Analysis of combustion waves arising in the presence of a competitive endothermic reaction

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Abstract

We consider travelling wave solutions of a reaction-diffusion system corresponding to a single-step homogeneous premixed combustion scheme competitively coupled with an endothermic reaction. Properties of the travelling combustion fronts, such as the wave speed and the burnt temperature are derived numerically over a range of different parameter values, such as those describing the relative enthalpies, rates and activation energies of the endothermic and exothermic reactions. Unique combustion wave solutions are shown to exist for each distinct combination of the parameter values. These solutions are linearly stable if the heat release from the exothermic reaction is sufficiently large, otherwise the combustion waves develop pulsation. In particular, using a finite element package to numerically integrate the governing partial differential equations, period-1 and period-2 type oscillatory behaviour was observed prior to wave extinction.

1. Introduction

This work concerns the existence and propagation of reaction fronts through reactive media where diffusive processes are present and where a main exothermic reaction is accompanied by an endothermic reaction as well. A number of authors have addressed problems where an independent endothermic process affects the progress of a combustion front [Gray et al. 2002, Please et al. 2003, Simon et al. 2003, 2004, and references therein]; our concern in this paper is with the possibility of *competitive* endothermic and exothermic reactions, where the same reactive material provides the feed for both reactive steps [Hmaidi et al. 2010].

Though most observed physico-chemical phenomena are a consequence of several, often numerous, concurrent or consecutive reactive processes, some of which are exothermic and some endothermic, and a full representation of even the simplest reaction usually comprises a large number, perhaps hundreds, of individual step, much useful understanding may often be gained by considering much simpler "lumped" models which reproduce the essential phenomenology. In some cases, notably when thermal effects are prominent in the process, the simplest useful model comprises a pair of reactions, one exothermic and one endothermic, characterised by different chemical kinetics. These reactions may feed on the same unique reactant material, so-called *competitive* reactions, or each reaction may independently consume a different reactant, so-called *parallel* reactions [Ball et al. 1999]. In the parallel case the coupling between the reactions is solely thermal, whereas in the competitive case there is a second coupling through the reactant consumption.

In contrast to the case of parallel reactions, which has been widely studied as exemplified in the references above, competitive reactions, which are often appropriate to model decomposition or pyrolysis processes [Antal and Varhegyi 1995; Wu et al. 1994], have received little attention, though a study by Calvin et al. [1987] established the existence of combustion wave multiplicity in the case of competing *exothermic* reactions. Whereas, in the parallel case, the net enthalpy production by complete consumption of both reactants is uniquely determined, this is not true for competitive reactions, where the net production depends on the full time history of the process; if the temperature is kept relatively low, by thermal diffusion or other extraneous effect e.g. Newtonian or radiative cooling, the net production may be, counter-intuitively, actually increased. This result will be discussed elsewhere [Hughes et al. 2011, in preparation] in the context of initiation and self-propagation of combustion fronts in the presence of both competitive and parallel endothermic effects..

Hmaidi et al. [2010] have investigated the existence and stability of travelling one-dimensional reaction fronts propagating through a solid reactive slab (infinite Lewis number), effectively extending the work of Matkowsky and Sivashinsky [1978] to the case where heat is lost through a competitive endothermic reaction term. The behaviour of the competitive system was modelled by regarding the endothermic reaction as a perturbation to an exothermic reaction. This necessitated some restrictions on the ordering of the kinetic parameters of the endothermic step. Specifically, the endothermic reaction was assumed to have larger activation energy than the exothermic reaction and a pre-exponential frequency term much greater than that for the exothermic reaction. These assumptions about the relative magnitudes of the pre-exponential frequencies and

the activation energies enabled a large activation energy analysis to be adopted and analytical solutions to be calculated for the burning rate. The analyses also established the existence of regions of oscillatory instability for a number of practical cases. However, the assumptions restricted the analyses to particular regions of the kinetic parameter space.

