Skeletal Mechanism Generation for Surrogate Fuels Using Directed Relation Graph with Error Propagation and Sensitivity Analysis

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Abstract

A novel implementation, using directed relation graph with error propagation and sensitivity analysis (DRGEPSA), for the skeletal reduction of large detailed reaction mechanisms was developed and presented. DRGEPSA integrates two previous methods, directed relation graph with error propagation (DRGEP) and directed relation graph aided sensitivity analysis (DRGASA), by first applying DRGEP to efficiently remove many unimportant species prior to sensitivity analysis to further eliminate unimportant species. A skeletal reduction of a detailed *n*-heptane mechanism was performed to illustrate the individual weaknesses of DRGEP and DRGASA and to show that DRGEPSA diminished these weaknesses. Furthermore, a comprehensive skeletal mechanism for *n*-decane was generated using DRGEPSA to demonstrate the applicability of the DRGEP method to the skeletal reduction of large surrogate fuel mechanisms. Specifically, the detailed mechanism of *n*-decane containing 940 species and 3887 reactions was reduced to a skeletal mechanism containing 211 species and 794 reactions, which exhibits good performance in predicting ignition delays over a wide range of equivalence ratios, temperatures, and pressures.

1. Introduction

Combustion of hydrocarbon fuels currently provides 85% of energy in the modern United States [1]. While renewable forms of energy are being pursued to supplement combustion-based sources, hydrocarbons will remain the major component for the next few decades. There is high demand to improve the efficiency of combustion technology to decrease the amount of fuel consumed and to reduce the emissions in an effort to lessen the environmental impacts. In addition, fuel-flexible designs that can run on both conventional and alternative fuels are desired.

Since computational modeling drives the design of new combustors and engines for aerospace, transportation, and energy applications, accurate prediction of fuel combustion and pollutant emissions requires comprehensive detailed chemical reaction mechanisms. Detailed reaction mechanisms for surrogates of gasoline [2,3], diesel [3,4], and jet fuels [5] have been developed that typically contain large numbers of species and reactions. For instance, a recent detailed mechanism developed for *n*-alkane hydrocarbons C_8–C_{16} [6] contains 2116 species and 8130 reactions. Despite rapid advancements in computing power, it is generally formidable to integrate such detailed reaction mechanisms into large-scale computational simulations, in terms of CPU time and memory requirements. In addition, the wide range of time scales (from nanosecond to second) and the nonlinear coupling between species and reactions induces stiffness when governing equations are solved. Due to these computational demands, practical simulations using detailed chemistry are unfeasible with modern computational tools.

Skeletal reduction is typically the first step of mechanism reduction, where species and reactions deemed negligible to important phenomena over the range of conditions of interest (e.g. pressure, temperature, and equivalence ratio) are removed from the detailed mechanism. The reader is referred to reviews of skeletal reduction methods, e.g. [7,8]. Important techniques include sensitivity analysis [9-11], principal component analysis [12], lumping [13-15], genetic algorithms [16,17], optimization [18,19], adaptive reduction [20], directed relation graph (DRG) [21-27], and an error minimization approach [28].

The DRG method has recently been shown to be particularly applicable to efficiently and reliably reduce large reaction mechanisms [23,24]. In DRG, the coupling of species is mapped on a directed graph, which is then analyzed to find unimportant species for removal. Recently, further development of this method has branched into two directions: (1) DRG-aided sensitivity analysis (DRGASA) [26], which performs sensitivity analysis on species not removed by DRG to further reduce the mechanism, and (2) DRG with error propagation (DRGEP) [22,27], which considers the propagation of species coupling down reaction pathways. In the current work, an approach, DRG with error

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propagation and sensitivity analysis (DRGEPSA), that integrates the major aspects of DRGASA and DRGEP is presented. It is illustrated that this combined approach overcomes the weaknesses of the two individual methods.

