Original Contribution

KINETICS MODELING FOR METHANE/AIR AUTOIGNITION: COMPARISON BETWEEN DRG & CSP METHODS

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ABSTRACT
Detailed chemical kinetic models coupled with transport process models require tremendous computational resources in numerical simulation of reactive flows. In order to reduce the computational cost in numerical simulations, skeletal and reduced chemical kinetics mechanisms are used instead of detailed chemical kinetics mechanism. The Directed Relation Graph (DRG) method is applied to GRI-3 kinetics mechanism for a spatially homogeneous constant-pressure model of methane/air autoignition at 1 atm pressure, 1000 k initial temperature and equivalence ratio of 1. The algorithm is used to identify species which their presence has little effect on the final results. These species are referred to as unimportant. The elementary reactions containing the unimportant species are eliminated from kinetics mechanism. The DRG simulation results are compared and validated by detailed chemical kinetics results. Also the results are compared with Computational Singular Perturbation method (CSP) which identifies unimportant elementary reactions. DRG method proved to be computationally more efficient, since it eliminates unimportant species instead of elementary reactions from the full mechanism as in CSP.

Key words: Directed Relation Graph; Computational Singular Perturbation; Chemical Kinetics Mechanism; Autoignition; Methane

INTRODUCTION
Application of chemical kinetics mechanisms in combustion simulations of chemically reactive flows and multi-zone models of combustion chambers are widely developed. Such numerical simulations require the accurate prediction of chemical features like heat release, ignition time, consumption and production of main reactants and products or pollutant formation. The detailed chemical kinetics mechanisms of hydrocarbon fuels are usually designed to model accurately fuel oxidation over a large range of temperature and pressure and can include thousands of elementary reactions and hundreds of species.

This large number of species and elementary reactions prohibits the direct implementation of detailed chemical kinetic mechanisms in reactive

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flow numerical simulations. Large system of governing equations and high computational effort in order to solve them is one of the main challenges for numerical simulations. The numerical simulations are further complicated by the existence of stiff governing equations.

Stiffness of governing equations is due to differences in the time scales of species production and consumption. Therefore, it is necessary to develop reduced mechanism with fewer species and elementary reactions, and with moderate stiffness while maintaining the required accuracy and comprehensiveness. There are two approaches to reduce the size of chemical kinetic mechanisms (1). The first approach is time scale analysis methods. In these methods, the main objective is to reduce the stiffness of the governing equations. The kinetic mechanism can further be simplified by identification of elementary reactions with least effect on the final results. These elementary

reactions are referred to as unimportant elementary reactions. Elimination of unimportant elementary reactions leads to the simplified mechanism (2). This method is based on the observation that frequently highly reactive radicals or fast reactions in detailed chemistry result in vastly different time scales and stiffness in the system (2). Some of the differential equations in the governing equations are replaced by algebraic relations through the quasi steady-state (QSS) species assumptions and partial equilibrium (PE) reactions to reduce the stiffness.

Computational Singular Perturbation (CSP) is one of the methods used to reduce stiffness and simplify the chemical kinetics. This method produces a small number of global steps whose rates are computed on the basis of the elementary reactions rates.

Another approach to simplify kinetics mechanisms is skeletal reduction. In these methods, only the size of kinetic mechanism decreases. One of the earliest methods is sensitivity analysis (3). Sensitivity analysis does not directly provide decoupled information about the reactions and species. Further post processing is required. The method of principal component analysis based on sensitivity analysis, operates on sensitivity matrices and systematically identifies the redundant reactions (3). The optimization methods such as integer programming, aim at obtaining an optimal set of reactions where reactions are declared unimportant, if their rates are smaller than a prescribed value.

M. Valorani et al. (2) proposed a simplification algorithm to construct skeletal mechanisms based on CSP method for autoignition of methane. This method is based on identification and elimination of unimportant elementary reactions. When the kinetic mechanism is large, these methods are time consuming. Methods which can identify and eliminate unimportant species instead of elementary reactions are more efficient. Lu and Law (3, 4) used a species selection process to automatically generate skeletal mechanisms. The identification of the important species set was carried out by constructing a Directed Relation Graph (DRG)

with nodes as the species to be included in the skeletal mechanisms.