The purpose of the work reported here is therefore to explore the behaviour of competitive systems over a wider range of values of chemical kinetics and other physical properties of the reactant material and its products. We again consider propagation of a burning front in a reactive material in which the driving exothermic reaction competes with an endothermic reaction which consumes both reactant and heat within the system. Our competitive scheme, similar to that first considered by Hmaidi et al. [2010], neglects heat loss through physical processes such as radiation and conduction, where heat loss is typically modelled by inclusion of Newtonian cooling, or quenching effects through endothermic reactions that occur in parallel or in sequence with the exothermic combustion reaction. It does, however, include diffusion of reactant as well as heat, so that Lewis number effects may be exposed, and lifts the restrictions on the activation energy and pre-exponential frequency of the endothermic reaction.

2. Problem description and mathematical modelling

Since our main purpose is to explore the qualitative phenomenology of competitive reaction processes, we adopt a simple physico-chemical description of the propagation of a burning front through a reactant in one spatial dimension with combustion described by the kinetic scheme: *Reactant* $\rightarrow P_1 + heat$. Additionally, we suppose that heat is lost through a competitive endothermic chemical pathway: *Reactant* $\rightarrow P_2$ - *heat*. A real world example of such a configuration would be a long, insulated cylinder containing a solid fuel undergoing a decomposition reaction, with an appropriate *a priori* averaging over the transverse spatial dimension of the reaction front.

Such a configuration has, for example, been used in laboratory experiments on the burning of ammonium nitrate (AN), in the context of emulsion explosives [Turcotte et al .2008; Chan and Turcotte 2009]. The extensive literature on the dissociation of AN reveals a surprising variety of representations of the chemistry involved. Common to virtually all, however, is the phenomenon of *competitive* processes feeding on the same initial AN resource. Importantly, some are exothermic and some endothermic, and it has been common to assume a lumped representation of just two competing processes, one endothermic, for example [Sinditskii et al, 2005]

$$AN \rightarrow NH_3 + HNO_3$$

and one exothermic

$$AN \rightarrow N_2O + 2H_2O$$

In numerical simulations of the ignition of AN [Hughes et al. 2011], self propagating fronts were not found when values of the kinetic parameters appropriate for ‘pure’ AN were used; this is in accord with the extensive literature on AN combustion. However, for values modified to take a crude account of the effect of additives [Chan and Turcotte

2009], such travelling combustion fronts were observed to develop for wide ranges of initial conditions and parameter values.

2.1 Mathematical model

Following Hmaidi et al. [2010], we consider a system of reaction diffusion equations describing the combustion dynamics. Unlike Hmaidi et al. [2010], however, we allow for the possibility of a non-solid reactant and diffusion of the reactant species. We assume that the reactant undergoes two competitive reactions, one exothermic and one endothermic, and that the reaction products are chemically inert and have no effect on physical properties such as diffusivities. In practice this will rarely be true, but in the spirit of our exploratory investigation we leave refinements of the model for the future.

Arrhenius kinetics are assumed for both reactions, with the endothermic reaction kinetics characterised by the activation energy E_1, the pre-exponential factor A_1 and heat release $-Q_1 < 0$. The exothermic reaction drives the combustion and is characterised by the activation energy E_2, the pre-exponential constant A_2, and heat release $Q_2 > 0$.

The governing equations for the system described above are then simply the heat and mass balance equations accounting for reaction and diffusion of heat and reactant. Similar equations can be found in Calvin et al. [1987].

$$\rho \mathrm{c_p} \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + \rho\left(-Q_1 A_1 e^{-E_1/RT} + Q_2 A_2 e^{-E_{21}/RT}\right)C \tag{2.1.1}$$

$$\rho \frac{\partial C}{\partial t} = \rho D \frac{\partial^2 C}{\partial x^2} - \rho\left(A_1 e^{-E_1/RT} + A_2 e^{-E_{21}/RT}\right)C \tag{2.1.2}$$

Here T and C denote the temperature and reactant mass fraction, respectively. Time and space coordinates (in the laboratory frame) are denoted by t and x, ρ is the density (assumed constant), k is the thermal conductivity, D is the coefficient of mass diffusion, R is the universal gas constant and $\mathrm{c_p}$ is the heat capacity at constant pressure of the reactant.

