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Rate-Controlled Constrained-Equilibrium Calculations of the Combustion Products in the Expansion Stroke of an Internal Combustion Engine

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Rate-controlled constrained-equilibrium calculations of the expansion of combustion products of isooctane during the power cycle of an internal combustion engine were conducted. It is assumed that ignition occurs under adiabatic, constant volume conditions at the top dead center. The constraints used in this study are the elemental oxygen, hydrogen, carbon and nitrogen together with other 4 dynamic constraints of total number of moles, moles of CO, moles of free valence and moles of free oxygen. This set enables accurate predictions of all H₂/O₂ and CO/CO₂ compounds and temperature history. Constrains are added one at a time in order to study their effectiveness.

1. Introduction

Based on the fundamental premise of the rate-controlled constrained-equilibrium (RCCE) technique, slow reactions in a complex reacting system impose constraints on its composition, which control the rate at which it relaxes to chemical equilibrium, while the fast reactions equilibrate the system subject to the constraints imposed by the slow reactions. Consequently, the system relaxes to chemical equilibrium through a sequence of constrained-equilibrium states at a rate controlled by the slowly changing constraints [1]. The nature of the controlling constraints depends on how far the system initially is from its chemical equilibrium state. Previous work involving systems that are initially far-from-equilibrium have revealed that, for fuels as different as Methane, Methanol, Ethanol, *n*-Heptane and Isooctane, there are several constraints that are responsible for the dynamic evolution of the system, and that, with few exceptions, the list is almost identical for different cases [2-6].

Another important class of problems is one in which the system is initially in an equilibrium state and undergoes either work or heat interactions with the surrounding environment. Under these circumstances, any small change of a system parameter or system energy will cause the internal dynamics of the system to shift in a direction towards re-establishing the equilibrium consistent with the instantaneous amount of energy and physical parameters. If the internal relaxation processes (chemical and/or physical) are slower than the externally imposed process, then the system lags behind in establishing the equilibrium and the kinetics of finite relaxation rate processes have to be considered. Relevant examples include CO quenching in the exhaust of

an internal combustion engine or a gas turbine.

Morr and Heywood [7] considered the problem of sudden cooling of the combustion products of Aviation Kerosene, under the specification of JET A-1, by passing the combustion products through a heat exchanger at constant pressure as a model for gas turbine. They compiled a model for CO oxidation chemistry based on the fact that three body and CO oxidizing reactions are generally slower than other reactions and confirmed the notion through comparison against experimental data.

In this paper we look at the expansion of Isooctane combustion products in the power stroke of an internal combustion engine using the Rate-Controlled Constrained-Equilibrium (RCCE) method. This method enables a systematic analysis of the underlying kinetics by examining the effect of different constraints and can be easily implemented.

2. Physical Model

The physical model is shown in Fig. 1. It is assumed that combustion occurs at constant volume, corresponding to the case where piston is at top dead center, and that the power stroke begins with the combustion products at the stable equilibrium state.

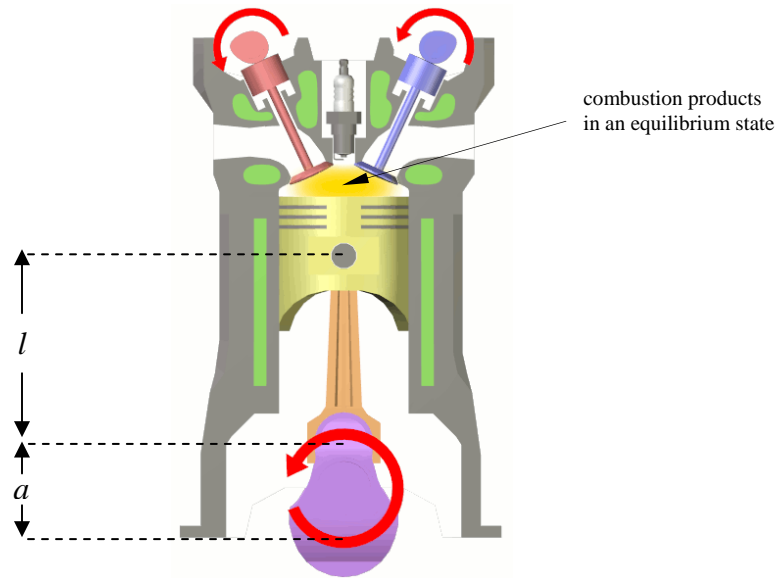


Fig.1 Schematic of the physical model

Volume is assumed to be a prescribed function of time [6]:

