Systematic simplification of chemical kinetic mechanisms with DRG and CSP methods

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Abstract

The algorithm of directed relation graph (DRG) recently developed for skeletal mechanism reduction is extended to overall linear time operation, thereby greatly facilitating the computational effort in mechanism reduction, particularly for those involving large mechanisms. This algorithm is applied to a spatially homogeneous constant-pressure autoignition of methane combustion and result are compared with CSP method. It is observed that   the accuracy of skeletal mechanisms is equivalently bounded by the user-specified error threshold value. DRG method because of directly eliminate unimportant species instead of elementary reactions, computationaly is more efficient.

keywords: Directed relation graph; computational singular perturbation; skeletal mechanism

1. Introduction

Detailed chemical kinetic for hydrocarbon oxidation consist of hundreds species and thousands elementary reactions. The large typical sizes of detailed mechanisms frequently result in high demand for computation time, therefore we need to reduce the mechanisms to acceptable sizes before they applied in large combustion simulations, such as those involving turbulence or complex geometries. Consequently, substantial effort has been devoted toward the development of theoretical and numerical methodologies for systematic mechanism reduction.

Two main classes of methods aim at alleviating the CPU time and memory overhead required to solve reactive flows with detailed kinetics; namely model simplification and model reduction. The first trims unimportant species and reactions from the detailed mechanism, the other method produces a small number of global steps, whose rates are computed on the basis of the elementary rates. The latter approach, usually referred as the time scale analysis. This method is basis on the observation that there are frequently highly reactive radicals or fast reactions in detailed chemistry, resulting in vastly different time scales and stiffness in the system, and making the system reducible by replacing some differential equations with algebraic relations through the assumptions of quasi-steady-state (QSS) species and partial equilibrium (PE) reactions.

Model reduction can be achieved by a number of different mathematical methods. An extensive survey, of particular relevance for hydrocarbon oxidation, may be found, for example, in [1,2]. One of the earliest methods is sensitivity analysis (SA) [3]. However, SA does not directly provide decoupled information about the reactions and species, and further post processing is required. The method of principal component analysis (PCA) [4], based on SA, operate on sensitivity matrices and systematically identifies the redundant reactions.

The same task is also achieved by a different class of methods that are based on the observation that, due to the wide range of chemical time scales appearing in a typical combustion system, a low-dimensional manifold develops in the species space, which possesses the properties of being invariant and exponentially attractive for the trajectory flow of the kinetic system. Reduction method belonging to this class are the techniques based on the quasi-steady-state-assumption (QSSA) [5,6], the Fraser and Roussel method [7,8], the computational singular perturbation (CSP) [9,10], the rate-controlled constrained equilibrium (RCCE) method [11], the intrinsic low-dimensional manifold (ILDM) approach [12] and the method of integral manifold (MIM) [13]. These reduction approaches are distinguished from each other by their strategies of approximating or directly evaluating the slow invariant manifold, where higher accuracy can be found by adopting the iterative methods FR and CSP.

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Most of these methods label the species in the detailed mechanism either as major (or slow) or minor (fast); the latter are computed from strongly nonlinear algebraic equations, needed for the evaluation of the former via the reduced kinetics model. The computational cost of solving these equations on line increases as the number of minor species grows, thus eliminating to a large extent the benefits expected from the use of the reduced model.

From the discussion above, it is clear that there exists a strong motivation to filter out from a given large detailed mechanism the portion of information deemed not absolutely relevant to the description of the problem of interest, i.e., to construct a simplified kinetic model.

Model simplification aims at modifying the detailed kinetics by trimming (i) the species whose kinetics are not tightly coupled with those of interest and (ii) the reactions judged unimportant to the retained species. The outcome of this procedure is a smaller kinetic mechanism, which is a subset of the detailed mechanism. By construction, this "skeletal" mechanism is supposed to be accurate only with respect to the species declared of interest and when it is used inside its domain of applicability. This domain is defined on the basis of (i) the specific reference problems (ignition, flames, PSR, plug flow reactor, etc.) and (ii) the specific range of pressure, initial temperature, and equivalence ratio within which the reference problems have been investigated in order to construct the database of CSP inputs for the procedure of generation of the skeletal mechanism.