In the present study, DRG method which is described in the next sections, has been applied to the detailed kinetics mechanism of methane. GRI-Mech. 3.0 (5) is used for a spatially homogeneous, adiabatic, isobaric, N dimensional, autoignition problem to identify unimportant species by resolving species coupling with the objective of having high efficiency and minimal dependency on the required system knowledge. The results are compared with the results from detailed chemical kinetics and a CSP-based (2) method.

DRG THEORETICAL BACKGROUND
Directed relation graph (DRG) is designed to reduce large detailed mechanisms with high efficiency (4). 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 of species A in a mechanism with I reversible elementary reactions is expressed as:

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

$$q_i = [M]_i \left(k_{fi} \prod_{k=1}^{N_s} C_k^{\nu'_{ki}} - k_{bj} \prod_{k=1}^{N_s} C_k^{\nu''_{ki}} \right) \tag{2}$$

Where the subscripts i and k indicate the ith elementary reaction and the kth species, respectively, and the subscripts f and b denote forward and backward directions of a reaction, respectively. Furthermore, ν 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, T the temperature, N_s number of species, and q_i is the reaction progress variable. 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}, is defined as follows:

$$r_{AB} = \frac{\sum_{i=1}^{I} |\nu_A q_i \delta_{Bi}|}{\sum_{i=1}^{I} |\nu_A q_i|}$$

(3)

$\delta_{Bi}=1$, if the ith elementary reaction involves species B

$\delta_{Bi}=0$, otherwise

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 $A \rightarrow B$ 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 **Figure 1**, in which vertices A, B. . . F corresponds to the respective species, and each directed edge indicates an immediate requirement of one species of another.
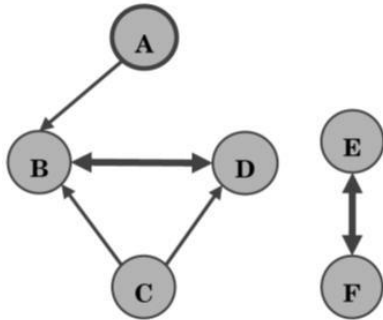

Figure 1. Typical configuration of the directed relation graph (DRG); the vertices correspond to the species and the directed edges correspond to the requirement of one species to another.

The starting vertex A, enclosed in a bold circle, is a major species in the mechanism. The skeletal species in Figure 1correspond 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 consists 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. In this study directed relation graph (DRG) method is used in order to simplify GRI-Mech. 3. Modification of DRG is applied in step 2 for graph searching procedure.

CSP THEORETICAL BACKGROUND
The Computational Singular Perturbation (CSP) method 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 [2].

$$\frac{du}{dt} = g(u)$$

(4)

In the following equation g indicates chemical source term vector and u is the vector of mass fractions. We can decompose the chemical source term in slow and fast manifolds. **a** and **b** are dual basis vectors.

$$\frac{du}{dt} = \sum_{r=1}^{M} a_r h^r + \sum_{s=M+1}^{N-N_c} a_s h^s = g_{fast} + g_{slow}$$

(5)

a and **b** are dual basis vectors and the modal amplitude h is:

$$h(u) = b(u).g(u)$$

(6)

In CSP terms, therefore, the solution of Equation (4) is constrained to lie close to the slow manifold and its slow evolution is governed by

the non stiff simplified system. The CSP fast/slow decomposition prompts the introduction of a "slow" importance index, 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 assessing the relative influence of the kth reaction on the M species affected most by the M fastest time scales. The slow and fast important indices can be defined, respectively, as

$$\left(I_k^i\right)_{slow} = \frac{\sum_{s=M+1}^{N-N_c} a_s^i (b^s.S_k)R^k}{\sum_{j=1}^{N_P}\left|\sum_{s=M+1}^{N-N_c} a_s^i (b^s.S_j)R^j\right|} \quad (7)$$

$$\left(I_k^i\right)_{fast} = \frac{\sum_{r=1}^{M} a_r^i (b^r.S_k)R^k}{\sum_{j=1}^{N_P}\left|\sum_{r=1}^{M} a_r^i (b^r.S_j)R^j\right|} \quad (8)$$

The method for the simplification of the kinetic mechanism is the elimination of all the reactions whose importance indices relative to a specific set of species are both smaller than a prescribed user-specified threshold value.

In the present study, the simplification of GRI-Mech. 3.0 kinetics is obtained by selecting both methane and nitric oxide as kernel species $(S_0 = [CH_4, NO])$, as they respectively represent a major reactant and product.

