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In the late 1960s Gray and Yang developed the first reduced kinetic model for the oxidation of hydrocarbon fuels that qualitatively described many features observed experimentally. Since then a number of reduced kinetic models have been proposed in the literature. In this contribution we analyse the steady-state behaviour of one such scheme. The chemical component of the model contains four chemical species undergoing six reactions. By making a pool-chemical approximation this system is reduced to three coupled non-linear differential equations: a temperature equation and equations for two reactive chemical intermediates. It is shown that any steady-state solution of this model having a steady-state temperature greater than 420 (K) is non-physical as the steady-state concentration of the chemical species are negative. Hence this particular scheme does not simulate closed-vessel experiments and is defective as an extension of the Gray-Yang model.

Keywords

Autoignition, hydrocarbons, batch, reactor, Analysis, reduced, model

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Autoignition of hydrocarbons in a batch reactor. Analysis of a reduced model.

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Abstract

In the late 1960s Gray and Yang developed the first reduced kinetic model for the oxidation of hydrocarbon fuels that qualitatively described many features observed experimentally. Since then a number of reduced kinetic models have been proposed in the literature. In this contribution we analyse the steady-state behaviour of one such scheme. The chemical component of the model contains four chemical species undergoing six reactions. By making a pool-chemical approximation this system is reduced to a system comprising three coupled non-linear differential equations: a temperature equation and equations for two reactive chemical intermediates. It is shown that any steady-state solution of this model having a steady-state temperature greater than 420 (K) is non-physical as the steady-state concentration of the chemical species are negative. Hence this particular scheme does not simulate closed-vessel experiments and is defective as an extension of the Gray-Yang model.

Key Words: autoignition, batch reactor, reduced kinetic model.

1 Introduction

Combustion scientists and engineers require mathematical descriptions of the combustion of hydrocarbons in order to design and predict the performance of practical combustion processes such as automotive engines. The combustion of hydrocarbons is a complex process. Detailed kinetic models for the low-temperature oxidation of simple hydrocarbon fuels, at the level of elementary chemical reactions, may contain many thousands of elementary steps among hundreds of chemical species [1]. Although such schemes have many uses, there is still

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an on-going interest in the use of reduced kinetic schemes [1]. For example, reduced kinetic schemes may be used in the simulation of combustion systems where the complexities of the complex fluid dynamic flow preclude the use of very detailed mechanisms. Reduced kinetic schemes may also be used for simulations of fuels, or fuel blends, where knowledge of the fundamental chemistry is not detailed-enough to develop a comprehensive mechanism. Finally, there is an interest in knowing how far simple mechanisms can predict generic behaviour observed during experimental studies.

The use of reduced kinetic schemes to model the oxidation of hydrocarbon fuels can be traced back to the mechanism developed by Yang and Gray [2, 3]. This scheme is shown in table 1. In this scheme reaction (1) is an initiation process in which the fuel species, F , decomposes to produce a radical intermediate, X . Reaction (3) is an autocatalytic branching process in which one radical produces two radicals. The branching process, reaction (3), competes with two termination steps, (2) and (4), in which the intermediate is removed. Termination step (2) is usually taken to be a surface reaction with a zero activation energy. This simple scheme contains both chemical and thermal feedback mechanisms and has been found to describe many of the qualitative features observed during the oxidation of hydrocarbons [4].

initiation	$F \rightarrow X$	(1)
termination 1	$X \rightarrow \text{inert}$	(2)
branching	$X \rightarrow 2X$	(3)
termination 2	$X \rightarrow \text{inert}$	(4)

Table 1: The Gray-Yang kinetic model [3]. Numbering of reactions from Griffiths [1].

Note that in this scheme, as in many reduced schemes, the chemical ‘reactions’ do not represent specific steps in the oxidation mechanism. Rather, by limiting the number of chemical variables, it is hoped that the scheme will provide insights into experimental observations.

Since the work of Yang and Gray [2, 3] a number of reduced schemes have been proposed of increasing degrees of chemical complexity[1]. In this paper we analyse the steady-state behaviour of a scheme that contains four chemical species undergoing six chemical reactions. This scheme has been used to examine ideas relating to the onset of autoignition and knock in engines [5]. It differs from the Gray-Yang model by excluding the second termination step, reaction (4), and including three additional steps, reactions (8, 13 & 14). Reaction (8) introduces a second autocatalytic branching step and involves an interaction between the fuel and radical. Reactions (13) & (14) are included to force chain branching in the second stage of ignition from the product of reaction (13) [5]. The role played by the chemical species P_2 in reactions (13 & 14) is similar to that played by the decomposition of hydrogen peroxide in the oxidation of hydrocarbons [5]. The autoignition chemistry used in this model is given in table 2.