The decision about which reactions can be removed from a detailed mechanism without altering the number of species can be taken by using optimization approaches, such as integer programming (IP), aimed at obtaining an optimal set of reactions for given constraints as done in the adaptive kinetics (AK) concept developed in [14], or as done in [15], where reactions are declared unimportant if their rates are smaller than a prescribed value.

However, the computational cost of a calculation involving detailed kinetics typically scales linearly with the number of reactions, and quadratically with the number of species. Therefore, the largest CPU cost savings in reactive flow simulations are obtained by reducing the number of species retained in the skeletal mechanism; this is especially so because removing species not only alleviates the cost of calculating the source term of kinetic nature, but also cuts the cost of evaluating the transport terms in the reactive flow equations. As a consequence, it is critical to achieve the correct identification of the species that do not play an important role in the reactive flow and their removal from the pertinent kinetic mechanism, together with all the reactions solely involving the removed species.

Most of the techniques aimed at reducing the number of species present in a skeletal mechanism follow a similar procedure. The selection process of the species to be retained in the skeletal mechanism starts with a set of target species deemed of interest to the investigator. Next, some nondimensional measure quantifying the interactions existing between species is introduced, the definition of this measure being the feature distinguishing the different techniques. Finally, species strongly interacting, with respect to the chosen measure and a user-defined threshold, with the target species are recursively included in the set of important species. The recursion stops when no more species need to be added to this set.

M. Valorani et al. [16], introduced a new skeletal reduction algorithm, according to which the criterion for selecting the subset of reactions and species to be retained is based on their relevance to the fast or slow dynamics of a prescribed set of "kernel" species, the concentration of which is desired to be accurately reproduced by the skeletal mechanism. Given that the dynamics of chemical kinetic systems exhibit a wide range of time scales, the rationale for constructing skeletal mechanisms is grounded in the decomposition of the system dynamics into distinct fast and slow dynamics; the fast dynamics constraining the system evolution within a low-dimensional manifold, and the slow dynamics driving the system along the manifold. The algorithm guarantees that both the fast and slow dynamics of the kernel species are accurately reproduced by the skeletal mechanism. This algorithm is based on the ability to decompose the chemical kinetic processes into fast and slow components, as offered by the computational singular perturbation (CSP) method [17], and to identify the processes that produce the most significant contribution in either the fast or slow components.

Lu and Law [18] used a species selection procedure similar to the one proposed by Bendtsen et al. [19] to automatically generate skeletal mechanisms. The identification of the set of important species is carried out by constructing a directed relation graph (DRG), whose nodes are the species to be included in the skeletal mechanism. The DRG connects the target species with all the species having a strong interaction with them. As a measure of the degree of interaction Lu and Law resort to a matrix of normalized interaction coefficients r_{ij}, Species are added to the DRG when the corresponding entry of the reaction matrix is above a user-defined tolerance ε. Note that the same value of ε, when applied to different mechanisms, will return different species reduction ratios and accuracies.

In the present study the method of directed relation graph (DRG) has been applied to detailed mechanism of methane, GRI-Mech. 3.0, for a spatially homogeneous, isobaric, adiabatic, N dimensional, autoignition problem to identify unimportant species by resolving species coupling with high efficiency and minimal requirement of systemdependent knowledge. In addition, DRG is compared with the CSP-based method in [16].

2. DRG theoretical background

DRG is designed to reduce large detailed mechanisms with high efficiency. More specifically, species couplings are mapped to a graph and strongly coupled species are identified by linear-time graph searching. Since species are coupled through reactions, the definition of species relations in DRG starts from the rate expressions of the species and reactions in a detailed mechanism. For example, the production rate RA of species A in a mechanism with I reversible elementary reactions is expressed as

$$k_{fi} = \left[A_i T^{n_i} \exp\left(-\frac{T_{ai}}{T}\right) \right] F_i \tag{1}$$

