# Design of Flexible Reduced Kinetic Mechanisms

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*Reduced mechanisms are often used in place of detailed chemistry because the computational burden of including all the species continuity equations in the reactor model is unreasonably high. Contemporary reduction techniques produce mechanisms that depend strongly on the nominal set of problem parameters for which the reduction is carried out. Effects of variability in these parameters on the reduced mechanism are the focus of this work. The range of validity of a reduced mechanism is determined for variations in initial conditions. Both sampling approaches and quantitative measures of feasibility, such as the flexibility index and the convex hull formulation, are employed. The inverse problem of designing a reduced mechanism that covers the desired range of initial conditions is addressed using a multiperiod approach. The effect of the value of a user-defined tolerance parameter, which determines whether the predictions made by the reduced mechanism are acceptable, is also assessed. The analytical techniques are illustrated with examples from the literature.*

## Introduction

The chemistry of several reacting systems is often described by detailed mechanisms that consist of a large number of species, $n_s$, and elementary reactions, $n_r$. Examples can be drawn from fields as diverse as combustion, polymerization, environmental science, materials technology, and microelectronics processing. Table 1 shows the values of $n_s$ and $n_r$ for some combustion mechanisms. To establish the material and energy balances for such systems in a reactor, the number of component mass balances required is $n_s$. Depending on the type of reactor, these balances could be nonlinear algebraic equations, ordinary differential equations, partial differential equations, or a combination of such equations. The CPU requirement to solve such problems rigorously thus increases in proportion with $n_s$. This difficulty has motivated the development of reduced mechanisms that retain only the limited set of species and reactions necessary to capture the essential features of the chemistry. For example, a reduced combustion mechanism is deemed successful if it matches the predictions of laminar flame speed, adiabatic temperature rise, auto ignition delay time, extinction time, and concentration profiles of key species with a prespecified accuracy. Once obtained, the reduced mechanism can be directly incorporated into the chemical source terms of a reactor model having any level of complexity.

The reduction of kinetic models for combustion is extremely crucial and has received considerable attention in recent times. Most industrial furnaces for power generation such as stokers, fluidized beds, and boilers have complicated geometry. Consequently, both the fluid mechanics and the heat transfer are extremely complex. The highly turbulent nature of the flow and the strong influence of radiation can be modeled only with the help of computational fluid dynamics, which is highly CPU-intensive. In the past, the rapid combustion reactions in CFD codes have been modeled under the equilibrium assumption. This is adequate to describe the heat transfer and the overall mass balance. However, with the increasing environmental concerns over the emissions of CO, $NO_x$, hydrocarbons, and chlorinated compounds into the atmosphere, the equilibrium assumption must be relaxed if the evolution of these pollutants is to be accurately predicted.

A comprehensive review of reduction techniques for kinetic models with an emphasis on combustion can be found

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**Table 1. Size of Commonly Encountered Combustion Mechanisms**

| Mechanism | Version | Chemistry | $n_s$ | $n_r$ |
|---|---|---|---|---|
| Hydrogen-oxygen | 1, Low pressure | H/O | 9 | 20 |
| | 2, Low pressure | H/O | 10 | 45 |
| | 1, High pressure | H/O | 8 | 19 |
| $CO/H_2$/air | 1 | C/H/O | 14 | 47 |
| Natural gas | | | | |
| GRI mechanism | | | | |
| | 1.2 | C/H/O | 32 | 177 |
| | 2.11 | C/H/O/N | 49 | 279 |
| | 3.0 | C/H/O/N | 53 | 325 |
| Leeds mechanism | 1.4 | C/H/O | 37 | 190 |
| | 1.4 with *N*-Extension | C/H/O/N | 43 | 354 |
| | 1.4 with *N*,*S*-Extension | C/H/O/N/S | 65 | 446 |

in Griffiths (1995) and Tomlin et al. (1997). The techniques for *a priori* mechanism reduction fall into three major categories: (1) quasi-steady-state/partial-equilibrium hypothesis (Peters and Williams, 1987), (2) time-scale analysis (Maas and Pope, 1992; Lam and Goussis, 1994), and (3) mathematical programming methods (Petzold and Zhu, 1999; Edwards and Edgar, 2000; Androulakis, 2000). Here a simplified reactor model such as batch, plug-flow, or perfectly stirred tank is used to study the relative influence of individual reactions on the features of the combustion process. Transport effects are neglected while performing the reduction, but their influence is sometimes checked *a posteriori* by testing the full and reduced mechanisms on a simplified model that includes these effects.

The reduced mechanism obtained by these methods depends on the parameters of the kinetic model, viz., initial conditions of composition, temperature, and pressure, and parameters such as specific reaction-rate constants and thermodynamic properties. In reality, the initial conditions may undergo considerable variation and the values of the parameters are not known exactly. For example, a change in the mode of operation from fuel-rich to fuel-lean combustion corresponds to a change of the initial conditions. Likewise, the rate constants are associated with confidence intervals or uncertainty factors. The reduction techniques also have internal tolerances that determine whether the predictions of the reduced and detailed mechanisms are acceptably close. As will be shown later, there is no universal way in which the internal parameters can be specified.

In this article, the effects of parameter variability on a reduced mechanism are assessed in a quantitative manner. In particular the effects of initial conditions variability is addressed. Uncertainty in kinetic parameters is of extreme importance, as pointed out in the literature by various researchers, such as McRae and coworkers (1997), and will be a subject of future publication. The concepts of feasibility and flexibility analysis (Biegler et al., 1997) are utilized to allow the efficient computation of the range of validity with respect to initial conditions. The inverse problem of determining the reduced mechanism for a prespecified range of validity is also solved. The techniques are demonstrated with the combustion mechanisms listed in Table 1. It may be noted that although the examples focus on combustion, the mathematical formulation is sufficiently general to be applicable to the reduction of kinetic mechanisms arising in other fields.

## Reduction Method

The reduction technique employed in this work follows the mathematical programming approach of Androulakis (2000), which is based on determining the reactions that can be omitted from the mechanism without causing the predictions of the reduced mechanism to deviate from those of the full mechanism by a user-specified tolerance. Since a reaction is either included in a mechanism or absent from it, this step involves decision making or choosing among alternatives and gives the problem a combinatorial nature.

The reduction process begins with the choice of a reactor model and a discrepancy function, which is a measure of the error incurred in dropping reactions from the mechanism. The reactor model is solved once with the full mechanism in place, and the values of the key quantities (such as laminar flame speed, adiabatic temperature rise, auto ignition delay time, extinction time, and concentration profiles of key species) are stored for subsequent evaluation of the discrepancy function. A tolerance on the acceptable value of the error function is selected and an optimization problem involving integer variables is solved to obtain the reduced mechanism. The reduction strategy is described in detail elsewhere (Androulakis, 2000). The model used is described briefly in the following section.

### *Optimization problem*

The reduced mechanism is determined by solving the following mathematical model:

$$\min_{\lambda} \Phi = \sum_{k=1}^{n_r} \lambda_i \tag{1}$$

subject to:

$$\chi(\boldsymbol{\lambda}) \leq \epsilon, \tag{2}$$

where $\Phi$ is the objective function representing the sum of the binary variables ($\lambda_i$) that correspond to the existence of reaction (i) in the reduced mechanism, $\chi$ is the discrepancy function that depends on $\lambda$ and is given by the following form:

$$\chi(\lambda) = \left[ \sum_{j=1}^{M} w_j \int_{t_0}^{t_f} \left[ E_j(t) \right]^2 dt \right]^{1/2}, \tag{3}$$

where $M$ is the number of matched quantities, $w_j$ is the weight assigned to the $j$th quantity, and $E_j$ is the time-dependent error between the predictions of the full and reduced models. The standard form for $E_j$ is a scaled residual

$$E_j(t) = \frac{u_j^f(t) - u_j^r(t)}{\sigma_j(t)}, \tag{4}$$

where $u$ represents the value of a matched quantity, superscripts $f$ and $r$ denote full and reduced, respectively, and $\sigma$

is a scale factor used to evaluate the relative error for all observables. Both $u$ and $\sigma$ may be time-dependent.

It is convenient to represent the integral in Eq. 3 in a discretized form. If the total time horizon is composed of $n_t$ points, including the start point, the step-size in the time domain is

$$\Delta t = \frac{t_f - t_0}{n_t - 1}. \tag{5}$$

The observables $u$ are evaluated at times

$$t_l = t_0 (l-1)\Delta t \qquad l = 1, \ldots, n_t \tag{6}$$

along with the corresponding errors

$$e_{jl} = \frac{u_{jl}^r - u_{jl}^f}{\sigma_{jl}} \qquad j = 1, \ldots, M; \quad l = 1, \ldots, n_t. \tag{7}$$

Applying the trapezoidal rule to Eq. 3 yields

$$\chi(\lambda) = \left[ \frac{\Delta t}{2} \sum_{j=1}^{M} w_j \left( e_{j,1}^2 + 2 \sum_{l=2}^{n_t - 1} e_{jl}^2 + e_{j,n_t}^2 \right) \right]^{1/2}. \tag{8}$$

The three types of scale factors for each residual are

$$\begin{aligned} \sigma_{jl} &= 1 \\ &= \max\left(\kappa, u_{jl}^f\right) \\ &= \max\left[\kappa, \max_{1 \le l \le n_t} \left(u_{jl}^f\right)\right], \end{aligned} \tag{9}$$

corresponding to no scaling, scaling the residuals of an observable with the maximum value of that observable over the entire time horizon for the full mechanism, and scaling residuals of an observable with the corresponding value of the full mechanism at each time step. The lower limit ($\kappa$) (typically $10^{-15}$) on $\sigma$ avoids scaling by extremely small quantities; $\sigma$ values are numerical scaling factors that are used to reduce the bias toward tracked variables that are very large in magnitude compared to the smaller variables.

