

Complex CSP for Chemistry Reduction and Analysis

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The method of computational singular perturbation for the analysis and reduction of complicated chemical mechanisms has been extended to the complex eigensystem. The characteristic time scale for each species was defined by using the time scales of the independent modes weighted by radical pointers, and the time scale of each species normalized by a characteristic time scale of the system was used as a criterion in determining the quasi-steady-state species. Furthermore, for oscillatory modes the radical pointer and the importance index of the previous computational singular perturbation theory were redefined. Results show that the time scales of chemical species change dramatically and non-monotonically, and the oscillatory modes appear frequently in large chemical reaction mechanisms. The present method was then employed to generate a 4-step and a 10-step reduced mechanism for the high-temperature H_2/air and CH_4/air oxidation, respectively. The validity of these reduced mechanisms were evaluated based on the responses of the perfectly stirred reactors and the one-dimensional planar propagating premixed flames. Comparisons between the reduced and detailed chemistries over a wide range of pressures and equivalence ratios show good agreement on the flame speed, flame temperature, and flame structure. A software package based on the present algorithm was compiled to generate reduced mechanisms for complex chemical mechanisms. The validity and efficiency of the present algorithm is demonstrated. © 2001 by The Combustion Institute

INTRODUCTION

It is well established that, even for the simplest hydrocarbon fuels, the detailed chemistry for combustion still involves tens of species and hundreds of elementary reactions. This large number of species and reactions results in various modes and time scales for the destruction and production of species during combustion, and render the computation of complex combustion phenomena, such as turbulent flames, either very difficult or basically untenable. Recently, efforts have been made in deriving local and/or global reduced chemistries for understanding complex chemical processes and for numerical simulation by employing partial equilibrium and quasi-steady-state (QSS) assumptions [1]. Reduced mechanisms for hydrogen and simple hydrocarbon fuels have been developed by several groups using the methods of reaction rate analysis [2–6], computational singular perturbation (CSP) [7–11], and intrinsic low-dimensional manifolds [12].

The key step in deriving a reduced chemistry is to identify and remove the QSS species with small time scales. The conventional method is to use a criterion based on small mole fractions, normalized net production rates, and sensitivity

analysis [2–6]. However, this method does not always work well because it does not ensure that all the smallest time scales are identified. In addition, the sensitivity analysis cannot provide any information on the destruction or production modes.

The CSP method [7–10] can successfully identify the steady-state species and the time scales of different modes. However, if higher than leading order accuracy is required, the refinement procedure for the time-dependent Jacobian might result in difficulties in the accurate calculation of the derivatives of the basis vectors. Furthermore, oscillatory modes are not considered. Because kinetic and thermal-diffusional oscillations frequently occur in flames [13, 14], prediction and identification of the amplitude and frequency of the oscillatory modes are also of importance. In addition, in determining the QSS with CSP, a reference time criterion is needed to separate the fast and slow subspaces and to identify the species projected mostly to the fast subspace, i.e., the fast modes. In a recent study of the one-dimensional planar propagating premixed flame [10–11], the thermal diffusion time was used as the criterion. Although the thermal diffusion time is meaningful to indicate the overall time scale of reactions across the flame zone, it is system dependent. Furthermore, the dramatic change

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of temperature and radical concentrations across the flame could lead to significant difficulties in choosing the proper weighting functions to integrate the CSP data across the flame. As such, it appears preferable to use a homogeneous reacting system such as the perfectly stirred reactor (PSR) to define a parameter that is more likely to be the chemical property of the mixture.

In view of the above discussions, the first objective of the present investigation was to present an extended CSP algorithm to determine the reaction modes, time scales, oscillation frequency and QSS species, and to obtain a comprehensive reduced chemistry by using complex eigensystem. The second objective was to develop a software package that can be almost fully automatic to generate reduced chemistries. In the following section, the algorithm of the complex CSP method is formulated. Then, time scales and reduced mechanisms of hydrogen/air and methane/air flames were obtained by using the PSR analysis for a wide range of pressures and equivalence ratios. This was followed by the generation of the reduced chemistry using the newly developed software package. Finally, the reduced chemistry was applied to the one-dimensional planar propagating flame, and the flame speeds, flame temperatures, and flame structures obtained by the reduced and detailed chemistries, respectively, are compared.

Formulation and Algorithm of Complex CSP

Basic Formulation

A general chemical reaction system can be expressed as:

$$\mathbf{g}(\mathbf{y}) \equiv \frac{d\mathbf{y}}{dt} = \mathbf{S} \cdot \mathbf{F}(\mathbf{y}) \quad (1)$$

where \mathbf{y} is the concentration vector of all the species, \mathbf{S} the stoichiometric coefficient matrix, and $\mathbf{F}(\mathbf{y})$ the rate vector of the elementary reactions. By taking the time derivative of Eq. 1, we obtained:

$$\frac{d\mathbf{g}}{dt} = \mathbf{J} \cdot \mathbf{g} \quad (2)$$

where $\mathbf{J} = d\mathbf{g}/d\mathbf{y}$ is the time-dependent Jacobian matrix. By using the decomposition of $\mathbf{J} = \mathbf{A}\mathbf{\Lambda}\mathbf{B}$, Eq. 2 can be written as:

$$\frac{d\mathbf{f}}{dt} = \mathbf{\Lambda} \cdot \mathbf{f}, \quad \mathbf{f} \equiv \mathbf{B} \cdot \mathbf{g} \quad (3)$$

where \mathbf{A} is the matrix of basis vectors and \mathbf{B} the inverse matrix of \mathbf{A} . In Eq. 3, if \mathbf{A} is a matrix built up by ideal basis vectors, then $\mathbf{\Lambda}$ reduces to a diagonal matrix and its diagonal elements are the eigenvalues of \mathbf{J} .

