

A Computationally Efficient Method for the Solution of Methane - Air Chemical Kinetics with Application to HCCI Combustion

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ABSTRACT

The Rate-Controlled Constrained-Equilibrium (RCCE) method is applied to the numerical solution of methane-air combustion. The RCCE method offers a reduction in computation time for complex chemically reacting systems because the rate equations for a small number of slowly evolving constraints need to be solved. The current work focuses on presenting both the principles of the RCCE method and its application to methane-air Homogeneous Charge Compression Ignition (HCCI) combustion. This work takes into consideration some of the previously unexplored numerical issues associated with solving the RCCE equation set. Application of the RCCE method is first demonstrated in constant and variable volume adiabatic environments and compared to the integration of the full set of kinetic rate equations for each species. Results presented here show a reduction in computational time. For large molecules, which require larger chemical mechanisms, it is expected that the computational time associated with the RCCE method should continue to improve over direct integration. The latter part of this work uses a thermo-kinetic HCCI model coupled with the RCCE method to simulate the combustion process in a methane-fueled internal combustion engine operating under HCCI conditions. This is the first known application of this method to HCCI simulations. Results are compared in light of HCCI experiments.

INTRODUCTION

Homogeneous Charge Compression Ignition (HCCI) engines are essentially a combination of conventional spark ignited (SI) and compression ignited (CI) engines. As in a conventional SI engine, a homogeneous air-fuel mixture is achieved either in the inlet system or early during the compression stroke (direct injection). As in the diesel combustion process, ignition is achieved by compressing the mixture until it auto-ignites. HCCI engines show promise for reducing harmful pollutants like oxides of nitrogen and particulate matter while maintaining elevated thermal efficiencies. However, the

concept is not without its challenges. The HCCI combustion process does not have direct or indirect control of the onset of the main heat release event. The lean burn combustion (i.e. equivalence ratio < 0.35) results in carbon monoxide and unburned hydrocarbon pollutants. It is a further challenge to oxidize these incomplete products at the low exhaust gas temperatures ($\sim 300\text{C}$). Numerical simulation of HCCI combustion can be a valuable tool in addressing some of these difficulties.

A survey of the HCCI literature has shown that model development in the HCCI field has taken one of three main approaches: (i) the zero-dimensional thermo-kinetic approach [1], (ii) the segregated, sequential fluid mechanic – thermo-kinetic multi-zone approach [2], (iii) and multi-dimensional approaches [3]. The reader is referred to Fiveland and Assanis [1] for detailed model taxonomy. Each of these models uses a detailed chemical kinetic solution scheme coupled to models that range in thermal and fluid-mechanic resolution.

The evolution of chemical reaction can, in principle, be solved accurately if a chemical mechanism for the conversion of fuel to products is available. In practice, a number of difficulties are encountered when trying to accomplish this. These difficulties, which result in numerical computations taking large amounts of CPU time, are discussed in the following section. Current computing capability makes it possible to simulate homogeneous chemically reacting systems, but detailed chemical kinetic calculations coupled with computational fluid dynamic (CFD) simulations of chemically reacting flows are still unrealistic as the basis for a parametric simulation tool. Agarwal and Assanis resolved the ignition event, for the direct injection of natural gas in a high-pressure bomb, using KIVA and the GRI-1.2 chemistry scheme. It took 7 days to simulate 2.8msec of physical engine time [5].

Some method to speed up the calculation of chemical kinetics without sacrificing accuracy is necessary if computer simulation of HCCI is to be computationally

efficient. Many such methods are found in the literature including the quasi-steady state assumption (QSSA) [6], partial equilibrium assumption (PEA) [7], computational singular perturbation [8], intrinsic low dimensional manifolds [9], and *in-situ* adaptive tabulation [10]. Many of these methods rely on the fact that processes occurring at fast time-scales are not of interest at large time-scales and their effect on the system can be represented in some simplified form, thus saving computational effort. Perhaps the most common method used is the QSSA where certain species are set into “steady state” and algebraic relations describe their evolution, thus eliminating the need to solve differential equations. While this method is extremely useful in increasing computational efficiency, it suffers from two main drawbacks. First, the chemical mechanism derived using steady state assumptions replicates the behavior of the detailed mechanism only in the neighborhood of the conditions for which it was derived. Second, the resulting reduced mechanism may be stiffer than the original mechanism [11]. Increased stiffness of the equations to be integrated typically leads to an increased computational demand.

One method that is based on similar ideas of eliminating the fast time-scales in the system is the rate-controlled constrained-equilibrium (RCCE) method first proposed by Keck and Gillespie [12] and extensively developed by Metghalchi and co-workers [13]. Keck [14] has presented a review of the RCCE method. The general basis of the idea is that the chemical composition is constrained from equilibrium, at any time, due to slowly occurring processes occurring within the system. The objective of this work is to further the work done by Metghalchi and co-workers by applying the RCCE method to HCCI combustion of methane. A secondary objective is to understand the characteristics of the numerical solution of the RCCE method.

