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Behaviour of an elementary oxidation reaction in a semi-batch reactor

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Abstract

The dynamics of a non-isothermal bi-molecular gas-phase reaction in a semi-batch reactor is investigated. It is assumed that one of the reactants flows into a reactor containing the second. A reduced model is obtained by making a ‘pool-chemical’ approximation on the concentration of the reactant initially in the reactor. The region in parameter space in which oscillations are observable in the full transient model is estimated by determining the Hopf bifurcation locus in the reduced system. The contribution of the current work is its comparative study of the behaviour of the full system to that of the pool-chemical model. Although the reaction scheme is symmetric with respect to the reactants the regions of oscillatory behaviour are not identical because the reactants have different heat capacities.

Keywords: Semi-batch reactor; Gas-phase oxidation reaction; Pool-chemical approximation; Oscillations; Hopf bifurcation

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1. Introduction

The two most commonly used reactors in which reactions are studied are the batch reactor and the continuous flow reactor. However semi-batch operation is desirable in some applications involving highly exothermic reactions since it provides for a better control of the system. For such reactions, the heat generated by the chemical reaction may be controlled by manipulating the rate at which one of the reactants enters the reactor. In addition to this safety aspect, semi-batch reactors may be used to increase the selectivity of the reaction process. Stoessel and Ubrich [1] provide a well written account of the safety assessment and optimization of semi-batch reactors. Other industrial applications of semi-batch reactors include the manufacture of fine chemicals, biological fermentation and waste treatment plants. These types of reactors are also used in the administration of therapeutic drugs. It has also been suggested that the semi-batch mode of operation is a potentially powerful tool for the experimental study of reactions that are known to exhibit oscillatory kinetics in a CSTR [2,3].

The most common reaction used in the semi-batch operation is the liquid–liquid reaction. van Woezik and Westerterp [4] investigated the nitric acid oxidation of 2-octanol (a two-phase reaction system). Grau et al. [5] investigated an acid-base reaction and an oxidation-reduction reaction with a high reaction rate for both batch and semi-batch operation. Grau et al. [6] and Nougues et al. [7] used genetic algorithms to determine the optimal feeding profile for highly exothermic reaction. Donati and Paludetto [8] have reviewed the basic theory of semi-batch reactors, showing how it can be extended to more complicated situations involving non-ideal mixing that may arise in practice. Srinivasan and Bonvin [9] examined the method of determining the optimal feed-rate in semi-batch reactors for two-reaction schemes governed by power-law kinetics in which one reaction is considered to be desirable. The characterization of the region in which thermal runaway is possible in semi-batch reactors using lyapunov exponents was shown in [10], whereas a general

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runaway criterion based on the divergence of the system was presented in [11]. The advantage of the latter method is that it is sufficiently general and can be applied to different types of reactors and can be easily implemented on-line using only temperature measurements.

The motivation of our work is the suggestion by Griffiths [12] that studies in which one *gaseous* reactant flows at a controlled rate into a semi-batch reactor containing another reactant has potential safety applications since this scenario mimics a combustion hazard where an inadvertent leakage of a chemical occurs through a valve. Coppersthwaite et al. [13] have shown for the $H_2 + Cl_2$ system in a semi-batch reactor that during oscillations the temperature excursions can be significantly large. The dynamics of the decomposition of di-tert butyl peroxide has also been investigated in a semi-batch rector [14–16].

In experimental investigations it is useful to know in advance the region in parameter space where oscillatory behaviour occurs, particularly for safety reasons. In this paper we investigate the dynamic behaviour of a simple non-isothermal bi-molecular gaseous reaction. We assume that the reaction vessel contains initially one of the reactants, possible diluted by the addition of nitrogen. The second reactant flows into the reactor. A pool-chemical approximation is made on the species initially in the reactor. We investigate the circumstances under which the predictions of the reduced pool-chemical system serve as a good initial guess for the transient system and also state conditions when the pool-chemical approximation fails. In addition we examine how the dynamics depend upon the choice of inflowing reactant. The dynamics of our reaction scheme have also been investigated in a continuously stirred tank reactor [17] and in a batch reactor [18]. Taken together, including the present analysis, these papers show the range of behaviour that can be exhibited by a simple non-isothermal chemical scheme depending upon the choice of reactor.

2. Description of the model and governing equations

We consider the dynamics of a gaseous fuel undergoing an oxidation reaction in a semi-batch reactor. Two scenarios are considered: fuel flowing into a reactor initially containing only oxygen and nitrogen; oxygen flowing into a reactor initially containing only fuel and nitrogen.

For simplicity the rate of oxidation is given by a global Arrhenius reaction rate that is first order with respect to both of the reactants. One mole of fuel reacts with one mole of oxygen to produce n moles of products, that is

$$\mathcal{F} + \mathcal{O}_2 \to n\mathcal{C} \tag{1}$$

2.1. Transient dimensional equations

Under the assumptions described above the following governing equations can be derived.

- Inflow of fuel into an oxygen–nitrogen mixture:

Fuel concentration: $$\frac{d\mathcal{F}}{dt} = \frac{q\mathcal{F}_0}{V} - A\exp\left[\frac{-E}{RT}\right]\mathcal{F}\mathcal{O}_2, \tag{2}$$

Oxygen concentration: $$\frac{d\mathcal{O}_2}{dt} = -A\exp\left[\frac{-E}{RT}\right]\mathcal{F}\mathcal{O}_2, \tag{3}$$

Temperature:

$$\begin{aligned}\rho c_v V\frac{dT}{dt} &= QVA\exp\left[\frac{-E}{RT}\right]\mathcal{F}\mathcal{O}_2 - \chi S(T-T_a)\\ &\quad + q\mathcal{F}_0 c_{v,m_{\mathcal{F}}}(T_0 - T),\end{aligned} \tag{4}$$

