Sensitivity analysis based on intersection approach for mechanism reduction of cyclohexane

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ARTICLE INFO

ABSTRACT

An intersection approach aided sensitivity analysis (ISASA) is proposed for mechanism reduction. In this approach, sensitivity analysis is carried out using mechanisms based on intersections of a set of skeletal mechanisms from various mechanism reduction methods. Number of species in the large-size and small-size mechanisms required in sensitivity analysis is reduced to a large extent. ISASA is thus more efficient than other sensitivity analysis methods such as the direct relation graph (DRG) aided sensitivity analysis (DRGASA) and the achieved reduced mechanism is more compact. A detailed mechanism for cyclohexane with 1081 species and 4269 reactions is reduced using ISASA over a wide range of conditions with ignition delay times as criteria for selecting species and a 61-species mechanism is obtained. However, large error is found on temperature after ignition at low initial temperature and on laminar flame speeds. This failure indicates that mechanism reduction using ignition delay times as the only criteria may result in large error on laminar flame speeds. ISASA using ignition delay times and the maximum mole fraction of CO as criteria is carried out in reduction of the cyclohexane mechanism and a 70-species mechanism is achieved. This 70-species mechanism is shown to afford autoignition delay times, temperature after ignition, species profiles in jet-stirred reactor (JSR), brute-force sensitivity coefficients, laminar flame speeds and reaction paths that are in good agreement with those of the detailed mechanism.

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1. Introduction

Chemical kinetic models for combustion of practical fuels such as gasoline, diesel, and jet fuels are playing a more important role recently for improving performance and reducing emissions in engine design [1,2]. However, detailed chemical kinetic models are becoming increasingly large in size. For example, a chemical kinetic mechanism for a series of n-alkanes and iso-alkanes developed by Lawrence Livermore National Laboratory (LLNL) contains more than 7000 species and 30,000 reactions [3]. These models are too large to be incorporated in 2D or 3D combustion simulations [4]. Detailed mechanisms should thus be reduced to accommodate the demands of computational fluid dynamic (CFD) calculations. Furthermore, reduced mechanisms can greatly facilitate mechanism analysis and provide insights on generation of chemical kinetic models.

Many mechanism reduction methods have been developed such as principle components analysis (PCA) [5], computational singular perturbation (CSP) method [6–8], level of importance analysis (LOI) [9,10], quasi-steady-state approximation (QSSA) [11]. In addition, automated and theory-based methods also exist, such as directed relation graph (DRG) related methods [12–19], dynamic adaptive chemistry (DAC) method [20–23], flux projection tree method (FPT) [24] and simulation error minimization connectivity method (SEM-CM) [25,26]. One of the most popular mechanism reduction approaches is based on connectivity graph, i.e. DRG, originally proposed by Lu and Law [12] in 2005. Many other closely related methods have been developed since then, e.g. DRG with error propagation (DRGEP) [13], path flux analysis (PFA) [14], revised-DRG approach [15], DRG with expert knowledge (DRGX) [16–19]. Furthermore, DRG aided sensitivity analysis (DRGASA) proposed by Lu et. al. [27,28] is able to achieve reduced mechanisms with a rather small size. A 561-species mechanism for n-heptane has been reduced to a 78-species mechanism using DRGASA while still retaining reliability of the detailed mechanism [29]. Sensitivity analysis based on DRGEP has also been introduced by Niemeyer et. al. [30,31] and they found DRGEPSA can produce a smaller reduced mechanism given the same simulation error compared to DRGASA in reduction of n-heptane mechanism [29]. In DRGASA

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or DRGEPSA, two mechanisms with different size are first generated using two different thresholds based on DRG or DRGEP. Species included in the small-size mechanism are treated as important species, while sensitivity of the other species in the large-size mechanism is evaluated based on a one-by-one analysis. Computational effort of DRGASA or DRGEPSA is thus rather demanding. Sensitivity analysis (SA) can also be performed with two mechanisms of different size obtained from other mechanism reduction approaches. Efficiency of the SA approach depends on the number of species in the large-size mechanism while size of the achieved reduced mechanism depends on the number of species in the small-size mechanism. Recently, Wang [32] proposed an intersection approach for mechanism reduction. In the approach, the final skeletal mechanism is achieved based on intersection of skeletal mechanisms from various reduction methods. In another word, only species appeared in all the skeletal mechanisms are retained in the final skeletal mechanism. Their results indicate that intersection approach can reduce size of skeletal mechanism without sacrificing accuracy. The large-size and small-size mechanisms required in SA may be generated from the intersection approach. One would expect that intersection approach aided sensitivity analysis (ISASA) will be more efficient than other similar methods such as DRGASA and DRGEPSA. Moreover, it is possible to achieve reduced mechanisms with an even smaller size since the number of species in the two mechanisms required in SA can be reduced with the intersection approach.

Cycloalkanes are important chemical components in practical fuels, with concentrations up to 35% by weight in diesel, 20% by volume in jet fuel [33]. In the past decade, chemical kinetic of cyclohexane combustion received much attention since cyclohexane is one of the most important cycloalkanes and is often used as a surrogate for practical fuels [34]. Several detailed chemical kinetic models for oxidation of cyclohexane have been developed, which can be applied to either high-temperature [35–37] or both high- and low-temperature range [38–45].

