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Development of skeletal chemical mechanisms with coupled species sensitivity analysis method*#

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Abstract: In this paper, we propose a chemical kinetic mechanism reduction method based on coupled species sensitivity analysis (CSSA). Coupled species graph of uncertain species was calculated using the interaction coefficient in the directed relation graph (DRG) approach and listed first, whereas species having large interaction coefficients were regarded as one unit and removed in the sensitivity analysis process. The detailed mechanisms for ethylene with 111 species and 784 reactions, and for n-heptane with 561 species and 2539 reactions, under both low and high temperatures were tested using the proposed reduction method. Skeletal mechanisms were generated, comprising a 33-species mechanism for combustion of ethylene and a 79-species mechanism for n-heptane. Ignition delay times, laminar flame speeds, perfectly stirred reactor (PSR) modeling as well as species and temperature profiles, and brute-force sensitivity coefficients obtained using the skeletal mechanisms were in good agreement with those of the detailed mechanism. The results demonstrate that the CSSA reduction approach can achieve compact and accurate skeletal chemical mechanisms and is suitable for combustion modeling.

Key words: Combustion chemical model; Skeletal reduction; Sensitivity analysis; Directed relation graph (DRG) method; Computational fluid dynamics (CFD)

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1 Introduction

Chemical kinetic models for combustion of practical fuels such as gasoline, diesel, and jet fuels provide important information about the ignition, flame propagation, species distribution, formation of pollutants, and many other key characteristics of their combustion process (Westbrook et al., 2005; Dagaut and Cathonnet, 2006; Liao et al., 2018; Shan et al., 2019; Tang et al., 2019). Development of chemical kinetic models of various fuels is a critical step towards computational fluid dynamics (CFD) analysis of engineering combustion devices, in which the governing equations for flows are integrated with chemical kinetic rates. Detailed chemical kinetic models for practical fuels consist of hundreds of species and thousands of reactions, which prevents them from being used in multi-dimensional CFD simulations due to their huge memory usage and CPU time (Lu and Law, 2009; Pitz and Mueller, 2011; He et al., 2017; Yao et al., 2017; Pucilowski et al., 2019). As a compromise, skeletal chemical kinetic mechanisms are widely used in CFD simulations (Yoo et al., 2013; Liu et al., 2016; Yao et al., 2017). Often skeletal mechanisms are developed for specific conditions and they are poor in predicting combustion for more general conditions. Thus, more accurate and robust

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skeletal mechanisms are required. In particular, there is a strong demand for developing methods that can systematically simplify the detailed chemical kinetics while retaining the essential features of the reaction system and without sacrificing the accuracy of the detailed chemical kinetic mechanism. There are some automated and theory-based methods and their revised versions for skeletal mechanism reduction including directed relation graph (DRG) (Lu and Law, 2005), DRG with error propagation (DRGEP) (Pepiot-Desjardins and Pitsch, 2008), path flux analysis (PFA) (Sun et al., 2010), and flux projection tree method (FPT) (Liu et al., 2014). Sensitivity analysis combining DRG-based approaches, such as DRG-aided sensitivity analysis (DRGASA) (Sankaran et al., 2007; Zheng et al., 2007), DRGEP and sensitivity analysis (DRGEPSA) (Niemeyer et al., 2010; Niemeyer and Sung, 2014; Li R et al., 2016, 2018, 2019a, 2019b), species-targeted sensitivity analysis (STSA) (Stagni et al., 2016), decoupling methodology (Chang et al., 2015, 2016), combined reduction methods (Tian et al., 2019a, 2019b), and other reduction methods (Wang et al., 2012, 2013; Li SH et al., 2016), are frequently employed as further skeletal reduction methods. These methods have been adopted in skeletal mechanism generation for various fuels, including n-heptane, iso-octane, n-decane primary reference fuels (PRFs), and biofuels.

