Systematic Approach To Obtain Analytic Solutions of Quasi Steady State Species in Reduced Mechanisms

Tianfeng Lu* and Chung K. Law

Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey 08544

Received: July 14, 2006; In Final Form: September 23, 2006

A systematic approach was developed to obtain analytic solutions for the concentrations of the quasi steady state (QSS) species in reduced mechanisms. The nonlinear algebraic equations for the QSS species concentrations were first approximated by a set of linear equations, and the linearized quasi steady state approximations (LQSSA) were then analytically solved with a directed graph, namely a QSSG, which was abstracted from the inter-dependence of QSS species. To obtain analytic solutions of high computational efficiency, the groups of strongly connected QSS species were first identified in the QSSG. The inter group couplings were then resolved by a topological sort, and the inner group couplings were solved with variable elimination by substitution. An efficient algorithm was developed to identify a near-optimal sequence for the variable elimination process. The proposed LQSSA-QSSG method was applied to generate a 16-step reduced mechanism for ethylene/air, and good accuracy and high efficiency were observed in simulations of auto-ignition and perfectly stirred reactors with the reduced mechanism.

1. Introduction

The importance of applying detailed chemical kinetics in combustion simulations is now generally recognized. It is further recognized that, limited by current computer power, it is necessary to reduce these mechanisms to smaller sizes and with less stiffness such that the simulations are efficient and reasonably accurate. The need is particularly relevant in studies on turbulence and flow fields with complex geometries.

Various methods have therefore been developed for mechanism reduction, generally falling within the two major categories of skeletal reduction and reduction based on time-scale analysis. In skeletal reduction unimportant reactions and species are eliminated from the detailed mechanisms with negligible reduction error. Representative methods include sensitivity analysis,[1] principal component analysis,[2] Jacobian analysis,[3] detailed reduction,[4] computational singular perturbation (CSP),[5,6] optimization,[7] directed relation graph (DRG),[8−10] and DRG with error propagation.[11]

While skeletal mechanisms are smaller than the detailed ones, they are typically still stiff in that many radicals with short time scales are important species and cannot be eliminated in skeletal reduction. To remove the stiffness, methods based on time scale analysis, such as quasi steady state approximation (QSSA)[12−18] and rate-controlled constrained equilibrium,[19] can be exploited. More systematic approaches involve the separation of fast and slow subspaces by decoupling the Jacobian matrix, notably those of intrinsic low dimensional manifold (ILDM)[20] and CSP.[21] Because time scale separation requires time-consuming matrix operations, as well as iterations in many cases, it frequently needs to be combined with methods of tabulation, such as in-situ adaptive tabulation (ISAT)[22] and pre-imaged curves.[23] On the other hand, the QSSA approach, developed almost a century ago,[24,25] is simple to apply and has been widely adopted in studies on mechanism reduction in the last two decades.[12−18] Specifically, a systematic procedure for lumping elementary reactions into semi-global reactions for QSSA based reduction was developed,[14] the error induced by QSSA was analyzed,[26] and the effects of QSSA on the element conservation and entropy production were studied.[27]

The consequence of invoking QSSA is frequently the need to solve a set of coupled, nonlinear, algebraic equations to obtain the concentrations of the quasi steady state (QSS) species, which are required to evaluate the global reaction rates. In most of the previous studies, these equations were solved by algebraic iterations, which may require a large number of computation loops to converge. As such, the time savings gained by the elimination of species and reactions are compromised, rendering the reduced mechanisms inefficient to apply.[28] Even worse, the algebraic iterations may diverge and consequently lead to failure in obtaining trustable final solutions in large simulations. To resolve this problem, empirical methods have been applied to truncate terms in the nonlinear algebraic equations[29] such that the resulting system is sufficiently simple to be solved analytically. The errors associated with such truncations, however, are frequently difficult to assess. It is therefore of interest to develop a systematic and efficient approach to obtain accurate analytic solutions for the equations of QSSA. In response to such a need, a method based on graph theory was developed to obtain analytic solutions for the QSS species concentrations with user specified accuracy, and as such significantly improves the efficiency and applicability of QSS based reduced mechanisms. This method is presented in the following.

2. Methodology

A QSS species typically features a fast destruction time scale such that its small or moderate creation rate is quickly balanced by the self-depleting destruction rate, causing it to remain in low concentration after a transient period. The net production rate of the QSS species is therefore negligible compared with both the creation and the destruction rates, resulting in an

---

* To whom correspondence should be addressed. E-mail: tlu@princeton.edu.

10.1021/jp064482y CCC: $33.50

algebraic equation for its concentration. If a system consists of multiple QSS species, the algebraic equations are in general nonlinearly coupled, and analytic solutions are difficult to obtain. Consequently, these nonlinear equations are frequently solved by algebraic iterations. In the following we shall, however, demonstrate that the nonlinear terms are not important in many instances such that the nonlinear system can be approximated in a rational manner by a set of linear equations.

2.1. Linearized Quasi Steady State Approximation (LQSSA). In a reaction mechanism consisting of I irreversible elementary reactions and K species, with the first N of which assumed to be in steady state without loss of generality, the group of algebraic equations of QSSA can be expressed as

$$\omega_{C,i} = \omega_{D,i} \qquad i = 1, 2, ..., N$$

$$\omega_{\mathrm{C},i} = \sum_{j=1}^{I} \nu''_{i,j}\Omega_j \qquad \omega_{\mathrm{D},i} = \sum_{j=1}^{I} \nu'_{i,j}\Omega_j \qquad \Omega_j = k_j \prod_{k=1}^{K} x_k^{\nu'_{k,i}} \tag{1}$$

where the subscripts i, j, and k indicate the ith QSS species, the jth reaction, and the kth species respectively, ω_C and ω_D are the creation and destruction rates, respectively, x is the mole concentration, ν' and ν'' are the stoichiometric coefficients of the reactants and products respectively, Ω is the reaction rate, and k is the product of the Arrhenius rate expression and relevant rate corrections, such as the third body concentration and the falloff correction.