From the mathematical viewpoint it is convenient to consider a non-dimensional version of the system (2.1.1, 2.1.2). We therefore introduce the dimensionless temperature and space and time coordinates:

$$u = \frac{RT}{E_2}, \quad x' = \sqrt{\frac{\rho Q_2 A_2 R}{k E_2}}\, x, \quad t' = \frac{Q_2 A_2 R}{\mathrm{c_p} E_2} t. \tag{2.1.3}$$

Writing the system (2.1.1, 2.1.2) in terms of (2.1.3) and omitting the primes, the following dimensionless system of equations is obtained:

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} + Ce^{-1/u} - qrCe^{-f/u} \tag{2.1.4}$$

$$\frac{\partial C}{\partial t} = \frac{1}{Le}\frac{\partial^2 C}{\partial x^2} - \Theta Ce^{-1/u} - \Theta Cre^{-f/u} \tag{2.1.5}$$

The new parameters Θ, q, f, r and Le are defined as follows:

$$\Theta = \frac{\mathrm{c_p} E_2}{R Q_2}, \quad q = \frac{Q_1}{Q_2}, \quad f = \frac{E_1}{E_2}, \quad r = \frac{A_1}{A_2}, \quad Le = \frac{k}{\rho \mathrm{c_p} D} \tag{2.1.6}$$

We will refer to the parameter Θ as the exothermicity parameter, q as the ratio of heats, f as the ratio of activation energies, r as the ratio of rate constants and Le as the Lewis number. We note in particular the similarity of the parameterisation (2.1.6) with that of Please et al. (2003). We also note for reference that the important 'channelling parameter' β defined in Hmaidi et al. (2010) can be written in terms of (2.1.6) as

$$\beta = r(q+1) \tag{2.1.7}$$

As discussed by Hmaidi et al. (2010) this parameter reflects the degree to which the endothermic and exothermic reactions compete with one another.

2.2 Travelling wave formulation

Assuming that the temperature and reactant concentration profiles that constitute the combustion fronts may be realised as stationary planar waves, it is natural to consider the model problem in terms of the frame of reference that moves with the combustion front. We therefore seek solutions to (2.1.4, 2.1.5) in the form of stationary fronts moving with a speed v, namely

$$u(x,t) = u(\xi), \quad C(x,t) = C(\xi)$$

where $\xi = x - vt$ is a coordinate in the frame moving with speed v. Invoking this travelling wave ansatz we obtain two ordinary differential equations:

$$u_{\xi\xi} + v u_\xi + C\left(e^{-1/u} - qre^{-f/u}\right) = 0 \tag{2.2.1}$$

$$Le^{-1} C_{\xi\xi} + v C_\xi - C\Theta\left(e^{-1/u} + re^{-f/u}\right) = 0 \tag{2.2.2}$$

Introducing $Y = u_\xi$ and $W = C_\xi$ to denote the derivatives of the temperature u and reactant concentration C, we may write the system (2.2.1, 2.2.2) as a first-order system of ordinary differential equations over $\mathbf{R}^4$.

$$u_\xi = Y \tag{2.2.3}$$

$$Y_\xi = -vY - C\left(e^{-1/u} - qre^{-f/u}\right) \tag{2.2.4}$$

$$C_\xi = W \tag{2.2.5}$$

$$W_\xi = Le\left(-vW + C\Theta\left(e^{-1/u} + re^{-f/u}\right)\right) \tag{2.2.6}$$

