IGNITION AND TRANSITION CONDITIONS IN THE THEORY OF COMBUSTION

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Abstract

In branched-chain thermal explosion theory, it is usually impossible to obtain analytical solutions and sometimes a substantial computation may be required to calculate the temperature, activation energy and modiûed Semenov's number at transition from discontinuous to continuous behaviour. Invariably, it is possible to reduce the governing equation to accommodate other important mathematical model in the theory of combustion. With this aspect of the equation, transition temperature, activation energy and Semenov's number can be estimated analytically. Previously obtained results are special cases of ours.

1. Introduction

Using the dimensionless variables, θ, β, Φ, a of the variable approach of the author [6, 7] and the literatures contained there - in, the homogeneous equation for a branched - chain thermal reaction in an adiabatic vessel that modelled the competition between a heat production (due to exothermic reaction) and heat loss to the surroundings (cooling) represented by the standard power - law form for the temperature can be written as

$$\frac{d\theta}{d\tau} = a + \theta^m (1+\beta\theta)^n \exp\left(\frac{\theta}{1+\beta\theta}\right) - \frac{(\beta^{-1}+\theta)^r - \beta^{-r}}{\Phi}, \qquad (1)$$

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where

$$\theta = \frac{E}{RT_0^2}(T - T_0), \qquad (2)$$

$$\beta = \frac{RT_0}{E}, \qquad (3)$$

$$\alpha = \frac{A}{B_0}\left(\frac{\alpha}{\beta T_0}\right)^m \left(\frac{\nu\hbar\rho}{KT_0}\right)^n \exp\left(\frac{1}{\beta}\right), \qquad (4)$$

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$$\Phi = \frac{B_0 Q}{\mu \alpha^r \alpha_0}\left(\frac{\beta T_0}{\alpha}\right)^{m-r}\left(\frac{KT_0}{\nu\hbar\rho}\right)^n \exp\left(-\frac{1}{\beta}\right), \tag{5}$$

$$\tau = B_0 t(\beta T_0/\alpha)^{m-1}(KT_0/\nu\hbar\rho)^n \exp(-1/\beta), \tag{6}$$

$$\mu = \begin{cases} \chi s/V, & \text{If r = 1, for conductive losses} \\ \sigma S\varepsilon/V, & \text{If r = 4, for radiative losses} \end{cases} \tag{7}$$

The initial condition for the exothermic reaction is given by

$$\theta(0) = 0. \tag{8}$$

In the above formulation A is the rate of initiation of radicals, B_0 is the m^{th} order rate constant for the chain branching, C_p is the specific heat capacity, E is the activation energy, h is the planck's constant, Q is the exothermicity per mole reactant, R is the Universal gas constant, S is the surface area, t is the time, T_o is the initial temperature, T is the temperature, V is the volume, α is the energy released, ε is the emissivity of the radiant, K is the Boltzmann's constant, μ is the heat loss term, ν is the vibration frequency, σ is the Stefan-Boltzmann's constant, χ is the heat transfer coefficient, ρ is the density, m is the order of branching reaction, n is the numerical exponent of the pre-exponential factor arising from the Arrhenius rate constant and $n \in \{-2, 0, 1/2\}$, α_0 is a constant number, r is the order of heat loss and $r \in \{0, 1, 4\}$.

Of interest in this formulation are values of β and Φ at which the solution θ is to be determined as a smooth function of β and Φ. In most cases, the value of Φ is ïxed and the control parameter is β.

The nonlinear ordinary differential equation (1) and the initial condition (8) and related problems have been studied both analytically for $\beta = m = 0$ and $r = 1$ (see [4, 5, 9]). In the event that $m \neq 0$, analysis have been carried out both analytically and numerically in [1, 10]. In the above reactions with $\beta = 0$, $\Phi(\theta)$ reaches a maximum after starting from zero, and increase without limit. When β is small ($\beta < \beta_{tr}$), $\Phi(\theta)$ passes first through a maximum, then through a minimum, and finally grows without bound as $\theta \to \infty$. When $\beta = \beta_{tr}$, $\Phi(\theta)$ passes through a point of horizontal inflexion corresponding to the merging of the maximum and minimum. The corresponding values of Φ and θ are referred to as Φ_{tr} and θ_{tr}. The authors of [2, 4, 6, 7] studied the transitional set $\{\Phi_{tr}, \beta_{tr}, \theta_{tr}\}$ under realistic assumptions on equation (1).