Equation 1 is nonlinear in general in terms of x_k, mostly because there are frequently reactions containing more than one QSS reactants, resulting in nonlinearity in Ω_j. While an analytic solution of eq 1 is in general not available, we recognize that the concentrations of QSS species are typically small such that the collision frequency of two QSS species is small. Consequently, reactions with more than one, mostly two, QSS reactants may not be important in the mechanism in most cases. Furthermore, it is well recognized that the effects of QSS species in the third body concentration and other correction terms in k_j are typically negligible. As such, after the unimportant reactions and species are eliminated from detailed mechanisms by skeletal reduction, it is expected that the existence of important nonlinear terms in QSS relations for skeletal mechanisms is of low probability, and a linear approximation of the equations is likely to exist. This point will be demonstrated in section 3 with ethylene as an example.

To assess the importance of the nonlinear terms, the normalized contributions of the nonlinear terms to the destruction and creation rates of the ith QSS species can be quantified as

$$\alpha_i = \frac{\sum_{j=1}^{I} \nu'_{i,j}\Omega_j\delta_j}{\omega_{\mathrm{D},i}} \qquad \beta_i = \frac{\sum_{j=1}^{I} \nu''_{i,j}\Omega_j\delta_j}{\omega_{\mathrm{C},i}} \tag{2}$$

where

$$\delta_j = \begin{cases} 1, \text{ if reacton } j \text{ has more than one QSS reactants} \\ 0, \text{ otherwise} \end{cases}$$

The nonlinear terms can therefore be eliminated from the QSS relations for a given reaction state if

$$\alpha_{\max} < \epsilon \qquad \text{and} \qquad \beta_{\max} < \epsilon \tag{3a}$$

$$\alpha_{\max} = \max_{i=1,...,N}(\alpha_j) \qquad \beta_{\max} = \max_{i=1,...,N}(\beta_j) \tag{3b}$$

where ϵ is a user-specified small threshold value, for example 0.1. Furthermore, if (3) is satisfied for all the reaction states of interest, the nonlinear terms can be completely eliminated, and the QSS relations in (1) are then approximated by a set of linear equations:

$$D_i x_i = \sum_{k \neq i} C_{ik} x_k + C_{i0} \qquad i = 1, 2, ..., N$$

$$D_i = \frac{\omega_{\mathrm{D},i}}{x_i} \qquad C_{ik} = \frac{\sum_{j=1}^{I} \nu''_{i,j}\Omega_j \operatorname{sign}(\nu'_{k,j})}{x_k}$$

$$\operatorname{sign}(\nu'_{k,j}) = \begin{cases} 1, \text{ if } \nu'_{k,j} > 0 \\ 0, \text{ if } \nu'_{k,j} = 0 \end{cases}$$

$$C_{i0} = \sum_{j=1}^{I} \nu''_{i,j}\Omega_j\delta'_j$$

$$\delta'_j = \begin{cases} 1, \text{ if reacton } j \text{ has no QSS reactant} \\ 0, \text{ otherwise} \end{cases} \tag{4}$$

It is readily seen that D_i, C_{ik}, and C_{i0} are independent of QSS species concentrations and as such are treated as constants in solving x_i. It is further noted that D_i is positive, and C_{ik} and C_{i0} are non-negative. This observation will be exploited in solving eq 4 in the following sections.

We next note that although the linear equations in eq 4 can be solved with Gaussian elimination, the time complexity is a cubic function of the number of QSS species. Furthermore, though algebraic iterations can be more efficient because the coefficient matrix in eq 4 is frequently sparse, the procedure may suffer from the difficulty in convergence. The computation, however, can be greatly facilitated by deriving an analytic solution based on the sparse coefficient matrix. This was accomplished in the present study through graph theory, to be discussed next.

2.2. QSS Graph (QSSG). *2.2.1. Graph Construction.* To obtain a sequence to solve eq 4, it is transformed to the following standard form:

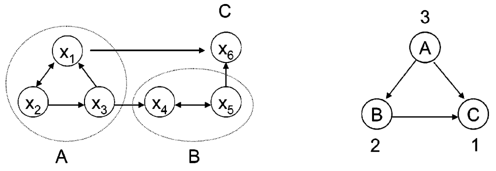
$$x_i = \sum_{j \neq i} A_{ij} x_j + A_{i0} \qquad i = 1, 2, ..., N \tag{5}$$

where

$$A_{ij} = \frac{C_{ij}}{D_i} \qquad A_{i0} = \frac{C_{i0}}{D_i}$$

It is seen that A_{ij} and A_{i0} are both non-negative in that D_i is positive, and C_{ij} and C_{i0} are non-negative, as mentioned earlier. If $A_{ij} > 0$, the concentration x_j is needed to directly solve for x_i in eq 5. Such directed requirement of one QSS species by another can be mapped to a directed graph, namely the QSSG, in which each QSS species is a vertex, and there is an edge $x_i \rightarrow x_j$ if and only if $A_{ij} > 0$. A representative configuration of QSSG is shown in Figure 1a and will be discussed later.