Note that the current work is a follow-up of the initial presentation of the DRGEPSA method [25] that compared DRGEPSA with other DRG-based methods using the skeletal reduction of 1,3-butadiene. In the following, the methodology of DRGEPSA for skeletal reduction of large detailed reaction mechanisms is first discussed. The specific weaknesses of DRGASA and DRGEP, and the subsequent improvement of DRGEPSA, are demonstrated with a skeletal reduction of the *n*-heptane mechanism of [29]. A skeletal mechanism for *n*-decane from the detailed mechanism of [6] generated with DRGEPSA is then presented to illustrate the capability of the current method for the reduction of large surrogate fuel mechanisms.

2. Methodology

The reduction procedure begins with the use of SENKIN [30] in conjunction with CHEMKIN-III [31] to generate the numerical solutions of constant volume combustion with the detailed mechanism over a range of input conditions. These SENKIN evolution results are used for the subsequent chemical kinetic analysis, while the ignition delay times are used to assess the overall performance of the resulting skeletal mechanisms.

Based on the SENKIN solutions with the detailed mechanism, the DRGEP method is performed in an iterative manner. The threshold used to identify unimportant species for removal is increased until the global error in ignition delay prediction reaches a set limit. When species are removed from the detailed mechanism, all reactions containing such species are also removed. Species are then divided into three groups: unimportant species for direct removal, "limbo" species for further sensitivity analysis, and important species for retention. Sensitivity analysis is then performed on the limbo species to further identify unimportant species. Again, such unimportant species are removed until the global error reaches the set limit. Specifics of each phase for skeletal reduction are detailed as follows.

2.1 DRGEP Phase

The first phase of DRGEPSA is based on the DRGEP of Pepiot-Desjardins and Pitsch [27], which in turn is an extension of the original DRG of Lu and Law [21,23,24]. This DRGEP phase includes an improved definition of the direct interaction coefficients motivated by the shortcomings of the original [22] in situations with long chemical paths involving fast modes as discussed in [23]. In the current DRGEP, it uses a directed graph to map the coupling of species in a reaction system. The graph vertices represent species and directed edges represent species dependencies based on a contribution to overall production rate. This contribution is expressed as the direct interaction coefficient:

$$r_{AB} \equiv \frac{\left|\sum_{i=1}^{n_R} \nu_{A,i}\omega_i\delta_B^i\right|}{\max\left(P_A, C_A\right)}, \tag{1}$$

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

$$P_A = \sum_{i=1}^{n_R} \max\left(0, \nu_{A,i}\omega_i\right), \tag{3}$$

$$C_A = \sum_{i=1}^{n_R} \max\left(0, -\nu_{A,i}\omega_i\right), \tag{4}$$

where A and B represent the species of interest (with dependency in the $\mathrm{A} \rightarrow \mathrm{B}$ direction), i is the ith reaction, n_R the total number of reactions, $\nu_{A,i}$ the stoichiometric coefficient of species A in the ith reaction, and ω_i the overall reaction rate of the ith reaction. P_A and C_A are simply the net production and consumption rates of species A, respectively. These coefficients are calculated for all species at each data point from the SENKIN simulation, and the maximum values are used in the following analysis.

After mapping the system, a depth first search is performed starting at certain target species (e.g. fuel, oxidizer, important pollutants) to find the dependency pathways for all species relative to the targets. To represent the error propagation down a certain pathway, a path-dependent interaction coefficient is defined as the product of intermediate interaction coefficients between the target species A and species of interest B:

$$r_{AB,p} = \prod_{i=1}^{n-1} r_{S_i S_{i+1}}, \tag{5}$$

where n is the number of species between A and B in pathway p and S is a placeholder for the intermediate species. An overall interaction coefficient is then defined as the maximum of all path-dependent coefficients between each species and the targets:

$$R_{AB} \equiv \max_{\text{all paths } p}\left\{r_{AB,p}\right\}. \tag{6}$$

For example, Fig. 1 shows a simple reaction system where the overall dependence of species A on species D is expressed as:

$$\begin{aligned} R_{AD} &= \max_{\text{paths 1, 2, 3}}\left\{r_{AD,p}\right\} \\ R_{AD} &= \max\left\{\left(r_{AB}\cdot r_{BD}\right), \left(r_{AC}\cdot r_{CD}\right), \left(r_{AC}\cdot r_{CE}\cdot r_{ED}\right)\right\} \end{aligned}, \tag{7}$$

where path one is $\mathrm{A} \rightarrow \mathrm{B} \rightarrow \mathrm{D}$, path two is $\mathrm{A} \rightarrow \mathrm{C} \rightarrow \mathrm{D}$, and path three is $\mathrm{A} \rightarrow \mathrm{C} \rightarrow \mathrm{E} \rightarrow \mathrm{D}$. Species with overall interaction coefficients below a threshold ε_{EP} are considered negligible to the overall production rates of the

target species and therefore can be removed from the reaction mechanism.

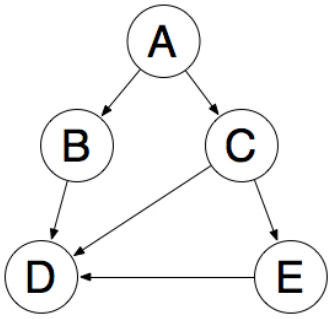

Fig. 1. A directed relation graph showing path-dependent species coupling.

The DRGEP removal is performed in an iterative manner. After an initially low threshold, ε_{EP}=0.01, is used, the error of the subsequent skeletal mechanism is evaluated with respect to the detailed mechanism. As mentioned earlier, in this implementation, ignition delay is used to measure error. If the initial value is too high to remove species while keeping within the error limit, ε_{EP} is decreased an order of magnitude. Otherwise, ε_{EP} is increased by 0.01 and the procedure is repeated. Once the skeletal mechanism error passes the error limit, ε_{EP} reverts to the last valid value. The iterative approach generates an optimal skeletal mechanism for the specified error limit before moving to the sensitivity analysis phase.

2.2 Sensitivity Analysis Phase

The second phase of DRGEPSA is based on the brute-force sensitivity analysis of Zheng *et al.* [26]. In particular, species with overall interaction coefficient values above the final ε_{EP} but below some intermediate value (e.g. 0.5) are analyzed for removal. These so-called "limbo" species are first removed from the mechanism one-by-one then sorted in ascending order based on the following:

$$\delta_B = \left| \delta_{B,ind} - \delta_{DRGEP} \right|, \quad (8)$$

where $\delta_{B,ind}$ is the induced error of species B and δ_{DRGEP} is the error of the DRGEP-generated mechanism. By first removing species with low induced error compared to the error of the DRGEP-generated mechanism, the least important species can be identified. Any species with an induced error above the overall error limit is automatically removed from the list of limbo species and is retained in the mechanism. The species are then removed in order and the overall error is evaluated after each removal. If the error passes the limit, the last removed species and associated reactions are reinserted into the mechanism so that the final skeletal mechanism error is below the set limit.

3. Results and Discussion

3.1 *n*-Heptane Skeletal Reduction

A skeletal reduction of the detailed mechanism for *n*-heptane from [29], containing 561 species and 2539 reactions, was performed using DRGASA, DRGEP, and DRGEPSA to illustrate the individual weaknesses of the two original methods and the subsequent improvement of the combined method. The DRGEP and DRGEPSA methods used the iterative procedure described previously to determine the optimal ε_{EP} value, while the DRGASA method used the standard ε_{DRG} of 0.1 [21,23,24,26] during the DRG phase. The ignition delay error limit was 30% for the iterative procedures of DRGEP and DRGEPSA as well as the sensitivity analysis of DRGASA and DRGEPSA. A SENKIN initial condition of 1.0 atm, 1000 K, and equivalence ratio of 1.0 was used for the reduction. This constant volume simulation provided kinetics data covering 1.0–2.8 atm and 1000–2430 K. Oxygen, nitrogen, and *n*-heptane were the target species used for all three reduction methods.