In general, skeletal reduction methods work in the following way. Firstly, the sensitivity of species in the detailed mechanism is checked by calculating the direct interaction coefficient (DIC). Second, species with sensitivity lower than a user-specified threshold are regarded as redundant species and removed. The sensitivity of species in the sensitivity analysis reduction method is obtained by running simulations rather than from the interaction coefficient in graph search approaches. However, the aided sensitivity analysis method is much more time-consuming than graph search approaches, because the sensitivity index of each species needs to be calculated under all the target conditions. Secondly, owing to the highly nonlinear nature of the kinetic mechanism due to strong couplings among species, it is possible that errors and instability may be generated in the reduction process by removing species in a one-by-one manner. In this study, coupled species sensitivity analysis (CSSA) is proposed to resolve these disadvantages. A species-coupled graph between species is calculated and listed first, and two species with strong coupling are regarded as one in the sensitivity analysis reduction process, i.e. redundant species are removed in a two-at-a-time and one-by-one way. Thus, sensitivity analysis with a species-coupled graph should be more efficient than the conventional sensitivity analysis (CSA) method.

Ethylene is a key intermediate species in the oxidation of higher alkanes and alkenes, and is a reactive component in the decomposition product of kerosene, which makes ethylene attractive in the research community and industry, especially in the area of supersonic combustion (Sun et al., 2015; Tian et al., 2015; Wang et al., 2015; Liu et al., 2017; Yuan et al., 2017; Cai et al., 2018; Huang et al., 2018). Therefore, a chemical mechanism for combustion of ethylene was used to reduce and validate the new proposed method. A typical and main component of aviation kerosene (Hua et al., 2010) and PRFs (Niemeyer et al., 2010; Voglsam and Winter, 2012; Niemeyer and Sung, 2014), n-heptane, was also reduced and analyzed.

This paper is organized as follows. First, the proposed mechanism reduction method is presented. The method is based on the CSSA and the DGR methods. Next, the new reduction method is applied to generate an accurate and compact skeletal reaction model of ethylene combustion. Then, the validation of the mechanism is presented. At last, the low- and high-temperature detailed n-heptane mechanism is reduced using CSSA, and the validation work is presented.

2 Methodology

A large-size mechanism and a small-size mechanism are required in sensitivity analysis, generated by choosing a large and a small threshold, respectively, in DRG-based methods. The sensitivity of the ith species in the current uncertain species set is defined as the maximum absolute simulation error induced by removing this species compared with the detailed mechanism, as shown in Eq. (1). Z represents all the target conditions of interest in generation of the skeletal mechanism, j denotes the jth condition, and δ is the combustion character, which in this study is the

ignition delay time, calculated using the detailed or skeletal mechanism.

$$E_i = \max_j \frac{\left|\delta^j(\text{skel}_i) - \delta^j(\text{detail})\right|}{\delta^j(\text{detail})}, \quad j \in \{Z\}. \quad (1)$$

E_i of each species in the uncertain set is calculated, then the species with the smallest E_i is removed from the uncertain set, and the process proceeds in a one-by-one way. The reduction process is repeated until the maximum absolute simulation error of the skeletal mechanism is larger than a user-specified threshold (ξ). The flowchart of this process is shown in Fig. 1.

Considering that there is a strong coupling between two species of the uncertain set, it would be time-saving and more reasonable if two species that coupled strongly with each other were regarded as a unit and removed together in the sensitivity analysis, i.e. removing redundant species in a two-at-a-time and one-by-one way. A coupled species graph of the uncertain set is calculated in the large-size mechanism and listed first, according to Eqs. (2) and (3):

$$R_{AB} = r_{AB}^{\text{DRG}} + r_{BA}^{\text{DRG}}, \quad (2)$$

$$r_{AB}^{\text{DRG}} = \frac{\sum_{i=1,I}\left|v_{A,i}\omega_i\varphi_B^i\right|}{\sum_{i=1,I}\left|v_{A,i}\omega_i\right|}, \quad r_{BA}^{\text{DRG}} = \frac{\sum_{i=1,I}\left|v_{B,i}\omega_i\varphi_A^i\right|}{\sum_{i=1,I}\left|v_{B,i}\omega_i\right|}. \quad (3)$$