In rare cases, all equations in (5) are explicit, which means that there is a sequence of i in which the equations can be solved one after another without substitution. This indicates an acyclic QSSG, such that the graph can be transformed to a tree structure, and the solution of each node x_i only requires the information of the nodes in the subtree rooted by x_i. In most practical problems, some subsets of the QSS species are strongly coupled and cycles exist in QSSG. In such cases, the QSS species can be decomposed into groups. The inner-group couplings of the



(a) (b)

Figure 1. Sample QSSG showing (a) the existence of SCCs, which are enclosed in dotted circles, and (b) the acyclic graph derived from (a) by treating each SCC as a composite vertex. The topological order of vertices is marked in (b), indicating the sequence in which the SCCs are to be solved, e.g., $\{x_6\} \rightarrow \{x_4, x_5\} \rightarrow \{x_1, x_2, x_3\}$.

species form cycles in QSSG, and the inter-group couplings are acyclic, such that the QSS species can be solved group by group in a semi-explicit manner. Although only a single group can be found in QSSG if **A** is a full matrix, multiple groups can be found if **A** is sufficiently sparse. Therefore, the first step in solving eq 5 is to reduce the QSSG by eliminating unnecessary graph edges, the importance of which is measured by the normalized contribution, r_{ij}, of the jth QSS species to the creation rate of the ith QSS species:

$$x_i \rightarrow x_j \quad \text{iff} \quad r_{ij} > \epsilon \qquad r_{ij} = \max_{\mathbf{S}}\left(\frac{A_{ij}x_j}{\sum_{k\neq i} A_{ik}x_k + A_{i0}}\right) \tag{6}$$

where **S** is the set of all possible reaction states of interest. When r_{ij} is compared with a user specified small threshold value ϵ, the terms with negligible contribution to the creation rate of x_i are truncated, resulting in the elimination of the corresponding edges in the QSSG. A sparser graph can therefore be obtained.

2.2.2. Strongly Connected Component (SCC) and Topological Sort of QSSG. The reduced QSSG is expected to be sparse in that each QSS species typically only interacts with a few of the others. In an example QSSG shown in Figure 1a, three SCCs, namely A, B, and C, each of which is a group of species connected by at least one cyclic path, are enclosed in dotted circles. The species inside each SCC form a set of implicit equations that need to be solved with variable elimination by substitution. However, when all the SCCs are identified, the dependence of one SCC on another is acyclic, and the SCCs can be solved one after another in a sequence. In such cases, a block upper-triangular coefficient matrix can be obtained by rearranging the sequence of the variables. The solution of eq 5 is therefore decomposed into solving several smaller equation sets, the total cost of which is lower than that of solving the large equation set, in that the cost of solving linear problems is a worse-than-linear, typically a quadratic, function of the number of variables.

To identify the SCCs in a QSSG, existing methods in graph theory can be employed. Formally, a SCC is defined as a maximal subgraph in a directed graph, and there is a directed path between any pair of vertices inside the SCC. A method based on depth-first search (DFS) can be applied to systematically and efficiently identify all the SCCs.[30] For convenience, a brief explanation of this method is presented below.

For a directed graph consisting of N vertices, all labeled "undiscovered" initially, let **E** denote the adjacent matrix of the graph, where

$$E_{ij} = \begin{cases} 1, \text{ if there is an edge } x_i \rightarrow x_j \\ 0, \text{ otherwise} \end{cases} \tag{7}$$

Starting from each "undiscovered" vertex x_i, a DFS is performed on both graph G and graph G^T with the transposed adjacency matrix $\mathbf{E}^T$; a vertex is labeled "discovered" if it is reached by the DFS in both G and G^T. All the vertices newly "discovered" by the current DFS then constitute an SCC. This procedure is repeated until all the vertices are "discovered".

As aforementioned, each QSS species in an SCC requires the concentrations of all the other QSS species in the same SCC either directly or indirectly. The inner-SCC couplings are strong, and each of the SCCs can be treated as a single composite vertex, the incoming and outgoing edges of which being the union of those of its member vertices. As such, an acyclic graph can be obtained, as shown in Figure 1b for the graph in Figure 1a. Each composite vertex in Figure 1b is labeled a unique number, namely the topological order, such that the species in the SCC with order n only depends on the species in the SCCs with orders not larger than n. Therefore, the SCCs can be solved one after another in the topological order. The process to find a topological order for acyclic graphs is known as topological sort, asdescribed in ref 30.

2.2.3. Resolving Inner-SCC Couplings. After the identification of the SCCs and the topological sort, the last step is to solve the species concentrations within each SCC with variable elimination by substitution. Although the species in each SCC are strongly connected, the subgraph of each SCC may still be sparse, and the length of the expressions of the analytic solution can be minimized by the proper selection of a sequence for variable elimination, as what is frequently done when solving algebraic equations with pencil and paper. To automate this process, an algorithm similar to that for computing pageranks[31] in worldwide-web search engines is developed to find an optimal or near-optimal sequence for variable elimination. This is accomplished by ranking the normalized expansion cost, c_i, of each variable, defined recursively as

$$\mathbf{c} = \mathbf{L}\cdot\mathbf{c}$$

$$\mathbf{c} = (c_1, c_2, ..., c_M)^T \qquad \text{and} \qquad L_{ij} = \frac{E_{ij}}{\sum_{k=1}^{M} E_{kj}} \tag{8}$$