The system (2.2.3 – 2.2.6) is considered over an infinite domain and is supplemented with the following boundary conditions, where we have used $U = (u, Y, C, W)^{\mathrm{T}}$ for notational brevity:

$$U \to U^- = (u_b, 0, 0, 0)^T \quad \text{as} \quad \xi \to -\infty \tag{2.2.7}$$

$$U \to U^+ = (0, 0, 1, 0)^T \quad \text{as} \quad \xi \to +\infty \tag{2.2.8}$$

The boundary condition (2.2.7) corresponds to the burnt region where all the reactant has been consumed. The 'burnt temperature' u_b is treated as a free parameter. The boundary condition (2.2.8) corresponds to the unburnt region where the reactant has yet to be consumed and the temperature is at its ambient value, in this case zero. The assumption of zero ambient temperature is assumed here to circumvent the cold boundary problem, which has been discussed by many authors (e.g. see discussion in Weber et al. [1997]). The model considered here also differs from that considered by Hmaidi et al. [2010] in that the initial reactant mass fraction is equal to unity due to the nondimensionalisation.

2.3 Numerical scheme

Solutions to the system (2.2.1, 2.2.2) are obtained through numerical solution of the associated first order system (2.2.3 – 2.2.6). Linearization of (2.2.3 – 2.2.6) about U^+ yields the set of eigenvectors:

$$k^+_{1,3} = (1, \mu^+_{1,3}, 0, 0)^T, \quad k^+_{2,4} = (0, 0, 1, \mu^+_{2,4})^T \tag{2.3.1}$$

with eigenvalues given by

$$\mu^+_1 = -v, \quad \mu^+_2 = -vLe, \quad \mu^+_{3,4} = 0 \tag{2.3.2}$$

Similarly, linearization of (2.2.3 – 2.2.6) about U^- yields the set of eigenvectors:

$$k^-_{1,2} = \left(1, \mu^-_{1,2}, -\Omega_1^{-1}\mu^-_{1,2}(v + \mu^-_{1,2}), -\Omega_1^{-1}{\mu^-_{1,2}}^2(v + \mu^-_{1,2})\right)^T, \quad k^-_{3,4} = (1, \mu^-_{3,4}, 0, 0)^T \tag{2.3.3}$$

with eigenvalues given by

$$\mu^-_{1,2} = \frac{-vLe \pm \sqrt{v^2Le^2 + 4Le\Omega_2}}{2}, \quad \mu^-_3 = -v, \quad \mu^-_4 = 0 \tag{2.3.4}$$

where

$$\Omega_1 = e^{-1/u_b} - qre^{-f/u_b}, \quad \Omega_2 = \Theta(e^{-1/u_b} + re^{-f/u_b}) \tag{2.3.5}$$

We note in particular that $\Omega_2 > 0$.

For fixed values of the parameters v, q, f, r and Le the system (2.2.3 – 2.2.6) is first considered as an initial value problem over $[0, L]$, where L is sufficiently large, with initial conditions given by

$$U_0 = U^- + \varepsilon k^-_1 \tag{2.3.6}$$

where ε is a sufficiently small fixed parameter, which defines a small departure from the unstable point U^- along the unstable direction defined by k_1^-.

The parameters Θ and u_b are considered as free parameters and are adjusted through application of a shooting algorithm based on the standard fourth-order Runge-Kutta integrator. The shooting algorithm is applied with an initial guess for the values of Θ and u_b. The parameters are then adjusted accordingly and the process repeated until the solution at $\xi = L$ fits the corresponding boundary conditions to a specified accuracy.

The solution obtained through implementation of the shooting algorithm is then refined using a relaxation scheme, which is applied iteratively until a solution with a maximum average error of less than 10^{-15} is delivered. The numerical procedure briefly described above is discussed in more detail in Gubernov et al. [2003]. Once an accurate solution and its corresponding set of parameters have been found, solutions corresponding to nearby parameter values are obtained by slightly varying the values for which the solution is known and reapplying the relaxation method, which also provides the updated values of the free parameters Θ and u_b. Repeating this process enables the determination of solutions over a wide range of the control parameters.