$$k_{ri} = \frac{k_{fi}}{K_{ci}} \tag{2}$$

$$q_i = \left(\sum_{k=1}^{K} (a_{ki})[X_k] \right)\left(k_{fi} \prod_{k=1}^{K} [X_k]^{\upsilon'_{ki}} - k_{ri} \prod_{k=1}^{K} [X_k]^{\upsilon''_{ki}} \right) \tag{3}$$

$$R_A = \sum_{i=1,I} \nu_{A,i} q_i \tag{4}$$

where the subscripts i and j indicate the ith elementary reaction and the j th species, respectively, and the subscripts f and r denote forward and backward directions of a reaction, respectively. Furthermore, $R_A = \sum_{i=1,I} \nu_{A,i} q_i$ is the net stoichiometric coefficient of species A, ν' and ν'' are the stoichiometric coefficients for the reactants and products, respectively, C the species molar concentration, A, n, and T_a are the reaction parameters, and F is a correction term including the third body concentration, fall-off, and other special effects, T the temperature, and K_c the equilibrium constant.

To quantify the relation of one species to another, the normalized contribution of species B to the production rate of species A, namely r_{AB}, was defined as follows:

$$r_{AB} = \frac{\sum_{i=1,I} \left| \nu_{A,i} q_i \delta_{Bi} \right|}{\sum_{i=1,I} \left| \nu_{A,i} q_i \right|} \tag{5}$$

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

The dependent set of a major species can be identified efficiently by mapping the species coupling to a directed relation graph, which can be constructed using the following rules:

(1) Each vertex in DRG is uniquely mapped to a species in the detailed mechanism.

(2) There exists a directed edge A → B if and only if $r_{AB} \geq \varepsilon$.

(3) The starting vertices of DRG correspond to the major species in the mechanism.

A sample configuration of DRG is shown in Fig. 1, in which vertices A, B, . . . , F correspond to the respective species, and each directed edge indicates an immediate requirement of one species of another.
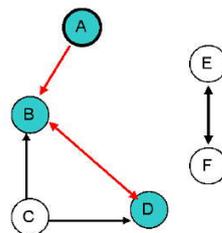

Fig. 1. Schematics showing typical configuration of the directed relation graph (DRG); the vertices correspond to the species and the directed edges correspond to the immediate requirement of one species to another.

The starting vertex A, enclosed in a bold circle, is a major species in the mechanism. The skeletal species in Fig. 1 correspond to all the vertices reachable from the starting vertex. Graph searching methods such as depth first search (DFS) can thus be exploited to efficiently find all the vertices reachable from the starting one.

Species A, B, and D are therefore identified as the species of the skeletal mechanism in the current example. The global algorithm of DRG method in order to construction skeletal mechanism consist of 3 main steps

1- Graph construction

2- Graph searching

3- Create skeletal mechanism

In the step 3 those species that are marked with values smaller than ε are eliminated from the mechanism and those elementary reactions that involving eliminated species are removed from the mechanism. Retain species and elementary reactions are involved in skeletal mechanism.

3. CSP theoretical background

The Computational Singular Perturbation (CSP) method [20] was first developed for the solution and analysis of stiff ODEs and later extended for the treatment of stiff PDEs when the stiffness is produced by a source term. So far the method has been applied to a number of combustion problems involving stirred reactors, laminar flames, and shock induced combustion. Here an overview of the method will be presented in order to point out the parts of the method that are incorporated in the algorithm for the construction of skeletal mechanisms. In this study, CSP is especially devoted to the analysis of spatially homogeneous, N-dimensional, autonomous systems governed by stiff ODEs,

$$\frac{d\mathbf{u}}{dt} = \mathbf{g}(\mathbf{u}) \tag{6}$$

$$\frac{d\mathbf{u}}{dt} = \mathbf{S}_1 R^1 + \mathbf{S}_2 R^2 + ... + \mathbf{S}_{N_P} R^{N_P} = S\mathbf{R} \tag{7}$$

where $\mathbf{u}$ is the N-dimensional vector ($N = N_s + 1$) of unknowns $(Y_1, . . . , Y^{Ns}, T)^T$, with Y_i being the ith species mass fraction, T the temperature, and $N_p = 2N_r$ is the total number of chemical processes comprising forward and backward reactions, N_r being the total number of reversible elementary reactions. Further, the stoichiometric vectors $\mathbf{S}_1$ to $\mathbf{S}_{N_p}$ define the $(N \times N_p)$-dimensional generalized stoichiometric matrix S as

