Application of Jacobian defined direct interaction coefficient in DRGEP-based chemical mechanism reduction methods using different graph search algorithms

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Submitted for full-length article with black and white printing

Abstract

The graph search based approaches, such as the directed relation graph (DRG) and DRG with error propagation (DRGEP) methods, are efficient as the first-cut reduction for large detailed chemical mechanisms. In this study, the DRGEP-based methods are further improved by using a Jacobian for evaluating direct interaction coefficient (DIC). Both the Dijkstra's algorithm and the AStar algorithm are studied to assess the effect of graph search algorithms on the performance of DIC using the Jacobian implementation. Additionally, the target search algorithm (TSA) is used for exploring the further reduction potential by initializing with the skeletal mechanisms generated by the graph search methods. High temperature methane and low temperature n-heptane auto-ignition are selected as the testing conditions. For methane with high temperature conditions, the Jacobian DIC with the AStar algorithm has the best performance with 31% species less compared to the previously defined DIC with the Dijkstra's algorithm for the 10% limited error. By restarting TSA initialized with the skeletal mechanisms generated by graph search methods and TSA, an identical 19-species skeletal mechanism is generated. For n-heptane with NTC region conditions, the Jacobian DIC enhances both the two graph search algorithms as well as the methane skeletal reduction. With the combination of the proposed Jacobian DIC and the AStar algorithm, the n-heptane skeletal mechanism generated by repeatedly restarting TSA is 16% smaller (~20 species less) than the one purely developed from multi-round TSA for the 10% error. The validation of n-heptane laminar flame speed against detailed mechanism shows that the skeletal mechanisms developed by the DRGEP-based approaches can retain the chemistry of laminar flames by targeting only 30 cases near NTC regions.

Key Words: DRGEP; Sensitivity; Skeletal mechanism; Dijkstra; A-star

Nomenclature

DFS: depth first search

DIC: direct interactive coefficient

DRG: directed relation graph

DRGEP: directed relation graph with error propagation

GIC: global interactive coefficient

NTC: negative temperature coefficient

PIC: path interactive coefficient

TSA: target search algorithm

ε : cutoff tolerance in graph search methods

t_{ign} : auto-ignition delay time

1. Introduction

Since numerical simulations are routinely used in assisting designs of efficient combustion devices, kinetic modeling plays an essential role in simulating combustion processes. However, comprehensive detailed reaction mechanisms covering a wide range of conditions can have thousands of species for heavy fuels [1, 2], which are prohibitively expensive for large-scale three-dimensional computations in terms of memory and CPU time. Additionally, stiffness is another issue when wide ranges of time scales and nonlinear coupling among species exist in the detailed mechanisms. For these reasons, there is great interest in reducing the size of the kinetic model while maintaining sufficient species and reaction steps to adequately reproduce relevant physical phenomena at target conditions [3].

Since the Directed Relation Graph (DRG) method was first proposed a decade ago [4], approaches based on graph search algorithms have received significant attention to develop skeletal mechanisms. DRG and its derivatives are useful for the first-step reduction of large detailed mechanisms due to the efficient features of this type of methods. Additionally, the skeletal mechanisms can be used with analytical Jacobian approaches [5, 6] for efficient computations. However, the efficient characteristic requires that the removal of species in DRG-based methods

must be accurate enough so that the resulting skeletal mechanism can be as small as possible to satisfy a fixed relative error. Past experiences revealed that only one improper removal of important species would cause the relative error to increase rapidly. Therefore, two notable approaches have been developed on the basis of DRG: (1) Path Flow Analysis (PFA) [7] and (2) DRG with Error Propagation (DRGEP) [8]. In the original DRG, the Direct Interaction Coefficient (DIC) is a pair-wise relation between a pair of two species. The PFA redefines the DIC by considering the production and consumption fluxes separately, and uses the first (A-B) and second generations (A-M-B) for calculating the DIC. The DRGEP modifies the DRG method by considering the path dependence of a target species on others, and take the path product that is searched by the chosen graph search algorithm as the Global Interaction Coefficient (GIC) for each species. DRGEP assumes that the reduction error decays geometrically along the graph searching paths.

