

Bioethanol combustion based on a reduced kinetic mechanism

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Received: 20 December 2012 / Accepted: 14 March 2013 / Published online: 28 March 2013
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Abstract Bioethanol is a fuel additive or a fuel substitute that has the benefit of being cleaner and price competitive with gasoline. Therefore, we develop a reduced kinetic mechanism capable of modeling the ethanol combustion and the generation of the combustion products H_2O , CO_2 , CO , H_2 , C_2H_4 and OH . Based on a mechanism composed by 372 reversible elementary reactions among 56 reactive species, we propose a reduction strategy to obtain an eight-step mechanism for the ethanol. The reduction strategy consists in estimating the order of magnitude of the reaction rate coefficients, defining the main chain, applying the steady-state and partial equilibrium hypotheses, and justifying the assumptions through an asymptotic analysis. The main advantage of the obtained reduced mechanism is the decrease of the work needed to solve the system of chemical equations proportionally to the number of elementary reactions present in the complete mechanism. Numerical tests are carried out for a jet diffusion flame of ethanol and the results compare well with available data in the literature.

Keywords Combustion · Kinetics · Reduced mechanism · Simulation

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Mathematics Subject Classification 80A25 · 80A30**1 Introduction**

Bioethanol is one of the most important biofuels because it can be used in full or in partial replacement of gasoline in modern internal combustion engines [1]. Brazil has a fleet of about 30 million cars, of which over 50% can use ethanol as fuel in any fraction of mixture or even pure. This is because, in Brazil, the price of ethanol is similar to that of gasoline and the fuel has the advantage of being greener. For a light-duty vehicle using bioethanol, the net CO₂ emission is less than 7% of that from the same car using reformulated gasoline [2].

Chemical kinetic modeling has become an important tool for interpreting and understanding observed combustion phenomena. Its application requires as an input a valid chemical reaction mechanism [3]. The chemical kinetic mechanisms together with CFD (Computational Fluid Dynamics) codes are used to develop more efficient and clean systems and to optimize the operating behavior of practical combustion devices [4]. It is a common practice in the analysis of complex chemical systems to consider only a few reactions steps, which in general do not correspond to the mechanism of the reaction on a molecular scale, but which describes the overall chemical processes [5].

Computer simulations with detailed mechanisms turn more complicated due to the existence of highly reactive radicals, which induce significant increase of the stiffness of the governing equations. Consequently, there exists the need to develop from these detailed mechanisms the corresponding reduced mechanisms, of fewer variables and moderated stiffness, while maintaining a good level of accuracy and comprehensiveness of the detailed mechanism [6].

Various reduced mechanisms were obtained and published in the mid-1980s for premixed and nonpremixed methane flames. In the 1980s some research groups focused their attention on methane flames, developing techniques useful for the systematic reduction of detailed kinetic mechanisms [7]. It was found that the kinetic models for hydrocarbons have a logical hierarchy, where the kinetic mechanism of any fuel contains as a subset, information of the mechanisms of the smaller fuel molecules. This reduces the time and the effort required to develop reaction mechanisms of large species [8].

Although the ethanol is an attractive fuel for use as a renewable energy source of low pollution, important questions remain about its combustion chemistry. The ethanol mechanism is an increase of the mechanisms developed for the combustion of hydrogen, carbon monoxide, methane, ethane, ethylene, acetylene, propane, propylene, allene and methanol. Simplifications have been done considering certain temperatures, pressures, and strain rates. These restrictions, for example, prevent the soot formation and cool flames [9].

The reduction of detailed kinetic mechanisms for hydrocarbons has been treated in the works from Warnatz [10], Bongers et al. [11], Lindstedt and Meyer [12], Yalamanchili et al. [13], Li et al. [14], Röhl and Peters [15], Komninou and Rakopoulos [16], among others. Saxena and Williams [9] investigated the ethanol combustion

based on a chemical kinetic mechanism consisting of 192 elementary steps among 36 species, augmented by 53 additional steps and 14 additional species, to address the formation of oxides of nitrogen, and 43 steps and 7 species, to address the formation of compounds involving three carbon atoms. A detailed chemical kinetic mechanism describing the ethanol combustion was presented by Marinov [17], and has been validated using experimental data from shock tubes, burning velocity measurements in constant volume bombs, and burning velocity measurements employing the twin flame configuration [9].

In this paper we develop a reduced kinetic mechanism for ethanol based on the detailed kinetic mechanism presented by Marinov [17], capable of modeling the burning of this fuel with good approximation.

2 Obtainment of a reduced kinetic mechanism for the ethanol combustion

The chemical kinetics of ethanol combustion has been studied by Marinov [17], Li et al. [18], Saxena and Williams [9], Seiser et al. [19], among others.

A detailed chemical kinetic model for high temperature oxidation of ethanol was developed and validated against a variety of experimental data by Marinov [17]. This mechanism, composed by 372 elementary reactions among 56 reactive species, is used here to obtain a reduced mechanism with 8 reactions among 11 species for ethanol. Information about its thermodynamic and transport data are found in the same reference. We define the main chain based on the order of magnitude of the reaction rate coefficients, apply the hypotheses of steady-state and partial equilibrium, and justify the assumptions by an asymptotic analysis.

