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MODELING OF COMBUSTION OF MONO-CARBON FUELS USING THE RATE-CONTROLLED CONSTRAINED-EQUILIBRIUM METHOD

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ABSTRACT

Modeling of a non-equilibrium combustion process involves the solution of large systems of differential equations with as many equations as species present during the process. The process of chemical reaction and combustion is complicated since it may be governed by hundreds, sometimes thousands of microscopic rate processes. Integration of these equations simultaneously becomes more difficult with the complexity of the combustible. In order to reduce the size of these systems of equations, the Rate-Controlled Constrained-Equilibrium method (RCCE) has been proposed to model non-equilibrium combustion processes. This method is based on the Second Law of Thermodynamics, assuming that the evolution of a complex system can be described by a small number of rate-controlling reactions which impose slowly changing constraints on all allowed states of the system, therefore a non-equilibrium system will relax to its final equilibrium state through a sequence of rate controlled constrained equilibrium states. Oxidation induction times and concentration of species during a combustion process are found in a less complicated way with this method, as equations for constraints rather than for species determine the composition and evolution of the system. The time evolution of the system can be reduced since the number of constraints is much smaller than the number of species present, so the number of equations to solve.

The RCCE method has been applied to the stoichiometric combustion of mono-carbon fuels using 29 chemical species and 139 chemical reactions at different sets of pressure and temperature, ranging from 1 atm to 100 atm, and from 900 K to 1600 K respectively. Results of using 8, 9, 10 and 11 constraints compared very well to those of the detailed calculations at all conditions for the cases of formaldehyde (H_2CO), methanol (CH_3OH) and methane (CH_4). For these systems, ignition delay times and major species concentrations were within 5% of the values given by detailed calculations, and computational saving times up to 50% have been met.

KEYWORDS: C1 Oxidation, Ignition Delay, RCCE, Rate-Controlled Constraint-Equilibrium, Combustion Modeling

INTRODUCTION

The development of models for describing the time evolution of chemically reacting systems is a fundamental objective of chemical kinetics. The conventional approach to this problem involves (1) specifying the state and species variables included in the model, (2) compiling a full set of rate-equations for these variables, and (3) integrating this set of equations to obtain the time-dependent behavior of the system. Such calculations are frequently referred to as comprehensive or fully detailed although, except for the hydrogen/oxygen system, they contain only a small fraction of the species and reactions possible. Extensive work and mechanisms have been developed by Westbrook [1] and Wang [2]. For complex systems, this approach can involve formidable computational tasks requiring the tabulation of a great many reaction rates and the integration of a large number of stiff differential equations. Indeed, for hydrocarbon systems involving the possibility of literally thousands of chemical species and isomers, and millions of reactions, a truly fully detailed solution is difficult, if not impossible to conceive.

Over the past several decades, numerous methods for simplifying the kinetics of large chemical systems have been proposed. These can be roughly divided into two classes. The first involves reducing the number of rate equations and reactions required by truncation of the species list [3-11]; the

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second involves the use of various mathematical approximations to simplify the system by converting differential equations to algebraic equations without reducing the number of species [12-15]. The methods in the first class increase the speed of the calculations but reduce the level of detail of the results. The methods in the second class maintain a reasonable level of detail but it is not clear that the speed or calculations increases. Important advances in model reduction, and in the accuracy of the results has been more recently made with the method of low-dimensional manifolds (ILDM) [16-19] proposed by Maas and Pope and also with the method of computational singular perturbation (CSP), proposed by Lam [20-21]

Here, we investigate an alternative approach, the Rate-Controlled Constrained-Equilibrium (RCCE) method, originally proposed by Keck and Gillespie [22] and later developed by Keck and co-workers [23-31]. The method is based on the maximum-entropy principle of thermodynamics and involves the fundamental assumption that slow reactions in a complex reacting system impose constraints on its composition, which retard its relaxation to chemical equilibrium, while the fast reactions equilibrate the system subject to the constraints imposed by the slow reactions. Consequently, the system relaxes to chemical equilibrium through a sequence of constrained-equilibrium states at a rate controlled by the slowly changing constraints. Systems solved with RCCE always evolve to the right equilibrium state and concentrations for all species are calculated.