In this study, a discussion of the RCCE method with details about governing equations is first presented. The RCCE method is used to describe the time-evolution of methane-air combustion in adiabatic bombs. Temperature and species concentration histories calculated using the RCCE method are compared to solutions obtained through integration of detailed chemistry for different initial conditions. Induction delay times for stoichiometric methane-air combustion calculated using the RCCE method are compared to detailed chemistry calculations. This is followed by a discussion of numerical issues with the RCCE method such as stiffness. Finally, integration of the RCCE calculation with the thermo-kinetic model and comparison of simulation results to experimental data is presented. Engine simulations in this study are based on the previous work of Fiveland *et al.* [1,4] who have successfully used a thermo-kinetic combustion model to simulate the HCCI combustion process in a natural gas fueled HCCI engine.

RATE-CONTROLLED CONSTRAINED-EQUILIBRIUM

SOLUTION OF COMPLEX CHEMICAL SYSTEMS

We consider a complex reacting system with ns species. If a complete reaction mechanism that describes the evolution of these species is known, the time history of species concentrations may be obtained by integrating an ordinary differential equation (ODE) for the rate of change of concentration of each species given by:

$$\dot{N}_i = \frac{d[N_i]}{dt} = \dot{\omega}_i, \quad (1)$$

where N_i is the molar concentration of species i and $\dot{\omega}_i$ the molar production rate, which can be determined from the law of mass action [15]. Given an initial temperature and pressure, equations (1) may be integrated along with an equation for the rate of change of temperature to obtain the composition of the system at any time, t . This is, in principle, the most accurate way to solve for the composition given a reaction mechanism.

The method of solution described above has some difficulties associated with it. One problem that must be overcome is that chemical mechanisms for even simple fuels such as methane contain a large number of intermediate species. For example, the GRI 3.0 mechanism [16], used later in this work, contains about 35 species to describe oxidation of hydrocarbon species up to C_3H_8 . This number rapidly increases as the size of the fuel molecule becomes larger. For example, a chemical mechanism that describes the oxidation of n-heptane has 544 species [17]. Since ODEs of the form of (1) must be solved for each species, CPU time increases with the number of species. It has been shown [2] that the CPU time grows as the square of the number of species. A second, and probably more important, problem is that of numerical stiffness. This problem is often over-looked in the literature and a discussion of stiffness is presented in a later section.

To overcome some of these difficulties, we use the RCCE method to determine an approximate solution to the set of equations (1). Much of the discussion in this section follows Hamiroune *et al.* [18]. The RCCE approach is based on the following assumptions:

1. A complex chemically reacting system can be described by a relatively small number of degrees of freedom.
2. These degrees of freedom are constraints imposed on the system by slowly evolving reactions.
3. Other reactions are fast enough that they can equilibrate the system subject to the constraints imposed by the slow reactions.
4. The system thus progresses to chemical equilibrium through a series of quasi-equilibrium states.

The RCCE method is thus comparable to partial equilibrium methods of reducing chemical kinetics models. Fast reactions are implicitly assumed to be in

partial equilibrium by the RCCE method and constraints are imposed on the system by slow reactions.

An important aspect of the RCCE method is the identification of these constraints. A discussion of constraints is given by Keck [14], and a brief discussion of constraints used in this study is presented in Appendix A.

The time-dependant constraints are a linear combination of species given by:

$$C_j = \sum_{i=1}^{ns} a_{ij} N_i, \quad (2)$$

where C_j is the molar concentration of constraint j and a_{ij} the number of moles of species i in constraint j . The rate equations for the constraints may be obtained by differentiating equations (2) as:

$$\dot{C}_j = \sum_{i=1}^{ns} a_{ij} \dot{N}_i, \quad (3)$$

with \dot{N}_i given by equations (1). Once equations (3) have been integrated, the constrained equilibrium composition may be determined with the method of element potentials using Lagrange undetermined multipliers as outlined by Keck [14] and Reynolds [19]. We refer to this method as RCCE-A. Using this method, once the Lagrange multipliers are determined, the species compositions are found by:

$$N_i = Q_i \exp\left(-\sum_{j=1}^{nc} a_{ij} \gamma_j\right), \quad (4)$$

$$Q_i = \frac{p_0 V}{RT} \exp(-\mu_i), \quad (5)$$

where γ_j is the undetermined multiplier conjugate to constraint j and μ_i is the Gibbs free energy of species i . Keck [14] points out that the computation of the constrained equilibrium at each time-step may be expensive because of the iterative procedure involved in determining the Lagrange multipliers. He presents an alternative method of solving for the constrained equilibrium composition. We refer to this alternative method as RCCE-B and discuss it below. All RCCE calculations in this work use the RCCE-B method.

Rather than solve equations (3) for the constraints and then solve equations (4) and (5) for the species, rate equations for the Lagrange multipliers may be derived with some manipulations. The equations for the rate of change of the Lagrange multipliers are given as follows:

$$\sum_{n=1}^{nc} C_{jn} \dot{\gamma}_n - C_{jT} \frac{\dot{T}}{T} - C_{jV} \frac{\dot{V}}{V} + \sum_{i=1}^{ns} a_{ij} \dot{\omega}_i = 0, \quad (6)$$

where $C_{jn} = \sum_{i=1}^{ns} a_{ij} a_{in} N_i$, $C_{jT} = \sum_{i=1}^{ns} a_{ij} \frac{E_i}{RT} N_i$, and