The reaction rate coefficient k is obtained using the modified equation of Arrhenius

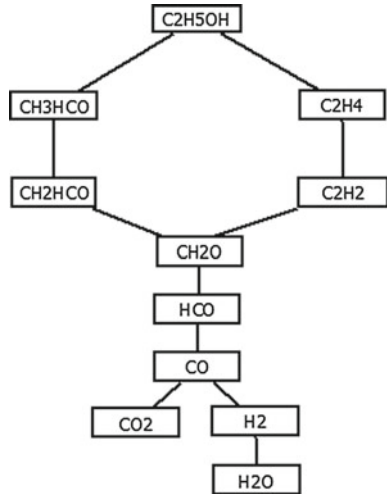
$$k = AT^\beta \exp\left(-\frac{E}{RT}\right) \quad (1)$$

where A is the frequency factor, T the temperature, β the temperature exponent, E the activation energy, R the gas constant, and the units are mol, cm³, s, K and cal/mol. Through this formula it is calculated the magnitude of the rate coefficients, with $T = 800$ K, and it is defined the main chain of the combustion process. Figure 1 shows the main chain for the ethanol combustion.

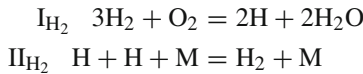
For the oxidation of the hydrogen, consider the set of reactions 1–20 shown in the Table 1 [17]. The assumptions frequently employed to obtain reduced kinetic mechanisms are those of steady-state and partial equilibrium. In a homogeneous system, the assumption of steady-state is valid for those intermediate species that are produced by slow reactions and consumed by fast reactions, so that their concentrations remain small [20]. The partial equilibrium hypothesis is justified when the reaction rate coefficients of forward and backward reactions are much larger than all the other reaction rate coefficients of the mechanism [21].

After applying the hypothesis of partial equilibrium for the reactions with high rate coefficients of the forward and backward reactions, it remains the reactions 3, 11, 12, 13 and 14, helping to eliminate the species O, HO₂ and H₂O₂.

Fig. 1 Diagram of the main chain for the ethanol combustion



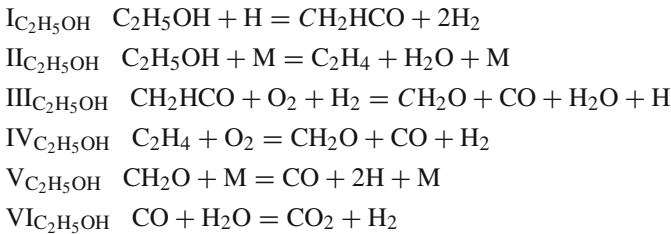
The steady-state hypothesis is applied for the species OH, resulting in the following two-step mechanism among four species for hydrogen flames



where M is an inert needed to remove the bond energy that is liberated during recombination.

For the oxidation of the ethanol, consider the set of reactions shown in the Table 2 [17], obtained from the order of magnitude of the reaction rate coefficients. We apply the hypothesis of partial equilibrium for the reactions with high rate coefficients of the forward and backward reactions; it remains the reactions 1, 2, 17, 21, 22, 23, 29, 30, 31, 34, 35, 36, 37, 38 and 39.

The application of the steady-state assumption for the species CH₃HCO, H₂O₂, C₂H₂, CH₃, O, HCO and OH, results in the following mechanism



After adding the steps I_{H₂} and II_{H₂} it results the eight-step mechanism among 11 species for ethanol flames.

Table 1 Hydrogen mechanism rate coefficients ($k = AT^\beta \exp(-E/RT)$); units are mol, cm³, s, K and cal/mol

	Reaction	A	β	E
1	OH + H ₂ = H + H ₂ O	2.14E+08	1.520	3,449
2	O + OH = O ₂ + H	2.02E+14	-0.400	0
3	O + H ₂ = OH + H	5.06E+04	2.670	6,290
4	H + O ₂ + M = HO ₂ + M	4.52E+13	0.000	0
	Low pressure limit	1.05E+19	-1.257	0
	Enhanced third body efficiencies: H ₂ O = 0, H ₂ = 0, N ₂ = 0, CH ₄ = 10, CO ₂ = 3.8, CO = 1.9			
5	OH + HO ₂ = H ₂ O + O ₂	2.13E+28	-4.827	3,500
6	H + HO ₂ = OH + OH	1.50E+14	0.000	1,000
7	H + HO ₂ = H ₂ + O ₂	6.63E+13	0.000	2,126
8	H + HO ₂ = O + H ₂ O	3.01E+13	0.000	1,721
9	O + HO ₂ = O ₂ + OH	3.25E+13	0.000	0
10	2OH = O + H ₂ O	3.57E+04	2.400	-2112
11	H + H + M = H ₂ + M	1.00E+18	-1.000	0
12	H + OH + M = H ₂ O + M	2.21E+22	-2.000	0
13	H + O + M = OH + M	4.71E+18	-1.000	0
14	O + O + M = O ₂ + M	1.89E+13	0.000	-1788
15	HO ₂ + HO ₂ = H ₂ O ₂ + O ₂	4.20E+14	0.000	11,982
16	OH + OH + M = H ₂ O ₂ + M	1.24E+14	-0.370	0
	Low pressure limit	3.04E+30	-4.630	2,049
	Troe parameters: $a = 0.47$, $T^{***} = 100$ $T^{**} = 1.0E + 15$, $T^* = 2000$			
17	H ₂ O ₂ + H = HO ₂ + H ₂	1.98E+06	2.000	2,435
18	H ₂ O ₂ + H = OH + H ₂ O	3.07E+13	0.000	4,217
19	H ₂ O ₂ + O = OH + HO ₂	9.55E+06	2.000	3,970
20	H ₂ O ₂ + OH = H ₂ O + HO ₂	2.40E+00	4.042	-2162

