

# A directed relation graph method for mechanism reduction

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## Abstract

A systematic approach for mechanism reduction was developed and demonstrated. The approach consists of the generation of skeletal mechanisms from detailed mechanism using directed relation graph with specified accuracy requirement, and the subsequent generation of reduced mechanisms from the skeletal mechanisms using computational singular perturbation based on the assumption of quasi-steady-state species. Both stages of generation are guided by the performance of PSR for high-temperature chemistry and auto-ignition delay for low- to moderately high-temperature chemistry. The demonstration was performed for a detailed ethylene oxidation mechanism consisting of 70 species and 463 elementary reactions, resulting in a specific skeletal mechanism consisting of 33 species and 205 elementary reactions, and a specific reduced mechanism consisting of 20 species and 16 global reactions. Calculations for laminar flame speeds and nonpremixed counterflow ignition using either the skeletal mechanism or the reduced mechanism show very close agreement with those obtained by using the detailed mechanism over wide parametric ranges of pressure, temperature, and equivalence ratio.

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**Keywords:** Reduced mechanism; Directed relation graph

## 1. Introduction

Detailed chemical reaction mechanisms for hydrocarbon oxidation have been developed for the comprehensive description of the pathways and rates of the myriad elementary reactions and reaction intermediates that constitute these mechanisms over wide ranges of system parameters such as pressure, temperature, equivalence ratio, and residence time. However, their typically large sizes frequently prevent them from being readily applicable to the computation of even moderately complex combustion phenomena such as unsteady, two- and three-dimensional laminar

flames. Furthermore, their employment in the simulation of combustion phenomena frequently induces substantial differences in the time scales of the system variables because of the vastly disparate reactivities of the various chemical species. The resulting stiffness of the system can significantly restrict the application of many fast and simple numerical methods and thereby renders the problem difficult to solve. Thus, there exists much incentive to develop systematic methodologies that can reduce the detailed mechanisms to smaller sizes and with less stiffness.

Mechanism reduction can be conducted at two levels of detail. The first level is skeletal reduction, which eliminates the unimportant reactions and species based on either comprehensive consideration or for a particular application. Several techniques have been developed, each

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with its merits and restrictions. For example, two methods for identifying redundant species in large mechanisms were developed through reaction rate analysis and Jacobian analysis, respectively [1–3]. The method of reaction rate analysis assumes a species to be redundant if elimination of all its consuming reactions induces no significant error to the remaining species. This method is simple to use. However, it is time consuming due to the validation for each eliminated species. The method through Jacobian analysis can identify species coupled with the important species. However, it requires an iterative procedure [3], and the selection of threshold values is arbitrary [1]. The method of detailed reduction [4] can systematically identify the unimportant reactions by comparing its reaction rate with that of a pre-selected controlling reaction. The identification of the controlling reaction is however not easy, especially for large mechanisms, due to the lack of a universally rigorous definition of the controlling behavior and the possible change of controlling processes under different conditions. Furthermore, a slow reaction is not necessarily unimportant.

Lastly, as far as skeletal reduction is concerned, computational singular perturbation (CSP) can be used to identify and to eliminate only the elementary reactions that are not important for any species through the use of the importance index [5–7]. Consequently, the potential extent of reduction at the skeletal level is small. Reduction of species by CSP is realized only with the further assumption of the states of the reactions and species, which constitute the second level of reduction, to be discussed next.

The second level of reduction involves the application of partial equilibrium and quasi-steady-state (QSS) assumptions [8] to the skeletal mechanism, using the methods of reaction rate analysis with the criteria of small mole fractions, normalized net production rates, and sensitivity analysis [9–13]. These methods mostly require strong mechanism-dependent knowledge and could be inefficient to remove the modes of short time scale. The method of lifetime analysis [14] is partly empirical and subjected to occasional failure in identifying the QSS species. The intrinsic low-dimensional manifolds (ILDM) method is more rigorous mathematically [15], although the constant Jacobian assumption could reduce the accuracy while the demand for storage space is high due to the need for tabulation to solve the fast subspace. The CSP method [16–18] fully considers the time dependency of the Jacobian matrix and can accurately identify the fast modes, although the refinement procedure for the time-dependent Jacobian demands heavy computation time. Consequently, for practical purposes in generating static reduced mechanisms, CSP is often used together with the constant Jacobian assumption.