3. Combustion wave profiles and properties

The system (2.2.3 – 2.2.6) was solved numerically using the scheme described above. The results were also checked independently by solving the system of partial differential equations (2.1.4, 2.1.5) using the finite element package FlexPDE™. Fig. 1 shows dimensionless temperature and reactant mass fraction combustion wave profiles for Le = 1, f = 2, r = 1, v = 0.355 and q = 1, 2 and 4. The corresponding values of the exothermicity parameter are Θ = 0.98592, 0.75692 and 0.305770, respectively. An interesting feature of the temperature profiles in Fig. 1 is that the burnt temperature varies non-monotonically as q is varied. This is indicative of the complex compensatory interaction between the endothermic and exothermic reactions that is required to maintain a combustion wave of constant speed. Fig. 2a illustrates in more detail how the burnt temperature and exothermicity must vary with q to maintain a constant wave speed of v = 0.355. We note here for clarity that Θ decreases as the combustion reaction becomes more exothermic. Fig. 2a therefore indicates that to maintain a constant wave speed as the heat absorbed by the endothermic reaction increases, the exothermic reaction must compensate in a way that initially increases the burnt temperature up until a point where the endothermic reaction dominates, beyond which the burnt temperature decreases rapidly.

Fig. 2b illustrates how the wave speed varies with the exothermicity parameter for various values of the Lewis number. The remaining parameters have been set as follows: f = 2, q = 1 and r = 1. The figure indicates that for a specific value of the exothermicity parameter, the associated combustion wave has a unique wave speed. This is in contrast to combustion waves subject to radiative heat loss, which typically possess two distinct wave speeds for each value of the exothermicity parameter [Spalding 1957; Gubernov et al. 2004]. The single-valued wave speed seen here is in fact similar to that exhibited by adiabatic combustion waves [Gubernov et al. 2003]. This result highlights the differences that different heat loss mechanisms can have on the resulting combustion wave dynamics.

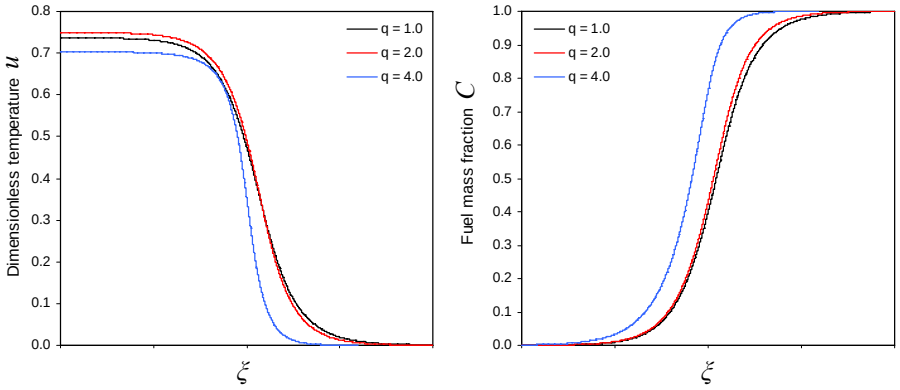

Figure 1. Combustion wave profiles arising in the competitive exothermic-endothermic scheme (2.1.1, 2.1.2) for three different values of the ratio of heats: q = 1.0, 2.0 and 4.0. The left panel shows profiles of the dimensionless temperature u_b, while the right panel shows the corresponding reactant mass fraction C. All of the profiles shown have dimensionless wave speed v = 0.355.