Fall-off reaction in the Lindemann–Hinshelwood form with: $k = k_0[M]/(1+k_0[M]/k_\infty)$; fall-off reaction in the Troe form with: $k = k_0[M]/(1+k_0[M]/k_\infty)F$, $\log F = \{1 + [\kappa/(N-d\kappa)]^2\}^{-1} \log F_{cent}$, $\kappa = \log(k_0[M]/k_\infty) + C$, $C = -0.4 - 0.67 \log F_{cent}$, $N = 0.75 - 1.27 \log F_{cent}$, $d = 0.14$, $F_{cent} = (1-a) \exp(-T/T^{***}) + a \exp(-T/T^*) + \exp(-T^{**}/T)$ [17]

Now, we justify these assumptions making an asymptotic analysis, which is a method used to describe limiting behaviors. It employs the concept of a limit to identify reactions, critical conditions or other important parameters in nonlinear natural phenomena. Here, it consists in assuming the steady-state condition for a species, and in obtaining the corresponding algebraic equations among the reaction rates. The steady-state assumption for a species i leads to an algebraic equation among some reaction rates. For the set of elementary reactions shown in the Table 1, the balance equations for the hydrogen can be written as

Table 2 Ethanol mechanism rate coefficients ($k = AT^\beta \exp(-E/RT)$); units are mol, cm³, s, K and cal/mol

	Reaction	A	β	E
1	OH + H ₂ = H + H ₂ O	2.14E+08	1.520	3,449
2	O + OH = O ₂ + H	2.02E+14	-0.400	0
17	H ₂ O ₂ + H = HO ₂ + H ₂	1.98E+06	2.000	2,435
21	H + H ₂ O = OH + H ₂	2.29E+09	1.404	18,320
22	O ₂ + H = O + OH	3.55E+15	-0.406	16,600
23	CH ₃ + O = CH ₂ O + H	8.00E+13	0.000	0
24	CH ₃ + M = CH + H ₂ + M	6.90E+14	0.000	82,469
25	CH ₃ + M = CH ₂ + H + M	1.90E+16	0.000	91,411
26	CH ₃ OH + M = CH ₂ + H ₂ O + M	2.84E+10	1.000	83,871
	Low pressure limit	1.78E+49	-8.810	93,369
	Troe parameters: $a = 0.9$, $T^{***} = 740$ $T^{**} = 5100$, $T^* = 980$			
	Enhanced third body efficiencies: H ₂ O = 10, H ₂ = 2, CO ₂ = 3, CO = 2			
27	CH ₃ OH + M = HCOH + H ₂ + M	4.20E+09	1.120	85,604
	Low pressure limit	5.02E+47	-8.400	94,823
	Troe parameters: $a = 0.9$, $T^{***} = 615$ $T^{**} = 4615$, $T^* = 915$			
	Enhanced third body efficiencies: H ₂ O = 10, H ₂ = 2, CO ₂ = 3, CO = 2			
28	CH ₃ OH + M = CH ₂ O + H ₂ + M	2.03E+09	1.000	91,443
	Low pressure limit	9.78E+47	-8.400	101,761
	Troe parameters: $a = 0.9$, $T^{***} = 825$ $T^{**} = 5700$, $T^* = 1125$			
	Enhanced third body efficiencies: H ₂ O = 10, H ₂ = 2, CO ₂ = 3, CO = 2			
29	CH ₂ O + M = HCO + H + M	3.31E+16	0.000	81,000
30	HCO + M = H + CO + M	1.86E+17	-1.000	17,000
31	CO + OH = CO ₂ + H	9.42E+03	2.250	-2,351
32	C ₂ H ₅ OH + M = CH ₂ OH + CH ₃ + M	5.94E+23	-1.680	91,163
	Low pressure limit	2.88E+85	-18.900	109,914
	Troe parameters: $a = 0.5$, $T^{***} = 200$ $T^{**} = 4600$, $T^* = 890$			
	Enhanced third body efficiencies: H ₂ O = 5, H ₂ = 2, CO ₂ = 3, CO = 2			
33	C ₂ H ₅ OH + M = C ₂ H ₅ + OH + M	1.25E+23	-1.540	96,005
	Low pressure limit	3.25E+85	-18.810	114,930
	Troe parameters: $a = 0.5$, $T^{***} = 300$ $T^{**} = 5000$, $T^* = 900$			
	Enhanced third body efficiencies: H ₂ O = 5, H ₂ = 2, CO ₂ = 3, CO = 2			

