Asociación Argentina
de Mecánica Computacional

Mecánica Computacional Vol XXIX, págs. 2655-2661 (artículo completo)
Eduardo Dvorkin, Marcela Goldschmit, Mario Storti (Eds.)
Buenos Aires, Argentina, 15-18 Noviembre 2010

DEVELOPMENT OF REDUCED REACTION MECHANISMS FOR ETHYLENE AND ETHANOL DIFFUSION FLAMES

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Keywords: Diffusion flames, ethanol, reduced mechanisms, REDIM.

Abstract. The ethanol (C_2H_5OH) is frequently mentioned as an alternative fuel that can be produced from renewable energy resources. It can be used as an automotive fuel in the hydrated form or mixed with gasoline. A skeletal chemical kinetic mechanism describing the combustion of ethanol is presented by Marinov; this mechanism is composed by 351 reversible reactions among 56 species, describing the high temperature oxidation of it. The aim of this work is the development of reduced reaction mechanisms for ethanol and ethylene diffusion flames. The process to obtain the reduced mechanism for ethanol and ethylene is initially based on the velocity and concentration of each elementary reaction, then one employs the Intrinsic Low-Dimensional Manifold (ILDM) technique. Numerical tests show that the main advantage of the reduced reaction mechanism is the decrease of the cost necessary to solve the system of equations for diffusion flames.

1 INTRODUCTION

Combustion is very important in our life and also in industrial processes. About 90% of the World energy requirements (e.g., in electrical power generation, heating, chemical industry, etc.) is provided by combustion. However, the fundamental processes occurring in combustion and their interactions with each other are not completely understood. A large variety of models describing several processes occurring in combustion, as chemistry and turbulence, and a variety of numerical tools needed to solve the underlying equation systems, have been developed (Chrys Correa, 2000).

The simulation of reactive flows using detailed chemistry introduces a large number of species and reactions. One major challenge in combustion modelling is the simplification of detailed reaction mechanisms without significant loss of accuracy. The main difference for the existing reduction methods appears in the strategy to distinguish between slow and fast processes (Bongers et al., 2002).

Mathematical modeling of reactive flows has gained increasing importance in the last decades (Bauer and Maas, 2006). Peters (1992) introduced the Systematic Reduction Method (SRM). This method applies steady-state assumptions for intermediate species and partial equilibrium assumptions for fast reactions. The steady-state technique is based on the assumption that many of the elementary reactions of the full mechanism does not contribute significantly to the determination of the rate governing the overall combustion process (Warnatz et al., 2006), and some elementary reactions can be considered as being in partial equilibrium.

Moreover, it is advantageous if a technique to reduce the calculations to find a solution incorporates as much as possible information from the original system. In methods such as the Intrinsic Low-Dimensional Manifolds (ILDM) and the Reaction Diffusion Manifolds (REDIM), it is possible.

In the ILDM method, slow and fast processes are separated based on a time-scale analysis of the Jacobian of the chemical source term (Bongers et al., 2002). The Jacobian contains the necessary numerical information about the linearization of the system at a point, and the solution of the linearized system describes the local behavior of the system near that point. The ILDM can be generated using a locally adapted parametrization, but in most applications in Computational Fluid Dynamic (CFD) it is used in terms of a fixed parametrization. In this case, the governing equations system is projected in the major species concentrations directions, characterizing the reaction progress (e.g. CO_2, H_2O) (Bauer and Maas, 2006).

The REDIM corresponds to an evolution of the Intrinsic Low-Dimensional Manifolds method. This technique is based on the solution of an evolution equation for a low-dimensional manifold in the thermo-kinetic space. It overcomes many of the deficiencies of the ILDM concept, because it takes into account the coupling of reaction and molecular transport processes.

In this paper, we use both the assumptions of steady-state, partial equilibrium together with the REDIM method. The set of 351 irreversible reactions, which are part of ethanol oxidation, are reduced resulting in fewer reactions and species. The fact that the development of reduced reaction mechanisms for fuels such as ethanol is not very frequent in the literature, and its understanding can simplifies the calculation of flames involving alcohols, are motivating our studies. Results are obtained for an ethanol/air diffusion flame, based on the 1D-REDIM technique.

2 REDUCED KINETIC MECHANISMS FOR ETHANOL AND ETHYLENE

The numerical cost for solving the equations of chemical kinetics of combustion systems is generally high. Techniques to facilitate the numerical solution of diffusion flames using kinetic chemical reaction mechanisms are based on hypothesis such as the steady-state or the partial equilibrium.