The coupling coefficient between two species is evaluated by R_{AB}, where r_{AB} and r_{BA} are the interaction coefficients defined in the DRG approach (Lu and Law, 2005), $v_{A,i}$ is the net stoichiometric coefficient of species A in the ith reaction, while $v_{B,i}$ is the net stoichiometric coefficient of species B in the ith reaction. ω_i is the net reaction rates of the ith reaction, and I is the total reaction number. The value of φ_B^i is 1 when species B is involved in the ith reaction, and is 0 when species B is absent in the ith reaction. Species A and B are regarded as coupled if R_{AB} is larger than a selected threshold value. In the present work, R_{AB} was assigned a value of 1.0. After all R_{AB} between any pairs of two species in the uncertain set are calculated, they are listed in descending order. R_{AX} and R_{BY} (where X represents species except A, and Y represents species except B) would not be considered if they are smaller than R_{AB} (Fig. 2a). Five tested species, i.e. A_1, A_2, A_3, A_4, and A_5, can be replaced by three new groups, i.e. C_1, C_2, and C_3 (Fig. 2b). The two grouped species are regarded as one in calculating the E_i in Eq. (1). If a certain coupled species group has the smallest E_i, then those two species will be removed. Sensitivity analysis using a species-coupled graph should be more efficient than the CSA method since the number of testing simulations required is reduced significantly.

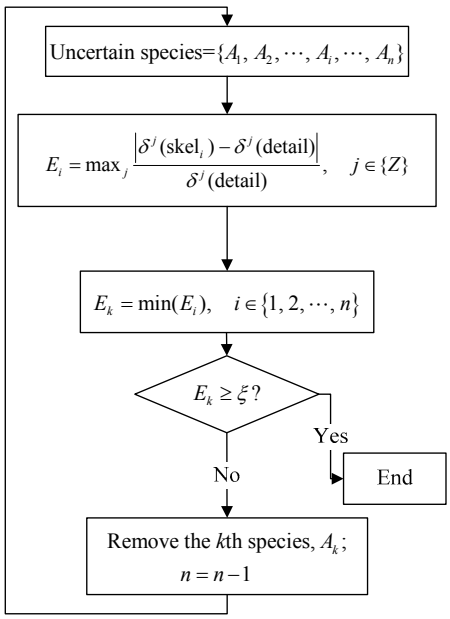

Fig. 1 Flowchart of the sensitivity analysis reduction method

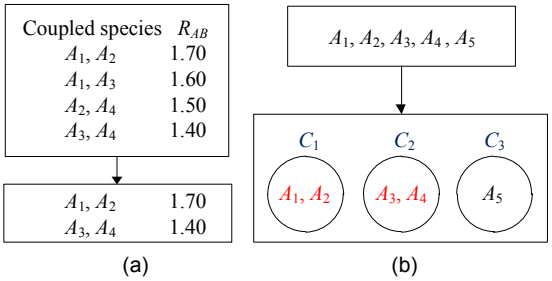

Fig. 2 Sketch map of coupled species graph
(a) Calculation of R_{AB}; (b) Coupled species graph

3 Skeletal reduction of the ethylene mechanism

The kinetic model used here is a detailed mechanism of ethylene from the University of Southern California (USC-II) (Wang et al., 2007),

consisting of 111 species and 784 elementary reactions, which has been extensively validated against experimental data. The USC-II model predicts auto-ignition and laminar burning velocity well, as validated by Xu and Konnov (2012). The auto-ignition process in a homogeneous reactor with constant pressure was simulated with Chemkin II (Kee et al., 1989), and simulations were carried out under 81 different conditions in the range of equivalence ratios Φ={0.5, 1.0, 2.0}, pressures P={1, 5, 10, 30 atm} (1 atm=1×10^5 Pa), and temperatures T={1000, 1100, 1200, 1300, 1400, 1500, 1600, 1700, 1800 K}. Nine temperature points with temperature increments of 5, 25, 50, 100, 250, 375, 400, 425, and 800 K over the initial temperature of the target cases were selected. Oxygen and ethylene were selected as target species in the first-stage reduction. A 45-species skeletal mechanism (large-size mechanism) was achieved with the DRGEP method, and the maximum auto-ignition error was 3.5% over the above simulation conditions. The small-size mechanism contained 20 species. The threshold in DRGEP of ethylene was 0.035 for the large-size mechanism and 0.24 for the small-size mechanism. There were 25 uncertain species in the uncertain set, which included 16 elements (9 coupled and 7 single) to be tested (Table 1). Finally, a skeletal mechanism with 33 species and 211 reactions model was generated for combustion of ethylene using the CSSA method, and the maximum error of the ignition delay time was about 10%.