where M is the number of variables in the SCC, and the matrix **L** is derived from the adjacency matrix **E** in eq 7 with normalized columns, such that the sum of each column is unity. It is readily seen that the solution of **c** in (8) is the eigenvector associated with the principal eigenvalue of matrix **L**, because each entry of **L** is non-negative and the sum of each column is unity. The value of c_i empirically indicates the extent of expansion in the length of the equations due to the elimination of the ith species in the SCC. The system typically expands quickly in the beginning of the substitutions; however, the extent of the expansion becomes restricted in the later substitution stage because the size of the system is becoming smaller. Therefore, variables with the lowest expansion cost should be solved first to maintain a system as sparse as possible in the initial stage, and consequently the overall computation cost of the solution can be restricted to a minimal level. As such, the sequence through which each variable is to be eliminated by substitution can be determined by sorting the expansion costs of the variables in the SCC in ascending order.

The method of LQSSA-QSSG is so far complete. It is now applied to an example mechanism for ethylene/air in the next section.

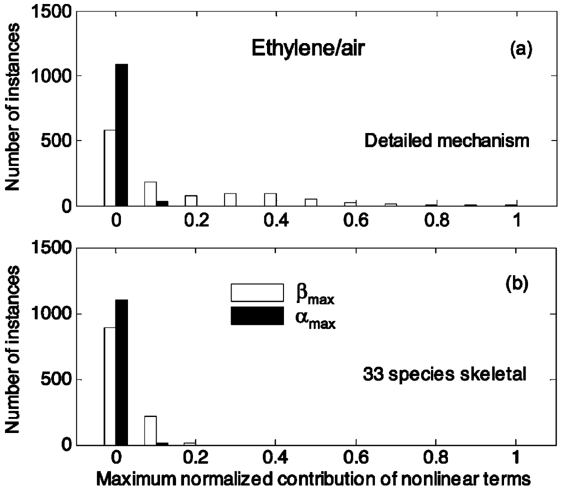


Figure 2. Distribution of α_{max} and β_{max}, the maximum normalized contribution to the destruction and the creation rates respectively as defined in eq 3b, for more than 1000 densely sampled reaction states from PSR and auto-ignition, calculated with (a) the detailed mechanism with 70 species, and (b) the 33 species skeletal mechanism.

3. Results and Discussion

To demonstrate the algorithm described in section 2, a detailed mechanism with 70 species[32] and a corresponding skeletal mechanism with 33 species[8] were selected as target mechanisms for reduction based on QSSA. First, using a threshold value of $\epsilon = 0.1$ for normalized species time scales as that in ref 8, a set of 24 QSS species, namely C, CH, CH_2, CH_2*, HCO, CH_2OH, CH_3O, C_2H, C_2H_3, C_2H_5, HCCO, CH_2CHO, C_3H_2, n-C_4H_3, i-C_4H_3, n-C_4H_5, i-C_4H_5, C_4H_7, C_6H_3, A_1^-, C_5H_4OH, n-C_3H_7, i-C_3H_7, and CH_3CCH_2, were identified in the detailed mechanism using the method in ref 6. Second, the same 12 QSS species as those in ref 8 were assumed in the 33 species skeletal mechanism, resulting in a 16-step reduced mechanism. To derive an analytic solution to the QSSA equations valid over a wide parameter range, more than 1000 reaction states were densely sampled from simulations of the perfectly stirred reactor (PSR) and auto-ignition, which are typical homogeneous applications for extinction and ignition phenomena, respectively, with pressures from 1 to 30 atm, equivalence ratios from 0.5 to 1.5, and initial temperatures from 1000 to 1600 K for auto-ignition and 300 K for PSR. The sampled reaction states are then applied as the data source for the algorithm in section 2.

To check the validity of LQSSA for the QSS species, the normalized contributions of the nonlinear terms to the creation rate and destruction rates of the QSS species were calculated using eqs 2 and 3b. Figure 2a shows the histogram of α_{max} and β_{max} defined in eq 3b, calculated with the detailed mechanism for all the sampled reaction states. It is seen that the contributions of the nonlinear terms to the destruction rates of the QSS species are generally small, e.g., less than about 0.1, and their contributions to the creation rates are non-negligible in many cases, with the worst case value being close to unity. Therefore, LQSSA does not seem to be applicable to the detailed mechanism. However, considering that when the contributions of the nonlinear terms to the destruction rates of all the QSS species are small, as shown in Figure 2a, reactions with more than one QSS species, e.g., A and B, can only control unimportant reaction pathways with smaller rates as compared to the major destruction pathways of A and B. If these slow reaction pathways are the major creation terms for a certain downstream QSS species C, species C is likely to be unimportant for the production rate of the major species, and as such can be eliminated in a skeletal reduction. To demonstrate this point, Figure 2b shows the histogram of α_{max} and β_{max} for the 33 species skeletal mechanism derived from the detailed mechanism with the DRG method.[8] It is seen that, once the unimportant species and reactions are removed, contributions of the nonlinear terms to both the creation and destruction rates are small, e.g., about 0.1−0.2, for all the QSS species. Therefore, LQSSA is applicable after the skeletal reduction, in which all the unimportant QSS species are removed.

