THE DEVELOPMENT AND USE OF RATE-CONSTRAINED CHEMICAL EQUILBRIUM WITH HCCI COMBUSTION MODELING

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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. Thus, the energy release event is dominated by the kinetic timescales. Accurate modeling requires the coupling of a detailed chemical kinetic description to the proper fluid-dynamic resolution (1).

The evolution of chemical reaction can, in principle, be solved accurately if a chemical mechanism for the conversion of fuel to products is available. The solution of practical chemical kinetic systems requires numerical methodologies that resolve the chemical process, down to the highest frequency mode, while maintaining numerical stability. As a result, the numerical solution of chemical kinetics problems is very computationally expensive because the process is occurring on multiple timescales, as some radical species are being formed and depleted rapidly while other species exhibit a slow evolution (such as H_2O or CO_2). The presence of a range of timescales is known as stiffness (13). Stiff kinetic systems require a large number of time-steps, thus making the numerical solution time-consuming. 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 (1).

The solution of the kinetic system, even when using the most efficient solver, may be too computationally expensive. Therefore, the modeler must sacrifice some details within the kinetic scheme to improve the solution speed. Many techniques have been developed to generate reduced mechanisms such as quasi-steady state analysis (QSSA) (9), intrinsic low dimensional manifolds (ILDM) (10), partial equilibrium assumption (PEA), (8), computational singular perturbation (CSP) (5), sensitivity analysis (17), integral and local reaction flow analysis (17), time-scale analysis (15), and computer augmented reduced mechanism (CARM), (16). The application of these tools sets out to eliminate both species and reactions. The disadvantage of these reduction approaches is that the reduced mechanism is valid only for a very limited range of thermodynamic conditions. If the combustor conditions, such as pressure, temperature, or equivalence ratio (i.e. load range) increase or decrease outside the applicable range, the reduction procedure must be repeated and a new reduced equation set developed.

Several techniques exist to speed the solution of the chemistry while not reducing the chemical kinetic mechanism information, and hence the accuracy of the system. The common ones are rate-constrained chemical equilibrium (RCCE) and *in-situ* adaptive tabulation (ISAT) (7). The RCCE method was first proposed by Keck (4) and extensively developed by Metghalchi and co-workers (3). This work focuses on the extension of the RCCE method to model HCCI ignition events with the introduction of automatic constraint generation.

Rate Constrained Chemical Equilibrium – Overview

The general basis of the RCCE idea is that the chemical composition is constrained from equilibrium, at any time, due to slowly evolving constraints that are imposed in the system. The system evolves in time through a series of quasi-equilibrium states. The physical premise for the idea is that only equations describing the slowly evolving constraints need to be integrated. Much of the discussion in this section follows Hamiroune *et al.* (3). The RCCE approach is based on the following stated 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.

RCCE Mathematical Formulation

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

$$C_j = \sum_{i=1}^{ns} a_{ij} N_i \,, \tag{1}$$

where C_j is the molar concentration of constraint j and a_{ij} the number of moles of species i in constraint j. Once the differentiated form of equation (1) has been integrated, the constrained equilibrium composition may be determined with the method of element potentials using Lagrange undetermined multipliers as outlined by Keck (4) and Reynolds (13). We refer to this method as RCCE-A. Using this method, once the Lagrange multipliers are determined, the species compositions are found by:

$$N_i = Q_i \exp\left(-\sum_{j=1}^{nc} a_{ij}\gamma_j\right),\ Q_i = \frac{p_0 V}{RT}\exp\left(-\mu_i\right) \tag{2}$$

where γ_j is the undetermined multiplier conjugate to constraint j and μ_i is the Gibbs free energy of species i. Keck (4) 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 (11).
Rather than directly integrate the constraints and then solve equation (2) 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:

$$\sum_{n=1}^{nc} C_{jn}\dot{\gamma}_n - C_{jT}\frac{\dot{T}}{T} - C_{jV}\frac{\dot{V}}{V} + \sum_{i=1}^{ns} a_{ij}\dot{\omega}_i = 0\,, \quad (3)$$