A major advantage of the RCCE method is that it is unnecessary to start with a complete reaction model that must then be simplified by various approximations. Instead, one starts with a small number of constraints to which more can be added to improve the accuracy of the calculations if desired. In the limit where the number of constraints equals the number of species specified for a system, the method reduces to an exact calculation. However, as with all thermodynamic systems, the number of constraints necessary to describe the state of the system within measurable accuracy is in general very much smaller than the number of species in the system. In addition, reactions that do not change any constraint do not affect the evolution of the system. Thus, only the rates of slow reactions which change the constraints are required and these are the ones most likely to be known.

In previous studies, the RCCE method has been applied to stoichiometric mixtures [29-31]. In this paper we will discuss the rational for the formulation of this model, starting with the non dynamic methods of equilibrium calculations using Lagrange multipliers, then constrained-equilibrium calculations and finally the non-equilibrium dynamic method of RCCE. The results for the case of the formaldehyde/oxygen mixture will be presented as well.

Modeling a Chemical Reaction Process

Two techniques, Lagrange multipliers and constrained-equilibrium (CE), to calculate final equilibrium using constraints is discussed previous to the dynamic method of RCCE. The Lagrange multipliers method uses only the elemental constraints that reflect the conservation of elements. The CE method uses also the elemental constraints and additional constraints that are imposed to better define the system subject to extremely slow rate controlling reactions. Finally, time evolution through the constrained shifting equilibrium is included in order to completely describe the processes. This last technique is the so called Rate-Controlled Constrained-Equilibrium (RCCE)

a)Equilibrium Calculation Using Lagrange Multipliers

This method for chemical equilibrium provides a superior means for solution of complicated problems and it is used by the NASA and STANJAN programs. Its implementation in the interactive program STANJAN has been well described by W.C. Reynolds [25].

Equilibrium is calculated by minimizing the Gibbs energy function subject to elemental constraints of the form:

$$C_i = \sum_{j=1}^{n_s} a_{ij} N_j \qquad (1)$$

Where N_j is the number of moles of the jth element in the system, a_{ij} is the number of atoms of the ith element in the jth species, ns is the number of different species and C_i is the elemental constraint i.

These elemental constraints are the sum of each independent atom present in the system, and due to mass conservation, these constraints are always constant.

The method relates the mol fractions of each species to quantities called element potentials γ_i (Lagrange Multipliers of the constraints). There is one element potential for each constraint in the system, and these element potentials, plus the total number of mols in each phase, are the only variables that must be adjusted for the solution. In large problems this is a much smaller number than the number of species, and hence far fewer variables need to be adjusted.

Concentration composition subject to constraints is:

$$\frac{N_j}{V} = (\frac{1}{RT})\exp(-\mu_j^0 - \sum_n a_{ij}\gamma_i) \qquad (2)$$

The model assumes that the gas phase is a mixture of ideal gases and that condensed phases are ideal solutions.

b) Constrained-Equilibrium Calculation (CE)

Constraints in addition to the elemental ones can be imposed to any system. These are called generalized constraints.

These additional constraints are of the same for as (2) and they are imposed to better define the system subject to extremely slow rate controlling reactions. The GNASA and GSTANJAN codes [28], Generalized NASA and Generalized STANJAN respectively, have been developed by our Research group to use this technique to find the constrained equilibrium composition of complex systems. For systems which include a large number of species, the number of constraints is much smaller than the number of species, therefore solving for the constraint potentials is much easier than solving for the species concentrations using the method of equilibrium constants. The primary difference between GNASA and GSTANJAN is in the techniques used to solve these equations and the manner in which the calculations are initialized.

Two examples of constraints imposed by chemical reactions in gas-phase systems are the total moles of mixture (M) which is controlled by slow three-body association and dissociation reactions and the free valence (FV), number of unpaired electrons, which is controlled by slow branching and termination reactions. These additional constraints are required for dynamic calculations as we will see in the RCCE method as well.

c) Rate-Controlled Constrained-Equilibrium (RCCE)

For the systems of interest in combustion, the number of species is of order 10^2 and the number of reactions is of order 10^4. Thus the tabulation of reaction rate constants and the integration of rate equations using the detailed kinetics method are difficult tasks and usually they involve a significant time of computation. In addition, accurate rate constants are known only for a small fraction of the possible reactions. The RCCE method requires only solving the rate equations for a few constraints to predict the time evolution of all species and to guarantee the right final equilibrium state.

This method is based on the assumption that complex chemical systems evolve through a sequence of quasi-equilibrium states determined by the instantaneous values of internal constraints on the system's composition. These constraints, as in the case of the Constrained-Equilibrium method, are imposed by slow rate-limiting reactions. The technique involves direct integration of either the rate equations for the constraints or the rate equations for the constraint potentials (Lagrange multipliers conjugate to the constraints).

