $\text{CH}_3 + \text{M} = \text{CH}_2 + \text{H} + \text{M}$	1.90E+16	0.00	91411
41. $\text{CH}_3\text{OH} + \text{M} = \text{CH}_2 + \text{H}_2\text{O} + \text{M}$	2.84E+10	1.00	83871
42. $\text{CH}_3\text{OH} + \text{M} = \text{HCOH} + \text{H}_2 + \text{M}$	4.20E+09	1.12	85604
43. $\text{CH}_3\text{OH} + \text{M} = \text{CH}_2\text{O} + \text{H}_2 + \text{M}$	2.03E+09	1.00	91443
109. $\text{CH}_2\text{O} + \text{M} = \text{HCO} + \text{H} + \text{M}$	3.31E+16	0.00	81000
112. $\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}$	1.86E+17	-1.00	17000
126. $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$	9.42E+03	2.25	-2351
130. $\text{C}_2\text{H}_5\text{OH} + \text{M} = \text{CH}_2\text{OH} + \text{CH}_3 + \text{M}$	5.94E+23	-1.68	91163
131. $\text{C}_2\text{H}_5\text{OH} + \text{M} = \text{C}_2\text{H}_5 + \text{OH} + \text{M}$	1.25E+23	-1.54	96005
132. $\text{C}_2\text{H}_5\text{OH} + \text{M} = \text{C}_2\text{H}_4 + \text{H}_2\text{O} + \text{M}$	2.79E+13	0.09	66136
133. $\text{C}_2\text{H}_5\text{OH} + \text{M} = \text{CH}_3\text{HCO} + \text{H}_2 + \text{M}$	7.24E+11	0.09	91007
174. $\text{C}_2\text{H}_5\text{HCO} + \text{O}_2 = \text{C}_2\text{H}_5\text{HCO} + \text{H}_2\text{O}_2$	2.32E+11	0.40	14864
180. $\text{CH}_2\text{HCO} + \text{O}_2 = \text{CH}_2\text{O} + \text{CO} + \text{OH}$	3.00E+10	0.00	0
208. $\text{C}_2\text{H}_4 + \text{M} = \text{C}_2\text{H}_2 + \text{H}_2 + \text{M}$	1.80E+14	0.00	87000
224. $\text{C}_2\text{H}_2 + \text{OH} = \text{C}_2\text{H}_3 + \text{CO}$	4.83E-04	4.00	-2000
231. $\text{C}_2\text{H}_2 + \text{M} = \text{C}_2\text{H} + \text{H} + \text{M}$	4.20E+16	0.00	107000
248. $\text{CH}_2\text{CO} + \text{M} = \text{CH}_2 + \text{CO} + \text{M}$	3.00E+14	0.00	70980
266. $\text{C}_3\text{H}_8 + \text{M} = \text{C}_2\text{H}_5 + \text{CH}_3 + \text{M}$	7.90E+22	-1.80	88629
293. $\text{C}_3\text{H}_6 = \text{C}_2\text{H}_2 + \text{CH}_4$	2.50E+12	0.00	70000
294. $\text{C}_3\text{H}_6 = \text{H}_2\text{C}=\text{CH}_2 + \text{H}_2$	3.00E+13	0.00	80000

Making the rates $w_{I''''}$, $w_{II''''}$, $w_{III''''}$ and $w_{IV''''}$ equal to $w_{I''''} = 0.5(w_{132} + w_{133})$, $w_{II''''} = 0.5(w_{132} - w_{133} + w_{180})$, $w_{III''''} = 0.5(-w_{132} + w_{133} + w_{208})$ and $w_{IV''''} = w_{109}$, one obtains the linear combinations

$$\begin{aligned}
L(\text{C}_{\text{H}_2}) &= +2w_{I''''} - w_{II''''} + w_{III''''} \\
L(\text{C}_{\text{H}}) &= -w_{I''''} + w_{II''''} + 2w_{IV''''} \\
L(\text{C}_{\text{O}_2}) &= -w_{II''''} - w_{III''''} \\
L(\text{C}_{\text{H}_2\text{O}}) &= +w_{I''''} + w_{II''''} \\
L(\text{C}_{\text{CO}}) &= +w_{II''''} + w_{III''''} + w_{IV''''} \\
L(\text{C}_{\text{C}_2\text{H}_5\text{OH}}) &= -2w_{I''''} \\
L(\text{C}_{\text{C}_2\text{H}_4}) &= +w_{I''''} - w_{III''''} \\
L(\text{C}_{\text{CH}_2\text{HCO}}) &= +w_{I''''} - w_{II''''} \\
L(\text{C}_{\text{CH}_2\text{O}}) &= +w_{II''''} + w_{III''''} - w_{IV''''}
\end{aligned}$$

