Amirkabir Univ. of Technology
Aerospace Engineering Dept.

The Third Fuel & Combustion Conference of IRAN

Tehran - IRAN Feb. 2010

Iranian Combustion Institue

FCCI2010-1163

# Computational Singular Perturbation Method for Kinetics Mechanism Simplification in Methane/Air Autoignition under V94.2 Gas Turbine Conditions

Sajjad Yousefian[*, §], Akbar Ghafourian [**], Masoud Darbandi [***], Shahrokh Sorkhkhah[****]

[*, ****] Department of Research and Development
MAPNA Turbine Engineering and Manufacturing Company (TUGA)
Head Office: 231 Mirdamad Ave. Tehran - I.R.Iran; P.O.BOX:15875-5643;

[**, ***] Aerospace Engineering Department
Sharif University of Technology
Azadi Ave. Tehran - I.R.Iran; P.O.BOX: 11365-1115

([§] yousefian.sajjad@mapnaturbine.com)

**ABSTRACT** Computational Singular Perturbation (CSP) algorithm is used for detailed mechanism reduction of methane/air combustion. Detailed chemical kinetic models coupled with transport process models require tremendous computational resources. In order to reduce the computational cost in numerical simulations, skeletal mechanisms are used instead of detailed mechanism. Chemical kinetics mechanism of methane (GRI-3) consists of 53 species and 325 elementary reactions. The algorithm is applied to a spatially homogeneous constant-pressure autoignition of methane/air combustion at the conditions in combustion chambers of V94.2 gas turbine. The algorithm is used to identify elementary reactions which their presence has little effect on the final results. Results from CSP method and detailed kinetics mechanism are compared for accuracy.

**Keywords** Computational Singular Perturbation, Skeletal Mechanism, Autoignition, Methane.

## INTRODUCTION

Application of chemical kinetic 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 kinetic 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 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. The first approach is time scale analysis methods. In these methods, the main objective is to reduce the stiffness of the governing equations. The kinetics 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. 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. 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. Massias, A., Diamantis, D., Mastorakos, E., and Goussis, D.A. [1999] developed a reduced seven-step mechanism for detailed chemical kinetic mechanism of laminar premixed methane flame.

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. 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. 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.

Valorani, M., Creta, F., Goussis, Dimitris A., Lee, J. C., Najm, H. N. [2006] 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 kinetics mechanism is large, these methods are time consuming. Those methods which can identify and eliminate unimportant species instead of elementary reactions are more efficient. Lu, T. and Law, C.K. [2006] 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, CSP method has been applied to the detailed kinetics mechanism of methane. GRI-Mech. 3.0 [Smith, G.P., Golden, D.M. , Frenklach, M., Moriarty, N.W., Eiteneer, B., Goldenberg, M., Bowman, C.T., Hanson, R.K. , Song Jr., S., Gardiner, W.C., Lissianski,V.V., Zhiwei, Q.,] is used for a spatially homogeneous, adiabatic, isobaric, N

dimensional, autoignition problem to identify unimportant elementary reactions. Initial conditions in this problem are similar to the combustion chamber of V94.2 gas turbine. This gas turbine in its premixed combustion mode uses natural gas as fuel.

## 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.

$$\frac{d\mathbf{u}}{dt} = \mathbf{g}(\mathbf{u}) \tag{1}$$

In the following equation $\mathbf{g}$ indicates chemical source term vector and $\mathbf{u}$ 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

$$\frac{d\mathbf{u}}{dt} = \sum_{r=1}^{M} \mathbf{a}_r \mathbf{h}^r + \sum_{s=M+1}^{N-N_c} \mathbf{a}_s \mathbf{h}^s = \mathbf{g}_{fast} + \mathbf{g}_{slow} \tag{2}$$

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

$$h(\mathbf{u}) = \mathbf{b}(\mathbf{u}).\mathbf{g}(\mathbf{u}) \tag{3}$$

In CSP terms, therefore, the solution of Equation (1) 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 importance indices can be defined, respectively, as

$$(I_k^i)_{slow} = \frac{\sum_{s=M+1}^{N-N_c} a_s^i (b^s . S_k) R^k}{\sum_{j=1}^{N_p} \left| \sum_{s=M+1}^{N-N_c} a_s^i (b^s . S_j) R^j \right|} \tag{4}$$

$$(I_k^i)_{fast} = \frac{\sum_{r=1}^{M} a_r^i (b^r . S_k) R^k}{\sum_{j=1}^{N_p} \left| \sum_{r=1}^{M} a_r^i (b^r . S_j) R^j \right|} \quad (5)$$

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 ($S_0$ = [CH4,NO]), as they respectively represent a major reactant and product.

## 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. 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 10 atm The initial temperature 1300 k and equivalence ratio of Φ=1.The temporal change of species mass fraction, $Y_i$, and temporal change of temperature is calculated from:

$$\frac{dY_k}{dt} = \dot{\omega}_k \frac{W_K}{\rho} \quad (6)$$

$$\frac{dT}{dt} = -\frac{1}{\rho \bar{C}_p} \sum_{k=1}^{K} H_K \dot{\omega}_k \quad (7)$$

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 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 1 and 2 show the number of active reactions and species in skeletal mechanisms as a function of threshold value **ε.** Note that mechanism simplification is achieved when the number of active species is lower than 53, for threshold value $>10^{-7}$ in CSP.