The skeletal reduction results are given in Table 1. Through the iterative procedure, 0.03 was selected as the optimal ε_{EP} to generate an initial mechanism of 40 species using DRGEP. The DRGEP and DRGASA methods generate skeletal mechanisms of comparable size and error while DRGEPSA produces a skeletal mechanism that is smaller with similar error. It is expected that the discrepancy between the sizes of the skeletal mechanisms would be larger for a more complex reduction (i.e. greater range of conditions). The difference between the DRGEP and DRGEPSA results is explained by the sensitivity analysis performed.

Method	# Species	# Reactions	Error
DRG	74	440	13.9%
DRGASA	39	143	27.7%
DRGEP	40	189	27.8%
DRGEPSA	35	152	28.1%

Table 1: Comparison of *n*-heptane skeletal mechanism sizes generated by DRG, DRGEP, DRGASA, and DRGEPSA methods.

Figure 2 shows the species analyzed by sensitivity analysis in the DRGEPSA method. It can be seen that the relative value of the overall interaction coefficient for a species does not always correspond to the induced error. Hence, DRGEP alone is not sufficient to identify and remove all unimportant species. For example, species such as CH_2, CH, and CH_2(s), identified as unimportant and removed by sensitivity analysis, would not be removed even by using a slightly higher ε_{EP}.

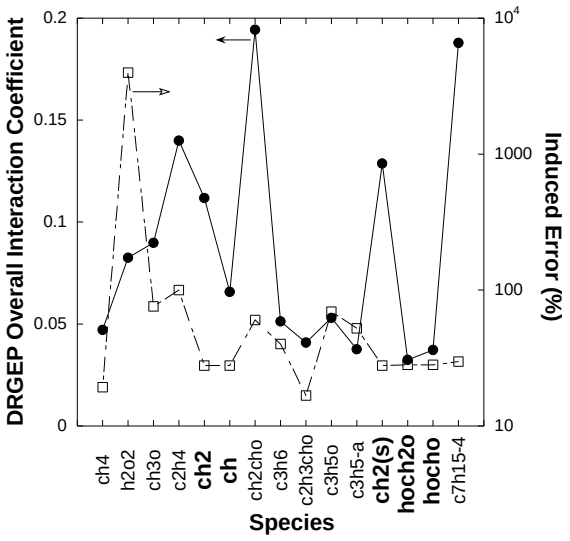

Fig. 2. Comparison of DRGEP overall interaction coefficients to the individual induced error for species considered with sensitivity analysis in DRGEPSA. Species in bold were removed after sensitivity analysis.

The improvement of DRGEPSA over DRGASA consists of two parts. First, certain species are "shielded" from sensitivity analysis in DRGASA due to a high level of importance given by the DRG phase. The DRGEP method considers species dependence propagation down reaction pathways so that species further from the targets will have lower overall interaction coefficients. In the current results, nine of the 27 species retained by DRGASA without analysis were removed by DRGEPSA; eight of the nine species were actually removed by the DRGEP phase. Second, the DRGEPSA method is more efficient than DRGASA in that more species are removed in the DRGEP phase so that a smaller number of species are considered with sensitivity analysis. In the current case, DRGASA performed sensitivity analysis on 47 species, while only 15 were considered in DRGEPSA.

Furthermore, an interesting comparison between DRGEPSA and DRGASA is the fate of carbon dioxide. At stoichiometric conditions carbon dioxide is a major product and is typically of interest in combustion modeling. A simple way to assure accurate reproduction of carbon dioxide production would be to select it as a DRG/DRGEP target. However, in the current results, carbon dioxide was actually removed from the mechanism during sensitivity analysis in the DRGASA method. DRGEPSA, on the other hand, retained the species without analysis.

