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Skeletal mechanism generation for high-temperature oxidation of kerosene surrogates

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ABSTRACT

A skeletal mechanism with 106 species and 382 reactions is developed from a detailed kerosene combustion chemical kinetic mechanism that includes 209 species and 1673 reversible reactions for a tricomponent surrogate mixtures, consisting of *n*-decane, *n*-propylcyclohexane, and *n*-propylbenzene. The directed relation graph (DRG) method for skeletal mechanism reduction is applied as the first step for reduction of mechanisms with large numbers of species. A revised DRG approach (Z.Y. Luo, T.F. Lu, et al., Energy Fuels 24 (2010) 6283–6293) is compared with the original one and it is shown to be more stable than the original DRG method. The simplified iterative screening and structure analysis method (ISSA) is used subsequently based on the reduced mechanism generated by the DRG method to remove redundant species and reactions simultaneously. A minimal skeletal mechanism from the detailed mechanism for kerosene combustion is thus obtained. It is found that the discrete local reaction rates rather than the time-averaged reaction rates should be adopted when using the ISSA method for mechanism reduction due to large temperature difference and different reaction pathways in combustion at different simulation conditions. Although reduced in size by a factor of 2 for species and a factor of 4 for reactions, the skeletal mechanism exhibits high accuracy for high-temperature applications in predicting global combustion parameters, such as ignition delay, detailed profiles of species concentrations, and laminar flame speed. Furthermore, numerical simulation results of different mixture compositions are also comparable with those based on the detailed mechanism, indicating that the major reaction pathways of each component are captured by the reduced mechanism and the hierarchical structure of the detailed mechanism is maintained.

1. Introduction

It is generally recognized that realistic numerical simulation of combustion must necessarily require both realistic descriptions of the laws of fluid mechanics and chemical kinetics of fuels [1]. Therefore, in recent years there has been an increasing effort to incorporate more realistic reaction mechanisms in numerical simulations beyond the simplistic descriptions assuming either equilibrium chemistry or one-step overall reaction. However, detailed combustion mechanisms of fossil fuels usually consist of hundreds of species and thousands of reactions and the employment of large detailed mechanisms in large scale numerical simulations demands huge amount of computational resources. Although the available computational power is growing rapidly, the computational cost associated with numerical simulations of turbulent combustion using detailed chemical kinetic mechanism at practical conditions remains challenging. Therefore, in order to make numerical simulations of combustion computationally affordable and comprehensively reliable, the development of computational approaches for rigorous reduction of detailed chemical kinetic mechanisms is essential.

Kerosene is a mixture of a large number of hydrocarbon compounds with varying chemical structures, and it is not practical to model the combustion processes of every involved fuel component [2]. For simplification, a surrogate containing two to six pure compounds is usually adopted to mimic jet-fuel behaviors [3–7]. Such multi-component surrogates can be adjusted to match multiple experimental targets such as ignition delay, flame propagation speed, and physical properties of real kerosene. However, detailed chemical kinetic mechanism of kerosene combustion is highly complex, even for surrogate mixtures with only a few components. Therefore, numerical investigations with detailed combustion chemistry are severely restricted to some zero- and one-dimensional applications in which the governing equations of fluid mechanics are greatly simplified [2–7]. Consequently, these

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limitations have forced scientists to develop mechanism reduction methods for substantially decreasing the numbers of chemical species and reactions without significant loss of accuracy of the detailed mechanisms.

Mechanism reduction has been extensively studied and a variety of methodologies have been developed as reviewed in Ref. [1]. Mechanism reduction methods can be classified into two classes [8]: the first is skeletal reduction, which removes unimportant species and reactions from the detailed mechanism, usually referred as "model simplification"; the other approach produces a number of global reaction steps, whose rates are computed on the basis of the elementary reaction rates. The latter approach, usually referred as "model reduction," can effectively be applied after skeletal reduction.

Skeletal reduction is typically the first step in mechanism reduction. It can be achieved through species reduction methods or by removing unimportant reactions from the detailed mechanisms. Elimination of redundant species and corresponding reactions from a large reaction mechanism can reduce the simulation time significantly, since the computational effort of simulation typically scales quadratically with the number of species, while only linearly with the number of reactions [1]. Various methods for species reduction have been reviewed by Nagy and Turanyi [9]. Species elimination now can be achieved through the computational singular perturbation (CSP) method [8], detailed reduction [10], level of importance (LOI) [11], connectivity method (CM) [9,12], element flux analysis [13], directed relation graph (DRG) [14–16] and other DRG-based methods such as DRG with error propagation (DRGEP) [17] as well as path flux analysis method [18], etc. The DRG-based methods combined with sensitivity-based methods, e.g., the DRG-aided sensitivity analysis (DRGASA) [19], and DRGEP with sensitivity analysis (DRGEPSA) [20] are also developed to achieve a minimal skeletal mechanism with larger computational cost. Some of these methods, e.g., element flux analysis, and DRG are also incorporated into CFD simulations through adaptive reduction or on-the-fly reduction [21–24].