$$C_{jV} = \sum_{i=1}^{ns} a_{ij} N_i.$$

In the case where the temperature is not constant, an additional equation for the temperature (or energy) must be solved and this is given as:

$$\sum_{i=1}^{ns} \sum_{n=1}^{nc} E_i a_{in} N_i \dot{\gamma}_n - \sum_{i=1}^{ns} C_{iE} N_i \frac{\dot{T}}{T} - \sum_{i=1}^{ns} E_i N_i \frac{\dot{V}}{V} + \dot{E} = 0, \quad (7)$$

where $C_{iE} = \left(c_{v,i} T + \frac{E_i^2}{RT}\right)$ and E is the internal energy

of the system. The rate of energy change in the system is described using the energy equation with the appropriate source and sink terms for work and heat transfer [1]. Once the values of the Lagrange multipliers are determined by numerically integrating equations (6) and (7), the constrained equilibrium composition may be determined without any iteration using equations (4). The equations are integrated using an implicit stiff ODE solver based on a backward differencing formulae (BDF) method [20].

NUMERICAL SOLUTION OF RCCE EQUATIONS

A summary of the numerical calculation method is as follows:

1. Solve equations (1) until a minimum concentration of every species is achieved.
2. Calculate initial values of constraint potentials, γ . See equation (8) below.
3. Integrate equations (6) and (7) in time to determine time evolution of constraint potentials and temperature.
4. Use equations (4) to determine constrained equilibrium composition at each time-step.

Initialization of the RCCE calculation in step 2 above is an important step as the method of initialization can affect the RCCE solution. The initialization method used in this work is described below.

Initialization of RCCE Calculation

In order to integrate the set of equations (6) and (7), we must determine initial values of the constraint potentials, γ , that satisfy the initial concentrations of species. Hamiroune *et al.* [18] discuss this initialization problem. They point out that we have a system of ns equations in

nc equations ($ns > nc$); thus, the system is over-determined. To overcome this difficulty, they pick nc species as independent ones, and solve for the constraint potentials. While this method works well for a small system where $ns - nc$ is not large, this method can fail in a practical system where $ns - nc$ is much larger. One difficulty is choosing what species are independent ones and the other problem is that the concentrations for the remaining $ns - nc$ species obtained from equation (4) can be significantly different from the specified initial condition.

A different method for determining the initial values of the constraint potentials arises from realizing that the initial values of constraint potentials must satisfy the set of equations (2). We substitute equations (4) in equations (2) to obtain the following nc coupled equations:

$$\sum_{i=1}^{ns} \left(a_{ij} Q_i \exp \left(- \sum_{j=1}^{nc} a_{ij} \gamma_j \right) \right) - C_{j0} = 0, \quad (8)$$

where C_{j0} is the initial value of constraint j . We solve the above nc equations using a damped Newton-Raphson iteration method [21]. Hamiroune [22] points out that equation (8) can be used to determine the value of the undetermined multipliers. However, this formulation was not used by Hamiroune to initialize the RCCE calculation who instead used the method described in [18].

The value of the constraint potentials determined using equations (8) might not satisfy the initial conditions for the species concentrations. However, the composition that results upon substituting the initial values of γ in equations (4) is the constrained equilibrium composition of the system subject to nc constraints. This composition and the initial conditions for species concentrations must be as close to each other as possible.

ADIABATIC BOMB CALCULATIONS

In order to demonstrate the RCCE calculation method, a number of calculations were performed for methane-air combustion in an adiabatic "bomb". All the RCCE calculations are compared to detailed chemistry calculations using the GRI 3.0 mechanism [16]. The detailed mechanism has 35 species for the hydrocarbon chemistry and the RCCE calculations used 11 constraints (discussed in Appendix A). Initial Conditions are shown in table 1 for the cases whose results are presented here.

Case No.	Equivalence Ratio	Temperature (K)	Pressure (atm)
1	Stoichiometric	1500	1
2	Lean ~ 0.7	1250	100
3	Rich ~ 1.8	900-1700	10
4	Lean-Rich	450	2 (Varying Volume)

Table 1: Initial Conditions for RCCE validation cases

Figure 1 shows the comparison of temperature vs. time for the detailed calculation and the RCCE calculation. It can be seen that the temperature reaches the correct equilibrium value; however, the induction time is over-predicted by about 0.7 ms with the RCCE calculation.

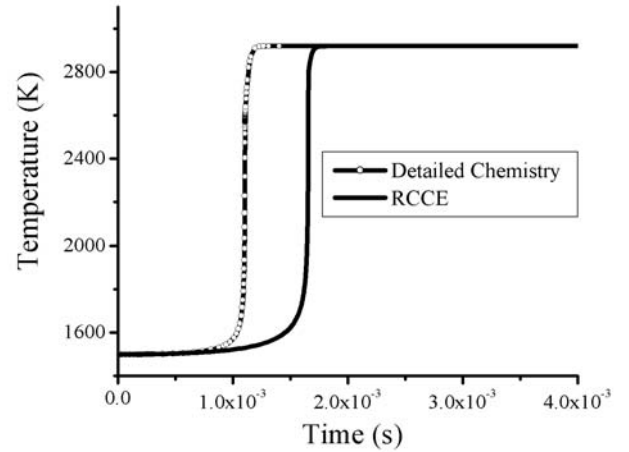


Figure 1: Temperature vs. time for case 1

Species concentrations for fuel and CO_2 are shown in figures 2 and 3. The species concentrations follow the same trends as the temperature. Note that the fuel and CO_2 concentrations also reach their correct equilibrium values.