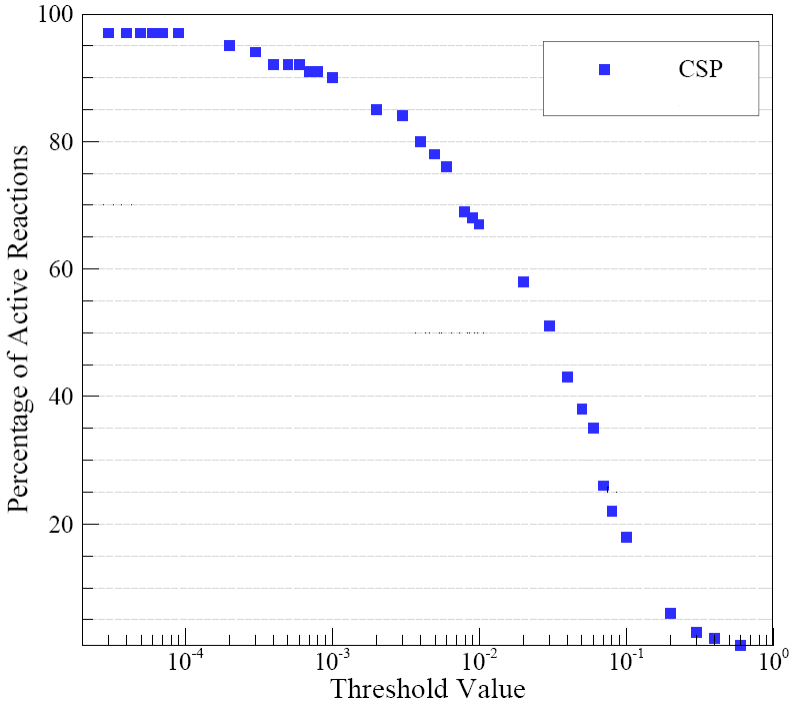


Figure 1. Percentage of active reactions as a function of threshold value in CSP method.

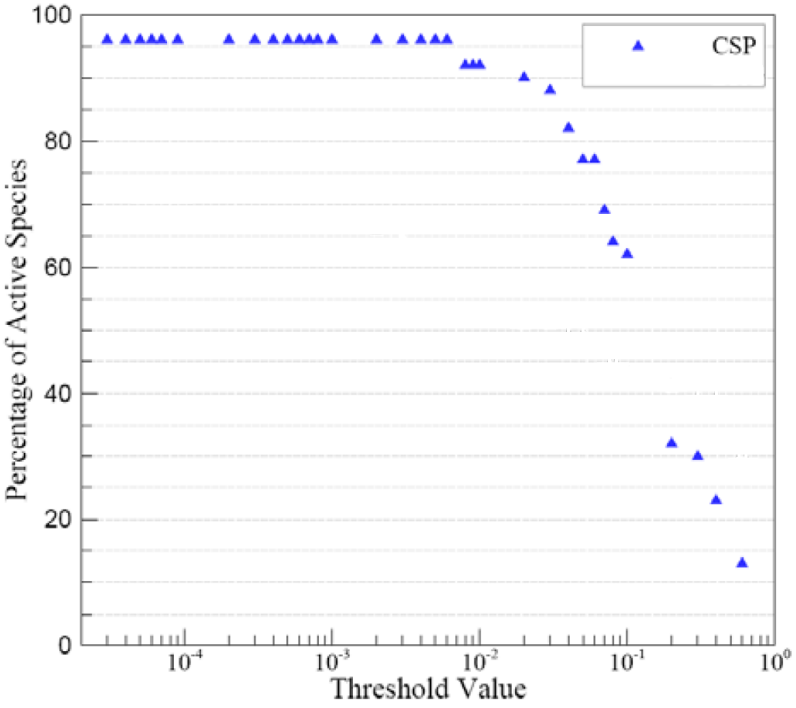


Figure 2. Percentage of active species as a function of threshold value in CSP method.

If we normalize the run time of skeletal mechanisms with the run time of detailed mechanism, we can define the parameter of CPU speed-up that is a criterion in order to compare computational effort. Figure 3 shows the CPU speed-up as a function of number of active species in skeletal mechanisms for CSP method.