Ethanol combustion is investigated here using a skeletal chemical-kinetic mechanism consisting of 351 elementary steps among 56 species (Marinov, 1999). As it is necessary to solve several differential equations, we try to reduce the number of reactions and species involved in the system. The elimination of the unimportant reactions is based on assumptions of partial equilibrium and steady-state. The justification for this approximation is generally provided by physical terms because the rate at which species k is consumed is much faster than the rate by which it is produced, being the time derivative of the concentration of these species set to zero

$$\frac{d[C_k]}{dt} = 0. \tag{1}$$

The resulting mechanism is given by

$$\begin{array}{ll}
\text{I.} & C_2H_5OH(+M) = C_2H_4 + H_2O(+M) \\
\text{II.} & C_2H_4(+M) = C_2H_2 + H_2(+M) \\
\text{III.} & C_2H_2(+M) = C_2H + H(+M) \\
\text{IV.} & C_2H + O_2 = CO + CO + H \\
\text{V.} & C_2H + H_2 = C_2H_2 + H \\
\text{VI.} & C_2H + OH = HCCO + H \\
\text{VII.} & HCCO + OH = C_2O + H_2O \\
\text{VIII.} & C_2O + O_2 = CO + CO + O \\
\text{IX.} & CO + O_2 = CO_2 + O \\
\text{X.} & CO + OH = CO_2 + H \\
\text{XI.} & OH + H_2 = H + H_2O \\
\text{XII.} & OH + OH = O + H_2O \\
\text{XIII.} & O + H_2 = OH + H \\
\text{XIV.} & H + O_2 = HO_2 \\
\text{XV.} & H + HO_2 = H_2 + O_2 \\
\text{XVI.} & H + HO_2 = 2OH \\
\text{XVII.} & H + H(+M) = H_2(+M) \\
\text{XVIII.} & H + O = OH
\end{array} \tag{2}$$

From the direct decomposition of ethanol surge some species, such as CH_2OH, C_2H_5, C_2H_4, CH_3CHOH, CH_3CH_2O and others. The ethylene (C_2H_4) is an important intermediate since its concentration is high. It is produced not only by this direct decomposition, but also by decomposition of others species (Saxena and Williams, 2007).

Note that for the ethylene the reduced mechanism corresponds to the equations II to XVIII and their corresponding coefficients are given in Table 1. Using the coefficients presented in this table, we obtain the specific velocity of each elementary reaction, using the relation

$$k^f = AT^b \exp\left(-\frac{E_a}{RT}\right), \tag{3}$$

where k^f is the reaction rate coefficient of the forward reaction, A the frequency factor, T the temperature, E_a the activation energy, and $R = 1.98[$ cal/mol $\cdot$ K$]$ denote the gas constant. Units are Moles, cm^3, Seconds, Kelvin, and Calories/Mole.

Step	A	b	E_a
I	2.79E+13	0.09	66136
II	1.80E+14	0	87000
III	4.20E+16	0	107000
IV	9.04E+12	0	-457
V	4.09E+05	2.39	864.3
VI	2.00E+13	0	0
VII	3.00E+13	0	0
VIII	2.00E+13	0	0
IX	2.53E+12	0	47688
X	9.42E+03	2.25	-2351
XI	2.14E+08	1.52	3449
XII	3.57E+04	2.4	-2112
XIII	5.06E+04	2.67	6290
XIV	4.52E+13	0	0
XV	6.63E+13	0	2126
XVI	1.50E+14	0	1000
XVII	1.00E+18	-1	0
XVIII	4.71E+18	-1	0

Table 1: Chemical kinetics data for modeling ethanol combustion.

A still more reduced scheme for the ethanol can be found at De Bortoli et al. (2010), which is useful to obtain the principal species for ethanol/air burning at high temperatures. In the following, the reduction strategy using the REDIM is briefly discussed.

3 1D-REDIM STRATEGY

In this section one discusses how to build a 1D-REDIM, which will be applied to partially premixed diffusion flames. The fluid is considered to be a Newtonian fluid, the viscous dissipation is neglected, and the Lewis number of all species is assumed to be equal to unity. Under these hypotheses, the related thermo-chemical processes can be modeled by the following equation

$$\frac{\partial \Psi}{\partial t} + \mathbf{u} \cdot \nabla \Psi - \frac{1}{\rho} \nabla \cdot (D \nabla \Psi) = \frac{1}{\rho} F(\Psi), \tag{4}$$

where Ψ and $F(\Psi)$ are $n = 2 + n_{sp}$-dimensional vectors, $\Psi = (h, p, Y_1, ..., Y_{n_{sp}})$ and $F(\Psi) = (0, 0, \dot{w}_1, ..., \dot{w}_{n_{\mathrm{sp}}})$. The $n \times n$-dimensional diffusion matrix is $D = -\lambda / c_p \cdot I$.