Table 1 Coupled species of the uncertain set in ethylene reduction

Coupled species		R_{AB}	Uncoupled species
aC_3H_5	C_3H_6	1.57	C_2O
HCCO	C_2H_2	1.53	CH_2OCH
C_3H_8	nC_3H_7	1.50	CH_2^*
C_3H_3	aC_3H_4	1.41	C_2H_6
C_4H_{8}-1	C_4H_7	1.32	H_2O_2
C_4H_4	C_4H_6	1.31	CH_2CO
CH_3OH	CH_3O	1.20	CH_4
C_2H	C_4H_2	1.17	
CH	pC_3H_4	1.14	

Fig. 3 shows experimental ignition delay times (Kalitan et al., 2005) of $C_2H_4/O_2/Ar$ at the equivalence ratio of 1.0, as well as the model predictions. The ignition delay times in the simulations are defined as the moment of the maximum rise of the OH mole fraction. It can be seen that the 33-species skeletal model and the USC-II detailed model could each predict the ignition delay times for low and high-temperature conditions. Fig. 4 shows the laminar burning velocities of ethylene/air mixtures at different pressures measured by Jomaas et al. (2005) and Hassan et al. (1998). The new compact skeletal model replicated the results of the detailed model well, and both models gave results in good agreement with the experimental data for a wide range of equivalence ratios, especially at the pressure of 1 atm.

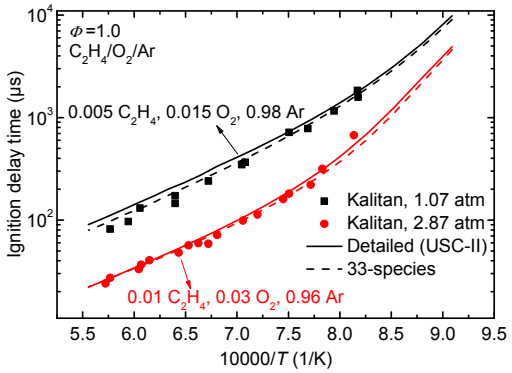

Fig. 3 Comparison of experimental ignition delay times with predicted results using the detailed and skeletal (33-species) chemical kinetic models (Kalitan et al., 2005)

The laminar flame structure was also validated to evaluate the skeletal reaction mechanisms (Fig. S1, Electronic Supplementary Materials). The temperature and species profiles in a 1D laminar premixed ethylene/air flame under standard conditions calculated using the 33-species skeletal model agree very well with the results from the detailed model. The concentrations of C_2H_4, O_2, H_2O, CO, CO_2, and important intermediate radicals, such as OH and CH_2O, calculated using the skeletal model adequately replicated the results from the detailed mechanism.

4 Skeletal reduction of the n-heptane mechanism

CSSA method was applied to the reduction of the oxidation mechanism of n-heptane. The detailed mechanism for n-heptane was from the Lawrence

Livermore National Laboratory (LLNL) model. The reduction target conditions in this study covered the temperature range of 600–1800 K, pressures of 1–50 atm, and equivalence ratios of 0.5–1.5. The negative temperature coefficient (NTC) region was also included in the target conditions. The large-size mechanism contained 176 species and 808 reactions and the maximum auto-ignition error was 10%, while the small-size mechanism included 31 species and 112 reactions. The large-size and small-size mechanisms of n-heptane were taken from Li R et al. (2016) using the intersection method from various DRG-based methods. There were 56 coupled species and 33 uncoupled species from testing using Eqs. (2) and (3) as well as the rules in Fig. 2 (Table S1, Electronic Supplementary Materials).