In the present study, we shall generate the skeletal mechanism by applying the theory of directed relation graph (DRG) to identify the unimportant species, and thereby the unimportant elementary reactions associated with them, based on a pre-set numerical criterion. While we shall defer the discussion of the merits of this method to the next section, it suffices to note herein that this method can generate skeletal mechanisms much faster than other available methods, and that the resulting skeletal mechanisms can predict the reaction rates of the remaining species with a definable accuracy. We shall apply this method to a detailed ethylene mechanism to generate a skeletal mechanism, which is reduced further through the use of CSP [7,16–18] and the QSS assumption. The final reduced mechanism consists of 16 lumped steps and 20 species, and shows excellent performance in mimicking the original detailed mechanism in the description of combustion phenomena of different nature, with wide parametric variations.

We shall sequentially present the reductions using the graph theory and CSP, and the results obtained therein as follows.

## 2. Skeletal reduction using directed relation graph

We first note that while it is straightforward to identify and to eliminate the unimportant elementary reactions that contribute negligibly to the production rate of every species, it is more complicated to identify and to eliminate the unimportant species because of the coupling of the species. For example, a species  $A$  can be strongly coupled to species  $B$  either directly if they appear together in a fast reaction or indirectly if each of them is strongly coupled to another species  $C$ , even if they themselves do not appear together in any reaction [1]. In the presence of such couplings, removal of a single species from the detailed mechanism may require the removal of a group of species strongly coupled to it. By the same reasoning, if it is necessary to keep a species in the skeletal mechanism, it is also necessary to keep the group of species strongly coupled to it.

The theory of directed relation graph is well suited to abstract the couplings among the species. Specifically, each node in a DRG represents a species in the detailed mechanism, and there exists an edge from vertex  $A$  to vertex  $B$  if and only if the removal of species  $B$  would directly induce significant error to the production rate of species  $A$ . That is, an edge from  $A$  to  $B$  means that  $B$  has to be kept to correctly evaluate the production rate of  $A$ .

Consider the expression of the production rate of, say, species  $A$ :

$$R_A = \sum_{i=1,I} \nu_{A,i} \omega_i, \quad (1)$$

$$\omega_i = k_{fi} \prod_{j=1}^K C_j^{v'_{ij}} - k_{bi} \prod_{j=1}^K C_j^{v''_{ij}}, \quad (2)$$

$$k_{fi} = [A_i T^{m_i} \exp(-E_i/RT)] F_i, \quad (3)$$

where the subscripts  $i$  and  $j$ , respectively, designate the  $i$ th elementary reaction and the  $j$ th species,  $v_{A,i}$  is the stoichiometric coefficient of species  $A$ ,  $\omega_i$  is the production rate,  $k_{fi}$  and  $k_{bi}$  are the forward and backward reaction rates, respectively,  $C_j$  is the molar concentration,  $v'_{ij}$  and  $v''_{ij}$  are respectively the forward and backward stoichiometric coefficients,  $A_i$  is the frequency factor,  $T$  is the temperature,  $E_i$  is the activation energy, and  $F_i$  is a correction term that includes the concentrations of the third body species, fall-off effects, and other special correction terms. To quantify the direct influence of one species on another, a normalized contribution of species  $B$  to the production rate of species  $A$ ,  $r_{AB}$ , can be defined as:

$$r_{AB} \equiv \frac{\sum_{i=1,I} |v_{A,i} \omega_i \delta_{Bi}|}{\sum_{i=1,I} |v_{A,i} \omega_i|}, \quad (4)$$

$$\delta_{Bi} = \begin{cases} 1 & \text{if the } i\text{th elementary reaction} \\ & \text{involves species } B, \\ 0 & \text{otherwise.} \end{cases} \quad (5)$$

It is seen that if the normalized contribution  $r_{AB}$  is sufficiently large, the removal of species  $B$  from the skeletal mechanism is expected to induce significant error on the production rate of species  $A$ . Consequently, if  $A$  has to be kept,  $B$  should also be kept. In such a case, we say species  $A$  strongly depends on species  $B$ .

To quantify the dependence of  $A$  on  $B$ , we define a small threshold value  $\varepsilon$  such that, for  $r_{AB} < \varepsilon$ , the dependence can be considered to be negligible, and there is no edge from  $A$  to  $B$ . Therefore, the DRG can be constructed by the following rules:

- (1) Each node in DRG is uniquely mapped to a species in the detailed mechanism.
- (2) There exists a directed edge from  $A$  to  $B$  if and only if  $r_{AB} \geq \varepsilon$ .

