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THERMAL INSTABILITY IN A MODEL CHAIN BRANCHING - CHAIN BREAKING KINETICS.

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Abstract

Thermal instabilities such as thermal explosion and thermal ignition are examined in a two-step reactions mechanism, comprising of a chain-branching and a chain-breaking step. The aim of this study is to examine the influence of the chain-breaking step on these instabilities and then compare our findings with the existing results for the one step model, which is mainly a branching step. The resulting mathematical equations were subjected to a variational method executed on the Mathematica package for the analysis of thermal explosion, while the thermal ignition is amenable to simple integration. These results show that the chain branching step leads to a complete departure from existing results for the one step model. It is established that the Frank-Kamenetskii parameter (δ_{cr}) and the ignition time (τ_i) are monotonically decreasing functions of the heat parameters.

1. Introduction

Instabilities are frequently occurring phenomena in reaction kinetics. In reactive fluid dynamics, these instabilities include thermal explosion, thermal ignition, flame propagation, isothermal oscillations etc. These phenomena are known to have different nature and the way they occur are not the same. For example, thermal explosion occurs at the steady state (time-independent), while thermal ignition is a time dependent process.

In addition, thermal ignition requires an external influence such as spark, compression wave, etc., for its propagation, while thermal explosion is brought about by the thermal properties of the mixture and geometries of the reacting vessel.

The classical theory of thermal explosion and thermal ignition was originally developed to deal with a single irreversible exothermic reaction [Stolin et al.[19], Okoya and Ajadi [2], Boddington et al. [4, 5]]. Subsequently, this study has been extended to a system of two or more reactions [Boddington et al.[6, 7], Nunziato [13], Graham-Eagle [8], Okoya [14, 15, 16], Ajadi and Okoya [2] and Makino [12]]. Mathematically, thermal explosion is measured by a parameter δ, a dimensionless measure of heat release, while the critical Frank-Kamenetskii (δ_{cr}), marks the onset of thermal explosion. Thus, for $\delta > \delta_{cr}$ and a corresponding temperature, θ_{cr}, explosion occurs and for $\delta < \delta_{cr}$, a stable behaviour is obtained. Similarly, thermal ignition may be described as a sharp or unexpected increase in temperature, while the ignition time (τ_i) is the time for which thermal runaway is reached.

Our purpose here is to study the thermal explosion and thermal ignition theory in a model two-step reactions mechanism of the form,

$$F + X \rightarrow 2X \qquad E_1 = \infty, \qquad (I)$$

$$2X + M \rightarrow 2P + M \qquad E_2 = 0, \qquad (II)$$

where E_1 and E_2 are the activation energies of steps (I) and (II) respectively, F is the reactant(Fuel), X is the radical, P is a product, while M is a third or inert body. The elementary step (I) is the branching step, which is a reaction capable of producing a net increase in the number of chain carrier (X), while (II) is the chain-breaking step (termination) leading to the termination of the chain.

In their studies, Boddington et al. [6] considered a system of exothermic simultaneous reactions. Analytical solution was obtained for the special case of two parallel reactions for the slab geometry.

Graham-Eagle and Wake [8] extended this investigation to other geometries such as cylinder and the sphere. As the analytical method considered by Boddington [6] does not always generalize to these geometries, a variational method is used. The results obtained have been observed to be 98% accurate when compared to the exact solution.

In the ignition theory, a variation of (I) and (II) has been investigated by Ayeni [3].

Of particular interest, he provided an upper bound for the ignition time as function of the activation energy.

Ajadi [1], examined the effect of the activation energy parameter as well as the parameter which measures the ratio of the oxygen consumption to that of the fuel, using a one-step porous medium combustion model. The fact that oxygen supports combustion is well established.

Nunziato et al. [13] derived an expression for the thermal ignition time of a homogeneous explosive which is exothermically decomposing by two parallel Arrhenius reactions. The result involves the thermal ignition time of each reaction alone and is expressed in terms of the hypergeometric function. An application of their analysis to the case of nitromethane ignition is illustrated.