$$\frac{V(t)}{V_c} = 1 + \frac{1}{2}(r_c - 1)[R + 1 - \cos\theta(t) - \sqrt{R^2 - \sin^2\theta(t)}], \quad R = \frac{l}{a} \quad (1)$$

where $V(t)$, V_c , r_c and θ represent the instantaneous volume of the cylinder, clearance volume, compression ratio and the instantaneous crank angle respectively. The numerical values used in this study are $V_c = 125 \text{ mlit}$, $r_c = 11$, and $R=3$ and $\dot{\theta} = 100\pi \text{ (1/sec)}$. The power stroke is also identified by $0 \leq \theta \leq 180$.

3. Governing Equations in RCCE form

The detailed formulation of RCCE in constrained-potential form can be found in earlier works [2], and only the most relevant features will be repeated here.. In the present work, as well as all previous applications of the RCCE method, the constraints imposed on the system by the reactions have been assumed to be a linear combination of the mole number of the species present in the system,

$$C_i = \sum_{j=1}^{N_s} a_{ij} N_j, \quad i = 1, \dots, N_c \quad (2)$$

where a_{ij} is the value of the i^{th} constraint for the j^{th} species, N_c is the number of constraints and, N_s is the number of species in the system. The constrained-equilibrium composition of a system found by maximizing the entropy or minimizing the Gibbs free energy, subject to a set of constraints, using the method of LaGrange multipliers is

$$N_j = \frac{V}{RT} \exp(-\mu_j^0 - \sum_{i=1}^{N_c} a_{ij} \gamma_i), \quad j = 1, \dots, N_s \quad (3)$$

where $\mu_j^0 = (h_j^0 - Ts_j^0)/RT$ is the non-dimensional standard Gibbs free energy of species j , γ_i is the constraint potential (LaGrange multiplier) conjugate to the constraint i . In the absence of any physical diffusion processes and fluid convection, equations governing the constraint potentials take the following form,

$$\sum_{n=1}^{N_c} C_{in} \dot{\gamma}_n - C_{iV} \frac{\dot{V}}{V} - C_{iT} \frac{\dot{T}}{T} + \sum b_{ik} r_k = 0, \quad i = 1, \dots, N_c \quad (4)$$

where

$$\begin{aligned} C_{in} &= \sum_{j=1}^{N_s} a_{ij} a_{nj} [N_j], \\ C_{iV} &= \sum_{j=1}^{N_s} a_{ij} [N_j], \\ C_{iT} &= \sum_{j=1}^{N_s} a_{ij} \frac{E_j}{RT} [N_j]. \end{aligned} \quad (4-a)$$

r_k is the net rate of the k^{th} chemical reaction and b_{ik} represents the value of the i^{th} constraint in the k^{th} reaction. Obviously, a reaction for which $b_{ik} = 0$ is in equilibrium, and is therefore redundant. Also, E_j , represents the molar energy of species j . In order to close the system of equations, equation (4) has to be coupled with an energy equation which, for the given parameters, takes the following form[2].

$$\sum_{n=1}^{N_c} C_{En} \dot{\gamma}_n + C_{EV} \frac{\dot{V}}{V} + C_{ET} \frac{\dot{T}}{T} - \dot{E} = 0 \quad (5)$$

where

$$C_{En} = -\sum_{j=1}^{N_s} E_j a_{nj} [N_j], \quad (5-a)$$

$$C_{EV} = \sum_{j=1}^{N_s} E_j [N_j], \quad (5-b)$$

$$C_{ET} = \sum_{j=1}^{N_s} \left(c_{vj} T + \frac{E_j^2}{RT} \right) [N_j], \quad (5-c)$$

$$\dot{E} = -p\dot{V}. \quad (5-d)$$

c_{vj} is the molar heat capacity of species j at constant volume and p is pressure. Upon solving the differential equations for the γ_i vector, the constrained-equilibrium composition of the system can be found at each time step by evaluating equation (3).