Thus, species  $A$  depends on species  $B$  if and only if there exists a directed path from  $A$  to  $B$  in DRG, i.e.,  $B$  is reachable from  $A$ . For each species  $A$ , there exists a group of species, which are reachable from  $A$ , and this set of species is defined as the dependent set of  $A$ , denoted as  $S_A$ . If species  $A$  is an important species to be kept in the skeletal mechanism, its dependent set  $S_A$  should be kept as well.

Figure 1 shows the typical relations between the species in a DRG. The arrow shows the direction of dependence of one species on another, with its width indicating the strength of the depen-

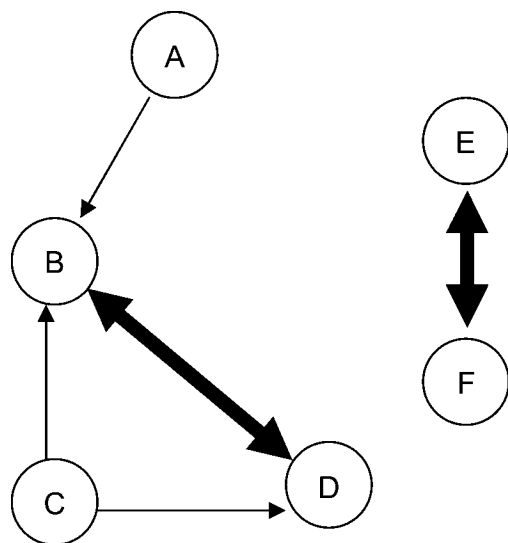


Fig. 1. A directed relation graph showing typical relations of the species.

dence. Thus, for a species  $A$  that has to be kept, it is seen that  $A$  depends on  $B$ , but  $B$  does not depend on  $A$ . Furthermore, since species  $B$  and  $D$  are strongly coupled, they form the dependent set  $\{B, D\}$  of  $A$ , and has to be kept to correctly predict  $A$ . However, species  $C$ ,  $E$ , and  $F$  can be eliminated because they are not required by either  $A$  or any species in the dependent set of  $A$ . Furthermore, species within the strongly coupled groups,  $\{B, D\}$  and  $\{E, F\}$ , should be either kept or eliminated together.

Procedurally, given the rates of the elementary reactions, the DRG can be constructed in linear time proportional to the number of reactions by evaluating the contribution of each elementary reaction,  $\omega_i$ , to the edges affected by it, as shown in Eq. (4). Subsequently, we select the “starting set” of species, which has to be kept. The starting set can simply consist of a single species, the fuel, because through it the oxidizer, as well as the radicals that are products of reactions involving them, is coupled. If we are also interested in such auxiliary phenomena as  $\text{NO}_x$  formation, in addition to oxidation,  $\text{NO}$  should also be included as a starting species. Note that for simplicity in the present study, a species is not considered to be involved in an elementary reaction in Eq. (4) if it only participates as a third body species. Thus, inert species are also included in the starting set, and consequently they are automatically retained in the skeletal mechanism.

Consequently, for each starting species  $A$ , a deep first search (DFS) is applied to the graph to identify the dependent set  $S_A$  recursively. By identifying the dependent set for each starting species, the species constituting the skeletal mecha-

nism is then the union of these dependent sets. The elementary reaction set of the skeletal mechanism can therefore be obtained by eliminating all the elementary reactions in the detailed mechanism, which do not contain any of the species in the skeletal mechanism.

The skeletal mechanism obtained has errors bounded by the user-specified small value of  $\varepsilon$  for the conditions under which it is developed. To obtain such a skeletal mechanism over a sufficiently wide range of parameters such as those for pressure, temperature, equivalence ratio, and residence time, a group of points in the parametric space are sampled for typical applications. While these applications can include the homogeneous systems of the perfectly stirred reactor (PSR) and auto-ignition, and diffusive systems of planar laminar flame propagation as well as counterflow ignition and extinction, it is however more appropriate and expedient to base the sampling on homogeneous systems because they are chemistry-controlled phenomena and because of the significantly reduced calculation time. Furthermore, the use of the PSR is expected to capture the high-temperature chemistry relevant for burning and extinction, while auto-ignition should describe the low-temperature through moderately high-temperature ignition chemistry. Given a sufficiently wide range of pressure, equivalence ratio, and initial temperature, the sampled data points should cover most of the typical conditions under which the mechanism is to be applied.