Rate-equations for Constraints

From detailed kinetics theory we must remember that the rate of change of moles of any species is given by:

$$\dot{N}_j = V\sum_{k=1}^{nr} \nu_{jk} r_k \qquad j=1,\ldots ns \qquad (3)$$

The constraints imposed on the system by the reactions have been assumed to be a linear combination of the mole number of the species present in the system. In the present work, as well as most previous applications of RCCE method [27-31], the constraints for a system of *nc* constraints and *ns* species, they can be written in matrix notation as:

$$\mathbf{C} = \mathbf{AN} = \mathbf{A}_{11}\mathbf{N}_1 + \mathbf{A}_{12}\mathbf{N}_2 \qquad (4)$$

where $\mathbf{C}$ is the constraint vector, $\mathbf{N}$ is the species vector, $\mathbf{A}$ is the constraint matrix, $\mathbf{A}_{11}$ is a square matrix relating $\mathbf{C}$ to the major species vector $\mathbf{N}_1$, and $\mathbf{A}_{12}$ is the remaining part of matrix $\mathbf{A}$ relating $\mathbf{C}$ with the rest of species. Differentiating equation (4) and gives the rate-equation for the constraints

$$\dot{\mathbf{C}} = \mathbf{BR} \qquad (5)$$

where matrix $\mathbf{B}$ contains the change of constraints due to each reaction, and matrix $\mathbf{R}$ contains the net reaction rates, therefore $\mathbf{B}$ can be expressed as

$$\mathbf{B} = \mathbf{A}\boldsymbol{\nu} \qquad (6)$$

where $\boldsymbol{\nu}$ is the matrix of stoichiometric coefficients.

The elements of $\mathbf{B}$ then can be written as:

$$b_{ik} = \sum_{j=1}^{ns} a_{ij}\nu_{jk} \qquad (7)$$

then, b_{ik} is the change of constraint *i* due to the reaction *k*. Since elements are conserved the corresponding $b_{ik} = 0$. This reduces the number of rate-equations to be integrated by *ne,* where *ne* is the number of elemental constraints.

Given the initial conditions the *nc-ne* rate-equations (5) for the constraints can be integrated in stepwise fashion. At each step, the constrained-equilibrium composition

$$N_j(t) = N_j(V(t), T(t), C_1, \ldots C_{ne}, C_{ne+1}(t), \ldots C_{nc}(t)) \qquad (8)$$

must be evaluated using a generalized equilibrium code such as GNASA or GSTANJAN [28,35].

Rate-equations for Constraint-Potentials

An alternative and more time efficient method is to solve the equations for the conjugate to the constraints, or constraint potentials. The constrained-equilibrium composition of a system found by maximizing the entropy or by minimizing the free energy subject to a set of constraints using the LaGrange multipliers method is

$$N_j = (V/\widetilde{R}T)\exp(-\mu_j^0 - \sum_{i=1}^{nc} a_{ij}\gamma_i) \qquad j=1,\ldots ns \qquad (9)$$

where $\mu_j^0 = (h_j^0 - Ts_j^0)/RT$ is the standard Gibbs free energy for species *j* divided by RT and γ_i is the constraint potential (LaGrange multiplier) conjugate to the constraint *i*. Differentiating equation (9) with respect to time, and substituting the result into equation (5) leads to the implicit rate-equation for the constraint-potentials.

$$\dot{C}_i = C_{iV}\dot{V}/V + C_{iT}\dot{T}/T - \sum_{n=1}^{nc} C_{in}\dot{\gamma}_n \qquad i=1,\ldots nc \qquad (10)$$

where,

$$C_{in} = \sum_{j=1}^{ns} a_{ij}a_{nj}N_j \qquad (11a)$$

$$C_{iV} = \sum_{j=1}^{ns} a_{ij}N_j \qquad (11b)$$

$$C_{iT} = \sum_{j=1}^{ns} a_{ij}\frac{e_j}{RT}N_j \qquad (11c)$$

Equation (10) can be written in matrix form as:

$$\boldsymbol{\mu} = \ln \mathbf{P} + \boldsymbol{\mu}^0 = -\mathbf{A}^T\boldsymbol{\gamma} \qquad (12)$$

where $\mathbf{A}^T$ is the transpose of $\mathbf{A}$.