Table 2 continued

	Reaction	A	β	E
34	$C_2H_5OH + M = C_2H_4 + H_2O + M$	2.79E+13	0.090	66,136
	Low pressure limit	2.57E+83	-18.850	86,452
	Troe parameters: $a = 0.7, T^{***} = 350$			
	$T^{**} = 3800, T^* = 800$			
	Enhanced third body efficiencies:			
	$H_2O = 5$			
35	$C_2H_5OH + M = CH_3HCO + H_2 + M$	7.24E+11	0.095	91,007
	Low pressure limit	4.46E+87	-19.420	115,586
	Troe parameters: $a = 0.9, T^{***} = 900$			
	$T^{**} = 3500, T = 1100$			
	Enhanced third body efficiencies:			
	$H_2O = 5$			
36	$CH_3HCO + HO_2 = CH_2HCO + H_2O_2$	2.32E+11	0.400	14,864
37	$CH_2HCO + O_2 = CH_2O + CO + OH$	3.00E+10	0.000	0
38	$C_2H_4 + M = C_2H_2 + H_2 + M$	1.80E+14	0.000	87,000
	Low pressure limit	1.50E+15	0.000	55,443
39	$C_2H_2 + OH = CH_3 + CO$	4.83E-04	4.000	-2,000
40	$C_2H_2 + M = C_2H + H + M$	4.20E+16	0.000	107,000
41	$CH_2CO + M = CH_2 + CO + M$	3.00E+14	0.000	70,980
	Low pressure limit	3.60E+15	0.000	59,270
42	$C_3H_8 + M = C_2H_5 + CH_3 + M$	7.90E+22	-1.800	88,629
	Low pressure limit	7.24E+27	-2.880	67,448
	Troe parameters: $a = 1, T^{***} = 1.0E - 15$			
	$T^{**} = 1.0E + 15, T^* = 1500$			
	Enhanced third body efficiencies:			
	$H_2O = 5, H_2 = 2, CO_2 = 3, CO = 2$			
43	$C_3H_6 = C_2H_2 + CH_4$	2.50E+12	0.000	70,000
44	$C_3H_6 = H_2CCCH_2 + H_2$	3.00E+13	0.000	80,000

Fall-off reaction in the Troe form with: $k = k_0[M]/(1 + k_0[M]/k_\infty)F$, $\log F = \{1 + [\kappa/(N - d\kappa)]^2\}^{-1} \log F_{cent}$, $\kappa = \log(k_0[M]/k_\infty) + C$, $C = -0.4 - 0.67 \log F_{cent}$, $N = 0.75 - 1.27 \log F_{cent}$, $d = 0.14$, $F_{cent} = (1 - a) \exp(-T/T^{***}) + a \exp(-T/T^*) + \exp(-T^{**}/T)$ [17]

$$w_{H_2} = -w_1 - w_3 + w_7 + w_{11} + w_{17} \quad (2)$$

$$w_H = +w_1 + w_2 + w_3 - w_4 - w_6 - w_7 - w_8 - 2w_{11} \quad (3)$$

$$-w_{12} - w_{13} - w_{17} - w_{18}$$

$$w_{O_2} = +w_2 - w_4 + w_5 + w_7 + w_9 + w_{14} + w_{15} \quad (4)$$

$$w_O = -w_2 - w_3 + w_8 - w_9 + w_{10} - w_{13} - 2w_{14} - w_{19} \quad (5)$$

$$w_{H_2O} = +w_1 + w_5 + w_8 + w_{10} + w_{12} + w_{18} + w_{20} \quad (6)$$

$$w_{OH} = -w_1 - w_2 + w_3 - w_5 + 2w_6 + w_9 - 2w_{10} - w_{12} \quad (7)$$

$$+w_{13} - 2w_{16} + w_{18} + w_{19} - w_{20}$$

$$w_{HO_2} = +w_4 - w_5 - w_6 - w_7 - w_8 - w_9 - 2w_{15} + w_{17} \quad (8)$$

$$+w_{19} + w_{20}$$

$$w_{H_2O_2} = +w_{15} + w_{16} - w_{17} - w_{18} - w_{19} - w_{20} \quad (9)$$

where w_i represents the reaction rate. The positive sign refers to a species which appears in the right side of the equal sign of reactions of the Table 1, while the negative sign in the left side of them. For example, in 1. $\text{OH} + \text{H}_2 = \text{H} + \text{H}_2\text{O}$, $w_{\text{H}} = +w_1$ and $w_{\text{OH}} = -w_1$ (see the Table 1).

The species O, OH, HO_2 and H_2O_2 are assumed to be in steady-state and, therefore, $w_i = 0$, which leads to four algebraic equations among the reaction rates w_k ,

$$w_6 = +w_4 - w_5 - w_7 - w_8 - w_9 - w_{15} + w_{16} - w_{18} \tag{10}$$

$$w_{12} = -w_1 - 2w_2 + 2w_4 - 3w_5 - 2w_7 - w_8 - 2w_9 - w_{10} - 2w_{14} - 3w_{15} - w_{16} + w_{17} + w_{19} \tag{11}$$

$$w_{13} = -w_2 - w_3 + w_8 - w_9 + w_{10} - 2w_{14} - w_{19} \tag{12}$$

$$w_{20} = +w_{15} + w_{16} - w_{17} - w_{18} - w_{19} \tag{13}$$

Making the rates $w_{\text{I}_{\text{H}_2}}$ and $w_{\text{II}_{\text{H}_2}}$ equal to

$$w_{\text{I}_{\text{H}_2}} = -w_2 + w_4 - w_5 - w_7 - w_9 - w_{14} - w_{15} \tag{14}$$

$$w_{\text{II}_{\text{H}_2}} = -w_1 - 3w_2 - w_3 + 3w_4 - 3w_5 - 2w_7 - 3w_9 + w_{11} + w_{17} - 3w_{14} - 3w_{15} \tag{15}$$

one obtains the following linear combinations

$$w_{\text{H}_2} = -3w_{\text{I}_{\text{H}_2}} + w_{\text{II}_{\text{H}_2}} \tag{16}$$

$$w_{\text{H}} = +2w_{\text{I}_{\text{H}_2}} - 2w_{\text{II}_{\text{H}_2}} \tag{17}$$

$$w_{\text{O}_2} = -w_{\text{I}_{\text{H}_2}} \tag{18}$$

$$w_{\text{H}_2\text{O}} = +2w_{\text{I}_{\text{H}_2}} \tag{19}$$

The stoichiometry of these balance equations corresponds to the global mechanism of two-step for the hydrogen formed by reactions I_{H_2} and II_{H_2} .