Consequently, for each application, a sub-skeletal mechanism can be obtained for each sampling point, and the union of all these sub-skeletal mechanisms constitutes the application-specific skeletal mechanism that is valid at every sampled point in the parametric space, within  $\varepsilon$  accuracy. Finally, by forming the union of these application-specific skeletal mechanisms, a comprehensive skeletal mechanism, valid for all sampled applications, is obtained.

Strictly speaking, the skeletal mechanism developed using DRG should only be applied to those applications and parametric spaces based on which it is developed. However, it is often the case that a skeletal mechanism developed from simple applications can be applied to more complicated simulations and still has satisfactory accuracy [19]. For example, it is reasonable to apply the skeletal mechanisms developed from the homogeneous systems of PSR and auto-ignition to problems with diffusive transport, provided some sort of pre-validation is performed. Indeed, this is often the only option in acquiring comprehensive skeletal mechanisms from very large detailed mechanisms for calculations involving flames.

We also note that skeletal mechanisms with different levels of accuracy can be obtained by assigning different threshold  $\varepsilon$  values. The smaller

the  $\varepsilon$ , the larger is the skeletal mechanism such that it will converge to the detailed mechanism as  $\varepsilon$  approaches zero. Furthermore, it is reasonable to expect that strongly coupled groups frequently exist in large mechanisms, and as such intra-group couplings are strong while inter-group couplings are relatively weak. Consequently, the number of species in the skeletal mechanism could vary abruptly as the threshold value  $\varepsilon$  is varied, and jumps in the number of species would occur around certain values of  $\varepsilon$  across which a group of strongly coupled species is eliminated. The existence of such jumps facilitates selection of specific candidate threshold values in that reduction of the mechanism size is most efficient neighboring such jumps.

We now discuss the merits of the DRG in the elimination of unimportant species and elementary reactions as compared to the previous method of Jacobian analysis [1–3], both of which identify the species, which are strongly coupled to the important species. First, DRG significantly reduces the time cost for the reduction process by exploiting Eq. (4), which is much easier to compute as compared to the Jacobian analysis. Furthermore, DRG can identify all the candidate skeletal mechanisms, sorted by accuracy, in a single run, with the time linearly proportional to the number of edges in the graph, while the Jacobian analysis method requires iterations to identify a single skeletal mechanism. Second, DRG provides a universally specifiable threshold value normalized between 0 and 1, which at the same time specifies the upper error bound for the reduced mechanism. The above two features together render it possible for mechanism reduction over wider ranges of the parametric space, and with the possibility of real time, dynamic reduction. Third, since the development of skeletal mechanism involves the elimination of species and reactions, it is more appropriate to directly evaluate the effect of the elimination, which is expressed as in Eq. (4), rather than through the Jacobian, which is a linear approximation calculated by local perturbation of species concentration. This is particularly true when there are many terms in the Jacobian matrix, which are nonlinear functions of the species concentrations.

### 3. Further reduction based on QSS assumptions

Since a skeletal mechanism contains only elementary reactions, it is applicable in the same manner as the detailed mechanism. However, the size of a skeletal mechanism is usually still too large for many demanding simulations. Further reduction can be accomplished by eliminating species with short time scales by approximating them to be in steady state. The removal of the short time scales effectively reduces the stiffness of the

system as well as the number of differential equations. This combined benefit usually dominates over the costs incurred by the internal algebraic iteration in solving the concentrations of the QSS species, and consequently results in an overall time saving in using QSS-based reduced mechanisms.

The short time scales can be identified by several methods, such as those of ILDM and CSP; we shall use the latter [7,16–18] in the present study. Briefly, the time scales of independent modes are summed to an indicator weighed by sufficiently large radical pointers, the reciprocal of which can be defined as the time scale of the species. A critical time scale is selected to normalize the time scales of species, such that the time scale of the major species controlling the overall reaction rate of the system is normalized to unity. Species are considered to be QSS if their normalized time scales  $\bar{\tau}_i$  are smaller than a specified critical value,  $\alpha$ ,

$$\bar{\tau}_i < \alpha, \quad \bar{\tau}_i = \tau_i / \tau_{\text{ch}}, \quad \tau_i = -1 / \sum_{r=1}^K \mathbf{R}_{ir} \lambda_r, \quad (6)$$

where  $\tau_{\text{ch}}$  is the critical time for the progress of the chemical reaction,  $K$  is the total number of species;  $\mathbf{R}_{ir}$  is the radical pointer associated with the  $i$ th mode and the  $r$ th species, and  $\lambda_r$  is an eigenvalue of the  $r$ th mode.