CSP Data in Complex Space

Because the Jacobian matrix \mathbf{J} is actually time dependent, a refinement procedure was used previously [8] to obtain a group of real number ideal base vectors. This is necessary for certain time-integration processes in which the time-dependent properties of the Jacobian matrix \mathbf{J} must be considered. Another advantage of the refinement procedure is that only the fast subspace needs to be decomposed [10]. However, if higher than leading order accuracy is required, the refinement procedure requires evaluation of the time derivative of the ideal base vectors. This might be difficult in some cases. If only the time scales of the modes or species are of interest, the Jacobian matrix can be assumed to be locally time independent, and the refinement procedure can be replaced by performing a full decomposition of the Jacobian matrix. Furthermore, because oscillatory modes frequently appear in a large chemical reaction system, it is necessary to decompose \mathbf{J} in complex space in order to strictly diagonalize $\mathbf{\Lambda}$ such that the frequencies and amplitudes of the oscillatory modes can be obtained accurately. As such, the definitions of the modes, their time scales, the radical pointer, and the participation index in the original CSP theory [7–11] need to be modified accordingly.

Because \mathbf{A} and \mathbf{B} are complex matrices when oscillatory modes appear, complex conjugate pairs of columns and rows in each of them need to be treated in the definitions of CSP data:

$$\mathbf{A}_i = \mathbf{A}_{iR} + i\mathbf{A}_{iI} \quad (4a)$$

$$\mathbf{A}_{i+1} = \mathbf{A}_{iR} - i\mathbf{A}_{iI} \quad (4b)$$

$$\mathbf{B}^i = \mathbf{B}_R^i + i\mathbf{B}_I^i \quad (4c)$$

$$\mathbf{B}^{i+1} = \mathbf{B}_R^i - i\mathbf{B}_I^i \quad (4d)$$

where the i th and $(i + 1)$ th columns of \mathbf{A} and the i th and $(i + 1)$ th row of \mathbf{B} are complex conjugate pairs, and the subscript R and I designate the real and imaginary parts, respectively. After simple algebraic manipulation, each pair of complex conjugate modes in Eq. 3 can be converted into a pair of real modes:

$$f_i = \mathbf{B}_R^i \cdot \mathbf{g} \quad (5a)$$

$$f_{i+1} = \mathbf{B}_I^i \cdot \mathbf{g} \quad (5b)$$

These two modes were coupled with each other through the complex conjugate eigenvalue pair $\lambda_i = \lambda_{iR} + i\lambda_{iI}$ and $\lambda_{i+1} = \bar{\lambda}_i$. This implies that these two modes have the same characteristic time scale of $1/\lambda_{iR}$ and oscillatory frequency λ_{iI} with a phase difference of π . The corresponding projection matrices associated with the pair of oscillatory modes in Eq. 5 are:

$$\mathbf{Q}_i = 2\mathbf{A}_{iR} \cdot \mathbf{B}_R^i \quad (6a)$$

$$\mathbf{Q}_{i+1} = 2\mathbf{A}_{iI} \cdot \mathbf{B}_I^i \quad (6b)$$

The radical pointers $\mathbf{R}_{i,r}$ and $\mathbf{R}_{i+1,r}$ are the r th diagonal elements of \mathbf{Q}_i and \mathbf{Q}_{i+1} , respectively. The radical pointer $\mathbf{R}_{i,r}$ is normalized with respect to either i or r . It indicates how parallel the axis of the r th species is to the i th mode, and can be used to identify the QSS species [7–11].

The participation index for the pair of oscillatory modes are given as:

$$\mathbf{P}_r^i = \frac{(\mathbf{B} \cdot \mathbf{S})_{rR}^i \cdot \mathbf{F}^r}{\sum_{r=1}^H \left| (\mathbf{B} \cdot \mathbf{S})_{rR}^i \cdot \mathbf{F}^r \right|} \quad (7a)$$

$$\mathbf{P}_r^{i+1} = \frac{(\mathbf{B} \cdot \mathbf{S})_{rI}^i \cdot \mathbf{F}^r}{\sum_{r=1}^H \left| (\mathbf{B} \cdot \mathbf{S})_{rI}^i \cdot \mathbf{F}^r \right|} \quad (7b)$$

The participation index \mathbf{P}_r^i is the normalized contribution of the r th elementary reaction to the i th mode [7–9].

For non-oscillatory modes, the radical pointers are the diagonal elements of $\mathbf{A}_i \cdot \mathbf{B}^i$ and the participation index can be obtained by Eq. 7a. The importance index is the same as that in the original CSP algorithm [7–11]

$$\mathbf{I}_r^i = \frac{\mathbf{S}_r^i \cdot \mathbf{F}^r}{\sum_{r=1}^H \left| \mathbf{S}_r^i \cdot \mathbf{F}^r \right|} \quad (8)$$

where \mathbf{I}_r^i indicates the normalized contribution of the r th reaction to the reaction rate of i th species.