The Jacobian is widely applied in chemical kinetics including the solution of stiff ODE, the calculation of local sensitivities and the time-scale analysis [9]. Among them, the local sensitivity calculation is an accurate way to define coupled species from the Jacobian matrix element magnitude [10], and has been employed to identify redundant species [11-13] and reactions [14] in chemical mechanism reduction approaches. Recently, the Jacobian has been used in development of dynamic adaptive chemistry [15] and a linearized error propagation model for skeletal mechanism reduction [16], showing its usefulness in providing key information. However, as a key element in the graph search methods, almost all the DICs are defined by the contribution of production rate from one species to the other. Although there are graph search approaches with the name of DRG-aided Sensitivity Analysis (DRGASA) [17], DRGEP and Sensitivity Analysis (DRGEPSA) [18] and others [19, 20], they are combined methods to check the redundant species by running simulations instead of involving the calculation of sensitivities. For another key factor which is the graph search algorithm, Niemeyer and Sung [21] developed a DRGEP-based method with the Dijkstra's algorithm [22], and compared it with other algorithms, such as Depth-First-Search (DFS) and Breadth-First-Search (BFS) [23, 24] considering the calculation of GIC in DRGEP as a single-source shortest path problem. The results showed that the DRGEP-Dijkstra method is superior to the other algorithms. Thus the graph search algorithms can play an important role to improve the performance

of DRGEP-based approaches. For the DIC, almost all the graph search approaches focused on the improvements of the definition of production rate contribution from one species to the other [8, 25-27].

In this study, high-temperature methane auto-ignition using the GRI-3.0 mechanism [28] and low-temperature n-heptane auto-ignition using the Lawrence Livermore National Lab (LLNL) v3.1 [2] mechanism are selected to be the testing cases. The Jacobian DIC, which employs a semi-normalized local sensitivity coefficient is defined and applied to the DRGEP-based methods. The Dijkstra's algorithm [22] and the AStar algorithm [29] are used to study the effect of graph search algorithms on the Jacobian DIC implementation. Then the Target Search Algorithm (TSA) [30] is applied to compare the further reduction potential by initializing with the skeletal mechanisms developed by graph search methods.

2. DRG and DRGEP methodology

In DRG [25] and DRGEP [8] methods, the DICs are related to rAG and $rABDRGEP$ defined below to measure the relative importance of species B in the chemical activities of species A. These two parameters in DRG and DRGEP are calculated by:

$$rABDRG = \ln R_{vA,i} R_i \delta B_{ii} = \ln R_{vA,i} R_i, \quad (1)$$

$$rABDRGEP = \ln R_{vA,i} R_i \delta B_{i \max}(PA, CA), \quad (2)$$

where

$$\begin{aligned} R_i &= R_{f,i} - R_{b,i} \\ &= k_{f,i,j} \ln r_{i,j} [C_j] v_{i,j}' - k_{b,i,j} \ln r_{p,i} C_j v_{i,j}'', \end{aligned} \quad (3)$$

$$PA_i = \ln R_{\max}(O, v_{A,i} \omega_i), \quad (4)$$

$$CA_i = \ln R_{\max}(O, -v_{A,i} \omega_i), \quad (5)$$

$$v_{i,j} = v_{i,j}'' - v_{i,j}' \quad (6)$$

The sequence of AB denotes the direction from species A to B, which means A is dependent on B. The symbols R_i , $R_{f,i}$ and $R_{b,i}$ are the net, forward and backward reaction rates of the i -th reaction, where $v_{i,j}$, $v_{i,j}'$ and $v_{i,j}''$ are the net, reactant and product side stoichiometric coefficients of the j -th species and the i -th reaction, respectively. C_j is the molar concentration of species j . $k_{f,i}$ and $k_{b,i}$ are the forward and backward rate coefficients in the i -th reaction. $n_{r,i}$ and $n_{p,i}$ are the reactant and product numbers in reaction i . n_R is the total number of reactions in the mechanism. δB_i equals to 1 if the i -th reaction involves species B, otherwise it equals to 0.