The selection of the critical time scale  $\tau_{\text{ch}}$  depends on the system. The extinction time for the PSR, and the auto-ignition time, can be, respectively, used as the characteristic time for extinction and ignition problems.

## 4. Demonstration of methodology: ethylene

### 4.1. Skeletal mechanism

We have selected the detailed ethylene oxidation mechanism of [20] for demonstration of the present reduction procedure and capability. This detailed mechanism consists of 70 species and 463 elementary reactions. PSR and auto-ignition were used as the data source for reduction, as mentioned earlier, with pressure ranging from 0.1 to 30 atm, equivalence ratio from 0.7 to 1.3, initial temperature of 300 K for PSR and 1000 to 1800 K for auto-ignition, and residence time covering the entire ignition and extinction ranges. Data points were densely sampled over the above parametric space to ensure that all specific relations among the species can be represented by the sample set. In the present study, more than 1000 data points were sampled, although it was found that much less sampling points, say about 100, are adequate for the specified accuracy. The entire process for the DRG reduction, using all the sampled data points, takes only about 1 s on a moderate PC.

Ethylene was selected as the starting species. Figure 2 shows the dependence of the number of species in the skeletal mechanism on the value of  $\varepsilon$  selected. It is seen that, for very small  $\varepsilon$ , say 0.01, the number of species in the skeletal mechanism is close to that of the detailed mechanism. This number then decreases as  $\varepsilon$  increases, as expected. As  $\varepsilon$  approaches unity, only the species initially selected remains in the skeletal mechanism since all the couplings are truncated. Figure 2 also shows that there exist jumps in the number of species at certain values of  $\varepsilon$ , most prominently around  $\varepsilon = 0.02$  and 0.14. These jumps are due to the elimination of strongly coupled species groups as anticipated earlier. Since these groups should be either eliminated or kept together, the accuracy criterion  $\varepsilon$  should be selected either before or after such jumps. The identification of such strongly coupled groups can significantly reduce the number of candidate skeletal mechanisms, and consequently save the effort of mechanism validation. We have consequently selected the criterion  $\varepsilon = 0.16$ , an  $O(0.1)$  quantity, as the value, which is just slightly larger than that at the second jump, and obtained a skeletal mechanism consisting of 33 species, as shown in Fig. 2. The species constituting this skeletal mechanism are:  $\text{H}_2$ ,  $\text{H}$ ,  $\text{O}$ ,  $\text{O}_2$ ,  $\text{OH}$ ,  $\text{H}_2\text{O}$ ,  $\text{HO}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{C}$ ,  $\text{CH}$ ,  $\text{CH}_2$ ,  $\text{CH}_2^*$ ,  $\text{CH}_3$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{HCO}$ ,  $\text{CH}_2\text{O}$ ,  $\text{CH}_2\text{OH}$ ,  $\text{CH}_3\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_3$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_5$ ,  $\text{HCCO}$ ,  $\text{CH}_2\text{CO}$ ,  $\text{CH}_2\text{CHO}$ ,  $n\text{-C}_3\text{H}_7$ ,  $\text{C}_3\text{H}_6$ ,  $\alpha\text{-C}_3\text{H}_5$ ,  $\text{Ar}$ , and  $\text{N}_2$ . By eliminating all elementary reactions in the detailed mechanism that has any reactants or products not included in the above set of species, 205 elementary reactions were retained for the skeletal mechanism.

It is reasonable to expect that skeletal mechanisms of even smaller sizes can be obtained

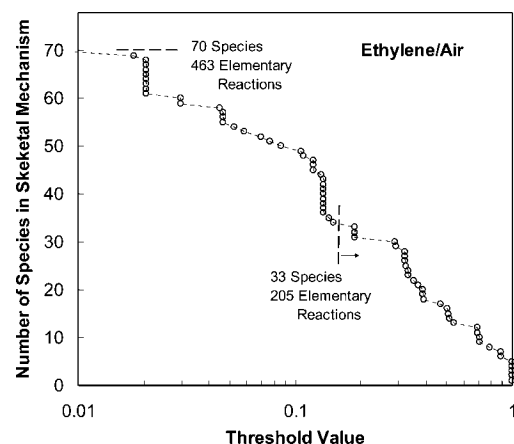


Fig. 2. Dependence of the species number of the skeletal mechanism on the threshold value  $\varepsilon$ , specified to truncate the weak relations of the species. The jumps in species number show the existence of strongly coupled groups.



