Rate-Controlled Constrained-Equilibrium Modeling of Chemical Kinetics and Mixing

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Abstract

The objective of this study is to assess the computational efficiency and accuracy of the Rate-Controlled Constrained-Equilibrium (RCCE) method to represent systems involving chemical reaction and mixing. The RCCE is a dimension reduction technique for chemical kinetics based on thermodynamics laws. It describes the time evolution of reacting systems using a series of constrained-equilibrium states determined by RCCE constraints. The full chemical composition at each state is obtained by maximizing the entropy subject to instantaneous values of the constraints. The RCCE rate equations can be formulated in terms of constraints or constraint potentials. Although these two forms are mathematically equivalent, they involve different numerical procedures and thus show different computational performances. In the first part of this study, both of these formulations are implemented and applied to simulate a well stirred reactor involving methane combustion in oxygen. The results show that both methods provide quite accurate representation of the kinetics. It is also demonstrated that while the constraint form involves less numerical stiffness, the constraint potential implementation results in more saving in computation time. The constraint potential formulation is therefore used in the second part of this work to investigate the influence of mixing on the accuracy and computational efficiency of RCCE predictions. This formulation allows considering mixing alongside chemical reaction without time-splitting. Simulations are conducted of methane oxygen combustion in a spatially homogeneous constant pressure partially stirred reactor (PaSR). RCCE predictions are compared with those of detailed kinetics model (DKM), in which the same chemical mechanism as in the RCCE calculations is directly integrated. The RCCE shows accurate prediction of combustion in PaSR at different mixing intensities. It also results in reduced numerical stiffness and overall computational cost compared to DKM.
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I dedicate this thesis to

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Chapter 1

Introduction

Despite all the progress in renewable energy research to date, combustion-based energy conversion is still the dominant technology, particularly in transportation and power generation industries. As this dominance is expected to continue in the foreseeable future, it is crucial to further improve combustion system technologies to meet the global challenge of producing clean and efficient energy. It is now widely recognized that development of improved combustion devices rely strongly on fundamental understanding of turbulent reacting flow processes. Simulation tools with higher fidelity are, therefore, instrumental to provide further insight into details of such processes. Among various challenges in predictive simulation of turbulent reactive flows, handling of detailed chemical kinetics, incorporating hundreds of species in thousands of reactions, is particularly daunting and requires prohibitive computational power, especially if high fidelity simulation methods such as direct numerical simulation (DNS) and large eddy simulation (LES) are to be employed [1–7]. This difficulty is, on one hand, because of the large number of species and reaction steps involved, which grow rapidly as the complexity of fuel increases. On the other hand, the numerical stiffness associated with kinetics makes the integration of chemical reaction source term the most expensive part of the simulation. To remedy the problem, methods of simplifying chemical kinetic models for such complex reacting flow simulations have attracted interest among researchers in combustion discipline. Some of the promising methods include the Directed Relations Graph (DRG) [8], DRG with error propagation (DRGEP) [9], Quasi Steady-state Assumption (QSSA) [10, 11], Partial Equilibrium Approximation [3], Computational Singular Perturbation (CSP) [12], Intrinsic Low-Dimensional
Manifold (ILDM) [2], Trajectory-Generated Low-Dimensional Manifolds (TGLDM) [13], Invariant Constrained Equilibrium-Edge Pre-Image Curve (ICE-PIC) [14], In Situ Adaptive Tabulation (ISAT) [15, 16], Piecewise Reusable Implementation of Solution Mapping (PRISM) [17], Artificial Neural Network (ANNs) [18] and Rate-Controlled Constrained-Equilibrium (RCCE) [6, 7, 14, 19–34, 34–37]. Among these methods, the RCCE is particularly appealing due to its basis in classical thermodynamics. This method was originally introduced by Keck and Gillespie [6]; it was further developed and applied by Keck and co-workers [7, 19–22] and employed in many other investigations [14, 23–34, 34–38].

In RCCE, it is assumed that the evolution of a complex system can be described with acceptable accuracy by a relatively small number of slowly changing constraints on the allowed states of the system. The fast reactions are assumed to relax the system to the associated constrained-equilibrium state on a time scale that is short compared to that on which the constraints are changing. The dynamical evolution of the kinetically controlled species is determined by the kinetics alone. The unrepresented species are assumed to be temporarily in an equilibrium state, called constrained equilibrium state, which is constrained by the composition of the represented species. Concentration of these species are determined by maximizing entropy subject to the instantaneous values of the constraints. As the reacting system evolves, the constrains for this state also evolve according to the differential equations of chemical kinetics. Therefore, a non-equilibrium system will relax to its final equilibrium state through a sequence of rate-controlled constrained-equilibrium states.

Following the original works as referenced above, the RCCE has been employed in many investigations. These include development of ISAT-RCCE [28], in which the dimension reduction is done via RCCE and the tabulation is performed by ISAT. The ISAT-RCCE is applied to a constant pressure adiabatic pairwise mixing stirred reactor (PMSR) in which mixing and reaction are handled in separate fractional steps. In a following study [29], the ISAT-RCCE method is further advanced and an alternative projection based on the close parallel inertial manifold is developed. In this study, simulations are performed of an adiabatic, isobaric plug-flow reactor (PFR) using rate equations for constraint potentials. Later on, three different implementations of RCCE for computing the reaction mapping in the ISAT-RCCE approach are presented [39]. In Refs. [34, 35, 40], the RCCE method is presented in differential-algebraic equations (DAE) and constraint potential form. These formulations are applied to homogeneous and pairwise-mixed
stirred reactors as well as laminar premixed and nonpremixed flames. The RCCE formulation is coupled with the transport equations, including those for RCCE constraints. An operator-splitting approach is employed in which transport of kinetic constraints is considered in a separate step; subsequently, the reaction step is carried out. In this step, using a system of algebraic equations the constraints are first transformed into constraint potentials, which are then advanced in time with either the DAE or the corresponding rate equations. The RCCE formulation, presented in Refs. \[34, 35, 40\], is combined with ANN and probability density function (PDF) methods \[41\] in Reynolds Averaged Navier Stokes (RANS) to study turbulent nonpremixed flames \[42\]. Application of RCCE to turbulent flames in large eddy simulation (LES) has been considered via two approaches: the formulation presented in Refs. \[34, 35, 40\] combined with conditional moment closure \[36, 37\], and the ISAT-RCCE along with PDF methods \[32, 43\]. Recently, the effects of combined dimension reduction and tabulation on the simulations of a turbulent lean-premixed propane air is studied using LES-PDF method \[44\].

An important issue in RCCE is identifying a proper set of constraints to represent the kinetics. Janbozorgi et al. \[22, 23\], studied the \(C_1\) hydrocarbon fuel oxidation process and developed a very successful set of structurally valid constraints based on studying reaction pathways. Algorithms for automated selection of constraints include that developed by Yousefian \[25\] in which a set of constraints that are a linear combinations of species are derived based on a prior knowledge of equilibrated reactions as well as other methods based on level of importance (LOI) to identify single species constraints by determining the species governed by fast/slow scales \[45\]; greedy algorithm \[31, 46\] to select single species constraints by cyclic direct integration of chemical kinetics; and a new methodology \[24, 38\] for systematic identification of the best constraints for a given range of thermodynamic conditions that is based on an algebraic analysis of the results of a preliminary simulation of the underlying detailed kinetics model (DKM), which is focused on the behavior of the degrees of disequilibrium (DoD) of the individual chemical reactions. The important issue in constraint selection is to ensure that correct reactions are considered as rate-limiting based on the constraints selected. The constraints used in this study are those identified by Janbozorgi et al. \[22, 23\].

The RCCE theory can be implemented via two general approaches: constraint and constraint potential. Despite previous contributions, there has been severely limited studies on comparing the accuracy and computational efficiency of these forms. In Chapter 2, comparison is made of
numerical implementation and performance of these two methods. The constraint potential form involves rate equations for constraint potentials, solution of which fully determines the state of the system [22–24, 47–49]. In the constraint form, the rate equations are solved for constraints. This form requires additional constrained equilibrium calculations [20, 26, 27]. In previous work [20, 26, 27], these calculations are handled using NASA CEA [50] and STANJAN [51] codes and it is determined that these codes result in excessive computation times. A better software for this purpose is the CEQ which is a Fortran library to compute equilibrium compositions using Gibbs function continuation method [52, 53]. This method is guaranteed to determine the chemical equilibrium state for all well-posed constrained and unconstrained problems [54]. Detailed description of this approach is provided in Ref. [52]. In this study, the CEQ software is utilized because of its shorter computation time compared to the aforementioned codes [54]. In both RCCE forms, time integration of rate equations is performed using the stiff ordinary differential equation (ODE) solver DVODE [55]. The solver divides each reaction time step into smaller sub-time steps internally according to numerical stiffness of the reacting system. Such subdivision has important consequences in RCCE, as discussed in the following. It is important to note that the constraint potential and constraint forms of RCCE are mathematically equivalent; however, their computational efficiency and numerical error are different because the two formulations result in different numerical stiffness and mathematical operations performed during each sub-time step. As stated in Ref. [28], the constraint potential form is expected to be superior to the constraint one in terms of computational efficiency. The objective of this study is to provide a quantitative comparison of these two forms concerning accuracy and computational cost. The goal is to determine the most efficient implementation of RCCE to be employed in turbulent combustion simulations which is shown to be the constraint potential formulation [56].

In Chapter 3, the RCCE formulation, involving rate equations for constraint potentials, temperature and density, is used to describe the dynamics of reacting gas mixtures. As discussed above, this form of RCCE is computationally more advantageous than the constraint form as it avoids conversion of constraints to constraint potentials at each time step which is a demanding calculation [56]. Another important benefit of this method is that it allows simultaneous consideration of both mixing and reaction effects with no additional splitting scheme. In all previous contributions as discussed above mixing and reaction are accounted for in separate fractional steps.
Besides introducing additional errors, such treatment requires the expensive constraints to constraint potentials conversion at each time step. The RCCE rate equations, including both mixing and reaction, are solved to fully determine the constrained-equilibrium state of the system. At this state the concentration of all mass fractions are obtained using the method of undetermined Lagrange multipliers by maximizing the entropy. The method is applied to study methane/oxygen combustion in a partially stirred reactor (PaSR), which is characterized by mixing, chemical and residence time scales. The numerical solution procedure in PaSR is similar to that in PDF methods. It thus provides a simplified test case to assess the performance of RCCE in turbulent combustion simulation using PDF methods. The main objectives of Chapter 3 are (1) to conduct a comprehensive study to demonstrate the efficiency and accuracy of the method, and (2) to demonstrate its capacity to accurately predict reacting systems with different mixing intensities. The mixing process in PaSR involves both macro- and micro-mixing which are represented by residence and mixing time scales, respectively. The former is associated with bulk fluid motion while the latter occurs at molecular scales. Both mixing mechanisms can have important consequences in the RCCE predictions. Despite, they have not been addressed in detail in previous studies. The importance of this issue is because mixing can influence the constrained-equilibrium state and thus, effectiveness of constraints representing chemical kinetics. It is thus essential to study the capacity of RCCE to predict the coupling between chemical reaction and fluid motion at different levels of mixing. Besides accuracy, the computational performance of RCCE is also assessed in this study by measuring its overall central processing unit (CPU) time as well as its effectiveness in reducing the numerical stiffness of chemical kinetics. The constraints used are those shown to be very effective in previous work [22]. The ultimate goal of this work is to fully assess the potential of RCCE for reliable description of detailed kinetics in turbulent combustion simulations using PDF methods.