The combustion is assumed to take place in an isobaric batch reactor with premixed reactants and well-mixed contents operating isothermally or adiabatically. Transport effects are excluded from the model. The initial composition and temperature are specified. The reactor model is solved with the full mechanism in place for the evaluation of source terms in the material and energy balances

$$\frac{dy_k}{dt} = \frac{R_k M_k}{\rho} \qquad k = 1, \ldots, n_s \tag{10}$$

$$\frac{dT}{dt} = \sum_{k=1}^{n_s} \frac{R_k M_k h_k}{\rho \bar{c}_p}. \tag{11}$$

Here $R_k$ is the net rate of the production of species $k$, and can be evaluated from knowledge of the intrinsic rates $q_i$ of individual reactions and the stoichiometry as follows:

$$R_k = \sum_{i=1}^{n_r} \lambda_i \left( \nu_{ki}^r - \nu_{ki}^f \right) q_i, \tag{12}$$

where $q_i$ is given by the familiar power-law expression of mass-action kinetics:

$$q_i = k_{f,i} \left( \prod_{k=1}^{n_s} c_k^{\nu_{ki}^f} - \frac{1}{K_{c,i}} \prod_{k=1}^{n_s} c_k^{\nu_{ki}^r} \right). \tag{13}$$

The temperature dependence of the specific reaction rate constant is given by the Arrhenius law:

$$k_{f,i} = A_i T^{\beta_i} \exp - \left[ \frac{E_i}{R_g T} \right]. \tag{14}$$

In order to include the characteristics of nonelementary reactions, three-body reactions, pressure-dependent reactions, and reactions involving vibrational energy transfer prevalent in combustion, the basic expressions for $q_i$ and $k_{f,i}$ are modified as described in Chemkin-III (Kee et al., 1996).

### *Numerical methods*

The differential equations representing the batch reactor model are generally stiff. They are also badly scaled in that the absolute values of the variables vary by several orders of magnitude. Hence, integration was performed using the code LSODE (Hindmarsh, 1983) based on Gear's method that can solve this problem both efficiently and accurately. The thermophysical properties and reaction rates appearing on the righthand sides of the ODEs were evaluated using the CHEMKIN-III package. For each set of values $\lambda$, the reactor equations were solved to evaluate $\chi$ using Eq. 8.

The overall problem of mechanism reduction is a nonlinear integer programming (INLP) problem. The INLP was solved using a branch-and-bound (B&B) strategy (Floudas, 1995; Adjiman et al., 2000). The relaxed INLP at each node of the B&B tree was solved using a sequential quadratic programming (SQP) code. Both NPSOL (Gill et al., 1986) and FSQP (Zhou et al., 1991) have been used.

The derivatives required for the SQP method were provided numerically with finite differences determined based on a stepsize that takes into account the truncation and round-off errors in the approximation, and the noise in the constraint function. When solving the relaxed problem, an infeasible path strategy for NLPs such as SQP may allow the bounds on the binary variables to be violated. This was found to have a deleterious influence on the performance of the NLP solver. Hence, special care was taken to ensure feasibility with respect to the bounds at each iteration. Further, the function $\chi$ is nonconvex and as such can have multiple local minima. Since the SQP method can only guarantee a local minimum, the results of the B&B strategy do not necessarily yield the smallest set of reactions, as was also pointed out by

Androulakis (2000). Multiple starting points implemented in the current procedure serve only as a verification of the solution rather than proof of its global optimality.

### *Effect of error tolerance*

The error tolerance $\epsilon$ represents the degree to which the reduced mechanism must match the predictions made by the full mechanism for the quantities of interest. If the parameter $\epsilon$ is too small, all the reactions may have to be included in the reduced mechanism. On the other hand, too large a value of $\epsilon$ results in a reduced mechanism that poorly describes the combustion process. Hence, an intermediate value of $\epsilon$ must be judiciously selected. Unfortunately, the value of $\epsilon$ that can be considered adequate for a reduced mechanism cannot be specified in advance. One of the factors governing the absolute value of $\epsilon$ is the choice of error function and the scaling employed. Since the mole fractions of individual components vary by several orders of magnitude and differ from the temperature by at least three orders of magnitude, the scale factors appearing in each $e_{j,l}$ are crucial to the success of the reduction scheme. In the absence of scaling, the error function $\chi$ is biased toward the quantities with a large magnitude. Experience has shown that each residual must be scaled by the corresponding quantity for the full mechanism, which is the third choice of scale factors in Eq. 9.

### *Case studies*

The ideas proposed in this paper have been demonstrated with two examples: hydrogen-oxygen combustion at low pressure and $CO/H_2/O_2$ combustion (Androulakis, 2000). The details of the mechanism can be found in the reference cited.

*$H_2/O_2$ Combustion at Low Pressure.* The full mechanism involving 20 reactions and 9 species is given in Table 1. Table 2 shows the effect of changing $\epsilon$ on the reduced mechanism for $H_2/O_2$ combustion for various initial conditions. In all cases, the temperature was chosen to be sufficiently high for ignition to occur, and the pressure was held at 1 atm. The matched quantities were the concentration profiles of $H_2$, $O_2$, and $H_2O$, and the temperature and the error is evaluated over a time period of 1.6 ms.

As $\epsilon$ decreases from 0.1 to 0.001 for any set of initial conditions, the size of the reduced mechanism increases, which is consistent with the expected behavior of the MINLP model for reduction. The actual error achieved, $\chi(\epsilon)$, is smaller than the desired error by a factor of 2 to 9, but not more than an order of magnitude. Since the reaction indices take on inte-