In the DRGEP-based method, the importance of path is included by calculating the Path Interaction Coefficient (PIC), rTB, p , which is the product of DICs between the target species T (such as fuel and oxidizer) and the species of interest B along the path p connecting them:

$$rTB, p = \prod_{j=1}^{n-1} S_j S_{j+1} DRGEP, \quad (7)$$

where n is the number of species along the path p . S_j is the species along the path p by the direction from T to B. As such the error propagation method will assign smaller PICs to the species far from the starting species in a long path since DICs are less than 1. After searched by different graph search algorithms, which will be discussed later, the maximum value of rTB, p will be called RTB corresponding to the assigned location of B by the searching. Finally, by repeating the proceeding process for all the target species of the preset group $\{X\}$, the Global Interactive Coefficient (GIC), RB , is determined for species B:

$$R_B = \max_{T \in \{X\}} R_{TB} \quad (8)$$

Construction of a skeletal mechanism is based on DICs ($=rABDRG$) in DRG and on GICs in DRGEP which are compared to a preset cutoff tolerance (ϵ). In DRG, after exploring all the species by the chosen search algorithm which uses DICs as a guide, the species without directed edge to any other species will be removed from the detailed mechanism along with its associated reactions. In DRGEP, species with $GIC < \epsilon$ are removed from the

species list which is created by searching with a descending order of GICs. In this study, the DICs of Eqs. (1) and (2) are used for the non-Jacobian defined DRG and DRGEP-based methods, respectively.

3. Jacobian DIC formulation

The most frequently used form of Jacobian is the first-order local sensitivity coefficient that indicates how a target variable changes as a consequence of a change in a parameter by a small amount, with all the other parameters fixed at their nominal values. In this study, a semi-normalized sensitivity coefficient is calculated as the Jacobian matrix element, which is defined as:

$$J_{i,j} = Y_j \frac{\partial}{\partial Y_j} \frac{dY_i}{dt} \quad (9)$$

$$= Y_j W_i \rho \frac{\partial \omega_i}{\partial Y_j} \quad (10)$$

$$= Y_j W_i \rho \omega_i P, T, Y_j + \Delta Y_j - \omega_i P, T, Y_j \Delta Y_j \quad (11)$$

Y_i and Y_j are the mass fraction of the i -th and j -th species. W_i and ω_i are the molecular weight and the molar production rate of the i -th species, respectively, and ρ is the density. The local sensitivity shown in Eq. (11) is computed numerically. The Jacobian DIC is defined in Eq. (12), which is the ratio between the absolute Jacobian matrix element and the maximum absolute values among the elements in the same row. Physically, through changing the mass fraction of the species B, the perturbed production rate of the species A is resulted from a globally synergy effect by all the related reactions that species B are involved. In comparison, the original DICs shown in Eqs. (1) and (2) only define the local interactions by considering the reactions including both species A and B.

$$r_{ABJAC} = J_{A,B} \max_{1 \leq j \leq n_{sp}} (J_{A,j}, 10^{-40}) \quad (12)$$

4. Graph search algorithms in DRGEP-based methods

In Figure 1, a 5-node directed graph is plotted as an example with the DIC value for each edge. The nodes represent the species in a detailed reaction mechanism. The arrow from species X to species Y denotes that X is dependent on Y. The searching processes of the three graph search algorithms are explained through the DRGEP-

based methods to reveal their effects on the species list ranking. Node A is the pre-defined target species, such as fuel and oxidizer, to be kept in the skeletal mechanisms. Because Niemeyer and Sung [21] showed the incompatibility performance between the DFS algorithm [31] and the DRGEP-based methods, the DFS algorithm is only used in the original DRG method and won't be shown for the searching process in this section.

Figure 1. A 5-node directed graph with the DIC value for each edge.