Assuming $\mathbf{A}_{11}$ is non-singular, i.e. its determinant is non-zero, and that $\mathbf{A}_{12}\mathbf{N}_2$ in Eq. (4) can be neglected, equation (12) can be inverted to give

$$\boldsymbol{\gamma}_1 = -(\mathbf{A}_{11}^T)^{-1}\boldsymbol{\mu}_1 = -(\mathbf{A}_{11}^T)^{-1}(\ln\,\mathbf{P}_1 + \boldsymbol{\mu}_1^0) \qquad (13)$$

where the subscript 1 denotes initial values.

The solution of equation (13) is simplified and the calculations proceed more smoothly if the $\mathbf{A}_{11}$ matrix is diagonalized. This can be accomplished by a transformation of the constraint vector. Multiplying equation (4) by $\mathbf{A}_{11}^{-1}$ gives

$$\widetilde{\mathbf{C}} = \mathbf{A}_{11}^{-1}\mathbf{C} = \mathbf{A}_{11}^{-1}\mathbf{A}\mathbf{N} = \mathbf{I}_{11}\mathbf{N}_1 + \mathbf{A}_{11}^{-1}\mathbf{A}_{12}\mathbf{N}_2 = \widetilde{\mathbf{A}}\mathbf{N} \qquad (14)$$

and equation (12) becomes

$$\boldsymbol{\mu} = \ln\mathbf{P} + \boldsymbol{\mu}^0 = -\widetilde{\mathbf{A}}^T\boldsymbol{\Gamma} = -(\mathbf{A}_{11}^{-1}\mathbf{A})^T\boldsymbol{\Gamma} \qquad (15)$$

$\widetilde{\mathbf{C}} = \mathbf{A}_{11}^{-1}\mathbf{C}$ and $\boldsymbol{\Gamma}$ are the transformed constraint and constraint-potential vectors, $\mathbf{I}_{11}$ is the unit matrix, and $\widetilde{\mathbf{A}} = \mathbf{I}_{11} + (\mathbf{A}_{11}^{-1}\mathbf{A}_{12})\,\widetilde{\mathbf{A}}$ is the transformed constraint matrix. The relation between $\boldsymbol{\gamma}$ and $\boldsymbol{\Gamma}$ found by equating equations (12) and (15) is

$$\boldsymbol{\Gamma} = (\mathbf{A}_{11})^T\boldsymbol{\gamma} \qquad (16)$$

and the initial value of $\boldsymbol{\Gamma}$ obtained from equation (13) is

$$\boldsymbol{\Gamma}_1 = -\boldsymbol{\mu}_1 = -(\ln\,\mathbf{P}_1 + \boldsymbol{\mu}_1^0) \qquad (17)$$

The transformed reaction rate matrix is

$$\widetilde{\mathbf{B}} = \widetilde{\mathbf{A}}\,\boldsymbol{\nu} = \mathbf{A}_{11}^{-1}\mathbf{B} \qquad (18)$$

In cases where state variables other than T and V are used, additional equations for these are required. For example, if the energy

$$E = \sum_{j=1}^{ns} e_j N_j \qquad (19)$$

is used to replace T, differentiating equation (19) provides the equation

$$\dot{E} = C_v\dot{T} - V\sum_k^{nr} E_k r_k \qquad (20)$$

where,

$$C_v = \sum_{j=1}^{ns} c_{vj} N_j \qquad (21a)$$

$$E_k = \sum_{j=1}^{ns}(h_j - RT)\nu_{jk} \qquad (21b)$$

and $c_{vj} = \partial e_j / \partial T$ is the constant volume specific heat for species j, and $h_j = e_j + RT$ is the enthalpy of species j at temperature T. Note that only reactions which change constraints contribute to the sum in equation (20) since all others which are in equilibrium and r_k is zero for these. Combining equations (10) and (20) then gives,

$$\sum_n^{nc} C_{in}\dot{\gamma}_n = C_{iV}\dot{V}/V + C_{iT}(E - V\sum E_k r_k)/C_v T - \dot{C}_i \quad i = 1,..nc \qquad (22)$$

Given $E(t)$ and $V(t)$ and initial values for γ_i, the energy equations (20) and the implicit equations (22) for the γ's can be integrated with respect to time using integration routines such as DASSL or LSODI to obtain the constraint-potentials. These can then be used in equation (9) to obtain the composition as function of time. The number of unknowns is reduced from the number of species *ns* included in the detailed calculations to the number of constraints *nc* used in the RCCE calculations. In addition, the rate-constants for those reactions which do not change any of the constraints are not needed.