Initial conditions: $$\mathcal{F}(0) = 0, \quad c_r = \mathcal{N}_2 + \mathcal{O}_2(0), \quad T(0) = T_0, \tag{5}$$

Algebraic relationships: $$\rho c_v = \frac{5R}{2}(\mathcal{O}_2(0) + \mathcal{N}_2), \quad c_{v,m_{\mathcal{F}}} = 3R. \tag{6}$$

- Inflow of oxygen into an fuel-nitrogen mixture:

Fuel concentration: $$\frac{d\mathcal{F}}{dt} = -A\exp\left[\frac{-E}{RT}\right]\mathcal{F}\mathcal{O}_2, \tag{7}$$

Oxygen concentration:

$$\frac{d\mathcal{O}_2}{dt} = \frac{q\mathcal{O}_{2,0}}{V} - A\exp\left[\frac{-E}{RT}\right]\mathcal{F}\mathcal{O}_2, \tag{8}$$

Temperature:

$$\begin{aligned}\rho c_v V\frac{dT}{dt} &= QVA\exp\left[\frac{-E}{RT}\right]\mathcal{F}\mathcal{O}_2 - \chi S(T-T_a)\\ &\quad + q\mathcal{O}_{0,2} c_{v,m_{\mathcal{O}_2}}(T_0 - T),\end{aligned} \tag{9}$$

Initial conditions: $$\mathcal{O}_2(0) = 0, \quad c_r = \mathcal{N}_2 + \mathcal{F}(0), \quad T(0) = T_0, \tag{10}$$

Algebraic relationships:

$$\rho c_v = \frac{5R}{2}\mathcal{N}_2 + 3R\mathcal{F}(0). \quad c_{v,m_{\mathcal{O}_2}} = \frac{5R}{2}. \tag{11}$$

The terms that appear in Eqs. (2)–(11) are defined in the nomenclature. Since the governing equations for the two cases are similar, for the sake of brevity we shall only describe the equations for the case when fuel is flowing into an oxygen–nitrogen mixture.

In Eq. (2) the first term on the right-hand side gives the increase in fuel concentration due to its inflow into the reactor.

The second term represents the decrease in fuel concentration due to the oxidation reaction. In this scenario oxygen does not flow into the reactor and accordingly Eq. (3) only contains the depletion term. In Eq. (4) the first term on the right-hand side is heat production due to oxidation, the second represents heat loss due to Newtonian cooling and the final term gives the rate of increase of enthalpy due to reactant inflow. In previous studies of semi-batch reactors [13–16,19,20] the inflow was assumed to be instantaneously heated to the temperature inside the reactor. Consequently this term was absent.

Eq. (5) give the initial conditions. As we consider fuel flowing into an oxygen–nitrogen mixture the initial concentration of fuel is zero. The first expression in (6) defines the initial heat capacity of the reaction mixture, which appears on the left-hand side of Eq. (4). The heat capacity of the fuel species, which appears in the third term on the right-hand side of Eq. (4) is given by the second expression in (6). For simplicity we assume that we have tight control of the coolant temperature, so that there is no requirement to include an equation for the jacket temperature as it is regarded as constant (isoperibolic mode).

2.2. Non-dimensionalised transient equations

Our aim in non-dimensionalising the model equations is to ensure that each of the parameters of main experimental interest appears in only one continuation parameter. We do not retain the pressure at which the initial mixture is assembled as a distinct continuation parameter, as it is uncommon for pressure to be used as a primary bifurcation parameter. In non-dimensionalising the governing equations we introduce a non-dimensionalised fuel concentration ($\mathcal{F}^*$), non-dimensionalised oxygen concentration ($\mathcal{O}_2^*$), non-dimensionalised temperature (T^*), and a non-dimensionalised time-scale (t^*). These are all defined in the nomenclature.

- Inflow of fuel into an oxygen–nitrogen mixture:

$$\frac{d\mathcal{F}^*}{dt^*} = k_f^* T_0^* - \frac{A^*}{T_0^*} \exp\left[\frac{-E^*}{T^*}\right] \mathcal{F}^* \mathcal{O}_2^*, \tag{12}$$

$$\frac{d\mathcal{O}_2^*}{dt^*} = -\frac{A^*}{T_0^*} \exp\left[\frac{-E^*}{T^*}\right] \mathcal{F}^* \mathcal{O}_2^*, \tag{13}$$

$$\frac{5}{2}\frac{dT^*}{dt^*} = \frac{Q^* A^*}{T_0^*} \exp\left[\frac{-E^*}{T^*}\right] \mathcal{F}^* \mathcal{O}_2^* - T_0^*(T^* - T_a^*) + 3k_f^* T_0^*(T_0^* - T^*), \tag{14}$$

Non-dimensionalised initial conditions:

$$\mathcal{N}_2^* = \gamma, \quad \mathcal{F}^*(0) = 0, \quad \mathcal{O}_2^*(0) = \beta, \quad T^*(0) = T_0^*, \tag{15}$$

Relationship between the initial non-dimensionalised

$$\text{concentrations:} \quad \beta + \gamma = 1. \tag{16}$$

- Inflow of oxygen into a fuel-nitrogen mixture:

$$\frac{d\mathcal{F}^*}{dt^*} = -\frac{A^*}{T_0^*} \exp\left[\frac{-E^*}{T^*}\right] \mathcal{F}^* \mathcal{O}_2^*, \tag{17}$$

$$\frac{d\mathcal{O}_2^*}{dt^*} = k_f^* T_0^* - \frac{A^*}{T_0^*} \exp\left[\frac{-E^*}{T^*}\right] \mathcal{F}^* \mathcal{O}_2^*, \tag{18}$$

$$\frac{5+\alpha}{2}\frac{dT^*}{dt^*} = \frac{Q^* A^*}{T_0^*} \exp\left[\frac{-E^*}{T^*}\right] \mathcal{F}^* \mathcal{O}_2^* - T_0^*(T^* - T_a^*) + \frac{5}{2}k_f^* T_0^*(T_0^* - T^*), \tag{19}$$