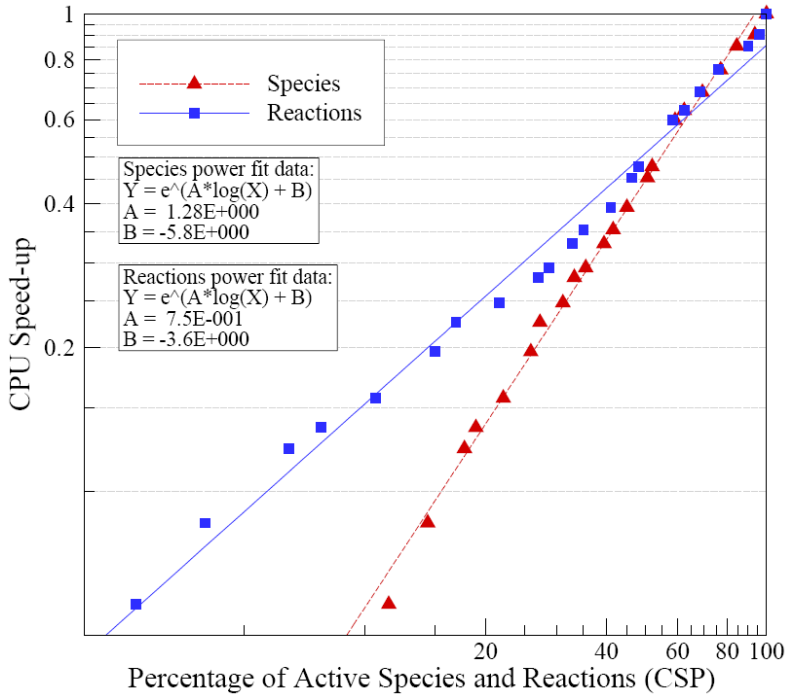


Figure 3. CPU speed-up as a function of percentage of active species and reactions in CSP method.

Figure 4 shows the percentage of ignition time error as function of number of active species in skeletal mechanisms for CSP method. The criteria in order to find ignition time is the time need to temperature reaches to 5 percent of its maximum value. In this figure values of CSP method compared with detailed solution

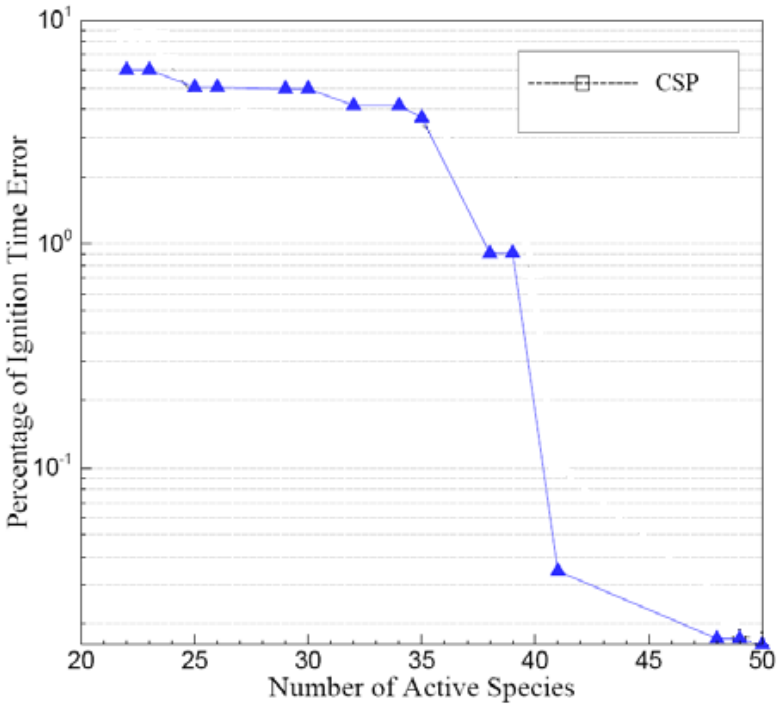


Figure 4. Percentage of ignition time error as function of number of active species in skeletal mechanism for CSP method.

## CONCLUSION

The method of CSP constructed based on a detailed solution, to make a decision about which elementary reactions 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 under the condition of Siemens' V94.2 gas turbine. Model reduction is achieved when elementary reactions deemed unimportant with respect to the elementary reactions in the specified kernel are eliminated. 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 detailed solution. For large kinetics mechanisms with large number of elementary reactions, using species based simplification method initially is more efficient. After using such methods CSP method can be used with its high accuracy.

## REFERENCES

Lu, T., Law, C. K., [2006], On the applicability of directed relation graphs to the reduction of reaction mechanisms. Combustion and Flame Vo.146, pp. 472–483.

Lu, T., Law, C. K., [2006], Linear time reduction of large kinetic mechanisms with directed relation graph: *n*-Heptane and iso-octane.Combustion and Flame Vo.144, pp. 24–36.

Massias, A., Diamantis, D., Mastorakos, E., and Goussis, D.A., [1999], An Algorithm for the Construction of Global Reduced Mechanisms With CSP Data. Combustion and Flame Vo. 117, pp. 685–708.

Smith, G.P., Golden, D.M. , Frenklach, M., Moriarty, N.W., Eiteneer, B., Goldenberg, M., Bowman, C.T., Hanson, R.K. , Song Jr., S., Gardiner, W.C., Lissianski,V.V., Zhiwei, Q., GRI.3 [online], University of Berkley.
Available from:
http://www.me.berkeley.edu/gri_mech/.

Valorani, M., Creta, F., Goussis, Dimitris A., Lee, J. C., Najm, H. N., [2006], An automatic procedure for the simplification of chemical kinetic mechanisms based on CSP. Combustion and Flame Vo.146, pp.29–51.