Identification of QSS Species

Eq. 3 shows that if the i th eigenvalue of \mathbf{J} is a large negative number, the i th mode will be quickly exhausted. Therefore, if the radical pointer associated with a species and this fast mode is almost unity, i.e., if the species is almost only associated with one exhausted mode, this species can be identified as a QSS species [7–11]. However, in most cases, each species is projected onto several modes of different time scales. Therefore, special procedures were required to obtain an overall parameter that can be used to identify the QSS species in such cases. The projection of a species onto the fast subspace is used in Refs. 10 to 11. When a species is projected more onto the fast space than another species, it is a better QSS candidate. The concentrations of the species are also weighted into the indicator based on the common phenomenon that QSS species generally have lower concentrations than other major species. Although most QSS species can be successfully identified by using this indicator, a problem still remains. That is, if species A is projected onto several fast modes in the fast subspace and species B is projected to other modes with longer time scales than those of species A , and the two species have the same radical pointer to the fast subspace, species A should be a better QSS candidate than species B . This happens because this indicator does not reflect the internal distribution of how the species is projected onto the fast subspace.

To resolve this problem, the time scales of independent modes can be summed to an indicator weighed by sufficiently large radical pointers, and this indicator can be defined to be the reciprocal time scale of the species. That is, a species belonging to a faster subspace, which consists of a group of faster modes, can be exhausted faster than a species belonging to a

less fast subspace. The definition is provided in Fig. 9, in which a critical time scale is used to normalize the time scales of those major species that control the overall reaction of the system to be around $O(1)$. It is difficult to find the critical time scale from the Jacobian matrix itself and, hence, it has to be chosen from the many time scales associated with the reacting system. Once this critical time scale is found, the normalized time scale of the species can be defined. In the present study, species were considered to be QSS if their time scales τ_i satisfy:

$$\tau_i \equiv \frac{-1}{\lambda_{pi}} < \frac{\tau_{ch}}{\alpha}, \lambda_{pi} \equiv \sum_{r=1}^{KK} \mathbf{R}_{ir} \lambda_r, |\mathbf{R}_{ir}| > \epsilon \quad (9)$$

where τ_{ch} is the critical time scale for the progress of chemical reaction and will be given later; KK is the total number of species; \mathbf{R}_{ir} , which is the r th diagonal elements of the projection matrix \mathbf{Q}_i , is the radical pointer associated with the i th mode and the r th species; ϵ is a small number below which the species and the mode are almost orthogonal, as indicated by the a radical pointer, and the weak projection from the species to the mode can be considered negligible subsequently. For example, $\epsilon = 0.01$ was used in the present study. The parameter α is the threshold factor, which should be chosen according to the accuracy requirement. For example, $\alpha = 100$ means that species with time scales at least 100 times shorter than that of the critical time scale, or the time scale of the controlling species as stated above, can be selected as QSS species.

As will be shown later, the criterion of Eq. 9 works very well for H_2/air and CH_4/air mixtures. However, to avoid limiting cases, verification is needed for the reduced mechanism obtained from Eq. 9 before it is applied. Of course, a more accurate reduced mechanism can always be obtained by specifying a sufficiently large value for α .

Obtaining “Global” QSS Species

It is shown in CSP theory that different reduced mechanisms are required for different initial conditions and reaction times. A good QSS species candidate at a certain time may become a poor QSS species candidate as time progresses

or as a result of other changes in the initial conditions. The CSP data above are only the local chemistry information at a certain time step under a specified condition, and the QSS species identified by the above information is therefore only valid locally. In many cases, however, a comprehensive reduced mechanism with fixed numbers of QSS species and global steps that can work for a certain range of initial conditions is more convenient to use. In order to identify the QSS species that is valid for a wide range of conditions, global indicators need to be generated from the local CSP data under various temperatures and pressures and equivalence ratios.

In previous work [10–11], integration of the radical pointers across a flame was used to choose the global QSS species. The integrated indicator therefore reflects the overall behavior of the species across the entire flame. However, by using this integrated indicator without a sufficiently comprehensive weighting function, which may be very difficult to find, the possibility that a species could be a poor QSS candidate in only a very narrow zone can be overlooked. As such, inaccurate results may be obtained if this zone is very important even although it is very narrow.

In the present study, a QSS species is selected if it can satisfy the conditions in Eq. 9 everywhere within the range of interest. However, it is not applicable if the global data are obtained across a flame. This is because the temperature and radical concentrations change dramatically across the flame, leading to correspondingly dramatic changes in the time scales of the species. Consequently, it may not be adequate to normalize the time scales of the species with a single critical time scale across the entire flame zone. A preferred choice is to use a homogeneous reacting system without transport processes. The advantage is that the reactivity of a species, which is a chemical property determining whether a species can be selected as a QSS species, can be assessed more clearly without the influence of transport. PSR was used in the present study to generate the data source for CSP analysis.

The critical time scale τ_{ch} must be selected for each system according to Eq. 9. A well-defined time scale in PSR is obviously the extinction

residence time, which is the shortest time for the major radical pool to build up given a sufficiently high temperature and radical concentrations such that the reactions can sustain themselves. For ignition phenomena, the ignition time is the appropriate choice, which measures the time required for the controlling species to build up. Obviously, a comprehensive reduction should take into account of both the ignition and extinction phenomena. For simplicity, we shall nevertheless conduct the following illustration based only on strongly burning and near-extinction situations.