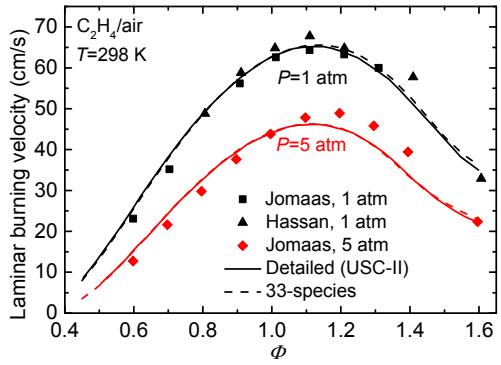

Fig. 4 Comparison of experimental data and modeling of the laminar burning velocities for the ethylene/air mixture at the temperature of 298 K and at two pressures, using the detailed and the skeletal (33-species) chemical kinetic models (Hassan et al., 1998; Jomaas et al., 2005)

Fig. 5 presents the maximum error against the species number of the skeletal mechanism generated by the CSA method and CSSA approaches. The mechanism with CSSA had a slightly larger maximum error than those of the CSA when the number of retained species in the skeletal mechanisms was between 150 and 100. CSSA performed better than the CSA when the number of retained species was less than 100. Moreover, there was less non-monotonic behavior in results from the CSSA mechanism than in results from CSA. It is possible that the non-monotonic behavior is induced by removing only one species of two strongly coupled species. Since the CSSA considers two coupled species as one and removes them at the same time, it can efficiently avoid this kind of behavior. The reduction time of the CSSA method was 55 h, which was less than half that of the CSA method (136 h).

A skeletal mechanism model with 79 species and 339 reactions was obtained for combustion of n-heptane using the CSSA method, and the maximum error of the ignition delay time was 22%. The ignition delay times of the 79-species skeletal mechanism of n-heptane were compared with those from the detailed mechanism at the initial temperature and under constant pressure at various pressures and equivalence ratios (Fig. 6). There was good agreement between results from the 79-species mechanism and those from the detailed mechanism over high and low temperatures.

The validation of the skeletal mechanism for the perfectly stirred reactor (PSR) modeling for n-heptane/air mixtures at various pressures and equivalence ratios is shown in Fig. 7. The simulated results from the 79-species mechanism were close to those from the detailed mechanism. Laminar flame speeds were also investigated at the pressure of 1 atm and temperatures of 300 and 400 K. The laminar flame speeds versus equivalence ratios obtained with the 79-species and detailed mechanisms, as well as experimental results (Kumar et al., 2007; Chong and Hochgreb, 2011; Sileghem et al., 2013), are shown in Fig. 8. The 79-species skeletal mechanism performed quite well for equivalence ratios of 0.5–1.6. At worst, the 79-species skeletal mechanism under-predicted the laminar flame speeds of the detailed mechanism by 5.2% (2.5 cm/s).

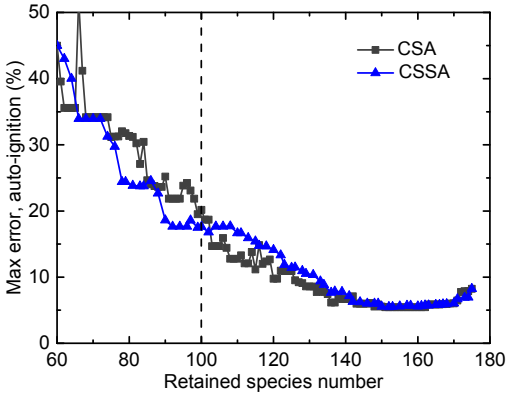

Fig. 5 Maximum error in ignition delay time against species number of the skeletal mechanisms (for n-heptane) generated using CSA and CSSA methods