Non-dimensionalised initial conditions:

$$\mathcal{N}_2^* = \gamma, \quad \mathcal{F}^*(0) = \alpha, \quad \mathcal{O}_2^*(0) = 0, \quad T^*(0) = T_0^*, \tag{20}$$

Relationship between the initial non-dimensionalised

$$\text{concentrations:} \quad \alpha + \gamma = 1. \tag{21}$$

2.3. Pool-chemical approximation

Bifurcation theory can not be used to analyse the transient model equations presented in Section 2.2 because they do not possess a steady state. The concentration of the inflowing species increases without bound after the concentration of the second species becomes negligible. In order to obtain a set of equations suitable for analysis we make a pool-chemical approximation on the concentration of the reactant species initially inside the reactor. Thus we ignore depletion of this species.

- Inflow of fuel into an oxygen–nitrogen mixture:

  We ignore depletion of oxygen and assume that it remains at its initial value.

$$\frac{d\mathcal{F}^*}{dt^*} = k_f^* T_0^* - \frac{A^*}{T_0^*} \exp\left[\frac{-E^*}{T^*}\right] \mathcal{F}^*(1-\gamma), \tag{22}$$

Non-dimensionalised temperature

$$\frac{5}{2}\frac{dT^*}{dt^*} = \frac{Q^* A^*}{T_0^*} \exp\left[\frac{-E^*}{T^*}\right] \mathcal{F}^*(1-\gamma) - T_0^*(T^* - T_a^*) + 3k_f^* T_0^*(T_0^* - T^*), \tag{23}$$

Non-dimensionalised initial conditions:

$$\mathcal{F}^*(0) = 0, \quad T^*(0) = T_0^*. \tag{24}$$

- Inflow of oxygen into a fuel-nitrogen mixture:

We ignore depletion of the fuel and assume that it remains at its initial value.

$$\frac{\mathrm{d}\mathcal{O}_2^*}{\mathrm{d}t^*} = k_\mathrm{f}^* T_0^* - \frac{A^*}{T_0^*} \exp\left[\frac{-E^*}{T^*}\right] \mathcal{O}_2^*(1-\gamma), \tag{25}$$

$$\frac{5+\alpha}{2}\frac{\mathrm{d}T^*}{\mathrm{d}t^*} = \frac{Q^* A^*}{T_0^*} \exp\left[\frac{-E^*}{T^*}\right] \mathcal{O}_2^*(1-\gamma) - T_0^*(T^* - T_\mathrm{a}^*) + \frac{5}{2} k_\mathrm{f}^* T_0^* (T_0^* - T^*), \tag{26}$$

Non-dimensionalised initial conditions:

$$\mathcal{O}_2^*(0) = 0, \quad T^*(0) = T_0^*. \tag{27}$$

3. Results

The pool-chemical models above consist of two coupled ordinary differential equations. For such systems Gray and Roberts [21] have provided the defining conditions necessary to determine all bifurcations of codimension zero, one, and two. In Section 3.1 we show that both models have a unique steady-state solution. Thus the only bifurcation that can occur is the Hopf bifurcation. This type of bifurcation marks the location on the steady-state curve beyond which oscillatory solutions are possible when a certain control parameter is varied.

3.1. Steady-state analysis

- Inflow of fuel into oxygen–nitrogen mixture:

  The unique steady-state solution of Eqs. (22) and 23) is given by

$$T^* = \frac{k_\mathrm{f}^* Q^* + 3k_\mathrm{f}^* T_0^* + T_\mathrm{a}^*}{1 + 3k_\mathrm{f}^*},$$

$$\mathcal{F}^* = \left[\frac{k_\mathrm{f}^* {T_0^*}^2}{A^*(1-\gamma)}\right] \exp\left[\frac{E^*}{T^*}\right]. \tag{28}$$

  In non-isothermal problems response diagrams usually show the variation in the steady-state temperature as a function of the bifurcation parameter. We do not show a steady-state diagram since it is a single-valued function that is either monotonic increasing or monotonic decreasing depending upon the choice of bifurcation parameter and the values of the remaining parameters.

- Inflow of oxygen in fuel-nitrogen mixture:

  The unique steady-state solution of Eqs. (25 and 26) is given by

$$T^* = \frac{2Q^* k_\mathrm{f}^* + 5k_\mathrm{f}^* T_0^* + 2T_\mathrm{a}^*}{2 + 5k_\mathrm{f}^*},$$

$$\mathcal{O}_2^* = \left[\frac{k_\mathrm{f}^* {T_0^*}^2}{A^*(1-\gamma)}\right] \exp\left[\frac{E^*}{T^*}\right]. \tag{29}$$

3.2. Numerical results

3.2.1. Pool-chemical approximation

In this section we investigate the region in parameter space in which Hopf bifurcations are found. We note that the $H2_1$ degeneracy does not occur as the initial composition of the reaction mixture is varied. Thus, for a given fuel, there are two experimentally ‘tunable’ parameters of interest: the reactor temperature and the inflow rate.

Fig. 1a shows the Hopf bifurcation locus when fuel flows into oxygen. Although the solution curve approaches arbitrarily close to the origin it is not defined there. Of course, the ideal gas law, and consequently the model, are not valid at very low temperatures. Generically the steady-state diagram contains either no Hopf points, in which case the steady-state solution given by Eqs. (28) and (29) is always stable, or two Hopf points, in which case stable limit cycles exist at parameter values inside the locus. Although the cool flame boundary is commonly associated with the Hopf locus (see [22]) this may only be a approximation since there is a possibility that one or both of the Hopf points are subcritical in which case the cool-flame region is larger than the Hopf locus (see [23] for an example of this case). The two points marked (A) represent $H2_1$ degeneracies. Thus Hopf bifurcations do not occur if either the ambient temperature or the flowrate is too high. In semi-batch experiments [13–16], the inflow rate was normally fixed and the ambient temperature varied—it is much easier to vary the temperature of the reactor in a controlled manner. For a given inflow rate this figure provides a range of ambient temperatures over which oscillations are expected to be observed experimentally.