Identification of the Fast Elementary Reactions

For each QSS species, a fast elementary reaction can be eliminated so that the reaction rate of this fast elementary reaction will not appear in the global reaction rates in the reduced mechanism [3, 10, 11]. This fast reaction can be chosen by CSP analysis using the importance index defined in Eq. 8, and the elementary reaction with the largest importance index for each QSS species is selected and eliminated. In the previous CSP theory [10, 11], an algorithm to identify the fast elementary reaction by using the integrated importance index across the flames was provided. In the present study, the minimum values of the importance index of the elementary reactions for each species in the entire range of initial conditions are used as a global importance index. For reversible reactions, the forward and backward reactions are considered separately so that reactions in partially equilibrium state will not be overlooked. The elementary reaction with the largest global importance index for each species is the best candidate to be eliminated for this species. The advantage of using the minimum value of the importance index, rather than the integrated value, is that it can account for effects due to the existence of narrow regimes within which the importance index could be very small.

By using Eq. 8, a skeletal mechanism can also be obtained by eliminating the unimportant elementary reactions that have negligible importance index for every species. The accuracy of the resulting skeletal mechanism depends on the small, user-specified threshold value under

which an importance index can be considered negligible. Reduced mechanisms can then be generated from these skeletal mechanisms with fewer species and global reaction numbers. These two steps can also be performed together [10–11].

Once the QSS species and their corresponding fast elementary reactions are identified, an algebraic procedure in matrix form can be used to generate the minimum set of linearly independent global reactions and to evaluate the global reaction rates [3].

Applying the Reduced Mechanisms

When the time scale of transport is slower than that of chemical extinction, the QSS species obtained from PSR data by using the present method should be valid in general. For those applications with transport time scales faster than the chemical extinction time scales, such as those associated with distributed turbulent combustion, an appropriate choice of α and pre-tests of the reduced mechanism have to be conducted. In laminar premixed flames, the chemical extinction time (τ_{ext}) is expected to be shorter than the global diffusion time (τ_{diff}). They assume similar order only when the flame approaches the extinction state. Therefore, in most cases, it is adequate to apply the reduced chemistry generated from PSR to laminar premixed flames. For weak turbulent flames, the situation is almost the same as that for laminar flames. For strong turbulent flames, however, a sufficiently large α should be used to obtain the reduced mechanism.

In addition, in applying the reduced mechanisms in flame calculations, special procedures are frequently needed to deal with the incorrect concentrations calculated for some QSS species. Specifically, abnormally high concentrations of QSS species may be obtained in the low- and intermediate-temperature zones of flames, implying that the QSS assumption is not applicable there. A previous method used to solve this problem is to truncate some elementary reactions [11]. The advantage of this method is that the concentrations of the QSS species in low-temperature zone will change smoothly. However, problems will arise when the elementary reactions are important in both high- and low-

temperature zones. Another method is to set upper and lower bounds for the concentrations of the QSS species such that truncation of the concentration of QSS species will be effected only when they are out of the bounds. The second method is used in the present study because the abnormally high concentrations should not occur where the reduced mechanism is generated if the QSS species are identified successfully, and the concentrations of the QSS species in the low-temperature flame zone are always lower than those of the non-QSS radicals and have a weaker effect on flames.

Software Package ARC-CSP

A software package based on the PSR data, and termed automatic reduction of chemistry with CSP (ARC-CSP), was developed by using the present algorithm. It can automatically create the skeletal mechanism, analyze the CSP data from PSR outputs, determine the QSS species, and create the global reduced chemistry. It is compatible with CHEMKIN-II and uses Windows interface. Detailed information on this package is available by contacting the authors. Here, we only give a brief description of its input and output. The inputs of the package are the detailed chemistry, the threshold error of the skeletal mechanism, the threshold factor α defined in Eq. 9, and the range of pressure, temperature, and equivalence ratio. The package first automatically creates the extinction profiles of PSR at different pressures, temperatures, and equivalence ratios, and generates the skeletal mechanism and builds the CSP data by using the specified error threshold and Eqs. 4–9, respectively. Second, the steady-state species are selected and the reduced chemistry was created automatically by using the threshold factor α . The package also provides a choice for users to disable the recommended selection and to select their own QSS species and preferred reduced chemistries. Specifically, after identifying the QSS species, all the possible linearly independent global reactions are shown to the user. The user then sequentially selects his preferred global reactions, being aided by displaying the remaining linearly independent reactions after the selection. Third, a set of CHEMKIN-II compatible FORTRAN subrou-

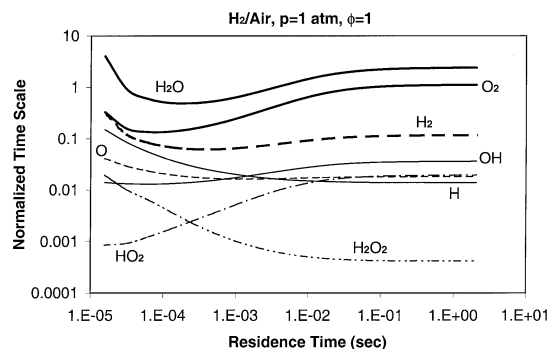


Fig. 1. Dependence of the reciprocal of time scale of species normalized by the extinction residence time of PSR for H_2 /air oxidation.

tines are generated for application purpose, and comparison of the reduced chemistry with the detailed chemistry are made based on the PSR and SENKIN data.