with the same accuracy threshold by restricting the application and parametric range to those of special cases. For example, we can restrict the phenomena of interest to those involving only ignition at all pressures, or burning and extinction at all pressures, or ignition and burning at atmospheric pressure, etc. However, we have found that the additional number of species that can be further eliminated is rather modest, say only a few. This is ostensibly due to the fact that although we have imposed additional restrictions on the phenomena or parametric range of interest in developing the specialized mechanisms, the remaining phenomena and parametric ranges are still sufficiently extensive such that the chemistry identified for the comprehensive description is mostly retained. We are therefore led to the belief that it is preferable that skeletal reduction be developed for comprehensive coverage because the additional small reduction for restricted descriptions is not worth the loss of comprehensiveness. On the other hand, we also recognize the potential of significant reduction with the method of the DRG for *severely* restricted parametric range, e.g., when performing dynamic reduction—a topic that merits further investigation.

#### 4.2. Reduced mechanism

The 33-species skeletal mechanism developed above was further reduced by using CSP to identify the QSS species. By again using PSR and auto-ignition as the databases, the time scales for each species were calculated for each data point, with their characteristic times being those of the extinction and ignition times, respectively. The longest normalized time for each species, obtained through Eq. (6), was taken as the characteristic time scale for this species because it describes approximately its worst-case characteristic time. Figure 3 shows the number of species in the reduced mechanism for the normalized time scales of the radicals in the worst-case of the entire parametric range. A species is assumed to be a QSS species if its worst-case normalized time scale is shorter than the specified threshold value,  $\alpha$ . Consequently, the species indicated in Fig. 3 are those assumed to be QSS with progressive extent of reduction.

Figure 4 plots the normalized time scales of most of the radicals for PSR and auto-ignition. The larger of these two values represents the worst-case, global consideration. It is seen that most of the fast-reacting radicals have short time scales for both the extinction and ignition cases. The high reactivity of these radicals renders them ideal QSS candidates over the entire parametric range, being valid for low to high temperatures, lean and rich fuel compositions, and whether or not the radical pool is established.

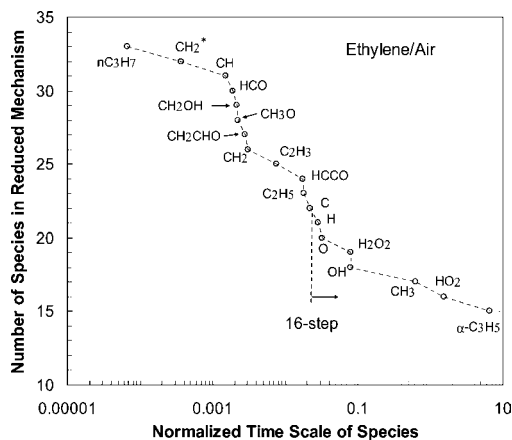


Fig. 3. The number of species in the reduced mechanism as a function of the critical normalized time scale of the species,  $\tau_{ch}$ .

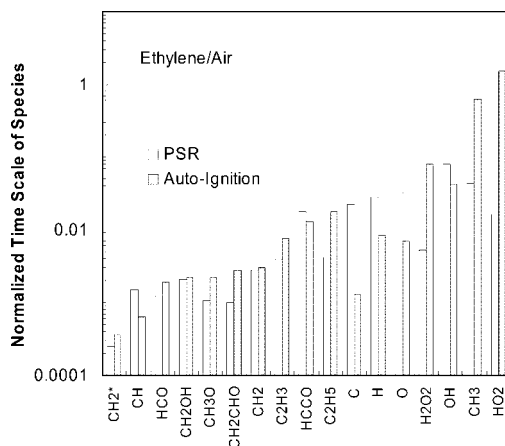


Fig. 4. Comparison of the normalized time scales of the radicals for PSR and auto-ignition for ethylene/air mixture.