This model has been presented as a development of the Gray-Yang scheme [1]. Whereas the Gray-Yang scheme has one reactive intermediate species (X) this scheme has two (X and P_2). We investigate the behaviour of this scheme when the chemical reaction takes place in a well-stirred batch reactor, which was the experimental

		$Z/$ m^3mols	$(E/R)/$ K	Exothermicity q/kJmol^{-1}	
initiation	$F \rightarrow X$	5×10^6	12000	0	(1)
termination 1	$X \rightarrow P_1$	50	0	0	(2)
branching 1	$X \rightarrow 2X$	2×10^5	3500	100	(3)
branching 2	$X + F \rightarrow 2X + P_1$	5×10^7	10^4	100	(8)
propagation	$X \rightarrow P_2$	4×10^7	7000	50	(13)
branching	$P_2 \rightarrow 2X$	3×10^{11}	2×10^4	-200	(14)

Table 2: The kinetic model used by Griffiths *et al* [5]. Parameter values and numbering of reactions from [1].

configuration investigated by Yang & Gray [3]. The oxidation of hydrocarbons in batch reactors has been extensively studied, thermokinetic features of such studies are described by Griffiths [4].

2 Model

The reaction is assumed to occur in a well-stirred batch reactor in which heat-transport between the reaction vessel and its surroundings is modelled by Newtonian heat transfer. The reactor contains reactants, total pressure \mathcal{P} , and a small amount of nitrogen, pressure \mathcal{P}_N . The initial conditions are given by

$$[F](t=0) = \frac{\mathcal{P}}{RT_a},$$

$$[N_2](t=0) = \frac{\mathcal{P}_N}{RT_a}.$$

(All symbols are defined in the nomenclature). As depletion of the reactants is assumed to be negligible we assume that the volumetric heat-capacity is given by its initial value. Thus, assuming ideal gas behaviour, we have

$$\begin{aligned}
C_v &= C_{v,[F]} [F](t=0) + c_{v,[N_2]} [N_2](t=0) \\
&= 3R \left[\frac{\mathcal{P}}{RT_a} \right] + \frac{5R}{2} \left[\frac{\mathcal{P}_N}{RT_a} \right] \\
&= \frac{6\mathcal{P} + 5\mathcal{P}_N}{2T_a}.
\end{aligned} \tag{1}$$

3 Equations

The mass and conservation equations for fuel, the intermediate species (X , P_1 & P_2) and temperature for the kinetic model shown in table 2 are

$$\frac{d[F]}{dt} = -k_1 [F] - k_8 [F] [X], \quad (2)$$

$$\frac{d[X]}{dt} = k_1 [F] + (k_3 - k_2 - k_{13}) [X] + k_8 [F] [X] + 2k_{14} [P_2], \quad (3)$$

$$\frac{d[P_1]}{dt} = k_8 [F] [X] + k_2 [X], \quad (4)$$

$$\frac{d[P_2]}{dt} = k_{13} [X] - k_{14} [P_2], \quad (5)$$

$$V c_v \frac{dT}{dt} = V q_3 k_3 [X] + V q_8 k_8 [F] [X] + V q_{13} k_{13} [X] + V q_{14} k_{14} [P_2] - S\chi (T - T_a), \quad (6)$$

Initial conditions

$$F(t=0) = \frac{\mathcal{P}}{RT_a},$$

$$X(t=0) = 0, \quad P_1(t=0) = 0, \quad P_2(t=0) = 0,$$

$$T(t=0) = T_a,$$

Note that the rate constants k_i are non-linear functions of the temperature

$$k_i = Z_i \exp\left[\left(\frac{-E}{R}\right)_i \cdot \frac{1}{T}\right].$$

The heat capacity is defined by equation (1).

In analysing this system the simplifying assumption is made that the concentration of the fuel species (F) does not change significantly during the early parts of the reaction (the pool chemical approximation). This approximation is often made in the analysis of thermodynamically closed systems [6, chapters 2–5] and was made in the original analysis of the Gray-Yang scheme [2, 3]. Furthermore equation (4) is ignored as the product species P_1 does not appear in the remaining equations. This leads to a system of three non-linear differential equations, equations (3), (5) & (6), in which the value for F is given by its initial condition.

3.1 Numerics

The path-following software Auto 97 [7] was used to obtain the steady-state diagram. In this the standard representation is used; solid lines are stable steady states; dotted lines are unstable steady states; squares are Hopf bifurcation points; open circles are unstable periodic orbits and filled-in circles are stable periodic solutions. For a periodic orbit the maximum and minimum over the period of the solution are plotted.