RESULTS AND DISCUSSION

Time Scales of Chemical Species

The reciprocals of the time scales of species in the stoichiometric H_2 /air reaction under 1 atm calculated from PSR data are plotted in Fig. 1 as a function of the residence time. Here, the time scale of each species is normalized by the extinction residence time. It is seen that normalized time scales of the major species such as H_2 , O_2 , and H_2O are close to $O(1)$, whereas other highly reactive radicals such as H_2O_2 and HO_2 have much shorter time scales. This result indicates that the extinction residence time of PSR is a good indicator of the characteristic time for the progress of the chemical reaction. It shows that the time scale of H is smaller than those of O , OH , and HO_2 when the residence time is long. However, as the residence time decreases the time scale of H becomes larger than those of O , OH , and HO_2 , particularly near the extinction limit. This result implies that the local time scales of the reacting species should not be used alone to derive a comprehensive reduced chemistry. Furthermore, Fig. 1 shows that the time scales of H_2O_2 , OH , and O are much shorter than those of the reactants and products, and thus can be assumed to be QSS. In addition, it is also seen that OH and HO_2 are better QSS than

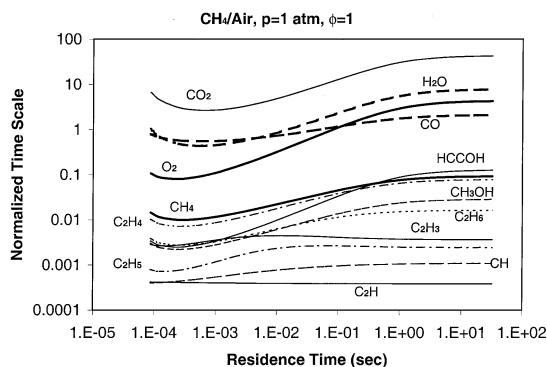


Fig. 2. Dependence of the reciprocal of time scale of species normalized by the extinction residence time of PSR for CH_4/air oxidation.

O and H. These results agree well with those obtained by the analyses of net production rates [5, 15].

Near the extinction limit, for short residence times, Fig. 1 shows that the time scales of the reactants and main radicals decrease rapidly as the mixture approaches the extinction state. This implies that the QSS assumption becomes poor at the extinction state, as there is not enough time for the radical pool to build up. By truncating a very short residence time segment next to the extinction point, a reduced mechanism with a much smaller size can be obtained while it is still adequate for most flame applications for which the operating conditions are generally sufficiently far from the extinction limit. On the other hand, when the residence time approaches infinity, the extinction time will no longer be a good critical time scale to normalize the time scales of species because there is no more controlling species in this limit, and most species are actually in quasi-steady state here. As such, only the data points with residence times less than a critical value, say 100 times the extinction time, need to be considered to obtain the global reduced mechanism.

The time scales of species in stoichiometric CH_4/air mixture calculated from PSR data are plotted in Fig. 2. Similar to the H_2/air mixture, the time scales of reactants and products are longer than those of the radicals and are close to the extinction residence time. Numerical results at higher and lower pressures as well as for near-limit mixtures also support this observation. Therefore, it can be concluded that the

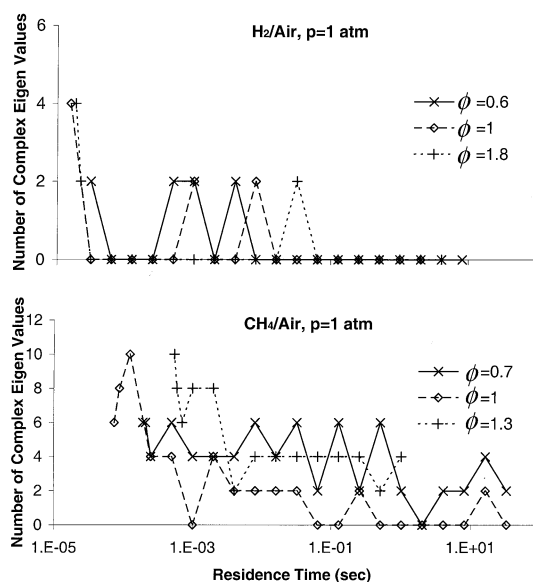


Fig. 3. Number of complex eigenvalues of Jacobian matrix $J = dg/dy$ as a function of residence time scale of PSR in H_2/air and CH_4/air system.

extinction residence time is a reasonable choice as the characteristic time for the progress of chemical reactions. This characteristic time will be used as the time criterion defined in Eq. 9 to determine the QSS. It can be clearly seen that species such as C_2H , C_2H_5 , and CH are the best candidates for QSS. The results also agree with those of previous works [1, 2, 6]. Therefore, by checking the criterion in Eq. 9 for all the mixtures of interest, comprehensive reduced chemistries for H_2/air and CH_4/air flames can be obtained within 1 min on a modest PC by using the current software package.

To demonstrate the existence of oscillatory modes, the number of oscillatory modes appearing in stoichiometric H_2/air and CH_4/air flames at various equivalence ratios is plotted in Fig. 3 as a function of the residence time. It is clearly seen that oscillatory modes frequently appear in chemical reactions. In addition, as the flame approaches the extinction limit, the number of oscillatory modes increases. This result suggests that it is important to include the oscillatory modes in CSP analysis. It may be noted that the present algorithm can also be directly extended to identify the oscillatory modes caused by thermal-diffusion in flame or heat loss to the chamber wall in PSR if the temperature term is added to the Jacobian matrix computation.