MODELING OF AUTOIGNITION FOR METHANE/AIR
Methane is an important reference fuel, and the best detailed mechanism for its oxidation is GRI-Mech. 3.0 [5]. This mechanism contains 53 species and 325 elementary reactions. The process of ignition CH_4/air mixtures is computed with using a homogenous model at constant enthalpy and pressure of 1 atm. The initial temperature is 1000 k and equivalence ratio is $\phi = 1$.

Three criteria have been presented for calculation of autoignition delay time. A first criterion is the time elapsed before the reactants in a perfectly-stirred reactor show a 5% temperature rise with respect to the initial conditions. Second has been defined by peaks in the profile of species OH concentration and third definition has been Defined by the temperature

inflection point at the profile of temperature versus time. In this study the first criteria have been chosen for numerical estimation of autoignition delay time.

Autoignition delay time is investigated by using a zero- dimensional closed homogenous model . The SENKIN code [6] 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 $S_0 = [CH_4, NO]$. 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.

Governing equations for a homogenous reactor consist of conservation of species equations and energy equations. The general conservation of species equation is:

$$\frac{dY_k}{dt} = \dot{\omega}_k \frac{W_k}{\rho} \quad (9)$$

n above equation Y_k is the mass fraction of kth species, $\dot{\omega}_k$ is the molar rate of production of the *k*th species bygas-phase chemical reaction per unit volume, and W_k is the molecular weight of the *k*th species. In energy equation H_k is the molar enthalpy of kth species.

$$\frac{dT}{dt} = -\frac{1}{\rho \bar{C}_P} \sum_{k=1}^{K} H_k \dot{\omega}_k \quad (10)$$

RESULTS AND DISCUSSION
In this section the results of kinetics mechanism simplification with using DRG method for Methane/Air autoignition are presented. **Figure 2** shows the number of active species in skeletal mechanisms as a function of threshold value ε in DRG method. Also **Figure 3** shows the number of active reactions in skeletal mechanisms as a function of threshold value ε in DRG method. Simplification of mechanisms is achieved when the number of active species is lower than 53 species with threshold value in DRG method.
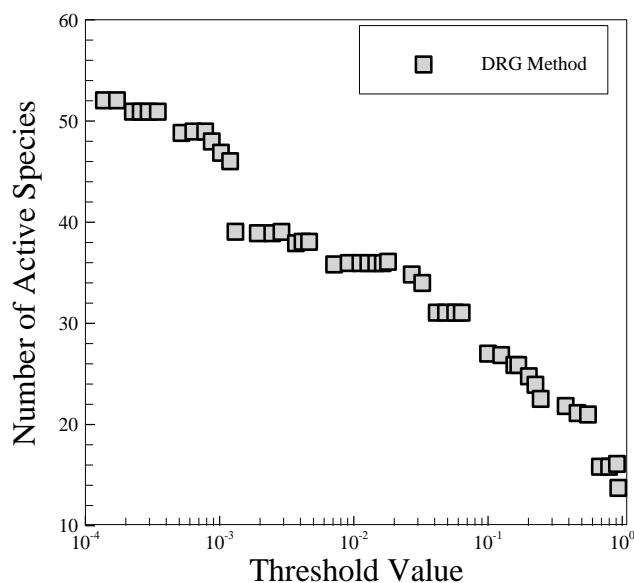
Figure 2. Number of active species in skeletal mechanisms as a function of threshold value ε in DRG method
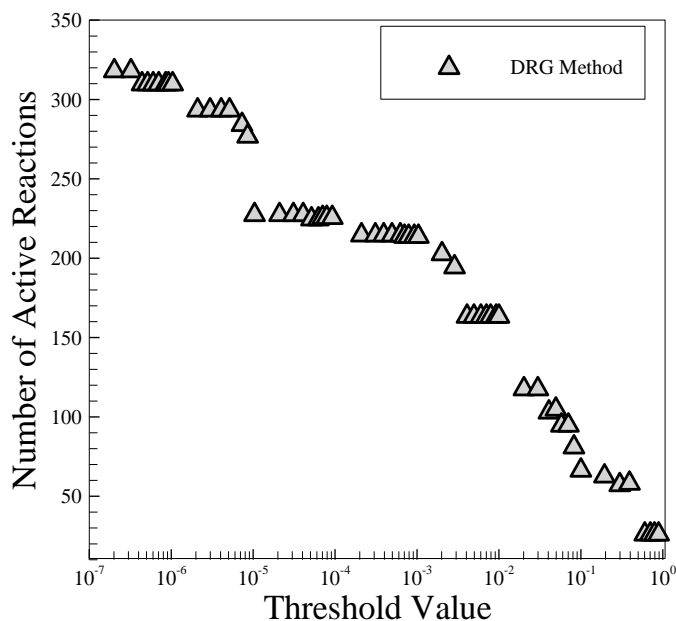

Figure 3. Number of active reactions in skeletal mechanisms as a function of threshold value ε in DRG method.