4 Results

Figure 1 shows the steady-state diagram when the ambient temperature is $T_a = 670$ (K). This is the classic ‘S’ shaped combustion curve — the high-temperature branch is not shown. This steady-state diagram has two limit points, the extinction limit point is not shown, and one Hopf bifurcation point. The limit cycles generated at the Hopf bifurcation point, at a total reactant pressure $\mathcal{P}_h \approx 1.282 \times 10^3$ (Nm⁻²), are terminated by a homoclinic orbit, at a total reactant pressure $\mathcal{P}_{hc} \approx 1.195 \times 10^3$ (Nm⁻²).

Figure 1 has an unexpected feature that none of the steady-state solutions for positive pressure are physically meaningful: the concentration of the chemical species X and P_1 are negative for $\mathcal{P} > 0$. To understand this consider the steady-state equations corresponding to equations (3) & (5). The steady-state value of P_2 is obtained from equation (5) as

$$P_{2,ss} = \frac{k_{13}X_{ss}}{k_{14}}. \quad (7)$$

From equations (3) & (7) the steady-state concentration of the free radical species X is given by

$$X_{ss} = \frac{k_1 F}{k_2 - (k_3 + k_{13} + k_8 F)}. \quad (8)$$

This is positive if

$$k_2 > (k_3 + k_{13} + k_8 F). \quad (9)$$

The left-hand side of inequality (9) is independent of temperature ($E_2 = 0$) whereas the right-hand side of the inequality is a monotone increasing function of the temperature. There is a unique temperature at which equality holds, the value depending upon the fuel concentration. Call the equality temperature $T_e(F)$. It is easy to show that when $F \geq 0$, $T_e(F)$ is a monotone decreasing function of F . Thus $T_e(F = 0) > T_e(F)$ if $F > 0$.

The equality

$$k_2 = (k_3 + k_{13}) \quad (10)$$

holds when

$$T_{ss} = \frac{-E_3}{\ln z}, \quad (11)$$

where

$$z = \frac{-Z_3 + \sqrt{Z_3^2 + 4Z_{13}Z_2}}{2Z_{13}}. \quad (12)$$

This gives

$$T_e(0) \approx 419.6(\text{K}). \quad (13)$$

(In obtaining equations 11 & 12 use is made of the condition $2E_3 = E_{13}$.) Thus if $F > 0$ and $T_{ss} > 420$ (K) inequality (9) does not hold and the steady-state values for the free radical (X) and product (P_2) concentrations are negative. Note that figure 1 shows the variation in the steady-state temperature with reactant pressure — the temperature is *positive* even though the concentrations are *negative*.

5 Conclusions

Many reduced kinetic schemes have been proposed to model the oxidation of hydrocarbons. In this paper we have investigated the steady-state behaviour of one such scheme in a batch reactor by making a pool chemical approximation. The scheme that we investigated is a four-species six-step reduced kinetic scheme for the oxidation of hydrocarbons proposed by Griffiths *et al* [5].

The kinetic scheme used here has the defect that any steady-state with a temperature greater than $T_e \approx 420(\text{K})$ is unphysical as the corresponding chemical concentrations are negative. Furthermore, even if the chemical concentrations were positive figure 1 would not correspond to experimental reality. The reason for this is that at sufficiently low reactant pressure the model should exhibit a stable steady-state branch that corresponds in an experiment to a slow reaction with a negligible temperature increase. Figure 1 does have a steady-state solution branch but it is unstable. Thus we conclude that the model originally proposed in [5], and presented in [1] as a development of the Gray and Yang model, is defective.

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6 Nomenclature

The subscript $_{ss}$ is used to denote a steady-state value.

C_v	Volumetric heat-capacity at constant volume.	$(\text{JK}^{-1}\text{m}^{-3})$
$C_{v,i}$	Heat capacity of species i at constant volume.	$(\text{JK}^{-1}\text{mol}^{-3})$
$[F]$	The concentration of the fuel species F .	(mol m^{-3})
$[N]_2$	The concentration of nitrogen.	(mol m^{-3})
$[P_i]$	The concentration of product species P_i ($i=1,2$).	(mol m^{-3})
\mathcal{P}	The initial pressure of fuel.	(Nm^{-2})
\mathcal{P}_h	The pressure at a Hopf bifurcation point.	(Nm^{-3})
\mathcal{P}_{hc}	The pressure at a homoclinic orbit.	(Nm^{-3})
\mathcal{P}_N	The initial pressure of nitrogen.	(Nm^{-2})
R	The ideal gas constant.	$(\text{JK}^{-1}\text{mol}^{-1})$
S	The surface area of the reactor.	(m^2)
T_a	The temperature of the reactor walls.	(K)
V	The volume of the reactor.	(m^3)

$[X]$	The concentration of intermediate species $[X]$.	(mol m^{-3})
k_i	The rate constant for reaction i . $k_i = Z_i \exp\left[\left(\frac{-E}{R}\right)_i \cdot \frac{1}{T}\right]$.	(varying)
q_i	Exothermicity of reaction i	(kJ mol^{-1})
t	Time.	(s)
χ	Surface heat transfer coefficient.	$(\text{J s}^{-1} \text{m}^{-2} \text{K}^{-1})$

We take the following typical parameter values: $\mathcal{P}_N = 0.01 \text{N m}^{-3}$, $S = 5 \times 10^{-2} \text{m}^{-2}$, $V = 10^{-3} \text{m}^3$ and $\chi = 30 \text{J s}^{-1} \text{m}^{-2} \text{K}^{-1}$.