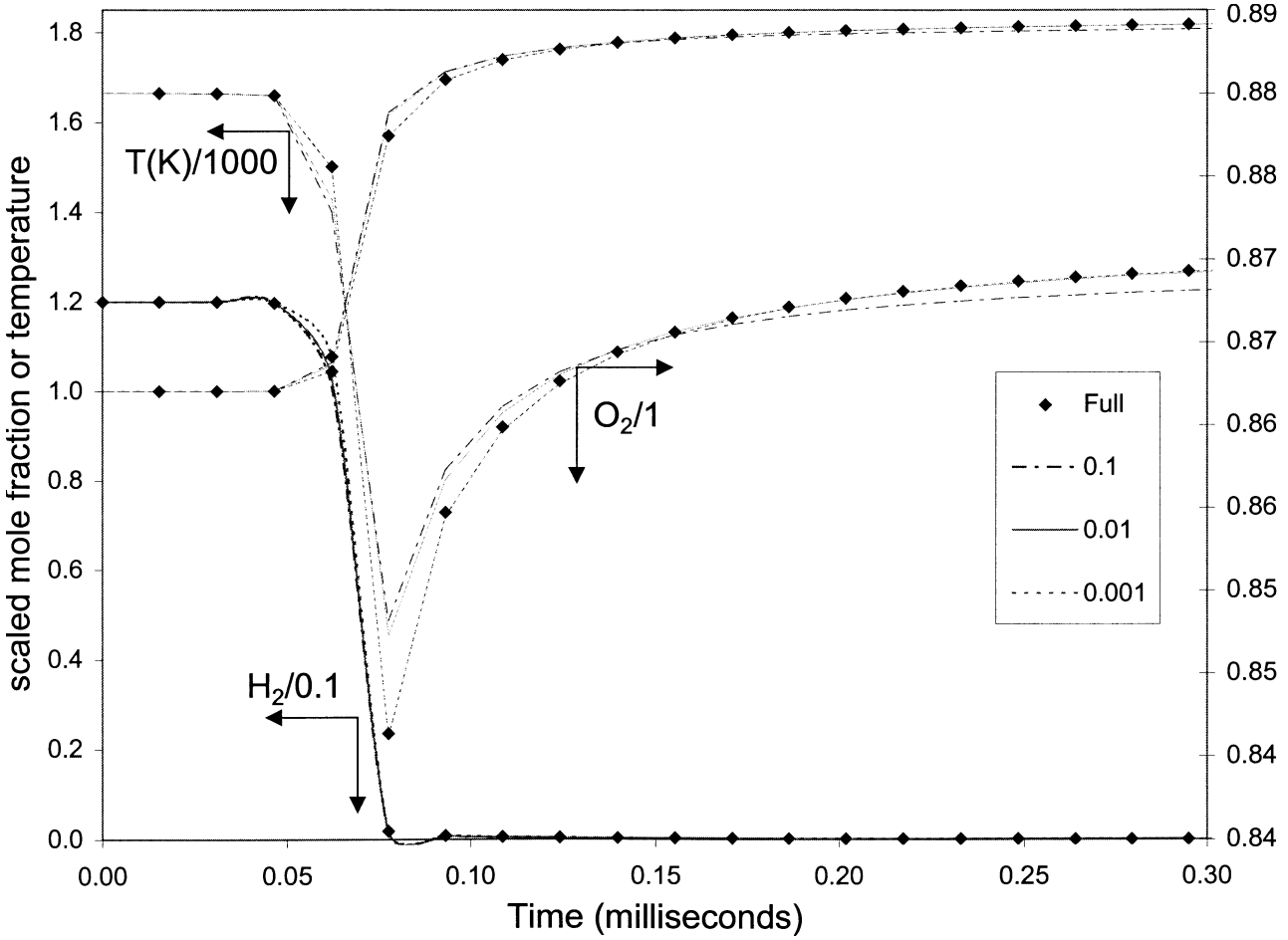


**Figure 1. Error tolerance effect on reducing the mechanism for $H_2/O_2$ combustion at 1 atm with $[O_2]_0 = 0.88$ and $T_0 = 1{,}000$ K: temporal evolution of concentration profiles of $H_2$, $O_2$, and temperature.**

**Table 2. $H_2$ Combustion Network**

| No. | Reaction | A | $n$ | $E$ |
|---|---|---|---|---|
| 1 | $H_2+O_2 \leftrightarrow 2OH$ | $1.70\times10^{13}$ | 0.0 | 47,780 |
| 2 | $OH+H_2 \leftrightarrow H_2O+H$ | $1.17\times10^{13}$ | 1.3 | 3,626 |
| 3 | $H_2+OH \leftrightarrow H_2O+H$ | $4.00\times10^{14}$ | −0.5 | 0 |
| 4 | $O+H_2 \leftrightarrow OH+H$ | $5.06\times10^{14}$ | 2.7 | 6,290 |
| 5 | $H+O_2+M \leftrightarrow HO_2+M$ | $3.61\times10^{17}$ | −0.7 | 0 |
| 6 | $OH+HO_2 \leftrightarrow H_2O+O_2$ | $7.50\times10^{12}$ | 0 | 0 |
| 7 | $H+HO_2 \leftrightarrow OH+OH$ | $1.40\times10^{14}$ | 0 | 1,073 |
| 8 | $O+HO_2 \leftrightarrow OH+O_2$ | $1.40\times10^{13}$ | 0 | 1,073 |
| 9 | $OH+OH \leftrightarrow O+H_2O$ | $6.00\times10^{8}$ | 1.3 | 0 |
| 10 | $H+H+M \leftrightarrow H_2+M$ | $1.00\times10^{18}$ | −1.0 | 0 |
| 11 | $H+H+H2 \leftrightarrow H_2+H_2$ | $9.20\times10^{16}$ | −0.6 | 0 |
| 12 | $H+H+H_2O \leftrightarrow H_2+H_2O$ | $6.0\times10^{19}$ | −1.2 | 0 |
| 13 | $H+OH+M \leftrightarrow H_2O+M$ | $1.6\times10^{22}$ | −2.0 | 0 |
| 14 | $H+O+M \leftrightarrow OH+M$ | $6.2\times10^{16}$ | −0.6 | 0 |
| 15 | $O+O+M \leftrightarrow O_2+M$ | $1.89\times10^{13}$ | 0 | −1,788 |
| 16 | $H+HO_2 \leftrightarrow H2+O2$ | $1.25\times10^{13}$ | 0 | 0 |
| 17 | $HO_2+HO_2 \leftrightarrow H_2O_2+O_2$ | $2.00\times10^{12}$ | 0 | 0 |
| 18 | $H_2O_2+M \leftrightarrow OH+OH+M$ | $1.30\times10^{17}$ | 0 | 45,500 |
| 19 | $H_2O_2+H \leftrightarrow HO_2+H_2$ | $1.60\times10^{12}$ | 0 | 3,800 |
| 20 | $H_2O_2+OH \leftrightarrow H_2O+HO_2$ | $1.00\times10^{13}$ | 0 | 1,800 |

ger values of 0 and 1 only, $\chi(\epsilon)$ cannot be represented as a continuous function of $\epsilon$ for given reaction sets. In other words, not every value of $\epsilon$ corresponds to an integer set $\lambda$. Although the number of reactions in the reduced set, $N_r$, is less than that in the full set, $n_r$, and varies with $\epsilon$, the number of species remains practically constant at 6 or 7. Hence, only 2 or 3 species are dropped in this example.

The four initial conditions represent operating conditions ranging from fuel-lean to fuel-rich combustion. The basic set of reactions is always {1, 2, 3, 4}, but there is considerable variability in the remaining reactions that are selected for various $\epsilon$. In particular, given error tolerances $\epsilon_1$ and $\epsilon_2$ with $\epsilon_2 < \epsilon_1$, the reaction set $\{\lambda\}_1$ for $\epsilon_1$ is not necessarily a subset of the reaction set $\{\lambda\}_2$ for $\epsilon_2$. This shows that variability in the initial conditions requires different reduced mechanisms. Hence, it is important to deduce the reduced mechanism that is valid for the widest range of expected initial conditions.

Another important point is that if the basic set of reactions is known *a priori*, one can use this information to improve dramatically the efficiency of the solution procedure, since the binary variables that correspond to these reactions can be fixed, thus resulting in smaller solution space in terms of binary variables combinations.

Figures 1 and 2 are a comparison of the full profiles, with the reduced profiles for various values of $\epsilon$ corresponding to initial conditions of $T_0 = 1000$ K, $[H_2] = 0.12$, and $[O_2] = 0.88$. The reduced mechanisms appear to be satisfactory for both

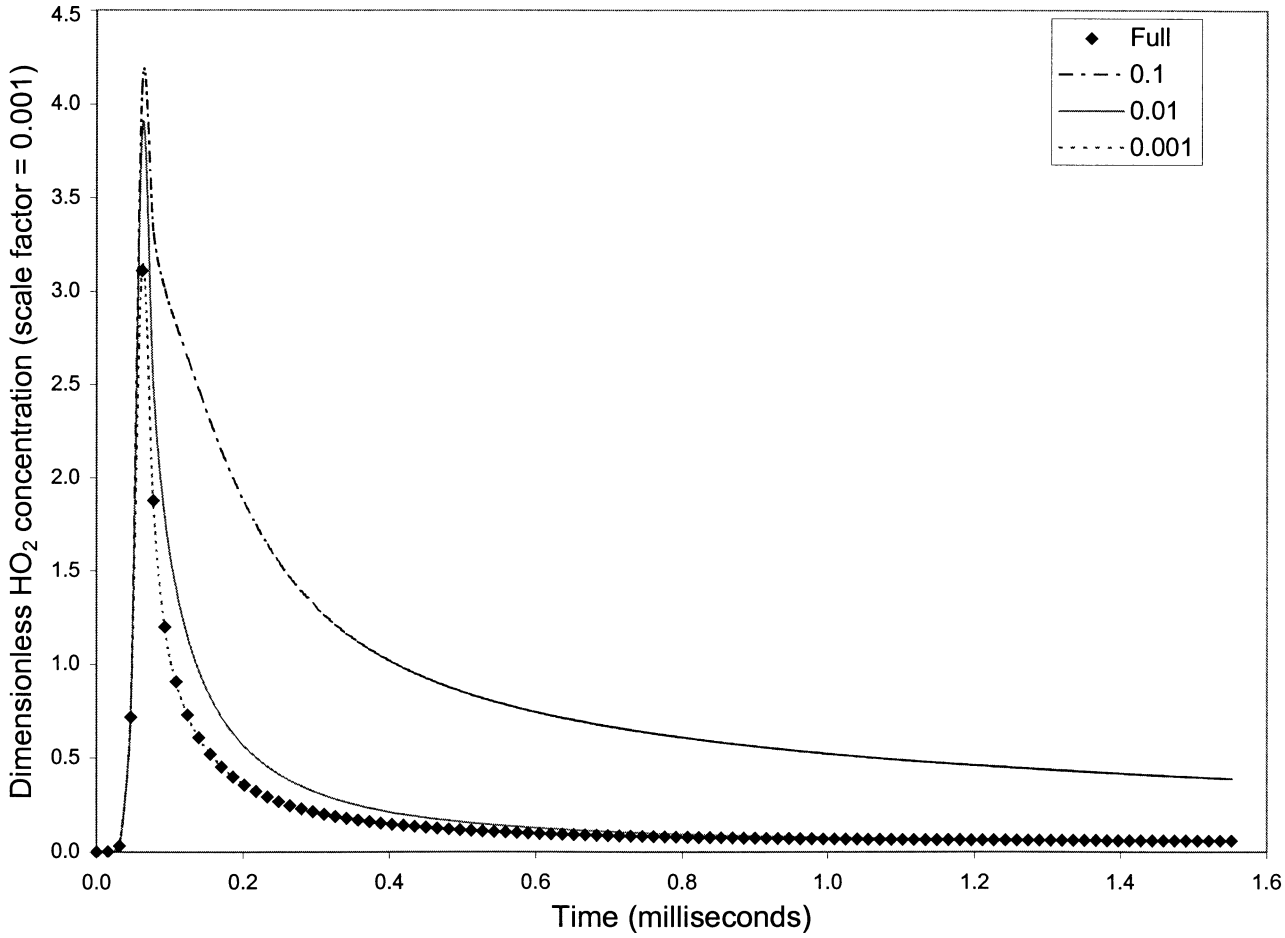


**Figure 2. Error tolerance effect on reducing the mechanism for $H_2/O_2$ combustion at 1 atm with $[O_2]_0 = 0.88$ and $T_0 = 1{,}000$ K: temporal evolution of concentration profiles of $HO_2$.**