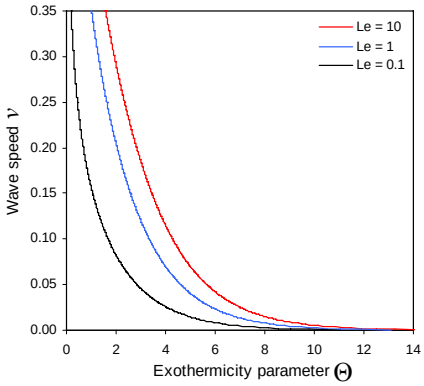

Figure 2. (a) Burnt temperature u_b and exothermicity parameter Θ plotted against the ratio of heats q for combustion waves of constant speed v = 0.355. (b) Wave speed v plotted against the exothermicity parameter Θ for different values of the Lewis number Le = 0.1, 1 and 10.

Fig. 3a illustrates the dependence of the burnt temperature on the ratio of rate constants r required to maintain combustion waves of constant speed v = 0.355, for various values of the Lewis number. In Fig. 3 we have assumed f = 2 and q = 1. For Lewis number sufficiently smaller that unity the burnt temperature decreases monotonically as the ratio of reaction rates increases. In contrast if the Lewis number is sufficiently greater than unity u_b exhibits a monotonic increase as r increases. However, when Le = 1 there is a non-monotonic dependence of u_b on r. Indeed, Fig. 3b attests to a complex interaction similar to that evident in Fig. 2a. In this case, as the rate of the endothermic reaction increases in proportion to the rate of the exothermic reaction, the constant wave speed

can only be maintained by a compensatory change in the exothermicity. Initially this results in a decrease in the burnt temperature to a local minimum. As r increases further the burnt temperature increases to a local maximum before the proportional increase in the endothermic reaction rate causes the burnt temperature to decrease more rapidly.