$$S = [\mathbf{S}_1,...,\mathbf{S}_{N_P}] = Q[\dot{\mathbf{S}}_1,...\dot{\mathbf{S}}_{N_r}, \dot{\mathbf{S}}_1,...,\dot{\mathbf{S}}_{N_r}] = Q[\dot{S},\dot{S}] \tag{8}$$

where is the $(N_s \times N_r)$ matrix of stoichiometric coefficients whose entry $\dot{S}_k^{\,i} = \Delta\nu_{ik}$ is the net stoichiometric coefficient of species i in reaction k. The $(N \times N_s)$ matrix Q in Eq. (8) takes different expressions for different definitions of the generalized state vector $\mathbf{u}$.

The rates R^1 to $R^{Np} = R^{2Nr}$ in Eq. (7) define the generalized (N_p)-dimensional vector $\mathbf{R} = \{R^k\}_{k=1}^{N_P}$ as

$$\mathbf{R} = [r_{f,1},...,r_{f,N_r}, -r_{b,1},...,-r_{b,N_r}] \tag{9}$$

where r_f and r_b are the third-body and pressure-falloff corrected (if applicable) forward and reverse elementary rates of progress of the N_r reversible reactions. At each point in time and space the CSP method provides two sets of N-dimensional column basis vectors $\mathbf{a}_i$, which define the fast and slow subdomains of $\mathbf{u}$:

$$a_r = [a_1, a_2,...,a_M] \tag{10}$$
$$a_s = [a_{M+1}, a_{M+2},...,a_N]$$

where M is the number of time scales, which are faster than the locally dominant ones and varies from 0 to N-1. On the basis of these vectors, Eq. (6) can be cast in the form:

$$\frac{d\mathbf{u}}{dt} = \sum_{r=1}^{M} \mathbf{a}_r \mathbf{h}^r + \sum_{s=M+1}^{N-N_c} \mathbf{a}_s \mathbf{h}^s = \mathbf{g}_{fast} + \mathbf{g}_{slow} \tag{11}$$

where

$$\mathbf{h}^r = \mathbf{b}^r \mathbf{g}$$
$$\mathbf{h}^s = \mathbf{b}^s \mathbf{g}$$

and the N row vectors in $\mathbf{b}^r$ and $\mathbf{b}^s$ form the dual basis. The CSP vectors were approximated by their leading order expressions, i.e., by the local eigenbasis of the Jacobian of $\mathbf{g(u)}$. When the M fastest modes are declared exhausted, the *M* nonlinear algebraic equations

$$\mathbf{h}^r = \mathbf{b}^r \mathbf{g} \approx 0 \qquad r = 1,...,M \qquad\qquad (12)$$

In CSP terms, therefore, the solution of Eq. (6) is constrained to lie close to the slow manifold and its slow evolution is governed by the nonstiff simplified system obtained by enforcing Eq. (12) in Eq. (11),

$$\frac{d\mathbf{u}}{dt} \approx a_{M+1}h^{M+1} + ... + a_{N-N_c}h^{N-N_c} = \mathbf{g}_{slow} \qquad\qquad (13)$$

The CSP fast/slow decomposition prompts the introduction of a "slow" importance index $(I_k^i)_{slow}$ assessing the relative influence of a given reaction *k* in the production/consumption of a given species *i* in the context of its slow evolution on the manifold. In addition, it prompts the introduction of a "fast" importance index $(I_k^i)_{fast}$ assessing the relative influence of the *k*th reaction on the *M* species affected most by the *M* fastest time scales. The slow and fast importance indices can be defined, respectively, as

$$(I_k^i)_{slow} = \frac{\displaystyle\sum_{s=M+1}^{N-N_c} a_s^i (b^s S_k) R^k}{\displaystyle\sum_{j=1}^{N_p} \left| \sum_{s=M+1}^{N-N_c} a_s^i (b^s S_j) R^j \right|} \qquad\qquad (14)$$

$$(I_k^i)_{fast} = \frac{\displaystyle\sum_{r=1}^{M} a_r^i (b^r S_k) R^k}{\displaystyle\sum_{j=1}^{N_p} \left| \sum_{r=1}^{M} a_r^i (b^r S_j) R^j \right|} \qquad\qquad (15)$$