**Table 3. Effect of Error Tolerance on Low-Pressure $H_2/O_2$ Combustion Mechanism Reduction**

| $x_{O_2}$ | $x_{H_2}$ | $T$,K | $\epsilon$ | $N_r$ | $N_s$ | $\chi(\epsilon)$ | Reaction Set |
|---|---|---|---|---|---|---|---|
| 0.88 | 0.12 | 1,000 | 0.1 | 6 | 7 | $3.82\times10^{-2}$ | {1, 2, 3, 4, 5, 7} |
| | | | 0.01 | 7 | 7 | $4.70\times10^{-3}$ | {1, 2, 3, 4, 5, 6, 7} |
| | | | 0.001 | 11 | 7 | $6.86\times10^{-4}$ | {1, 2, 3, 4, 5, 6, 7, 8, 9, 13, 16} |
| 0.8 | 0.2 | 1,275 | 0.1 | 6 | 7 | $2.68\times10^{-3}$ | {1, 2, 3, 4, 5, 8} |
| | | | 0.01 | 6 | 7 | $2.68\times10^{-3}$ | {1, 2, 3, 4, 5, 8} |
| | | | 0.001 | 7 | 7 | $9.83\times10^{-4}$ | {1, 2, 3, 4, 5, 6, 7} |
| 0.5 | 0.5 | 1,200 | 0.1 | 4 | 6 | $2.50\times10^{-2}$ | {1, 2, 3, 4} |
| | | | 0.01 | 5 | 6 | $7.12\times10^{-3}$ | {1, 2, 3, 4, 14} |
| | | | 0.001 | 6 | 7 | $4.28\times10^{-4}$ | {1, 2, 3, 4, 5, 7} |
| 0.15 | 0.85 | 1,250 | 0.1 | 5 | 6 | $1.71\times10^{-2}$ | {1, 2, 3, 4, 13} |
| | | | 0.01 | 5 | 6 | $7.23\times10^{-3}$ | {1, 2, 3, 4, 12} |
| | | | 0.001 | 9 | 7 | $3.32\times10^{-4}$ | {1, 2, 3, 4, 5, 7, 11, 12, 13} |

$\epsilon = 0.001$ and $\epsilon = 0.01$. However, Figure 1 shows that the concentration profile of $O_2$ deviates considerably from the full profile for $\epsilon = 0.1$, although profiles for $H_2$ and temperature are reasonably close. Figure 2 shows the profiles for $HO_2$, a species that was not included in the discrepancy function. As $\epsilon$ decreases, the reduced profile for this species begins to approach the full mechanism profile, although it is not being matched. Hence, at lower values of the tolerance, the reduced mechanism can achieve more than the requested accuracy.

The results in Figures 1 and 2 and Table 3 throw light on some of the features of this problem that make the *a priori* selection of $\epsilon$ difficult. The only difference between the reduced mechanisms corresponding to $\epsilon$ values of 0.1 and 0.01 is the inclusion of reaction 6, but the effect on the profile of $O_2$ is significant. On the other hand, although the reduced mechanisms for $\epsilon$ values of 0.01 and 0.001 differ by four reactions, the effect on the profiles is negligible. Finally, all values of $\epsilon$ yield reduced mechanisms with 6 or 7 species, which shows that the number of species in the mechanism need not be altered although the number of reactions changes.

The computational requirements for the reduction methodology based on our current implementation of B&B optimization procedure, are 273.6 CPU s (5 nodes) for $\epsilon = 0.1$, 114.3 CPU s (3 nodes) with $\epsilon = 0.01$, and 321.5 CPU s (5 nodes) for $\epsilon = 0.001$. The average time per node spent for the solution of NLP is approximately 50 CPU s. Note that the CPU time is not proportional to the tolerance used. All computations are performed in SUN Ultra 60 workstation.

*$CO/H_2/O_2$ Combustion.* For the $CO/H_2/O_2$ mechanism reduction the observables are CO, $H_2$, $O_2$, $CO_2$, $H_2O$, and temperature, and the integration time is 1.6 ms. The observations regarding the effect of $\epsilon$ in the preceding example are corroborated by the results shown in Table 4 and Figure 3. Clearly, $\epsilon = 0.1$ is an unacceptable choice for this mechanism since the reduced mechanism predicts an adiabatic temperature rise that is 667 K lower than the true value causing the concentration profiles to deviate significantly. A decrease in $\epsilon$ to 0.01 results in better agreement with $N_r = 9$ and $N_s = 9$. A further decrease in $\epsilon$ to 0.001 leaves $N_s$ unchanged, but $N_r$

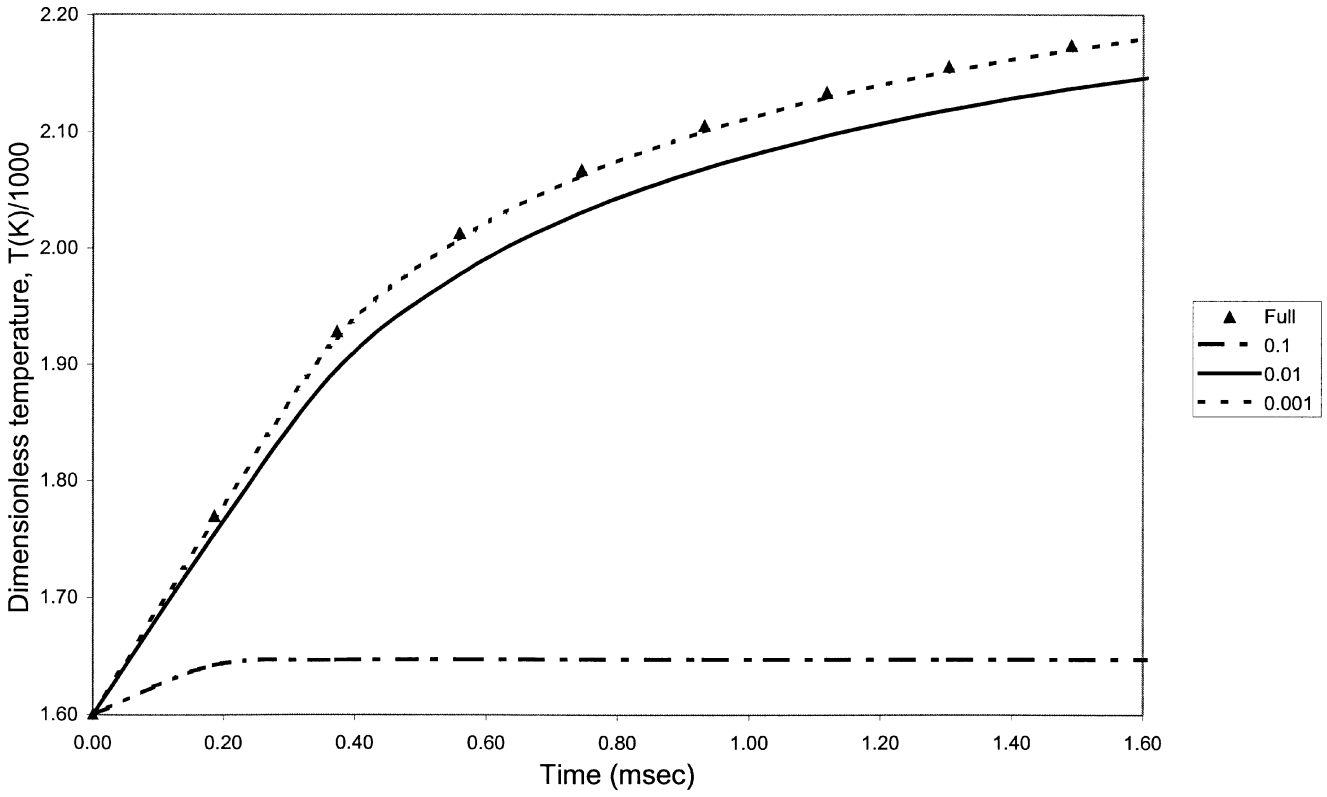


**Figure 3. Error tolerance effect on reducing the mechanism for $CO/H_2/$air combustion at 1 atm with the initial conditions in Table 3: temporal evolution of the temperature profile.**