4.1 Dijkstra's algorithm

The Dijkstra's algorithm [22, 31] is a shortest path searching algorithm. The purpose of calculating GIC in DRGEP-based methods is to determine the maximum product value of DIC between the target species and the species of interest in all possible paths. As an important feature, the Dijkstra's algorithm is guided by PIC considering all the unexplored species. In Figure 2, the searching process using the Dijkstra's algorithm is shown for the directed graph in Figure 1. The numbers inside the brackets and parentheses indicate the searching sequences and the GICs ($RB=RTB$ due to one target), respectively. Starting from the target Node A, Node B is reached first due to the highest PIC among all the species related to A. Then Node D is recorded due to its higher DIC ($r_{BD}=0.9$) than the other unexplored species related to B ($r_{BC}=0.4$ and $r_{BE}=0.1$). The word "recorded" here means the Node D has not been flagged as a "searched" node because its PIC ($r_{ABD,p}=0.63$) needs to be compared with the PICs of the other unexplored species related to A ($r_{AC,p}=0.5$, $r_{AD,p}=0.4$ and $r_{AE,p}=0.6$). The subscript "ABD" is used to be distinguished from the path involves only A and D. Since the $r_{ABD,p}$ is the largest among them, Node D is searched. Then $r_{ABDE,p}=0.126$ is recorded and compared with the unexplored $r_{AC,p}=0.5$ and $r_{AE,p}=0.6$. Thus Node E is searched, followed by Node C. Therefore, the species list is B(0.7)>D(0.63)>E(0.6)>C(0.5).

Figure 2. Searching processes and results of the Dijkstra's algorithm through a DRGEP-based method.

4.2 AStar algorithm

Figure 3. Searching process and result of the AStar algorithm through a DRGEP-based method.

5. Target search algorithm (TSA)

In order to assess the performances and further reduction potential of DRG and DRGEP-based methods, the Target Search Algorithm (TSA) [30, 33] is used as a reference. The TSA is a trial and error method to develop skeletal mechanisms and it has been demonstrated to generate accurate skeletal mechanisms. However, TSA becomes expensive when the starting mechanism is large [30, 34]. In the TSA, the species in the detailed mechanism are tested for removal in ascending order by their maximum mole fractions. After the removal of each test species and associated reactions, the relative error of the new skeletal mechanism is compared to the original mechanism by running flame or kinetics codes at each target condition. If the relative errors do not exceed pre-defined thresholds, the tested candidate will be removed from the mechanism; otherwise, the species and reactions are re-inserted into the mechanism. The above process is repeated for all species. TSA becomes time-consuming for large detailed mechanisms, especially when there are flame speed target cases. Therefore, the graph search methods can be employed as the first step of the reduction process. Then the TSA is applied once the graph search method can't satisfy the relative error threshold. This reduction strategy would benefit from a smallest starting mechanism generated by DRG or DRGEP-based methods with good accuracy.

6. Results and discussion

The application of Jacobian DIC in DRGEP-based methods is implemented with the Dijkstra's algorithm (Dijkstra-JAC) and the AStar algorithm (AStar-JAC), which are compared with the DRGEP-Dijkstra [21], the DRGEP-AStar and the original DRG [4] for high-temperature methane and low-temperature n-heptane auto-ignition. The maximum relative error between the predicted results of detailed and skeletal mechanisms is defined in Eq. (15), where x denotes a key feature to be computed accurately by the skeletal mechanism. Z represents the collection of all the target cases of interest.

$$\delta_{\text{skel}} = \max_{x \in Z} \frac{|x_{\text{det}} - x_{\text{skel}}|}{x_{\text{det}}} \quad (15)$$

In this study, an in-house Well-Mixed Reactor (WMR) model [35] is used for evaluating the relative error of auto-ignition delay time (t_{ign}) with the threshold of 10% by assuming adiabatic constant volume calculation. For the inputs of chemical state samples in WMR model to the graph search approaches, six temperature points at temperature increments of 20 K, 50 K, 150 K, 300 K, 550 K and 1000 K over the initial temperature of the target cases are selected.