The method for the simplification of the kinetic mechanism is the elimination of all the reactions whose importance indices, $(I_k^i)_{slow}$ and $(I_k^i)_{fast}$, relative to a specific set of species S_0 are both smaller than a prescribed user-specified tolerance. In the present study, the simplification of GRI-Mech 3.0 kinetics is obtained by selecting both methane and nitric oxide as kernel species (S_0 = [CH4,NO]), as they respectively represent a major reactant and product.

4. Skeletal mechanisms for autoignition of methane

Methane is an important reference fuel, and the best detailed mechanism for its oxidation is GRI-Mech. 3.0 [21]. This mechanism contains 53 species and 325 elementary reactions. The process of ignition CH4/air mixtures is computed with using a homogenous closed reactor model at constant enthalpy and pressure of 1 atm. The initial temperature 1000 k and equivalence ratio of Φ=1. The temporal change of species mass fraction, Y_i, and temporal change of temperature is calculated from:

$$\frac{dY_k}{dt} = \dot{\omega}_k \frac{W_K}{\rho} \qquad\qquad (16)$$

$$\frac{dT}{dt} = -\frac{1}{\rho \bar{C}_p} \sum_{k=1}^{K} H_K \dot{\omega}_k$$

Thermodynamic and kinetic parameters are computed with an in-house code. Also the DVODE code is used in order to solve the stiff governing equations to find molar concentration and temporal change of temperature. These values are used in order to find production rate of each species and consequently determination of r_{AB} for each pair of species. If we have k species, we should find $k^2 - k$ values for r_{AB}. The kernel species or starting

vertices is S_0=[CH4,NO]. After using DRG and CSP method we have local skeletal mechanisms in each time step that union of species in each step help us to construct global skeletal mechanism.

