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Approximate critical conditions in thermal explosion theory for a two-step kinetic model

S. O. Ajadi · O. Nave

Abstract Approximate critical conditions for a thermal explosion problem is developed for a two-step reactions based on theories of Semenov and Frank-Kamenetskii. The aim is to examine the contributions of the radical termination step and the temperature dependent pre-exponential factor on the critical parameters within the framework of classical stationary and non-stationary theories. In the non-stationary case, a more general expression for the critical Semenov parameter (Ψ_{cr}) and critical temperature (θ_{cr}) were obtained by asymptotic procedure. In the stationary case, numerical estimates for the critical Frank-Kamenetskii parameter (δ_{cr}) and the critical temperature (θ_{cr}) were obtained by variational method technique. It was observed that the Semenov and Frank-Kamenetskii parameters are greatly influenced by the termination step and the variable pre-exponential factor. Apart from elucidating hitherto unknown features in the theory of thermal explosion, the results are more general as some known results are easily recovered.

Keywords Thermal explosion · Asymptotic procedure · Two-step reaction · Radical termination

S. O. Ajadi · O. Nave
Department of Mathematics, Ben-Gurion University of Negev, PO Box 653, 84105 Beer-Sheva, Israel

O. Nave
e-mail: naveof@cs.bgu.ac.il

S. O. Ajadi (✉)
Department of Mathematics, Obafemi Awolowo University, Ile Ife 220005, Nigeria
e-mail: sajadi@oauife.edu.ng; sajadi@bgu.ac.il; soajadi@yahoo.co.uk

1 Introduction

The studies and investigations of the theory of thermal explosion are not only relevant to the development of physics of thermal explosion but also to fundamental branches of knowledge such as chemical kinetics and heat transfer theory. The phenomenon of thermal explosion is used in the laboratory as a method of physicochemical investigation. In most cases, the practical interest in thermal explosion processes arises mainly from problems of industrial safety in some operations with explosive systems(chemical storage, processing, coal mining, etc.).
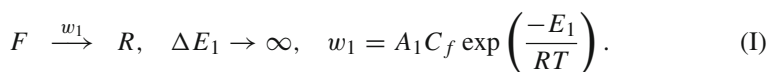
The theory of thermal explosion was initiated by Semenov and Frank-Kamenetskii several decades ago. Semenov (1928) considered the classical problem of a spatially homogeneous gaseous thermal explosion model, while Frank-Kamenetskii (1939) considered the impossibility of the steady state represented as the point where the heat loss is tangent to the heat of reaction curve [22]. Thus, Semenov theory of self-ignition follows the time variation of spatially averaged temperature of the reacting gas mixture in a vessel in order to determine the threshold at which the temperature rapidly increases in a seemingly boundless manner. The Frank-Kamenetskii's spontaneous ignition analysis involves a delineation of the conditions under which the steady state energy equation possesses a physically valid solution from those under which it does not. In a response to Semenov and the Frank-Kamenetskii theories, several works in this direction have been reported in literature, further developments in the Semenov model have been undertaken [1–22].

The pre-exponential factor is a very important thermo-physical parameter in the kinetic theory of gases but is often assumed constant. It characterises the total number of collisions of molecules at the average thermal velocity, which in turn affects the rate of reactions. Thus, in recent times, the use of the temperature dependent pre-exponential factor is on the increase [1–3]. In particular, [1] used a power law temperature dependent pre-exponential factor to study the critical behaviour in a three step reactions kinetics model. The effect of chain termination reaction step on the thermal explosion parameter was established based on the Frank-Kamenetskii thermal explosion theory.
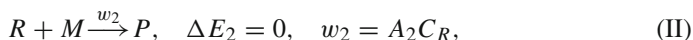
Most of the works reported in literature in the direction of Semenov theory were directed at one-step reaction system. But in reality, a reaction involving reactants(fuels) leads to liberation of the chain-carriers(radicals) and need to be accounted for. Motivated by this, the present work extends the classical one-step reaction to a two step reaction system by adding the chain termination step. Approximate and improved approximate Semenov number were obtained by the Semenov and an improved approximation by the Mischenko and Rozov asymptotic technique respectively. Furthermore, the thermal explosion theory of the steady state system has been considered using a variational method, leading to the determination of numerical estimates for the Frank-Kamenetskii parameter (δ_{cr}) and the critical temperature (θ_{cr}).

2 Problem formulation and basic equation

We consider a system of exothermic reactions occurring in a closed vessel in the form
Initiation:

$$F \xrightarrow{w_1} R, \quad \Delta E_1 \to \infty, \quad w_1 = A_1 C_f \exp\left(\frac{-E_1}{RT}\right). \tag{I}$$

Termination:

$$R + M \xrightarrow{w_2} P, \quad \Delta E_2 = 0, \quad w_2 = A_2 C_R, \tag{II}$$

where F is the fuel and R is the radical, M is the inert (third) body, P is the product, E_1 and E_2 are the activation energies of the initiation and termination steps respectively, w_1 and w_2 are the local reaction rates of the initiation and termination steps respectively. Let W_F and W_R be the global reaction rates for the fuel and radical, then

$$W_F = -w_1, \quad \text{and} \quad W_R = w_1 - w_2. \tag{III}$$

A typical example of the reaction scheme (I–II) is the thermal decomposition of nitromethane (CH_3NO_2) at low pressure, given by

$$CH_3NO_2 \to CH_3^\bullet + NO_2, \quad E_1 = 53,600 \, kJ,$$
$$\frac{1}{2}CH_3^\bullet \to C_2H_6 + \text{heat}, \quad E_2 = 0,$$
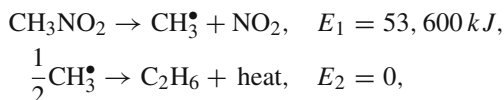
where $CH_3^\bullet$ is the methyl radical formed and consumed in (I) and (II) respectively [12]. Nitromethane is regarded as a very good propellant from the point of view of its physical properties and handling.