**Table 4. Effect of Error Tolerance on the $CO/H_2$/Air Combustion Mechanism Reduction**

| $\epsilon$ | $N_r$ | $N_s$ | $\chi(\epsilon)$ | Reaction Set |
|---|---|---|---|---|
| 0.1 | 4 | 7 | $6.87\times10^{-2}$ | {3, 10, 17, 38} |
| 0.01 | 9 | 9 | $8.74\times10^{-3}$ | {3, 6, 10, 12, 15,17, 24, 32, 38} |
| 0.001 | 16 | 9 | $9.60\times10^{-4}$ | {1, 3, 4, 6, 10, 12, 13, 14, 15, 17, 22, 24, 32, 34, 35, 38} |

*Note:* Nominal initial conditions: $T_0 = 1600$, mole fractions: $CO = 0.095$, $H_2 = 0.005$, $O_2 = 0.189$, $N_2 = 0.711$.

almost doubles to 16. Again, the choice between 0.01 and 0.001 for $\epsilon$ is difficult to make, although the mechanism for $\epsilon = 0.001$ clearly has excellent agreement.

These observations emphasize the importance of choosing $\epsilon$ for any function $\chi(\epsilon)$ that has been appropriately scaled. A reduced mechanism showing reasonable agreement with a full mechanism is characterized by a constant number of species, $N_s$. Imperceptible improvements in the predictions may be characterized by large increases in $N_r$ as $\epsilon$ decreases. Further, since the error constraint is rarely active at a bound, the actual accuracy achieved is greater than that desired. However, as mentioned earlier, since the variables of the problem are restricted to binary values only, an integer solution with $\chi(\lambda^r) = \epsilon$ need not exist.

Increased computational time is required in this case due to an increased number of binary variables. In particular, 1513 CPU s (5 nodes) for $\epsilon = 0.1$, 701 CPU s (7 nodes) for $\epsilon = 0.01$, and 1780 CPU s (9 nodes) for $\epsilon = 0.001$. One should notice that possible computational improvement is possible since no work has been done along this direction.

## Range of Validity of Reduced Mechanisms

### *Problem definition*

A mechanism describes the intrinsic chemistry of a reacting process, that is, the rates of the actual molecular events leading to the transformation of reactants to products. The rate expressions involve parameters such as specific reaction-rate constants, thermodynamic equilibrium constants, and third-body efficiencies. The values of these parameters are often determined by applying regression techniques to the experimental data obtained in the laboratory. The measurement errors that are present in the experiments and the regression errors that arise when the rate law is fitted to the experimental data using the maximum likelihood approach can be statistically described as confidence limits or uncertainty factors. When describing the reaction process in a reactor, parameters such as thermophysical and transport properties appear, and are additional sources of uncertainty. Further, the reactor-model equations are solved subject to initial conditions such as feed composition and temperature. These operating conditions can undergo large variability from process to process. Hence, it is important to determine

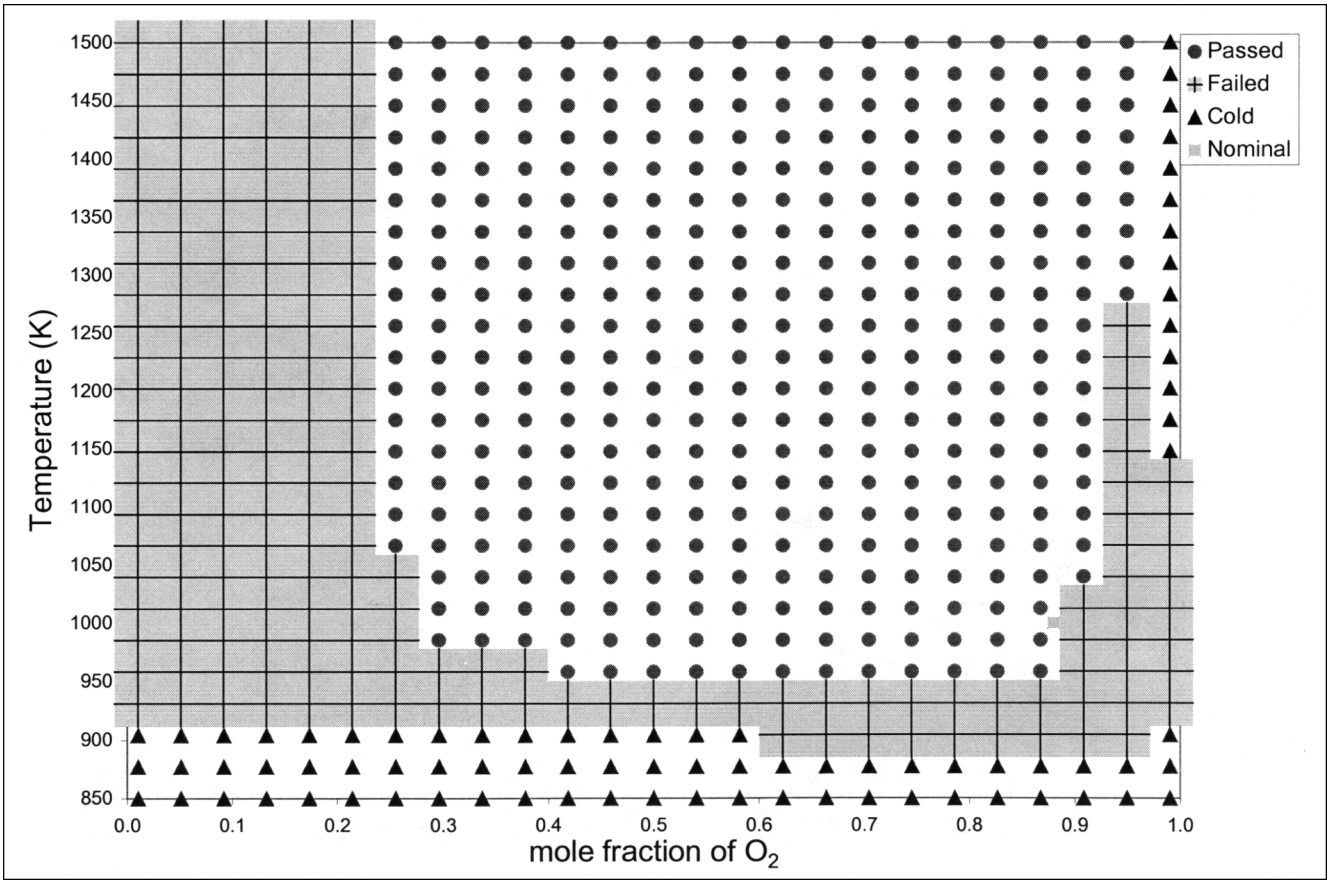


**Figure 4. Feasible region map showing "pass," "fail" and "cold" regions for $H_2/O_2$ combustion at 1 atm with nominal conditions of $[O_2]_0 = 0.88$ and $T_0 = 1000$ K, and $\epsilon = 0.001$.**

whether the reduced mechanism is valid for other operating conditions and values of the parameters apart from the nominal values that are used for performing the reduction. In the case of combustion, such uncertainty is of paramount importance in predicting the evolution of pollutant species that are present at PPM levels and are extremely sensitive to the parameter values used for simulation.

In the combustion mechanisms used in this work, the uncertain or variable parameters are the initial conditions of composition and temperature, and the rate constants. The range of validity of the reduced mechanism is examined in two ways. First, reduced mechanisms are obtained with nominal values of the parameters, and the feasible range is determined a *posteriori* using sampling methods and flexibility analysis. Second, the reduction is performed to ensure that the reduced mechanism is valid for a range of parameter values specified *a priori*.

### *Effects of variability in the initial conditions*

The reduced mechanisms have been developed for a fixed set of initial conditions. Industrial combustors operate under a variety of initial conditions, such as fuel-lean or fuel-rich. The results in Table 3 have demonstrated that the reduced mechanism changes with the initial conditions. In this section, the range of validity of the reduced mechanism is determined through the generation of feasible region plots. The effect of variability is also quantified using the flexibility-index method (Swaney and Grossmann, 1985a,b) and the recent convex hull formulation (Ierapetritou, 2001).