3.2 *n*-Decane Skeletal Reduction

A skeletal mechanism for *n*-decane was generated using the DRGEPSA method from the detailed mechanism for *n*-alkanes, *n*-octane through *n*-hexadecane, of [6], with portions of the full mechanism describing C_{13}–C_{16} kinetics being removed. This leads to a detailed mechanism for *n*-decane with 940 species and 3887 reactions. Using SENKIN input settings covering 650–1250 K at 13.32 atm and stoichiometric conditions along with a maximum 30% error in ignition delay, a skeletal mechanism with 232 species and 822 reactions is generated with a maximum error of 29.1%. Reduction is again performed on the first skeletal mechanism with a maximum error of 10% (compared to the baseline skeletal mechanism) to generate a final skeletal mechanism with 211 species and 794 reactions. Table 2 contains the details of the reduction procedures for both iterations.

Step	ε_{EP}	Species Removed
DRGEP #1	6×10^{-5}	555
SA #1		153
DRGEP #2	5×10^{-5}	12
SA #2		9

Table 2: Specific details of *n*-decane skeletal reduction with DRGEPSA.

Such a two-stage skeletal reduction was performed primarily for comparison with the multi-stage strategy of Lu and Law [32] but also to investigate the benefit of multiple iterations of the DRGEPSA method. In this case, 30% error was the limit used for the first case and 10% was the error limit used for the second. As such, the error of the final skeletal mechanism compared to the original detailed mechanism is approximately 27–33% for the SENKIN input condition. Again, the first stage reduced the mechanism from 940 to 232 species, a reduction of approximately 75%, while the second stage reduced the first skeletal mechanism from 232 to 211 species, a reduction of approximately 10% but only 2% compared to the initial mechanism. It is mainly a judgment call whether to perform multiple stages of reduction depending on the computational demands of the simulation to be performed using the skeletal mechanism.

Validation of the skeletal mechanism is performed and shown in Fig. 3, covering temperatures of 650–1250 K, pressures of 1.0, 13.32, and 40.0 atm, and equivalence ratios of 0.5, 1.0, and 1.5. Noticeable discrepancy between the ignition delay results of the skeletal and detailed mechanisms occurs at higher pressures and temperatures and the negative temperature coefficient region for stoichiometric and fuel-rich conditions. Nevertheless, this final skeletal mechanism exhibits reasonable good performance over a wide range of conditions. Table 3 further lists the maximum error in ignition delay for each of the pressure/equivalence ratio combinations considered. While stoichiometric conditions at 13.32 atm were used to generate the skeletal mechanism, the present DRGEPSA can include the desired range of thermodynamic parametric variations for particular applications specified by the user.

