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A global pathway selection algorithm for the reduction of detailed chemical kinetic mechanisms

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ABSTRACT

A Global Pathway Selection (GPS) algorithm for the reduction of detailed kinetic mechanisms is proposed and validated. The approach consists of (1) the construction of element flux graphs for each considered element from the simulation data obtained using detailed chemical mechanisms, (2) the selection of important species that act as hubs that transfer significant element flux, and (3) the subsequent identification of the global pathway for each hub species by searching a certain number of shortest paths with the constructed element flux graphs from the initial reactants to the final products through the considered hub species. The skeletal mechanism is then obtained by removing the species and reactions that are not important to any identified global pathways. Validations are performed to generate skeletal mechanisms for the combustion of two fuels: *n*-dodecane, and the mixture of toluene, iso-octane, and *n*-heptane. For both cases, a series of mechanisms are generated using GPS, and the maximum error of ignition delays is similar or smaller comparing to the skeletal mechanisms generated using Path Flux Analysis method (Sun et al., 2010) with similar number of species. GPS is further compared with two methods using sensitivity analysis, which is usually effective but time consuming. By comparing simulation results of ignition delay, perfect stirred reactor (PSR) temperature, and laminar flame speed over a wide range of operating conditions, it is observed that a 35-species skeletal mechanism generated by GPS for *n*-dodecane shows similar overall accuracy compared with the 31-species skeletal mechanism obtained by Direct Relation Graph Aided Sensitivity Analysis (Vie et al., 2015). Further validation is conducted for the combustion of the mixture of toluene, *n*-heptane and iso-octane. A 276-species mechanism generated using DRG with error propagation followed by sensitivity analysis and reaction elimination (Niemeyer et al., 2014) shows larger errors for PSR temperature and ignition delay with fuel composition different from the raw database. However these errors can be reduced significantly if GPS-generated mechanism of similar size is tested.

1. Introduction

Numerical simulations play an increasingly important role in the study of combustion. However, the detailed chemical mechanisms describing the combustion process typically involve hundreds of species and thousands of reactions. Their large sizes prohibit them from being implemented into complex CFD calculations due to extremely expensive CPU time. A significant portion of the computation time in the simulation of combustion systems is used for the calculation of chemical reactions. Furthermore, the vastly disparate reactivities of the various chemical species frequently induce chemical stiffness as an additional obstacle for numerical simulations.

1.1. State of the art

To address this challenge, a great number of systematic methodologies have been proposed to alleviate the computational complexity while still retain acceptable accuracy. The general rationale behind these approaches is to reduce the dimension of the system. This can be done with timescale decoupling, for example, using Computational Singular Perturbation (CSP) [1–3]. The dimension can also be reduced by mapping the complex chemical solution to states parameterized by a small set of state variables (tabulation, or "storage and retrieval" scheme), e.g., Intrinsic Low-Dimensional Manifolds (ILDM) [4–7], and progress variables with flamelet-based approaches [8–11]. Another kind of low-dimension representation of a chemical kinetic system is the skeletal mechanisms. A set of species and elementary reactions is trimmed from the detailed mechanism if the removal does not induce significant error.

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Nomenclature

Symbol	
$A_{e,\ i\to j}$	The total element flux of the eth element from the ith species to the jth species (mol/s cm^3)
$a_{e,\ r,i\to j}$	The element flux of the eth element from the ith species to the jth species contributed from the rth elementary reaction (mol/s cm^3)
$B_{e,i\to j}$	reciprocal of $A_{e,\ i\to j}$ (s cm^3/mol)
$C_{e,r,i\to j}$	The number of atoms of the eth element transferred from the ith to the jth species by the rth elementary reaction per unit of reaction rate (dimensionless)
K	The number of global pathways searched for each hub species (dimensionless)
$N_{e,i}$	The number of atoms of the eth element in a molecule of the ith species (dimensionless)
$n_{e,r,i}$	The number of atoms of the eth element transferred into or out from the ith species in the rth elementary reaction per unit of reaction rate (dimensionless)
$n_{e,r}$	The total number of the eth atoms transferred in the rth elementary reaction per unit of reaction rate (dimensionless)
p	Pressure (atm)
$\dot{R}_r$	rth elementary reaction (mol/s cm^3)
T_0	Initial temperature (for autoignition) or inlet temperature (for flame or perfectly-stirred reactor) (K)
$\alpha_{e,i}$	The normalized total flux of the eth element passing through the ith species (dimensionless)
α_{crit}	The threshold value for selection of hub species (dimensionless)
$\beta_{e,i\to j,r}$	The contribution to $A_{e,\ i\to j}$ from the rth elementary reaction (dimensionless)
ϕ	Equivalence ratio (dimensionless)
β_{crit}	The threshold value for selection of most contributing reactions for a given conversion (dimensionless)
$\upsilon_{r,i}$	The stoichiometric coefficient of the ith species in the rth elementary reaction (dimensionless)