4. Constraints

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

Table I. Definition of the Constraints Used in This Study

	Constraint	Definition of the Constraint
1	EN	Elemental nitrogen
2	EC	Elemental carbon
3	EO	Elemental oxygen
4	EH	Elemental hydrogen
5	M	Total number of moles
6	CO	Moles of CO
7	FO	Moles of free oxygen (any oxygen not directly attached to another oxygen)
8	FV	Moles of free valance (any unpaired valence electron)

5. Results and Discussion

The reaction model used in this study is shown in table II. Since the chemistry is assumed to start from a high-temperature equilibrium state, the mixture composition is mainly dominated by CO/CO₂ and H₂/O₂ species. The fuel-independency of the equilibrium combustion products is the feature of lean, stoichiometric and slightly rich mixtures.

Equations (4) and (5) were integrated using DASSL [8] for the combustion products of isooctane with an equivalence ratio of 0.7 and the results are shown in figures (2)-(9). It is important to note that since nitrogen has been assumed to be chemically inert, equilibrium temperature is over-estimated and so is the temperature after expansion. The initial conditions were also obtained from STANJAN [9].

Given the fact that the system is initially at equilibrium, the elemental constraints are the only nonzero constraints. In the case of a slow expansion, the state of the system follows the expansion and cooling, and all rate processes are in equilibrium. Consequently, the instantaneous thermodynamic state of the system is completely determined by the elemental constraints. Calculations describing this type of process are referred to as shifting equilibrium calculations. Clearly, this is a limiting case and the actual degree of disequilibrium depends upon the relative order of the expansion time scale compared to the controlling chemical and physical time scales.

Results show that during the early stage of expansion, when the expansion process occurs very slowly, the state of the gas exactly follows the predictions of shifting equilibrium. However, as the rate of expansion increases, departures from the equilibrium state predicted by the elemental constraints emerge.

According to the principle of Le Châtelier, any increase in volume will cause a subsequent reduction in the total number of moles to minimize the cooling effect of expansion. This forces the recombination reactions to come into play. The constraint characterizing this class of reactions is the total number of moles (M), and including this constraint can be seen to improve the agreement with the detailed calculation.

Another important set of reactions are reactions oxidizing CO to CO₂, with the most important ones being CO+OH=CO₂+H and CO+HO₂=CO₂+OH. Putting a constraint on CO will allow all the reactions involving CO to play an active role in the calculation.. Including this constraint can be seen to result in a further improvement in the agreement with the detailed calculation.

Inclusion of constraints on free valence and free oxygen, which are faster constraints, as the third and fourth dynamic constraints, results in excellent agreement with the detailed kinetics calculation. Looking at table II and the reactions chosen by these constraints, these constraints tend to resolve the interaction of OH and HO₂ with H₂/O₂ species, which results in the correct prediction of their mole fractions. Also, reactions 24-29 do not change any of the constraints and are, therefore, in equilibrium.