In rare cases where a few non-negligible nonlinear terms still remain after the skeletal reduction, three strategies can be assumed: (1) Remove some species from the QSS species list, such that the resulting algebraic equations are linear. Because important reactions with more than one QSS species are rare, it is expected that only very few species need to be removed from the QSS species list to form a linear system. Thus the size of the resulting reduced mechanism is not significantly increased. (2) If there are only very few, e.g., one or two, nonlinear relations in eq 1, the nonlinear equations can be solved as the last ones in the process of variable elimination by substitution. Because these nonlinear equations are treated only in the last couple of steps, the system of equations is already sufficiently small to be readily solved. (3) In extreme cases where many nonlinear terms remain even after the skeletal reduction, a hybrid method that combines the iteration and analytic solution of the linear components can be applied. Specifically, in each loop of the hybrid method, the linear components are first solved analytically with the nonlinear terms treated as constants, which are then updated with the latest results from the linear component. It is expected that it takes fewer iterations, consequently less computation cost, to converge with the hybrid scheme than with simple algebraic iterations if the linear component is convergence-rate limiting. It is noted nevertheless that though more can be discussed on the hybrid method, it exists only under extremely rare situations and as such is not the primary interest of this work.

We therefore proceed with the linear system obtained after the skeletal reduction. The sparsity of the QSSA equations is consequently to be examined. With the equations organized in the form of eq 5, QSSGs were constructed from (6), in which r_{ij}, the maximum normalized contributions of terms involving x_j to x_i, were computed using all the sampled reaction states and compared with the small threshold value ϵ. An edge $x_i \rightarrow x_j$ in the QSSG is neglected if x_j contributes negligibly to x_i for all instances. The dependence of the number of edges in the QSSG as a function of the small threshold value ϵ is shown in Figure 3. It is seen that with $\epsilon = 0$, there are about 40 edges, each of which indicates a nontrivial coefficient A_{ij} in eq 5. Compared with the full coefficient matrix of size 12 by 12, there are only less than 30% nontrivial coefficients in **A**, which is fairly sparse. Further selection of $\epsilon \approx 0.1$ leaves only 25 edges in the reduced QSSG, as shown in Figure 3. The fraction of nontrivial entries in **A** consequently decreases to less than 20%, and such a sparse graph results in the highly efficient solution of the LQSSA equations.

The QSSG obtained with $\epsilon = 0.11$ is shown in Figure 4, in which four SCCs were identified, three of which contain only a single species. The topological order obtained with the method in section 2.2 indicates the sequence in which the QSS species concentrations can be solved as groups. The solutions of groups 2−4 are straightforward because there is only a single species in each group, but group 1 contains 9 coupled species and an efficient sequence for variable elimination is needed and can be found with the algorithm in eq 8. The result is listed in Table

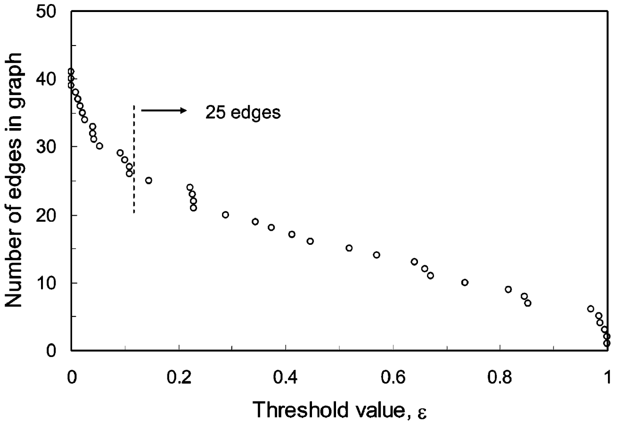


Figure 3. Number of edges in the QSSG as a function of the threshold value ϵ, showing that linear equations of LQSSA are sparse, and the sparsity increases with larger threshold value ϵ.

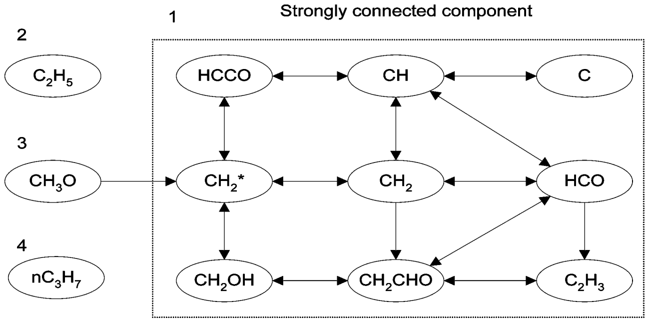


Figure 4. Directed graph for QSS species with four SCCs, three of which contain a single species, calculated with the skeletal mechanism of 33 species, 12 of which are in QSS, with a threshold value $\epsilon = 0.11$. The topological order is marked at the top-left corner of each SCC.

TABLE 1: Optimal Sequence of Elimination by Substitution for 9 QSS Species in a Strongly Connected Component in the QSSG of the 33 Species Skeletal Mechanism with $\epsilon = 0.11$

no.	QSS species	expansion cost
1	C_2H_3	0.06
2	C	0.14
3	CH_2OH	0.19
4	CH_2CHO	0.26
5	HCCO	0.26
6	CH_2*	0.38
7	HCO	0.39
8	CH_2	0.46
9	CH	0.55

1. It is seen from Figure 4 and Table 1 that the species that are coupled weakly with other species, such as C_2H_3 and C, are to be eliminated first, and the species that are coupled strongly with others, such as CH_2 and CH, are eliminated later. Such a sequence therefore effectively reduces the expansion of the expressions in the beginning stage of the variable elimination process and improves the overall efficiency of the solution. This method does not guarantee the exact optimal solution, but it finds suboptimal solutions close to the optimal one. To demonstrate this point, a set of 10 000 randomly generated variable elimination sequences, each of which occurs with the same probability, were tested. A FORTRAN code was generated for each sequence, and the number of operations, including multiplications and divisions, in each of the FORTAN codes was counted. The result of the random test is shown in Figure 5. It is seen from the histogram that the number of instances as a function of the number of operations, consequently the computation cost, is approximately in normal distribution. The most efficient sequence discovered in the 10 000 tests consists of 91 operations, and the sequence identified with the proposed algorithm has 92 operations, which is almost the minimum value. It is further observed in Figure 5 that a randomly selected variable elimination sequence may result in higher computation costs than the optimal sequence by a factor of about 2 on average and about 3 in the worst cases, demonstrating the necessity of searching for an optimized sequence.