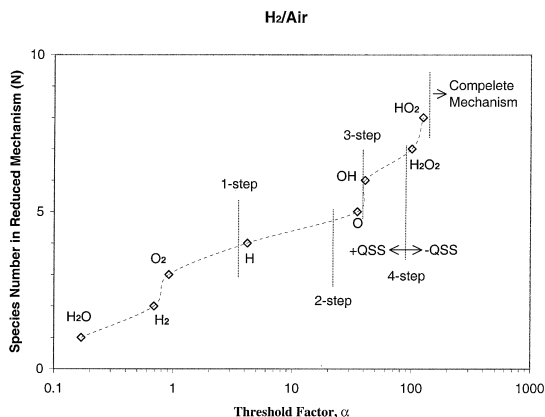


Fig. 4. Size of reduced mechanisms as a function of the value of α in H_2/air mixture.

The number of QSS species identified depends on the choice of the threshold value α as shown in Figs. 4 and 5, in which we have plotted the number of species in the reduced mechanism for the α value used, with indication of the specific species that is either removed ($-QSS$, for larger α) or added ($+QSS$, for smaller α). Inspecting Fig. 4, it appears that a regime of insensitivity in the choice of α would be $40 < \alpha < 100$ in that smaller values of α could result in unacceptable degradation in the accuracy in reduction, whereas the larger value of α would lead to “too many” species in the reduced mechanism. As such, we have put HO_2 and H_2O_2 as the QSS species and used $\alpha = 100$ to generate the reduced mechanism relevant for high-temperature hydrogen oxidation. For methane/air mixture, Fig. 5 shows that most

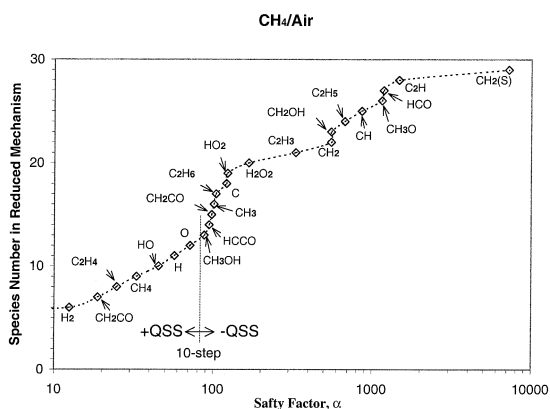


Fig. 5. Size of reduced mechanisms as a function of the value of α in CH_4/air mixture.

QSS species candidates have normalized time scales close to or well above 100. There are only a few species, with time scales less than or close to 50, which can be considered to be marginal QSS species. These marginal QSS species such as O and OH should be selected with care and subsequent verification. Perhaps the best strategy is not to include the marginal species as QSS species because there are only a few of them in a large mechanism anyway.

Reduced Mechanisms for H_2/Air and CH_4/Air Flames

The detailed H_2/air mechanism [16] used here involves nine species: H_2 , O_2 , N_2 , H_2O , O, OH, H, HO_2 , and H_2O_2 . The choice of α in Eq. 9 depends on the requirement of the accuracy for the resulting reduced chemistry. The larger the value of α , the higher is the accuracy of the reduced chemistry. By choosing $\alpha = 100$, with initial pressure between 0.2 atm and 20 atm and equivalence ratio from 0.7 to 2, for example, the software package ARC-CSP automatically recommends two species, HO_2 and H_2O_2 , as the QSS, finds and eliminates the corresponding fast reactions, and yields the following four-step reduced mechanism:

- 1: $\text{H}_2 + \text{O} = \text{OH} + \text{H}$
- 2: $\text{O}_2 + \text{H} = \text{O} + \text{OH}$
- 3: $\text{H}_2 + \text{OH} = \text{H}_2\text{O} + \text{H}$
- 4: $\text{H} + \text{H} + \text{M} = \text{H}_2 + \text{M}$

This reduced mechanism resembles the three-step reduced mechanism in Refs. 10 to 11, which includes OH as an additional QSS species. Clearly, the same three-step reduced mechanism could be obtained by the current algorithm if a smaller value of α , ~ 40 , is used to include OH as a QSS species.

For CH_4/air flames, we used the GRI MECH 1.2 as the detailed mechanism. It is shown in Fig. 5 that there are about five species which have global normalized time scales very close to 100. They are very difficult to be differentiated and should be included as QSS species as a group. By decreasing α slightly to ~ 80 , with the same pressure range as above and the equivalence ratio range between 0.7 and 1.3, for example, ARC-CSP generates a 10-step reduced mechanism. Reduced mechanisms with smaller sizes require much smaller values of α ,

which would result in substantial degradation of the results because the important radicals such as O and H will be included as QSS species. The selected QSS in the 10-step reduced mechanism are CH_3 , CH_2 , CH , CH_2O , HCO , HO_2 , H_2O_2 , C_2H_6 , C_2H_5 , C_2H_3 , C_2H , HCCO , CH_3OH , CH_2OH , CH_3O , $\text{CH}_2(\text{S})$, C, and the global reactions are:

- 1: $\text{CH}_4 + 3\text{O} = \text{CO} + \text{H}_2 + 2\text{OH}$
- 2: $\text{O} + \text{O} + \text{M} = \text{O}_2 + \text{M}$
- 3: $\text{H} + \text{OH} = \text{H}_2\text{O}$
- 4: $\text{CO} + \text{O} = \text{CO}_2$
- 5: $3\text{O} + \text{C}_2\text{H}_2 = 2\text{CO} + \text{H} + \text{OH}$
- 6: $\text{H}_2 + \text{O} = \text{H} + \text{OH}$
- 7: $\text{H} + \text{O} = \text{OH}$
- 8: $\text{H} + 3\text{O} + \text{C}_2\text{H}_4 = 2\text{CO} + 2\text{H}_2 + \text{OH}$
- 9: $\text{H} + \text{CH}_2\text{CO} = \text{OH} + \text{C}_2\text{H}_2$
- 10: $\text{HCCOH} = \text{CH}_2\text{CO}$

This reduced mechanism resembles the 12-step reduced mechanism of Ref. 6, which includes HO_2 and H_2O_2 as non-QSS species. These two species are found to have slow time scales only in ignition and low-temperature/high-pressure cases and are very good QSS candidates for extinction and high-temperature/low-pressure phenomena. The radical O is found to be a marginal QSS species with a global normalized time scale ~ 70 , and has a large effect on the PSR temperature if it is included as QSS species.