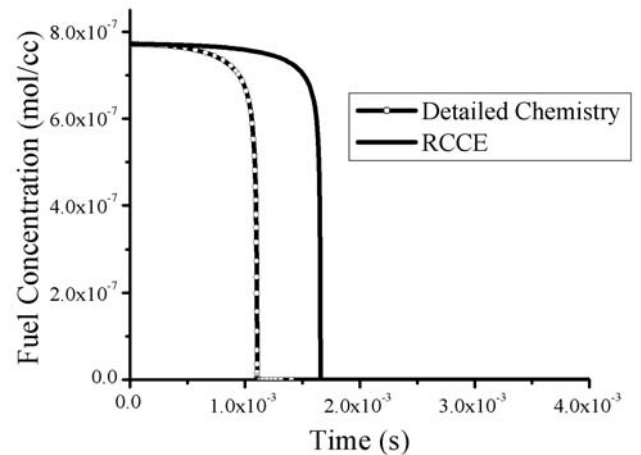


Figure 2: Fuel Concentration vs. time for case 1

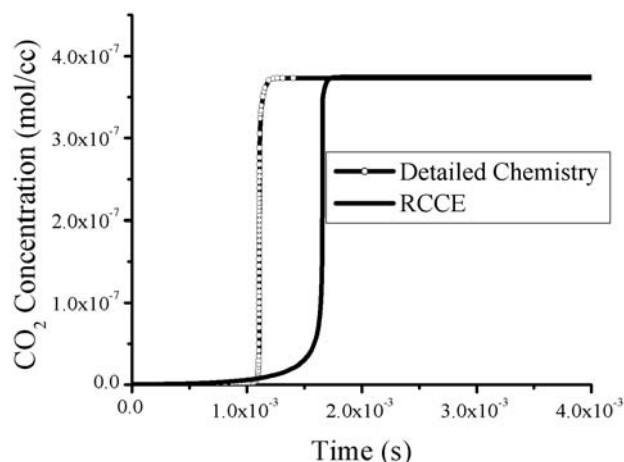


Figure 3: CO_2 Concentration vs. time for case 1

In understanding the RCCE method, it is instructive to look at the values of the constraint potentials as the constraints evolve over time. Figure 4 shows the constraint potentials for two “fixed” constraints, elemental nitrogen and elemental hydrogen, and two time-dependant constraints, total moles and free valences. The potentials for the time-dependant constraints reach a value of 0 as the system reaches equilibrium while the potentials for the fixed constraints reach their equilibrium values. This is because, at equilibrium, the system is constrained only by the elemental constraints and thus the potentials for the other constraints must be zero. It may be useful to note that an elemental constraint potential represents the contribution of the element to the chemical potential of a species which contains that element.

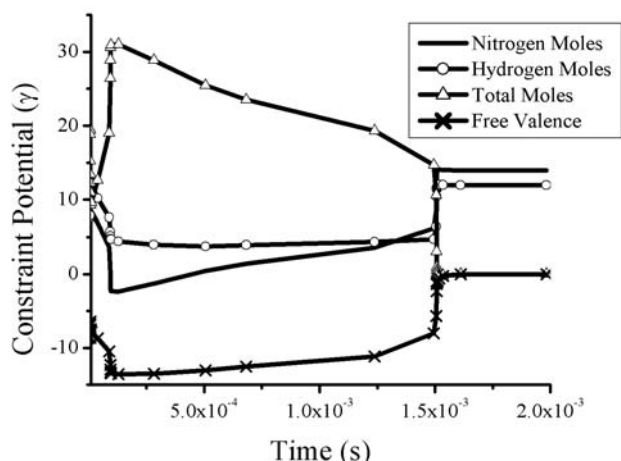


Figure 4: Constraint potentials vs. time for case 1

To test the RCCE method under a different condition, the RCCE solution was compared to the detailed chemistry solution for the initial conditions for case 2. The temperature history is shown in figure 5. In this case, also, the RCCE calculation reaches the correct equilibrium, but the induction time is over-predicted by

about 0.25 ms. Note that the over-prediction of induction time is less than that for case 1.

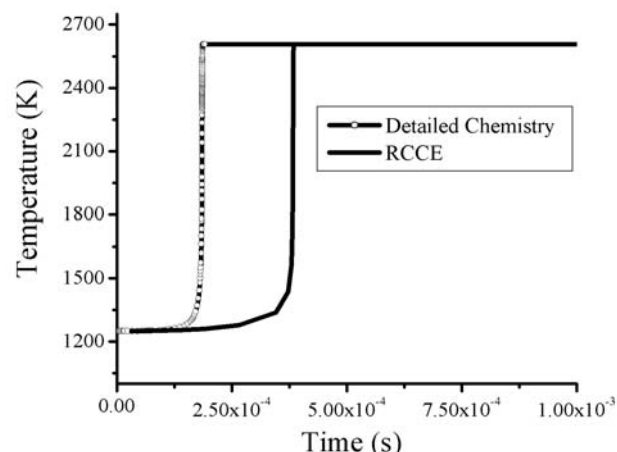


Figure 5: Temperature vs. time for case 2

As an additional validation test, the RCCE method was used to compute induction times for methane-air mixtures (case 3). Induction time is defined as the time required for a 400 K temperature rise. Induction times are not particularly sensitive to the choice of amount of temperature rise since the system is undergoing thermal runaway at this point. Comparisons of induction times for the RCCE calculation and detailed chemistry calculation are shown in figure 6.