6.1 Skeletal reduction of methane auto-ignition under high temperatures

The GRI-3.0 [28] mechanism with 53 species and 325 reactions is used for computing methane auto-ignition. Although GRI-3.0 is a relatively small mechanism compared to those of heavy fuels, the single-stage ignition is a good candidate for comparing the accuracy among the five methods under high temperature conditions. Twenty cases are run with conditions in the range of $T = \{1100 \text{ K}, 1300 \text{ K}\}$, $P = \{10 \text{ atm}, 40 \text{ atm}\}$ and equivalence ratio (ϕ) = $\{0.5, 0.8, 1.0, 1.2, 1.5\}$. The target species in the DRGEP-AStar related methods consist of CH_4 , O_2 , and N_2 , and the destination species contain CO_2 , H_2O and N_2 . Nine combinations can be made between the two groups but there are eight paths to be searched because the path of N_2 - N_2 is not needed. The target species in the DRG and DRGEP-Dijkstra methods consist of CH_4 , O_2 , N_2 , CO_2 , and H_2O . By setting different values of the cutoff level ε , skeletal mechanisms with different sizes can be developed. In Figure 4, the maximum relative error is plotted against the species number of the skeletal mechanism generated by various graph search approaches. The details of the species number, reaction number, maximum relative error of graph search methods, TSA and TSA-restart are summarized in Table 1. The red dashed line in Figure 4 denotes the 10% cutoff level that is acceptable for the subsequent reduction methods. If the maximum relative error is larger than 10% for the next species removal, the number of species and reactions, and the maximum relative error of the current skeletal mechanism are recorded in the second to fourth columns of Table 1, respectively. As seen in Figure 4 and Table 1, the DRGEP-AStar with Jacobian DIC is found to generate the smallest size of the skeletal mechanism (22 species) among the graph search approaches. Overall, the Jacobian DIC is seen to decrease the size of skeletal mechanism generated by the DRGEP methods using the same graph search algorithms. The AStar algorithm is found to perform better than the Dijkstra' algorithm with the same DICs. Although the TSA method is more time consuming than the graph search methods, the detailed mechanism can be reduced to 19 species satisfying the relative error threshold of 10% by

one-round running. Since the graph search methods can be used as the first-step reduction for a large mechanism, the TSA is run with the skeletal mechanisms as the initial mechanism shown in the second column of Table 1 until there is no species that can be removed to satisfy the 10% cutoff level. This exercise checks further reduction potential to the final skeletal mechanisms. The results in the last three columns of Table 1 indicate that the TSA-restart running initialized by the graph methods can lead to the identical 19-species skeletal mechanisms with TSA. In Figure 5, the comparison of methane ignition delay time between the detailed mechanism and the final 19-species skeletal mechanism is plotted. From the results, the high temperature region can be accurately predicted by the skeletal mechanism.

Figure 4. The maximum relative error against species number of skeletal mechanism developed by various graph search methods under high temperature conditions. The detailed mechanism is the GRI-3.0 mechanism [28] with 53 species.

Table 1

Figure 5. Comparison of methane ignition delay time between the detailed mechanism and the final 19-species skeletal mechanisms.

6.2 Skeletal reduction of n-heptane auto-ignition in NTC regions

For the graph search methods, the low-temperature combustion, Negative Temperature Coefficient (NTC) region and two-stage ignition, presents challenges to fulfill large scale reduction for a fixed threshold. In practice, the combustion process in engine conditions are mainly under these regions [30]. Therefore, n-heptane, which involves NTC region and two-stage ignition, is chosen as the next test fuel. The detailed mechanism by Lawrence Livermore National Lab (LLNL) v3.1 consisting of 654 species and 2827 reactions [2] was selected for reduction.

Thirty targets conditions covering the NTC regions are chosen in the range of $P = \{20 \text{ atm}, 40 \text{ atm}\}$, $\phi = \{0.5, 1.0, 2.0\}$ and $T = \{725\text{K}, 775\text{K}, 850\text{K}, 900\text{K}, 950\text{K}\}$ shown in Figure 6.

Figure 6. Thirty n-heptane target cases selected for LLNL v3.1 mechanism reduction with NTC regions.