Based on the sequencing of Fig. 3, a critical value of  $\alpha = 0.025$  was selected, resulting in a 16-step reduced mechanism, with the QSS species being: C, CH, CH<sub>2</sub>, CH<sub>2</sub><sup>\*</sup>, HCO, CH<sub>2</sub>OH, CH<sub>3</sub>O, C<sub>2</sub>H<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, HCCO, CH<sub>2</sub>CHO, and *n*-C<sub>3</sub>H<sub>7</sub>. This selection includes the most reactive radicals as the QSS species but retains the hydrogen reaction kernel intact. It is expected to keep the error at a low level since H is obviously an important radical for almost any hydrocarbon fuel oxidation. Indeed, further exploration with H and some additional species being assumed to be QSS resulted in significant inaccuracies in their performance and sometimes even difficulty in convergence. It may also be noted that a previous study on methane reduc-

tion using CSP [5] found critical values of the order of  $10^{-2}$  for  $\alpha$ , which agrees with the present value.

Figure 4 also shows that there exist radicals, such as  $\text{H}_2\text{O}_2$  and  $\text{HO}_2$ , which have much longer time scales for ignition than extinction. Such different time scales imply that these species may be very good QSS candidates for high-temperature burning and extinction, but very poor QSS candidates for ignition. Therefore, there again exists the possibility of developing specialized reduced mechanisms for specific applications. The consideration for specialization is different here than that for skeletal reduction in that, because of the small size of the reduced mechanism as compared to that of the skeletal mechanism, a further decrease in the number of global reactions by even two or three represents a proportionately larger extent of simplification.

## 5. Validation

To demonstrate the accuracy of the derived skeletal and reduced mechanisms, the results of PSR and auto-ignition are compared with those of the detailed mechanism. Figure 5 shows the temperature profiles calculated using PSR with the detailed, skeletal, and reduced mechanisms for the entire pressure, equivalence ratio, and residence time range of the reduction process. It is seen that both the skeletal and reduced mecha-

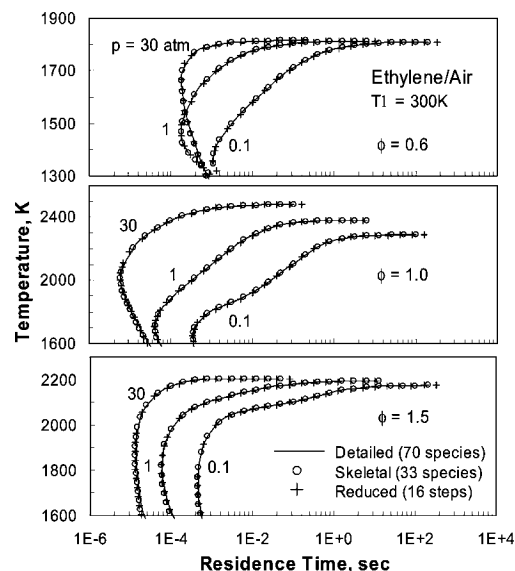


Fig. 5. The dependence of temperature on the residence time of PSR between the detailed, skeletal, and reduced mechanisms for ethylene/air mixtures at various pressures and equivalence ratios.

nisms track the temperature profiles almost exactly. Figure 6 shows the ignition time calculated using these mechanisms for the entire range of pressure, equivalence ratio, and initial temperature of the reduction process. It is seen that the skeletal mechanism again agrees very closely with the detailed one for the entire parameter range, exhibiting only hardly visible deviations for the high-pressure and high-initial temperature conditions. It is to be emphasized that while a close agreement is to be expected because the performance of the PSR and auto-ignition is the criterion based on which the skeletal and reduced mechanisms are developed, the very close agreement obtained is noteworthy.

We next extend our comparison to systems that are not part of the reduction process and are also more complex, involving diffusive transport. Figure 7 shows the calculated laminar flame speeds for the pressure range of 0.2–30 atm and equivalence ratio range of 0.55–1.7. It is seen that the comparison is still quite close for the entire parametric range, with maximum relative errors of a few percent. Figure 8 shows the calculated ignition temperature in nonpremixed counterflow ignition for the pressure range of 0.3–30 atm. Very close agreement is again observed. In both situations the inaccuracies seem to have incurred in the skeletal reduction stage.