A mathematical statement of the problem, which satisfy the above premises, leads to the familiar equations of the classical theory for the a system of first-order reactions that occur in the layer $-h < x < h$

$$\frac{\partial C_F}{\partial t} = D_1 \frac{\partial^2 C_F}{\partial x^2} - w_1 = D_1 \frac{\partial^2 C_F}{\partial x^2} - A_1 C_F \exp\left(\frac{-E_1}{RT}\right), \tag{1}$$

$$\frac{\partial C_R}{\partial t} = D_1 \frac{\partial^2 C_R}{\partial x^2} + w_1 - w_2 = D_1 \frac{\partial^2 C_F}{\partial x^2} + A_1 C_F \exp\left(\frac{-E_1}{RT}\right) - A_2 C_R, \tag{2}$$

and

$$\rho c_p \frac{\partial T}{\partial t} = K \frac{\partial^2 T}{\partial x^2} + Q_1 A_1 C_f \exp\left(\frac{-E_1}{RT}\right) + Q_2 A_2 C_R - \frac{S\chi}{V}(T - T_0). \tag{3}$$

(1) and (2) are the equations for the concentration of the fuel (C_F) and radical (C_R) respectively, while (3) is temperature field (T) equation. In as much as the reaction is symmetric, it will suffice to consider the equations in the half-layer $0 < x < h$. Thus the boundary conditions for the system (1)–(3) are the general Newtonian exchange of heat and the constancy of the temperature at the wall surfaces [22]

$$x = 0, \quad \frac{dT}{dy} + \frac{H}{K}(T - T_0) = 0 \quad \text{and} \quad x = \pm h, \quad T = T_0 \text{ on } \Omega. \tag{4}$$

The initial conditions are specified by the constancy of the reactants and temperature over the entire vessel volume:

$$C_F(0) = C_{F0}, \quad C_R(0) = C_{R0} \quad \text{and} \quad T(0) = T_0, \tag{5}$$

where C_F, C_R and T are the fuel concentration, radical concentration and temperature respectively, $A_1(T) = a_1 T^m$ and $A_2(T) = a_2 T^n$ are the variable pre-exponential factors for the initiation and termination reactions respectively, Q_1 and Q_2 are the heat of reactions for the initiation and termination reactions respectively, T_0 is the ambient temperature, S is the surface area, χ is the heat transfer coefficient, K is the thermal diffusivity, Ω is the surface of the vessel walls, and D_1 and D_2 are the fuel and radical diffusivities respectively, while m and n are numerical exponents.

By assuming negligible reactant diffusivities ($D_1 = D_2 = 0$) [4,5,15] and using the following dimensionless variables:

$$\eta = \frac{C_F}{C_{F0}}, \quad \xi = \frac{C_R}{C_{F0}}, \quad \theta = \frac{T - T_0}{\beta T_0}, \quad t' = a_1 \exp\left(\frac{-1}{\beta}\right) t,$$

$$\text{Bi} = \frac{H}{K}, \quad \beta = \frac{RT_0}{E} \quad \text{and} \, x' = \frac{x}{h}.$$

After dropping primes, the dimensionless governing Equations (1)–(3) become:

$$\frac{d\eta}{dt} = -\eta(1 + \beta\theta)^m \exp\left(\frac{\theta}{1 + \beta\theta}\right), \tag{6}$$

$$\frac{d\xi}{dt} = \eta(1 + \beta\theta)^m \exp\left(\frac{\theta}{1 + \beta\theta}\right) - \lambda\xi(1 + \beta\theta)^n, \tag{7}$$

$$\gamma\frac{\partial\theta}{\partial t} = \frac{1}{\delta}\frac{\partial^2\theta}{\partial x^2} + \eta(1 + \beta\theta)^m \exp\left(\frac{\theta}{1 + \beta\theta}\right) + \mu\xi(1 + \beta\theta)^n - \Psi\theta, \tag{8}$$

$$\eta(0) = 1, \quad \xi(0) = \xi_0, \quad \theta(0) = 0, \tag{9}$$

and

$$\frac{\partial\theta}{\partial x}(0) + \text{Bi}\,\theta(0) = 0, \quad \text{and} \quad \theta(1) = 0, \tag{10}$$

where

$$\gamma = \frac{\rho c_p R T_0^2}{C_{F0} Q_1 E}, \quad \Psi = \frac{S R T_0^2 \chi \exp\left(\frac{1}{\beta}\right)}{a_1 Q_1 E C_{F0} V \rho c_p}, \quad \xi_0 = \frac{C_{R0}}{C_{F0}}, \quad \lambda = \frac{a_2}{a_1}\xi_0 \exp\left(\frac{1}{\beta}\right),$$

$$\delta = \frac{Eh^2 q_1 a_1 C_{F0}}{K R T_0^2 \exp\left(\frac{1}{\beta}\right)},$$

where, $q = \frac{Q_1}{Q_2}$ and $\mu = q\lambda$, β is the dimensionless activation energy parameter, η and ξ are the dimensionless fuel and radical concentrations respectively, θ is temperature, Ψ is the heat loss parameter (Semenov parameter), while γ is the reciporcal of the adiabatic temperature rise and χ is the coefficient of heat transfer, ξ_0, a_1, and a_2 are constants.

Solution of the general system of Equations (6)–(10) present great mathematical difficulties. Therefore, approximate ways of approaching the problem-known as the stationary and the non-stationary theory of thermal explosion—have been developed within the framework of classical theories.