Figure 7 presents the maximum relative error against species number of the skeletal mechanism generated by various graph search approaches and the results are summarized in Table 2. The red line indicates the 10% cutoff level. The records of the species number, reaction number, maximum relative error of graph search methods, TSA and TSA-restart are shown in Table 2. From the results in Figure 7 and Table 2, the DRGEP-Dijkstra with Jacobian DIC is found to generate the smallest skeletal mechanism (247 species) with 8% error among graph search methods. Similar to the conclusion drawn in the high temperature skeletal reduction for methane, the Jacobian DIC is shown to improve the DRGEP-based methods compared to the previously defined. However, with the AStar algorithm, the improvement is small, i.e., 258 species versus 264 species. The one-round TSA can reduce the detailed mechanism to a much smaller size with 183 species satisfying 10% maximum relative error. Then the further reduction potential is tested by repeatedly running TSA-restart based on the skeletal mechanisms in the second column of Table 2 until there is no species removal for the fixed 10% cutoff level. The results in the last three columns of Tables 2 suggest that all the graph search methods lead to smaller final skeletal mechanisms than the TSA method alone. The DRGEP-AStar with Jacobian DIC leads to the smallest mechanism of 117 species compared to 139 species of the TSA method by 16% difference. The restart results with TSA also reveal that DRGEP-AStar leads to a smaller final mechanism than DRGEP-Dijkstra (123 species). The better performance of DRGEP-AStar than the DRGEP-Dijkstra with Jacobian DIC may be fortuitous as both algorithms perform similarly well. Based on the above results, the application of Jacobian DIC makes the Dijkstra's algorithm and AStar algorithm perform better compared to the original DICs.

Figure 7. The maximum relative error against species number of skeletal mechanism developed by various graph search methods in NTC regions.

Table 2

In Figures 8 and 9, the ignition delay times of the final n-heptane skeletal mechanisms are compared to those from the detailed mechanism. As seen in the figures, the skeletal mechanisms can match the detailed mechanism very well with the prescribed 10% error bound. Under some partially premixed engine conditions, the laminar flame speed is of great interest in chemical mechanism reduction [36]. In this study, only 30 target ignition cases covering the NTC regions under high pressures are used for development of various skeletal mechanisms. It would be too costly to include flame speed computation during the development. At the end of the first-step reduction, the skeletal mechanisms from various graph-based approaches are checked for their accuracy in predicting flame speeds using PREMIX [37] before further reductions. Figures 10 and 11 present comparisons of computed flames against experimental data at various initial temperatures and pressures revealing that all the graph-based methods in this study can generate skeletal mechanisms with very high accuracy compared to the detailed mechanism for all the conditions considered. Moreover, the results confirm that despite of their smaller sizes, the skeletal mechanisms generated by using Jacobian DIC retain the accurate predictability for the laminar flame speeds.

Figure 8. Comparison of n-heptane ignition delay time between the detailed mechanism and the final skeletal mechanisms for equivalence ratio of 0.5, 1.0 and 2.0 under the pressure of 20 atm.

Figure 9. Comparison of ignition delay time between the detailed mechanism and the final skeletal mechanisms for equivalence ratio of 0.5, 1.0 and 2.0 under the pressure of 40 atm.

Figure 10. Comparison of laminar flame speed between the detailed mechanism and skeletal mechanisms generated by DRGEP-based methods for unburned gas temperature of 298 K, 400 K and 470 K under the pressure of 1 atm. Symbols are experimental data: triangle: Kumar et al. [38]; square: Davis and Law [39]; circle: Huang et al. [40]; pentagon: Sileghem et al. [41].

Figure 11. Comparison of laminar flame speed between the detailed mechanism and skeletal mechanisms generated by DRGEP-based methods for pressure of 1 atm, 2 atm and 5 atm under the unburned gas temperature of 353 K. Symbols are experimental data: triangle: Kumar et al. [38]; hexagon: Smallbone et al. [42]; star: Kelley et al. [43].

7. Conclusion

In this study, a Jacobian-based direct interactive coefficient is proposed and applied to the DRGEP-based method with the Dijkstra's algorithm and the AStar algorithm. Comparisons of resulting skeletal mechanisms are made between the original and newly developed approaches for both the high temperature methane and the low temperature n-heptane auto-ignition. Moreover, the trail-and-error approach called TSA is used to explore the further reduction potential for the graph search methods. The major results and findings are:

- For methane with high temperature conditions, the Jacobian DIC with the AStar algorithm has the best performance with 31% species less compared to the original DIC with Dijkstra's algorithm for the 10% limited error. By restarting TSA with the skeletal mechanisms generated by graph search methods, an identical mechanism with 19 species is reached.
- For n-heptane with NTC region conditions, the Jacobian DIC enhances both the two graph search algorithms. With the combination of the proposed Jacobian DIC and the AStar algorithm, the n-heptane skeletal mechanism generated by restarting TSA is 16% smaller (~20 species less) than the one developed from multi-round TSA for the 10% error.
- The comparisons of laminar flame speeds among the detailed mechanism and the various skeletal mechanisms developed by the graph-based approaches over a wide range of equivalence ratio, temperature, and pressure indicate that the chosen target cases covering the NTC region are sufficient to retain the chemistry of the laminar flames. Therefore, the DRGEP-based methods with Jacobian DIC are advantageous to be used as the first-step reduction for the subsequent reduction methods such as TSA.