Different strategies are available to detect the redundant set for the generation of skeletal mechanisms. The first strategy is the sensitivity analysis. This method detects the potential redundant reaction/species by, for example, calculating the error after cutting the reaction rate [12], or removing species [13,14]. Although this approach provides very effective results, the process is extremely time consuming. Because of the coupling relationship between species, the redundancy does not satisfy additivity. For example, removal of species A and removal of species B is safe if done separately, but may be disastrous if done at the same time. Therefore, the sensitivity analysis needs to exam a great number of combinations and this usually is a brute-force method.

To explicitly calculate the error directly is time consuming; therefore approaches were proposed to estimate the importance of the species and/or elementary reactions. Strategies have been proposed to pick up species whose "score" is above some threshold. For example, methods are proposed to eliminate the reactions not contributing significantly to the heat production [15], or the total entropy production [16]. The score can also be defined on the relationship between species. One approach is to examine the element flux between species, a concept firstly proposed by Revel et al. [17] and then adapted in the studies [18–21] by Androulakis and coworkers. In these works [18–21], any pair of species will be retained in the skeletal mechanisms if the element flux between them is greater than the threshold (hereafter "pair element flux method"). Another approach is developed by Zhao et al. [22] recently. It is based on the "betweenness centrality" (BC), a concept originally emerged in the social network research in the 1970s. BC is adapted in this work to measure the frequency of a species to serve as a hub between a given pair of species, based on identified shortest chemistry pathways. The species of highly ranked BC values are retained to generate the skeletal mechanism.

Besides selecting the important species simultaneously as introduced above, it is also possible to find this set of important species by identifying species that are closely related to the species already assumed to be important, e.g., fuel and oxidizer. A well known family of approaches is the Directed Relation Graph (DRG) based methods [13,14,23–30], originally proposed by Lu and Law in 2005 [23]. The interaction coefficient between two species is defined to be high if most reactions that producing/consuming one of them also involve another [23]. Sensitivity analysis can be integrated with DRG to further reduce the mechanism size (DRG aided sensitivity analysis, DRGASA [14]). Pepiot-Desjardins et al. [28] extended DRG by incorporating the error propagation (DRGEP). However the potential risks of DRGEP is discussed in [31,32]. Another extension of DRG is the path flux analysis method (PFA) proposed by Sun et al. [31]. Unlike previous DRG-based methods only considering the direct relation between species, the interaction coefficients from multiple generations between species are defined in this algorithm in order to improve the prediction of reaction fluxes.

Other approaches used to improve the simulation efficiency include adaptive chemistry reduction (on-the-fly reduction technique [20,33–35]) and species/reactions lumping [36–40]. The afore-mentioned approaches can also be integrated together [3,13,20,23,34,41–43].

1.2. Remaining challenges

Although numerous algorithms are proposed to generate skeletal mechanisms, there still exist some challenges. It is possible for some methods to underestimate the importance of certain species. For example, for the hypothesized chemistry mechanism shown Fig. 1, if the object is to reduce the size of mechanism by approximately half, the appropriate set of species kept should be F, A_i (where $i=1$–12), D and P, since 69% of the total atoms pass through these 15 species. However, every *single* flux connected with D is small, thus if pair element flux method [18–21] is applied, D and A_i (where $i=1$–12) are neglected, but B_i (where $i=1$–13), F and P are selected. The obtained skeletal mechanism (B_{1-13}, F and P) includes totally 15 species but have two problems. Firstly, the pathway from F to P is broken because M1 and M2 are not selected (because the element flux to or from them are relatively small). Second, a significant portion of the reaction flux (through species D) is missed. The essential reason for missing species D is that only the first-generation relation between species (which is measured by the element flux for pair element method) is considered. One can find that 69% atoms from F passed D through three reaction steps, therefore F and D has a strong three-generation relation. Therefore, D could be kept if its multi-generation relation with F is properly considered. This example illustrates that the importance to consider the multi-generation relation between species. To address this issue, method such as PFA [31] has been proposed to consider such relation. PFA calculate the interaction coefficients of the $(m+1)$-th generation from the interaction coefficients of the mth generation. However the computation time for the reduction process of PFA increases fast with generations, as it is proportional to $(\text{species number})^{\text{generations}}$ [31]. Thus usually only up to two-generation relationship is considered by PFA. Therefore to develop a method that quantifying the relation