This paper reports some exact results for Φ_{tr}, β_{tr} and θ_{tr} and employs an obvious but powerful technique of taking the constant multiple of the $(r + 1)^{th}$ term from the Binomial expansion of the heat loss term on the right hand side of equation (1). Our results conform with readily derived special case of $r = 1$ in [2, 4, 7], allow earlier computational work for $r = 4$ in [6], to be appraised and provide new exact results for the generalized Newton's law of heat exchange.

2. The reduced model problem and result

Sequel to the fact that there is no general analytical solution for equation (1) when $r > 1$ and $a = 0$ [6], it is possible to establish analytically a lower bound for Φ_{tr} that is close to the numerically computed value. We assume that the heat loss term in equation (1) can be represented in the simple form $C\theta^r$, where C is a constant to be determined. More generally, we consider the heat loss term in equation (1) as the general term of the Taylor expansion of $(\beta^{-1} + \theta)^r \beta^r$ about $\theta = 0$ (see [8] for a similar consideration).

With this physically reasonable assumption on the heat loss term, the governing equation reduces to

$$\frac{d\theta}{d\tau} = a + \theta^m(1+\beta\theta)^n \exp\left(\frac{\theta}{1+\beta\theta}\right) - \frac{C\theta^r}{\Phi}, \tag{9}$$

The problem is now defined by equation (9). It is worth noting that equation (9) can be derived for some extreme situations where Newton's law of heat exchange $r = C = 1$ does not describe the typical features of the process: for instance, convective heat transfer to boiling helium is described by a cubic law ($r = 3$ and $C = 1$) [3].

The variation of transient temperature $d\theta/d\tau$ in equation (9) reveals the changing rate of reaction temperature or the difference between heat generated and heat removed. Larger values of $d\theta/d\tau$ reveal that the heat generated is higher than the removed heat. Finally, this accumulated heat leads to the system runaway or even branched-chain thermal explosion. Therefore the temperature variation rate at runaway is $[d^2\theta/d\tau^2]_{cr} = 0$. The modified Semenov's number at the critical point $\theta = \theta_{cr}$ of the system runaway or reduced branched-chain thermal explosion are

$$\Phi_{cr} = C\theta_{cr}^{r}\left\{a+\theta_{cr}^{m}(1+\beta\theta_{cr})^{n}\exp\left(\frac{\theta_{cr}}{1+\beta\theta_{cr}}\right)\right\}^{-1}$$

and

$$\Phi_{cr} = Cr\theta_{cr}^{r-1}[m\theta_{cr}^{m-1}(1+\beta\theta)^{n}+n\beta\theta_{cr}^{m}(1+\beta\theta_{cr})^{n-1}+\theta_{cr}^{m}(1+\beta\theta_{cr})^{n-2}]^{-1}\exp\left(-\frac{\theta_{cr}}{1+\beta\theta_{cr}}\right). \quad (11)$$

For the same value of Φ_{cr} in equation (10) and (11) when a = 0, we can obtain the quadratic equation

$$(m-r)(1+\beta\theta_{cr})^{2}+n\beta\theta_{cr}(1+\beta\theta_{cr})+\theta_{cr}=0. \quad (12)$$

The solutions of equation (12) depend on the sign of the quantity

$$D=(1+n\beta)^{2}+4\beta(m-r). \quad (13)$$

When D > 0, the two roots are real and unequal with the lower branch of the curves representing ignition while the higher branch of the curve represents extinction. Clearly, the case of D < 0, corresponds to a complex conjugate pair of roots which is not admissible. The special case of D = 0 admits repeated roots for which transition to continuous behaviour prevails and criticality is lost. This implies

$$\beta_{tr}=\beta_{tr}(m,n,r)=\left(\frac{\sqrt{r-m}-\sqrt{r-m-n}}{n}\right)^{2}, \quad (14)$$

provided $0\le m<r$ and m + n < r. Substituting equation (14) into the solution of (12) gives the transitional value of θ as

$$\theta_{tr}=\theta_{tr}(m,n,r)=\frac{(\sqrt{r-m}+\sqrt{r-m-n})^{2}\sqrt{r-m}}{\sqrt{r-m-n}}, \quad (15)$$

with $0\le m<r$ and m + n < r. We now turn our attention to the transitional value of Φ. A similar picture to β and θ emerges in the critical value of Φ. However, it is straightforward but laborious to show that

$$\Phi_{tr}=\Phi_{tr}(m,n,r)=C\left(\frac{2n^{2}(r-m)}{n^{2}+(n-2(r-m))Z}\right)^{r-m}\left(\frac{2n}{n-Z}\right)^{-n}\exp\left(\frac{-2n(r-m)}{n+Z}\right), \quad (16)$$