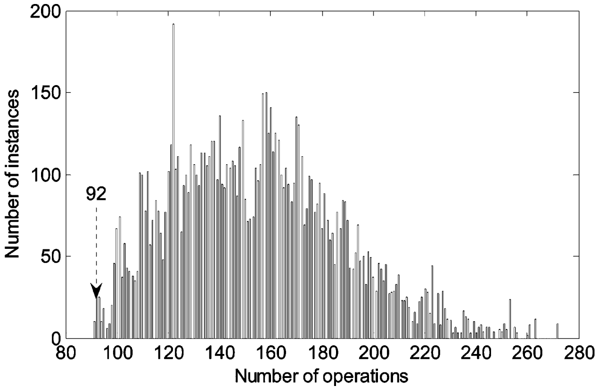


Figure 5. Distribution of number of operations, including multiplications and divisions, in 10 000 random tests, each with an automatically generated FORTRAN code solving the nine-species SCC shown in Figure 4.

It is further noted that, although the efficiency might be further improved slightly by using the exact optimal sequence, it is exceedingly more difficult to find such an exact solution because it involves the problem of integer programming, which is known to be NP-hard and inefficient to solve. Furthermore, it is difficult to formulate the exact optimization problem, both due to the difficulty in the exact timing of different operations in a general computation environment and because it is frequently not completely clear which target function and constraints are the best choice for the optimization of a reduced mechanism. Therefore, finding the exact optimal solution might not be of the best interest for many practical applications, because the proposed method is sufficiently fast to find a near-optimal sequence.

To demonstrate the accuracy of the proposed method, in Figures 6 and 7 the 16-step reduced mechanism with LQSSA-QSSG was compared with the 33-species skeletal mechanism and the 16-step reduced mechanism with QSSA solved with algebraic iterations, for auto-ignition and PSR respectively. It is seen from Figure 6 that although there is a slightly visible difference in the ignition delay time between the skeletal mechanism and the 16-step mechanism with iteration, the difference between the two 16-step reduced mechanisms is much smaller and basically invisible. In Figure 7, all the three mechanisms agree very well with one another, and the errors are not visible. Furthermore, although only stoichiometric mixtures are demonstrated in Figures 6 and 7, comparisons for off-stoichiometric mixtures show similar agreement.

To further show the magnitudes of the errors induced by the QSSA and the elimination of nonlinear and small linear terms in LQSSA-QSSG, the relative errors in the profiles of Figures 6 and 7 are plotted in Figures 8 and 9, respectively. It is seen that the difference between the 16-step mechanisms with LQSSA-QSSG and QSSA with algebraic iterations is much smaller than the error induced by QSSA; i.e., the additional accuracy loss induced by the elimination of nonlinear and small linear terms in the LQSSA-QSSG method is negligible compared with that induced by QSSA. Furthermore, the overall small

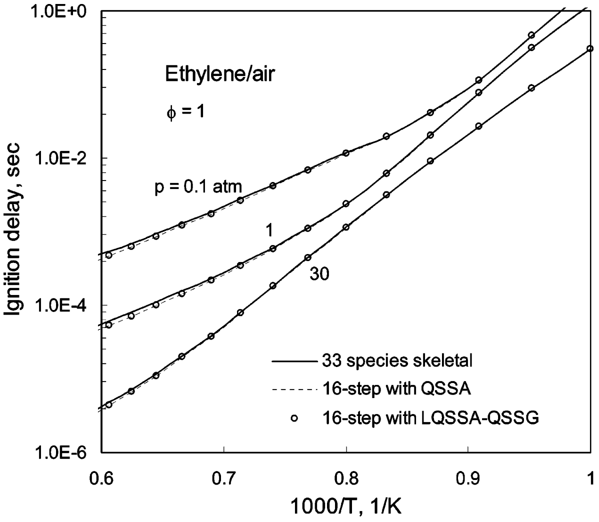


Figure 6. Dependence of ignition delay time on initial temperature for auto-ignition under constant pressure, calculated with the 33-species skeletal mechanism, the 16-step reduced mechanism with QSSA, and the 16-step mechanism with LQSSA-QSSG respectively.