Selection of Constraints

The selection of appropriate constraints is the key to the successful application of the RCCE method. Among the general requirements for the constraints are that they (1) be linearly independent combinations of the species mole numbers, (2) include the elements, (3) determine the energy and entropy of the system within experimental accuracy, and (4) hold the system in the specified initial state. In addition, they should reflect whatever information is available about rate-limiting reactions controlling the time evolution of the system.

In the temperature range important for chemical reactions, extremely slow nuclear reactions imply strict conservation of the elements on any observable time scale. Among the rate-limiting reaction of interest for chemical kinetics are:

1. Initiation reactions which hold the system in the specified initial state
2. Dissociation/recombination reactions which determine the total number of particles
3. Ionization reactions which determine the charge density in a system
4. Branching reactions which control the total free valence of the radicals
5. O-O bond breaking reactions which control the “fixed oxygen”
6. Reactions that change fuel radical
7. Carbon dioxide forming reactions
8. Reactions which form cyclic molecules.

In this work, three fixed elemental constraints: elemental carbon (EC), elemental oxygen (EO) and elemental hydrogen (EH) and from one to nine variable constraints: total number of moles (M), moles of free oxygen (FO), moles of free valence (FV), moles of fuel (FU), and moles of its radical (FR), moles of CO_2 (CO2) and moles of HO_2 (HO2). Other constraints used has been moles of alkanes (ALK), and moles of CH_3OO (CH3OO)

It should be noted that if only the elements are used as constraints, the RCCE method is identical independent constraints equals the number of species in a system the RCCE method is equivalent to a detailed calculation. This advantage of reducing significantly the number of equations by using the RCCE method is what makes it such a promising area for research.

Calculations for C1 systems

Illustrative calculations were carried out for premixed stoichiometric mixtures of C1-oxygen at constant energy in a constant volume chamber for initial pressures ranging from 1 atm to 100 atm and initial temperatures ranging from 900 K to 1600 K using 4 to 12 constraints. For comparison, corresponding rate-equations in a detailed model which includes 29 species and 139 reactions (20 species and 102 reactions in the GRI-Mech 3.0 model [36] along with other 9 species and 38 additional reactions [37-39]) were integrated using DASSL [34] to obtain exact solutions.

Formaldehyde-Oxygen System

The system was very well modeled with only 8 constraints. The constraints in the order that they were introduced in the RCCE calculations are defined in Table 1 which forms the constraint matrix A. The sub-determinant column shows the determinant of each sub square matrix A11. It can be seen that each of them is nonsingular which is a prerequisite described in the section of initial conditions for the calculation of initial constraint potentials. Only the reactions that change the constraints are used, all others are not needed and equilibrium composition is reached without them.

Table 1: Aij Matrix for the Formaldehyde-Oxygen mixture

		Species																											
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
N°	**Constraint**	**CO2**	**O2**	**H2**	**H2O2**	**HO2**	**H2O**	**H2CO**	**HCO**	CO	CH3OO	CH4	H	CH3OH	CH3OOH	HOCHO	HO	O	HOCO	OCHO	HOOCO	OOCHO	CH3	CH2	CH	C	CH2OH	CH3O	HOOCHO	CH2OOH
1	**EC**	**1**	**0**	**0**	**0**	**0**	**0**	**1**	**1**	1	1	1	0	1	1	1	0	0	1	1	1	1	1	1	1	1	1	1	1	1
2	**EO**	**2**	**2**	**0**	**2**	**2**	**1**	**1**	**1**	1	2	0	0	1	2	2	1	1	2	2	3	3	0	0	0	0	1	1	3	2
3	**EH**	**0**	**0**	**2**	**2**	**1**	**2**	**2**	**1**	0	3	4	1	4	4	2	1	0	1	1	1	1	3	2	1	0	3	3	2	3
4	**M**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
5	**FV**	**0**	**0**	**0**	**0**	**1**	**0**	**0**	**1**	0	1	0	1	0	0	0	1	2	1	1	1	1	1	2	3	4	1	1	0	1
6	**FO**	**2**	**0**	**0**	**0**	**0**	**1**	**1**	**1**	1	0	0	0	1	0	2	1	1	2	2	1	1	0	0	0	0	1	1	1	0
7	**FU**	**0**	**0**	**0**	**0**	**0**	**0**	**1**	**0**	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
8	**FR**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**1**	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Calculations for a broad range of pressures and temperatures have been performed. Figure 1 shows ignitions times (τ) at different pressures and temperatures. In all cases, RCCE calculations compare very well to detail calculations