3 Non-stationary theory

At the commencement of the reaction, no heat is released by the system and therefore no heat is loss. As the reaction proceeds, the system of equations thus reduce to:

$$\frac{d\eta}{dt} = -\eta(1 + \beta\theta)^m \exp\left(\frac{\theta}{1 + \beta\theta}\right), \tag{11}$$

$$\frac{d\xi}{dt} = \eta(1 + \beta\theta)^m \exp\left(\frac{\theta}{1 + \beta\theta}\right) - \lambda\xi(1 + \beta\theta)^n, \tag{12}$$

$$\gamma\frac{d\theta}{dt} = \eta(1 + \beta\theta)^m \exp\left(\frac{\theta}{1 + \beta\theta}\right) + \mu\xi(1 + \beta\theta)^n - \Psi\theta, \tag{13}$$

$$\eta(0) = 1, \quad \xi(0) = \xi_0, \quad \theta(0) = 0. \tag{14}$$

The profiles of η, ξ and θ for an adiabatic Arrhenius system is in line with the physics of the problems as shown in Fig. 1.

3.1 Semenov approximation

Based on the Semenov criterion, we ignore reactant consumption(as is usually done in thermal explosion theory) by setting

$$\eta = 1 \quad \text{and} \quad \xi = \xi_0, \tag{15}$$

which corresponds to the zero-order approximation ($\gamma \to 0$). The energy balance Equation (13) reduces to

$$\gamma\frac{\partial\theta}{\partial t} = (1 + \beta\theta)^m \exp\left(\frac{\theta}{1 + \beta\theta}\right) + \Lambda(1 + \beta\theta)^n - \Psi\theta = f(\theta; \beta) \equiv q_+ - q_-, \tag{16}$$

where q_+ and q_- are the heat produced and heat loss respectively and $\Lambda = \mu\xi_0$. The criterion for thermal runaway are identified by the two relations:

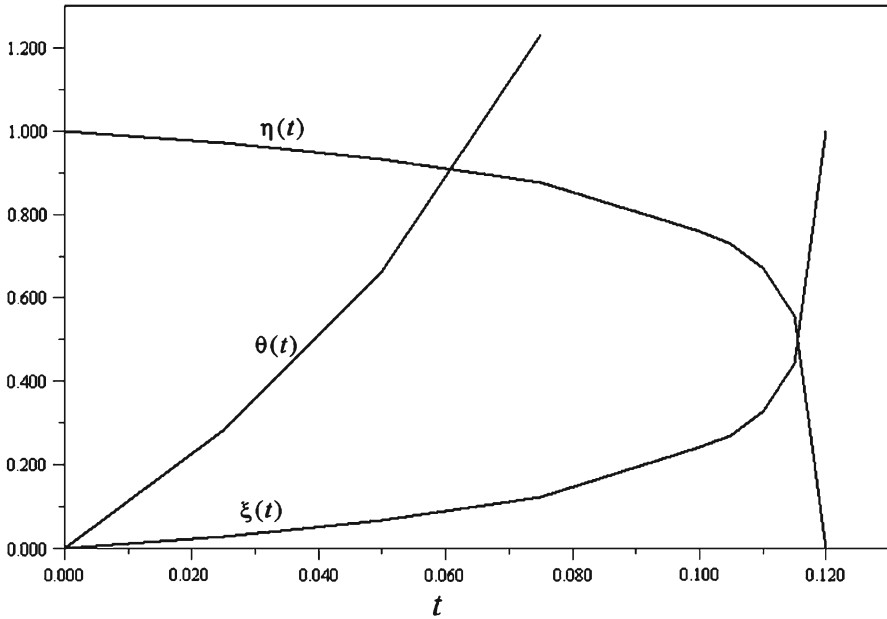$$q_+ = q_- \quad \text{and} \quad \frac{dq_+}{d\theta} = \frac{dq_-}{d\theta}, \tag{17}$$

Fig. 1 Plots of $\theta(t)$, $\eta(t)$ and $\xi(t)$ vs t, $\lambda = .01$, $\beta = .01$, $q = 1$

where $f = (1 + \beta\theta)^m \exp\left(\frac{\theta}{1+\beta\theta}\right) + \mu\xi_0(1 + \beta\theta)^n - \Psi\theta$, and Eq. (17)a refers to the meeting point of the heat loss line and the curve of heat of reaction, while (17)b represents the point (critical) at which the line is tangent to the curve. Using Eq. (17), we have

$$(1 + \beta\theta)^m \exp\left(\frac{\theta}{1 + \beta\theta}\right) + \Lambda(1 + \beta\theta)^n - \Psi\theta = 0, \qquad (18)$$

and

$$(1 + \beta\theta)^{m-2} \exp\left(\frac{\theta}{1 + \beta\theta}\right) + m\beta(1 + \beta\theta)^{m-1} \exp\left(\frac{\theta}{1 + \beta\theta}\right)$$
$$+ n\Lambda(1 + \beta\theta)^{n-1} - \Psi = 0. \qquad (19)$$

The combination of (18) and (19) leads to

$$(1 + \beta\theta)^2 - \theta[1 + m\beta(1 + \beta\theta)] + \Lambda[(1 + \beta\theta) - n\theta]\theta^{1+n-m}\left(\frac{-\theta}{1 + \beta\theta}\right) = 0. \qquad (20)$$