According to these figures, with increasing the threshold value the number of active species and elementary reactions in the skeletal mechanism decrease. **Figure 4** shows the percentage of active reactions as a function of threshold value in DRG method and its comparison with CSP method. Also **Figure 5** shows the comparison of

percentage of active species as a function of threshold value in DRG method and its comparison with CSP method. Simplification of mechanisms for CSP method is achieved when the number of active species is lower than 53 species with threshold value.
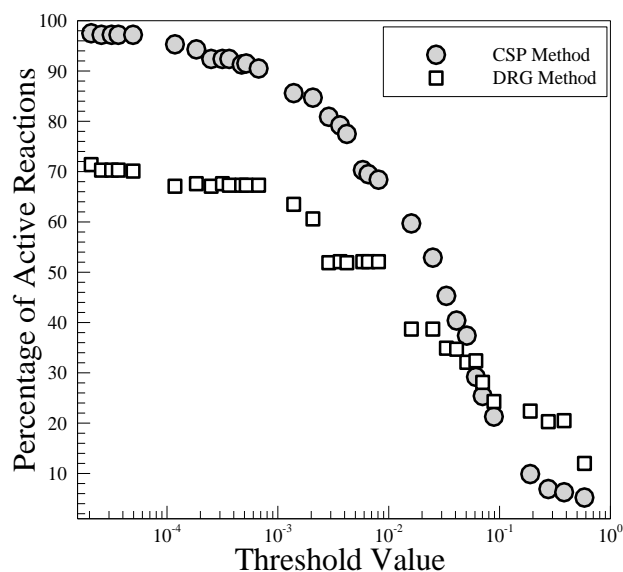
Figure 4. Percentage of active reactions as a function of threshold value in DRG and CSP [2] methods.
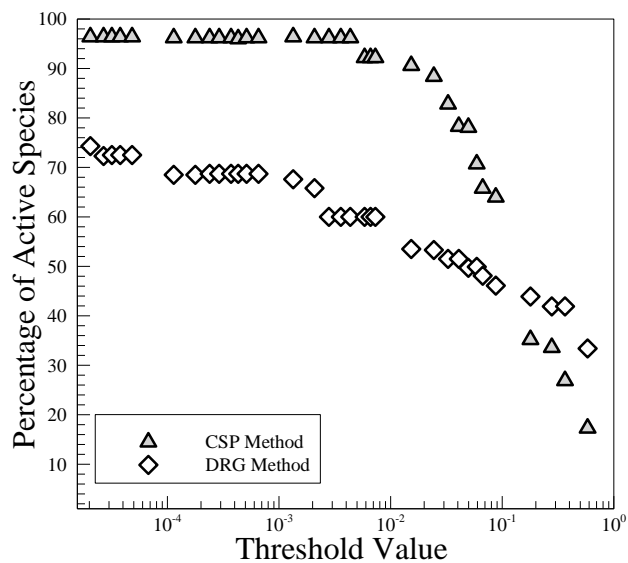

Figure 5. Percentage of active species as a function of threshold value in DRGand CSP [2] methods.

If the run time of skeletal mechanism is normalized with the run time of detailed mechanism, the parameter of normalized run time can be defined as a criterion in order to compare computational effort. **Figure 6** shows the normalized run time as a function of number of active species in skeletal mechanisms for CSP and DRG methods. Figure 6 shows that whit increasing the number of active species,