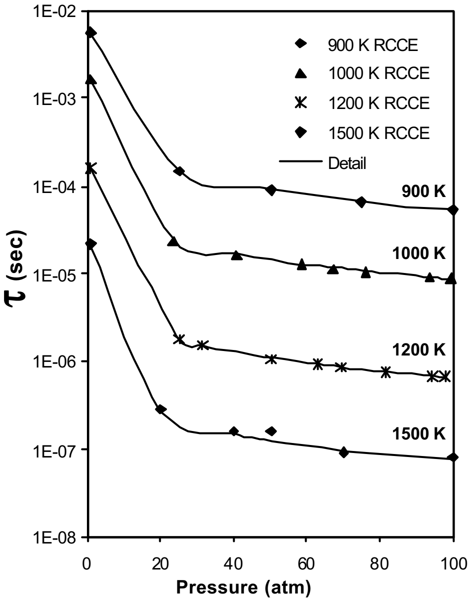

Figure 1 Ignition Delay Times (τ) at different Temperatures and Pressures for Formaldehyde-Oxygen Mixture Using Detailed Kinetics and 8 Constraints

Figure 2 shows the ignition delay for the case of 900 K and 100 atm of pressure; it can be seen that the ignition delay times agree within 0.5 % all calculations. Eight is the minimum number of constraints required to give very good agreement between ignition delay times at both high and low temperatures. Adding more constraints continuously improve the results for the time evolution of the minor species. Figure 3 shows the mole fraction evolution of CO2, O2, CO and H2CO for the same case, and Figure 4 shows the mole fraction evolution of H2O, HO2, H and HCO.

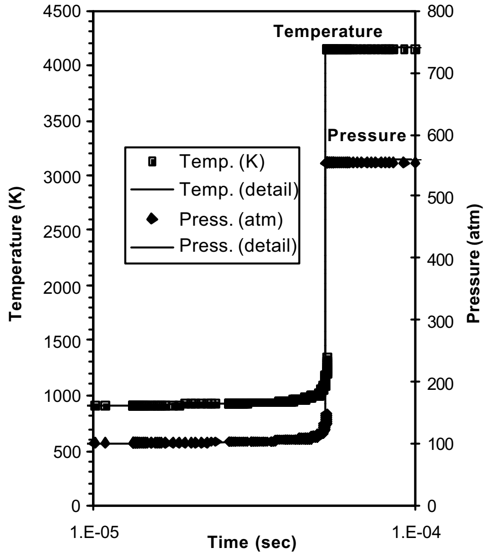

Figure 2 Temperature and Pressure Evolution for Formaldehyde-Oxygen Mixture at 900 K and 100 atm Using Detailed Kinetics and 8 Constraints

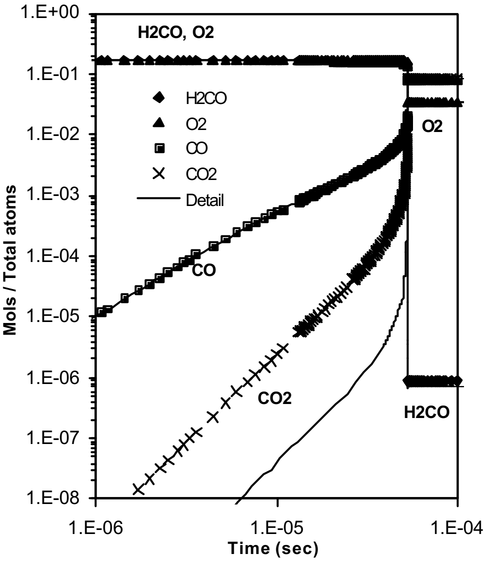

Figure 3 Mole Fraction Evolution of H2CO, O2, CO, and CO2 for Formaldehyde-Oxygen Mixture at 900 K and 100 atm Using Detailed Kinetics and 8 Constraints