Taking asymptotic expansion of the non-linear term in β, (20) leads to the quadratic equation

$$[(1 - m)\beta^2\theta^2 - \{1 - [(2 - m) + \Lambda e^{-1}(1 - n)]\}\theta + (1 + \Lambda e^{-1}) = 0, \qquad (21)$$

whose solutions are

$$\theta = \theta_I = (1 + \Lambda e^{-1})\{1 + [(2-m) + \Lambda e^{-1}(1-n)]\beta\} + O(\beta^2) \qquad (22a)$$

or

$$\theta = \theta_E = \frac{1 - [(2-m) + \Lambda e^{-1}(1-n)]\beta}{(1-m)\beta^2} - \theta_I, \qquad (22b)$$

where the critical temperature θ_I and θ_E refers to the ignition and extinction temperature respectively. The critical point θ_E is usually neglected due to the fact that it is extremely large to be considered a critical point [21]. Thus, the only realistic critical point is the ignition temperature $\theta_{cr} = \theta_I$. The expression for the approximate Semenov parameter can be obtained by substituting $\theta_{cr} = \theta_I$ into Eq. (18). Thus

$$\Psi_{cr} = \frac{(1 + \beta\theta_{cr})^m \exp\left(\frac{\theta_{cr}}{1+\beta\theta_{cr}}\right) + \Lambda(1 + \beta\theta_{cr})^n}{\theta_{cr}}. \qquad (23)$$

In the particular case of high activation energy asymptotics ($\beta \to 0$) and $\xi_0 = 0$, we recovered the the classical Semenov conditions for thermal runaway

$$\Psi_{cr} = e \quad \text{and} \quad \theta_{cr} = 1. \qquad (24)$$

One of the problems which concerns the non-stationary theory is the displacement of the thermal explosion limit caused by the combustion of material during the induction period, i.e. the variation of Ψ_{cr} with γ. For a normal non-degenerate system, this variation merely introduces a correction, but it becomes very significant for large values of γ(system with a relatively small heat of reaction). The derivation of a new approximate criterion starts from the approximate criterion of using asymptotic analysis. For a one-step model(first order reaction), [19] obtained asymptotic solution based on the assumption of infinite activation energy as

$$\Psi_{cr} = e\left[1 - \bar{\Omega}(\gamma)^{2/3}\right], \qquad (25)$$

where $\bar{\Omega} = 2.85$. Further approximations by [8,13] led to $\bar{\Omega} = 2.52$ and $\bar{\Omega} = 2.95$ respectively.

In order to get better approximation of (25), [5,14] have made use of the approximation formula [16]

$$\Psi_{cr} = eS(\beta)\left[1 - 2^{\frac{2}{3}}\Omega_0 Z(\beta)\gamma^{\frac{2}{3}} + \frac{4}{9}V(\beta)\gamma \ln\left(\frac{1}{\gamma}\right)\right] + O(\gamma + \beta^2), \qquad (26)$$

where $eS(\beta)$, $Z(\beta)$ and $V(\beta)$ are as defined in Appendix A. For the problem under consideration, after rigorous calculation, we obtain

$$
eS(\beta) = \frac{(e+n) + \left\{ (em+n\Lambda)(1+\Lambda e^{-1}) - (e+n)\left[(2-m)+\Lambda e^{-1}(1-n) \right] \right\} \beta}{1+\Lambda e^{-1}},
$$

$$
Z(\beta) = \frac{1+\Lambda e^{-1}}{(1-\Lambda e^{-1})^{1/3}} \left\{ 1 + \left[(2-m)+\Lambda e^{-1}(1-n) \right. \right.
$$
$$
\left. \left. - \frac{1+\Lambda e^{-1}}{3(1-\Lambda e^{-1})} \left(m - \Lambda e^{-1}+n\Lambda e^{-1} \right) \right] \beta \right\},
$$

$$
V(\beta) = (1+\Lambda e^{-1})^2 \left\{ (1 - 2\Lambda e^{-1}) + 2\left[(1+\Lambda e^{-1})(1+m - \Lambda e^{-1}+n\Lambda e^{-1}) \right. \right.
$$
$$
+ (1 - 2\Lambda e^{-1})(2 - m+\Lambda e^{-1} - n\Lambda e^{-1}) \tag{27}
$$
$$
\left. \left. - \frac{(1+\Lambda e^{-1})(1 - 2\Lambda e^{-1})}{(1 - \Lambda e^{-1})} (m - \Lambda e^{-1}+n\Lambda e^{-1}) \right] \beta \right\}
$$

Substituting (27) into (26) we obtain a generalized expression from which special cases could be recovered. For example, for $m = n = \beta = \Lambda = 0$, we recovered [14] as

$$
\Psi_{cr} = e \left[1 - 2.946(\gamma)^{2/3} + \frac{4}{9}\gamma \ln \frac{1}{\gamma} \right]. \tag{28}
$$

The case of $m = n = \Lambda = 0$, we also recovered [5] as

$$
\Psi_{cr} = e(1 - 2\beta) \left[1 - 2.946(1 + 2\beta)\gamma^{\frac{2}{3}} + \frac{4}{9}(1 + 6\beta)\gamma \ln \left(\frac{1}{\gamma} \right) + O(\gamma + \beta^2) \right]. \tag{29}
$$

In a recent work, the case $n = \Lambda = 0$, we recovered [3] as

$$
\Psi_{cr} = e \left[1 + 2(m - 1)\beta \right] \left\{ 1 - 2.946 \left[1 + \left(2 - \frac{4}{3}m \right) \beta \right] \gamma^{\frac{2}{3}} \right.
$$
$$
\left. + \frac{4}{9} \left[1 + 2(3 - m)\beta \right] \gamma \ln \left(\frac{1}{\gamma} \right) + O(\gamma + \beta^2) \right\}. \tag{30}
$$

The plot of Ψ_{cr}, θ_{cr} against γ, β, Λ are shown in Figs. 2,3,4,5,6, and 7.

