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Development of a Reduced Kinetic Mechanism for Ethanol based on DRG and Sensitivity Analysis

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Abstract. Ethanol is a important fuel that can be produced with renewable energy resources. Based on a mechanism with 377 reactions and 56 species, we combine two methods for mechanism reduction, Directed Relation Graph (DRG) and Sensitivity Analysis, to develop a 34 reactions and 23 species reduced mechanism. DRG is a method that shows the coupling of species through a coefficient based on the reaction rate, while sensitivity analysis uses the eigenvalues and eigenvectors of the sensitivity matrix to provide an absolute measure of significance for some species of the mechanism. The main advantage of the mechanism reduction is the decrease of computational cost needed to solve the chemical equations, of one order of magnitude for ethanol.

Key-words. Ethanol, Reduced Mechanism, DRG, Sensitivity Analysis

1 Introduction

Combustion of fossils fuels still is the principal process used for conversion of energy. In the beginning of XXI century, about 90% of the energy used all over the world came from combustion. Economical and specially the environmental restrictions induce the search for new energy sources, such as ethanol.

Ethanol is a very important energy carrier that can be produced from renewable energy resources. In 2013, Brazil's fleet of cars was about 30 millions, of which about 50% can use ethanol as fuel in any fraction of mixture or even pure [2]. Although most ethanol is generated by sugar cane fermentation, recent developments suggest that it can be derived efficiently from other types of biomass [4].

Reactive flow simulations, such as combustion, depends on the existence of detailed kinetics mechanisms for fuels. However, detailed mechanisms can have hundreds of species and thousand of reactions, which induces a significant stiffness in the system of governing equations. Consequently, there is the need to develop reduced mechanisms with fewer variables and moderate stiffness, maintaining a good level of accuracy and comprehensiveness of the detailed kinetic mechanisms [3].

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In this work, using Directed Relation Graph (DRG) and Sensitivity Analysis, we developed a new reduced mechanism for ethanol, based on the detailed mechanism developed by Marinov [7].

2 Directed Relation Graph

Directed relation graph (DRG), introduced by Lu and Law in 2005 [5], is an efficient method for obtaining skeletal mechanisms. The aim of the method is to resolve the coupling of species efficiently, estimating an index, which indicates that the removal of a species B from the mechanism induces an error on the production of species A. This index, noted as r_{AB}, can be expressed by

$$r_{AB} = \frac{\sum_{i=1}^{n} |\nu_{A,i}\omega_i\delta_{B,i}|}{\sum_{i=1}^{n} |\nu_{A,i}\omega_i|} \tag{1}$$

where n is the number of reactions, $\nu_{A,i}$ is the stoichiometric coefficient of species A in the reaction i, ω_i is the reaction rate of reaction i and $\delta_{B,i}$ is given by

$$\delta_{B,i} = \begin{cases} 1, & \text{if the } i^{th} \text{ reaction involves species B;} \\ 0, & \text{otherwise.} \end{cases} \tag{2}$$

The terms in the denominator of equation (1) are the contributions of the reactions to the production rate of species A, and the terms in the numerator are those in the denominator that involve species B.

Defining a threshold value ϵ, and if the value of r_{AB} is bigger compared to it ($r_{AB} > \epsilon$), then the removal of species B can induce an error in the production of species A, so that species B must be retained in the skeletal mechanism. Usually, the A-species is chosen to be one of the targets, i.e., species that have some desirable chemical features that the reduced mechanism is expected to reproduce [9].

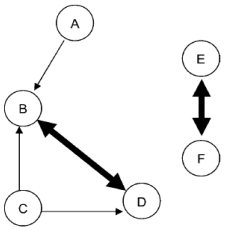

Figure 1: A DRG scheme [6].

The dependent set of each species can efficiently be identified with the directed relation graph, following three rules [6]:

1. Each vertex of the graph represents a species of the detailed mechanism;

2. There is an arrow from species A to species B if, and only if, $r_{AB} > \epsilon$;

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3. The beginning vertex of the graph represents the major species.

Figure (1) shows a typical DRG scheme. Note that the dependent set of species A is formed by species B and D, since B must be retained to form A, and D must be retained to form B. Species C can, thus, be eliminated, as well as species E and F, that are strongly coupled, but are not required by A or its dependent set.

To improve the performance of the method, graph search algorithms, such as the Depth First Search (DFS) can be used for efficiently finding all the vertices reachable from the starting vertex. In many cases, it is sufficient begin with only one species, such as the fuel.

3 Sensitivity Analysis

The term sensitivity analysis defines a collection of mathematical methods that can be used to explore the relationships between the values of the input parameters of a mathematical model and its solutions [12]. Sensitivity analysis can be used for mechanism reduction, help us to better understand the chemical processes and to identify those pathways which determine key model output or production distribution.