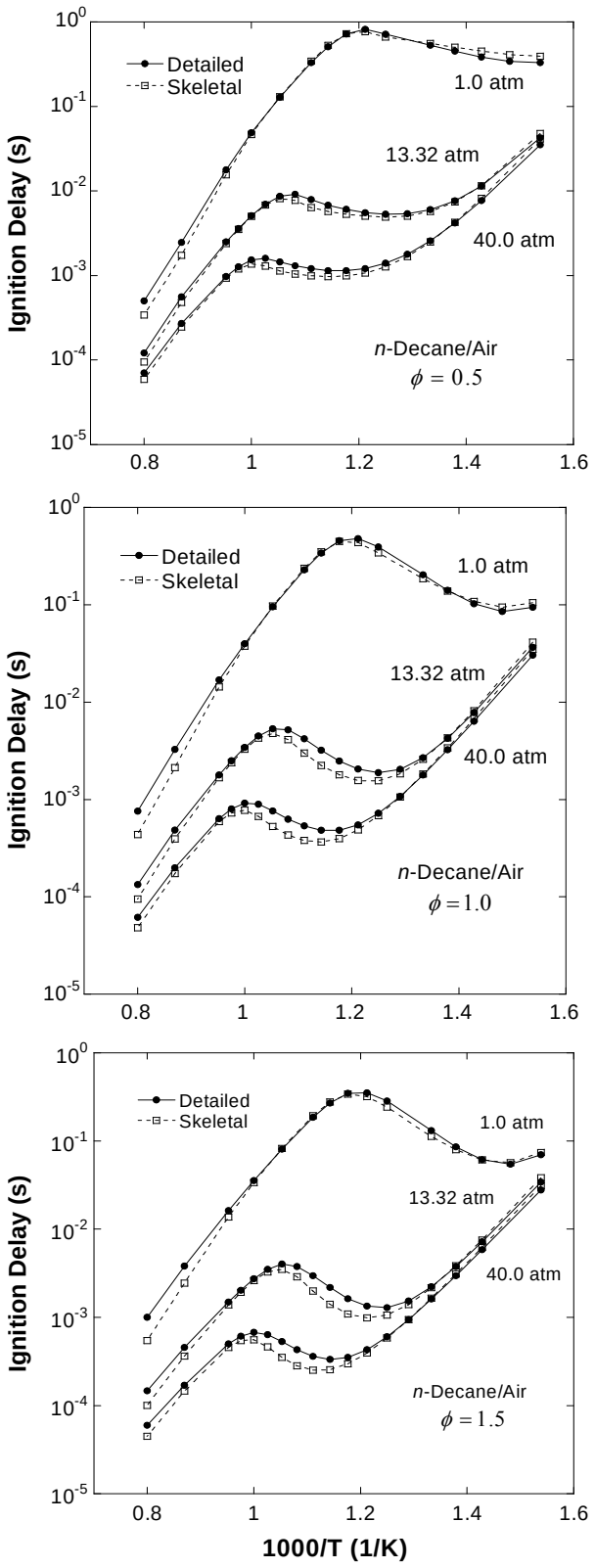

Fig. 3. Comparison of calculated ignition delays for detailed and skeletal mechanisms over a range of temperatures, pressures, and equivalence ratios.

ϕ	1.0 atm	13.32 atm	40.0 atm
0.5	31.91%	21.86%	22.00%
1.0	42.09%	29.94%	31.30%
1.5	45.17%	35.49%	34.34%

Table 3: Maximum ignition delay error of *n*-decane skeletal mechanism for initial temperatures covering 650 –1250 K and various pressures and equivalence ratios.

While a reduction of ~4.5:1 was achieved using DRGEPSA for the detailed mechanism *n*-decane, the final skeletal mechanism is still too large for full-scale simulations. Further reduction using techniques such as removal of unimportant reactions, isomer lumping, time-scale analysis (e.g. quasi-steady-state assumption), and diffusive species bundling [32] is required before realistic computational simulations are feasible.

4. Conclusions

In the present work the directed relation graph with error propagation and sensitivity analysis (DRGEPSA) method for skeletal mechanism reduction was presented and discussed. This approach, a combination of the DRGEP and DRGASA methods, utilized the specific strengths of each in order to diminish some of the weaknesses. DRGEP efficiently identifies and removes unimportant species/reactions but is unable to identify all unimportant species, while DRGASA uses sensitivity analysis to identify many unimportant species for removal at a greater computational expense. By combining the two, DRGEPSA is able to identify and remove more unimportant species than its precursors and at greater efficiency than DRGASA. A skeletal reduction of *n*-heptane was used to illustrate the improvement of DRGEPSA over DRGEP and DRGASA.

A skeletal reduction of *n*-decane was performed using DRGEPSA to demonstrate the applicability of the method to the reduction of large mechanisms of surrogate fuels. Starting with a detailed mechanism with 940 species and 3887 reactions, a final skeletal mechanism containing 211 species and 794 reactions was generated. Though a single pressure and equivalence ratio initial condition was used to provide kinetics data for the reduction, the resulting skeletal mechanism was shown to be mostly valid at lower and higher pressure and equivalence ratios.

Further reduction techniques are still needed for skeletal reaction mechanisms of surrogate fuels, but the DRGEPSA method has been shown to remove large numbers of unimportant species and reactions more efficiently and with greater reduction capabilities than previous DRG-based methods.

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