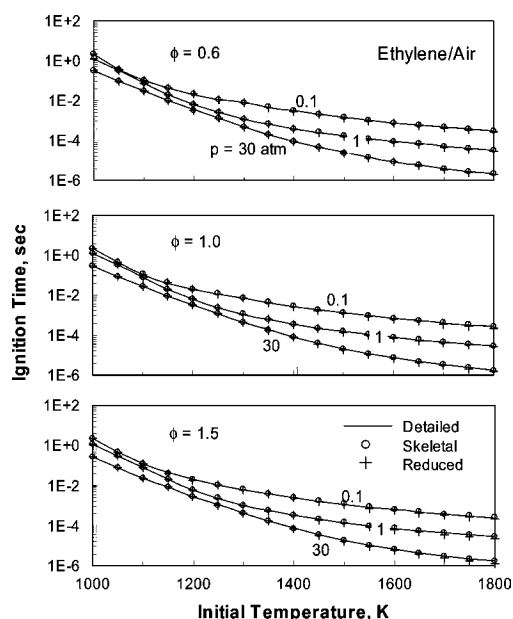


Fig. 6. The dependence of auto-ignition time on the initial temperature under constant pressure and enthalpy between the detailed, skeletal, and reduced mechanisms for ethylene/air mixture at various pressures and equivalence ratios.

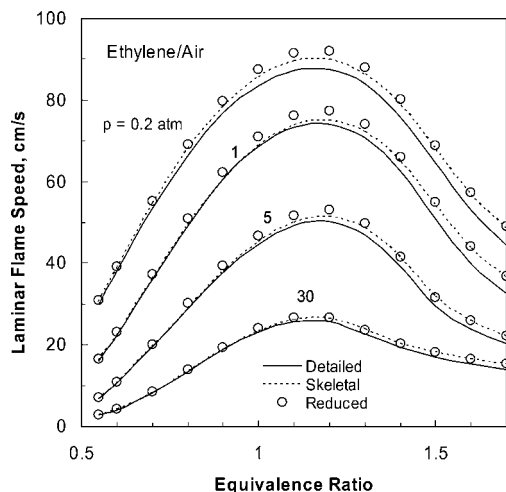


Fig. 7. The dependence of the laminar flame speed on the equivalence ratio between detailed, skeletal, and reduced mechanisms for ethylene/air flames at various pressures.

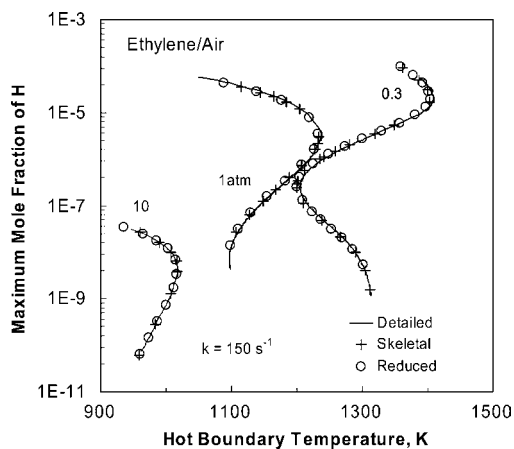


Fig. 8. The dependence of maximum mole fraction of the H radical on the hot boundary temperature of counterflow ignition between detailed, skeletal, and reduced mechanisms for ethylene/air mixtures at various pressures.

## 6. Concluding remarks

In the present investigation, we have successfully applied the method of directed relation graph to the reduction of detailed reaction mechanism to the level of skeletal mechanism, with specified accuracy. Strongly coupled species groups were observed in the reduction process, hence facilitating the identification of candidate skeletal mechanisms by eliminating or retaining the strongly coupled species in groups. The skele-

tal mechanism identified for ethylene oxidation, consisting of 33 species and 205 reactions, was found to mimic the performance of the detailed mechanism with high fidelity, not only for the homogeneous systems of PSR and auto-ignition based on which the mechanism was developed, but also for the diffusive systems of laminar flame propagation and counterflow ignition. The latter agreement demonstrates the dominance of chemistry in species coupling, and supports the utility of the present approach towards developing skeletal mechanisms for complex systems involving diffusive transport. Furthermore, because of the adoption of fast algorithms described in the above sections, such a reduction can be computationally accomplished very rapidly. Consequently, it holds the potential for further application and development in two directions: the reduction of extremely large detailed mechanisms consisting of hundreds of species and thousands of reactions, and its implementation for dynamic reduction in large simulation programs.

We have also shown that, by identifying the QSS species using CSP, this ethylene skeletal mechanism can be simplified further to a reduced mechanism consisting of 20 species and 16 semi-global reactions. High fidelity in simulation was again demonstrated.

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