$Z=(\sqrt{r-m}-\sqrt{r-m-n})^{2}$ $0\le m<r$

We observe that a special case of Semenov's treatment occurs when m = n = 0 and r = 1 in the above analysis. Thus, the transitional points of activation energy, temperature excess, Semenov's dimensionless number are $\beta_{tr}^{Sem}=\beta_{tr}(0,0,1)=1/4$, $\theta_{tr}^{Sem}=\theta_{tr}(0,0,1)=4$ and $\Phi_{tr}^{Sem}=\Phi_{tr}(0,0,1)=4\exp(-2)$, respectively.

Furthermore, from the analytical solutions (14)-(16) we notice the following profiles:

(i) For fixed values of m and n, β_{tr} is a monotonically decreasing function of r.

(ii) For fixed values of m and n, θ_{tr} is a monotonically increasing function of r.

(iii) For fixed values of m and n, Φ_{tr} increases with increasing r.

3. Conclusions

In a steady reaction and no chemical consumption up to the time of ignition, we can obtain the following results.

(i) The method expounded is quite general and enables the precision of recent work (Okoya [6], [7] and the references contained there-in) to be assessed.

(ii) The new results for transition of parameters in equations (14)-(16) are adequate for the generalized Newton's law of heat exchange.

(iii) Φ_{tr} depends on the constant C and we modify the constant to get the 'best' choice consistent with the restrictions in the approximate procedure. Hence it is a good estimate that can be remarkably close to the numerically computed values for the branched-chain thermal explosion.

(iii) The ex ıct solutions (14) and (15) which are good for the situation in (ii) are seen to underestimate the computation of transitional values for branched - chain thermal explosion and as such large relative errors are encountered in the study.

References

[1] Ayeni, R.O., Okedoye, A.M., Adegbie, K.S. and Okoya, S.S., 2003. Eûects of heat loss on ignition times in the theory of branched-chain explosions. *The Journal of the Mathematical Association of Nigeria* (ABACUS) 30, 2A, 52-57, 2003.

[2] Boddington, T., Gray, P. and Robinson, C., 1979. Thermal explosions and the disappearance of criticality at small activation energies: exact results for the slab. *Proc. Roy. Soc.* Lond. A 368, pp. 441-461.

[3] Kubicek, M. and Hlavacek, V., 1983. Numerical solutions of nonlinear boundary value problems with applications. Prentice-Hall, New Jersey.

[4] Luo, K.M., Lu, K.T. and Hu, K.H., 1997. The critical condition and stability of exothermic chemical reaction in a non-isothermal reactor. *J. Loss Prev. Process Ind.* 10 (3), 141-150.

[5] Makino, A., 2003. Ignition delay and limit of ignitability of a single sodium droplet: theory and experimental comparison. *Combustion and Flame* 134, pp. 149-152.

[6] Okoya, S.S., 2005. Radiative ignition of a branched-chain thermal reaction. Proceedings of the fourth Mediterranean Combustion Symposium, Lisbon, Portugal. (Edited by Prof. F. Beretta, Prof. N. Selcuk and M.S. Mansour), pp. 1-9.

[7] Okoya, S.S., 2006. Disappearance of criticality in a branched-chain thermal explosion with heat loss. *Combustion and Flame* 144 (1-2), pp. 410- 414.

[8] Okoya, S.S., 1996. Some exact solutions of a model nonlinear reaction diûusion equation. International Communications in Heat and Mass Transfer, 23(7), 1043-1052.

[9] Semenov, N.N., 1959. Some problems in chemical kinetics and reactivity part 2, Pergamon Press. London.

[10] Varatharajan, B. and Williams, F.A., 2000. Ignition times in the theory of branched-chain thermal explosions. *Combustion and Flame* 121, pp. 551-554.