1.1 Scope

This dissertation is organized as follows. In Chapter 2, a comparative assessment is made of two implementations of the RCCE method. These are the constraint and constraint potential formulations in which rate equations are solved for the RCCE constraints and constraint potentials, respectively. The two forms are equivalent mathematically; however, they involve different
numerical procedures and thus show different computational performance. The content of this chapter has been presented at several conferences [57–59] and is published in *Journal of Energy Resources Technology* [56]. In Chapter 3 a comprehensive study is conducted to demonstrate the efficiency and accuracy of the RCCE method as well as to demonstrate its capacity to accurately predict reacting systems with different macro- and micro-mixing intensities. The work described in this chapter has been presented at several conferences [60–62] and is published in *Journal of Non-Equilibrium Thermodynamics* [63]. For the convenience of the readers, both of these chapters are self-contained. In Chapter 4, conclusions and final remarks are provided along with some suggestions for future research.
Chapter 2

Comparison of Constraint and Constraint Potential Formulations

2.1 Introduction

The RCCE theory has thus far been implemented via two general approaches: constraint and constraint potential. Despite previous contributions, there has been severely limited studies on comparing the accuracy and computational efficiency of these forms. In this chapter, comparison is made of numerical implementation and performance of these two methods. The constraint potential form involves rate equations for constraint potentials, solution of which fully determines the state of the system [22–24, 47–49]. In the constraint form, the rate equations are solved for constraints. This form requires additional constrained equilibrium calculations [20, 26, 27]. It is important to note that the constraint potential and constraint forms of RCCE are mathematically equivalent; however, their computational efficiency and numerical error are different because the two formulations result in different numerical stiffness and mathematical operations performed during each sub-time step. The objective of this study is to provide a quantitative comparison of these two forms concerning accuracy and computational cost. The goal is to determine the most efficient implementation of RCCE to be employed in turbulent combustion simulations. This chapter is organized as follows. The mathematical description of constraint potential and constraint representations of RCCE is discussed in §2.2. Comparison of constraint potential and constraint forms is discussed in §2.3 and the concluding remarks are provided in §2.4.
2.2 Rate-Controlled Constrained-Equilibrium Formulation

The non-equilibrium evolution of reacting gas mixtures in a homogeneous system involving \( N_s \) chemical species is governed by

\[
\frac{dY_\beta}{dt} = S_\beta(t) \quad (\beta = 1, 2, \ldots, N_s)
\]  
(2.1)

where \( Y_\beta \) and \( t \) denote the mass fraction of chemical species \( \beta \) and time, respectively. The right hand side (RHS) includes the effect of chemical reaction \( S_\beta \). The reaction source term is defined as

\[
S_\beta(t) = \frac{\dot{\omega}_\beta M_\beta}{\rho}
\]  
(2.2)

where \( \dot{\omega}_\beta \) and \( M_\beta \) are the net production rate and molecular weight of species \( \beta \), respectively, and \( \rho \) is the density of the gas mixture. In RCCE formulation, the constraints are assumed to be linear combinations of gas mixture species concentrations [6]

\[
C'_\alpha = \sum_{\beta=1}^{N_s} A'_{\alpha\beta} \frac{Y_\beta M_\beta}{M_\beta} \quad (\alpha = 1, 2, \ldots, N_c)
\]  
(2.3)

where \( C'_\alpha \) and \( N_c \) represent the value and the number of constraints. The constant coefficient matrix \( A'_{\alpha\beta} \) is the transfer function of species to constraints and indicates the number of constraint \( \alpha \) in species \( \beta \). The coefficient matrix is obtained by identifying the slow reactions which impose slowly varying time-dependent constraints on the evolution of the reacting system. Following previous work [22], to improve robustness of calculations, the constant coefficient matrix is transformed to a new form, in which the square sub-matrix relating the constraints and the major species is diagonalized. The relation between transformed constraint vector and the species mass fractions is similar to Eq. (2.3),

\[
C_\alpha = \sum_{\beta=1}^{N_s} A_{\alpha\beta} \frac{Y_\beta M_\beta}{M_\beta}
\]  
(2.4)

where \( C_\alpha \) and \( A_{\alpha\beta} \) are transformed constraint and coefficient matrix, respectively. The RCCE provides a reduced representation of the kinetics in which the reacting system is governed by rate equations for constraints which is obtained by transforming Eq. (2.1) according to Eq. (2.4)
as
\[ \frac{dC_\alpha}{dt} = \sum_{\beta=1}^{N_s} A_{\alpha\beta} S_\beta \frac{M_\beta}{M_\beta} \] (2.5)

The constrained–equilibrium mass fraction of species can be obtained by maximizing the entropy, using the method of undetermined Lagrange multipliers subject to constraints [6]. This is done by adding entropy and instantaneous values of constraints as
\[ L = s + \sum_{\alpha=1}^{N_c} \lambda_\alpha \left( C_\alpha - \sum_{\beta=1}^{N_s} A_{\alpha\beta} Y_\beta \frac{M_\beta}{M_\beta} \right) \] (2.6)

where \( s \equiv s(p, h, Y_1, \ldots, Y_{N_s}) \) is the specific entropy and \( \lambda_\alpha \) denotes the Lagrange multiplier corresponding to constraint \( \alpha \). To optimize this relation with respect to mass fraction we set
\[ \frac{\partial L}{\partial Y_\beta} = 0 \quad (\beta = 1, \ldots, N_s) \] (2.7)

We, thus, have
\[ Y_\beta = \frac{M_\beta}{\rho} \frac{p_0}{R_u T} \exp \left( -\frac{\hat{g}_\beta^0}{R_u T} \right) \exp \left( -\sum_{\alpha=1}^{N_c} A_{\alpha\beta} \Lambda_\alpha \right) \] (2.8)

where \( p_0, R_u \) and \( T \) are standard pressure, universal gas constant and temperature, respectively. In this equation, \( \hat{g}_\beta^0 \) denotes the standard Gibbs free energy (of pure substance) per unit mole of species \( \beta \) and \( \Lambda_\alpha \) is the transformed constraint potential (dimensionless Lagrange multipliers) conjugate to the transformed constraint \( C_\alpha \). The total enthalpy
\[ h = \sum_{\beta=1}^{N_s} h_\beta Y_\beta \] (2.9)

is constant for an adiabatic isobaric reactor. In this equation, \( h \) and \( h_\beta \) denote specific enthalpy of the mixture and that of species \( \beta \), respectively. These equations are closed by the ideal gas equation of state
\[ p = \rho R_u T \sum_{\beta=1}^{N_s} Y_\beta \frac{M_\beta}{M_\beta} \] (2.10)

### 2.2.1 Constraint Potential Formulation

The constraint potential form is obtained following a procedure similar to Refs. [22–24] in which the time derivative of Eq. (2.8) is substituted into Eqs. (2.5,2.9,2.10). The final form is
obtained as

\[-C_α \frac{1}{ρ} \frac{dρ}{dt} + Q_{ca} \frac{1}{T} \frac{dT}{dt} + \sum_{θ=1}^{N_c} R_{cαθ} \frac{dΛ_θ}{dt} = \sum_{β=1}^{N_s} A_{αβ} \frac{S_β}{M_β} \]

(2.11a)

\[-h_1 \frac{1}{ρ} \frac{dρ}{dt} + Q_h \frac{1}{T} \frac{dT}{dt} + \sum_{θ=1}^{N_c} R_{hθ} \frac{dΛ_θ}{dt} = \frac{dh}{dt} \]

(2.11b)

\[Q_p \frac{1}{T} \frac{dT}{dt} + \sum_{θ=1}^{N_c} R_{pθ} \frac{dΛ_θ}{dt} = \frac{1}{p} \frac{dp}{dt} \]

(2.11c)

In these equations,

\[Q_{ca} = \sum_{β=1}^{N_s} A_{αβ} \frac{Y_β}{M_β} \cdot \hat{e}_β ; \quad R_{cαθ} = - \sum_{β=1}^{N_s} A_{αβ} A_{θβ} \frac{Y_β}{M_β} \]

\[Q_h = c_p T + \sum_{β=1}^{N_s} h_β Y_β \frac{\hat{e}_β}{R_u T} ; \quad R_{hθ} = - \sum_{β=1}^{N_s} A_{θβ} h_β Y_β \]

\[Q_p = M \sum_{β=1}^{N_s} \frac{Y_β}{M_β} \frac{\hat{e}_β}{R_u T} + 1 ; \quad R_{pθ} = -MC_θ \]

(2.12)

where \(c_p\) and \(\hat{e}_β\) denote specific heat capacity of the mixture at constant pressure and the internal energy per unit mole of species \(β\), respectively. Equation (2.11a) corresponds to rate equation of constraints (Eq. (2.5)). Equations (2.11b,2.11c) are the RCCE representation of transport of enthalpy and equation of state, respectively. In the isobaric, adiabatic reactor considered here we have \(\frac{dh}{dt} \approx 0\) and \(\frac{dp}{dt} \approx 0\). It is noticed that since chemical reaction conserves the atomic elements, in Eq. (2.11a) chemical reaction does not appear on the RHS for the elemental constrains. Given an initial thermodynamic state \((ρ,T,Y_1,\ldots,Y_{N_s})\), Eq. (2.11) is integrated to obtain \(T(t), ρ(t)\) and \(Λ_α(t) (α = 1,\ldots,N_c)\). These variables provide the mass fraction of all the species according to Eq. (2.8).

The algorithm used to obtain the RCCE predictions using constraint potentials is described in the following. At each reaction time step, constraint potentials, density and temperature are integrated from time \(t\) to \(t + Δt\), where \(Δt\) is the integration time step. The stiff ODE solver internally divides \(Δt\) into smaller sub-time steps. In each internal sub-time step, first, constrained equilibrium mass fractions are determined from Eq. (2.8). Afterwards, the variables are advanced in time by integrating Eq. (2.11). This step involves matrix inversion calculations because the coefficient matrix in Eq. (2.11) is not diagonal. Solution of this system provides the updated
constraint potential, density and temperature values which are used to advance the system to the next sub-time step. These calculations are continued until time \( t + \Delta t \) is reached as shown in Fig. 2.1.

### 2.2.2 Constraint Formulation

In the constraint formulation the rate equations of constraints, Eq. (2.5), are solved. Afterwards, the values of constraints are used in Eq. (2.3) along with Eq. (2.8) and the following relation

\[
\sum_{\beta=1}^{N_i} Y_\beta = 1
\]  

(2.13)

to obtain constraint potentials, mass fractions and density at the constrained equilibrium state. Normally, as performed in STANJAN, Newton’s method is considered to find constrained equilibrium composition. That is, an initial guess is made for \( \Lambda_\alpha \). Subsequently, \( \Lambda_\alpha \) is advanced iteratively until it satisfies Eqs. (2.3, 2.8, 2.13) while \( \dot{g}_\beta^0 \) is kept constant. However, this method is prone to singularity issues and sometimes \( d\Lambda_\alpha \) cannot be stably evaluated. The alternative method used here, the Gibbs function continuation method, is especially designed to overcome this issue [54]. We refer to Refs. [52, 54] for detailed discussion. This method is described briefly as follows. The numerical difficulties involved in the solution of Eqs. (2.3, 2.8, 2.13) are overcome by considering very small changes in the variables. Specifically, very small changes to \( d\Lambda_\alpha \) and \( d\dot{g}_\beta^0 \) and the corresponding variations in \( dY_\beta \) and \( dC_\alpha \) are appraised. This method originates from the observation that for arbitrary \( d\dot{g}_\beta^0 \), a corresponding value for \( d\Lambda_\alpha \) can always be stably evaluated. Based on this observation, an equivalent set of ODEs in pseudo-time, \( \xi \), is introduced to represent the constraint potential equations, Eqs. (2.3, 2.8, 2.13). Afterwards, the solution is obtained by integrating this set of equations. In this regard, the pseudo-Gibbs free energy \( \bar{g}_\beta(\xi) \), and constraint potentials \( \overline{\Lambda}_\alpha(\xi) \) are defined as functions of \( \xi \). The pseudo-Gibbs free energy is appointed to vary linearly from a known initial condition at \( \xi = 0 \) to the accurate value of the standard Gibbs free energy at \( \xi = 1 \). \( \overline{\Lambda}_\alpha(\xi) \) is obtained by integrating the set of ODEs from a specified initial condition \( \overline{\Lambda}_\alpha(0) \). The constraint potential values at \( \xi = 1, \overline{\Lambda}_\alpha(1) \), satisfy the constraint potential equations.
The algorithm used to solve the RCCE equations in the constraint form involves solving the transport equations of constraints, Eq. (2.5), using the same ODE solver as in the constraint potential formulation. During each reaction time step, constraints are advanced from time \( t \) to \( t + \Delta t \). In each sub-time step of the solver, constraints, enthalpy and pressure are used as input to constrained equilibrium calculation code. This step determines the constrained equilibrium state at which mass fractions, temperature and density are computed. These variables are then used to evaluate the source term on the RHS of Eq. (2.5), which is subsequently integrated in time to update the constraint values. In contrast to the constraint potential approach, this form of RCCE does not require matrix inversion. These calculations are continued until time \( t + \Delta t \) is reached as shown in Fig. 2.2.