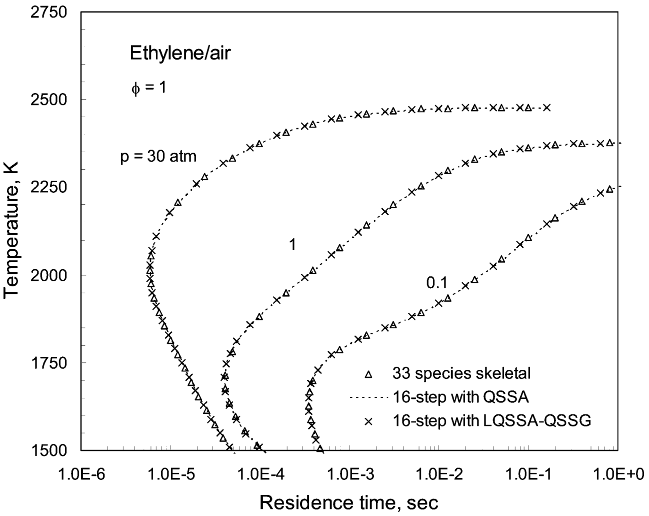


Figure 7. Dependence of temperature on residence time in perfectly stirred reactors under difference pressures, calculated with the 33-species skeletal mechanism, the 16-step reduced mechanism with QSSA, and the 16-step mechanism with LQSSA-QSSG respectively.

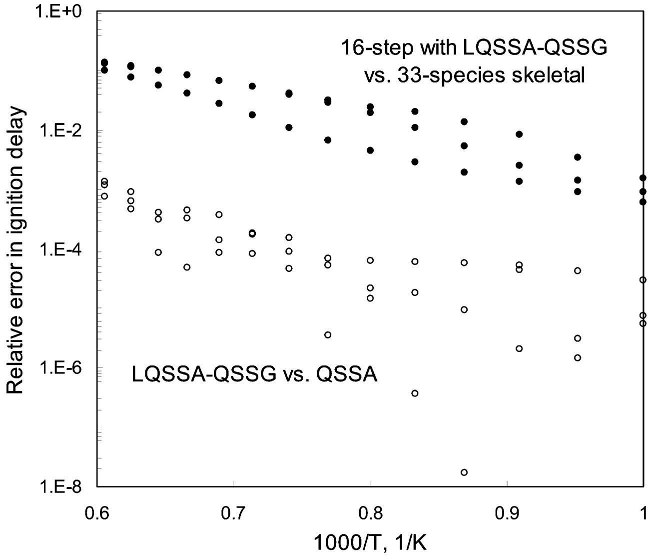


Figure 8. Relative error in calculated ignition delay time as a function of the initial temperature for profiles shown in Figure 6. The 16-step mechanism with LQSSA-QSSG is compared with the 33-species skeletal mechanism and the 16-step mechanism with QSSA respectively.

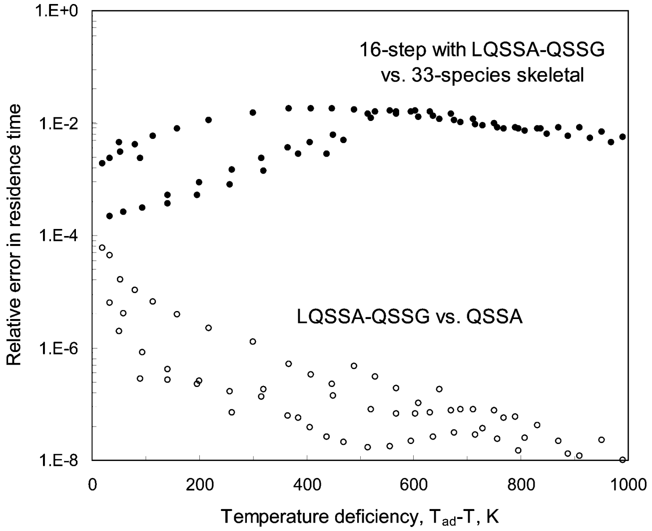


Figure 9. Relative error in calculated residence time as a function of temperature deficiency from the adiabatic flame temperature in perfectly stirred reactors for the profiles shown in Figure 7. The 16-step mechanism with LQSSA-QSSG is compared with the 33-species skeletal mechanism and the 16-step mechanism with QSSA respectively.

relative errors for both the ignition and extinction cases over the wide parameter ranges of pressure, temperature, and equivalence ratio show the validity of the LQSSA-QSSG method, in addition to the efficiency and feasibility demonstrated in earlier figures.

Finally, to further compare the properties of the current LQSSA-QSSG method with those of the classical QSSA, it is noted that though LQSSA and QSSA are based on the same physical observation that the destruction rate of a QSS species balances its creation rate after a transient period, the two methods have qualitatively different properties. For example, although neither existence nor uniqueness of the solution is guaranteed for general nonlinear equations of QSSA, both are guaranteed for the linearized system. It is further noted that, because the elimination of nonlinear terms and weak dependences between QSS species in LQSSA-QSSG can be equivalently achieved through elimination of the corresponding elementary reactions from the detailed or skeletal mechanisms, the method of LQSSA-QSSG does not induce any new source of element nonconservation or violation of the second law of thermodynamics in addition to those induced in the method combining skeletal reduction and QSSA.

4. Conclusions

In the above sections, the systematic approach of LQSSA-QSSG for obtaining analytic solutions for QSS species concentrations in reduced mechanisms was presented. It is shown that although the algebraic equations of QSSA are nonlinear in general, the equations can be approximated accurately by a linear system under most situations. This is based on the physical reasoning that QSS species typically exist in low concentrations and as such the probability of collisions between two QSS species is expected to be much lower than that involving the major species. Therefore, the majority of reactions involving more than one QSS reactant can be eliminated through skeletal reduction, resulting in a linear or near-linear set of equations for the QSS species in the skeletal mechanism. The linear system is found to be typically sparse and the QSSG method mapping the QSS species dependences to a directed graph is employed to solve the LQSSA equations analytically. By first identifying the SCCs in QSSG, we then solved the implicit inner-SCC couplings by substitution with an eigenvalue based algorithm, which was developed to efficiently find near-optimal sequences for variable elimination. The inter-SCC couplings were resolved by a topologically sort to obtain a sequence in which the SCCs can be solved one after another explicitly. The efficiency is high for both the algorithm and the automatically generated solver code.