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

$$\frac{d\mathbf{c}}{dt} = \mathbf{f}(\mathbf{c}, \mathbf{k}), \quad \mathbf{c}(0) = \mathbf{c}^0 \tag{3}$$

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 [3,12]. The right hand side of the ODE equation (3) can be obtained from the rate of reaction

$$f_i(\mathbf{c}, \mathbf{k}) = \sum_{j=1}^{n} \nu_{ij} R_j, \tag{4}$$

where f_i is the rate of production of species i, R_j is the rate of reaction j and ν_{ij} is the stoichiometric coefficient of the i^{th} species in the j^{th} reaction. Differentiating the above system with respect to the parameters k_j, results

$$\frac{d}{dt}\frac{\partial \mathbf{c}}{\partial k_j} = \frac{\partial \mathbf{f}}{\partial \mathbf{c}} \cdot \frac{\partial \mathbf{c}}{\partial k_j} + \frac{\partial \mathbf{f}}{\partial k_j} = \mathbf{J} \cdot \mathbf{S} + \mathbf{F}, \tag{5}$$

with initial condition $\dfrac{\partial \mathbf{c}}{\partial \mathbf{k}}(0) = 0$. Here $\mathbf{J}$ is the Jacobian matrix associated with the system, $\mathbf{S}$ is the sensitivity matrix and $\mathbf{F}$ is the rate sensitivity matrix. Since the parameters and the various output quantities of a model may have different units, a normalized sensitivity matrix $\tilde{\mathbf{S}}$ is defined

$$\tilde{\mathbf{S}} = \left(\frac{k_j}{c_i}\frac{\partial c_i}{\partial k_j}\right) = \left(\frac{\partial \ln c_i}{\partial \ln k_j}\right), \tag{6}$$

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and represents the fractional change in concentration c_i caused by a fractional change of parameter k_j [11].

Among various sensitivity analysis methods, the Principal Component Analysis (PCA) is based on the analysis of eigenvalues and eigenvectors of the sensitivity matrix. Eigenvalues will be shown to provide an absolute measure of significance for some part of the mechanism, providing a criterion for selecting a minimal reaction set [13], while eigenvectors reveal the related parameters [11].

In order to apply PCA, the matrix $\mathbf{S}$ is transformed to the symmetric square matrix $\mathbf{S}^T\mathbf{S}$, whose number of rows and columns are equal to the number of reactions in the detailed mechanism. Then the eigenvalues and eigenvectors are calculated and the groups of reactions that contribute the most to these eigenvectors are determined and referred to as principal components. The largest eigenvalues correspond to the principal components which are the most relevant to the description of selected important species.

Principal component analysis should be preferred to other methods because identifies groups of reactions that can be eliminated. Sometimes, the elimination of reactions one by one may cause significant errors in the solution, while eliminations of reaction pairs causes no significant consequences [10].

4 Reduced Kinetic Mechanism for Ethanol

The high computational cost of sensitivity analysis methods shows that it may be interesting to apply it on a smaller mechanism than the detailed. Coupling the two methods, DRG and sensitivity analysis, one can produce a better result with a time that is proportional to the number of reactions. In the DRGASA, i.e., directed relation graph aided sensitivity analysis, the DRG procedure is improved by identifying those species whose elimination cause only minor increase of the simulation error of the important species [8].

The detailed mechanism adopted for ethanol (C_2H_5OH) [7] consists of 377 reactions and 56 species. First, the DRG method was applied, to find the redundant species and eliminate them. The graphs of Figure (2) show the decrease of number of species and reactions as the threshold ϵ tends to unity.

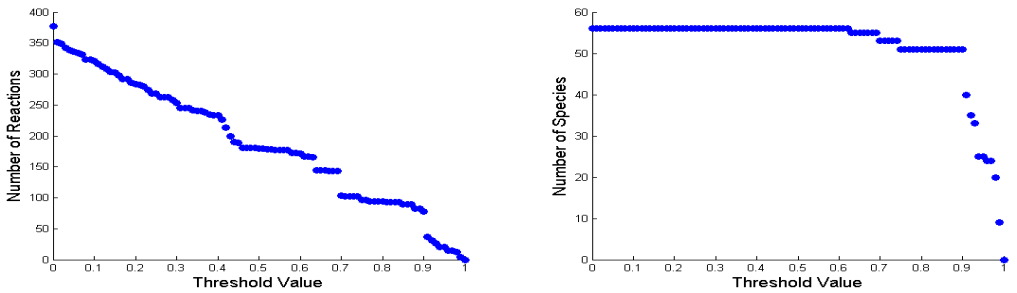

Figure 2: Dependence of number of reactions and species as a function of the threshold value ϵ.