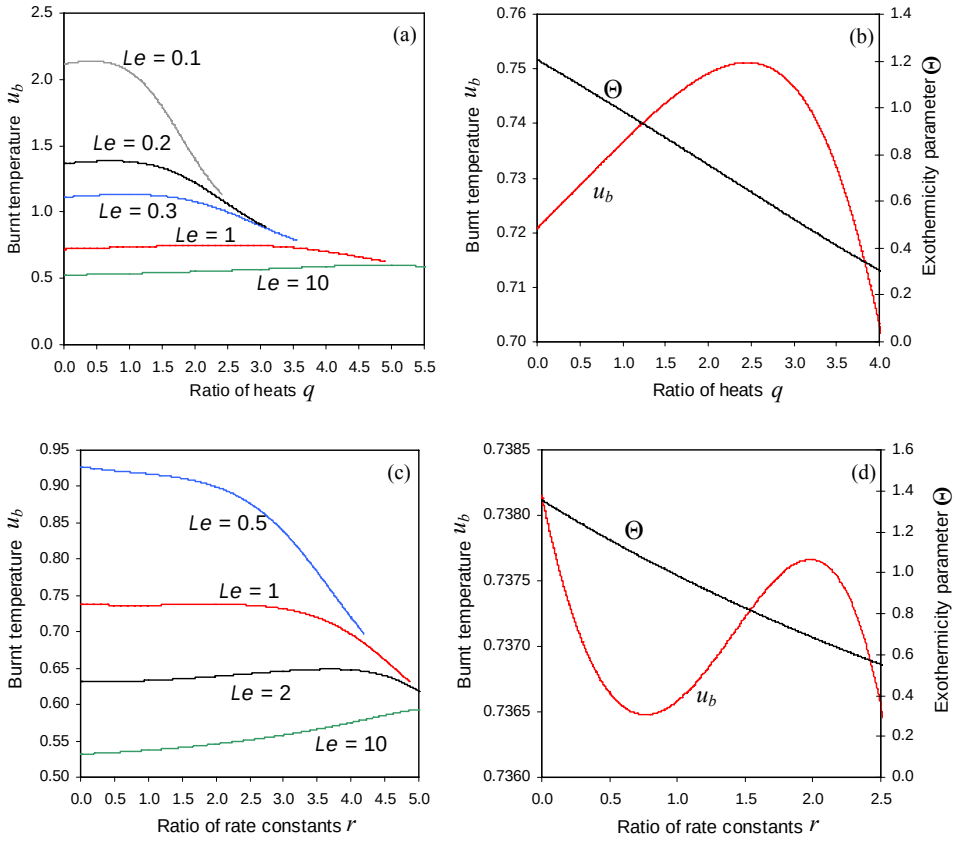

Figure 3. (a) Burnt temperature u_b plotted against the ratio of heats q for combustion waves of constant speed $v = 0.355$. (b) Same as panel (a) but zoomed in to illustrate the complex dependence of u_b on q when $Le = 1$; also included is the exothermicity parameter plotted against q. (c) Burnt temperature u_b plotted against the ratio of rate constants r for combustion waves of constant speed $v = 0.355$. (d) Same as panel (c) but zoomed in to illustrate the complex dependence of u_b on r when $Le = 1$; also included is the exothermicity parameter plotted against r.

4. Stability analysis

Stability refers to the capacity of a solution of a system of differential equations to re-establish itself when perturbed. In the physical world there generally exist enough sources of perturbation so that the only solutions that can be expected to manifest physically are the stable ones. Unstable solutions will generally not be realised in a physical sense. Determining the stability of travelling combustion waves is therefore an

important issue that has bearing on the types of behaviour that are likely to be observed in practice. Moreover, when a solution is unstable, the nature of the instability is important in determining the type of behaviour that can be expected. For example, and as will be shown, unstable travelling combustion waves can inherit oscillatory behaviour due to the presence of a Hopf instability, or Hopf bifurcation, so that ,whilst the travelling wave itself will not be observed in the laboratory, a pulsating combustion front may be. In other instances the travelling combustion wave will be uniformly unstable and will rapidly deteriorate, leaving no possibility of it being observed.

The stability of the travelling wave solutions to (2.2.1-2.2.2) was assessed using FlexPDE^{TM} to numerically integrate the corresponding partial differential equations. In this initial work only the case $f = 2$, $q = r = 1$ is considered. A more comprehensive range of parameter values will be considered in future work.

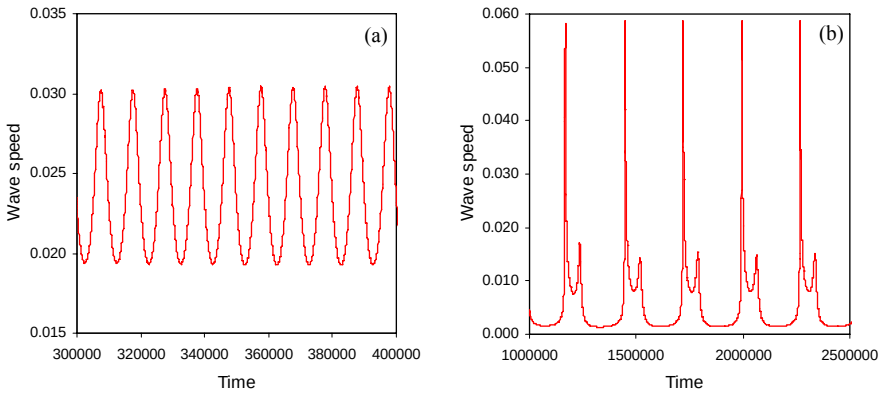

Figure 4. Wave speed derived from solution of (2.1.4-2.1.5) using FlexPDE^{TM} plotted against time for (a) $Le = 10$, $f = 2$, $q = r = 1$, $\Theta = 7.1$, (b) $Le = 10$, $f = 2$, $q = r = 1$, $\Theta = 9.16$.