Table II. CO-H₂-O₂ Mechanism used in this study

		EO	EH	EC	EN	M	O	LO	LV	Log ₁₀ (A)	Ea (kcal)
1	. H+O ₂ +M=HO ₂ +M	0	0	0	0	-1	0	0	0	15.4	-1.8
2	. OH+OH+M=H ₂ O ₂ +M	0	0	0	0	-1	0	-2	-2	12.5	-0.8
3	. H+O+M=OH+M	0	0	0	0	-1	0	0	-2	14.3	-2
4	. H+H+M=H ₂ +M	0	0	0	0	-1	0	0	-2	14.6	-2
5	. O+O+M=O ₂ +M	0	0	0	0	-1	0	-2	-4	13.6	-2
6	. OH+H+M=H ₂ O+M	0	0	0	0	-1	0	0	-2	15.5	-4
7	. CO+O+M=CO ₂ +M	0	0	0	0	-1	-1	0	-2	10.3	2.4
8	. H+H+H ₂ =H ₂ +H ₂	0	0	0	0	-1	0	0	-2	14.9	-1.2
9	. H+H+H ₂ O=H ₂ +H ₂ O	0	0	0	0	-1	0	0	-2	15.3	-2.6
10	. H+H+CO ₂ =H ₂ +CO ₂	0	0	0	0	-1	0	0	-2	13.9	-4
11	. H+O ₂ +H ₂ O=HO ₂ +H ₂ O	0	0	0	0	-1	0	0	0	16.3	-1.6
12	. H+O ₂ +O ₂ =HO ₂ +O ₂	0	0	0	0	-1	0	0	0	15.1	-2.5
13	. CO+O ₂ =CO ₂ +O	0	0	0	0	0	-1	2	2	12.4	47.8
14	. CO+OH=CO ₂ +H	0	0	0	0	0	-1	0	0	11.8	2.5
15	. CO+HO ₂ =CO ₂ +OH	0	0	0	0	0	-1	2	0	14.2	23.6
16	. HO ₂ +H=OH+OH	0	0	0	0	0	0	2	0	13.9	0.6
17	. HO ₂ +H=O+H ₂ O	0	0	0	0	0	0	2	0	12.6	0.7
18	. H ₂ O ₂ +H=OH+H ₂ O	0	0	0	0	0	0	2	0	13.0	3.6
19	. OH+O=O ₂ +H	0	0	0	0	0	0	-2	-2	12.9	-0.9
20	. HO ₂ +HO ₂ =O ₂ +H ₂ O ₂	0	0	0	0	0	0	0	-2	11.1	-1.6
21	. HO ₂ +O=OH+O ₂	0	0	0	0	0	0	0	-2	13.3	0
22	. HO ₂ +H=O ₂ +H ₂	0	0	0	0	0	0	0	-2	13.7	1.1
23	. HO ₂ +OH=O ₂ +H ₂ O	0	0	0	0	0	0	0	-2	13.1	-0.5
24	. OH+H=H ₂ +O	0	0	0	0	0	0	0	0	13.5	9.7
25	. H ₂ +OH=H+H ₂ O	0	0	0	0	0	0	0	0	13.5	6.4
26	. OH+OH=O+H ₂ O	0	0	0	0	0	0	0	0	12.8	2.7
27	. H ₂ O ₂ +H=HO ₂ +H ₂	0	0	0	0	0	0	0	0	13.9	9.2
28	. H ₂ O ₂ +OH=HO ₂ +H ₂ O	0	0	0	0	0	0	0	0	12.3	0.4
29	. O+H ₂ O ₂ =OH+HO ₂	0	0	0	0	0	0	0	0	13.8	8.0

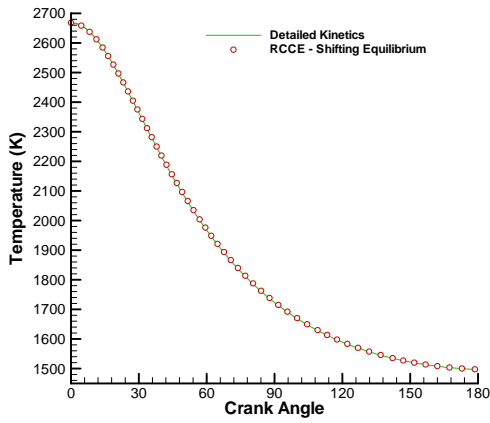


Fig.2: Temperature profile.

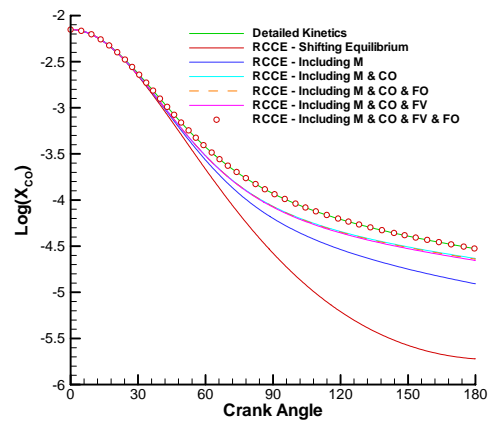


Fig.3: Profiles of CO mole fraction for different sets of constraints.

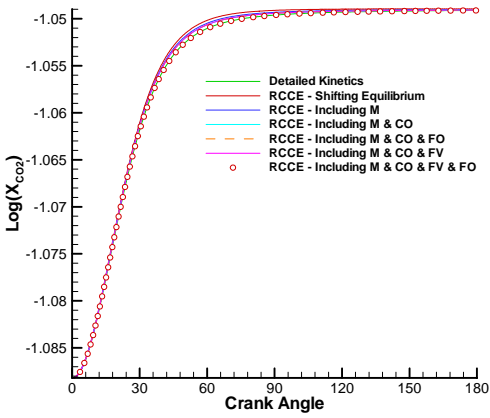


Fig.4: Profiles of CO₂ mole fraction for different sets of constraints.