### 2.3 Results

The two RCCE implementations are applied to a constant-pressure perfectly stirred reactor (PSR). The PSR case in the present study involves combustion of methane in oxygen. The reaction mechanism is that used in Ref. [22] which includes 29 species and 133 reaction steps. The \( \text{CH}_4/\text{O}_2 \) reacting system is represented by 12 RCCE constraints from Ref. [22] listed in Table 2.1. These constraints provide very accurate prediction of methane oxygen combustion as shown in previous work [22].

<table>
<thead>
<tr>
<th>Label</th>
<th>Constraint</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_1 )</td>
<td>H</td>
<td>Elements of hydrogen</td>
</tr>
<tr>
<td>( C_2 )</td>
<td>O</td>
<td>Elements of oxygen</td>
</tr>
<tr>
<td>( C_3 )</td>
<td>C</td>
<td>Elements of carbon</td>
</tr>
<tr>
<td>( C_4 )</td>
<td>M</td>
<td>Number of moles of gas</td>
</tr>
<tr>
<td>( C_5 )</td>
<td>FV</td>
<td>Number of moles of free valence</td>
</tr>
<tr>
<td>( C_6 )</td>
<td>FO</td>
<td>Number of moles of free oxygen</td>
</tr>
<tr>
<td>( C_7 )</td>
<td>FU</td>
<td>( \text{CH}_4 )</td>
</tr>
<tr>
<td>( C_8 )</td>
<td>FR</td>
<td>( \text{CH}_3 )</td>
</tr>
<tr>
<td>( C_9 )</td>
<td>APO</td>
<td>( \text{CH}_3\text{OOH} + \text{CH}_3\text{OO} + \text{CH}_2\text{OOH} )</td>
</tr>
<tr>
<td>( C_{10} )</td>
<td>ALCD</td>
<td>( \text{CH}_3\text{OH} + \text{CH}_3\text{O} + \text{CH}_2\text{OH} + \text{CH}_2\text{O} )</td>
</tr>
<tr>
<td>( C_{11} )</td>
<td>OHO</td>
<td>( \text{OH} + \text{O} )</td>
</tr>
<tr>
<td>( C_{12} )</td>
<td>DCO</td>
<td>( \text{HCO} + \text{CO} )</td>
</tr>
</tbody>
</table>
Chapter 2. **Comparison of RCCE Formulation**

The objective of this study is to compare RCCE results obtained from constraint potential and constraint methods in terms of efficiency and accuracy over a wide range of initial temperatures and equivalence ratios. This study is conducted by considering three sets of simulations:

I. ignition delay for a stoichiometric mixture at initial temperature of 1000 K,

II. stoichiometric mixtures at initial temperatures of 1000 – 1400 K,

III. nonstoichiometric mixtures with equivalence ratios 0.6, 0.9, 1.2, 1.6 and 2.0 at initial temperature of 1400 K.

Simulations are conducted on a computer with a 2.8 GHz Intel Core i7 processor. The accuracy of the results is assessed by comparing with those obtained from direct integration of the same kinetics, referred to as Detailed Kinetics Model (DKM). The relative error tolerance $\eta_r$ of the stiff ODE solver is the same for the RCCE and DKM calculations ($\eta_r = 10^{-7}$). However, the absolute error tolerance $\eta_a$ in the constraint potential RCCE simulations is assigned a larger value for temperature and constraint potentials, considering that these variables are 3 – 4 orders of magnitude larger than mass fractions and constraints; $\eta_a = 10^{-5}$ and $10^{-8}$ are used in constraint potential and constraint simulations, respectively.

In simulations I, DKM prediction of ignition delay for a stoichiometric mixture at initial temperature of 1000 K is conducted using a time step of $10^{-5}$ s. The DKM results at 17 equally spaced time intervals (10 – 170 ms) are used as initial compositions for the RCCE calculations which are conducted up to the next time interval. The interval 150 – 160 ms is divided into four subintervals because of high chemical activity in the region. The goal is to examine the efficiency and accuracy of RCCE formulations locally at different regions spanning the initial time to the equilibrium state. Prediction of temperature along with the percentage of relative difference ($\epsilon$) between the RCCE and DKM results are depicted in Fig. 2.3. The two RCCE methods show very small error at the initial time but relatively larger errors in the transition state. Both methods give an accurate prediction of equilibrium state with no error. The overall error in prediction of temperature is less than 3.5%. In Fig. 2.4, RCCE predictions of constraints are shown. For comparison, the constraints calculated from DKM mass fractions according to Eq. (2.3) are also displayed. This figure shows that the constraints are consistently predicted by the RCCE forms which demonstrates mathematical equivalence of the two formulations. The RCCE constraints
used here provide excellent predictions during the ignition process. Small differences between DKM and RCCE are, however, observed for a few constraints, which originate from less effectiveness of these constraints at particular times (Fig. 2.4i). It is also noticed that in Fig. 2.4a,b,c there are small differences between RCCE predictions of fixed elemental hydrogen $C_1$, oxygen $C_2$ and carbon $C_3$ constraints. These are because in constraint potential form, conservation of elements is not enforced as strict as that in the constraint approach. However, these deviations are very subtle (less that 0.5%) and can be ignored. In Fig. 2.5, mass fractions of some of species are shown. Concentration of all species are predicted quite well. This figure demonstrates the consistency and accuracy of RCCE formulations. Besides accuracy, an important issue with the RCCE is numerical performance. In this part, we provide a comparison of the overall CPU time and numerical stiffness of the two methods. Figure 2.6a shows the average computation time (described by the CPU time $t_{CPU}$) per time step for both forms. As depicted, constraint potential shows 50% less CPU time in this study. The overall computational cost is a function of both number of sub-time steps taken by the ODE solver and mathematical operations involved at each sub-time step. The number of sub-time steps is governed by stiffness of the system which is quite different between the two methods. Due to difference in their coefficient matrices (Eqs. (2.5, 2.11)), these methods carry different information regarding the time scales of the chemical kinetics. Figure 2.6b shows the number of function evaluations $n_f$. This parameter indicates the number of times the RHS and coefficient matrix of Eqs. (2.5, 2.11) is evaluated by the stiff ODE solver and gives an indication of the numerical stiffness of the system. As the numerical stiffness increases, the number of sub-time steps within the solver increases. This results in increased number of function evaluations. As shown in Fig. 2.6b, the constraint potential form shows 20% increase in number of function evaluations and thus higher stiffness in comparison with the constraint one. Although constraint potential method shows higher stiffness, it exhibits less computation time as demonstrated in Fig. 2.6a due to less intensive calculations per sub-time step [57, 58].

The second set of simulations are carried out over the initial temperatures of 1000 – 1400 $K$ using a time step of $10^{-5}$ s for both constraint potential and constraint methods. The RCCE temperature and mass fraction results are compared with those of DKM at the time when DKM temperature rises 10% over the initial temperature. In Figs. 2.7a,b the percentage of relative difference in prediction of temperature and ignition delay time $t_{ign}$ are shown, respectively.
The ignition delay time is defined as the time needed for 10% rise over the initial temperature. Both methods provide favorable predictions with almost similar accuracy for temperature; the constraint form shows slightly better accuracy as evidenced in Fig. 2.7a. The overall error in prediction of temperature and ignition delay time are less than 2% and 4.5%, respectively. Using current RCCE constraints results in slight underprediction of ignition delay time as shown in Fig. 2.7b. The accuracy of RCCE predictions can be further improved by adding more constraints, as discussed in Ref. [7]. The percentage of relative difference in prediction of CH\textsubscript{4} and O\textsubscript{2} mass fractions in comparison with DKM is shown in Fig. 2.8. Good agreement between the RCCE and DKM results is evident in this figure. The error in prediction of CH\textsubscript{4} and O\textsubscript{2} mass fractions is less than 1%. Similar agreement is obtained for other mass fractions. Figure 2.9a shows the average CPU time per time step. Consistent with stoichiometric results, as presented above, the constraint potential approach shows about 50% less CPU time for all initial temperatures considered. Figure 2.9b depicts the number of function evaluations. As shown, constraint potential approach shows 20% increase in number of function evaluations.

The third set of simulations involves lean (with equivalence ratios Φ = 0.6, 0.9) and rich (with Φ = 1.2, 1.6, 2.0) mixtures at initial temperature of 1400 K. The integration time step is $10^{-6}$ s. The RCCE temperature and mass fraction results are compared with those of DKM at $t = 4 \times 10^{-4}$ s. The percentage of relative difference in prediction of temperature as well as CH\textsubscript{4} and O\textsubscript{2} mass fractions are shown in Figs. 2.10 and 2.11, respectively. As shown, in these cases the constraint form yields slightly better predictions than the constraint potential one. As illustrated in Fig. 2.12a, the constraint potential shows 30% reduction in the CPU time for all equivalence ratios considered. The number of function evaluations for the constraint potential method, exhibits 20% rise over that for the constraint form, consistent with stoichiometric results (Fig. 2.9b). Therefore, constraint approach is superior to constraint potential one from the numerical stiffness standpoint. However, the overall computational cost of constraint potential is lower than that of constraint formulation considering combined effects of stiffness and mathematical operations per sub-time step (matrix inversion as opposed to constrained equilibrium calculations) [56–59].
2.4 Conclusions

The constraint potential and constraint forms of Rate-Controlled Constrained-Equilibrium (RCCE) method are applied to isobaric, adiabatic well stirred reactor involving combustion of methane in oxygen. The constraint potential implementation is based on solving rate equations for constraint potentials, density and temperature. In the constraint formulation the rate equations for constraints are solved. The two approaches, however, involve quite different mathematical operations. The former involves matrix inversion operation, while the latter requires constrained equilibrium calculations. Such difference in numerical solution procedure results in not only different number of mathematical operations but also dissimilar reduction in stiffness of the kinetics. As a result, the two forms of RCCE exhibit different numerical performance. To examine efficiency and numerical errors in these formulations, simulations are carried out over wide range of initial temperatures and equivalence ratios. Comparisons indicate that constraint potential shows 20% more number of function evaluations by the stiff ordinary differential equation solver, indicating higher numerical stiffness. However considering both stiffness and number of mathematical operations, the constrain potential formulation exhibits 50% and 30% less CPU times in stoichiometric and nonstoichiometric mixtures, respectively. The accuracy of RCCE predictions are assessed by comparing with those generated by direct integration of the same kinetics used in RCCE calculations. Compared to direct integration results, the two RCCE forms provide good prediction of the reacting system dynamics with almost similar accuracy.
Chapter 2. Comparison of RCCE Formulation

Figure 2.1: Algorithm used in the constraint potential form of RCCE calculations. The box represents the operations performed internally within the stiff ODE solver during each sub-time step.
Figure 2.2: Algorithm used in the constraint form of RCCE calculations. The box represents the operations performed internally within the stiff ODE solver during each sub-time step.
Figure 2.3: Ignition delay simulations for methane oxygen stoichiometric mixture in PSR at initial temperature of 1000 K. (a) time variation of temperature and (b) percentage of relative difference between the RCCE and DKM prediction of temperature. Solid and dashed lines denote the constraint potential and constraint results, respectively. The symbol (○) denotes DKM predictions.
Figure 2.4: Constraints in ignition delay calculations for stoichiometric methane oxygen mixture at initial temperature of 1000 K in PSR. Solid and dashed lines denote the constraint potential and constraint results, respectively. The symbol (◦) denotes DKM predictions. Constraints are listed in Table 2.1.
Figure 2.5: Mass fractions in ignition delay calculations for stoichiometric methane oxygen combustion at initial temperature of 1000 K in PSR. Solid and dashed lines denote the constraint potential and constraint results, respectively. The symbol (◦) denotes DKM predictions.
Figure 2.6: Performance of RCCE in ignition delay calculations for stoichiometric methane oxygen combustion in PSR at initial temperature of 1000 K. (a) Average CPU time in seconds; (b) number of function evaluations. The symbols (□) and (△) denote constraint potential and constraint results, respectively.
Figure 2.7: The percentage of relative difference in prediction of (a) temperature and (b) ignition delay time. Constraint potential (right set) and constraint (left set) forms are compared with DKM in stoichiometric methane oxygen combustion simulations in PSR for initial temperatures of 1000 – 1400 K.
Figure 2.8: The percentage of relative difference in prediction of (a) CH$_4$ and (b) O$_2$ mass fractions. Constraint potential (right set) and constraint (left set) forms are compared to DKM in stoichiometric methane oxygen combustion simulations in PSR for initial temperatures of 1000 – 1400 K.
Figure 2.9: Performance of RCCE in stoichiometric methane oxygen combustion simulations in PSR for initial temperatures of 1000 – 1400 K. (a) Average CPU time in seconds; (b) number of function evaluations. The symbols (□) and (△) denote constraint potential and constraint results, respectively.
Figure 2.10: The percentage of relative difference in prediction of temperature. The RCCE is compared with DKM in lean ($\Phi = 0.6, 0.9$) and rich ($\Phi = 1.2, 1.6, 2.0$) mixtures at initial temperature of 1400 K. Constraint potential and constraint forms are the right and left sets, respectively.
Chapter 2. Comparison of RCCE Formulation