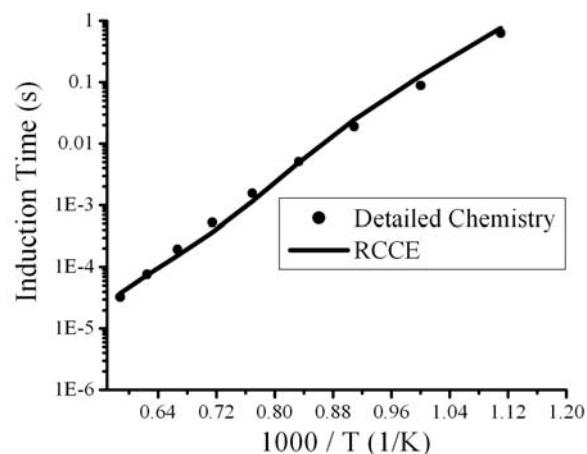


Figure 6: Induction times for methane-air mixture (Case 3)

It can be seen that the RCCE calculations and detailed chemistry calculations are in good agreement. The RCCE calculation, however, does not exactly pick up the linear dependence between the induction time and $1/T$. This dependence and agreement in induction times could have been improved by using a better set of constraints for the RCCE calculations; however since finding constraints was not a major objective of this work, not much effort was expended for that task.

The final validation for the RCCE method was comparing ignition delay times obtained using the RCCE method and detailed chemical kinetic calculations in a varying volume bomb. The volume was varied as in an internal combustion engine with a stroke of 190 mm; bore of 170 mm with 19:1 compression ratio running at 1500 rpm. Initial conditions are shown in table 1 (case 4). The initial fuel mass fraction was varied from 0.01 to 0.1 with the nitrogen mass fraction also being varied, while the initial oxygen mass fraction was kept constant at 0.23. Ignition time is defined as the time when the temperature first reaches 1600 K. Comparison between the RCCE calculation and the calculation with detailed chemistry is shown in figure 7. Ignition time is predicted well for mixtures that are lean and close to stoichiometric and the prediction is not very accurate far away from this region. However, we note that HCCI operation is primarily in the 0.2-0.5 equivalence ratio ($\sim 0.015 - 0.04$ initial CH_4 mass fraction) range and this agreement for ignition delay is acceptable under HCCI conditions.

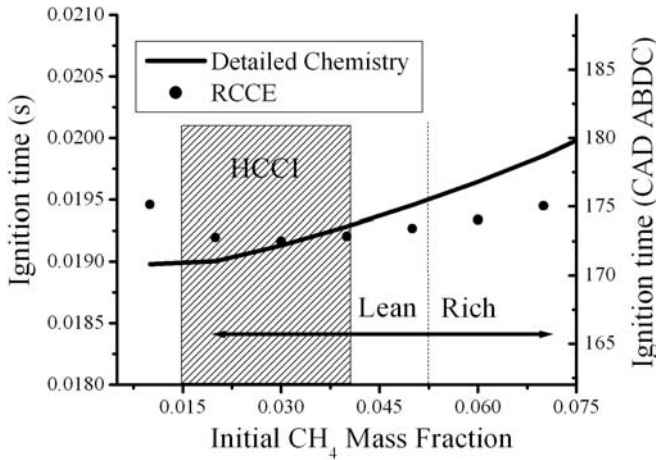


Figure 7: Ignition time for methane-air mixtures in a variable volume bomb (Case 4)

Figure 8 shows the reduction in CPU time using the RCCE method for all the computations of case 3 along with the error in the induction time calculation. The percentage savings in CPU time is defined as the difference in the CPU time for the RCCE and the detailed chemistry calculation normalized by the time for the calculation with full chemical kinetics. The error in induction time calculation is the difference between the RCCE calculation and the detailed chemistry calculation normalized by the detailed chemistry calculation. In each case, there was some savings in CPU time and the savings were significant in some cases. It is believed that as the number of species in the detailed chemical mechanism increases, the RCCE method offers the potential for even larger savings in CPU times. The error ranged from 30 % under-prediction of induction time to about 40 % over-prediction of induction time. Improvement in the agreement between the RCCE and detailed chemical kinetics solution can be brought about by selecting a better set of constraints for the RCCE solution. The following section explores some of the

characteristics that can be exploited for larger savings in CPU time.