Fig. 1(b) shows how the Hopf locus depends upon the initial pressure inside the reactor. As the initial pressure *decreases* the “cool-flame region” *increases*. Moreover the cool-flame region is slightly larger when fuel flows into oxygen than vice-versa. This is more apparent at lower pressures. As the reaction mechanism is symmetric with respect to the reactants this difference is due to the different heat capacities of the initial mixture.

Fig. 2 shows how the location of the $H2_1$ degeneracy depends upon the initial composition of the reactant mixture. The cool-flame region increases with increasing nitrogen fraction. This increase is more notable at low initial pressures and at high nitrogen fraction. As the nitrogen fraction increases the distinction between the two scenarios decreases. We noted that the differences between the two scenarios is due to the difference in the initial heat capacity of the reaction mixture. The initial heat-capacity of an oxygen–nitrogen mixture does not depend upon its composition. At high nitrogen fraction the total heat capacity of a fuel-nitrogen mixture is dominated by the contribution from the nitrogen and approaches that of an oxygen–nitrogen mixture. Thus at high nitrogen fraction the difference in initial heat capacities between the two scenarios decreases.

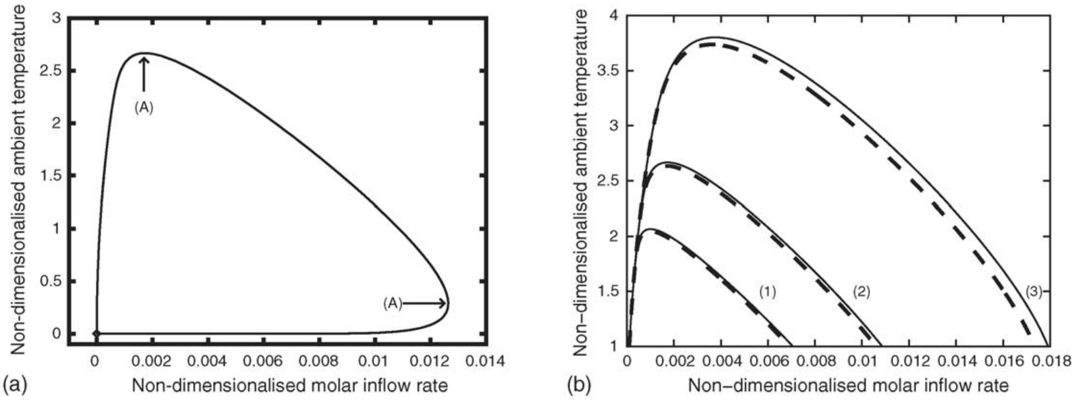

Fig. 1. (a) The Hopf bifurcation locus when fuel flows into a reactor containing oxygen. Note that the curve is not connected at the origin. (b) Part of the Hopf bifurcation locus when either fuel flows into a reactor containing oxygen (solid lines) or oxygen flows into a reactor containing fuel (dashed lines). Parameter values: nitrogen fraction: $\gamma = 0$, pressure: (b1) $\mathcal{P}^0 = \frac{1}{3} 1.01325 \times 10^5\ \mathrm{Jm}^{-3}$; (a and b2) $\mathcal{P}^0 = \frac{1}{30} 1.01325 \times 10^5\ \mathrm{Jm}^{-3}$; (b3) $\mathcal{P}^0 = \frac{1}{300} 1.01325 \times 10^5\ \mathrm{Jm}^{-3}$.

3.2.2. Transient semi-batch model

In this section, we find the region in parameter space in which oscillatory behaviour is found in the transient semi-batch model, Eqs. (12)–(14) for fuel flowing into an oxygen–nitrogen system, and Eqs. (17)–(19) for oxygen flowing into a fuel-nitrogen system.

Fig. 3 shows oscillatory behaviour taking place in the semi-batch reactor. True periodic solutions (such as those in a continuously stirred tank reactor) are impossible in the semi-batch as there is only fresh input of one reactant into the reactor. Consequently only a finite number of oscillations can occur. We define oscillations to occur in the semi-batch reactor when the peaks in the temperature profiles and the reactant that is flowing into the reactor are of equal or greater in amplitude to the previous peaks. Damped oscillations are therefore not considered to be a periodic solution. In the case described in Fig. 3, we have excluded nitrogen from the mixture (that is, we set $\gamma = 0$) since the inclusion of nitrogen had an insignificant impact on the numerical results. The concentration profiles for the fuel and oxygen are presented in Fig. 3a, whereas Fig. 3b shows the corresponding temperature profile. The results here clearly shows oscillatory behaviour taking place. Beyond time $t^* = 62$, the oscillatory behaviour ceases, and the fuel concentration gradually decreases to zero, while the oxygen concentration increases linearly according to the rate of inflow into the reactor. Furthermore, for $t^* > 62$, the temperature also gradually cools to the ambient temperature $T_a^* = 3.5$. Fig. 4 shows a case when there are no sustained oscillations occurring in the reactor. Here the parameter values were the same as those in Fig. 3 except that the ambient temperature was now increased to $T_a^* = 4.2$. Similar oscillatory and non-oscillatory behaviour were observed for the case when fuel was flowed into the reactor with oxygen already present.