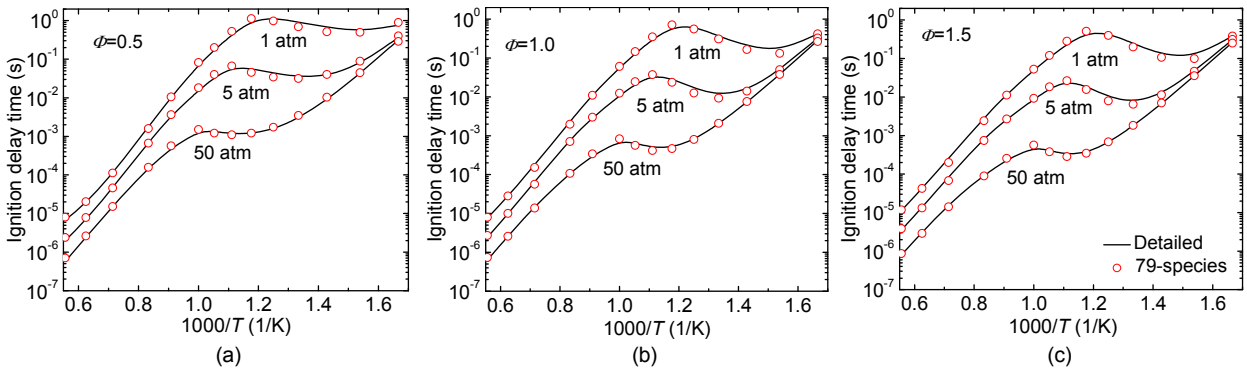

Fig. 6 Auto-ignition delay times with respect to the initial temperature for the n-heptane/air mixture at various pressures and equivalence ratios, with the detailed and 79-species skeletal mechanisms: (a) Φ=0.5; (b) Φ=1.0; (c) Φ=1.5

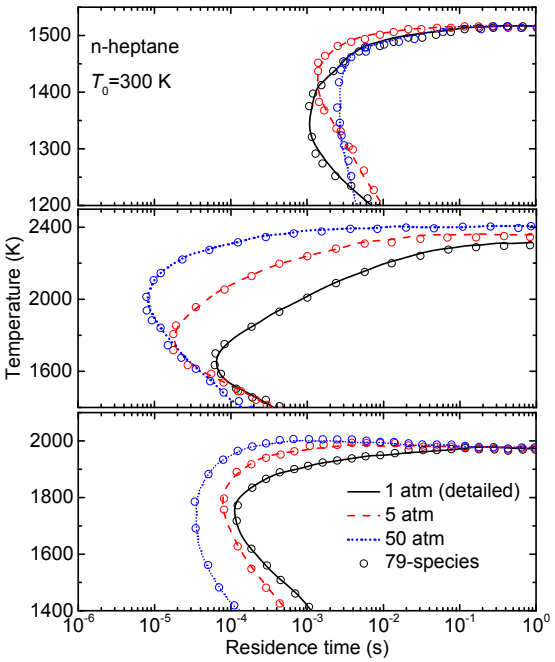

Fig. 7 Comparison of the calculated temperature profile in PSR as a function of the residence time for n-heptane/air with the detailed and the 79-species skeletal mechanisms, for equivalence ratios from 0.5 to 1.5, pressure from 1 to 50 atm, and the initial temperature of 300 K

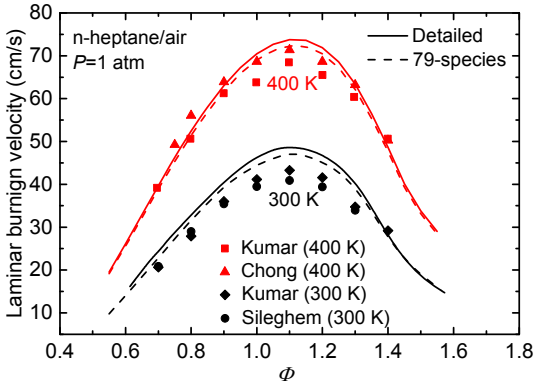

Fig. 8 Laminar flame speeds obtained from the detailed and 79-species skeletal mechanisms, together with experimental data at the pressure of 1 atm and temperatures of 300 and 400 K (Kumar et al., 2007; Chong and Hochgreb, 2011; Sileghem et al., 2013)

The time saving of the 33-species ethylene mechanism and 79-species n-heptane mechanism compared to the detailed mechanisms were measured with 0D ignition and 1D laminar flame modeling. The speedup factors were about 3.5 and 2.9 for the 33-species ethylene mechanism and about 12.5 and 8.6 for the 79-species n-heptane mechanism, for the 0D ignition and 1D laminar flame simulations, respectively.

To further evaluate the 79-species skeletal mechanism for combustion of n-heptane, validation of the skeletal and detailed mechanisms for engine conditions was performed using constant volume auto-ignition simulations. Fig. 9 shows temperature profiles obtained with the detailed and the 79-species skeletal mechanisms in a closed homogeneous reactor at constant volume conditions, initial temperatures of 700, 900, 1300, and 1800 K, an initial pressure of 40 atm, and equivalence ratios (ER) of 0.6, 1.0, and 1.5. Temperature-time profiles at constant pressure at initial temperatures of 800, 1000, 1100, and 1200 K, equivalence ratios of 0.6, 1.0, and 1.5 using the detailed and the 79-species skeletal mechanisms are included (Fig. S2, Electronic Supplementary Materials). The 79-species skeletal mechanism accurately reproduced the temperature profiles.