### *Feasible region plots*

A convenient graphical representation of the feasible region for a set of initial conditions can be obtained using a grid search procedure. The error function is evaluated at a

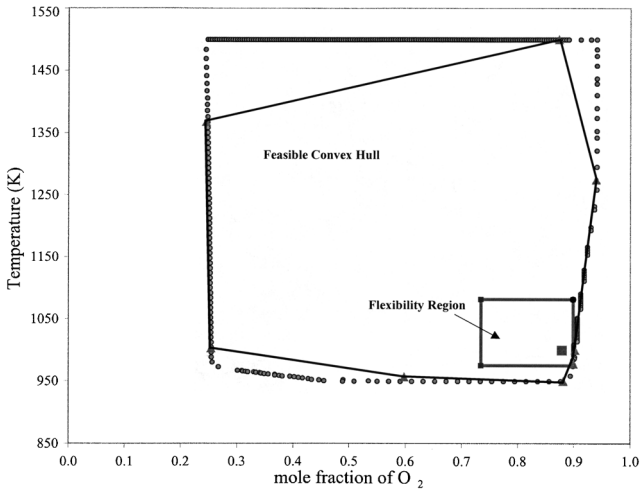


**Figure 5. Feasible region map showing the boundary of the feasible and predicted feasible regions based on the flexibility index and convex hull approach for $H_2/O_2$ combustion at 1 atm with nominal conditions of $[O_2]_0 = 0.88$ and $T_0 = 1{,}000$ K, and $\epsilon = 0.001$.**

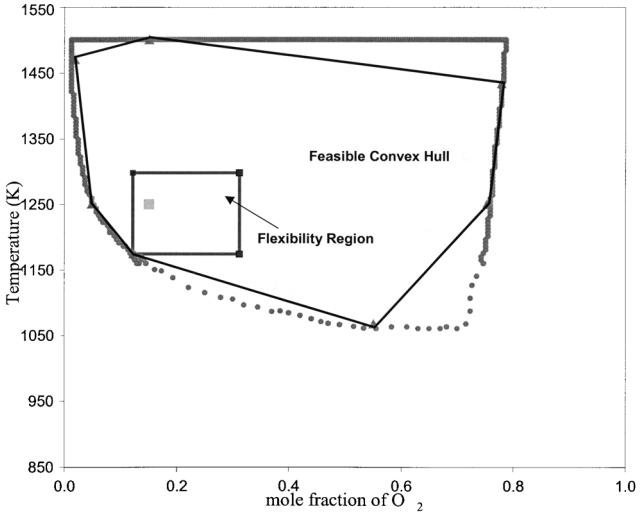


**Figure 6. Feasible region map showing the boundary of the feasible and predicted feasible regions based on the flexibility index and convex hull approach for $H_2/O_2$ combustion at 1 atm with nominal conditions of $[O_2]_0 = 0.5$ and $T_0 = 1{,}200$ K, and $\epsilon = 0.01$.**

set of equally spaced points covering the expected range of each initial condition that is expected to be variable. Each point is classified as "pass" or "fail" depending on whether the error constraint is satisfied or not. If the final temperature attained by the reactor contents does not exceed the feed temperature by a specified amount (say 100 K) in the residence time corresponding to the nominal conditions, the point is classified as "cold" regardless of the value of the error constraint. This does not necessarily mean that ignition cannot occur under the initial conditions of a "cold" point. As an alternative to the grid search, a Monte Carlo sampling method was also used, and the results obtained were similar. Since there are only two or three parameters in the problems considered, either method is acceptable. By keeping track of the changes in the type of points being generated, it is also possible to trace the boundaries of the "pass," "fail," and "cold," regions. Figure 4 shows the feasibility map for $H_2/O_2$ combustion at 1 atm, corresponding to nominal conditions of {0.88, 1000} and $\epsilon = 0.001$.

Figures 5–7 show the boundary of the feasible region corresponding to the reduced mechanisms shown in Table 3 for the three nominal conditions considered for $H_2/O_2$ combustion. The grid search was performed for initial oxygen mole fractions in the range {0.0001, 0.9999} and initial temperatures in the range {850, 1500}. With 50 grid points per variable, the reactor model was solved 2500 times. Hence, the method is computationally expensive.

A perusal of the plots shows that the area of each "pass" region is not the same for various nominal conditions. Further, the boundary of the region is not smooth everywhere and the region itself has a complicated shape. It can be noted from Figures 5–7 that parts of the boundary determined by the grid search procedure are highly irregular because of the high level of noise in the discrepancy function. However, for

a given nominal initial condition at which reduction is carried out, the corresponding reduced mechanism is valid over a large range of initial conditions. Since the equivalence ratio for these nominal conditions varies from fuel-rich to fuel-lean, it is unrealistic to expect one mechanism to represent the entire range of operating conditions.

The same analysis was repeated for the $CO/H_2/O_2$ combustion problem. In this case, three initial conditions are of interest: the initial temperature, and the mole fractions of CO and $H_2$. The grid search technique was applied to determine feasible-region plots of initial temperature against initial CO mole fraction with initial $H_2$ mole fraction as a parameter. Initial $H_2$ mole fraction was taken in the range {0.08, 0.64} in steps of 0.08. Initial CO mole fraction was allowed to vary between 0 and 0.6 while initial temperatures were uniformly sampled in the range {1,500, 1,600}. The reduced mechanism corresponding to an error level of $\epsilon = 0.001$ was chosen for analysis. The results showed that the region of validity of the reduced mechanism decreases as $H_2$ concentration in the feed increases.

### *Flexibility analysis*

The creation of the feasible region plots is computationally expensive and is only possible for problems up to three parameters. For larger problems, techniques from flexibility analysis can be applied to get an estimate of the feasible region (Ierapetritou and Androulakis, 1999). The basic formulation will be explained with the help of the low-pressure $H_2/O_2$ combustion example. Let the initial conditions of oxygen mole fraction and temperature be denoted by $\theta_1$ and $\theta_2$, respectively. Then if $\theta_i^+$ and $\theta_i^-$ are the maximum expected deviations in the parameters from their nominal values $\theta_i^N$, the expected range of each parameter is

$$\theta_i^N - \Delta\theta_i^- \le \theta_i \le \theta_i^N + \Delta\theta_i^+ . \tag{15}$$

To determine whether the mechanism is feasible over the expected parameter range, a new parameter $\delta$ is introduced, which allows the expected range to be represented by

$$\theta_i^N - \delta\Delta\theta_i^- \le \theta_i \le \theta_i^N \qquad \Delta\theta_i^+ . \tag{16}$$

The flexibility index $F$ for a given reduced mechanism set $\{\lambda^r\}$ is the value of $\delta$ that defines the critical parameter range responsible for the error function $\chi$ to be equal to its desired value $\epsilon$. We can determine $F$ in two ways: the vertex enumeration strategy (VES) and the active set method (ASM).

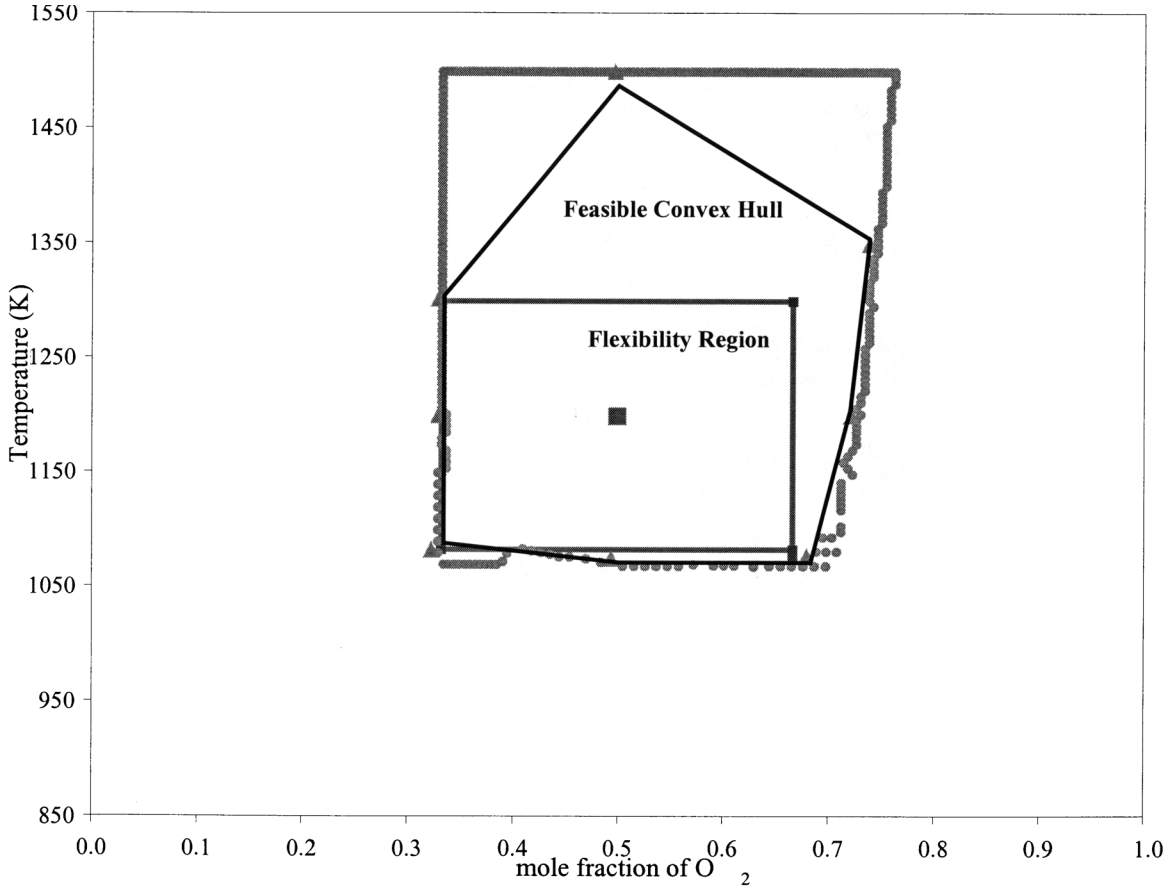


**Figure 7. Feasible region map showing the boundary of the feasible and predicted feasible regions based on the flexibility index for $H_2/O_2$ combustion at 1 atm with nominal conditions of $[O_2]_0 = 0.15$ and $T_0 = 1{,}250$ K, and $\epsilon = 0.001$.**