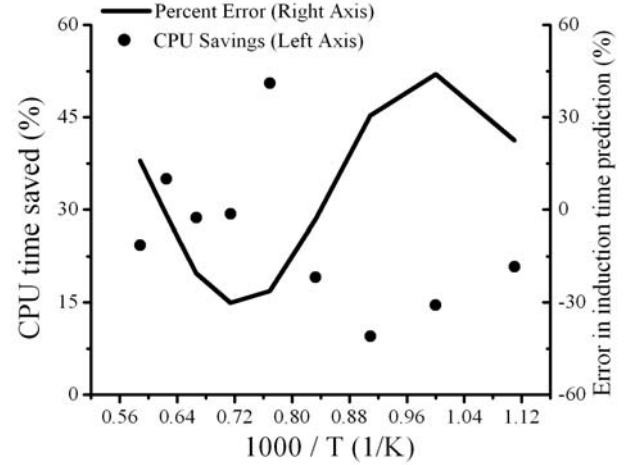


Figure 8: CPU time reduction over detailed chemistry calculation using RCCE method

NUMERICAL ISSUES

Stiffness

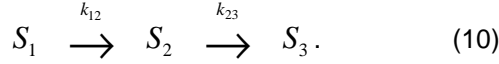
In order to reduce the computational time required to solve a set of ODEs, it does not suffice to merely reduce the number of equations being solved. ODE systems of the form of equations (1) suffer from a problem called stiffness [23]. For fast computation time, the stiffness of the system of equations formed with the reduced number of equations must be less than or the same as the stiffness of the original system of equations. Physically, stiffness occurs when the problem contains a wide range of time-scales. In a chemical kinetics problem, stiffness arises because some species are changing at slow timescales (such as CO_2) and others are changing extremely fast (such as radical species). Numerically, the smallest negative eigenvalue of the system imposes a stability constraint on the solution. The problem is said to be stiff when we wish to solve the problem over a large range of the independent variable and the small eigenvalues allow only a small time-step. This results in a need to take a large number of time-steps, thus making the numerical solution time-consuming.

Various definitions for stiffness are found in the literature, and we use the following definition for a stiffness coefficient in this work as adopted from [24]:

$$SC = 1 / \left(\max_{\text{Re}(\lambda) \leq 0} |\lambda| \right). \quad (9)$$

A small value of the stiffness co-efficient indicates that the governing equations are stiff and will take longer CPU time to integrate. A desirable property of a solution method is that the stiffness co-efficient be as large as possible.

To demonstrate the stiffness of the RCCE-B method using the constraint potentials, we follow Warnatz *et al.* [25] and consider a simple reaction system,



We consider two methods of integrating the equations that describe this system and compare stiffness for the two methods:

1. Direct integration of species conservation equations (1), and
2. Integration of equations for Lagrange multipliers, equations (6), with the constraint matrix set equal to the identity matrix; resulting in as many equations for the undetermined multipliers as species.

Note that method 1 and method 2 are equivalent calculations, because method 2 will result in a constrained equilibrium composition with all species constrained, which must be the same composition that results from the calculation procedure of method 1. Method 2 is an inefficient method of solving the equations governing system and would not be implemented in practice. We present this method only to discuss the stiffness of two equivalent calculations using different methods. Warnatz *et al.* [25] show that the eigenvalues of the Jacobian for method 1 are given as:

$$\lambda_1 = 0 \quad \lambda_2 = -k_{12} \quad \lambda_3 = -k_{23}. \quad (11)$$

It can be shown (see Appendix B) that the Jacobian for method 2 is given as:

$$J = \begin{pmatrix} 0 & 0 & 0 \\ k_{12} \frac{N_1}{N_2} & -k_{12} \frac{N_1}{N_2} & 0 \\ 0 & k_{23} \frac{N_2}{N_3} & -k_{23} \frac{N_2}{N_3} \end{pmatrix}, \quad (12)$$

with eigenvalues of the Jacobian:

$$\lambda_1 = 0 \quad \lambda_2 = -k_{12} \frac{N_1}{N_2} \quad \lambda_3 = -k_{23} \frac{N_2}{N_3}. \quad (13)$$

Depending on the numerical values of k_{12} and k_{23} , either λ_2 or λ_3 determine the stiffness characteristics of the system for method 1. For method 2, however, the ratios $\frac{N_2}{N_1}$ and $\frac{N_3}{N_2}$ are also important in determining the stiffness of the system. Towards the beginning of the calculation, when some species concentrations are small, this can cause the system to be extremely stiff and negatively impacts the speed of calculation. This effect

can be seen in figure 9 where the stiffness coefficient is plotted as a function of time for method 1 (detailed chemistry calculation) and method 2 (RCCE-B method). The initial conditions for this calculation are those of Case 3 with the initial temperature as 1500 K. It is clear that the RCCE calculation exhibits more stiffness in the early part of the calculation where some of the species concentrations are extremely small. It is also interesting to note that the RCCE calculation is less stiff during the thermal runaway period (~75 ms) where method 1 is the most stiff.

We note that this problem of increased stiffness should not occur with the RCCE-A method. This is because the RCCE-A method with the constraint matrix set equal to the identity matrix is the same calculation as integration equations (1). An evaluation of the relative merits of the two methods is necessary to decide which method will result in greater speed-up.