Okoya [14] obtained an analytic expression for the thermal ignition time of a two-step reactive system. He employed the effective activation energy approach which allows the elimination of previous difficulties arising in the estimation of ignition time. The result of this novel technique is compared with numerical result as well as those obtained previously, and there is good agreement in all cases.

Varatharajan and Williams [20] obtained an integral expression for the ignition times in terms of the branching reaction, branching and initiation rate parameters, energetic parameters, the activation temperature of the branching in the limit in which the ratio of the initiation rate to the branching rate is small.

More recently, Ajadi and Okoya [2] investigated the influence of variable pre-exponential factor on the ignition time of a system of homogeneous three-step reaction mechnaism. Based on a simple numerical analysis, it is shown that for the ignition time over a broad range of realistic constant, the variation of pre-exponential factor leads to a significant departure from the Arrhenius case.

While the above model mechanism has been well studied for flame propagation [Joulin [11], Niioka [19], etc.], not much has been done on the thermal explosion and thermal ignition theory. Hence the motivation for this work. In addition, the thermal runaway of chemical reactions occur frequently and disastrously in the chemical industries, sometimes with the tragic loss of human lives and considerable damage to property and other economic losses. There would be need to know the safe period (ignition time) prior to the occurrence of this phenomenon. The occurrence of thermal explosion (e.g spontaneous

combustion), resulting in wood forest disaster has given more impetus to this work

2. Mathematical Formulation

The mathematical description of the reaction mechanism is governed essentially by the species and energy equations. Thus, in the absence of convection, we have,

$$\frac{\partial F}{\partial t} = \frac{1}{x^i}\frac{\partial}{\partial x}\left(x^i D_1 \frac{\partial F}{\partial x}\right) - B_1 F X \exp\left(-E_1/(RT)\right), \tag{2.1}$$

$$\frac{\partial X}{\partial t} = \frac{1}{x^i}\frac{\partial}{\partial x}\left(x^i D_1 \frac{\partial X}{\partial x}\right) + B_1 F X \exp\left(-E_1/(RT)\right) - B_2 X^2, \tag{2.2}$$

and

$$\frac{\partial T}{\partial t} = \frac{1}{x^i}\frac{\partial}{\partial x}\left(x^i K \frac{\partial T}{\partial x}\right) + B_1 q_1 F X \exp\left(-E_1/(RT)\right) + B_2 q_2 X^2, \tag{2.3}$$

where D_1, D_2 and K are the diffusion coefficients of the fuel, radical and the thermal conductivity respectively, B_1 and B_2 are the pre-exponential factors for (I) and (II) respectively, x and t are the space and time variables respectively, while i is the geometry factor[i=0(Slab), i=1(Cylinder) and i=2(Sphere)]. Equations (2.1) and (2.2) are the species equations for the fuel and radical, while (2.3) is the energy equation.

The assumption that the reactant consumption is not negligible is known [Boddington et al.[7]]. However, we shall assume in this study that the reactant consumption is negligible, thus (2.1) - (2.3) reduce to the energy equation[see Okoya and Ajadi [2], Boddington et al. [4, 5] etc.],

$$\frac{\partial T}{\partial t} = \frac{K}{x^i}\frac{\partial}{\partial x}\left(x^i D_1 \frac{\partial T}{\partial x}\right) + B_1 q_1 F X \exp\left(-E_1/(RT)\right) + B_2 q_2 X^2, \tag{2.4}$$

with the boundary conditions,

$$T(-1,t) = T_0, \qquad T(1,t) = T_1 \tag{2.5}$$

and the initial condition

$$T(x,0) = T_2 \tag{2.6}$$

2.1 Thermal Explosion Theory

The steady state form of equation (2.4) results in the ordinary differential equation

$$\frac{K}{x^i}\frac{d}{dx}\left(x^i\frac{dT}{dx}\right) + B_1q_1FX\exp\left(-E_1/(RT)\right) + B_2q_2X^2 = 0, \tag{2.7}$$