For the reactions of the Table 2, the balance equations for the ethanol are written as

$$w_{\text{H}_2} = -w_1 + w_{17} + w_{21} + w_{24} + w_{27} + w_{28} + w_{35} + w_{38} + w_{44} \tag{20}$$

$$w_{\text{H}} = +w_1 - w_{17} - w_{21} - w_{22} + w_{23} + w_{25} + w_{29} + w_{30} + w_{31} + w_{40} \tag{21}$$

$$w_{\text{O}_2} = -w_{22} - w_{37} \tag{22}$$

$$w_{\text{O}} = +w_{22} - w_{23} \tag{23}$$

$$w_{\text{OH}} = -w_1 + w_{21} + w_{22} - w_{31} + w_{33} + w_{37} - w_{39} \tag{24}$$

$$w_{\text{H}_2\text{O}} = +w_1 - w_{21} + w_{26} + w_{34} \tag{25}$$

$$w_{\text{HO}_2} = +w_{17} - w_{36} \tag{26}$$

$$w_{\text{H}_2\text{O}_2} = -w_{17} + w_{36} \tag{27}$$

$$w_{\text{CO}} = +w_{30} - w_{31} + w_{37} + w_{39} + w_{41} \tag{28}$$

$$w_{\text{CO}_2} = +w_{31} \tag{29}$$

$$\begin{aligned}
 w_{\text{CH}_4} &= +w_{43} & (30) \\
 w_{\text{CH}_3} &= -w_{23} - w_{24} - w_{25} + w_{32} + w_{39} + w_{42} & (31) \\
 w_{\text{CH}_2} &= +w_{25} + w_{26} + w_{41} & (32) \\
 w_{\text{CH}} &= +w_{24} & (33) \\
 w_{\text{CH}_3\text{OH}} &= -w_{26} - w_{27} - w_{28} & (34) \\
 w_{\text{CH}_3\text{HCO}} &= +w_{35} - w_{36} & (35) \\
 w_{\text{CH}_2\text{O}} &= +w_{23} + w_{28} - w_{29} + w_{37} & (36) \\
 w_{\text{CH}_2\text{OH}} &= +w_{32} & (37) \\
 w_{\text{CH}_2\text{HCO}} &= +w_{36} - w_{37} & (38) \\
 w_{\text{CH}_2\text{CO}} &= -w_{41} & (39) \\
 w_{\text{HCOH}} &= +w_{27} & (40) \\
 w_{\text{HCO}} &= +w_{29} - w_{30} & (41) \\
 w_{\text{H}_2\text{CCCH}_2} &= +w_{44} & (42) \\
 w_{\text{C}_2\text{H}_5\text{OH}} &= -w_{32} - w_{33} - w_{34} - w_{35} & (43) \\
 w_{\text{C}_2\text{H}_5} &= +w_{33} + w_{42} & (44) \\
 w_{\text{C}_2\text{H}_4} &= +w_{34} - w_{38} & (45) \\
 w_{\text{C}_2\text{H}_2} &= +w_{38} - w_{39} - w_{40} + w_{43} & (46) \\
 w_{\text{C}_2\text{H}} &= +w_{40} & (47) \\
 w_{\text{C}_3\text{H}_8} &= -w_{42} & (48) \\
 w_{\text{C}_3\text{H}_6} &= -w_{43} - w_{44} & (49)
 \end{aligned}$$

The species O, OH, HO₂, H₂O₂, CH₄, CH₃, CH₂, CH, HCOH, HCO, H₂CCCH₂, CH₂OH, CH₃OH, CH₃HCO, CH₂CO, C₂H₅, C₂H₂, C₂H, C₃H₈ and C₃H₆ are assumed to be in steady-state and, therefore, $w_i = 0$, which leads to 20 algebraic equations among the reaction rates w_k ,

$$w_1 = -w_{31} + w_{37} + w_{38} \quad (50)$$

$$w_{17} = +w_{35} \quad (51)$$

$$w_{21} = +w_{38} \quad (52)$$

$$w_{22} = -w_{28} + w_{38} \quad (53)$$

$$w_{23} = -w_{28} + w_{38} \quad (54)$$

$$w_{24} = 0 \quad (55)$$

$$w_{25} = +w_{28} \quad (56)$$

$$w_{26} = -w_{28} \quad (57)$$

$$w_{27} = 0 \quad (58)$$

$$w_{28} = 0 \quad (59)$$

$$w_{30} = +w_{29} \quad (60)$$

$$w_{32} = 0 \quad (61)$$

$$w_{33} = 0 \quad (62)$$

$$w_{36} = +w_{35} \quad (63)$$

$$w_{39} = +w_{38} \quad (64)$$

$$w_{40} = 0 \quad (65)$$

$$w_{41} = 0 \quad (66)$$

$$w_{42} = 0 \quad (67)$$

$$w_{43} = 0 \quad (68)$$

$$w_{44} = 0 \quad (69)$$

Making the rates $w_{\text{IC}_2\text{H}_5\text{OH}}$, $w_{\text{II}_\text{C}_2\text{H}_5\text{OH}}$, $w_{\text{III}_\text{C}_2\text{H}_5\text{OH}}$, $w_{\text{IV}_\text{C}_2\text{H}_5\text{OH}}$, $w_{\text{V}_\text{C}_2\text{H}_5\text{OH}}$ and $w_{\text{VI}_\text{C}_2\text{H}_5\text{OH}}$ equal to