Figure 2 shows the percentage of active species and reactions versus threshold value in DRG method. This figure shows that with increasing the threshold value the number of active species and elementary reactions in the skeletal mechanism decrease. Note that mechanism simplification is achieved when the number of active species is lower than 53, i.e., for tol $>10^{-7}$. Figure 3 shows the same result but for CSP method. In this method for tol$>10^{-2}$ we have simplified mechanisms.
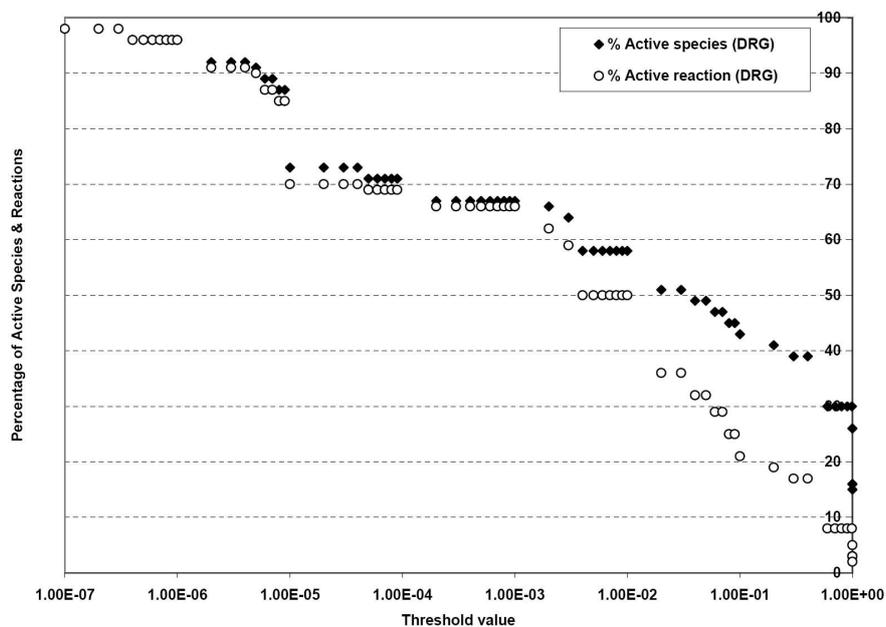
Fig. 2. Percentage of active species and reactions as a function of threshold value ε in DRG method for S_0=[CH4,NO] as kernel species
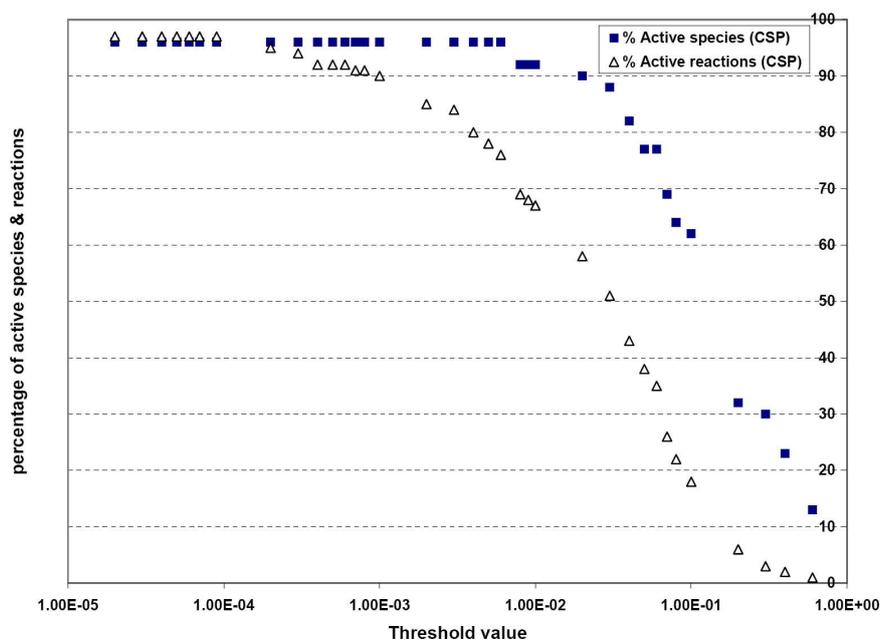

Fig. 3. Percentage of active species and reactions as a function of threshold value ε in CSPmethod for S_0=[CH4,NO] as kernel species

Figure 4 and 5 shows the dependence percentage of active reactions to percentage of active species for DRG and CSP methods. According to figures we can see that dependency of active reactions and species in DRG method is more linearly as compared with CSP method.
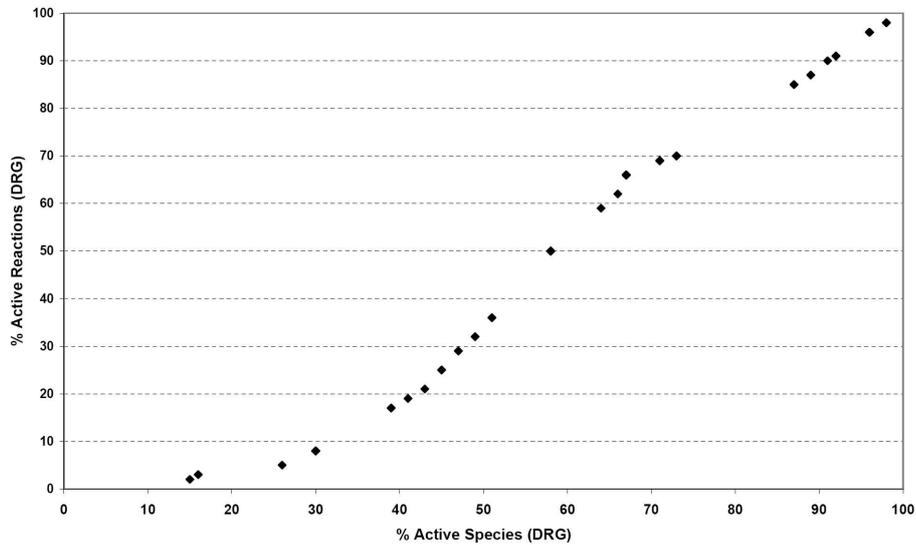