For the ethanol, considering the reaction set given by equations (2), it implies that $n = 2+15$. Here, ρ is the density, **u** denotes the velocity field, h the specific enthalpy, p the pressure, Y_k the mass fraction of the k-th species, $\dot{w}_k$ the reaction rate of the k-th species, λ the thermal conductivity and c_p the heat capacity.

This technique was recently developed by Bykov and Mass (2007), that proposed the REDIM equations defined as the stationary solution of:

$$\begin{aligned} &\frac{\partial \Psi(\theta)}{\partial t} = (I - \Psi_\theta \Psi_\theta^+) \cdot \left[F(\theta) + \frac{\lambda}{\rho c_p} \Psi_{\theta\theta} \circ \mathrm{grad}(\theta) \circ \mathrm{grad}(\theta) \right] \\ &\Psi^0 = \Psi^{\mathrm{ext}}(\theta) \end{aligned} \tag{5}$$

Now, let us assume that the REDIM is parameterized by the progress variable $\theta = Z$, the mixture fraction, which is simply defined by:

$$Z = \frac{\nu Y_F - Y_{O_2} + Y_{O_2,i}}{\nu Y_{F,i} + Y_{O_2,i}}, \tag{6}$$

where ν is the stoichiometric mass ratio, $Y_{O_2,i}$ and $Y_{F,i}$ denote the mass fraction of oxygen and fuel in the stream, respectively. Z is a conservative scalar ranging from 0 to 1, which relates the level of mixing between the oxygen and the fuel.

The gradient vector Ψ_θ is given by

$$\Psi_\theta = \left(\frac{\partial h}{\partial Z}, \frac{\partial p}{\partial Z}, \frac{\partial Y_1}{\partial Z}, ..., \frac{\partial Y_{n_{\mathrm{sp}}}}{\partial Z} \right). \tag{7}$$

Assuming that $\frac{\partial Y_1}{\partial Z} = \frac{\partial Y_F}{\partial Z}$, Ψ_θ and $\Psi_{\theta\theta}$ become

$$\Psi_\theta = \left(\frac{\partial h}{\partial Z}, 0, \frac{\nu Y_{F,i} + Y_{O_2,i}}{\nu}, \frac{\partial Y_2}{\partial Z}, ..., \frac{\partial Y_{n_{\mathrm{sp}}}}{\partial Z} \right), \tag{8}$$

$$\Psi_{\theta\theta} = \left(\frac{\partial^2 h}{\partial Z^2}, 0, 0, \frac{\partial^2 Y_2}{\partial Z^2}, ..., \frac{\partial^2 Y_{n_{\mathrm{sp}}}}{\partial Z^2} \right). \tag{9}$$

The pseudo inverse defined by $\Psi_\theta^+ := (\Psi_\theta^T \cdot \Psi_\theta)^{-1} \cdot \Psi_\theta^T$ is then given by

$$\Psi_\theta^+ = \left(0, 0, \frac{\nu}{\nu Y_{F,i} + Y_{O_2,i}}, 0, ..., 0 \right). \tag{10}$$

Moreover, the projected system of equations onto the REDIM in the non-stationary is simply given by

$$\frac{\partial Z}{\partial t} + \mathbf{u} \cdot \nabla Z - \nabla \cdot \left(\frac{\lambda}{c_p} \nabla Z \right) = 0, \tag{11}$$

which is the mixture fraction equation.

4 NUMERICAL RESULTS

Numerical tests using the REDIM technique are performed to determine a manifold on the mixture fraction space. All calculations are based on a reduced reaction mechanism consisting of 15 species and 18 elementary reactions listed in the set of equations 2. The resulting equations are then discretized by the standard second order space and first order time Finite Difference Method.

Figures 1 and 2 show the species concentration versus the mixture fraction. In Fig. 1 we show the species with higher concentrations for ethanol flames, and in Fig. 2 the species with smaller concentrations, but still significant, according to the reaction systems considered here. Here it was considered $Y_{O_2,i} = 0.1812$ and $Y_{C_2H_5OH,i} = 0.1385$ (Saxena and Williams, 2007). The products surge near the stoichiometric surface ($Z \sim 0.4$), where there are ideal conditions of burning.