Figure 2.11: The percentage of relative difference in prediction of (a) CH₄ and (b) O₂ mass fractions in comparison with DKM. Simulations are performed in nonstoichiometric methane oxygen combustion simulations in PSR for lean (Φ = 0.6, 0.9) and rich (Φ = 1.2, 1.6, 2.0) mixtures at initial temperature of 1400 K. Constraint potential and constraint forms are the right and left sets, respectively.
Figure 2.12: Performance of RCCE forms in nonstoichiometric methane oxygen combustion simulations in PSR for lean ($\Phi = 0.6, 0.9$) and rich ($\Phi = 1.2, 1.6, 2.0$) mixtures at initial temperature of 1400 $K$. (a) Average CPU time in seconds; (b) number of function evaluations. The symbols (□) and (△) denote constraint potential and constraint results, respectively.
Chapter 3

Interactions Between Mixing and Chemical Reaction Using the Rate-Controlled Constrained-Equilibrium Method

3.1 Introduction

The RCCE formulation, involving rate equations for constraint potentials, temperature and density, is used to describe dynamics of reacting gas mixtures. Compared to RCCE formulations based on constraints as dependent variables, this form is computationally advantageous as it avoids conversion of constraints to constraint potentials at each time step which is a demanding calculation [56]. Another important benefit of this method is that it allows simultaneous consideration of both mixing and reaction effects with no additional splitting scheme. Besides introducing additional errors, such treatment requires the expensive constraints to constraint potentials conversion at each time step. The RCCE rate equations, including both mixing and reaction, are solved to fully determine the constrained-equilibrium state of the system. The method is applied to study methane/oxygen combustion in a partially stirred reactor (PaSR), which is characterized by mixing, chemical and residence time scales. The main objectives
of this work are (1) to conduct a comprehensive study to demonstrate the efficiency and accuracy of the method, and (2) to demonstrate its capacity to accurately predict reacting systems with different mixing intensities. The mixing process in PaSR involves both macro- and micro-mixing which are represented by residence and mixing time scales, respectively. The former is associated with bulk fluid motion while the latter occurs at molecular scales. Both mixing mechanisms can have important consequences in the RCCE predictions. The importance of this issue is because mixing can influence the constrained-equilibrium state and thus, effectiveness of constraints representing chemical kinetics. It is thus essential to study the capacity of RCCE to predict the coupling between chemical reaction and fluid motion at different levels of mixing. Besides accuracy, the computational performance of RCCE is also assessed in this study by measuring its overall central processing unit (CPU) time as well as its effectiveness in reducing the numerical stiffness of chemical kinetics. The constraints used are those shown to be very effective in previous work [22]. This chapter is organized as follows. The mathematical description of constraint potential representation of RCCE is discussed in §3.2. Reactor configuration and selection of constraints are outlined in §3.3 and §3.4, respectively. The results of reactor simulations along with accuracy and efficiency of RCCE in comparison with DKM are discussed in §3.5. Concluding remarks are provided in §3.6.

3.2 Rate-Controlled Constrained-Equilibrium Formulation

The evolution of a macroscopically homogeneous, reacting system involving $N_s$ chemical species is governed by

$$
\frac{d\phi_\beta}{dt} = \mathcal{M}_\beta(t) + S_\beta(t) \quad (\beta = 1, 2, \ldots, N_s + 1)
$$

(3.1)

where compositional variables $[\phi_1, \phi_2, \ldots, \phi_{N_s+1}]$ constitute the full representation of the reacting system. These variables are $\phi_\beta \equiv Y_\beta$, for $\beta = 1, \ldots, N_s$ and $\phi_{N_s+1} \equiv h$, where $Y_\beta$ and $h$ denote mass fraction of chemical species and specific enthalpy of the mixture, respectively. The right hand side (RHS) includes the effects of micro-mixing $\mathcal{M}_\beta$ and chemical reaction $S_\beta$. For the micro-mixing term, we employ the linear mean square estimation (LMSE) model [64], also known as interchange by exchange with the mean (IEM) closure [65],

$$
\mathcal{M}_\beta(t) = -\frac{1}{\tau_{mix}} (\phi_\beta - \bar{\phi}_\beta)
$$

(3.2)
where \( \tau_{\text{mix}} \) denotes the mixing time scale and \( \bar{\phi}_j \) is the mean value of composition variables. The reaction source term is defined as

\[
S_\beta(t) = \frac{\dot{\omega}_\beta M_\beta}{\rho} \quad (\beta = 1, \ldots, N_s)
\]  

(3.3)

where \( \dot{\omega}_\beta \) and \( M_\beta \) are the net production rate and molar mass of species \( \beta \), respectively, and \( \rho \) is the density of the gas mixture. In low Mach number flows, we assume \( S_{N_s+1} \approx 0 \) for the specific enthalpy. The RCCE method provides a reduced representation of the reacting system using \( N_c \) slowly-varying scalars which impose constraints on the evolution of the system. These scalars, termed “constraints,” are linear combinations of chemical species [7],

\[
C_\alpha = \sum_{\beta=1}^{N_s} A_{\alpha\beta} \frac{Y_\beta}{M_\beta} \quad (\alpha = 1, 2, \ldots, N_c)
\]  

(3.4)

where \( C_\alpha \) denotes the value of constraint \( \alpha \). The transformation matrix \( A_{\alpha\beta} \), a predefined constant here, represents the contribution of the chemical species \( \beta \) to the constraint \( \alpha \). The reduced representation \([C_1, C_2, \ldots, C_{N_c}, h]\) is governed by rate equations for constraints and specific enthalpy. The former is obtained by transforming Eq. (3.1) according to Eq. (3.4),

\[
\frac{dC_\alpha}{dt} = \sum_{\beta=1}^{N_s} A_{\alpha\beta} \left( \dot{\omega}_\beta(t) + S_\beta(t) \right)
\]  

(3.5)

and the latter is described by Eq. (3.1) with \( \alpha = N_s + 1 \). In RCCE, Eq. (3.1) is replaced by Eq. (3.5) which is advantageous since Eq. (3.5) includes fewer ordinary differential equations (ODEs) with reduced numerical stiffness. The rapidly-varying (unconstrained) species are assumed to be instantaneously in a constrained-equilibrium state, at which the composition of chemical species are determined. The constrained-equilibrium state is specified using the method of undetermined Lagrange multipliers together with maximizing the entropy or minimizing an appropriate free energy subject to the instantaneous values of constraints [22]. We consider the summation of entropy and constraints

\[
L = s + \sum_{\alpha=1}^{N_s} \lambda_\alpha \left[ C_\alpha - \sum_{\theta=1}^{N_s} A_{\alpha\theta} \frac{Y_\theta}{M_\theta} \right]
\]  

(3.6)

where \( s \equiv s(p, h, Y_1, \ldots, Y_{N_s}) \) is the specific entropy of the mixture, \( p \) is pressure and \( \lambda_\alpha \) denotes the Lagrange multiplier corresponding to constraint \( \alpha \). To optimize this relation with respect to
mass fraction we set
\[
\frac{\partial L}{\partial Y_\beta} = 0 \quad (\beta = 1, \ldots, N_s)
\] (3.7)

We, thus, have
\[
\frac{\partial s}{\partial Y_\beta} - \sum_{\alpha=1}^{N_s} \lambda_\alpha \sum_{\theta=1}^{N_s} \frac{1}{M_\theta} \frac{\partial Y_\theta}{\partial Y_\beta} = 0
\] (3.8)

For a multicomponent system at constant specific enthalpy and pressure, the derivative of specific entropy with respect to mass fraction of species \( \beta \) can be written as
\[
\frac{\partial s}{\partial Y_\beta} = -\frac{\hat{\mu}_\beta}{M_\beta T}
\] (3.9)

Substituting Eq. (3.9) into Eq. (3.8) yields
\[
-\frac{\hat{\mu}_\beta}{M_\beta T} - \frac{1}{M_\beta} \sum_{\alpha=1}^{N_s} A_{\alpha\beta} \lambda_\alpha = 0
\] (3.10)

where \( \hat{\mu}_\beta \) is the chemical potential per unit mole of species \( \beta \). We divide both sides of this equation by universal gas constant \( R_u \). The normalized Lagrange multiplier conjugate to each constraint, called the “constraint potential,” is defined as
\[
\Lambda_\alpha = \frac{\lambda_\alpha}{R_u}
\] (3.11)

Equation (3.10) can thus be written as
\[
\frac{\hat{\mu}_\beta}{R_u T} = -\sum_{\alpha=1}^{N_s} A_{\alpha\beta} \Lambda_\alpha
\] (3.12)

where the LHS can be expanded according to the relationship between the chemical potential and the Gibbs free energy of the pure substance per unit mole of species \( \beta \) \( \hat{g}_\beta \)

\[
\hat{\mu}_\beta = \hat{g}_\beta + R_u T \ln X_\beta
\] (3.13)

The Gibbs free energy \( \hat{g}_\beta \equiv \hat{g}_\beta(T, p) \) is related to that at the standard pressure \( p_0 \) as
\[
\hat{g}_\beta = \hat{g}_\beta^0 + R_u T \ln \frac{p}{p_0}
\] (3.14)
where \( \bar{\hat{g}}_\beta^0 \equiv \hat{g}_\beta(T, p_0) \). Substituting Eqs. (3.13,3.14) into Eq. (3.12) gives

\[
\frac{1}{R_u T} \left[ \frac{\bar{\hat{g}}_\beta^0 + R_u T \ln \frac{pX_\beta}{p_0}}{R_u T} \right] = - \sum_{\alpha=1}^{N_c} A_{\alpha\beta} \Lambda_\alpha
\]  

(3.15)

Solving this equation for \( X_\beta \) gives

\[
X_{\beta}^{RCCE} = \frac{P_0}{p} \exp \left( -\frac{\bar{\hat{g}}_\beta^0}{R_u T} \right) \exp \left( - \sum_{\alpha=1}^{N_c} A_{\alpha\beta} \Lambda_\alpha \right)
\]  

(3.16)

where \( X_{\beta}^{RCCE} \) is the mole fraction evaluated at the RCCE state of the system. Equation (3.16) can also be written in terms of mass fractions as

\[
Y_{\beta}^{RCCE} = \frac{M_\beta p_0}{\rho R_u T} \exp \left( -\frac{\bar{\hat{g}}_\beta^0}{R_u T} \right) \exp \left( - \sum_{\alpha=1}^{N_c} A_{\alpha\beta} \Lambda_\alpha \right)
\]  

(3.17)

where \( Y_{\beta}^{RCCE} \) is the mass fractions at the constrained-equilibrium state.