Acknowledgments

This work at the University of California Berkeley was supported by National Science Foundation and U.S. Department of Energy under award No. CBET-1258653.

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Table 1

Comparison of methane skeletal mechanism sizes generated by different reduction methods*.

Method	# Species	# Reactions	Max. rel. error (%)	# Species by TSA-restart	# Reactions by TSA-restart	Max. rel. error (%) by TSA-restart
DRG	45	266	9.16	19	79	8.97
Dijkstra	32	165	9.07	19	79	8.97
AStar	26	138	9.16	19	79	8.97
Dijkstra-JAC	25	132	2.53	19	79	8.97
AStar-JAC	22	92	3.71	19	79	8.97
TSA	19	79	8.97	19	79	8.97

* Maximum relative error is set at 10%. The TSA-restart means keeping running TSA based on the skeletal mechanism in the 2nd column until there is no species removed by TSA. The detailed mechanism used is the GRI-3.0 with 53 species and 325 reactions.

Table 2

Comparison of n-heptane skeletal mechanism sizes generated by different reduction methods*.

Method	# Species	# Reactions	Max. rel. error (%)	# Species by TSA-restart	# Reactions by TSA-restart	Max. rel. error (%) by TSA-restart
DRG	341	1745	7.88	129	559	9.94
Dijkstra	273	1452	5.37	127	570	9.61
AStar	264	1395	9.23	118	528	9.84
Dijkstra-JAC	247	1198	7.96	123	536	9.58
AStar-JAC	258	1367	9.43	117	519	9.62
TSA	183	797	9.80	139	639	9.96

* Maximum relative error is set at 10%. The TSA-restart means keeping running TSA based on the skeletal mechanism in the 2nd column until there is no species removed by TSA. The detailed mechanism used is the LLNL v3.1 with 654 species and 2827 reactions.

Figure 1

Figure 2

Dijkstra

Figure 3

A-star

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 1. A 5-node directed graph with the DIC value for each edge.

Figure 2. Searching processes and results of the Dijkstra's algorithm through a DRGEP-based method.

Figure 3. Searching process and result of the AStar algorithm through a DRGEP-based method.

Figure 4. The maximum relative error against species number of skeletal mechanism developed by various graph search methods under high temperature conditions. The detailed mechanism is the GRI-3.0 mechanism [28] with 53 species.

Figure 5. Comparison of methane ignition delay time between the detailed mechanism and the final 19-species skeletal mechanisms.

Figure 6. Thirty n-heptane target cases selected for LLNL v3.1 mechanism reduction with NTC regions.

Figure 7. The maximum relative error against species number of skeletal mechanism developed by various graph search methods in NTC regions.

Figure 8. Comparison of n-heptane ignition delay time between the detailed mechanism and the final skeletal mechanisms for equivalence ratio of 0.5, 1.0 and 2.0 under the pressure of 20 atm.

Figure 9. Comparison of ignition delay time between the detailed mechanism and the final skeletal mechanisms for equivalence ratio of 0.5, 1.0 and 2.0 under the pressure of 40 atm.

Figure 10. Comparison of laminar flame speed between the detailed mechanism and skeletal mechanisms generated by DRGEP-based methods for unburned gas temperature of 298 K, 400 K and 470 K under the pressure of 1 atm. Symbols are experimental data: triangle: Kumar et al. [38]; square: Davis and Law [39]; circle: Huang et al. [40]; pentagon: Sileghem et al. [41].

Figure 11. Comparison of laminar flame speed between the detailed mechanism and skeletal mechanisms generated by DRGEP-based methods for pressure of 1 atm, 2 atm and 5 atm under the unburned gas temperature

of 353 K. Symbols are experimental data: triangle: Kumar et al. [38]; hexagon: Smallbone et al. [42]; star: Kelley et al. [43].