Assessment of the Reduced Mechanisms

The fidelity of these two reduced mechanisms was evaluated by comparing them with the detailed mechanisms using the PSR in the pressure range between 0.2 and 20 atm, and equivalence ratio range between 0.7 and 1.3. The comparison of the temperature dependence on the flow residence time in PSR for H_2/air and CH_4/air mixtures are shown in Figs. 6 and 7. For H_2/air mixtures, it is seen that the results of the reduced chemistry agree very well with those of the detailed chemistry over the entire range of pressure and equivalence ratio. The results for CH_4/air show similar agreement with the detailed chemistry. In addition, comparison of the mole fractions of the remaining species also shows equally good agreement. Therefore, it can be concluded that the reduced chemistry

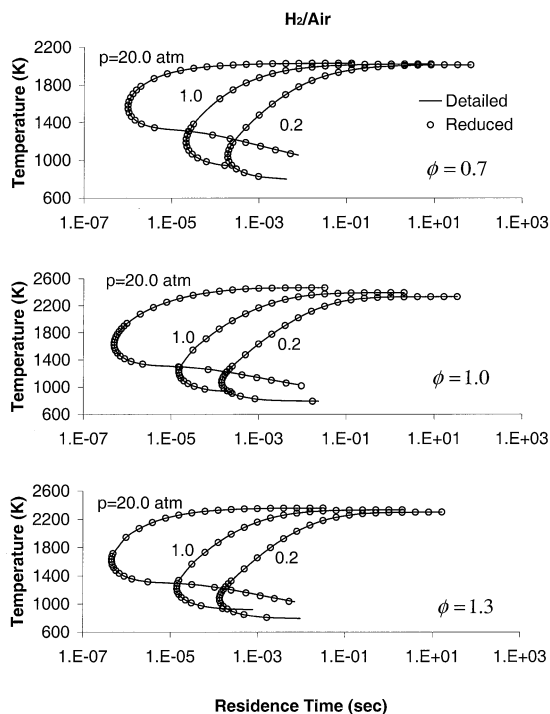


Fig. 6. Comparison of dependence of temperature on the residence time of PSR between the reduced and detailed mechanisms for various pressures and equivalence ratios in H_2/air flame.

generated by the present CSP algorithm can well reproduce the PSR data.

We next assess the reduced mechanism by using the one-dimensional planar propagating flame at the same pressure and equivalence ratio ranges. The code used was SANDIA's PREMIX. For hydrogen/air flames, Fig. 8 compares the flame structure at 1 atm, whereas Fig. 9 shows the dependence of the flame speed on the equivalence ratio and pressure. It is seen that the flame speed obtained by the reduced mechanism agrees quite well with the detailed chemistry on the lean side or at pressures less than 1 atm. The relative error increases slightly with increasing pressure on the rich side. At 20 atm, the relative error of flame speed is about 5%. The reason is that HO_2 and H_2O_2 , while being selected as the QSS at $\alpha = 100$, become increasingly important with increasing pressure. By comparing Figs. 8 and 9, we conclude that the QSS assumption for HO_2 and H_2O_2 only slightly affects the flame speed of rich hydrogen flames at high pressures. We note again that

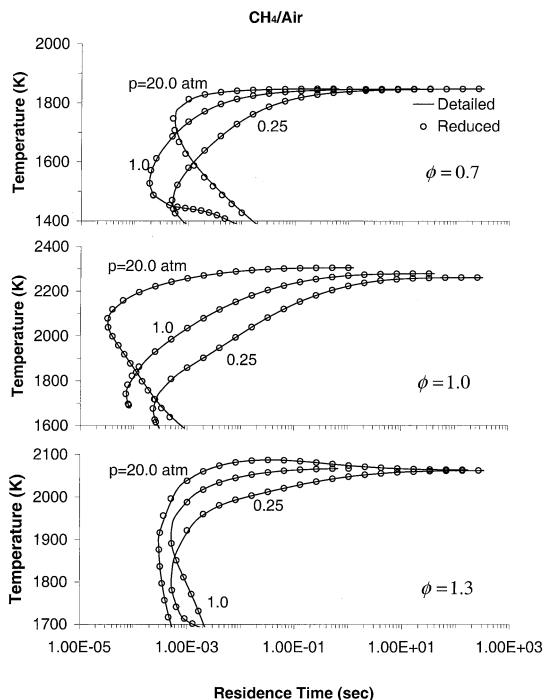


Fig. 7. Comparison of dependence of temperature on the residence time of PSR between the reduced and detailed mechanisms for various pressures and equivalence ratios in CH₄/air flame.

HO₂ and H₂O₂ have been found to be important in such lower temperature phenomenon as ignition [6], and as such cannot be treated as QSS in these cases.