The VES solves four problems, one at each vertex of the expected parameter range. The coordinates of the vertices $V^k$ for a two-parameter problem are

$$\begin{aligned} V^1 &= \{\theta_1 \quad \delta\cdot\Delta\theta_1^+, \theta_2 \quad \delta\cdot\Delta\theta_2^+\} \\ V^2 &= \{\theta_1 \quad \delta\cdot\Delta\theta_1^+, \theta_2 - \delta\cdot\Delta\theta_2^-\} \\ V^3 &= \{\theta_1 - \delta\cdot\Delta\theta_1^-, \theta_2 - \delta\cdot\Delta\theta_2^-\} \\ V^4 &= \{\theta_1 - \delta\cdot\Delta\theta_1^-, \theta_2 \quad \delta\cdot\Delta\theta_2^+\} \end{aligned} \tag{17}$$

where $\delta$ can be interpreted as the scaled step-length factor along each vertex direction.

At each vertex $k$, the following problem is solved:

$$\Theta^k = \max \delta \tag{18}$$

subject to:

$$\chi(\lambda^r, V^k) - \epsilon \le 0$$

$$\Delta T_{\min} - \left(T_{n_t}^f - T_0\right) \le 0. \tag{19}$$

The second inequality constraint in Eq. 19 avoids "cold" points under the given initial conditions. As mentioned earlier, $\Delta T_{\min} = 100$ K. The flexibility index is the smallest value among all the optima obtained from the solution of Eqs. 18–19:

$$F = \min_{1 \le k \le 4} \{\Theta^k\}. \tag{20}$$

The VES assumes that the point of constraint violation, if it exists, occurs at one of the vertices of the expected parameter range. This need not be true as shown by Biegler et al. (1997). Further, the number of optimization problems to be solved for a generic problem with $n$ parameters is $2^n$, which could be prohibitively large. The ASM exploits the fact that the value of $F$ is determined by the active inequality constraints (Grossmann and Floudas, 1987). In the present case, the ASM reduces to the solution of two problems. First, the constraint on the error function is assumed active and the following problem is solved:

$$\begin{aligned} \psi^1(\delta, \theta_1, \theta_2) &= \min \delta \\ \chi(\lambda^r, \theta_1, \theta_2) - \epsilon &= 0 \end{aligned} \tag{21}$$

subject to:

$$\begin{aligned} &\Delta T_{\min} - \left(T_{n_t}^f - \theta_2\right) \le 0 \\ &\theta_i - \left(\theta_i^N + \delta\Delta\theta_i^+\right) \le 0 \quad i = 1, \ldots, 2 \\ &\left(\theta_i^N - \delta\Delta\theta_i^+\right) - \theta_i \le 0 \quad i = 1, \ldots, 2. \end{aligned} \tag{22}$$

Then, the same problem is solved with the error constraint treated as an inequality and the "ignition constraint" assumed active to yield $\psi^2$. Finally, $F = \min(\psi^1, \psi^2)$. Thus, the ASM simultaneously determines the value of $F$ and the critical values of the initial conditions.

Table 5 shows the values of the flexibility index obtained by the ASM for the low-pressure $H_2/O_2$ problem. The VES was also employed for this problem, and the results were practically the same as those obtained with the ASM. The predicted rectangular feasible region based on the values of $F$ obtained by the ASM is inscribed in Figures 5–7, corresponding to three nominal conditions and $\epsilon = 0.001$. The boundary of the feasible region obtained by the grid search method is also included for comparison. As expected, the area of this rectangle increases with $F$ leading us to conclude that the nominal conditions {0.15, 1,250} yield a mechanism with the greatest flexibility. However, the results of the grid search show that the rectangular-shaped region predicted by flexibility analysis is a very poor approximation of the true feasible region. Although the mechanisms corresponding to all three nominal conditions are equally feasible, the nominal conditions {0.88, 1,000} have a smaller predicted flexibility due to the proximity of these conditions to the boundary of the feasible region. In contrast, the other initial points, which are farther away from the boundary, have a larger flexibility. These observations strengthen the case for a better measure of flexibility. It may be noted, however, that this conclusion was possible based on results of the grid search approach to determine the boundary of the flexible region. Since the grid search is not applicable to all problems, techniques based on flexibility analysis might be the only way to characterize the range of validity of the reduced model. An alternative measure has been recently developed by Ierapetritou (2001) and is described in the next section.

**Table 5. Flexibility Index for $H_2/O_2$ Combustion at 1 atm for Different Initial Conditions and Error Tolerances**

| | | | Flexibility Index | |
|---|---|---|---|---|
| $x_{O_2}^0$ | $T_0$ | $\epsilon$ | VES | ASM |
| 0.88 | 1,000 | 0.1 | 0.4306 | 0.4096 |
| | | 0.01 | 0.2153 | 0.2396 |
| | | 0.001 | 0.1648 | 0.1642 |
| 0.5 | 1,200 | 0.1 | 0.2592 | 0.2479 |
| | | 0.01 | 0.1017 | 0.0864 |
| | | 0.001 | 0.2073 | 0.1910 |
| 0.15 | 1,250 | 0.1 | 0.3952 | 0.3522 |
| | | 0.01 | 0.0481 | 0.0472 |
| | | 0.001 | 0.3356 | 0.3339 |

### *Convex hull approach*

The basic idea behind this approach is the inscription of the convex hull inside the feasible region. The basic steps of the proposed methodology are:

1. Solve a series of optimization subproblems to determine points at the boundary of the validity range. For the case of two variable parameters, eight subproblems must be solved: four in the direction of the vertices and four in the positive and negative directions of a Cartesian coordinate system, with the nominal point as the origin. The determination of each of these points using the bisection method may involve several evaluations of the error constraint.

2. Determine the convex hull defined by the points obtained at step (1). This is achieved by utilizing the *Quickhull algorithm* developed by Barber et al. (1996).

3. Determine the volume (area) of the convex hull obtained from step (3) using *Delaunay triangulation* (Berg et al., 1997). The volume of the overall expected region is determined simultaneously using the vertices of the expected range of variability of the uncertain parameters. In addition, the

linear functions describing the faces of the convex hull are determined.

4. Evaluate the feasible convex hull ratio (FCHR), which defines the ratio of the "volumes" of the feasible convex hull and the expected region:

$$\text{FCHR} = \frac{\text{Volume of the feasible convex hull}}{\text{Volume of the overall expected range}}. \quad (23)$$

FCHR is used as the new metric for measuring the feasible space or for the case of the reduced kinetic model as a metric for characterizing the range of validity and comparing different mechanisms.

The results obtained with the FCHR approach are presented in the Figures 5–7 and summarized in Table 6. A comparison with the results of the flexibility analysis procedure reveals that the range of validity as described by the inscribed feasible convex hull provides a better representation of the actual region than that predicted by flexibility analysis. As shown in Table 6, FCHR can be also used to compare different reaction schemes since it represents the relation between the actual region and the inscribed region more accurately. Using this metric, we find that the reaction scheme with the largest range is the one that corresponds to the initial conditions of 0.88 for the molar concentration of $O_2$ and 1000 K for temperature rather than the one that corresponds to the nominal conditions {0.15, 1250} as found by the flexibility analysis.

**Table 6. Feasible Region Described by Flexibility Analysis and Convex Hull Analysis Approach for $H_2/O_2$ Combustion with $\epsilon = 0.001$**

| | Flexibility Region Area | | | Convex Hull Area |
|---|---|---|---|---|
| Nominal Cond. | Flexibility | (% of Total Expected Area) | FCHR | (% of Total Expected Area) |
| 0.88, 1,000 | 0.1648 | 2.6 | 0.483 | 48.3 |
| 0.15, 1,250 | 0.33 | 3.64 | 0.351 | 35.1 |
| 0.5, 1,200 | 0.2 | 11.1 | 0.191 | 19.1 |

## Multiperiod Formulation

The previous sections have dealt with the problem of assessing the effects of variability in initial conditions on the feasible range of a reduced mechanism that was developed based on nominal values. In this section, the problem of finding the reduced mechanism that covers a prespecified range of initial conditions is addressed.