with the boundary condition

$$\frac{dT}{dx}(x=0) = T(1) = 0. \tag{2.8}$$

We non-dimensionalize (2.7) and (2.8) using the following variables

$$\theta = \frac{T-T_0}{\epsilon T_0}, \quad \epsilon = \frac{RT_0}{E_1} \quad \text{and} \quad \rho = \frac{x}{a}, \tag{2.9}$$

where T_0 is the surrounding temperature, a is the radius of the cylinder or sphere or the half width of the slab. Hence, equations (2.7) and (2.8) become

$$\frac{1}{\rho^i}\frac{d}{d\rho}\left(\rho^i\frac{d\theta}{d\rho}\right) + \frac{B_1q_1FX\exp(-E_1/(RT_0)a^2)}{KRT_0^2}\left(1 + \frac{B_2q_2X\exp(E_1/(RT_0))}{q_1F}\right) = 0, \tag{2.10}$$

r simply,

$$\frac{1}{\rho^i}\frac{d}{d\rho}\left(\rho^i\frac{d\theta}{d\rho}\right) + \delta\left(\exp(\theta/(1+\epsilon\theta)) + \beta\right) = 0 \tag{2.11}$$

This is subject to the realistic boundary condition ($a = 1$)

$$\frac{d\theta}{d\rho}(\rho=0), \quad \theta(\rho=1) = 0, \tag{2.12}$$

$$\text{where } \delta = \frac{B_1q_1FX\exp(-E_1/(RT_0))a^2}{KRT_0^2} \text{ and } \beta = \frac{B_2q_2X\exp(E_1/(RT_0))}{q_1F}$$

are the Frank - Kamemetskii parameter and heat parameter (due to the termination step) respectively.

We now apply the variational technique previously considered in Graham-Eagle et al [8] to calculate δ_{cr} and θ_{cr} in equations (2.11) and (2.12). Consider the functional,

$$F_\delta(\theta) = \int_0^1 \rho^i\left(\frac{d\theta}{d\rho}\right)^2 d\rho - \delta\int_0^1 \rho^i\left(\exp(\theta) + \beta\theta\right)d\rho \tag{2.13}$$

An example of functions satisfying the boundary condition (2.12) is

$$\theta(x) = A\cos\left(\frac{\pi x}{2}\right) + B\cos\left(\frac{3\pi x}{2}\right) \tag{2.14}$$

For the slab ($i = 0$), (2.13) becomes

$$F_\delta(A, B) = \frac{\pi^2}{8}\left(\frac{A^2}{2} + \frac{9}{4}B^2\right) - \delta\int_0^1 (\exp(\theta) + \beta\theta)d\rho,$$

and the equations to be solved are

$$\frac{\partial F_\delta}{\partial A} = 0, \quad \frac{\partial F_\delta}{\partial B} = 0 \tag{2.15}$$

and

$$\left(\frac{\partial^2 F_\delta}{\partial A^2}\right)\left(\frac{\partial^2 F_\delta}{\partial B^2}\right) = \left(\frac{\partial^2 F_\delta}{\partial A \partial B}\right)^2 \tag{2.16}$$

Thus, we solve these system of equations,

$$\frac{\pi^2 A}{8} - \delta\int_0^1 A\cos\left(\frac{\pi x}{2}\right)(\exp(\theta(\rho)) + \beta)\, d\rho = 0 \tag{2.17},$$

$$\frac{9\pi^2 B}{8} - \delta\int_0^1 A\cos\left(\frac{3\pi x}{2}\right)(\exp(\theta(\rho)) + \beta)\, d\rho = 0 \tag{2.18}$$

and

$$\left(\frac{\pi^2}{8} - \delta\int_0^1 A\cos^2(\frac{\pi x}{2})\exp(\theta(\rho))d\rho\right) \times \left(\frac{9\pi^2}{8} - \delta\int_0^1 \cos^2(3\frac{\pi x}{2})(\exp(\theta(\rho))d\rho\right)$$

$$= \left(\delta\int_0^1 \cos(3\frac{\pi x}{2})\cos(\frac{\pi x}{2})\exp(\theta(\rho))\right)^2, \tag{2.19}$$

simultaneously for A, B and δ_{cr}, where $\theta_{cr} = A + B$. The definite integrals in equations (2.17) - (2.19) were discretized using the Simpson numerical method and the equations are then solved numerically on the Mathematica system.