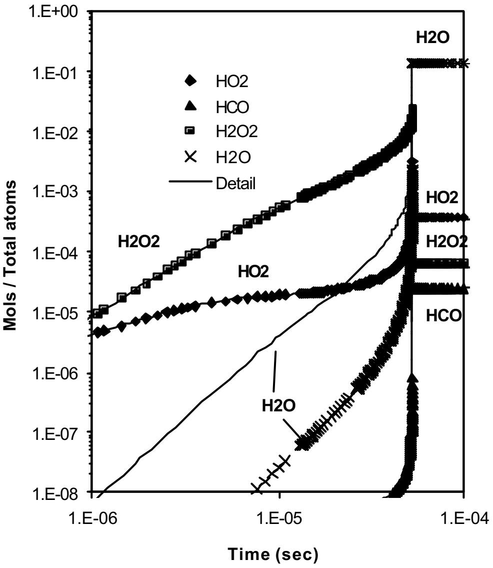

Figure 4 Mole Fraction Evolution of HO2, HCO, H2O2 and H2O for Formaldehyde-Oxygen Mixture at 900 K and 100 atm Using Detailed Kinetics and 8 Constraints

Methanol-Oxygen System

Figure 5 shows the ignition delay for the case of 1500 K and 1 atm of pressure; it can be seen that the ignition delay times agree within 0.5 % all calculations. Eight is the minimum number of constraints required to give very good agreement between ignition delay times at both high and low temperatures. Adding more constraints continuously improve the results for the time evolution of the minor species. Figure 6 shows the mole fraction evolution of CH3OH, O2, CO and CO2 for the same case, and Figure 7 shows the mole fraction evolution of HO2, CH2OH, H2O and H2.

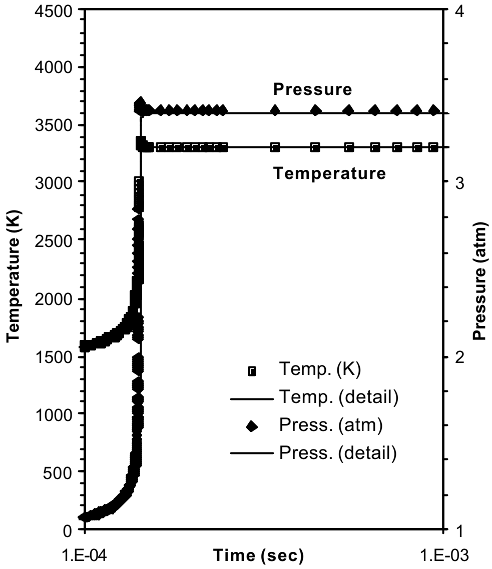

Figure 5 Temperature and Pressure Evolution for Methanol-Oxygen Mixture at 1500 K and 1 atm Using Detailed Kinetics and 9 Constraints

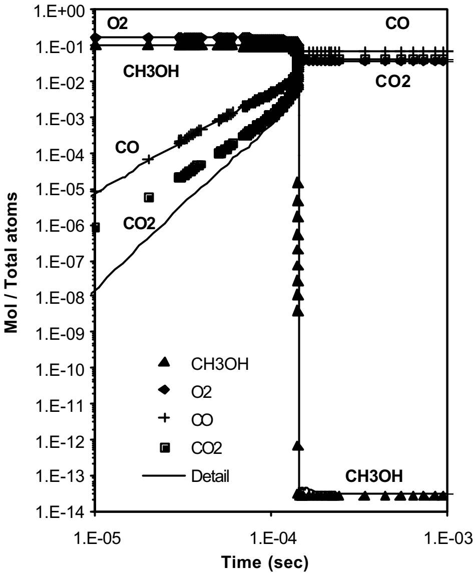

Figure 6 Mole fraction Evolution of CH3OH, O2, CO and CO2 for Methanol-Oxygen Mixture at 1500 K and 1 atm Using Detailed Kinetics and 9 Constraints

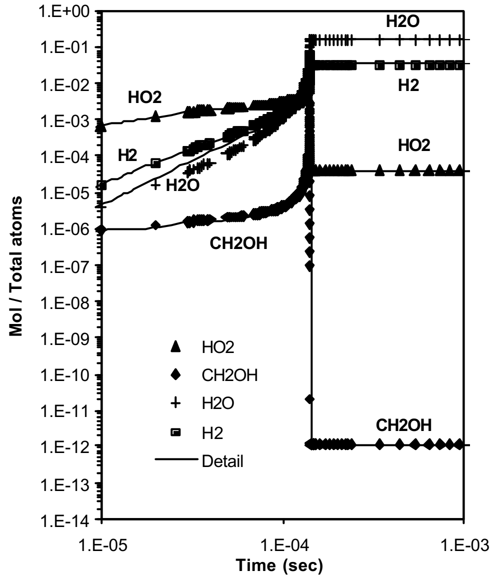

Figure 7 Mole fraction Evolution of HO2, CH2OH, H2O, and H2 for Methanol-Oxygen Mixture at 1500 K and 1 atm Using Detailed Kinetics and 9 Constraints