A general method for the solution of such problems was proposed by Halemane and Grossmann (1983) and is known as the multiperiod formulation for design under uncertainty. A population comprising $N_p$ vectors of uncertain parameters is initially generated using a suitable technique. Each member $k$ of the population is known as a scenario and is repre-

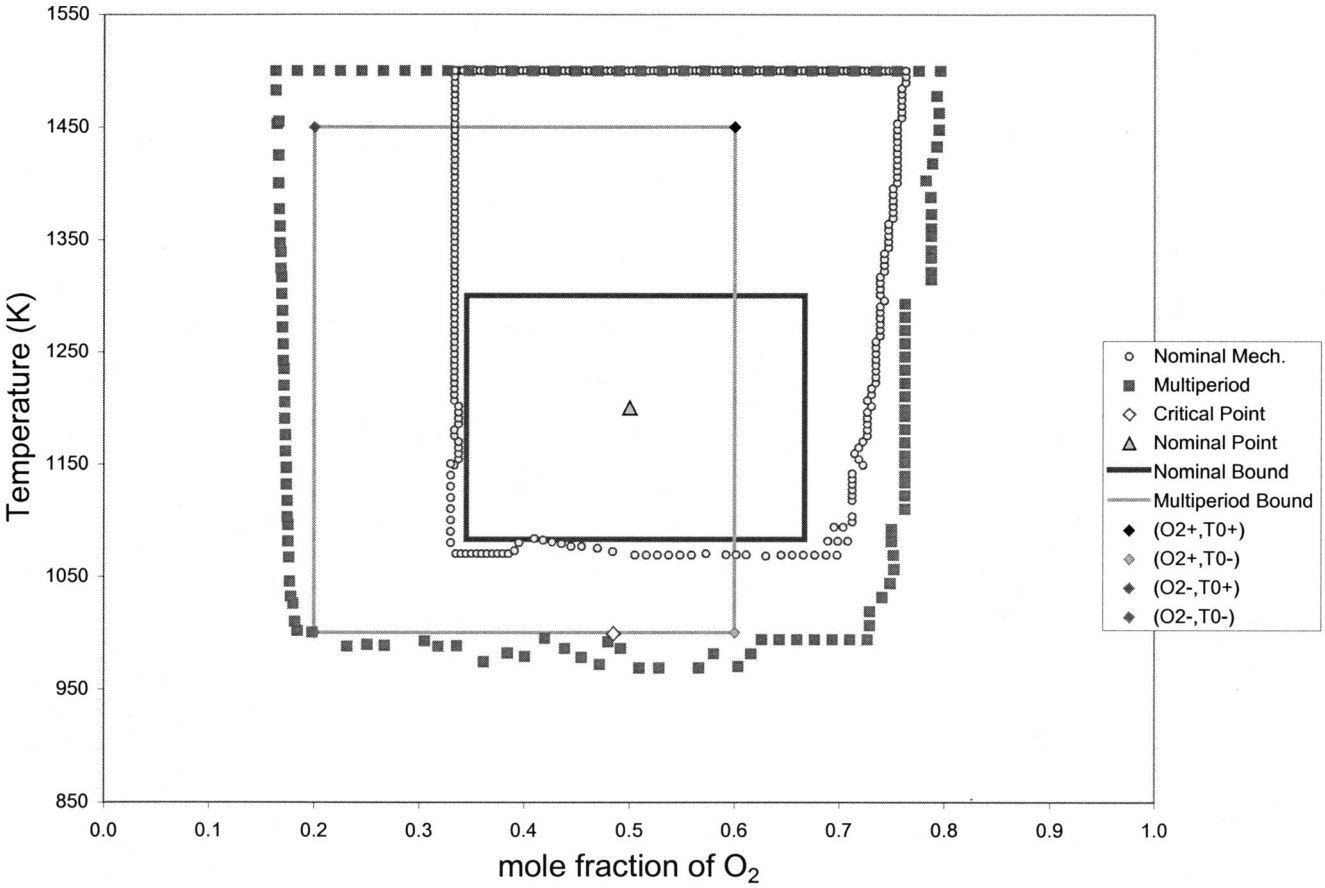


**Figure 8. Multiperiod formulation accounting for variability in the initial conditions.**

sented by the parameter vector $\theta^k$. The starting population of initial conditions is chosen to be the vertices of the desired feasible region. Then, the following integer nonlinear programming problem is solved by the B&B method to obtain a reduced mechanism:

$$\phi = \min_{\lambda} \sum_{i=1}^{n_r} \lambda_i \tag{24}$$

$$\text{subject to:} \quad \chi_k(\lambda, \theta^k) \leq \epsilon \quad k = 1, \ldots, N_p. \tag{25}$$

It can be noted that the problem represented by Eqs. 24–25 is similar to Eqs. 1–2, except that the number of error constraints to be satisfied is $N_p$ instead of one. Hence, this problem is more computationally intensive. Having obtained an optimal solution, the flexibility test problem is solved as described earlier. If the reduced mechanism has the desired flexibility as reflected by the value of the flexibility index $F$, the procedure is terminated. Otherwise, the critical point corresponding to the active constraint in Eq. 25 is added to the population of points and the procedure is repeated by solving Eqs. 24–25 with the larger population. As suggested by Beigler et al. (1997), only a few iterations of the method were found to be necessary.

The multiperiod formulation was applied to $H_2/O_2$ combustion at 1 atm with a tolerance of 0.001 using the nominal conditions of {0.5, 1,200 K} for initial oxygen mole fraction and temperature. The desired range of validity for initial oxygen concentration was taken to be {0.2, 0.6}, while that for temperature was {1,000 K, 1,450 K}. The algorithm was initiated with five scenarios corresponding to the nominal point and the following four vertices of the desired region: {0.6, 1,450 K}, {0.6, 1,000 K}, {0.2, 1,000 K}, {0.2, 1,450 K}. The first iteration yields the reduced flexible mechanism {1, 2, 3, 4, 5, 7, 12, 13, 16} satisfying the error condition for each of the five scenarios. Thus reactions 12, 13, 16 are added to the nominal mechanism {1, 2, 3, 4, 5, 7}. The flexibility index for this reduced mechanism is 1.004, corresponding to the nonvertex critical point {0.4851, 999.117 K}. The procedure terminates because the required flexibility is achieved (as indicated by $F > 1$). Figure 8 shows the coordinates of the five scenarios as points and the boundary of the feasible region described by $F$ as a solid line. Also shown are the actual boundaries of the feasible regions corresponding to the nominal and flexible mechanisms as obtained using the grid search method. As expected, the boundary of the flexible feasible region engulfs the boundary of the nominal feasible region.

## Concluding Remarks

The reduction of detailed mechanisms that rigorously describe many situations of industrial importance is crucial because inclusion of all the species and reactions is computationally prohibitive. The reduced mechanism obtained by most methods depends on the internal parameters specific to the reduction technique and the nominal values of the parameters. This article has addressed the issues related to the effects of variability in initial conditions and the choice of internal parameters, on the reduced mechanism. The reduction method proposed by Androulakis (2000) was used in this work, because the consequent reduced mechanisms maintain structural integrity and the technique is amenable to uncertainty analysis.

The reduced mechanism changes with the initial conditions used for its determination as demonstrated with $H_2/O_2$ combustion at 1 atm with feeds ranging from fuel-rich to fuel-lean. The feasible region for any nominal point can be represented by 2-D feasible-region plots that are convenient for visual inspection. However, since these plots are expensive to compute, the flexibility index approach outlined by Beigler et al. (1997) was also investigated in this work. The feasibility regions predicted by the value of $F$ was found to be much smaller than the actual feasible region for all three initial conditions chosen for the $H_2/O_2$ example. The main reason for the unsatisfactory behavior in this case appears to be the dependence of $F$ on the proximity of the nominal condition to the boundary of the feasible region. If the nominal condition happens to be close to a constraint boundary, the use of $F$ leads to a pessimistic estimate of the feasibility of the mechanism. An alternative flexibility measure based on the convex hull formulation of Ierapetritou (2001) has been found to yield more realistic estimates of the feasible region, and is recommended.

A multiperiod formulation based on the work of Swaney and Grossmann (1985) was applied to design reduced mechanisms that cover a wide range of initial conditions and directly incorporate the parametric uncertainty information. The results obtained for $H_2/O_2$ combustion at 1 atm and the SCWO mechanism were found to be consistent with the results obtained by the sampling approach.

An important internal parameter in the reduction process is the error tolerance that expresses the allowable deviation of the predictions of the reduced mechanism from those of the full mechanism for the important quantities of interest. Even when the discrepancy function is suitably scaled, it is not possible to determine an acceptable value of this parameter on an *a priori* basis. The results obtained for three combustion mechanisms has shown that excessive accuracy is characterized by a significant increase in the number of reactions and a constancy in the number of species. This observation can be used as a guideline for the selection of the tolerance parameter.

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