Comparison of the structure of the stoichiometric CH₄/air flame at 1 atm, obtained with the reduced as well as the detailed mechanisms, is

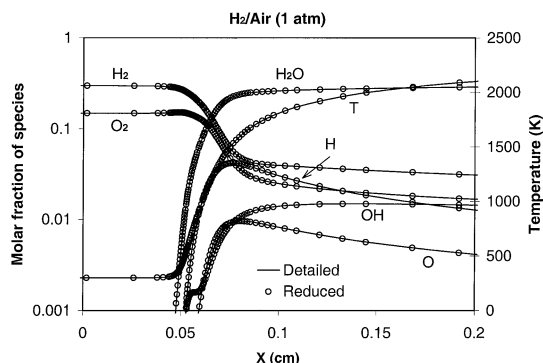


Fig. 8. Comparison of the flame structures of temperature and species predicted by the reduced and detailed mechanisms, respectively, for stoichiometric H₂/air flames at 1 atm.

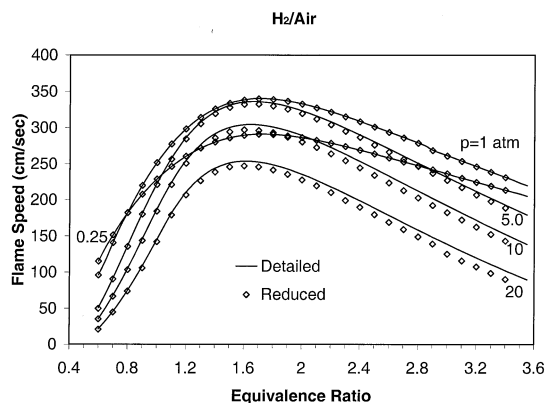


Fig. 9. Comparison of the dependence of flame speed on the equivalence ratio between reduced and detailed mechanisms for H₂/air flames at various pressures.

given in Fig. 10. It is seen that the distributions of temperature and mole fractions of the reactants and products calculated by using the reduced 10-step mechanism agree very well with those of the detailed chemistry. Figure 10b also shows that the reduced chemistry reproduces well the distributions of OH, O, H, HCCOH, and CH₂CO, and slightly under-predicts the peak mole fractions of C₂H₄ and C₂H₂.

The comparison of flame speed as a function of equivalence ratio and pressure for CH₄/air

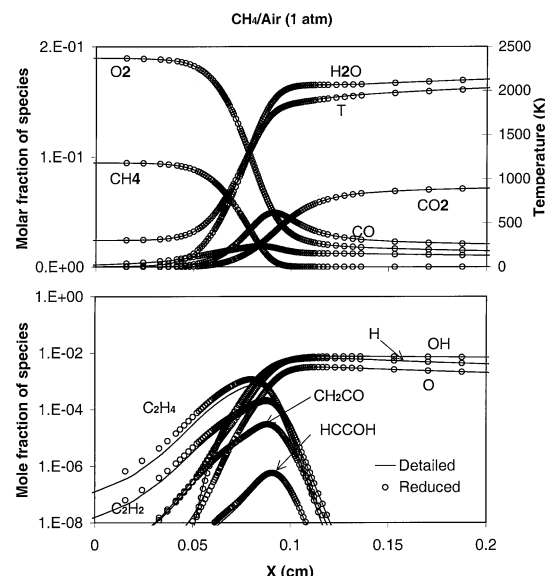


Fig. 10. Comparison of the flame structures predicted respectively by the reduced and detailed mechanisms for stoichiometric CH₄/air flames at 1 atm. 10a: temperature, reactants, and products; 10b: radicals.

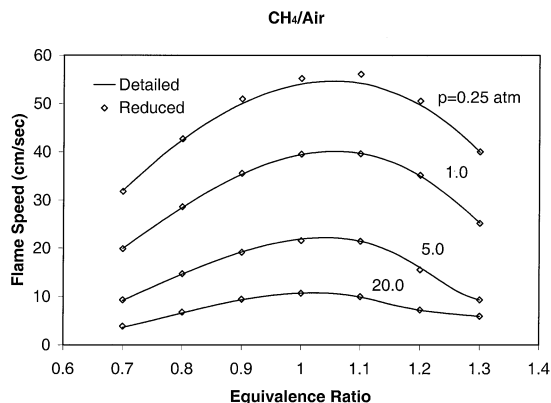


Fig. 11. Comparison of the dependence of flame speed on the equivalence ratio between reduced and detailed mechanisms for CH_4/air flames at various pressures.

flames is shown in Fig. 11. It is seen that the 10-step reduced chemistry agrees very well with the detailed chemistry at pressures greater than 1 atm. At pressures below 1 atm, the reduced mechanism slightly over-predicts the flame speed near $\phi = 1$, but still shows good agreement near both the lean and rich limits.

CONCLUSION

The previous CSP method for analysis and reduction of large chemical reaction mechanisms is extended to the complex eigensystem. An algorithm to identify the QSS species is presented by defining the characteristic time scale for each chemical species. The results show that the time scales of the chemical species change dramatically and non-monotonically, and oscillatory modes appear frequently in chemical systems. It is also shown that the extinction residence time of PSR is an appropriate characteristic time responsible for the progress of the chemical reaction for strongly burning and near-extinction situations. By using the present method, 4-step and 10-step reduced mechanisms of H_2/air and CH_4/air mixture were obtained and evaluated by using PSR and the one-dimensional planar propagating flames. The validity of the present algorithm is demonstrated through good agreements on the flame speed, flame temperature, and flame structure

obtained by the reduced and detailed chemistries, respectively, over a wide range of pressures and equivalence ratios.

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