For numerical solution of the RCCE rate equations, we transform Eq. (3.5) into differential equations for constraint-potentials. In previous studies [22–24], similar equations are derived for temperature and constraint potentials given equations for volume and energy. Here, we consider constraint-potentials along with temperature and density as independent variables for given enthalpy and pressure. We start with Eq. (3.4) and take derivative with respect to time

\[
\frac{dC_\alpha}{dt} = \sum_{\beta=1}^{N_c} A_{\alpha\beta} \frac{1}{M_\beta} \frac{dY_\beta}{dt} = \sum_{\beta=1}^{N_c} A_{\alpha\beta} \frac{Y_\beta}{M_\beta} \frac{d\ln Y_\beta}{dt}
\]  

(3.18)

The RHS is expressed by taking derivative of Eq. (3.17) with respect to time as

\[
\frac{d\ln Y_\beta}{dt} = - \frac{1}{\rho} \frac{d\rho}{dt} + \frac{1}{R_u T^2} \frac{dT}{dt} \left[ \bar{\hat{g}}_\beta^0 - T \frac{d\bar{\hat{g}}_\beta^0}{dT} - R_u T \right] - \sum_{\alpha=1}^{N_c} A_{\alpha\beta} \frac{d\Lambda_\alpha}{dt}
\]  

(3.19)

The second term on the RHS can be simplified to \( \frac{\bar{\hat{g}}_\beta^0}{R_u T^2} \frac{dT}{dt} \) where \( \bar{\hat{g}}_\beta \) denotes the internal energy per unit mole of species \( \beta \). For a pure chemical species, governed by ideal-gas equation of state, we have

\[
\bar{\hat{g}}_\beta^0 = \bar{h}_\beta - T \bar{s}_\beta^0 = \bar{\hat{e}}_\beta + R_u T - T \bar{s}_\beta^0
\]  

(3.20)

In this equation, \( \bar{h}_\beta \) and \( \bar{s}_\beta^0 \) denote the enthalpy per unit mole of species \( \beta \) and the entropy of
the pure substance at pressure $p_0$ per unit mole of species $\beta$, respectively. According to Gibbs fundamental equation, for a constant pressure and chemical composition process we have

$$\dot{s}_\beta = - \left( \frac{\partial \hat{g}_\beta}{\partial T} \right)_{p, n_1, n_2, \ldots, n_N} (3.21)$$

where $\dot{s}_\beta$ and $n_\theta$ denote the entropy of the pure substance per unit mole of species $\beta$ and the number of moles of species $\theta$, respectively. For a pure substance at pressure $p_0$ this relation along with Eq. (3.20) gives

$$\dot{e}_\beta = \hat{g}_\beta^0 - T \frac{d\hat{g}_\beta^0}{dT} - R_u T (3.22)$$

which relates the entropy to the Gibbs free energy and the temperature of the system. Therefore, the time derivative of constraints is obtained by substituting Eq. (3.19) into Eq. (3.18) as

$$\frac{dC_\alpha}{dt} = - \left( \sum_{\beta=1}^{N_s} A_{\alpha\beta} Y_\beta \right) \frac{1}{\rho} \frac{d\rho}{dt} + \left( \sum_{\beta=1}^{N_s} A_{\alpha\beta} Y_\beta \frac{\dot{e}_\beta}{M_\beta} \right) \frac{1}{T} \frac{dT}{dt}$$

$$- \sum_{\theta=1}^{N_s} \sum_{\beta=1}^{N_s} A_{\alpha\theta} A_{\theta\beta} Y_\beta \frac{d\Lambda_\theta}{M_\beta} dt (3.23)$$

To include the energy balance, we take time derivative of the specific enthalpy $h = \sum_{\beta=1}^{N_s} h_\beta Y_\beta$ to obtain

$$\frac{dh}{dt} = c_p \frac{dT}{dt} + \sum_{\beta=1}^{N_s} h_\beta Y_\beta \frac{d\ln Y_\beta}{dt} (3.24)$$

where $c_p$ is the specific heat capacity of the mixture at constant pressure and $h_\beta$ denotes specific enthalpy of species $\beta$. Employing Eq. (3.19) results in

$$\frac{dh}{dt} = -h \frac{1}{\rho} \frac{d\rho}{dt} + \left[ c_p T + \sum_{\beta=1}^{N_s} h_\beta Y_\beta \frac{\dot{e}_\beta}{R_u T} \right] \frac{1}{T} \frac{dT}{dt} - \sum_{\theta=1}^{N_s} \sum_{\beta=1}^{N_s} A_{\alpha\theta} h_\beta Y_\beta \frac{d\Lambda_\theta}{M_\beta} dt (3.25)$$

The set of equations corresponding to species concentrations and energy are closed by the ideal gas equation of state

$$p = \rho R_u T \sum_{\beta=1}^{N_s} \frac{Y_\beta}{M_\beta} (3.26)$$

Taking derivative of Eq. (3.26) with respect to time gives

$$\frac{1}{p} \frac{dp}{dt} = \frac{1}{\rho} \frac{1}{\rho} \frac{d\rho}{dt} + \frac{1}{T} \frac{dT}{dt} + M \sum_{\beta=1}^{N_s} \frac{Y_\beta}{M_\beta} \frac{d\ln Y_\beta}{dt} (3.27)$$
where \( M = \left( \frac{\sum_{\beta=1}^{N_s} Y_{\beta} Y_{\beta}}{M_{\beta}} \right)^{-1} \) is the average molar mass of the mixture. Using Eq. (3.19) we have

\[
\frac{1}{\rho} \frac{d\rho}{dt} = \left( M \sum_{\beta=1}^{N_s} \frac{Y_{\beta} \hat{e}_\beta}{M_{\beta} R_a T} + 1 \right) \frac{1}{T} \frac{dT}{dt} - M \sum_{\theta=1}^{N_c} \sum_{\beta=1}^{N_s} A_{\alpha \beta \theta} \frac{Y_{\beta} \Lambda_{\theta}}{M_{\beta}} \frac{d\Lambda_{\theta}}{dt}
\]

(3.28)

Equations (3.23, 3.25, 3.28) constitute the set of \( N_c + 2 \) equations describing the time variation of \( N_c \) constraint potentials, temperature and density. The final form of these equations are written as

\[
-C_{\alpha} \frac{1}{\rho} \frac{d\rho}{dt} + Q_{c\alpha} \frac{1}{T} \frac{dT}{dt} + \sum_{\theta=1}^{N_c} R_{c\theta \alpha} \frac{d\Lambda_{\theta}}{dt} = \sum_{\beta=1}^{N_s} A_{\alpha \beta} \frac{Y_{\beta}}{M_{\beta}} \left( \mathcal{M}_{\beta}(t) + S_{\beta}(t) \right) \quad (\alpha = 1, \ldots, N_c)
\]

(3.29a)

\[
-h \frac{1}{\rho} \frac{d\rho}{dt} + Q_{h \beta} \frac{1}{T} \frac{dT}{dt} + \sum_{\theta=1}^{N_c} R_{h \theta \beta} \frac{d\Lambda_{\theta}}{dt} = \mathcal{M}_{\beta+1}(t)
\]

(3.29b)

\[
Q_{p \beta} \frac{1}{T} \frac{dT}{dt} + \sum_{\theta=1}^{N_c} R_{p \theta \beta} \frac{d\Lambda_{\theta}}{dt} = \frac{1}{\rho} \frac{d\rho}{dt}
\]

(3.29c)

where the coefficients are

\[
Q_{c\alpha} = \sum_{\beta=1}^{N_s} A_{\alpha \beta} \frac{Y_{\beta}}{M_{\beta} R_a T} ; \quad R_{c\alpha \theta} = - \sum_{\beta=1}^{N_s} A_{\alpha \beta} A_{\beta \theta} \frac{Y_{\beta}}{M_{\beta}}
\]

\[
Q_{h \beta} = c_p T + \sum_{\beta=1}^{N_s} h_{\beta} Y_{\beta} \hat{e}_\beta \frac{R_a}{R_{T}} ; \quad R_{h \theta \beta} = - \sum_{\beta=1}^{N_s} A_{\theta \beta} h_{\beta} Y_{\beta}
\]

(3.30)

\[
Q_{p \beta} = M \sum_{\beta=1}^{N_s} Y_{\beta} \hat{e}_\beta \frac{R_a}{R_{T}} + 1 ; \quad R_{p \theta \beta} = -MC_{\theta}
\]

For systems with small pressure variations, we can assume \( \frac{1}{\rho} \frac{d\rho}{dt} \approx 0 \) on the RHS of Eq. (3.29c). It is also noticed that since chemical reaction conserves the atomic elements, in Eq. (3.29a) chemical reaction does not appear on the RHS of Eq. (3.29a) for the elemental constrains. Given an initial thermodynamic state \((\rho, T, Y_1, \ldots, Y_{N_s})\), Eq. (3.29) is integrated to obtain \( T(t), \rho(t) \) and \( \Lambda_{\theta}(t) \quad (\theta = 1, \ldots, N_c) \). These variables provide the mass fraction of all the species present in the chemical mechanism according to Eq. (3.17). An advantage of RCCE equations as presented in Eq. (3.29) is that the effects of mixing and chemical reaction can be accounted for simultaneously during numerical integration.
3.3 Reactor Configuration

The RCCE formulation is applied to a constant-pressure partially stirred reactor (PaSR) configuration \[66, 67\]. This reactor offers a simplified adiabatic, spatially homogeneous reactor to study interactions between chemical kinetics and turbulent mixing in a computationally efficient manner. In PaSR, the reacting system is represented by an ensemble of particles evolving in time. The particles are perfectly mixed macroscopically but poorly mixed at molecular level. The small-scale mixing in the reactor is described by the LMSE model with the characteristic mixing time \(\tau_{mix}\) (Eq. (3.2)). At small mixing time scales the PaSR becomes similar to perfectly stirred reactor (PSR), while for large mixing time scales its behavior is close to PFR. Besides mixing time scale, the reactor is also characterized by two other parameters: residence time scale \(\tau_{res}\) and reaction time scale \(\tau_{chem}\). The former is associated with large-scale mixing in the reactor. With constant mass, \(m\), within the reactor, the residence time is related to the mass flow rate \(\dot{m}\) of the inflow/outflow streams as \(\dot{m} = m/\tau_{res}\). The PaSR case in the present study involves combustion of methane/oxygen mixture. The reaction kinetics is that used in Ref. [22], which includes 29 species (Table 3.1) and 133 reaction steps. The PaSR has one inflow stream which carries stoichiometric \(\text{CH}_4/\text{O}_2\) mixture at 1500 \(K\) and 1 atm. The outflow particles are randomly substituted with the inflow ones at \(\tau_{res}\) intervals. The initial PaSR particles have the same mass fractions as the inflowing particles and the temperature is uniformly distributed between 1000 \(K\) and 1200 \(K\).

Table 3.1: Species in the methane oxygen chemical mechanism.

| Species   | \(\text{H}_2\) | \(\text{O}_2\) | \(\text{CO}_2\) | \(\text{H}_2\text{O}_2\) | \(\text{H}_2\text{O}\) | \(\text{CH}_4\) | \(\text{CH}_3\) | \(\text{CH}_2\text{O}\) | \(\text{OH}\) | \(\text{CO}\) | \(\text{H}_3\text{O}\) | \(\text{HCO}\) | \(\text{CH}\) | \(\text{C}\) | \(\text{O}\) | \(\text{CH}_2\text{OH}\) | \(\text{HOCO}\) | \(\text{HOCHO}\) | \(\text{OCHO}\) | \(\text{CH}_3\text{OO}\) | \(\text{CH}_2\text{OOH}\) | \(\text{HOOCHO}\) | \(\text{HOOCO}\) | \(\text{OOCHO}\) |
3.4 Rate-Controlled Constrained-Equilibrium Constraints

The CH$_4$/O$_2$ reacting system is represented by the 12 constraints from Ref. [22] listed in Table 3.2. These constraints provide very accurate prediction of a constant-volume constant-energy reactor as shown in previous work [22]. These constraints include 8 universal constraints: elemental hydrogen (H), elemental oxygen (O), elemental carbon (C), total number of moles of gas (M), number of moles of free valence (any unpaired valence electron) (FV), number of moles of free oxygen (any oxygen atom that is not directly attached to another oxygen atom) (FO), OH+O (OHO) and HCO + CO (DCO). These constraints are considered as “universal” constraints because they are independent of the initial reactants. Along with the equilibrium reactions, H$_2$ + O $\equiv$ OH + H, H$_2$ + HOO $\equiv$ H$_2$O$_2$ + H and HCO + O$_2$ $\equiv$ CO + HO$_2$, they are sufficient to determine the constrained-equilibrium mole fractions of the 11 major hydrocarbon combustion products H, O, HO, HO$_2$, H$_2$, O$_2$, H$_2$O, H$_2$O$_2$, HCO, CO and CO$_2$ under both high and low temperature conditions. Also considered are 4 additional fuel-dependent constraints which include a constraint on the fuel, FU $\equiv$ CH$_4$, a constraint on fuel radical, FR $\equiv$ CH$_3$ as well as APO $\equiv$ CH$_3$OOH + CH$_3$OO + CH$_2$OOH and ALCD $\equiv$ CH$_3$OH + CH$_3$O + CH$_2$OH + CH$_2$O. For more information about these constraints we refer to Ref. [22].