The species elimination procedure results in different reduced mechanisms with different number of necessary species, depending on the error of simulation tolerance and the simulation conditions where the skeletal mechanism is applied. After removal of redundant species, the reduced mechanisms can be reduced further via the elimination of unimportant reactions, and this can lead to a minimal skeletal mechanism, while the error of simulation remains essentially the same [9]. Methods for elimination of reactions include sensitivity analysis [25,26], principal component analysis (PCA) [27], computational singular perturbation (CSP) [8,28–32], genetic algorithm [33], etc. When skeletal mechanism has been achieved, model reduction methods, such as those based on time scale analysis [28–32], lumping [34–36], or quasi-steady state approximation [37,38] can be performed. Therefore, integrated strategies which combine these reduction methods in an appropriate sequence are often adopted to obtain a minimal skeletal mechanism or global reaction mechanism [1].

In the present work, we have used the DRG method combined with the iterative screening and structure analysis method (ISSA) [39,40] to construct a skeletal mechanism for combustion of kerosene on a large combustion domain by the removal of potentially redundant species and reactions without significant loss of the accuracy of the detailed mechanism. The different definitions of the direct interaction coefficient in DRG and the use of the ISSA method in combustion mechanism reduction are investigated. The paper is organized as following: in Section 2 we present the methodologies used for the mechanism reduction; results of the adopted methods and the performance of the skeletal mechanism are validated through a series of simulations including auto-ignition, perfectly stirred reactor (PSR), and 1-D flame propagation simulation by comparing with the detailed mechanism in Section 3, and the main conclusions are briefly summarized in Section 4.

2. Methodologies

The kinetic model for combustion of kerosene used here is proposed by Dagaut et al. It consists of 209 species and 1673 reversible reactions [2]. The molar composition of surrogates used in this modeling is *n*-decane (NC10H22) (74%), *n*-propylbenzene (PHC3H7) (15%), and *n*-propylcyclohexane (CYC9H18) (11%). The mechanism has been validated against a wide range of experimental results, especially the PSR experiments. Luche et al. [41] have used three different methods, i.e., element flux analysis, PCA and quasi-steady state approximation (QSSA) to reduce a three-component kerosene combustion mechanism. However, the reduced mechanism was generated and tested only based on PSR simulations. The skeletal mechanism derived in Luche's work by using element flux analysis and PCA methods involves 134 species and 1220 reactions. Further reduction to 33-species mechanism is obtained by introducing quasi-steady state approximation (QSSA). However, when a larger number of species are chosen to be in quasi-steady state, the validity of QSSA for some given species will be questionable in the entire simulation domain where temperature and pressure are beyond the pre-specified QSS conditions, and the traditional method for calculating the concentration of QSS species will be less efficient [1]. In the present work, an integrated method that combines DRG and ISSA methods will be employed to derive a reduced skeletal mechanism for combustion of kerosene, which can reduce the computational cost in numerical simulations significantly.

The DRG and ISSA methods are applied to reaction state points densely sampled from constant pressure auto-ignition simulations over a wide range of simulation conditions [42,43], and the important species and related reactions are captured by these two methods at each sample point. It has been previously confirmed that although reaction states are only sampled from auto-ignition in mechanism reduction, the generated skeletal mechanism still exhibited good performance in predicting the extinction turning point in PSR and laminar flame speed [11,20]. Though PSR and 1-D laminar flame simulations can be included in the data sampling for mechanism reduction and error control, the ignition demonstrates more restrictions for reaction eliminations than PSR [34]. In addition, auto-ignition simulations are much faster than 1-D laminar flame simulations. Consequently, in the present work, data sampling for mechanism reduction is only from auto-ignition simulation, and ignition delay time is selected as the only control parameter for error control in mechanism reduction [11,20]. The final reduced mechanism is the union of the sets of selected species and reactions. Another common feature in mechanism reduction is that the size of the reduced mechanism is controlled by a threshold value. Success of a mechanism reduction method can be judged by the size (number of species and reactions) of the reduced mechanism, the decrease in simulation time, and the error tolerance of the reduction. The latter is estimated based on comparison of the simulation results at sampling points using the full and the reduced mechanisms.

To achieve a skeletal mechanism suitable for jet-engine and other applications, the reduction is performed within the parameter range of pressure from 1 to 20 atm and equivalence ratio from 0.5 to 1.5. The initial temperature for constant pressure auto-ignition is set to be 1000–1600 K.

The reduced mechanism is tested over a wide parameter range in 0- and 1-dimensional applications that are relevant to high-temperature engine combustion. Based on the nature of the reduction approach which can maintain the major reaction path ways of each