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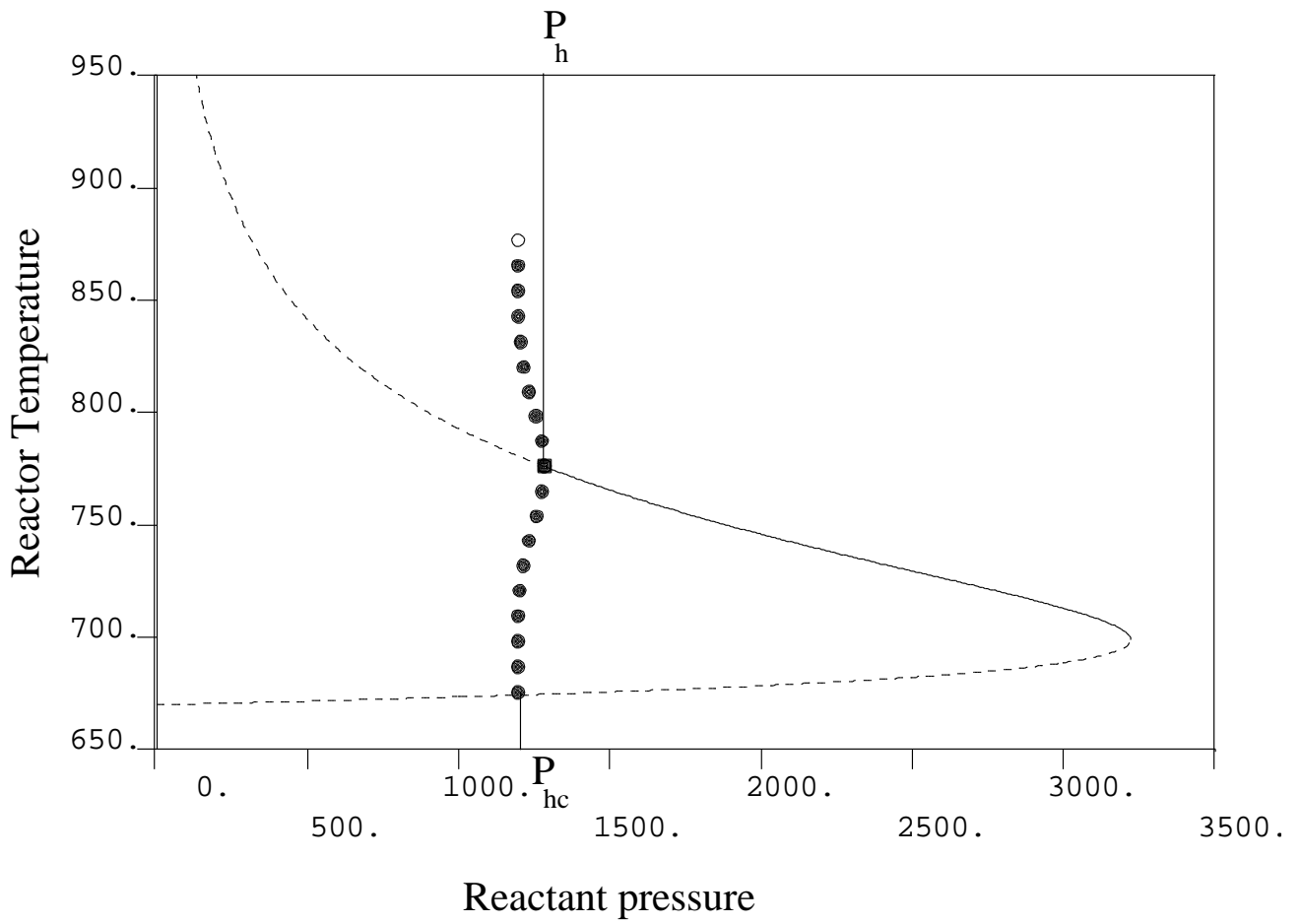


Figure 1: Steady-state diagram showing the variation of the reactor temperature T (K) with reactant pressure \mathcal{P} (Nm^{-2}). Parameter value: ambient temperature, $T_a = 670$.