Using the definition for oscillatory behaviour in the semi-batch reactor mentioned earlier, and by varying the flow rate and ambient temperature, we determined the boundaries between oscillatory and non-oscillatory behaviour in the

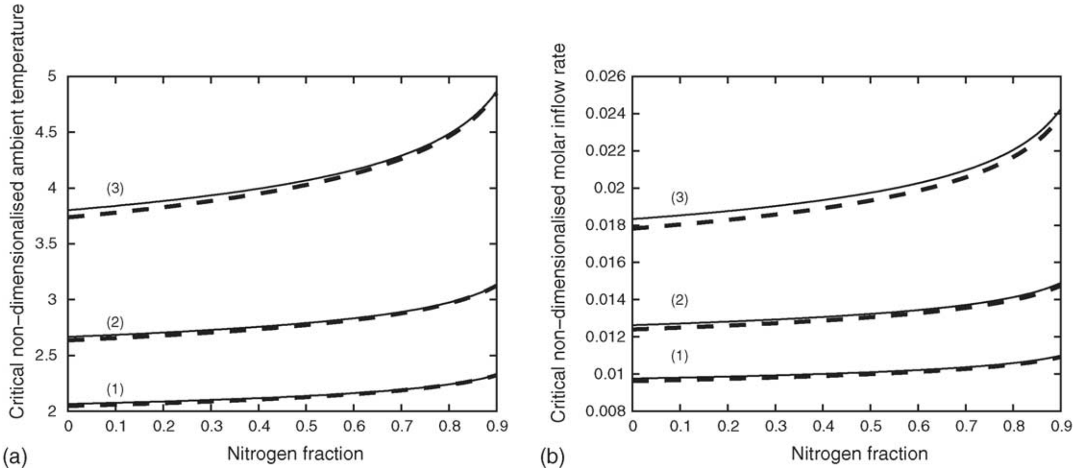

Fig. 2. The $H2_1$ locus in the ambient temperature/nitrogen fraction (a) and molar inflow rate/nitrogen fraction (b) planes. The solid lines represent fuel flowing into a reactor containing a oxygen–nitrogen mixture whereas the dashed lines represent oxygen flowing into a reactor containing a fuel-nitrogen mixture. Parameter values: Pressure, (b1) $\mathcal{P}^0 = \frac{1}{3} 1.01325 \times 10^5 \mathrm{Jm}^{-3}$; (b2) $\mathcal{P}^0 = \frac{1}{30} 1.01325 \times 10^5\ \mathrm{Jm}^{-3}$; (b3) $\mathcal{P}^0 = \frac{1}{300} 1.01325 \times 10^5\ \mathrm{Jm}^{-3}$.

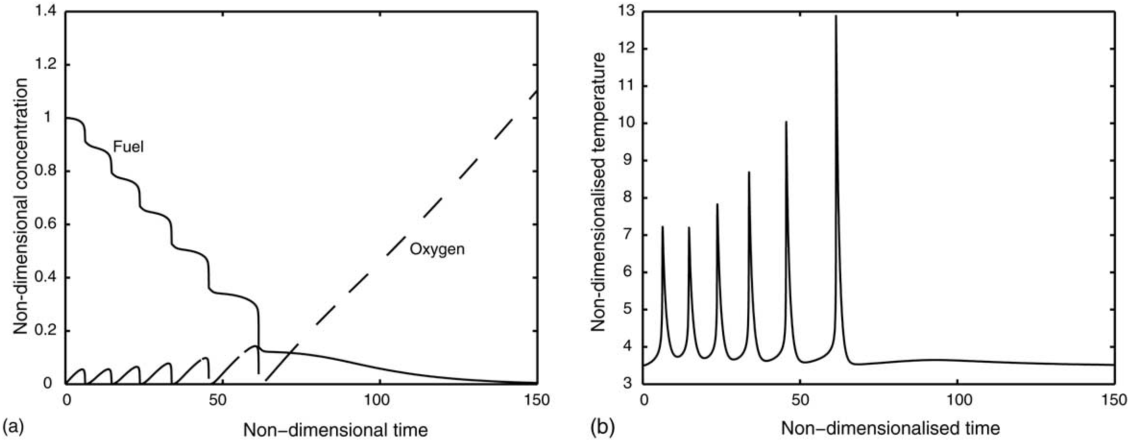

Fig. 3. An example of a case when oscillatory behaviour was observed in the transient semi-batch model. (a) The fuel and oxygen profiles and (b) the temperature profile for the case when oxygen is flowing into the semi-batch reactor with fuel already present. The parameter values used are: $k_f^* = 0.004$, $T_a^* = 3.5$ and $\mathcal{P}^0 = \frac{1}{300} 1.01325 \times 10^5\,\mathrm{Jm}^{-3}$.

(k_f^*, T_a^*)–parameter plane for both cases (i.e. oxygen flowing into the reactor with fuel already present, and vice-versa). These boundaries are shown in Fig. 5 for different values of pressures (noting that oscillatory behaviour were observed in the enclosed region). These diagrams show that there are important differences between the results from the pool-chemical approximation and those from the transient model.

Firstly, for the transient semi-batch model there appear to be a distinct “cut-off” value for the ambient temperature, below which no oscillatory behaviour occurs. This is not the case for the pool-chemical approximation. The “cut-off” value for the ambient temperature was identical for both scenarios (flow of oxygen into the reactor with fuel already present, and vice-versa). Secondly, although the pool-chemical approximation is valid for low values of inflow rates (that is, the boundaries for the onset of oscillations between the pool-chemical and the transient models correspond to each other), it predicts no oscillation whereas the numerical simulations of the transient semi-batch model indicate the presence of oscillations for higher inflow rates. For example referring to Fig. 5a and considering the case, when $\mathcal{P}^0 = \frac{1}{30} 1.01325 \times 10^5\mathrm{Jm}^{-3}$ (which is represented by curve 2 for the pool-chemical approximation and by the symbol + for the results for the transient semi-batch model) we can see that for $T_a^* = 2.5$, both the Hopf locus for the pool-chemical approximation and the boundary where oscillatory solution begins in the transient model, correspond to each other for low flow rates. However, as the flow rate of fuel into the reactor is increased, the pool-chemical approximation predicts that the oscillations ceases when $k_f^* \approx 0.004$, whereas this is not the case in the transient semi-batch model as there is still a significant region of parameter space in which oscillatory behaviour was observed. As the maximum reactor temperature can be significantly high in these regions (which are not ‘captured’ by the pool-chemical approximation), there are obviously serious safety implications if *only* the pool-chemical scheme was used to estimate the region of oscillatory behaviour. Finally, only for the case when fuel was flowing into the reactor with oxygen already present and at low pressures (curve 3 and the corresponding circles in