$$w_{\text{IC}_2\text{H}_5\text{OH}} = -w_{31} + w_{35} + w_{38} \quad (70)$$

$$w_{\text{II}_\text{C}_2\text{H}_5\text{OH}} = +w_{31} + w_{34} - w_{38} \quad (71)$$

$$w_{\text{III}_\text{C}_2\text{H}_5\text{OH}} = -w_{31} + w_{37} + w_{38} \quad (72)$$

$$w_{\text{IV}_\text{C}_2\text{H}_5\text{OH}} = +w_{31} \quad (73)$$

$$w_{\text{V}_\text{C}_2\text{H}_5\text{OH}} = +w_{29} \quad (74)$$

$$w_{\text{VI}_\text{C}_2\text{H}_5\text{OH}} = +w_{31} \quad (75)$$

one obtains the following linear combinations

$$w_{\text{C}_2\text{H}_5\text{OH}} = -w_{\text{IC}_2\text{H}_5\text{OH}} - w_{\text{II}_\text{C}_2\text{H}_5\text{OH}} \quad (76)$$

$$w_{\text{CH}_2\text{HCO}} = w_{\text{IC}_2\text{H}_5\text{OH}} - w_{\text{III}_\text{C}_2\text{H}_5\text{OH}} \quad (77)$$

$$w_{\text{C}_2\text{H}_4} = w_{\text{II}_\text{C}_2\text{H}_5\text{OH}} - w_{\text{IV}_\text{C}_2\text{H}_5\text{OH}} \quad (78)$$

$$w_{\text{CH}_2\text{O}} = w_{\text{III}_\text{C}_2\text{H}_5\text{OH}} + w_{\text{IV}_\text{C}_2\text{H}_5\text{OH}} - w_{\text{V}_\text{C}_2\text{H}_5\text{OH}} \quad (79)$$

$$w_{\text{CO}} = w_{\text{III}_\text{C}_2\text{H}_5\text{OH}} + w_{\text{IV}_\text{C}_2\text{H}_5\text{OH}} + w_{\text{V}_\text{C}_2\text{H}_5\text{OH}} - w_{\text{VI}_\text{C}_2\text{H}_5\text{OH}} \quad (80)$$

$$w_{\text{CO}_2} = w_{\text{VI}_\text{C}_2\text{H}_5\text{OH}} \quad (81)$$

$$w_{\text{O}_2} = -w_{\text{III}_\text{C}_2\text{H}_5\text{OH}} - w_{\text{IV}_\text{C}_2\text{H}_5\text{OH}} \quad (82)$$

$$w_{\text{H}_2\text{O}} = w_{\text{II}_\text{C}_2\text{H}_5\text{OH}} + w_{\text{III}_\text{C}_2\text{H}_5\text{OH}} - w_{\text{IV}_\text{C}_2\text{H}_5\text{OH}} \quad (83)$$

$$w_{\text{H}_2} = 2w_{\text{IC}_2\text{H}_5\text{OH}} - w_{\text{III}_\text{C}_2\text{H}_5\text{OH}} + w_{\text{IV}_\text{C}_2\text{H}_5\text{OH}} + w_{\text{VI}_\text{C}_2\text{H}_5\text{OH}} \quad (84)$$

$$w_{\text{H}} = -w_{\text{IC}_2\text{H}_5\text{OH}} + w_{\text{III}_\text{C}_2\text{H}_5\text{OH}} + 2w_{\text{V}_\text{C}_2\text{H}_5\text{OH}} \quad (85)$$

The stoichiometry of these balance equations correspond to the global mechanism of six-step for the ethanol formed by the reactions $\text{IC}_2\text{H}_5\text{OH}$ to $\text{VIC}_2\text{H}_5\text{OH}$.

As the hydrogen is an important intermediate species in the principal path of oxidation of ethanol, it results the eight-step mechanism for the ethanol (reactions IH_2 , IIH_2 , $\text{IC}_2\text{H}_5\text{OH}$, $\text{IIC}_2\text{H}_5\text{OH}$, $\text{IIIC}_2\text{H}_5\text{OH}$, $\text{IVC}_2\text{H}_5\text{OH}$, $\text{VC}_2\text{H}_5\text{OH}$, $\text{VIC}_2\text{H}_5\text{OH}$).

When, some species may be assumed to be in steady-state and some equations in partial equilibrium, such that the error between the solution of the simplified and the full system of equations is reduced to an acceptable level, the computational time

needed to obtain the chemical solution of diffusion flames is minimized [22]. However, these assumptions are not usually accurate in low temperature regimes.