4 Time-independent theory of thermal explosion

The time-independent theory of thermal explosion is based on the assumptions that the reactant mixture is motionless, that the heat losses are determined by the thermal conductivity of the reacting mixture and are proportional to the temperature gradient and that the reactant consumption is negligible. The theory of thermal explosion is viewed as the sudden impossibility of a stationary reaction in which the heat produc-
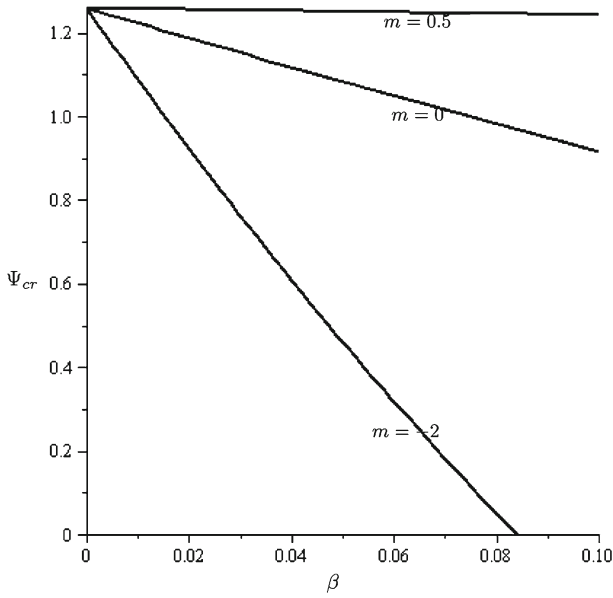
Fig. 2 Ψ_{cr} vs β for $n = -2$, $\gamma = 0.05$, $\Lambda = 0.05$ for $m = \{-2, 0, 0.5\}$
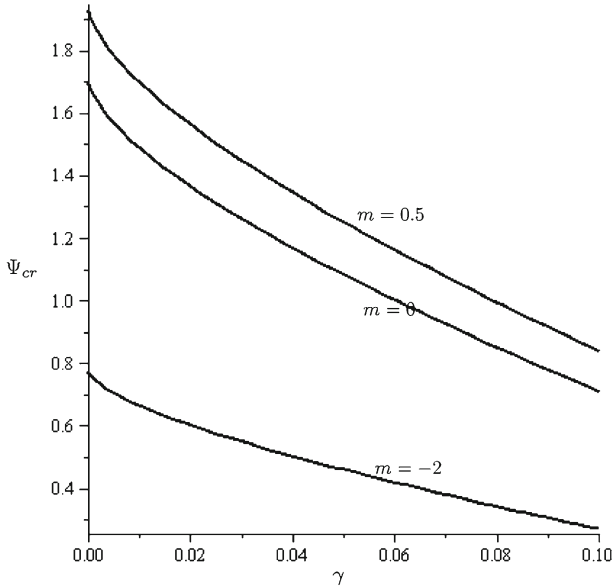

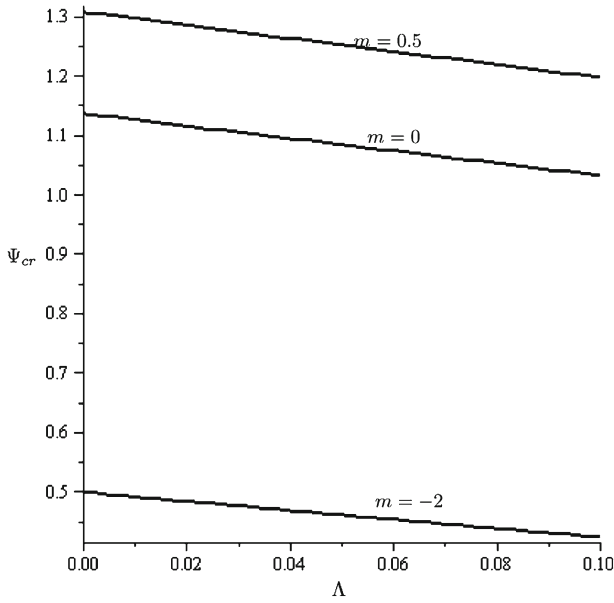**Fig. 3** Ψ_{cr} vs γ for $n = -2$, $\beta = 0.05$, $\Lambda = 0.05$ and $m = \{-2, 0, 0.5\}$