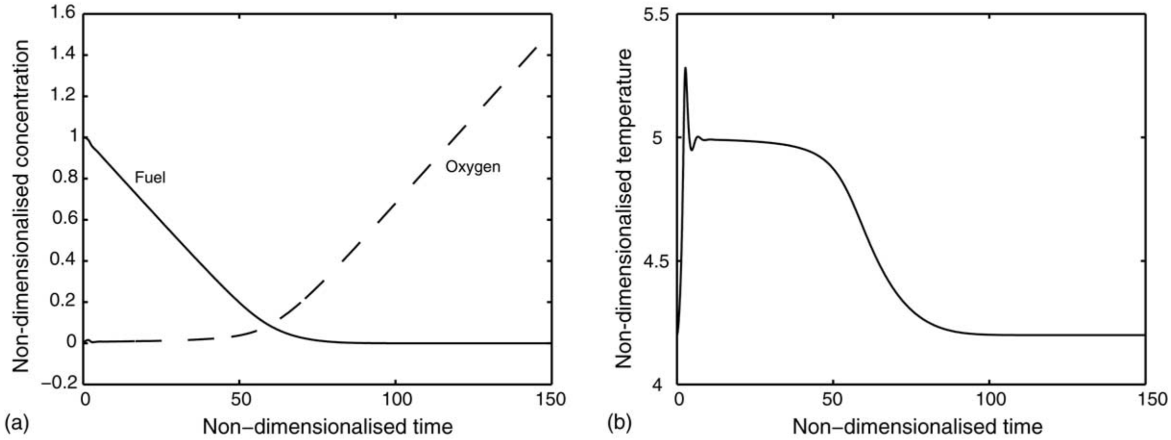

Fig. 4. An example of a non-oscillatory behaviour occuring in transient semi-batch model. Here oxygen is flowing into the reactor with fuel already present. The parameter values used are exactly the same as those in Fig. 3 except that the ambient temperature is $T_a^* = 4.2$.

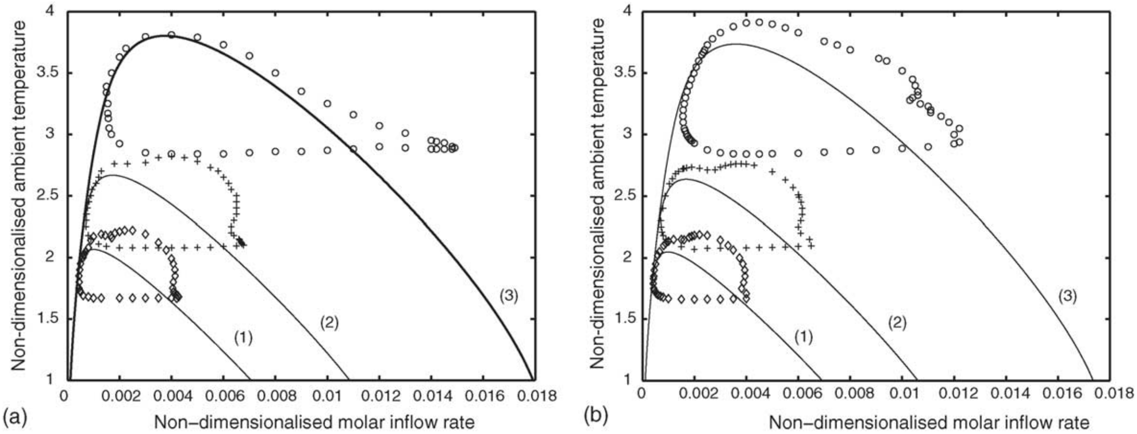

Fig. 5. The boundaries between oscillatory and non-oscillatory behaviour for the case of (a) inflow of fuel into oxygen and (b) inflow of oxygen into fuel. The bold curves refer to the Hopf locus from the pool-chemical approximation which are exactly the same as those shown in Fig. 1. The circle, cross and diamond symbols are the corresponding boundaries obtained for the transient semi-batch model. Curve 1 and the diamonds refer to results for $\mathcal{P}^o = \frac{1}{3}1.01325 \times 10^5\ \mathrm{Jm^{-3}}$, curve 2 and the crosses refer to $\mathcal{P}^o = \frac{1}{30}1.01325 \times 10^5\ \mathrm{J\,m^{-3}}$, and curve 3 and the circles correspond to $\mathcal{P}^o = \frac{1}{300}1.01325 \times 10^5\ \mathrm{J\,m^{-3}}$.

Fig. 5a) did the results match for both the pool-chemical and transient models for locating the $H2_1$ degenerate Hopf bifurcation points (maximum ambient temperature at which oscillatory behaviour can occur). In all other cases, the pool-chemical approximation under-estimates this value for the ambient temperature. We also note that only when the pressures were very low ($\mathcal{P}^0 = \frac{1}{3000}1.01325 \times 10^5\ \mathrm{J\,m^{-3}}$) did the maximum flow rates at which oscillatory behaviour can occur ($H2_1$ degenerate Hopf bifurcation points) correspond to each other in the two schemes.