TABLE 1
Variation of Frank-Kamenetskii parameter (δ_{cr}) and θ_{cr} with heat parameter(β)

β	0.0	0.25	0.5	0.75	1.0	1.25	1.5	1.75	2.0
θ_{cr}	1.1672	1.1667	1.1662	1.1655	1.1648	1.1640	1.1631	1.1622	1.1612
δ_{cr}	0.8784	0.7455	0.6476	0.5724	0.5129	0.8065	0.6931	0.6077	0.5410

2.2 Thermal Ignition Theory

The thermal ignition theory is usually based on the assumption that the system is spatially homogeneous or the thermal conductivity is being very poor. Thus equation (2.4) reduces to

$$\frac{dT}{dt} = B_1 q_1 F X \exp(-E_1/(RT)) + B_2 q_2 X^2, \tag{2.20}$$

with the initial condition

$$T(0) = T_0 \tag{2.21}$$

We non-dimensionalize (2.20) - (2.21) using the variables

$$\theta = \frac{T - T_0}{\epsilon T_0}, \quad \epsilon = \frac{RT_0}{E_1} \quad \text{and} \quad \tau = \frac{t}{t_0} \tag{2.22}$$

When (2.22) is substituted into (2.20) and (2.21), we obtain

$$\frac{d\theta}{d\tau} = \delta' \left(\exp(\theta/(1 + \epsilon\theta)) + \beta'\right) \tag{2.23}$$

with the initial condition,

$$\theta(0) = 0, \tag{2.24}$$

where

$$\delta' = \frac{B_1 q_1 E_1 F X \exp(-E_1/(RT_0))}{RT_0^2} \quad \text{and} \quad \beta' = \frac{B_2 q_2 t_0 X^2}{RT_0^2} \text{ are constants.}$$

We may integrate (2.23) to give

$$\tau = \int^{\theta} \frac{du}{\delta' \left(\exp(\theta/(1 + \epsilon\theta)) + \beta'\right)}. \tag{2.25}$$

As $\theta \to \infty$(runaway temperature), $\tau \to \tau_i$. In particular, for $\delta' = 1$, and using the initial condition (2.24). equation (2.25) becomes

$$\tau = \int_0^{\infty} \frac{du}{\left(\exp(\theta/(1 + \epsilon\theta)) + \beta'\right)}. \tag{2.26}$$

In the limit of $\epsilon \to 0$,

$$\tau_i = \frac{\ln(1 + \beta')}{\beta'} \tag{2.27}$$

TABLE 2.
Variation of ignition time (τ_i) with the heat parameter(β').

β'	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5
τ_i	1.00	0.81	0.69	0.61	0.55	0.50	0.46	0.43	0.40	0.38	0.36	0.34	0.32	0.31

3. Conclusion

The solutions of the thermal explosion theory and ignition theory have been presented in Table 1. and Table 2. above. In Table 1., δ_{cr} and the critical temperature (θ_{cr}) is monotonically decreasing function of β. Thus, as more heat is evolved, the tendency for the occurrence of thermal explosion increases. Similarly, Table 2., τ_i is monotonically decreasing function of β'. This also implies that as more heat is evolved from the system, the time to ignition reduces. This is physically reasonable since we have assumed that the rate at which heat is given out is low compared to the production of heat. From the tables, it is observed that the results of the one-step reaction (i.e. $\beta = \beta' = 0$), is in full agreement with the existing literature [Graham - Eagle and Wake [8], Boddington et al. [4, 5] and Zeldovich et al.[21]].

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