Fig. 4 Ψ_{cr} vs Λ for $n = -2$, $\gamma = 0.05$, $\beta = 0.05$ for $m = \{-2, 0, 0.5\}$
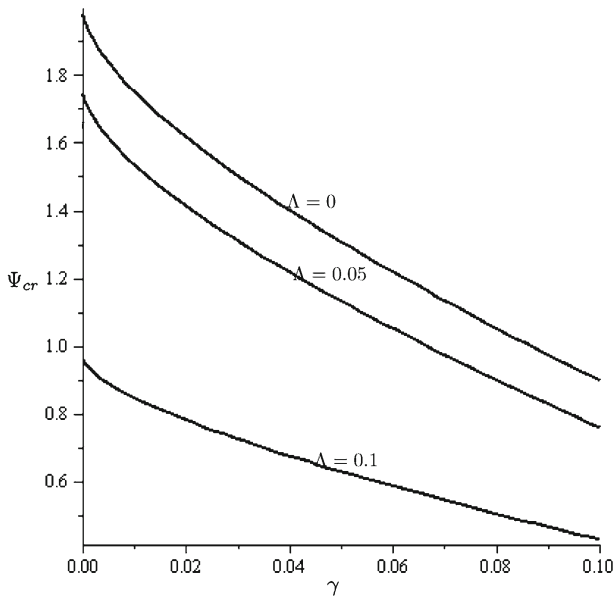
Fig. 5 Ψ_{cr} vs γ for $m = 0.5$, $n = -2$, $\beta = 0.05$ for $\Lambda = \{0, 0.05, 0.1\}$
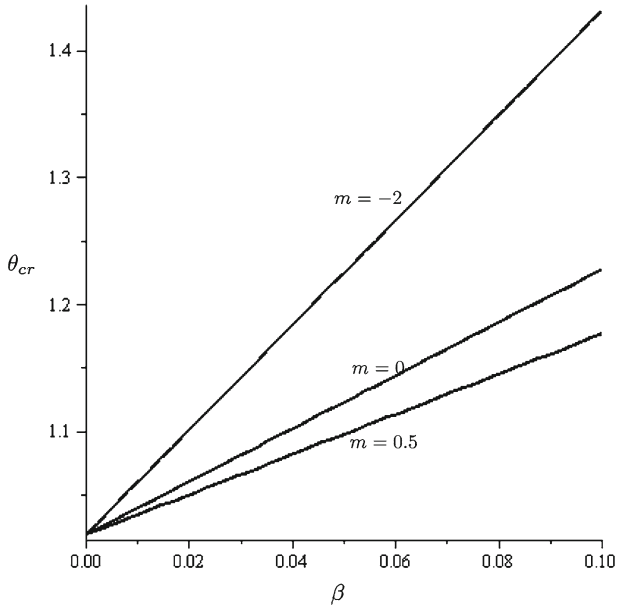
Fig. 6 θ_{cr} vs β for $n = -2, \gamma = 0.05, \Lambda = 0.05$ for $m = \{-2, 0, 0.5\}$
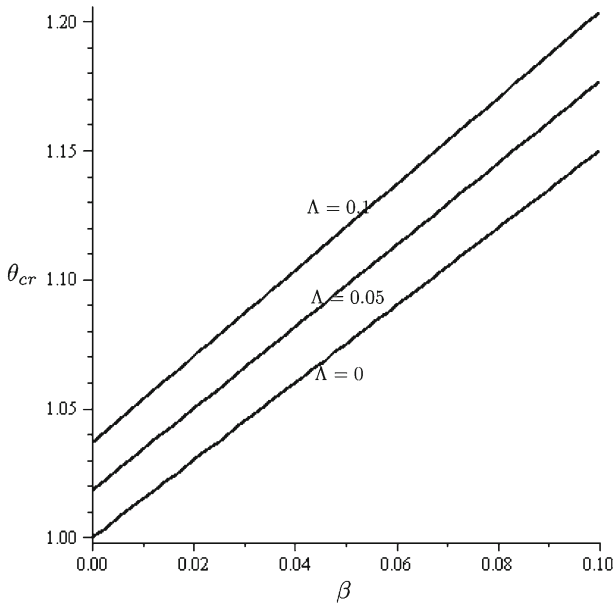

Fig. 7 θ_{cr} vs β for $n = -2, \gamma = 0.05, m = 0.5$ for $\Lambda = \{0, 0.05, 0.1\}$

tion is completely balanced by heat loss to the surrounding walls. Based on the above, the one-dimensional steady state equations to be examined in two limiting cases are

$$\frac{d^2\theta}{dx^2} + \delta \left[(1 + \beta\theta)^m \exp\left(\frac{\theta}{1 + \beta\theta}\right) + \Lambda(1 + \beta\theta)^n \right] = 0, \tag{31}$$

with boundary condition

$$\text{Bi} = 0, \quad \frac{d\theta}{dx}(0) = 0, \quad \text{and} \quad \theta(1) = 0, \tag{32}$$

$$\text{Bi} = \infty, \quad \theta(0) = 0, \quad \text{and} \quad \theta(1) = 0. \tag{33}$$

Due to the non-linear nature, an approximate solution based on the variational technique is considered [Appendix B]. Thus, the mathematical criteria for maximum critical ignition points is

$$\frac{d\delta}{d\theta} = 0, \quad \frac{d^2\delta}{d\theta^2} < 0, \tag{34}$$

from which the calculation of maximum temperature (θ_{cr}) and the corresponding critical parameter (δ_{cr}) are obtained. And beyond θ_{cr} and δ_{cr}, we have the onset of thermal explosion. Before transforming the problem to a variational form, for simplicity, we let

$$f(\theta) = (1 + \beta\theta)^m \exp\left(\frac{\theta}{1 + \epsilon\theta}\right) + \Lambda(1 + \beta\theta)^n, \tag{35}$$

and the primitive of $f(\theta)$ is:

$$F(\theta) = \int f(\theta)d\theta = \int \left[(1 + \beta\theta)^m \exp\left(\frac{\theta}{1 + \beta\theta}\right) + \Lambda(1 + \beta\theta)^n \right] d\theta.$$

The domain of H_δ is restricted to those functions satisfying the boundary conditions (32) and (33); an example of such a function is

$$\theta(y) = A \cos\left(\frac{\pi y}{2}\right) + B \cos\left(\frac{3\pi y}{2}\right). \tag{36}$$

Hence,

$$H_\delta(A, B) = \frac{1}{8}\pi^2(uA^2 + 6ABv + 9B^2w) - \delta \int_0^1 F(\theta)dy, \tag{37}$$

where $u = \frac{1}{2}, v = 0, w = \frac{1}{2}$. After substituting (37) into (B11) in Appendix B, we obtain $A, B (A + B = \theta_{cr})$ and δ_{cr}, by solving the simultanoeus equations:

$$\frac{1}{4}\pi^2(uA + 3vB) - \delta\frac{\partial}{\partial A}\left(\int_0^1 F(\theta)dy\right) = 0, \tag{38}$$

$$\frac{3}{4}\pi^2(vA + 3wB) - \delta\frac{\partial}{\partial B}\left(\int_0^1 F(\theta)dy\right) = 0, \tag{39}$$

$$\left(\frac{\pi^2 u}{4} - \delta\frac{\partial^2}{\partial A^2}\int_0^1 F(\theta)dy\right)\left(\frac{9\pi^2 w}{4} - \delta\frac{\partial^2}{\partial B^2}\int_0^1 F(\theta)dy\right)$$

$$= \left(\frac{3\pi^2 v}{4} - \delta\frac{\partial^2}{\partial A\partial B}\int_0^1 F(\theta)dy\right)^2. \tag{40}$$

5 Numerical results

We have considered the influence of chain consumption and variable pre-exponential factor on the critical parameters for determining thermal explosion and the corresponding maximum temperature in a two-step reactive system.

