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Some Mathematical Techniques in Obtaining Reduced Kinetic Mechanisms

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1 Introduction

The modelling of chemical kinetics is an important tool for interpreting and understanding the combustion phenomena. Researches have developed detailed and reduced kinetic mechanisms for hydrocarbon and oxygenated fuels combustion. Since the use of detailed mechanisms may imply the solution of hundreds of conservation equations, it is convenient to use simplified kinetic mechanisms [1].

The most widely used strategy for mechanisms reduction of sample fuels is the steady state assumption (QSSA), which allows the elimination of some species and, consequently, the conversion of differential equations in algebraic equations. But such strategy can be applied in mechanisms with a limited number of species, so that is necessary to combine it with other approaches. Several techniques have been developed in recent years.

2 Lumping, DRG and Sensitivity Analysis in Mechanisms Reduction

A chemical kinetic problem can be written as the following ODE's system

$$\frac{d\mathbf{c}}{dt} = \mathbf{f}(\mathbf{c}, \mathbf{k}), \mathbf{c}(0) = \mathbf{c}^0 \tag{1}$$

where $\mathbf{c}$ is the concentrations vector and $\mathbf{k}$ is the vector where each component is the specific rate $k_i = AT^{\beta}e^{-Ea/RT}$ of reaction i, in which A is the frequency factor, T the temperature with its respective exponent β, Ea is the activation energy and R is the constant of ideal gas [1, 5]. Differentiating the above system with respect to k_j, one obtains

$$\frac{d}{dt}\frac{\partial \mathbf{c}}{\partial k_j} = \frac{\partial \mathbf{f}}{\partial \mathbf{c}} \cdot \frac{\partial \mathbf{c}}{\partial k_j} + \frac{\partial \mathbf{f}}{\partial k_j} = J(\mathbf{c}) \cdot \frac{\partial \mathbf{c}}{\partial k_j} + \frac{\partial \mathbf{f}}{\partial k_j} \tag{2}$$

where $J(\mathbf{c})$ is the Jacobian matrix associated with the system.

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In the lumping approach, species with similar composition, functionalities or evolutionary history, such as isomers, are grouped into representative lumped species, so the number of species is reduced [4]. In the exact lumping, developed by Li and Rabitz [2], one ODE's system, given by equation (1) is projected into a smaller system, i.e.,

$$\frac{d\mathbf{c}}{dt} = \mathbf{f}(\mathbf{c}) \Rightarrow \frac{d\hat{\mathbf{c}}}{dt} = M\frac{d\mathbf{c}}{dt} = M\mathbf{f}(\mathbf{c}) = \hat{\mathbf{f}}(\hat{\mathbf{c}}), \tag{3}$$

where the matrix M has rows given by the eigenvectors of a matrix associated with the Jacobian $J(\mathbf{c})$ and $\hat{\mathbf{c}} = M\mathbf{c}$.

The DRG method [3], is adequate for generating skeleton mechanisms from the detailed mechanisms. The approach consists in determining the coupling degree among species,

$$r_{AB} = \frac{\sum_{i=}^{n} |\nu_{A,i}\omega_i\delta_{B,i}|}{\sum_{i=}^{n} |\nu_{A,i}\omega_i|} \quad \text{where} \quad \delta_{B,i} = \begin{cases} 1, & \text{if the } i^{th} \text{ reaction involves species B.} \\ 0, & \text{otherwise.} \end{cases} \tag{4}$$

Here, $\nu_{A,i}$ is the stoichiometric coefficient of species A and ω_i is the rate of reaction i. Redundant species, i.e., with low index r_{AB} compared with the important species, can be eliminated.

The Sensitiviy Analysis investigates the response of a mathematical model due to changes of one or more parameters [1]. Taking into account the systems (1) and (2) the following normalized sensitivity matrix $\tilde{S}$ can be obtained

$$\tilde{S}_{ij} = \frac{k_j \partial c_i}{c_i \partial k_j} = \frac{\partial \ln c_i}{\partial \ln k_j} \tag{5}$$

in which each element represents the fractional change in concentrations c_i caused by parameter changes [5]. Due to higher computational cost of this technique, it is advised to apply it in smaller mechanisms than those which we apply DRG and lumping.

3 Conclusions

Each strategy of mechanisms reduction has its own advantages and drawbacks. To minimize the computational time needed in the CFD (Computational Fluid Dynamics) treatment of reactive flows, we can combine different techniques taking advantage of each one. The contribution of the present work goes in this direction.

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