3 Numerical solution of a ethanol jet diffusion flame

Many jet diffusion flames are analyzed in the literature [23–25]. The numerical simulations shown here are based on an ethanol jet diffusion flame, and all calculations were done with the reduced kinetic mechanism consisting of 11 species and 8 elementary reactions listed in the Sect. 2, validating the reduced mechanism developed for the ethanol.

For the combustion process, the set of governing equations in nondimensional form includes the momentum (Navier–Stokes), enthalpy and mass fraction, given respectively by ($i, j = 1, 2, 3$)

$$\frac{\partial(\rho u_i)}{\partial t} + \frac{\partial(\rho u_i u_j)}{\partial x_j} = -\frac{1}{M^2} \frac{\partial p}{\partial x_i} + \frac{\partial}{\partial x_j} \left(\frac{\mu}{Re} \tau_{ij} \right) \quad (86)$$

$$\frac{\partial(\rho h)}{\partial t} + \frac{\partial(\rho u_j h)}{\partial x_j} = \frac{\partial}{\partial x_j} \left(\frac{\mu}{Pr} \frac{\partial(\rho h)}{\partial x_j} \right) \quad (87)$$

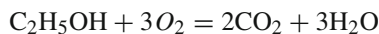
$$\frac{\partial(\rho Y_k)}{\partial t} + \frac{\partial(\rho u_j Y_k)}{\partial x_j} = \frac{\partial}{\partial x_j} \left(\frac{\mu}{Sc} \frac{\partial(\rho Y_k)}{\partial x_j} \right) + \dot{w}_k, \quad k = 1, \dots, n \quad (88)$$

where ρ is the density, u_i the velocity vector, t the time and p the pressure (given by a Poisson's equation). The viscous stress tensor is $\tau_{ij} = (\partial u_i / \partial x_j + \partial u_j / \partial x_i) - (2/3) \delta_{ij} \partial u_k / \partial x_k$, δ_{ij} is the Kronecker symbol, μ the dynamic viscosity, h the enthalpy, Y_k the mass fraction of the species k . The reaction rate of the species k is given by $\dot{w}_k = \pm \nu_F Da Y_F Y_O \exp(-Ze/T)$, ν_F is the stoichiometric coefficient of the fuel and He the heat released. In these equations M is the Mach, Re the Reynolds, Pr the Prandtl, Sc the Schmidt, Da the Damköhler, and Ze the Zel'dovich nondimensional numbers.

The resulting equations are coupled then discretized by the standard second order space and first order time finite difference method. The numerical simulation was performed using a code developed in Fortran90.

Consider that the burner, shown in the Fig. 2, used in the numerical simulation has a duct of cylindrical cross section with $De = 1$, a cylindrical tube that injects fuel with $D = 0.0267$, and the burner length is $L = 1$; all parameters are nondimensional.

The simulation for a C_2H_5OH /air jet diffusion flame uses the initial conditions, $Y_{O_2,0} = 0.1812$ and $Y_{C_2H_5OH,0} = 0.1385$. The results obtained with the reduced kinetic mechanism of 8 elementary reactions listed in the Sect. 2 are compared to the results computed with the following single-step global reaction scheme suggested by Turns [20]:



where

$$w_{C_2H_5OH} = A \exp\left(-\frac{E}{RT}\right) [C_2H_5OH]^m [O_2]^n \quad (89)$$