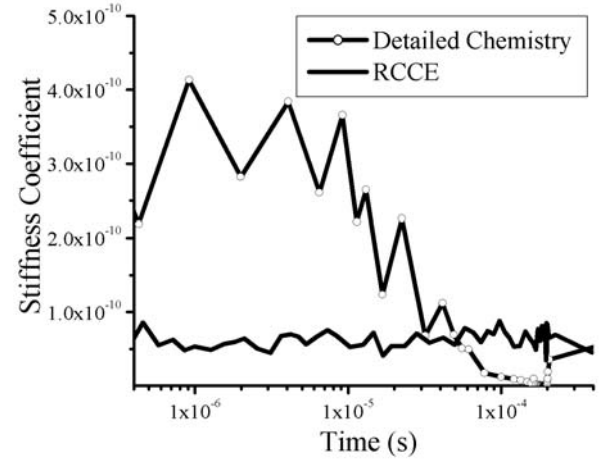


Figure 9: Stiffness Coefficient for Detailed Chemistry and RCCE calculation (Small values of SC are detrimental)

MODELING THE HCCI ENGINE

The compression ignition engine simulation of Fiveland and Assanis [1,4] was used as the parent model for RCCE integration. The main advantage of the full cycle simulation, over a variable volume reactor (i.e. closed cycle) model, is that it directly computes gas exchange as well as the internal residual trapped in the engine cylinder. Furthermore, it converges, through a series of iterations, to a steady state solution. The cycle simulation can be operated either i) over the full engine cycle calculation, which includes gas exchange and steady state iteration, or ii) over a partial engine cycle calculation (i.e. variable volume reactor).

SIMULATION ASSUMPTIONS

The HCCI thermodynamic formulation, the physical sub-models, and the simulation structure are discussed in detail by Fiveland and Assanis [1, 4]. Only the pertinent simulation assumptions will be briefly reviewed. The simulation is currently written in a single cylinder version, primarily because fundamental studies lend themselves

to this configuration. The engine simulation is a sequence of four-stroke processes. The gas exchange event is governed by quasi-steady, one-dimensional flow equations that are used to predict flow past valves. The compression event is defined from Intake Valve Closing (IVC) to a transition point prescribed when chemical reactions become important. The combustion event for the HCCI simulation differs from those of the SI and DICI types. Because of the premixed compression ignition principle, the rate of combustion is strictly limited by the chemical kinetics. The evolution of heat release and species is governed by a user-defined kinetic scheme and solved, for this work, with the RCCE methodology. The heat transfer modeling is handled via a turbulence kinetic energy cascade [1,4].

EXPERIMENTAL SETUP

The research engine originates from a Volvo truck engine. The in-line, six-cylinder engine has been modified for single cylinder operation. For this reason, only indicated values are presented in this paper. The engine specifications are shown in Table 2. The reader is referred to reference [4] for more detail on the engine experimental setup.

Combustion Chamber	Pancake
Bore (mm)	120.65
Stroke (mm)	140
Connecting Rod (mm)	260
Compression Ratio	19.8:1
Inlet Valve Diameter (mm)	50
Exhaust Valve Diameter (mm)	46
Exhaust Valve Open	39 CAD BBDC (at 1 mm lift)
Exhaust Valve Close	10 CAD BTDC (at 1 mm lift)
Inlet Valve Open	5 CAD ATDC (at 1 mm lift)
Inlet Valve Close	13 CAD ABDC (at 1 mm lift)
Valve Lift Exhaust (mm)	13.4
Valve Lift Intake (mm)	11.9

Table 2: Volvo TD100 Engine Specifications

The experiments were conducted at 1000 rpm under naturally aspirated conditions with several different fuel recipes [4]. This work will only focus on the methane-air experiments. During the tests, data was collected through a range of mixture temperatures that pushed the mixture from ignition at top center (TC) to misfire.

COMPARISON OF RCCE WITH EXPERIMENTS

The comparison of the RCCE method with HCCI experiments for the 2% mass fraction burned point obtained in the Volvo TD-100 is shown in figure 10 for a methane-air blend. This fuel study was a subset of a two-component fuel study [4]. For this particular case study, the engine was operated under naturally aspirated conditions at an equivalence ratio of 0.3, an intake manifold temperature that ranged from 175C to 162C, and an engine speed of 1000 RPM. The compression ratio in the engine tests was reported at 19.8. It is shown in the figure that the RCCE method does a reasonably good job of predicting the trend with decreasing manifold temperature. For example, at a manifold temperature 171C the model exhibits a 2 CA-deg error when

predicting the 2% mass fraction burned point. The RCCE prediction is closer to the experimental observation if the standard deviation (shown as error bars) in the experimental quantities is considered. It is noted that observed error could be a result of inaccuracies within the HCCI thermal description, the GRI kinetics mechanism or the assumed constraint matrix applied to the RCCE method.

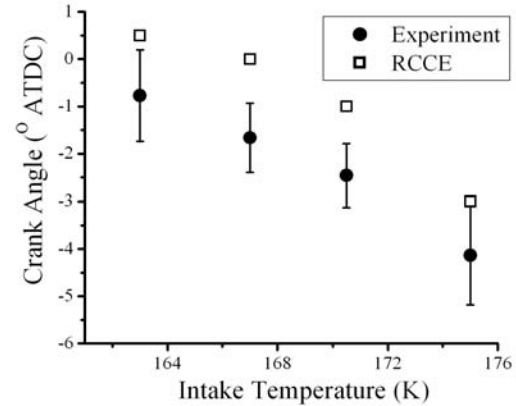


Figure 10: Cycle simulation vs. experimental 2% mass fraction burned point. The engine was operated at 1000rpm, an equivalence ratio of 0.3, an intake pressure of 1 bar, and with methane-air

CONCLUSION

The RCCE method has been successfully applied to describe the time-evolution of methane-air combustion in constant and variable volume environments. Good agreement between RCCE and detailed chemistry calculations is obtained for a variety of initial conditions in various environments. Temperature and species profiles are predicted well by the RCCE method, as are induction times and ignition delay times for methane-air mixtures. CPU time usage is reduced for RCCE calculations as compared to calculations utilizing detailed chemical kinetics. There is potential for further reduction in computational cost by improving the numerical characteristics of the system and improvement in the accuracy of the method through improved selection of constraints. The RCCE method is used to simulate HCCI combustion of methane in a Volvo engine and good agreement against experimental data for burn durations is obtained.