Methane-Oxygen System

For the case of the Methane-Oxygen system, Figure 8 shows the ignition delay time for the case of 1500 K and pressures varying from 1 atm to 20 atm using 9 constraints. Figure 9 shows the ignition delay time for the case of 1 atm and temperatures varying from 1200 K to 1600 K using 9 constraints.

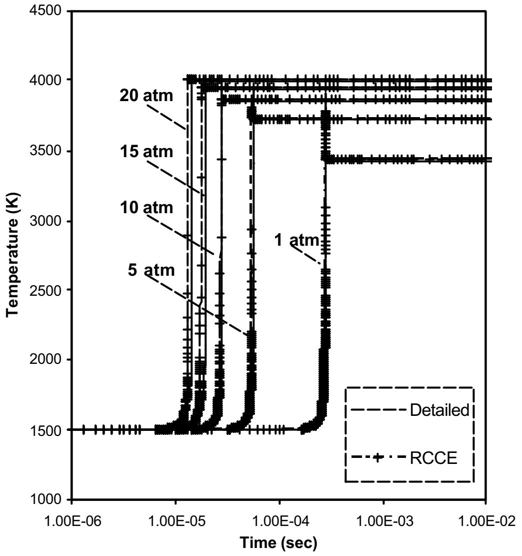

Figure 8 Ignition Delay for Methane-Oxygen Mixture at 1500K and Different Pressures Using Detailed Kinetics and 9 Constraints

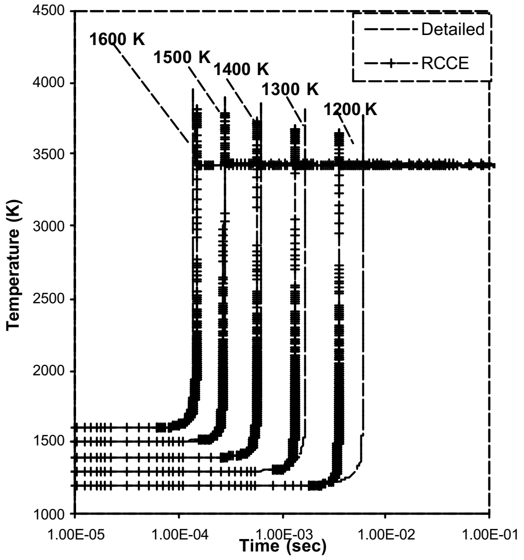

Figure 9 Ignition Delay for Methane-Oxygen Mixture at 1 atm and Different Temperatures Using Detailed Kinetics and 9 Constraints

For all cases, both RCCE and detailed calculations were done on a Sun workstation Sparc 10 machine. CPU time increases with the number of differential equations to be solved and the number of reactions involved. CPU time saved by the RCCE method is expected to improve by many folds for larger systems where detailed calculations can involve thousands of species and millions of possible reactions. Of equal importance is the potential reduction in the time required for the input of reaction mechanisms and the analysis of the resulting output.

Conclusions

Rate equations for the constraint potentials associated with the Rate-Controlled Constrained-Equilibrium (RCCE) method have been developed and successfully integrated for induction times of C1 chemistry systems at stoichiometric conditions over a wide range of initial temperatures and pressures.

RCCE calculation using 8 basic constraints gives reasonable results for ignition delay times and for the evolution of concentration of major species for the cases of H_2CO and methanol. These constraints include three elemental fixed constraints plus 5 variable constraints: Total number of moles (M), moles of free oxygen (FO), moles of free valence (FV), moles of fuel (FU) and moles of its radicals (FR). For the case of methane, 9 constraints (including the previous 8) were needed to obtain good results compared to detailed kinetics.

All results were within 5% of accuracy when compared to detailed calculations. Adding more variable constraints improved the calculation of the minor species concentration. Computer saving times up to 50% have been achieved for these cases. It is anticipated that for larger systems, larger time savings will be achieved.

Finally, the RCCE method gives valuable insight into the important reaction paths and rate-limiting reactions involved in the evolution of complex chemical systems in their journey through non-equilibrium states.

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