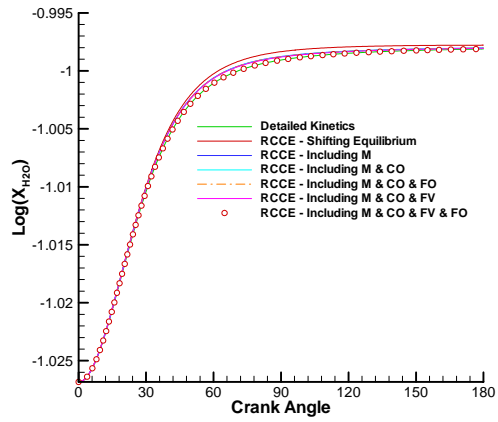


Fig.5: Profiles of H₂O mole fraction for different sets of constraints.

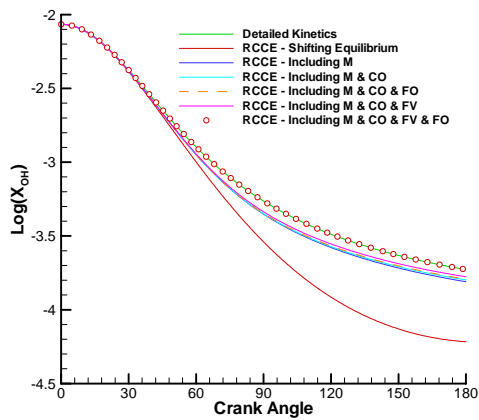


Fig.6: Profiles of OH mole fraction for different sets of constraints.

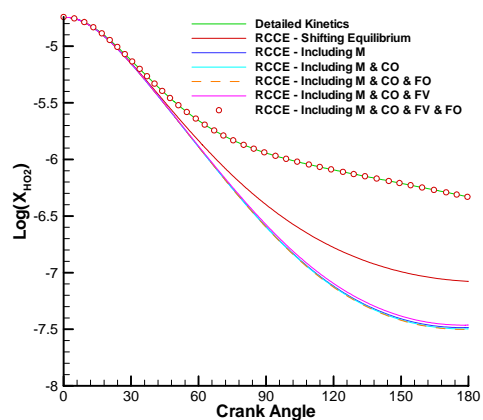


Fig.7: Profiles of HO₂ mole fraction for different sets of constraints.

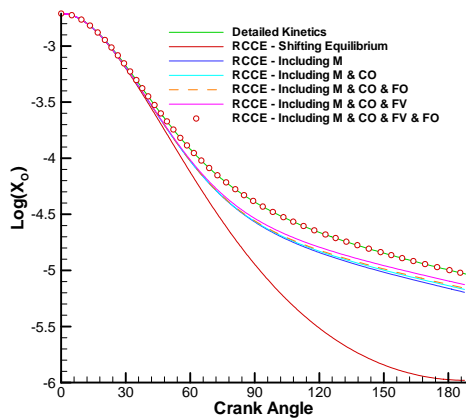


Fig.8: Profiles of O mole fraction for different sets of constraints.

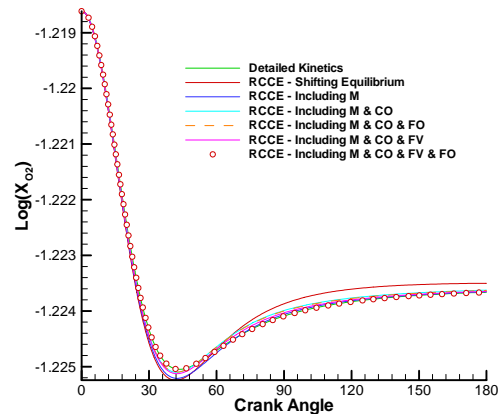


Fig.9: Profiles of O₂ mole fraction for different sets of constraints.

6. Concluding Remarks

Rate-controlled constrained-equilibrium calculations of the expansion of isooctane combustion products during the power cycle of an internal combustion engine were conducted. The dynamic constraints of total number of moles, moles of CO, moles of free valence and moles of free oxygen are able to reproduce the result of exact kinetic calculations. Within the temperature range studied in this paper, the non-equilibrium effects are mostly pronounced in time evolution of CO and H/O species and not in the temperature profile.

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