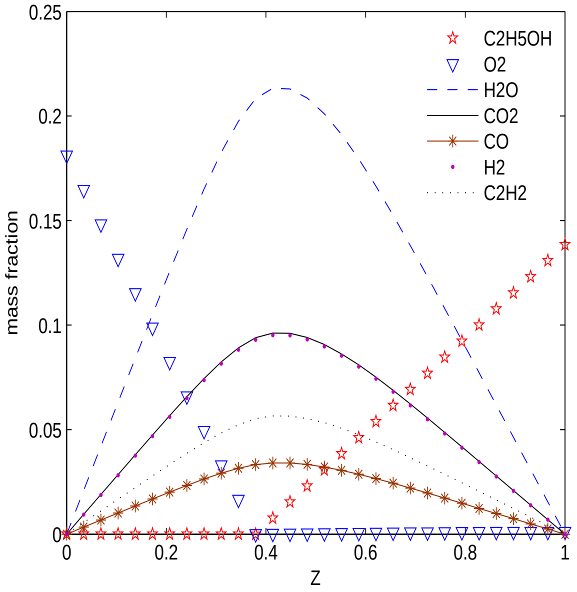

Figure 1: Mass fraction of C_2H_5OH, O_2, H_2O, CO_2, CO, H_2 and C_2H_2 in the mixture fraction Z, using REDIM.

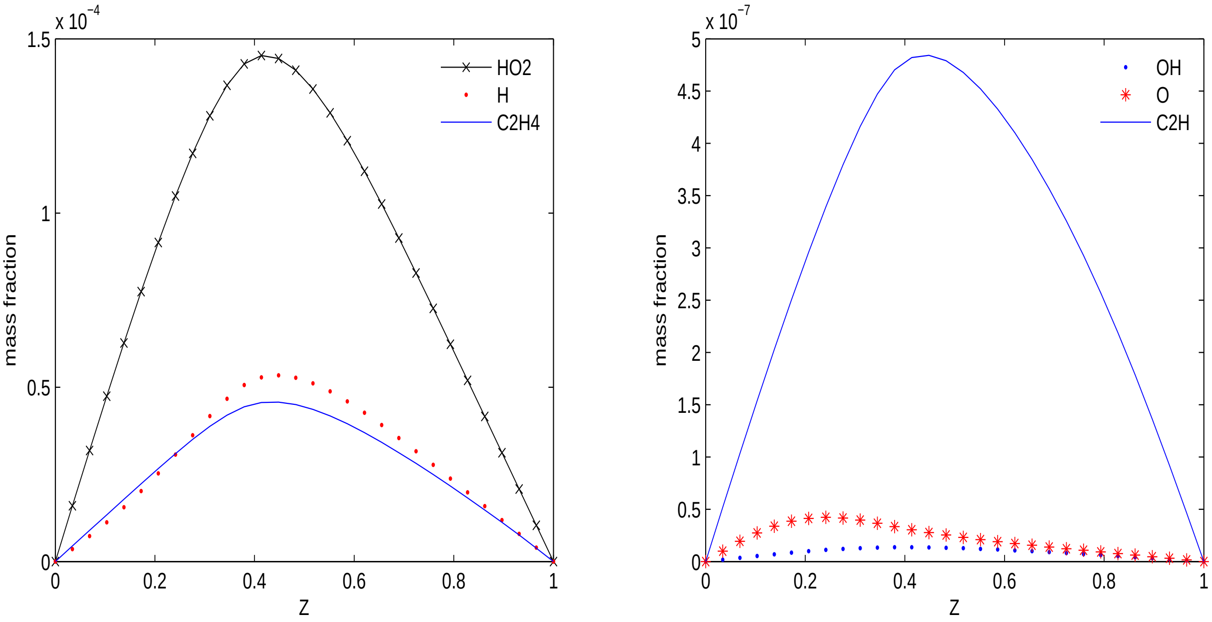

Figure 2: Mass fraction of HO_2, H, C_2H_4 (left) and OH, O, C_2H (right) in the mixture fraction Z, using REDIM.

5 CONCLUSIONS

In this work we have developed a reduced reaction mechanism for the ethanol, through the analysis of the specific velocity of each elementary reaction coming from a detailed chemical kinetic mechanism for high temperature ethanol oxidation. The hypothesis of partial equilibrium and steady-state, resulted in a system with 15 species and 18 elementary reactions. The 1D-REDIM technique helped us to obtain the solutions that describe the chemistry behavior of combustion of ethanol. Results show that the reduced reaction mechanism obtained using the 1D-REDIM technique produce good results.

6 ACKNOWLEDGMENTS

This research is being developed at UFRGS/Brazil. The first author gratefully acknowledges the financial support from CAPES, *Coordenação de Aperfeiçoamento de Pessoal de Nível Superior*, while Prof. De Bortoli acknowledges the financial support from CNPq, *Conselho Nacional de Desenvolvimento Científico e Tecnológico*, under process 303007/2009-5.

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