In the non-stationary system or spatially homogeneous system, we have obtained more general expressions for the critical parameter based on the classical Semenov theory and Mischenko and Rozov approximation formula. The heat transfer rate (Ψ_{cr}) decreases with increasing β, γ and Λ for some numerical exponent $m = \{-2.0, 0.0, 0.5\}$ as shown in Figs. 2,3,4, and 5, while the critical temperature (θ_{cr}) is on the contrary as revealed in Figs. 6 and 7. It could established that heat transfer rates increases with m, while θ_{cr} decreases with m.

In the time-independent system, we obtained numerical approximations based on the variational method. The level of approximation is within the tolerance limit of 98% when compared with known exact solution [1,2]. The variation of δ_{cr} and θ_{cr} with β for some m and Λ are shown in Figs. 8 and 9 respectively. It can be observed that for all Λ, θ_{cr} decreases with m, while δ_{cr} increases m. However, in the limit, $0 \leq \beta < 0.02$, θ_{cr} and δ_{cr} and decreases respectively with Λ. Thermal explosion is faster for a bimolecular reaction ($m = 0.5$) at a relatively higher temperature.

6 Conclusion

The study elucidates the significance of the variable pre-exponential factor and the radical termination step on the classical theory of thermal explosion. Although
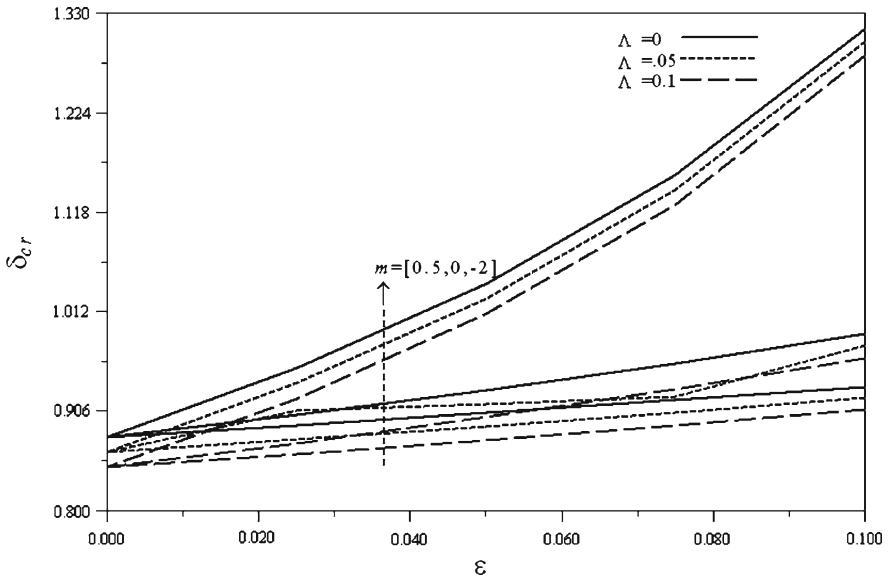
Fig. 8 δ_{cr} vs $\beta(=\epsilon)$ for $\Lambda = \{0, 0.05, 0.1\}$ and $m = \{-2, 0, 0.5\}$
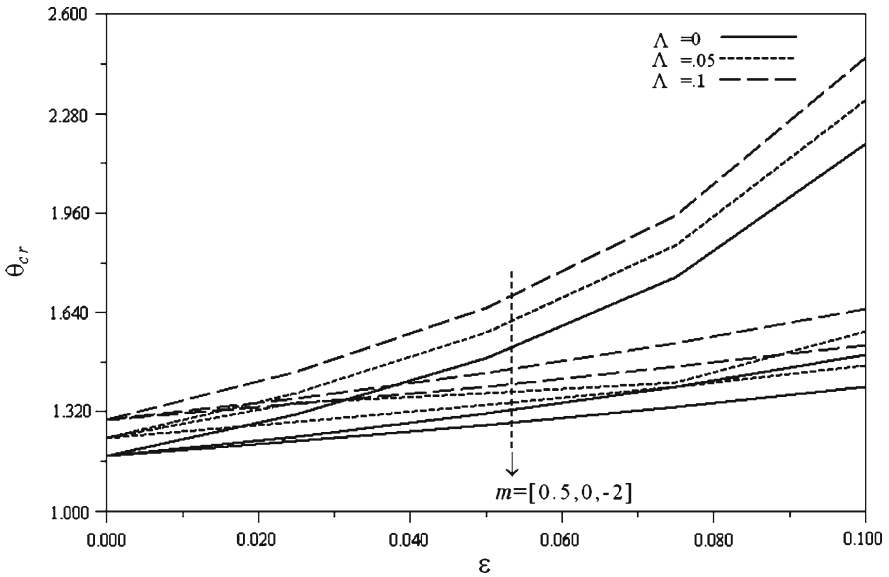

Fig. 9 θ_{cr} vs $\beta(=\epsilon)$ for $\Lambda = \{0, 0.05, 0.1\}$ and $m = \{-2, 0, 0.5\}$

previous studies have ignored the contribution of these in whole or in part, the termination step is a highly exothermic reaction and as such cannot be ignored. Furthermore, the behaviour of the numerical exponent (m), which determines the nature of reaction on the system, gave further insight.