<table>
<thead>
<tr>
<th>Constraints</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>Elements of Hydrogen</td>
</tr>
<tr>
<td>O</td>
<td>Elements of Oxygen</td>
</tr>
<tr>
<td>C</td>
<td>Elements of Carbon</td>
</tr>
<tr>
<td>M</td>
<td>Number of moles of gas</td>
</tr>
<tr>
<td>FV</td>
<td>Number of moles of free valence</td>
</tr>
<tr>
<td>FO</td>
<td>Number of moles of free oxygen</td>
</tr>
<tr>
<td>OHO</td>
<td>OH + O</td>
</tr>
<tr>
<td>DCO</td>
<td>HCO + CO</td>
</tr>
<tr>
<td>FU</td>
<td>CH$_4$</td>
</tr>
<tr>
<td>FR</td>
<td>CH$_3$</td>
</tr>
<tr>
<td>APO</td>
<td>CH$_3$OOH + CH$_3$OO + CH$_2$OOH</td>
</tr>
<tr>
<td>ALCD</td>
<td>CH$_3$OH + CH$_3$O + CH$_2$OH + CH$_2$O</td>
</tr>
</tbody>
</table>
3.5 Results and Discussion

The objectives of the PaSR simulations are to assess the efficiency and accuracy of RCCE and to demonstrate its predictive capacity over a wide range of mixing and residence time scales. The RCCE predictions are obtained by integrating the rate equations of constraint potentials, enthalpy and equation of state, Eq. (3.29), in time using the stiff ordinary differential equation (ODE) solver DASSL [68]. The results are assessed by comparing with those obtained from direct integration of the same kinetics, referred to as detailed kinetics model (DKM). Simulations are conducted of the PaSR configuration with and without mixing. In the former, mixing is not active ($\tau_{\text{mix}} \rightarrow 0$) and the reactor resembles a PSR; the objective is to access the predictive capacity and the computational performance of RCCE in a purely reacting system. In the latter, the ability of RCCE to predict reactors with inclusion of mixing are evaluated at various mixing and residence time scales. Specifications of these simulations along with the solver parameters are as listed in Table 3.3.

<table>
<thead>
<tr>
<th>Table 3.3: Numerical specifications.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSR</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>RCCE absolute error tolerance</td>
</tr>
<tr>
<td>RCCE relative error tolerance</td>
</tr>
<tr>
<td>DKM absolute error tolerance</td>
</tr>
<tr>
<td>DKM relative error tolerance</td>
</tr>
<tr>
<td>Time step (s)</td>
</tr>
<tr>
<td>Total number of time steps</td>
</tr>
<tr>
<td>Number of particles</td>
</tr>
<tr>
<td>Initial temperature ($K$)</td>
</tr>
<tr>
<td>Pressure (atm)</td>
</tr>
<tr>
<td>Temperature of inflow particles ($K$)</td>
</tr>
</tbody>
</table>

3.5.1 Accuracy of Rate-Controlled Constrained-Equilibrium description of chemical kinetics

Before studying the effect of mixing, we demonstrate the accuracy of RCCE. Two reaction mechanisms are considered: (1) $\text{H}_2/\text{O}_2$ kinetics [69] consisting of 9 species and 22 reaction steps (by eliminating Ar and He from the original kinetics) and (2) $\text{CH}_4/\text{O}_2$ kinetics [22] involving 29 species and 133 reactions. These mechanisms are integrated in time using RCCE equations and the results are validated by comparing with DKM of the underlying kinetics. In
the \( \text{H}_2/\text{O}_2 \) case, the number of constraints is chosen to be equal to the number of species. In this limiting case, \( \text{RCCE} \) and \( \text{DKM} \) must yield identical results. Calculations are performed for stoichiometric as well as lean and rich mixtures, and the system is allowed to relax to its final equilibrium state. The results, as shown in Fig. 3.1, demonstrate close agreements between \( \text{RCCE} \) and \( \text{DI} \) for all initial temperatures and equivalence ratios (\( \Phi \)). The \( \text{RCCE} \) calculations for \( \text{CH}_4/\text{O}_2 \) case are also carried out in a PSR with the initial temperatures 800-1800 K and the equivalence ratios \( \Phi = 0.25-2.0 \). Time variation of temperature for stoichiometric mixtures of methane and oxygen is shown in Fig. 3.2. Initial temperatures of 800, 1000, 1200, 1400, 1600 and 1800 K are considered with time step of \( 10^{-6} \). At initial times (not shown), temperature exhibits a slight decrease due to endothermic nature of initiation reactions. Subsequently, it increases as exothermic reactions become more important. The agreement between \( \text{RCCE} \) and \( \text{DKM} \) results is excellent over the entire range of temperatures considered as illustrated in Fig. 3.2. The temperature overshoot, caused primarily by unphased competition between the very fast heat releasing kinetics and the slow endothermic kinetics, is well predicted by \( \text{RCCE} \) under the chosen constraints. The fast kinetics involves 1) radical pool attack on fuel and 2) recombination of radicals as they become more populated due to depletion of fuel. Both such reactions involve zero or little activation energies. The slow endothermic kinetics, on the other hand, is due to dissociation reactions that involve high activation energy barriers, which make them slow. The same agreement is obtained for the lean (\( \Phi = 0.25 \) and \( \Phi = 0.4 \)) and the rich (\( \Phi = 1.33 \) and \( \Phi = 2.0 \)) mixtures as depicted in Figs. 3.3a and 3.3b, respectively. The \( \text{RCCE} \) predictions of ignition delay times for these mixtures are within \( 1 - 5\% \) of those obtained from \( \text{DKM} \). The ignition delay time is defined as the time needed for 10\% rise over the initial temperature. It is notable that the accuracy of \( \text{RCCE} \) predictions can be further improved by adding more constraints, as discussed in Ref. [7]. The \( \text{RCCE} \) prediction of mass fractions is shown in Fig. 3.4. Depicted are the mass fractions of \( \text{CH}_4, \text{CO}_2, \text{OH} \) and \( \text{H} \) whose predictions are within \( 1\% \) of those obtained from \( \text{DKM} \). It is noticed that mass fraction of minor species such as \( \text{H} \) is captured quite accurately by \( \text{RCCE} \) despite their very small values.

### 3.5.2 Numerical efficiency of Rate-Controlled Constrained-Equilibrium

The main advantage of \( \text{RCCE} \) is that it allows consideration of complex chemical kinetics at reduced computational cost. This reduction is due to both smaller number of rate equations to
solve as well as lower numerical stiffness caused by elimination of small time scales associated with fast reactions. It is evident that RCCE inherently involves more calculations than DKM at each sub-time step taken by stiff ODE solvers. This is, however, compensated by the lower number of sub-time step resulting from reduced stiffness in RCCE. As a result, the overall computational cost of RCCE is lower than that of DKM. To assess the RCCE computation time (measured by CPU time $t_{CPU}$), it is important to keep in mind that the performance of stiff ODE solvers are influenced by relative $\eta_r$ and absolute $\eta_a$ error tolerances. The former controls the error in the solution relative to dependent variable values. The latter provides a threshold below which the solution is insignificant. In the PSR simulations, these tolerances are set as the following in the RCCE and DKM calculations:

- **RCCE**: $\eta_r = 10^{-6}$; $\eta_a = 10^{-5}$ for temperature and constraint potentials; $\eta_a = 10^{-8}$ for density.
- **DKM**: $\eta_r = 10^{-6}$; $\eta_a = 10^{-8}$ for mass fractions; $\eta_a = 10^{-5}$ for temperature.

The RCCE and DKM simulations shown in Fig. 3.5 are conducted with the same relative error tolerance. However, the absolute error in RCCE is assigned a larger value for temperature and constraint potentials, considering that these variables are of 3 – 4 orders of magnitude larger than mass fractions. This figure shows the overall computation time in the PSR cases presented in Fig. 3.2 for RCCE and DKM. The CPU time is measured from the initial time until the mixture reaches the equilibrium state. As depicted, the RCCE shows reduced CPU times for all initial temperatures considered. This reduction is more significant at lower and higher temperatures. However, near 1200 $K$ the RCCE performance is relatively closer to that of DKM. This is an indication that in the vicinity of this temperature, equilibrated reactions that are not present in RCCE do not cause more substantial stiffness in the DKM calculations. It is important to keep in mind that such RCCE performance is obtained based on the specific constraints and solver parameters used. By reducing the stiffness associated with fast reactions, the former has a significant influence on the RCCE performance. Regarding the latter, the sensitivity of the RCCE results to the stiff ODE solver parameters is examined by varying the error tolerances and measuring the error in predicting the equilibrium temperature, ignition delay time as well as equilibrium $\text{CH}_4$, $\text{O}_2$, $\text{H}_2\text{O}$, $\text{CO}_2$, $\text{H}_2$, $\text{H}$, $\text{CO}$ and $\text{OH}$ mass fractions. To further illustrate the influence of error tolerances, two sets of simulations are considered in which $\eta_a = 0.01 \eta_r$. 

\[ \eta_a = 10 \eta_r \text{ with } \eta_r \text{ varied in the range of } 10^{-10} - 10^{-6}. \] A stoichiometric mixture with initial temperature of 1300 K is considered and the RCCE results are compared with those of highly accurate DKM simulations with \( \eta_a = 10^{-12} \) and \( \eta_r = 10^{-10} \). The CPU time for each case is shown in Fig. 3.6a, which indicates that larger \( \eta_r \) and \( \eta_a \) values decrease the RCCE computation time. For each \( \eta_r \) value, lowering \( \eta_a \) leads to significant increase in the CPU time. However, improvement in accuracy of the RCCE predictions is negligible as illustrated in Fig. 3.6b. This figure shows the relative difference (\( \epsilon \)) between the RCCE and DKM predictions of the equilibrium mass fractions and temperature. It is observed that while \( \eta_r \) has a significant influence on the error, \( \eta_a \) mostly affects the performance of RCCE without much increase in the error. The level of errors in this figure indicates that even with the largest \( \eta_r \) and \( \eta_a \) values the error in the RCCE results is very small. Increasing \( \eta_a \) by a factor 1000, causes 65% decrease in the CPU time. However, its effect on the resulting mass fractions is insignificant. In these calculations, the error in ignition delay time (not shown) has a maximum value of 1.45% and shows very small change with error tolerances.

The influence of error tolerances are further studied by considering three sets of simulations with the RCCE error tolerances set as:

I. \( \eta_r = 10^{-6}; \eta_a = 10^{-8} \) for temperature and constraint potentials; \( \eta_a = 10^{-11} \) for density,

II. \( \eta_r = 10^{-6}; \eta_a = 10^{-5} \) for temperature and constraint potentials; \( \eta_a = 10^{-8} \) for density,

III. \( \eta_r = 10^{-5}; \eta_a = 10^{-5} \) for temperature and constraint potentials; \( \eta_a = 10^{-8} \) for density.

These simulations involve stoichiometric mixtures with initial temperatures of 800, 1000, 1200, 1400, 1600 and 1800 K. The results are compared with DKM with \( \eta_r = 10^{-6} \) and \( \eta_a = 10^{-8} \) for mass fractions (\( \eta_a = 10^{-5} \) for temperature). Figure 3.7a shows the computation time and number of function evaluations \( n_f \). The latter indicates the number of times the RHS of Eq. (3.29) is evaluated by the stiff ODE solver and gives an indication of the numerical stiffness of the system. As the numerical stiffness increases, the number of integration sub-intervals within the solver increases. This results in an increased number of function evaluations. As \( \eta_a \) and \( \eta_r \) increase both the CPU time and the number of function evaluations decrease. Again, \( \eta_a \) does not show any notable influence on the accuracy but increasing \( \eta_r \) causes relatively more significant increase in the error. Despite, the error increase is not more than 1.5%. It can thus be concluded
that, for the range of values considered, as error tolerances increase the computational cost of RCCE declines without significant loss of accuracy. The relative error tolerance has a more significant influence on the error as it affects the accuracy over the whole range of dependent variable values. The absolute error, on the other hand, affects the solution near zero and thus, has a small effect on the overall accuracy of the results. With the selected tolerance values ($\eta_r = 10^{-6}$ and $\eta_a = 10^{-5}$) and RCCE constraints, the RCCE on the average shows more than 20% decrease in computation time (Fig. 3.7a) [62, 63]. It is useful to mention that RCCE involves much heavier calculations per time step compared to DKM. Therefore, implementation of more efficient numerical schemes is expected to improve the RCCE run time significantly.