The number of species only begins to decay considerably for $\epsilon > 0.63$. This happens

because, in DRG method, all species have the same level of importance.

Table 1: Reduced mechanism for Ethanol (units are mols for the reactions, seconds for the frequency factor A, Kelvin for the temperature exponent β and cal/mol for the activation energy E)

	Reaction	A	β	E
1	$C_2H_5OH = CH_2OH + CH_3$	$0.59E+24$	-1.680	91163.
2	$C_2H_5OH = C_2H_4 + H_2O$	$0.28E+14$	0.090	66136.
3	$C_2H_5OH = CH_3HCO + H_2$	$0.72E+12$	0.090	91007.
4	$CO + O = CO_2$	$0.62E+15$	0.000	3000.
5	$CH_3HCO + H = CH_2HCO + H_2$	$0.19E+13$	0.400	5359.
6	$CH_3HCO + HO_2 = CH_2HCO + H_2O_2$	$0.23E+12$	0.400	14864.
7	$CH_2HCO + H = CH_3 + HCO$	$0.50E+14$	0.000	0.
8	$C_2H_4 + OH = C_2H_3 + H_2O$	$0.20E+14$	0.000	5936.
9	$C_2H_4 = C_2H_2 + H_2$	$0.18E+15$	0.000	87000.
10	$C_2H_3 + H = C_2H_2 + H_2$	$0.90E+14$	0.000	0.
11	$C_2H_3 + O_2 = CH_2O + HCO$	$0.17E+30$	-5.310	6500.
12	$C_2H_3 + OH = C_2H_2 + H_2O$	$0.20E+14$	0.000	0.
13	$C_2H_2 + OH = C_2H + H_2O$	$0.34E+08$	2.000	14000.
14	$C_2H_2 + OH = CH_3 + CO$	$0.48E-03$	4.000	$-2000.$
15	$C_2H + O = CH + CO$	$0.50E+14$	0.000	0.
16	$CH_3 + OH = CH_2 + H_2O$	$0.20E+14$	0.000	550.
17	$CH_3 = CH + H_2$	$0.69E+15$	0.000	82469.
18	$CH_2 + H = CH + H_2$	$0.10E+19$	-1.560	0.
19	$CH_2 + OH = CH_2O + H$	$0.30E+14$	0.000	0.
20	$HCO + OH = H_2O + CO$	$0.10E+15$	0.000	0.
21	$CO + O_2 = CO_2$	$0.25E+13$	0.000	47688.
22	$CH_2OH + H = CH_2O + H_2$	$0.20E+14$	0.000	0.
23	$CH_2OH + O_2 = CH_2O + HO_2$	$0.16E+16$	-1.000	0.
24	$CH + O_2 = HCO + O$	$0.33E+14$	0.000	0.
25	$CH + OH = HCO + H$	$0.30E+14$	0.000	0.
26	$CH_2O + OH = HCO + H_2O$	$7.43E+08$	1.180	0.
27	$HCO + O_2 = CO + HO_2$	$2.71E+10$	1.180	$-469.$
28	$H_2O_2 + M = OH + OH + M$	$3.14E+19$	-1.370	51860.
29	$HO_2 + HO_2 = H_2O_2 + O_2$	$5.94E+17$	-0.660	53150.
30	$H_2 + OH = H_2O + H$	$2.16E+08$	1.510	83430.
31	$OH + HO_2 = H_2O + O_2$	$2.89E+13$	0.000	$-500.$
32	$H + O_2 + M = HO_2 + M$	$1.48E+12$	0.600	0.
33	$H + H_2O = OH + H_2$	$9.35E+08$	1.510	10580.
34	$O + H_2 = OH + H$	$5.08E+04$	2.670	96292.

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The DRG reduction was performed with $\epsilon = 0.87$ and after, sensitivity analysis was applied and the 34 reactions among 23 species reduced mechanism from Table (1) was obtained. This mechanism was compared with a reduced mechanism developed for ethanol using asymptotic analysis and partial equilibrium hypotheses [1, 2] and proved to be efficient, i.e., the path of combustion from the fuel to the formation of water and carbon dioxide was well defined. The comparison criteria was the final concentrations of the principal products (H_2O, H_2, CO_2, CO) for the reduced mechanisms.

5 Conclusions

The present work couples two methods for mechanism reduction. While in the DRG all species have the same level of importance, which can be a drawback of this simple and easy to apply method, sensitivity analysis has higher computational cost. Combining these two methods, better results appears. The DRG procedure identify those species whose elimination cause only minor increase of the simulation error of the important species.

To minimize computational cost in combustion simulations and the work needed to solve the system of chemical equations, DRG and sensitivity analysis methods were combined to produce a 34 reactions and 23 species mechanism for ethanol. Such corresponds to the principal contribution of the present work.

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