Fig. 4. dependence of active reactions on percentage of active species in DRG method for S_0=[CH4,NO] as kernel species
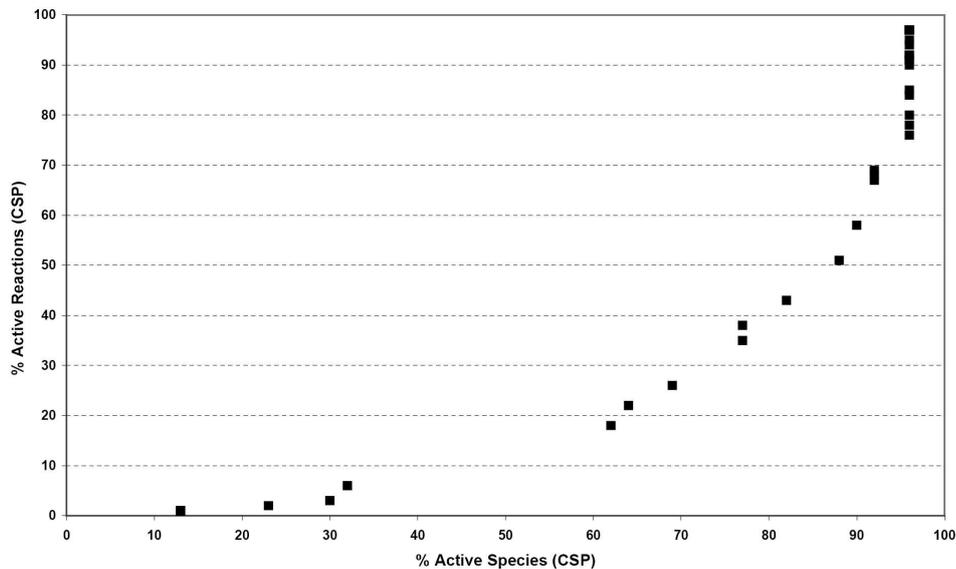

Fig. 5. dependence of active reactions on percentage of active species in CSPmethod for S_0=[CH4,NO] as kernel species

Figure 6 shows the percentage of active elementary reactions based on threshold value for both DRG and CSP method. Note that this comparison is for the same threshold value in both them. According to figure for the most threshold values the number of active elementary reactions in DRG method is less than CSP.
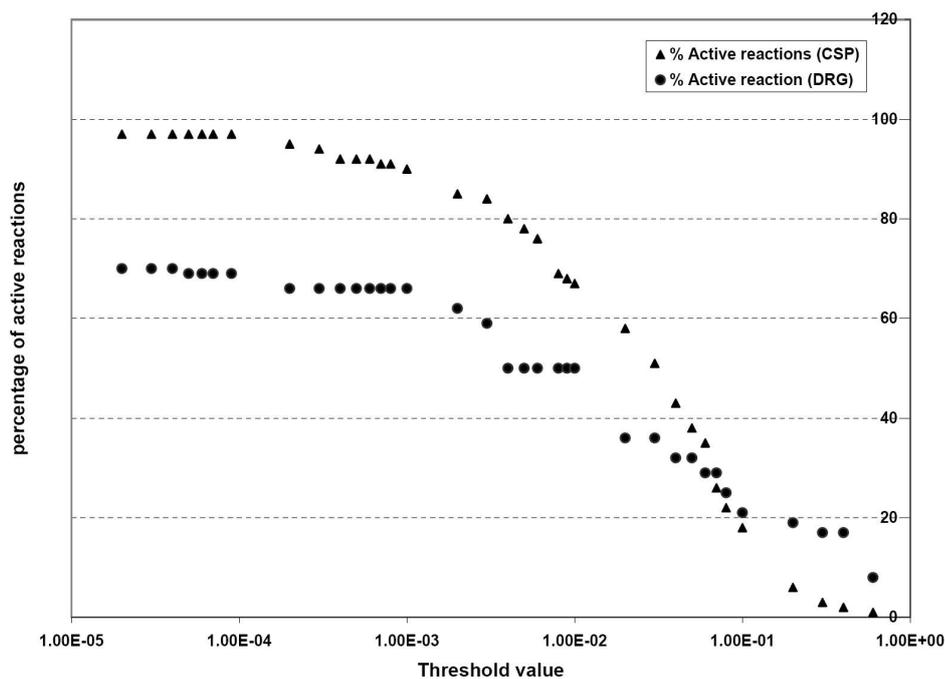
Fig. 6. Comparison of Percentage of active reactions as a function of threshold value ε in CSP and DRG method for S_0=[CH4,NO] as kernel species