4. Conclusions

We have investigated the dynamics of an exothermic bimolecular gaseous reaction in a semi-batch reactor. Considerable temperature excursions occur in the oscillatory region (Fig. 3). This has immediate safety implications and therefore we sought to examine the conditions under which oscillations occur. Due to reactant consumption, bifurcation theory can not be used to analyse the transient model in the semi-batch mode of operation. As a result we utilize the pool-chemical approximation similar to that used in [13] and [19] in an attempt to predict oscillatory behaviour in the semi-batch setting.

By comparing regions where oscillations are predicted in the pool-chemical scheme to those observed in the numerical solutions of the transient model, it is clear that the pool-chemical approximation is valid for low flow rates. However, its accuracy decreases as the pressure is increased as shown in Fig. 5. We also note that the accuracy between the pool-chemical approximation and the transient model is higher for the case when fuel is flowing into the reactor with oxygen already present. Furthermore when the flow rates of the reactants are higher, the boundaries predicted by the pool-chemical approximation is significantly different from the transient model. Thus the pool-chemical approximation has limited use when it comes to predicting oscillatory behaviour in the parameter space, and one has to be cautious when utilizing such an approach to approximate such reactions in the semi-batch setting. However, it may be useful as a tool to determine an initial region in parameter space to be analysed using the full model. We have shown that although the reaction scheme is symmetric with respect to the reactants, the regions of oscillatory behaviour are not identical due to the reactants having different heat capacities. However these differences became less apparent as the pressures were increased (see Fig. 1b).

The pool-chemical approximation used here depended critically on the fact that for a gas-phase reaction the volume of the reaction is constant. This is not the case for the more commonly investigated liquid–liquid reactions. It therefore remains an open question whether approximate techniques can be derived to analyse such systems.

Appendix A

A	pre-exponential factor for the oxidation reaction ($\mathrm{m^3\,mol^{-1}\,s^{-1}}$)
c_r	reference concentration (maximum concentration of a species assembled at a temperature T_0 and pressure $\mathcal{P}^o$, $c_\mathrm{r} = \frac{\mathcal{P}^o}{RT_\mathrm{r}}$
c_v	heat capacity of the reaction mixture at constant volume ($\mathrm{J\,K^{-1}\,kg^{-1}}$)
$c_{\mathrm{v},m_\mathrm{U}}$	molar heat capacity of species U at constant volume ($\mathrm{JK^{-1}\,mol^{-1}}$)
$\mathcal{C}$	the concentration of products in the batch reactor ($\mathrm{mol\,m^{-3}}$))
E	activation energy for the oxidation reaction ($\mathrm{J\,mol^{-1}}$)

$\mathcal{F}$	the concentration of fuel in the batch reactor (mol m^{-3})
$\mathcal{F}(0)$	the concentration of fuel at time $t = 0$ (mol m^{-3})
$\mathcal{F}_0$	the concentration of $\mathcal{F}$ in the inflow(mol m^{-3})
n	the number of moles of products ($\mathcal{C}$) produced by the combustion of one mole of fuel ($\mathcal{F}$) with one mole of oxygen ($\mathcal{O}_2$)
$\mathcal{N}_2$	the concentration of nitrogen in the batch reactor (mol m^{-3})
$\mathcal{O}_2$	the concentration of oxygen in the batch reactor (mol m^{-3})
$\mathcal{O}_2(0)$	the concentration of oxygen at time $t = 0$ (mol m^{-3})
$\mathcal{P}^0$	specified pressure at which reaction mixture is assembled (J m^{-}3)
q	the flowrate into the semi-batch reactor (m^3 s^{-1})
Q	exothermicity of the oxidation reaction (J mol^{-1})
R	ideal gas constant (J K^{-}1 mol^{-}1)
S	the surface area of the batch reactor (m^2)
t	time (s)
t_r	reference time-scale, $t_r = \frac{Vc_rR}{S\chi} = \frac{\mathcal{P}^o V}{T_r}\frac{1}{S\chi}$
T	the temperature inside the batch reactor (K)
$T(0)$	the temperature inside the batch reactor at time $t = 0$ (K)
T_a	the temperature of the walls of the batch reactor (ambient temperature) (K)
T_r	reference temperature (K)
T_0	the temperature of the inflow (K)
V	volume of the batch reactor (m^3)
α	the fraction of fuel in the reaction-mixture at time $t = 0$, $\alpha = \frac{\mathcal{F}(0)}{c_r}$
β	the fraction of oxygen in the reaction-mixture at time $t = 0$, $\beta = \frac{\mathcal{O}_2(0)}{c_r}$
γ	the fraction of nitrogen in the reaction-mixture at time $t = 0$, $\gamma = \frac{\mathcal{N}_2}{c_r}$
ρ	density of the reaction mixture (kg m^{-3})
χ	heat transfer coefficient between the reaction mixture and the vessel walls (J s^{-1} m^{-2} K^{-1})

The nondimensionalised terms are labelled with a superscript $*$ and are defined as:

$$A^* = A\frac{\mathcal{P}^{0^2}V}{RT_r^2S\chi}, \qquad E^* = \frac{E}{RT_r}, \qquad \mathcal{F}^* = \frac{\mathcal{F}}{c_r},$$

$$\mathcal{F}^*(0) = \frac{\mathcal{F}(0)}{c_r}, \qquad \mathcal{N}_2^* = \frac{\mathcal{N}_2}{c_r} = \gamma, \qquad \mathcal{O}_2^* = \frac{\mathcal{O}_2}{c_r},$$

$$\mathcal{O}_2^*(0) = \frac{\mathcal{O}_2(0)}{c_r} = \beta, \qquad Q^* = Q\frac{1}{RT_r}, \qquad T^* = \frac{T}{T_r},$$

$$T^*(0) = \frac{T(0)}{T_r}, \qquad T_a^* = \frac{T_a}{T_r}, \qquad T_0^* = \frac{T_0}{T_r},$$

$$k_f^* = q\mathcal{F}_0\frac{R}{S\chi} \quad \text{and} \quad t^* = \frac{t}{t_r}$$