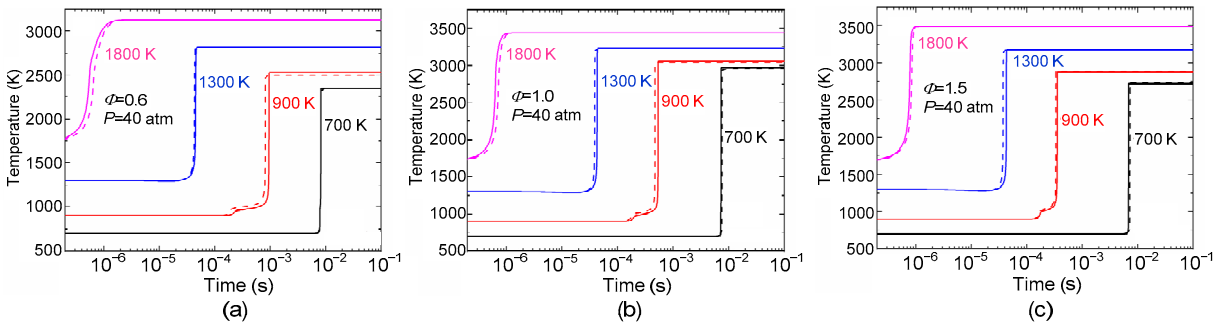

Fig. 9 Comparison of temperature profiles for various initial temperatures at the initial pressure of 40 atm, and ER=0.6, 1.0, and 1.5, calculated by the detailed and skeletal mechanisms under constant volume conditions. Solid line, detailed mechanism; dashed line, skeletal mechanism

Brute-force sensitivity analysis of the reaction coefficient was also performed using Eq. (4), which is a kind of local sensitivity analysis method proposed by Zeuch et al. (2008):

$$\text{Sensitivity}\ (i)=\frac{\tau_{\text{ign}}(2k_i)-\tau_{\text{ign}}}{\tau_{\text{ign}}}, \qquad (4)$$

where τ_{ign} and $\tau_{\text{ign}}(2k_i)$ are the ignition delay time of the original mechanism and of the mechanism with a doubled rate constant for the ith reaction, respectively. Reliability of the skeletal mechanisms can be evaluated by comparing sensitivity coefficients of the most important reactions with those from the detailed mechanism. The sensitivity indexes of all the 339 reactions in the 79-species skeletal mechanism were calculated and those of the same 339 reactions were also calculated using the detailed mechanism at a temperature of 1000 K. Reactions with a sensitivity coefficient larger than 5% are illustrated in Fig. 10, together with their sensitivity coefficients. This local sensitivity analysis result implies that the 79-species skeletal mechanism can describe auto-ignition reasonably because the most important reactions on auto-ignition were the same in the detailed and the 79-species skeletal mechanisms, and the sensitivity coefficients of their listed reactions agreed well.

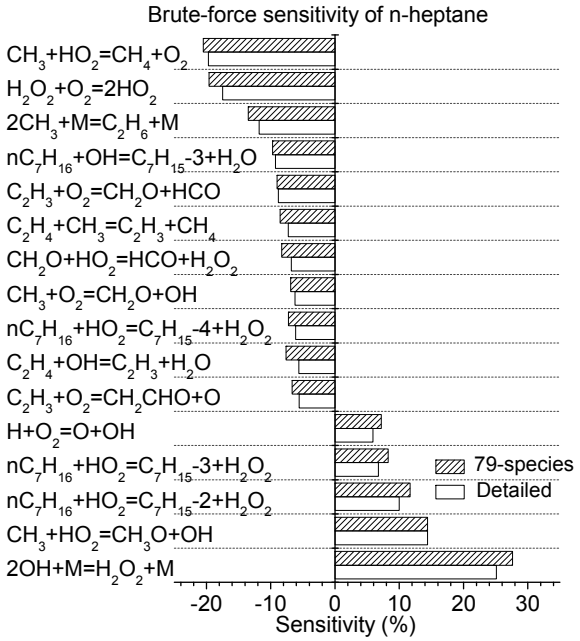

Fig. 10 Sensitivity of auto-ignition for the 79-species and detailed mechanisms of n-heptane at P=1 atm, Φ=1.0, and T=1000 K