### 3.5.3 Effect of mixing on Rate-Controlled Constrained-Equilibrium predictions

Following the initial appraisal of RCCE in the PSR, the method is applied to a constant pressure PaSR. The objective is to understand the influence of mixing on the accuracy of RCCE predictions. Mixing and residence time scales are considered to characterize the molecular and large scale mixing processes, respectively. The necessity of this study is clear considering that fast mixing may perturb the constrained-equilibrium states significantly and render the RCCE constraints ineffective for accurate representation of chemical kinetics. This is an important issue to address to ensure that RCCE provides reliable predictions when applied for complex turbulent combustion simulations. In Table 3.3 the numerical specifications and the simulation parameters of these simulations are listed. As a demonstration, Fig. 3.8 illustrates the RCCE and DKM results in a PaSR with $\tau_{res} = 0.2\ ms$ and $\tau_{mix} = 10\ ms$ using 100 particles. Such number of particles is sufficient to obtain reliable statistics, as also shown in Ref. [31]. The RCCE provides favorable prediction of the average temperature in the reactor. The resemblance of instantaneous particle temperature predicted by both methods is also evident. The inflowing particles with the temperature of 1500 $K$ are apparent. These particles subsequently ignite as they mix with higher temperature ones. The particles on top are at the equilibrium state. It is observed (Fig. 3.8a) that there is a slight discrepancy between the RCCE and DKM results. This stems from slight under prediction of ignition delay time by RCCE with the chosen set of constraints. With shorter ignition delay times, some particles reach the equilibrium temperature faster. Mixing and particle influx escalate this effect and as a result more particles ignite and
reach higher temperatures. Accordingly, at any instant, the average temperature of RCCE is slightly higher than that of DKM.

The influence of residence time scale in PaSR is examined in Fig. 3.9. Figure 3.9a shows the favorable agreement between RCCE and DKM predictions of average temperatures measured at statistically stationary states for various $\tau_{res}$ values and $\tau_{mix} = 10\,ms$. Figure 3.9b illustrates the time variation of mean temperature within the reactor predicted by both methods for different $\tau_{res}$ values. As shown, RCCE captures the dynamics of the system with various residence times reasonably well [61]. When $\tau_{res} \rightarrow \infty$ the rate of particle influx is zero and thus, there is no hot particle to ignite the reactor. In this case, it takes a long time ($10.5\,ms$ and $11.5\,ms$ for RCCE and DKM, respectively) for the system to reach equilibrium (not shown). With finite $\tau_{res}$ values, the system reaches the statistically stationary state much faster. When $\tau_{res} = 1\,ms$ the time to reach the statistically stationary state is $1.5\,ms$ for both RCCE and DKM. As $\tau_{res}$ decreases, the influx of hot particles increases. As a result, more particles ignite and the transition to stationary state occurs faster. The residence time essentially alters the initial rate of transition to the stationary state. It is also evident that the average temperature at stationary state declines with $\tau_{res}$. This is because more frequent replacement of ignited particles (at equilibrium state) with colder inflowing ones, along with relatively slower mixing, lowers the average temperature of the system.

At the extreme case of $\tau_{res} \rightarrow 0$, there are larger input/output activities and few particles reach ignition. Therefore, the average temperature of the reactor fluctuates around the temperature of inflowing particles. Figure 3.9c shows the error in average particle temperatures with respect to DKM $\epsilon(T)$ at statistically stationary state and the error for individual particle temperatures with respect to DKM averaged over all the particles within the reactor $\bar{\epsilon}(T)$. These errors are less than 6% and 10% for the mean and individual particle values, respectively. The higher averaged error for individual particles stems from the fact that the RCCE and DKM particles can ignite at slightly different times, which cause large difference between individual particle temperature values. It is also observed that there is a slight increase in error at intermediate residence times which is associated with the RCCE shorter ignition delay times as explained above. Nevertheless, this error declines drastically with shorter and longer residence time scales.

The interaction between micro-mixing and chemical reaction is studied by varying $\tau_{mix}$ in the PaSR. Figure 3.10 shows the comparison between the RCCE and DKM predictions of mean temperature. In Fig. 3.10a variation of mean temperature at the statistically stationary state with
respect to $\tau_{\text{mix}}$ for $\tau_{\text{res}} = 0.2\, ms$ is displayed. As shown, RCCE provides an accurate prediction of temperature in the reactor. Figure 3.10b depicts the good agreement between the instantaneous mean temperature in the reactor for different $\tau_{\text{mix}}$ values predicted by both methods. As the mixing time scale decreases (i.e., more effective mixing), the time-averaged temperature at the statistically stationary state approaches the equilibrium temperature of 3100 $K$ [60, 63]. This is because higher rate of mixing facilitates faster ignition of cold particles in the reactor.

In contrast to the residence time scale effect, the mixing time scale has almost no influence on the initial rate of increase in temperature (Fig. 3.10b); mixing only tends to redistribute energy among particles at the initial times. Two extreme cases are shown in this figure. With $\tau_{\text{mix}} \to 0$, the rate of mixing is high. In this case the PaSR is similar to PSR and the average temperature approaches that of chemical equilibrium state. When $\tau_{\text{mix}} \to \infty$, the rate of mixing is low and the PaSR behaves similar to a PFR. In this limit the stationary state depends more on the inflow stream condition. It is observed that the reactor with the highest mixing rate displays a distinctive behavior at earlier times. The intensive turbulent mixing in this case attenuates the instantaneous temperature fluctuations in the reactor. This leads to stabilization of the average temperature as the residing and inflowing particles are quickly mixed. After some time, however, more particles become energetic due to mixing with hot particles and as a result, an abrupt ignition occurs in the reactor. Same experiment is also conducted with smaller residence and mixing times (not shown). It is observed that higher mixing rates and more frequent input/output activities prevent the system from reaching higher average temperatures and thus, the stationary state temperature remains close to 1500 $K$. Figure 3.10c shows the error in average particle temperature at the statistically stationary state and the averaged error for individual particle temperature values. These errors are less than 6% and 11% for the mean and individual particle temperature values, respectively. It is evident that the error in the RCCE predictions of average temperature increases slightly for intermediate mixing time scales, but declines rapidly as the mixing time scale increases or decreases. This is due to the aforementioned discrepancy in ignition delay time, which is magnified by mixing. In ignited particles, heat release by combustion induces an increase in temperature which accelerates the rate of kinetics. High mixing delivers this energy to colder particles and helps them ignite faster. Due to competition between chain branching and chain breaking reactions this process is, however, very sensitive to temperature changes. Figures 3.11 and 3.12 show the mass fraction of CH$_4$, O$_2$, CO$_2$ and H$_2$O at the
statistically stationary state at different $\tau_{\text{mix}}$ and $\tau_{\text{res}}$ values. Consistent with Figs. 3.9 and 3.10, there is a good agreement between RCCE and DKM. The slight difference between the results at intermediate residence and mixing time scales is due to small difference in ignition delay time where there are stronger interactions between mixing and chemical kinetics. This causes a slight underprediction and overprediction of reactant and product mass fractions, respectively.

The RCCE is further applied to a pure mixing system. It is clear that kinetics reduction techniques such as RCCE are unnecessary in non-reacting flows. This study is however motivated by the fact that local pure mixing regions are often present in turbulent reacting flows. In the RCCE formulation employed in this study, constraints entirely replace concentrations to describe chemical composition in both mixing and reaction processes. Considering the influence of mixing on constraints, as discussed above, it is thus instructive to assess the accuracy of RCCE to represent pure mixing. Figure 3.13a shows almost identical RCCE and DKM predictions of average temperature for different residence time scales with $\tau_{\text{mix}} = 10\, ms$. In Fig. 3.13c, average temperature is shown for different mixing time scales with $\tau_{\text{res}} = 0.2\, ms$. The percentage error in individual particle temperature values averaged over all the particles before reaching the mean temperature is shown in Fig. 3.13b and Fig. 3.13d. These figures show that the agreement between RCCE and DKM results is excellent over the entire range of mixing and residence time scales considered.