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:

$$\sum_{i=1}^{ns}\sum_{n=1}^{nc} E_i a_{in} N_i \dot{\gamma}_n - \sum_{i=1}^{ns} C_{iE} N_i \frac{\dot{T}}{T} - \sum_{i=1}^{ns} E_i N_i \frac{\dot{V}}{V} + \dot{E} = 0\,, \quad (4)$$

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 (11). Once the values of the Lagrange multipliers are determined by numerically integrating equations (3) and (4), the constrained equilibrium composition may be determined without any iteration. The equations are integrated using an implicit stiff ODE solver based on a backward differencing formulae (BDF) method (2).

Constraints - Overview

The constraints that have been used in works using the RCCE method were based on constraints generated through physical intuition (3,6). 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.

Results & Discussion

In understanding the RCCE method, it is instructive to look at the values of the constraint potentials as the constraints evolve over time. Figure 1 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 that contains that element.

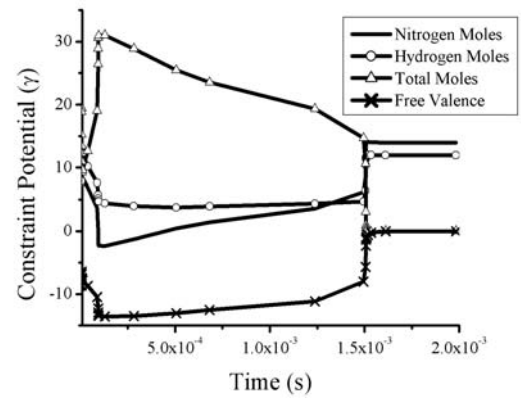

Figure 1. Evolution of Constraint Potentials vs. time

The constraints used in this study were based on constraints used by Gao and Methghalchi (6). In the work by Rao et al.(11), the RCCE method was compared to the detailed kinetic integration for lean and rich conditions through a range of gas temperatures.

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 2 for a methane-air blend. The reader is referred to Rao et. al. for a review of the experimental setup. This fuel study was a subset of a two-component fuel study (11) 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.

Automatic Constraint Generation

The use of this method for larger chain hydrocarbon molecules will depend on the ability to efficiently develop the constraint matrix (3, 18). Yousefian 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. Recently, work by Rao et al. has developed/demonstrated an automatic constraint methodology for use with a hydrogen-air combustion scenario (12). Specifically, their work used a novel partial equilibrium criterion with the constraint generation scheme proposed by Yousefian (18).

In order to validate the RCCE solution, induction times for H_2-O_2-Ar mixtures were computed using the RCCE method against shock tube experiments (12). The experiment was performed at a pressure of 5 atm. with a composition comprising 8 mole percent H2 and two mole percent O2 in Ar. The initial temperature was varied from 964 K to 1075 K. The computations were carried out assuming constant volume and adiabatic combustion. An example of a

comparison between the detailed solution and the RCCE method for a hydrogen-air mixture is shown in figure 3..

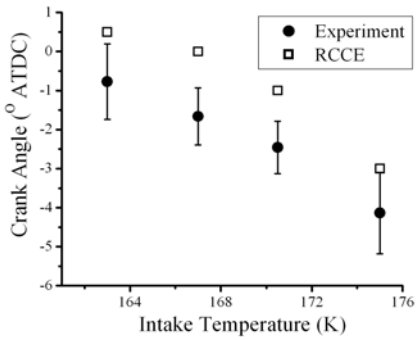

Figure 2: Methane-air simulation vs. experimental 2% mass burned point. 1000rpm, equivalence ratio (0.3), an intake pressure of 1 bar,

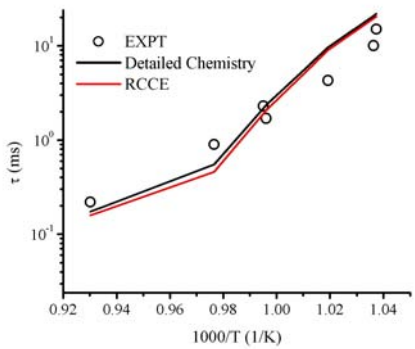

Figure 3: Comparison of computed and measured induction times for H_2-O_2-Ar mixtures

Conclusions

The RCCE method has been successfully applied to describe the time-evolution of hydrogen and 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. More work is needed to developed a robust automatic constraint generation method.