Reduction of mechanism for cyclohexane combustion received little attention, although many detailed chemical kinetic models and experimental data are available. A skeletal mechanism containing 60 species and 238 reactions based on a detailed mechanism with 499 species and 3348 reaction developed by Buda [41] is obtained by Hughes [46] using local sensitivity methods, and it is reduced to a 45-species mechanism via the QSSA method. Sensitivity analysis method is employed further to achieve a reduced mechanism with 26 species and 133 reactions. This reduction work focused on ignition at $\varphi = 1$ in air, pressures up to 350 kPa in the temperature range of 500–800 K. Systematic reduction of cyclohexane over a wide range of conditions including low temperature has not been reported previously. In the present work detailed mechanism for combustion of cyclohexane developed by Silke et al. [38] will be reduced with ISASA over a wide range of pressures and temperatures. The detailed mechanism adopted here can be applied to both low- and high-temperature combustion and it has been validated against experiment for species concentration profiles in jet-stirred reactor (JSR) [37,47] and rapid compression machine (RCM) [48]. Furthermore, Vranckx et. al. [49] noted that this model showed fair agreement with his own RCM experimental data, and ignition delay times were reproduced more reliably with this mechanism than those with Sirjean [43] and Jet-surf 2.0 [39] particularly in the negative temperature coefficient (NTC) regime. This paper is organized in the following manner: in Section 2, various mechanism reduction approaches employed in this work, i.e. DRG, DRGEP, revised-DRG, PFA and FPT as well as SA will be introduced. The achieved skeletal and reduced mechanisms and its validation against detailed mechanism will be present in Section 3.

2. Methodology

2.1. DRG and related methods

Species in a chemical kinetic model are coupled through chemical reactions and identification of unimportant species is crucial in a reduction method. In DRG method, coupling between species through chemical reactions are mapped into a directed relation graph. Dependence of one species on another, or coupling between two species is evaluated differently in different methods. Lu and Law used the following interaction coefficient in their original DRG approach [12]:

$$r_{AB(DRG)} = \frac{\sum_{i=1,I} \left| \nu_{A,i} \omega_i \delta_B^i \right|}{\sum_{i=1,I} |\nu_{A,i} \omega_i|}, \tag{1}$$

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

$$\omega_i = \omega_{f,i} - \omega_{b,i}, \tag{3}$$

where r_{AB} is the interaction coefficient and represents dependence of species A upon another species B, $\nu_{A,i}$ is the net stoichiometric coefficient of species A in the ith reaction, $\omega_{f,i}$, $\omega_{b,i}$ and ω_i are the forward, reverse and net reaction rates, respectively. To identify unimportant species in DRG, a set of target species is firstly chosen. Species B will be supplemented into this set if r_{AB} is larger than a threshold with A being a species in the target set. This process is iterated until all important species has been included in the target set.

To deal more efficiently with chemical kinetic mechanisms containing large isomer groups such as lipid and biodiesel mechanism, Luo et al. [15] proposed an alternative expression for the interaction coefficient:

$$r_{AB(revised-DRG)} = \frac{\max_i \left| \nu_{A,i} \omega_i \delta_B^i \right|}{\max_i |\nu_{A,i} \omega_i|}. \tag{4}$$

Alternatively, a more complicated method is introduced to calculate the interaction coefficient in PFA [14] and it reads:

$$r_{AB} = r_{AB}^{pro-1st} + r_{AB}^{con-1st} + r_{AB}^{pro-2nd} + r_{AB}^{con-2nd}, \tag{5}$$

$$r_{AB}^{pro-1st} = \frac{P_{AB}}{\max(P_A, C_A)}$$
$$= \frac{\sum_{i=1,I} \max(\nu_{A,i} \omega_i \delta_B^i, 0)}{\max(\sum_{i=1,I} \max(\nu_{A,i} \omega_i, 0), \sum_{i=1,I} \max(-\nu_{A,i} \omega_i, 0))}, \tag{6}$$

$$r_{AB}^{con-1st} = \frac{C_{AB}}{\max(P_A, C_A)}$$
$$= \frac{\sum_{i=1,I} \max(-\nu_{A,i} \omega_i \delta_B^i, 0)}{\max(\sum_{i=1,I} \max(\nu_{A,i} \omega_i, 0), \sum_{i=1,I} \max(-\nu_{A,i} \omega_i, 0))}, \tag{7}$$

$$r_{AB}^{pro-2nd} = \sum_{D_i \neq A,B} r_{AD_i}^{pro-1st} r_{D_i B}^{pro-1st}, \tag{8}$$

$$r_{AB}^{con-2nd} = \sum_{M_i \neq A,B} r_{AM_i}^{con-1st} r_{M_i B}^{con-1st}. \tag{9}$$

In PFA, contributions to the interaction coefficient r_{AB} due to production and consumption of A are calculated separately. P_A and C_A are production and consumption rate of species A, respectively, while P_{AB} and C_{AB} are production and consumption rate of species A in the presence of species B, respectively. $r_{AB}^{pro-1st}$ and $r_{AB}^{con-1st}$ are the first generation interaction coefficients, i.e. directed relation