3.6 Concluding Remarks

In this study, the effect of mixing on chemical reaction is investigated using the Rate-Controlled Constrained-Equilibrium (RCCE) method. A detailed evaluation of accuracy and computational efficiency is provided of the RCCE modeling of mixing/reacting systems. The RCCE formulation includes rate equations for constraint potentials, density and temperature. This method is computationally advantageous as it avoids the computationally expensive constraints to constraint potentials conversion at each time step and allows simultaneous implementation of micromixing and chemical reaction with no additional fractional step schemes. The method is applied to isobaric, adiabatic stirred reactors involving methane combustion in oxygen. The accuracy of RCCE predictions is fully appraised in a perfectly stirred reactor. The results show excellent agreement with those obtained by direct integration of the same kinetics, referred to as detailed
kinetics model (DKM). It is shown that RCCE using 12 constraints is able to accurately predict concentrations of all chemical species. To assess the ability of the method to describe the evolution of mixing/reacting systems, simulations are performed of a partially stirred reactor and the predictions are assessed over wide range of mixing and residence time scales. It is demonstrated that RCCE provides accurate prediction of chemical kinetics at all mixing and residence time scales. The method is also shown to be effective to reduce the overall computational time associated with kinetics calculations in comparison with DKM. With the constraints and solver parameters used here, it is shown that RCCE results in reduction of CPU time from 5% to 40% depending on the temperature range. On the average, RCCE shows 20% lower computation time than DKM in these simulations. This study demonstrates the accuracy and computational efficiency of RCCE in describing the dynamics of reacting systems in presence of mixing.
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Figure 3.1: Comparison of temperature predicted by RCCE (solid lines) and DI (dashed lines) in $H_2/O_2$ case for: (a) stoichiometric mixture at two initial temperatures of 800 and 1200 K, and (b) lean ($\Phi = 0.5$, bottom) and rich ($\Phi = 2.0$, top) mixtures at initial temperature of 1300 K.
Figure 3.2: Temperature variation vs. time for initial temperatures of 800, 1000, 1200, 1400, 1600 and 1800 K in RCCE (solid lines) and DKM (dashed lines) predictions of stoichiometric methane oxygen combustion in PSR.
Figure 3.3: Temperature variation vs. time in RCCE (solid lines) and DKM (dashed lines) predictions of methane oxygen combustion in PSR in (a) lean mixture at two equivalence ratios of $\Phi = 0.4$ (top) and $\Phi = 0.25$ (bottom) at initial temperature of 1800 K and (b) rich mixture at two equivalence ratios of $\Phi = 1.33$ (top) and $\Phi = 2.0$ (bottom) at initial temperature of 1800 K.
Figure 3.4: Mass fraction variation vs. time for (a) CH₄, (b) CO₂, (c) OH and (d) H for initial temperatures of 800, 1000, 1200, 1400, 1600 and 1800 K, from right to left, in RCCE (solid lines) and DKM (dashed lines) predictions of stoichiometric methane oxygen combustion in PSR.
Figure 3.5: The CPU time in simulation of stoichiometric methane oxygen combustion in PSR for initial temperatures of 800-1800 K. All CPU times are normalized by the corresponding DKM values. The solver error tolerances are specified as $\eta_a = 10^{-5}$ and $\eta_r = 10^{-6}$ for RCCE (left sets); and $\eta_a = 10^{-8}$ and $\eta_r = 10^{-6}$ for DKM (right sets).
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Figure 3.6: The effect of error tolerances on RCCE predictions of stoichiometric methane oxygen combustion in PSR for $\eta_a = 0.01 \eta_r$ (solid lines) and $\eta_a = 10 \eta_r$ (dashed lines). (a) The RCCE CPU time, normalized by that of RCCE simulations with $\eta_r = 10^{-6}$ and $\eta_a = 10^{-8}$; (b) the percentage error in RCCE predictions of the equilibrium mass fractions of CH$_4$ ($\bigcirc$), H ($\bigotimes$), OH ($\triangle$) and equilibrium temperature ($\square$). The RCCE mass fractions and temperature are compared to those by DKM ($\eta_a = 10^{-12}$ and $\eta_r = 10^{-10}$).
Figure 3.7: The effect of $\eta_a$ and $\eta_r$ values on the RCCE performance compared to DKM, in simulation of methane oxygen combustion in PSR. (a) The percentage of difference in CPU time (solid line) and number of function evaluations (dashed line); (b) the percentage error in RCCE predictions of equilibrium mass fractions of $\text{CH}_4$ (○), $\text{O}_2$ (△), $\text{H}_2\text{O}$ (+), $\text{CO}_2$ (×), $\text{H}_2$ (×), $\text{H}$ (○), $\text{CO}$ (□), $\text{OH}$ (△) and equilibrium temperature (□). The three RCCE simulations are performed with (I) $\eta_a = 10^{-8}$ and $\eta_r = 10^{-6}$, (II) $\eta_a = 10^{-5}$ and $\eta_r = 10^{-6}$ and (III) $\eta_a = 10^{-5}$ and $\eta_r = 10^{-5}$. The error tolerances in DKM simulations are $\eta_a = 10^{-8}$ and $\eta_r = 10^{-6}$.
Figure 3.8: Comparison of RCCE and DKM results for methane oxygen combustion in PaSR simulations with $\tau_{\text{mix}} = 10 \text{ ms}$ and $\tau_{\text{res}} = 0.2 \text{ ms}$. (a) Time variation of average temperature in RCCE (solid line) and DKM (dashed line); instantaneous temperature of PaSR particles in (b) RCCE and (c) DKM simulations.
Figure 3.9: Effect of residence time scale (with $\tau_{\text{mix}} = 10\, ms$) on prediction of average temperature in methane oxygen combustion simulations in PaSR. (a) Time variation of average temperature at the statistically stationary state for RCCE and DKM predictions; (b) time variation of average temperature for $\tau_{\text{res}} = 1, 0.33, 0.13$ and $0.04\, ms$ from top to bottom, respectively. The solid and dashed lines denote the RCCE and DKM predictions, respectively; (c) the percentage error in RCCE prediction of average temperature at the statistically stationary state (solid line) and the percentage error in individual particle temperature values averaged over all the particles within the reactor (dashed line).
Figure 3.10: Effect of mixing time scale (with $\tau_{\text{res}} = 0.2 \text{ ms}$) on prediction of average temperature in methane oxygen combustion simulations in PaSR. (a) Time variation of average temperature at the statistically stationary state for RCCE and DKM predictions; (b) time variation of average temperature, for $\tau_{\text{mix}} = 0.1, 2, 8 \text{ ms}$ and no mixing, from top to bottom, respectively. The solid and dashed lines denote the RCCE and DKM predictions, respectively; (c) the percentage error in RCCE prediction of average temperature at the statistically stationary state (solid line) and the percentage error in individual particle temperature values averaged over all the particles within the reactor (dashed line).
Figure 3.11: Variation of average mass fraction of (a) CH$_4$, (b) O$_2$, (c) CO$_2$ and (d) H$_2$O with respect to residence time scale ($\tau_{mix} = 10 \text{ ms}$) at the statistically stationary state in simulation of methane oxygen combustion in PaSR. The solid and dashed lines denote the RCCE and DKM predictions, respectively.
Figure 3.12: Variation of average mass fraction of (a) CH$_4$, (b) O$_2$, (c) CO$_2$ and (d) H$_2$O with respect to mixing time scale ($\tau_{res} = 0.2$ ms) at the statistically stationary state in simulation of methane oxygen combustion in PaSR. The solid and dashed lines denote the RCCE and DKM predictions, respectively.
Figure 3.13: The RCCE predictions of pure mixing with different residence and mixing time scales. (a) Time variation of average temperature for $\tau_{res} = 1, 0.33, 0.13$ and $0.04 \text{ ms}$ from bottom to top, respectively (with $\tau_{mix} = 10 \text{ ms}$); (b) temperature error percentage for different $\tau_{res}$ values; (c) time variation of average temperature for $\tau_{mix} = 0.1, 2, 8 \text{ ms}$ and no mixing (with $\tau_{res} = 0.2 \text{ ms}$); (d) temperature error percentage for different $\tau_{mix}$ values. The solid and dashed lines denote the RCCE and DKM results, respectively. The error is the percentage difference between RCCE and DKM prediction of individual particle temperature values averaged over all the particles before reaching mean temperature.
Chapter 4

Conclusions and Final Remarks

The Rate-Controlled Constrained-Equilibrium (RCCE) method has proven very effective as a dimension reduction technique in chemical kinetics. The objective of this dissertation is to assess the potential of RCCE for reliable description of detailed kinetics in turbulent combustion simulations. For this purpose, the most effective implementation of the method is determined and the ability of the method to describe chemical reaction in presence of mixing is evaluated. The RCCE is a dimension reduction technique for chemical kinetics based on thermodynamics laws. It describes the time evolution of reacting systems using a series of constrained-equilibrium states determined by RCCE constraints. The full chemical composition at each state is obtained by maximizing the entropy subject to instantaneous values of the constraints.

In the first part of this work different RCCE formulations are implemented and assessed. These are the constraint and constraint potential formulations. The two forms are equivalent mathematically; however, they involve different numerical procedures and thus show different computational performances. The two forms are applied to an isobaric, adiabatic well stirred reactor involving combustion of methane in oxygen. The constraint potential implementation is based on solving rate equations for constraint potentials, density and temperature. In the constraint formulation the rate equations for constraints are solved. The two approaches, however, involve quite different mathematical operations. The former involves matrix inversion operation, while the latter requires constrained equilibrium calculations. Such difference in numerical solution
procedure results in not only different number of mathematical operations but also dissimilar reduction in stiffness of the kinetics. As a result, the two forms of RCCE exhibit different numerical performance. To examine efficiency and numerical errors in these formulations, simulations are carried out over wide range of initial temperatures and equivalence ratios. Comparisons indicate that constraint potential shows 20% more number of function evaluations by the stiff ordinary differential equation solver, indicating higher numerical stiffness. However considering both stiffness and number of mathematical operations, the constraint potential formulation exhibits 50% and 30% less CPU times in stoichiometric and nonstoichiometric mixtures, respectively. The accuracy of the RCCE predictions are assessed by comparing with those generated by direct integration of the same kinetics used in the RCCE calculations referred to as detailed kinetics model (DKM). Compared to DKM results, the two RCCE forms provide good prediction of the reacting system dynamics with almost similar accuracy.

In the second part of this study, interaction between mixing and chemical reaction using RCCE is investigated. This study is important because mixing, an important attribute in turbulent flow, can influence the RCCE constrained equilibrium state. Therefore, the key objective of this study is to assess the accuracy and numerical performance of the method in predicting reacting systems in presence of mixing. The RCCE constraint potential formulation includes rate equations for constraint potentials, density and temperature. This method is computationally more advantageous than constraint form as it avoids the computationally expensive constraints to constraint potentials conversion at each time step and allows simultaneous implementation of micro-mixing and chemical reaction with no additional fractional step schemes. The method is applied to isobaric, adiabatic stirred reactors involving methane combustion in oxygen. The accuracy of the RCCE predictions is fully appraised in a perfectly stirred reactor. The results show excellent agreement with those obtained by DKM. It is shown that RCCE using 12 constraints is able to accurately predict concentrations of all chemical species. To assess the ability of the method to describe the evolution of mixing/reacting systems, simulations are performed of a partially stirred reactor and the predictions are assessed over wide range of mixing and residence time scales. It is demonstrated that RCCE provides accurate prediction of chemical kinetics at all mixing and residence time scales. The method is also shown to be effective to reduce the overall computational time associated with kinetics calculations in comparison with DKM. With the constraints and solver parameters used here, it is shown that RCCE results in
reduction of CPU time from 5% to 40% depending on the temperature range. On the average, RCCE shows 20% lower computation time than DKM in these simulations. This study demonstrates the accuracy and computational efficiency of RCCE in describing the dynamics of reacting systems in presence of mixing.

Some suggestions for possible future work are:

- Development of a constraint selection algorithm to select RCCE constraints based on identifying equilibrated reactions. Equilibrated reactions can be identified by a procedure introduced in Ref. [70]. These reactions can be used as input to an algorithm developed by Yousefian [25] to select constraints consisting of a linear combination of species.

- Application of RCCE to investigate combustion of more complex hydrocarbon fuels. This study requires derivation of a proper set of RCCE constraints which can be done by using the method proposed above. The accuracy and efficiency of RCCE can be assessed in comparison with DKM results, similar to that discussed in Chapter 3.

- Application of RCCE for large eddy simulation (LES) of turbulent flames. An effective approach for this purpose is by coupling the RCCE with the filtered density function (FDF) methodology [71, 72] which provides a closed form for chemical reaction effects. The RCCE provides a computationally efficient way to incorporate detailed kinetics in LES/FDF simulations.
Nomenclature

$A_{\alpha\beta}$ Transformation matrix ($\alpha = 1, \ldots, N_c; \beta = 1, \ldots, N_s$)

$C_{\alpha}$ Constraint $\alpha$ ($\alpha = 1, \ldots, N_c$), kmol/kg

$c_p$ Specific heat capacity at constant pressure, $J/kg.K$

$\dot{e}_{\alpha}$ Internal energy per unit mole of species $\alpha$ ($\alpha = 1, \ldots, N_s$), $J/kmol$

$\dot{g}_{\alpha}$ Gibbs free energy of the pure substance per unit mole of species $\alpha$ ($\alpha = 1, \ldots, N_s$), $J/kmol$

$\dot{g}_{\alpha}^0$ Gibbs free energy of the pure substance per unit mole of species $\alpha$ ($\alpha = 1, \ldots, N_s$) at pressure $p_0$, $J/kmol$

$\bar{g}_{\alpha}$ Pseudo-Gibbs free energy of the pure substance per unit mole of species $\alpha$ ($\alpha = 1, \ldots, N_s$), $J/kmol$

$h$ Specific enthalpy, $J/kg$

$h_{\alpha}$ Specific enthalpy of species $\alpha$ ($\alpha = 1, \ldots, N_s$), $J/kg$

$\dot{h}_{\alpha}$ Enthalpy per unit mole of species $\alpha$ ($\alpha = 1, \ldots, N_s$), $J/kmol$

$M$ Mixture molar mass, kg/kmol

$M_{\alpha}$ Molecular mass of species $\alpha$ ($\alpha = 1, \ldots, N_s$), kg/kmol

$\mathcal{M}_{\alpha}$ Mixing source term for species $\alpha$ ($\alpha = 1, \ldots, N_s$), 1/s

$N_c$ Number of constraints

$N_s$ Number of chemical species

$p$ Pressure, $N/m^2$

$p_0$ Standard pressure, $N/m^2$

$R_u$ Universal gas constant, $J/kmol.K$

$s$ Specific entropy, $J/kg.K$

$S_{\alpha}$ Chemical reaction source term for chemical species $\alpha$ ($\alpha = 1, \ldots, N_s$), 1/s

$\dot{s}_{\alpha}^0$ Entropy of the pure substance per unit mole of species $\alpha$ ($\alpha = 1, \ldots, N_s$) at pressure $p_0$, $J/kmol.K$

$T$ Temperature, K

$t$ Time, s
\( X_\alpha \) Mole fraction of species \( \alpha (\alpha = 1, \ldots, N_s) \)

\( Y_\alpha \) Mass fraction of species \( \alpha (\alpha = 1, \ldots, N_s) \)

**Greek Letters**

\( \Lambda_\alpha \) Constraint potential \( \alpha (\alpha = 1, \ldots, N_c) \)

\( \Lambda_\alpha \) Pseudo-constraint potential \( \alpha (\alpha = 1, \ldots, N_c) \)

\( \lambda_\alpha \) Lagrange multiplier corresponding to constraint \( \alpha (\alpha = 1, \ldots, N_c), J/kmol.K \)

\( \tilde{\mu}_\alpha \) Chemical potential per unit mole of species \( \alpha (\alpha = 1, \ldots, N_s), J/kmol \)

\( \xi \) Pseudo-time, \( s \)

\( \rho \) Fluid density, \( kg/m^3 \)

\( \tau_{mix} \) Mixing time scale, \( s \)

\( \tau_{res} \) Residence time scale, \( s \)

\( \phi_\alpha \) Scalar \( \alpha (\alpha = 1, \ldots, N_s + 1) \)

**Symbols**

\( \bar{f} \) Mean value of variable \( f \)

\([F]\) Molar concentration of species \( F \)
Bibliography