The proposed algorithm has been compiled into a computer code and a FORTRAN subroutine has been generated on the basis of a 33 species skeletal mechanism developed previously using DRG, and has been compared with the iterative QSSA solver employed in the previous work for the 16-step reduced mechanism. Results show that the elimination of the nonlinear terms and the weak dependences between QSS species induce negligible errors to the system compared with those by QSSA for the ethylene/air mixtures. As such, the LQSSA-QSSG method can serve as a rather general approach to eliminate the algebraic iterations in QSS-based reduced mechanisms. The various concepts and methodologies advanced herein are also expected to be of utility in other branches of science involving large systems of sparsely coupled entities.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research under the technical monitoring of Dr. Julian M. Tishkoff.

References and Notes

(1) Tomlin, A. S.; Turanyi, T.; Pilling M. J. *Comprehensive Chemical Kinetics*; Elsevier: Amsterdam, 1997; pp 293−437.

(2) Vajada, S.; Valko, P. and Turanyi, T. *Int. J. Chem. Kinet.* **1985**, *17*, 55−81.

(3) Turanyi, T. *New J. Chem.* **1990**, *14*, 795−803.

(4) Wang, H.; Frenklach, M. *Combust. Flame* **1991**, *87*, 365−370.

(5) Massias, A.; Diamantis, D.; Mastorakos, E.; Goussis, D. A. *Combust. Flame* **1999**, *117*, 685−708.

(6) Lu, T. F.; Ju, Y.; Law, C. K. *Combust. Flame* **2001**, *126*, 1445−1455.

(7) Bhattacharjee, B.; Schwer, D. A.; Barton, P. I.; Green, W. H. *Combust. Flame* **2003**, *135*, 191−208.

(8) Lu, T. F.; Law, C. K. *Proc. Combust. Inst.* **2005**, *30*, 1333−1341.

(9) Lu, T. F.; Law, C. K. *Combust. Flame* **2005**, *144*, 24−36.

(10) Lu, T. F.; Law, C. K. *Combust. Flame* **2006**, *146*, 472−483.

(11) Pepiot P.; Pitsch H. Systematic Reduction of Large Chemical Mechanisms. 4th Joint Meeting of the U.S. Sections of the Combustion Institute, Drexel University: Philadelphia, March 21−23, 2005.

(12) Peters, N. *Lecture Notes in Physics*; Glowinski, et al., Eds.; Springer: Berlin, 1985; p 90.

(13) Peters, N.; Kee, R. J. *Combust. Flame* **1987**, *68*, 17−29.

(14) Chen, J. Y. *Combust. Sci. Technol.* **1988**, *57*, 89−94.

(15) Smooke, M. D. *Lecture Notes in Physics 384*; Springer-Verlag: Berlin, 1991; p 1.

(16) Ju, Y.; Niioka, T. *Combust. Flame* **1994**, *99*, 240−246.

(17) Sung, C. J.; Law, C. K.; Chen, J. Y. *Proc. Combust. Inst.* **1998**, *27*, 295−304.

(18) Lovas, T.; Nilsson, D.; Mauss, F. *Proc. Combust. Inst.* **2000**, *28*, 1809−1815.

(19) Hamirouney, D.; Bishnuy, P.; Metghalchiy, M.; Keckz, J. C. *Combust. Theory Modelling* **1998**, *2*, 81−94.

(20) Maas, U.; Pope, S. B. *Combust. Flame* **1992**, *88*, 239−264.

(21) Lam, S. H.; Gousis, D. A. *Int. J. Chem. Kinet.* **1994**, *26*, 461−486.

(22) Pope, S. B. *Combust. Theory Modeling* **1997**, *1*, 41−63.

(23) Ren, Z.; Pope, S. B. *Proc. Combust. Inst.* **2005**, *30*, 1293−1300.

(24) Bodenstein, M. Z. *Phys. Chem.* **1913**, *85*, 329.

(25) Underhill, L. K.; Chapman, D. L. *J. Chem. Soc. Trans.* **1913**, *103*, 496.

(26) Turanyi, T.; Tomlin, A. S.; Pilling, M. J. *J. Phys. Chem.* **1993**, *97*, 163−172.

(27) Ren, Z.; Pope, S. B. *Combust. Flame* **2004**, *137*, 251−254.

(28) Law, C. K.; Sung, C. J.; Wang, H.; Lu, T. F. *AIAA J.* **2003**, *41*, 1629−1646.

(29) Mauss F.; Peters N.; Rogg R.; Williams F. A. In Reduced Kinetic Mechanisms for Applications in Combustion Systems. *Lecture Notes in Physics*; Peters, N., Rogg, B., Eds.; Springer-Verlag: Berlin, 1993; pp 29−43.

(30) Cormen, T. H.; Leiserson, C. E.; Rivest, R. L.; Stein, C. *Introduction to Algorithms*, 2nd ed.; MIT Press: Boston, 2001; pp 527−557.

(31) Brin S.; Page L. *Proc. 7th Intl. Conf. World Wide Web* **1998**, 107−117.

(32) Qin, Z.; Lissianski, V. V.; Yang, H.; Gardiner, W. C.; Davis, S. G.; Wang, H. *Proc. Combust. Inst.* **2000**, *28*, 1663−1669.