ACKNOWLEDGMENTS

The authors acknowledge the engine simulation group at Caterpillar, Inc., where this work was performed. The assistance of Yue Gao and Prof. Hameed Metghalchi at Northeastern University especially with providing an understanding of constraints was extremely helpful. The authors also gratefully acknowledge the valuable discussions with Prof. David Foster at the University of Wisconsin – Madison.

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NOMENCLATURE

$[i]$	Molar Concentration of species i
a_{ij}	Moles of species i in the j^{th} constraint
k	Reaction rate coefficient
nc	Number of constraints
ns	Number of species
p_0	Atmospheric pressure
C_j	Moles of constraint j per unit volume
E	Internal energy of System
E_i	Internal energy of Species i
J	Jacobian Matrix
N_i	Moles of species i per unit volume
Q_i	Partition function of species i

R	Ideal Gas Constant
$\text{Re}(\)$	Real part
S_i	Arbitrary species i
SC	Stiffness coefficient
T	Temperature
V	Volume
γ_j	Lagrange multiplier conjugate to constraint j
λ	Eigenvalue
μ_i	Dimensionless Gibbs free energy of species i
ω_i	Molar Production rate of species i

SUBSCRIPTS

i	Index for a chemical species
j	Index for a constraint

APPENDIX

A] DISCUSSION OF CONSTRAINTS USED

The constraints used in this study were based on constraints used by Gao and Methghalchi [27]. The most common constraints are conservation of elements. In this study, the system has four elements – C, H, O, and N and these are four “fixed” constraints, i.e. they do not depend on time. Time-dependant constraints include constraints on:

1. Total number of moles due to slow three body reactions,
2. Moles of ions due to slow radical reactions,
3. Moles of CO_2 due to slow oxidation of CO ,
4. Moles of fuel,
5. Moles of fuel radical,
6. Moles of oxygen, and
7. Moles of formaldehyde radical.

In this way, 11 constraints are used in this study. From the results in previous sections, it is seen that the formulation of a better set of constraints is necessary for improved accuracy of the RCCE solution. Yousefian [28] has presented an algorithm for the selection of constraints. The algorithm is based on using equilibrium relations for fast reactions, since the RCCE method implicitly assumes that all fast reactions are in equilibrium. Chen *et al.* [29] have also shown that the RCCE algorithm and the partial equilibrium assumption are identical provided the correct set of constraints is chosen. It is believed that an analysis of the detailed reaction mechanism can yield useful information about reactions in partial equilibrium and this information can be used to generate a set of constraints.

B] DERIVATION OF EINGENVALUES FOR RCCE-B

If we set the constraint matrix, a_{ij} , equal to the identity matrix and set $\dot{T} = \dot{V} = 0$, equations 6 may be written as

$$\dot{\gamma}_i N_i + \dot{\omega}_i = 0.$$

For the 3-species system, this may be written in matrix notation as:

$$\begin{bmatrix} \dot{\gamma}_1 \\ \dot{\gamma}_2 \\ \dot{\gamma}_3 \end{bmatrix} = \begin{bmatrix} -\dot{\omega}_1/N_1 \\ -\dot{\omega}_2/N_2 \\ -\dot{\omega}_3/N_3 \end{bmatrix}$$

Re-writing the molar production rate in terms of the reaction rate coefficients and simplifying,

$$\begin{bmatrix} \dot{\gamma}_1 \\ \dot{\gamma}_2 \\ \dot{\gamma}_3 \end{bmatrix} = \begin{bmatrix} -k_{12} \\ k_{12} \frac{N_1}{N_2} - k_{23} \\ k_{23} \frac{N_2}{N_3} \end{bmatrix}$$

Recognizing that $N_i = Q_i \exp(-\gamma_i)$, we can form the

Jacobian, $J = \frac{\partial \dot{\gamma}_i}{\partial \gamma_j}$:

$$J = \begin{pmatrix} 0 & 0 & 0 \\ k_{12} \frac{N_1}{N_2} & -k_{12} \frac{N_1}{N_2} & 0 \\ 0 & k_{23} \frac{N_2}{N_3} & -k_{23} \frac{N_2}{N_3} \end{pmatrix}$$

The eigenvalues of the Jacobian are the values that satisfy the characteristic equation of the Jacobian,

$$\det(J - \lambda I) = 0$$

We can easily see in this case, that

$$\lambda_1 = 0 \quad \lambda_2 = -k_{12} \frac{N_1}{N_2} \quad \lambda_3 = -k_{23} \frac{N_2}{N_3}$$