Fig. 2 Burner sketch

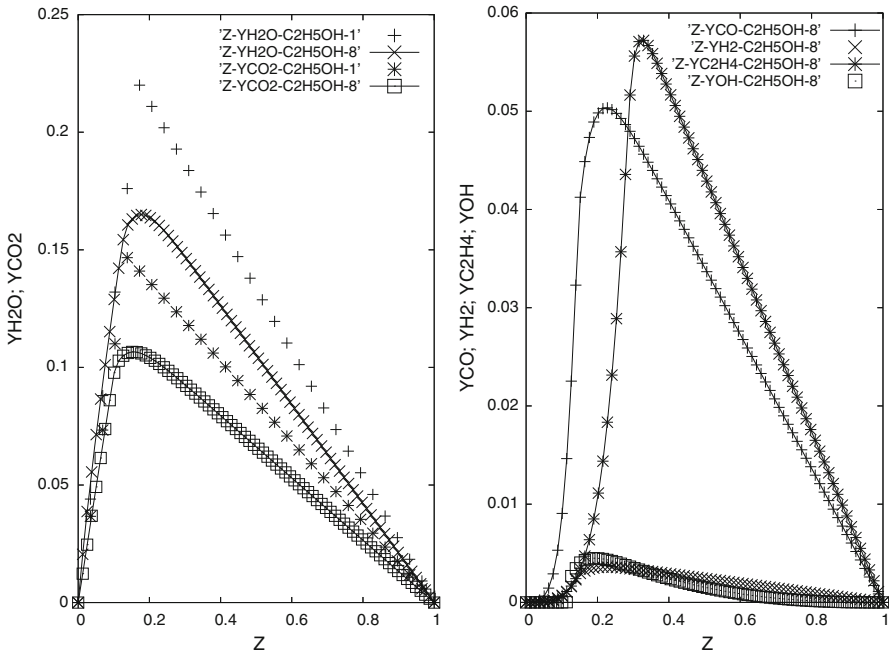
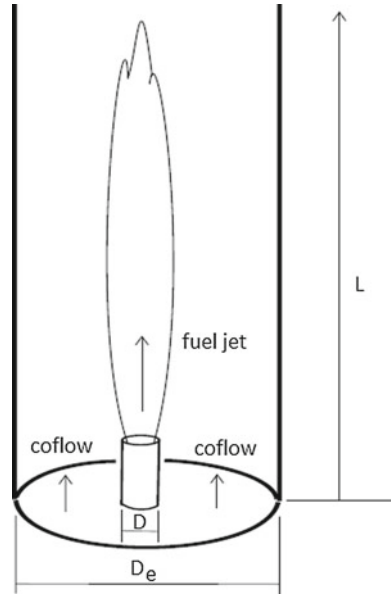
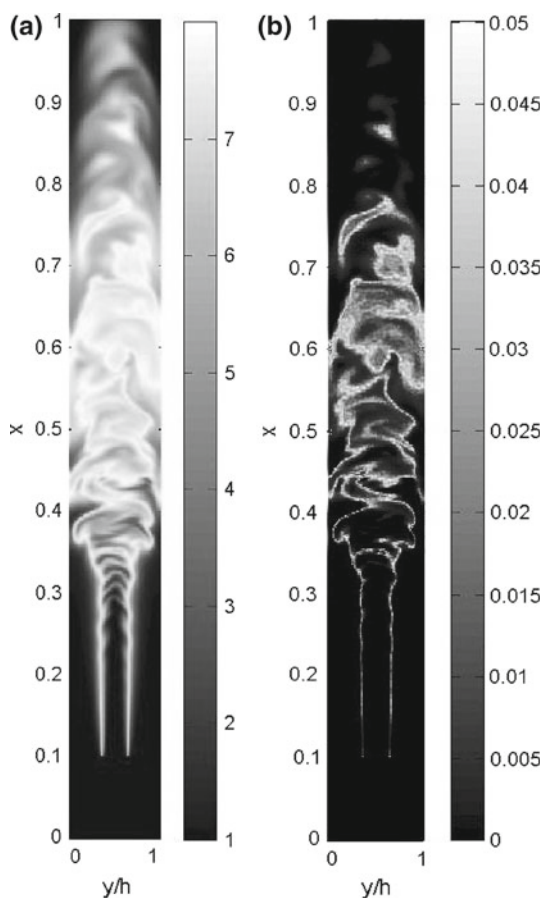


Fig. 3 Comparison of the mass fractions of H_2O and CO_2 (left) and of CO, H_2, C_2H_4 and OH (right) in the mixture fraction space of a reduced kinetic mechanism of 8-step with the global single-step reaction for the ethanol

Fig. 4 Temperature **a** and mass fraction map for CO **b** for an ethanol flame at 0.4 s



whose parameters $A = 1.5 \times 10^{12}$, $E/R = 15.098$, $m = 0.15$ and $n = 1.6$ are a result of the calibration of the formula with the experiment.

Figure 3 (left) shows the profiles of the mass fraction for the CO_2 and H_2O along the mass fraction space; the symbols “+” and “*” represent the results obtained with the single-step infinite-rate kinetic model according to the parameters given by Turns [20]. The products surge near the stoichiometric surface ($Z \sim 0.15$), where there are ideal conditions of burning. According to Saxena and Williams [9], the maximum concentrations of H_2O and CO_2 for ethanol partially premixed flames are approximately 0.18 and 0.11, respectively; these concentrations are in agreement with those found in this work. The results obtained with the single-step reaction mechanism overestimates the combustion principal products.

Figure 3 (right) shows the mass fractions of some species with smaller concentrations, but still significant, according to the reaction systems considered here. The mass fraction of the products H_2O , CO_2 , CO , H_2 , C_2H_4 and OH have their maximum value in the neighborhood of the stoichiometric surface.

Figure 4a, b show, respectively, the temperature and the instantaneous map for the product CO for ethanol flames, obtained at 0.4 s, for a longitudinal section of

the burner. The regions of higher temperature (white color) correspond to regions of higher mass fraction of combustion products. These regions correspond to those near the stoichiometric surface, where there are ideal conditions of burning.

Intermittent behavior is observed away from the nozzle exit. Intermittency, i. e., the growth of fluctuations, surges for many flows of practical interest, such as in turbulent jets, and boundary layers. These flow situations can have different levels of mixture depending on the conditions adopted [26]. The weakening of the eddies when the shear layer is partially developed is expected, resulting in a slower rate of entrainment and of axial velocity decrease. Greater intermittency in the values of mass fractions occurs when increasing the distance from the nozzle, and the reason for this may be explained by the decrease of the concentration [27].

4 Conclusions

The present work shows that a reduced kinetic mechanism for ethanol oxidation with eight-step can produce favorable results. Numerical tests were carried out for a jet diffusion flame and the results compare well with those obtained with optimized kinetic parameters found in the literature. The main advantage of the obtained reduced mechanism 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 full mechanism.

Acknowledgments This research is being developed at the Federal University of Rio Grande do Sul—UFRGS. Andreis and Vaz thank the financial support from the *Coordenação de Aperfeiçoamento de Pessoal de Nível Superior*—CAPES—Brazil, and Prof. De Bortoli gratefully acknowledges the financial support from the *Conselho Nacional de Desenvolvimento Científico e Tecnológico*—CNPq—Brazil, under process 303007/2009-5

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