normalized run time increases for both simplification methods. **Figure 7** shows the percentage of active reactions as a function of the percentage of active species for CSP and DRG methods. Figure 8 shows the percentage of ignition time error as a function of number of active species in skeletal mechanisms for DRG and CSP methods.
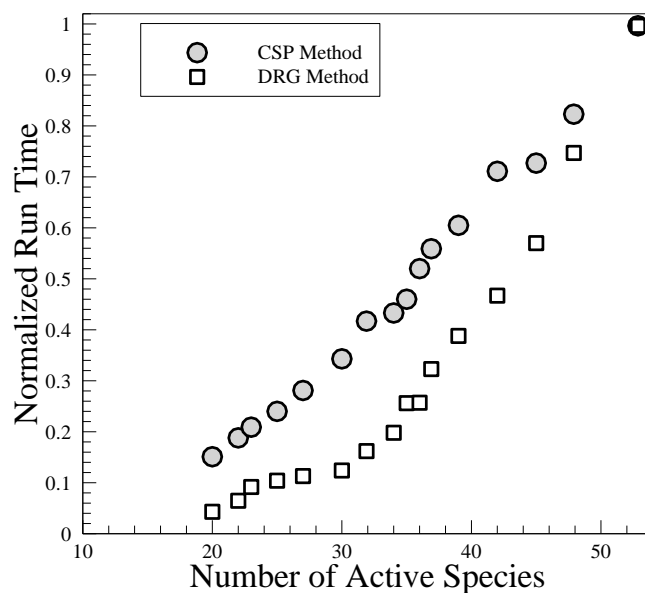
Figure 6. Comparison of normalized run time as a function of number of active species in skeletal mechanisms for DRG and CSP [2] methods.
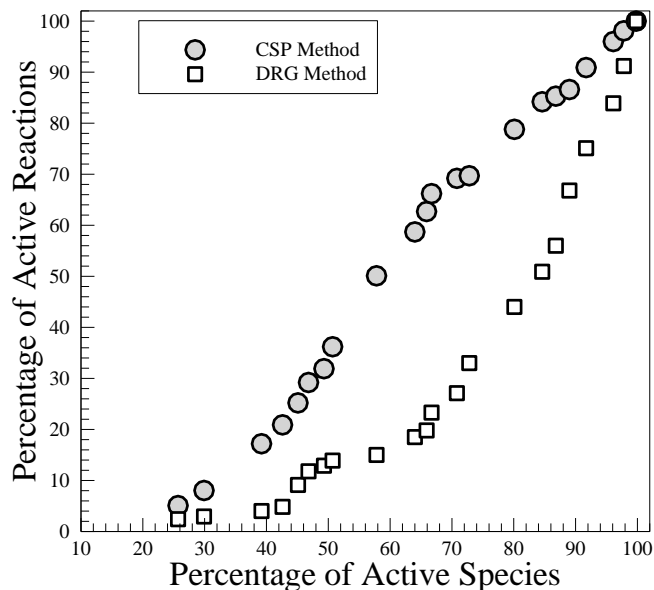

Figure 7. Comparison of percentage of active reactions as a function of percentage of active species for DRG and CSP [2] methods.

CONCLUSION

The method of DRG 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/air 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 which is in contrast with DRG method and is based on elimination of unimportant elementary reactions. In both methods the effect of elimination of species relative to elementary reactions is more important. 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.
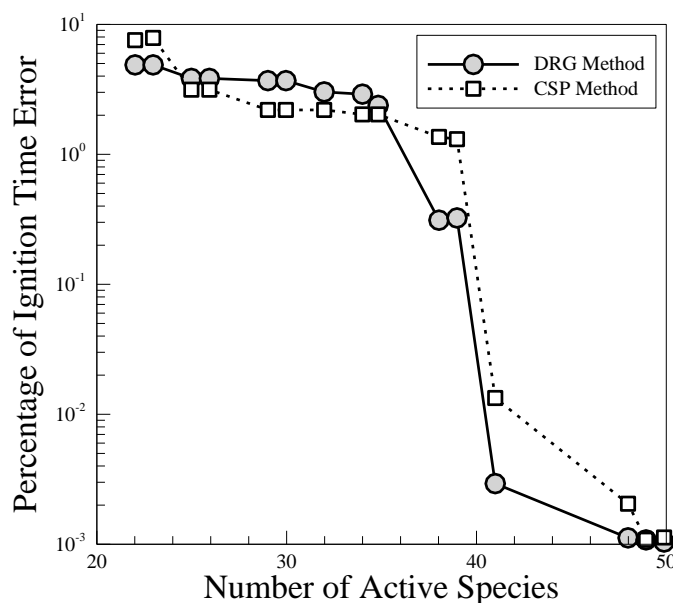

Figure 8. Percentage of ignition time error as function of number of active species in skeletal mechanism for DRG and CSP [2] methods.

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