5 Conclusions

In this paper, a new chemical reaction reduction method, i.e. coupled species sensitivity analysis (CSSA), is introduced. Two species having a large interaction coefficient are regarded as one coupled unit and removed together. The chemical mechanism of ethylene combustion using the detailed USC-II mechanism was reduced based on the CSSA method, and a 33-species skeletal reaction model was generated. The conditions for model validation covered Φ=0.5–2.0, temperatures 1000–1800 K, and pressures 1–30 atm. The model predicted the ignition delay time with a maximum error of about 10% compared with the parent model. The detailed mechanism for n-heptane with 561 species and 2539 reactions at both low and high temperatures was also reduced with the CSSA method, and a skeletal mechanism with 79 species was achieved. Ignition delay times, laminar

flame speeds, PSR modeling, temperature-time profiles, and brute-force sensitivity coefficients were in good agreement with those of the detailed mechanisms. The CSSA method is less time-consuming than the CSA method, and the achieved skeletal chemical mechanisms are suitable for combustion modeling.

Contributors

Guo-qiang HE, Fei QIN, and Rui LI designed the research. Rui LI wrote the first draft of the manuscript. Xiang-geng WEI, Duo ZHANG, Ya-jun WANG, and Bing LIU helped to organize the manuscript. Fei QIN and Rui LI revised and edited the final version.

Conflict of interest

Rui LI, Guo-qiang HE, Fei QIN, Xiang-geng WEI, Duo ZHANG, Ya-jun WANG, and Bing LIU declare that they have no conflict of interest.

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List of electronic supplementary material

Fig. S1 Temperature and species profiles in a 1D premixed flame with the detailed and 33 species skeletal mechanisms of ethylene at initial temperature of 300 K and pressure of 1 atm

Table S1 Coupled species in uncertain set of n-heptane reduction

Fig. S2 Comparison of temperature profiles for various initial temperatures at P=10 atm, ER=0.6, 1.0, and 1.5 calculated by the detailed mechanism and skeletal mechanisms at constant pressure condition

中文概要

题　目： **燃烧化学动力学机理的框架简化：组分耦合的灵敏性分析简化方法**

目　的： 发动机燃烧数值模拟需要高精度的、尺寸合适的化学反应机理，因此需要对复杂的详细化学反应机理进行简化。由于现有的灵敏性分析简化方法效率低且计算时间长，因此本文希望得出一种效率更高、计算时间更短的灵敏性分析简化方法。

创新点： 1. 利用直接关系图简化方法中的相互作用系数计算待删除组分之间的相互耦合关系，提出了组分耦合的灵敏性分析简化方法；耦合关系较大的两个组分被视为一个整体，有助于提高灵敏性分析简化的效率、缩短计算时间。2. 得到了较小尺寸的乙烯（33 组分）和正庚烷（79 组分）框架燃烧反应机理。

方　法： 1. 提出组分耦合的灵敏性分析简化方法，即先利用直接关系图简化方法中的相互作用系数计算待删除组分之间的相互耦合关系（公式（2）和（3），图 2）；在简化过程中，耦合关系较大的两个组分被视为一个整体被删除。2. 通过 0 维和一维计算验证得到的简化化学反应机理的精度。

结　论： 1. 本文所提出的组分耦合的灵敏性分析简化方法提高了灵敏性分析简化的效率、缩短了计算时间。2. 利用此方法对含有 111 组分和 784 基元反应的乙烯以及 561 组分和 2539 基元反应的正庚烷的燃烧化学机理进行简化，最终得到 33 组分的乙烯框架机理和 79 组分和 339 基元反应的正庚烷框架反应机理。3. 在较宽的工况范围内对得到的框架机理进行点火延时、层流火焰传播速度、温度曲线、组分浓度和反应的灵敏性分析等燃烧特性参数的验证与分析，结果表明得到的框架机理具有较高的精度和较小的尺寸，适用于燃烧数值模拟。

关键词： 燃烧化学反应机理；框架简化；灵敏性分析；直接关系图法；计算流体动力学