The results have shown that the additional heat contribution from the termination step leads to a reduction in the Semenov and Frank-Kamenetskii parameters and a corresponding increase in critical temperature. This implies that thermal explosion is hasten by the termination step with a corresponding increase in the explosion temperature. In addition, the bimolecular reaction ($m = 0.5$) reaches thermal explosion faster and at a higher temperature than the sensitized reaction ($m = -2$), while the Arrhenius reaction ($m = 0$) lies between them. This study would find application in the industry particularly for safety purposes and also extend the frontier of research in thermal explosion theory.

Appendix A

In line with [6, 16], the critical trajectory is obtained by the aproximation,

$$\Psi_{cr} = eS(\beta)\left[1 - 2^{\frac{2}{3}}\Omega_0 Z(\beta)\gamma^{\frac{2}{3}} + \frac{4}{9}V(\beta)\gamma \ln\left(\frac{1}{\gamma}\right) + O(\gamma + \beta^2)\right], \quad \text{(A1)}$$

where

$$eS(\beta) = \frac{(1 + \beta\theta_I)^m \exp\left(\frac{\theta_I}{1+\beta\theta_I}\right) + \Lambda(1 + \beta\theta_I)^n}{\theta_I}, \ Z(\beta) = \frac{\theta_I}{((2 - (1 - 2\beta)\theta_I)^{1/3}},$$

$$V(\beta) = \theta_I^2 \frac{3 - 2\theta_I(1 - 3\beta)}{((2 - (1 - 2\beta)\theta_I)^2}, \ \text{and} \ \theta_I = 1 + (2 - m)\beta. \quad \text{(A2)}$$

The coefficient Ω_0 is the least positive for the equation

$$J_{-1/3}\left(\frac{2}{3}\Omega^{3/2}\right) + J_{1/3}\left(\frac{2}{3}\Omega^{3/2}\right) = 0, \quad \text{(A3)}$$

where J_k is the Bessel function. Thus, $\Omega_0 = 2.338107$ [23].

Appendix B

The variational method

Consider a boundary value problem in the form

$$\nabla^2\theta + \delta f(\theta) = 0 \quad \text{in D,}$$
$$\theta = 0 \quad \partial D. \quad \text{(B1)}$$

Given the functional

$$H_\delta(\theta) = \int\limits_D \left(\frac{1}{2} |\nabla\theta|^2 - \delta F(\theta) \right) dV, \tag{B2}$$

where F is a primitive of f; i.e $F = \int f d\theta$. The variational principle suggests that $A_1, A_2,...,A_n$ be determined as the solution of the system

$$\frac{\partial H_\delta}{\partial A_k} = 0, \quad k = 1, 2, \ldots, n, \tag{B3}$$

giving an approximate solution $\theta = \sum A_k \theta_k$ corresponding to the chosen δ. The condition determining criticality is according to the implicit function theorem

$$\frac{\partial^2 H_\delta}{\partial A_k \partial A_l} = 0, \quad k, l = 1, 2, \ldots, n. \tag{B4}$$

After omitting a constant geometric factor, Eq. (B2) can be expressed as,

$$H_\delta(\theta) = \int\limits_0^1 \rho^j \left(\frac{d\theta}{d\rho} \right)^2 d\rho - \delta \int\limits_0^1 \rho^j F(\theta) d\rho. \tag{B5}$$

Equations (B3) and (B4) together give $(n + 1)$ equations for the unknowns $A_1, A_2,...,A_n$ and δ_{cr}, which in turn determine θ_{cr}. The numerical success of this procedure depends on a judicious choice of a trial function $\theta_1, \theta_2,...,\theta_n$. At this point, we take an example of such a function which satisfies the boundary conditions as

$$\theta(\rho) = A_1 g_1(\rho) + A_2 g_2(\rho), \tag{B6}$$

where the constants A_1, A_2 in (B6) are replaced by A and B respectively. Hence,

$$H_\delta(A, B) = \frac{1}{8} \pi^2 (uA^2 + 6ABv + 9B^2w) - \delta \int\limits_0^1 \rho^j G(\theta) d\rho, \tag{B7}$$

where

$$u = \int\limits_0^1 \rho^j \sin^2 \left(\frac{\pi\rho}{2} \right) d\rho = \begin{cases} \frac{1}{2}, & j = 0, \\ \frac{1}{2(j+1)} + \frac{1}{\pi^2} & j = 1, 2, \end{cases} \tag{B8}$$

$$v = \int\limits_0^1 \rho^j \sin \left(\frac{\pi\rho}{2} \right) \sin \left(\frac{3\pi\rho}{2} \right) d\rho = \begin{cases} 0, & j = 0, \\ \frac{-1}{\pi^2}, & j = 1, \\ \frac{-5}{4}, & j = 2, \end{cases} \tag{B9}$$

$$w = \int\limits_0^1 \rho^j \sin^2\left(\frac{3\pi\rho}{2}\right) d\rho = \begin{cases} \frac{1}{2}, & j = 0, \\ \frac{1}{2(j+1)} + \frac{1}{9\pi^2}, & j = 1, 2. \end{cases} \qquad (B10)$$

The simultaneous Equations (B3) and (B4) to be solved for A, B and δ are;

$$\frac{\partial H_\delta}{\partial A} = 0, \quad \frac{\partial H_\delta}{\partial B} = 0, \quad \left(\frac{\partial^2 H_\delta}{\partial A^2}\right)\left(\frac{\partial^2 H_\delta}{\partial B^2}\right) = \frac{\partial^2 H_\delta}{\partial A \partial B}, \qquad (B11)$$

where $\theta_{cr} = A + B$ and $\delta = \delta_{cr}$. By an interactive procedure on the Mathematica 6.0 software, we obtain solutions, which compare favourably with known analytic solutions in literature.

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