References

(1) Assanis, D.N., Lavoie, G.A., and Fiveland, S.B., Chapter 6, Overview of HCCI Modeling Approaches, *Homogeneous Charge Compression Ignition (HCCI) Engines Key Research and Development Issues,* SAE 2003.

1. (2) Brown, P. N., Hindmarsh, A. C. and L. R. Petzold (1994), *Using Krylov methods in the solution of large-scale differential-algebraic systems*, SIAM Journal of Scientific Computing, **15**: 1467-1488
2. (3) Hamiroune D, Bishnu P., Metghalchi M., and Keck J.C. (1998), "Rate-controlled Constrained-Equilibrium method using constraint potentials", Combustion Theory and Modeling, **2**:81-94
3. (4) Keck J.C. and Gillespie D. (1971), *Combustion and Flame*, **17**:237
4. (5) Lam S.H. and Goussis D. A. (1994), "The CSP Method of Simplifying Kinetics", *International Journal of Chemical Kinetics,* 26:461-486
5. (6) Gao Y. and Methghalchi M. (2002), Personal Communication
6. (7) Maas U.A. and Pope S.B. (1992), "Simplifying Chemical Kinetics: Intrinsic Low-Dimensional Manifolds in Composition Space", *Combustion and Flame*, **88**:239-264.
7. (8) Mott, David (1999), "New Quasi-Steady-State and Partial Equilibrium Methods for Integrating Chemically Reacting Systems", *Ph.D. Thesis*, Department of Aerospace Engineering and Scientific Computing, University of Michigan
8. (9) Peters, N. (1985), *Lecture Notes in Physics* Springer, Berlin, pg. 90–241.
9. (10) Pope S.B. (1997), "Computationally Efficient Implementation of Combustion Chemistry using In Situ Adaptive Tabulation," Combustion Theory and Modeling, **1**:41-63.
10. (11) Rao, S., Rutland C.J., and Fiveland S.B. (2003) "A Computationally Efficient Method for the Solution of Methane-air Chemical Kinetics with Application to HCCI Combustion," Submitted to SAE World Congress, 2003.
11. (12) Rao, S., Rutland, C.J., and Fiveland, S.B., Reduced Chemistry Modeling –A new method for identifying reactions in partial equilibrium, 16th AIAA Computational Fluid Dynamics Conference, Session: High Speed and Chemically Reacting Flows, 2003.
12. (13) Reynolds W.C. (1986), "The Element Potential Method for Chemical Equilibrium Analysis – Implementation in the Interactive Program STANJAN, Version 3", *Department of Mechanical Engineering*, Stanford University
13. (14) Shampine, L.F. (1985), "Measuring Stiffness", *Applied Numerical Mathematics*, 1:107-119.
14. (15) Soyhan, H. S., et al., (2000), "Automatic reduction of detailed chemical reaction mechanisms for autoignition under SI engine conditions," SAE Paper No. 2000-01-1895.
15. (16) Sung, C. J., Law, C. K., and Chen, J.-Y., "Further Validation of an Augmented Reduced Mechanism for Methane Oxidation: Comparison of Global Parameters and Detailed Structure," *Combust. Sci. Tech.,* 156, pp. 201-220 (2000).
16. (17) Warnatz J., Mass U., Dibble R.W. (1999), *Combustion Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation*, Springer, pg. 97.
17. (18) Yousefian V. (1998), "A Rate-Controlled Constrained-Equilibrium Thermochemistry Algorithm for Complex Reacting Systems", *Combustion and Flame*, 115:66-80