Figure 7 shows the percentage of active species based on threshold value for both DRG and CSP method. Note that this comparison is for the same threshold value in both them. According to figure for the most threshold values the number of active species in DRG method is less than CSP.
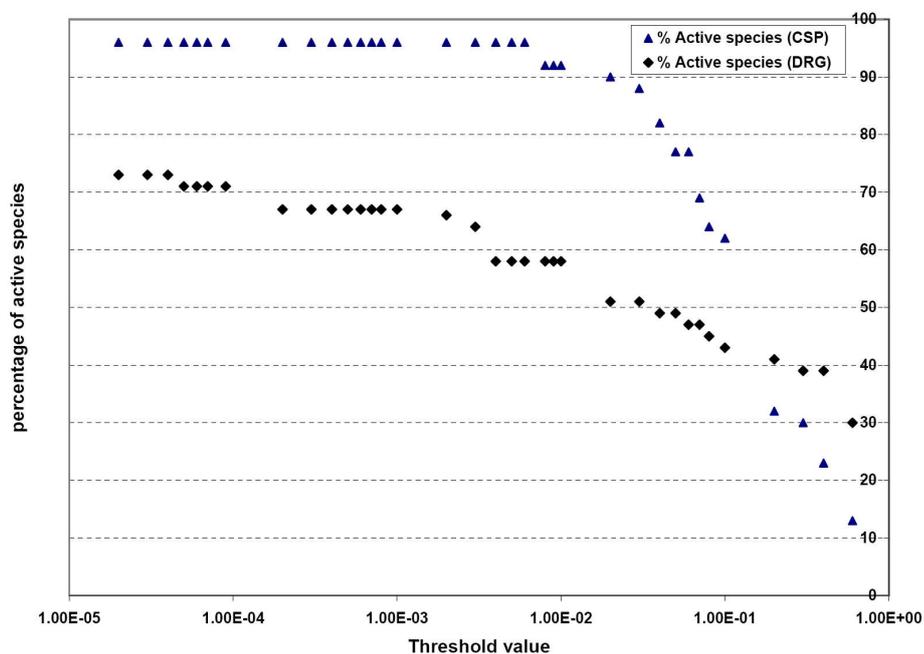

Fig.7. Comparison of Percentage of active species as a function of threshold value ε in CSP and DRG method for S_0=[CH4,NO] as kernel species

5. Conclusion

A DRG-based kinetic mechanism simplification algorithm is introduced. The algorithm uses a DRG database, constructed on the basis of a detailed solution, to make a decision about which species are deemed unimportant with respect to a user-specified kernel set of species. The degree of simplification is also user-

specified through a threshold value. The simplified mechanisms are tested for a spatially homogeneous constant-pressure autoignition of methane combustion. Model reduction is achieved when species deemed unimportant with respect to the species in the specified kernel are eliminated, along with the reactions involving them. The analysis of the simplified mechanisms offers a valuable diagnostic tool capable of providing insight on the analysis of reactive flows. The result is also compared with CSP method that in contrast with DRG method is based on eliminating unimportant elementary reactions. The usefulness of the present reduction algorithm and strategy clearly increases rapidly with increasing mechanism size. Indeed, this is probably the only approach that can expeditiously and automatically generate skeletal mechanisms from extremely large detailed mechanisms. We emphasize that the high efficiency of the present linear time algorithm, which is responsible for the extremely short time in mechanism generation.

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