The stoichiometry of these balance equations corresponds to the reactions



As the carbon monoxide is an important intermediate species in the principal path of oxidation of the ethanol too, we obtain the seven-step mechanism ($I_{\text{C}_2\text{H}_5\text{OH}}$, $II_{\text{C}_2\text{H}_5\text{OH}}$, $III_{\text{C}_2\text{H}_5\text{OH}}$, $IV_{\text{C}_2\text{H}_5\text{OH}}$, $V_{\text{C}_2\text{H}_5\text{OH}}$, $VI_{\text{C}_2\text{H}_5\text{OH}}$, $VII_{\text{C}_2\text{H}_5\text{OH}}$ given before), whose reaction rates are given by $w_{I_{\text{C}_2\text{H}_5\text{OH}}} = 0.5(w_{132} + w_{133})$, $w_{II_{\text{C}_2\text{H}_5\text{OH}}} = 0.5(w_{132} - w_{133} + w_{180})$, $w_{III_{\text{C}_2\text{H}_5\text{OH}}} = 0.5(-w_{132} + w_{133} + w_{208})$, $w_{IV_{\text{C}_2\text{H}_5\text{OH}}} = w_{109}$, $w_{V_{\text{C}_2\text{H}_5\text{OH}}} = w_{126}$, $w_{VI_{\text{C}_2\text{H}_5\text{OH}}} = -w_2 + w_4 - w_5 - w_7 - w_9 - w_{14} - w_{15} + w_{111}$ and $w_{VII_{\text{C}_2\text{H}_5\text{OH}}} = -w_1 + w_{1b} - 3w_2 - w_3 + 3w_4 - 3w_5 - 2w_7 - 3w_9 + w_{11} - 3w_{14} - 3w_{15} + w_{17} + 3w_{111} + w_{114} - w_{126}$.

The coupling of the reactions I' , II' , III' with I'''' , II'''' , III'''' , and I' , II' , III' with I'''' , II'''' , III'''' , IV''''

is possible because, typically, the mechanisms for hydrocarbon and oxygenated fuels are generated in a hierarchical way, starting with the hydrogen/oxygen system, adding the carbon monoxide subset, followed by the $\text{C}_1 - \text{C}_n$ species (Curran, 2009).

III. NUMERICAL RESULTS

Consider a burner whose duct has a cylindrical cross section with $De = 1$ and a cylindrical tube that injects fuel with $d = 0.025$, and the burner length is $L = 11$.

Figure 2 shows the principal combustion products (CO_2 , H_2O) along the mixture fraction space for the methanol and the ethanol. The mixture fraction measures the reactants mixing and is mainly related to the large scale motions of the flow. The maximum value of the mass fraction of the combustion products occurs at proximity of stoichiometric surface ($Z_{st} \sim 0.15$), where the fuel and the oxidizer mass fractions are both small, since they are consumed at this place.

The comparison of the principal products (CO_2 , H_2O) for the methanol is done with the experimental values (Müller *et al.*, 1993; Frassoldati *et al.*, 2008), shown in the figure 2. The numerical results agree with the experiment; the mass fraction is slightly over-predicted for the H_2O and underpredicted for the CO_2 at proximity of the stoichiometric region for the methanol. For the ethanol the tendency is the same.

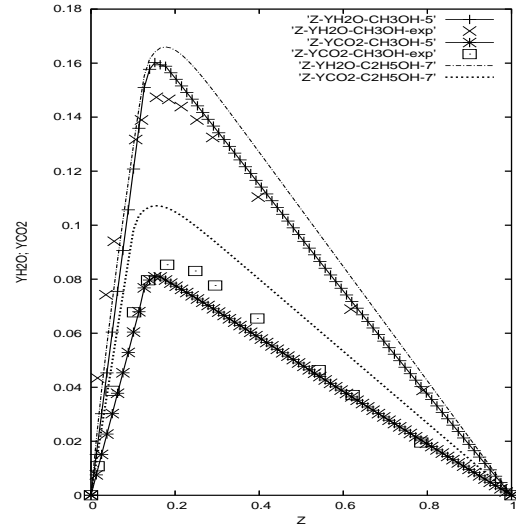


Figure 2: CO_2 and H_2O mass fractions for the methanol (5-step) compared with the experiment and numerical results for the ethanol (7-step)

The main advantage of the strategy is the decrease of the work needed to solve the resultant system of equations. The decrease of time for solving the set of the chemical equations is of one order of magnitude for the hydrogen, since the number of equations decrease in this order. For the methanol and ethanol such reduction in the computational time is of two orders of magnitude.

IV. CONCLUSIONS

The principal contribution of this work is the development of a strategy consisting of 4 steps to obtain reduced kinetic mechanisms for oxygenated fuels, such as the ethanol. We show that there is a coupling between the reduced kinetic mechanisms for the methanol and the ethanol flames, including the mechanisms for the hydrogen and for the carbon monoxide.

From the oxidation mechanism for ethanol presented by Marinov (1999), we obtained reduced mechanisms for the H_2 , the CO , the methanol and the ethanol. Moreover, the central idea that the kinetic models for common fuels have a hierarchical structure, helps to simplify the analysis.

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