Unless otherwise specified we take the following typical parameter values:

$A = 10^9\,\text{m}^3\text{mol}^{-1}\,\text{s}^{-1}$, $E = 114.7 \times 10^3\,\text{J mol}^{-1}$, $Q = 500 \times 10^3\,\text{J mol}^{-1}$, $S = 5.0 \times 10^{-2}\text{m}^2$, $T_a = 500\,\text{K}$, $\chi = 30\,\text{Js}^{-1}\,\text{m}^{-2}\,\text{K}^{-1}$, $V = 1 \times 10^{-3}\,\text{m}^3$ and

The appropriate values for physical constants are:

$\mathcal{P}^o = \frac{1}{30.0}1.01325 \times 10^5\,\text{Jm}^{-3}$, $R = 8.31441\,\text{JK mol}^{-1}$, and $T_{\text{ref}} = 298\,(\text{K})$.

References

[1] F. Stoessel, O. Ubrich, Safety assessment and optimization of semibatch reactions by calorimetry, J. Therm. Anal. Calorim. 64 (2001) 61.

[2] G. Rabai, I.R. Epstein, pH oscillations in a semibatch reactor, J. Am. Chem. Soc. 114 (1992) 1529.

[3] G. Rabai, I. Hanazaki, Oscillatory reaction in the hydrogen peroxide-sulfite ion-hydrogen ion-hexacynoferrate(II) ion system in a semibatch reactor, J. Phys. Chem. 98 (1994) 2592.

[4] B.A.A. Van Woezik, K.R. Westerterp, Runaway behaviour and thermally safe operation of multiple liquid–liquid reactions in the semibatch reactor: The nitric acid oxidation of 2-octanol, Chem. Eng. Process. 41 (2001) 59.

[5] M.D. Grau, J.M. Nougues, L. Puigjaner, Comparative study of two chemical reactions with different behaviour in batch and semibatch reactors, Chem. Eng. J. 88 (2002) 225.

[6] M.D. Grau, J.M. Nougues, L. Puigjaner, Obtention of the optimal feeding profile in a fed-batch reactor using genetic algorithms, Ind. Eng. Chem. Res. 40 (2001) 1488.

[7] J.M. Nougues, M.D. Grau, L. Puigjaner, Parameter estimation with genetic algorithm in control of fed-batch reactors, Chem. Eng. Process. 41 (2002) 303.

[8] G. Donati, R. Paludetto, Batch and semibatch catalytic reactors (from theory to practice), Catal. Today 52 (1999) 183.

[9] B. Srinivasan, D. Bonvin, Characterization of optimal temperature and feed-rate policies for discontinuous two-reaction systems, Ind. Eng. Chem. Res. 42 (2003) 5607.

[10] M.A. Alos, F. Strozzi, J.M. Zaldivar, A new method for assessing the thermal stability of semibatch processes based on Lyapunov exponents, Chem. Eng. Sci. 51 (1996) 3089.

[11] J.M. Zaldivar, J. Cano, M.A. Alos, J. Sempere, R. Nomen, D. Lister, G. Maschio, T. Obertopp, E.D. Gilles, J. Bosch, F. Strozzi, A general criterion to define runaway limits in chemical reactors, J. Loss Prevent. 16 (2003) 187.

[12] J.F. Griffiths, Reduced kinetic models and their application to practical combustion systems, Prog. Energ. Combust. Sci. 21 (1995) 25.

[13] D.P. Coppersthwaite, J.F. Griffiths, B.F. Gray, Oscillations in the $H_2 + Cl_2$ reaction: experimental measurement and numerical simulation, J. Chem. Phys. 95 (1991) 6961.

[14] P. Gray, Instabilities and oscillations in chemical reactions in closed and open systems, Proc. Roy. Soc., Ser. A 415 (1988) 1.

[15] J.F. Griffiths, S.R. Kay, S.K. Scott, Oscillatory combustion in closed vessels: theoretical foundations and their experimental verification, in: Proceedings of the 22nd Symposium on Combustion, 1988, p. 1597.

[16] P. Gray, J.F. Griffiths, Thermokinetic combustion oscillations as an alternative to thermal explosion, Combust. Flame 78 (1989) 87.

[17] H.S. Sidhu, M.I. Nelson, G.N. Mercer, R.O. Weber, Dynamical analysis of an elementary $X + Y \rightarrow P$ reaction in a continuously stirred tank reactor, J. Math. Chem. 28 (2000) 353.

[18] M.I. Nelson, Flammability limits in a batch reactor: a Semonov model, in preparation.

[19] H.S. Sidhu, M.J. Sexton, M.I. Nelson, G.N. Mercer, R.O. Weber, A simple combustion process in a semibatch reactor, in: R.L. May, G.F. Fitz-Gerald, I.H. Grundy (Eds.), Proceedings of the Fourth Eng. Math. Appl. Conf., EMAC, 2000, pp. 251–254.

[20] M.J. Sexton, L.K. Forbes, An exothermic chemical reaction with linear feedback control, Dynam. Stab. Sys. 11 (1996) 219.

[21] B.F. Gray, M.J. Roberts, A method for the complete qualitative analysis of two coupled ordinary differential equations dependent on three parameters, Proc. Roy. Soc., Ser. A 416 (1988) 361.

[22] P. Gray, S.K. Scott, Chemical Oscillations and Instabilities. Non-linear Chemical Kinetics, Clerendon Press, Oxford, 1990.

[23] H.S. Sidhu, L.K. Forbes, B.F. Gray, Analysis of the unified thermal and chain branching model of hydrocarbon oxidation, Proc. Roy. Soc., Ser. A 449 (1995) 493.