The travelling reaction front was found to be stable for values of the exothermicity parameter below a certain critical value Θ_h corresponding to a Hopf bifurcation. For example, for $Le = 10$ the Hopf point was found to be $\Theta_h \approx 7.01$. For $\Theta > \Theta_h$ the travelling reaction front was oscillatory unstable. Fig. 4a illustrates the oscillatory nature of the solution for $\Theta = 7.1$, where the wave speed was found to vary periodically between a minimum value of 0.0193 and a maximum value of 0.0304. Unlike Gubernov et al. [2010], who investigated an adiabatic model with a two-step chain branching reaction mechanism, we did not encounter a period doubling route to chaos before extinction. We did locate period-2 type oscillations beyond $\Theta \approx 7.9$. One such example, corresponding to $\Theta = 9.16$, is shown in Fig. 4b. For $\Theta \geq 9.17$ the system exhibits extinction, i.e. numerical integration of (2.1.4-2.1.5) did not yield any solutions. However, the exact nature of the transition to extinction remains open to further investigation.

Fig. 5 illustrates the Hopf and extinction loci for values of the Lewis number $Le \leq 10$. For values of (Θ, Le) to the left of the Hopf curve in Fig. 5, the system possess stable travelling wave solutions that propagate with a unique speed. For values of (Θ, Le) in the region to the right of the Hopf curve solutions are linearly unstable and various pulsating

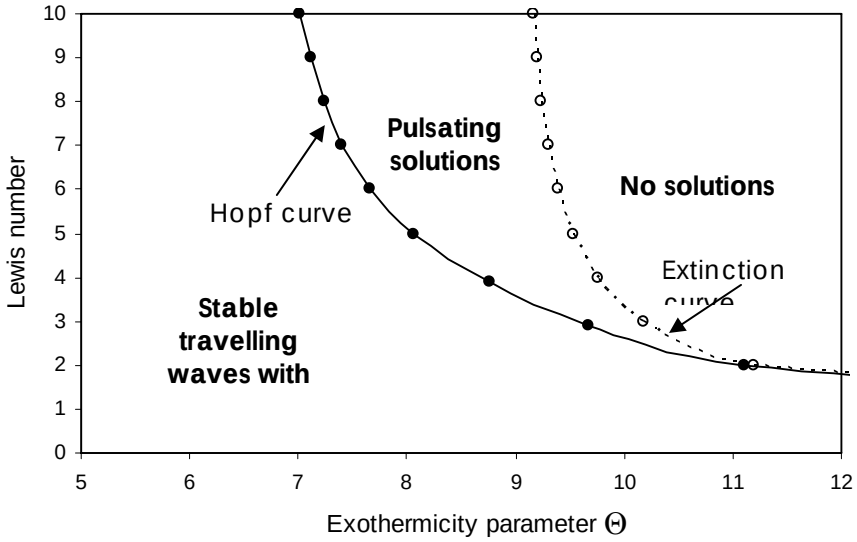

Figure 5. Stability diagram showing Hopf and extinction loci for $f = 2$, $q = r = 1$.

were observed. For (Θ, *Le*) in the region to the right of the extinction curve no solutions were detected using the FlexPDE^{TM} package. As the Lewis number approached unity, the Hopf and extinction loci were observed to coincide, with $\Theta_h \rightarrow \infty$.

5. Discussion and Conclusions

An analysis of combustion wave solutions arising in the presence of a competitive endothermic reaction has demonstrated that a unique travelling wave exists for each value of the exothermicity parameter Θ. Numerical integration of the governing partial differential equations using a finite element package indicates that the combustion waves are linearly stable for values of Θ below a certain value corresponding to a Hopf bifurcation. Above the Hopf point Θ_h the combustion waves were found to be oscillatory unstable. As Θ was increased further the oscillatory solutions were found to evolve period-2 type behaviour before exhibiting wave extinction. Though the parameter values used by Hmaidi et al., and also those used under current investigation by Hughes et al differ from those used here, in both cases the incidence of oscillatory behaviour was found to occur widely in parameter space for condensed phase competitive reactions (infinite Lewis number), which is clearly compatible with the broad parameter range of oscillatory behaviour demonstrated for large Lewis number in Figure 5. In future work the stability properties of the competitive exothermic-endothermic system will be investigated more thoroughly using an Evans function approach.

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