Thermal explosion of autocatalytic reaction

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Abstract

Analytical and numerical solutions are used to determine the critical conditions for thermal explosion of autocatalytic reaction. The solutions covers both the reaction governed by the Arrhenius kinetics equation and the Frank-Kamenetskii approximation for that equation. The definition of criticality as the point at which $d^2\theta/d\beta^2 = 0$, $d^3\theta/d\beta^3 = 0$ and $d\theta/d\beta\rangle 0$ is used here. The study is dealt with low and high exothermicity (B) of the reaction and their effects on the critical parameters. The numerical solutions cover the whole reaction from start at $\beta = 0$ up to the end at $\beta = 1.0$. All trajectories from subcritical, critical to supercritical are offered. The effects of different parameters such as B, ψ and θ_a (ambient temperature) on the critical conditions are presented. The results showed that the lower the autocatalytic factor (β_0) is, the pronounced autocatalytic reaction explosion. The analytical solution offered analytical expressions for the critical condition and the different limits of the solutions are clarified. It was found that the numerical results confirm the analytical solution.
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1. Introduction

The effect of reactant consumption has been considered in most cases solely in terms of a reaction rate decreasing uniformly with time, the effect on pre-explosion self heating being negligible when the heat of the reaction is sufficiently large. We will consider the type of autocatalytic reactions in which a reaction is proportional to its concentration so that, at least in the early stages, the rate of reaction (and the rate of heat generation) increases with time as the reaction proceeds. Thermal explosion in the presence of heat generation by an autocatalytic reaction was first discussed analytically by Todes and Meletiev (1940), and Merzhanov and Dubovitskii (1958). They defined criticality as the point at which the two lobes of the loci of maximal touch at $\beta = 1/2$ with using the Frank-Kamenetskii exponential approximation for the Arrhenius rate term. They defined that the Frank-Kamenetskii δ for an autocatalytic reaction is larger than those for the Semenov stead-state model, for the three basic geometries (slab, cylinder, and sphere) and a zero-order reaction. The notion of quasi-stationary behavior for the early stages of self-heating with autocatalysis was examined by Merzhanov and

Dubovitskii (1960) and has been extended to the analysis of thermal explosion with simple kinetics under dynamic regimes such as an ambient temperature increasing slowly with time by Merzhanov (1958). The definition of the critical Frank-Kamenetskii number in terms of the maximum rate for an autocatalytic process was assumed by Frank-Kamenetskii (1969) to be directly applicable to the thermal explosion when Biot number = ∞, i.e. for purely conductive loss. Numerical solution of the transient conduction problem for thermal explosion in solids with autocatalytic reaction, carried out for slabs, cylinders, and spheres with Biot number from 1.0 to ∞ by Barzkin, Gontkovskaya and Merzhanov (1966). The behavior of the induction period above and below criticality was also being studied in detail by Zelikman (1968). Recently, Shouman and El-Sayed (1992) reviewed the work on criticality and they defined criticality in the temperature-concentration plane as the point where the second and third derivatives of the governing function equal zero. They applied their definition on solids with homogenous reaction. El-Sayed (1996) studied analytically and numerically the condition of criticality for metal with heterogeneous reaction. Gray and Scott (1994) offered a more detailed discussions about autocatalytic reaction based on a nonlinear stability theorem.

In this article, analytical and numerical solutions for thermal explosion with autocatalytic reaction are presented. The applicability of that definition of criti-

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Nomenclature

A_n	frequency factor (s^{-1})
B	exothermicity of reaction $=QC_0R/\rho c_p E$
C	concentration (mol m^{-3})
C_0	Original concentration (mol m^{-3})
c_p	specific heat (J K^{-1} kg^{-1})
E	activation energy of reaction (J $mol^{-1)}$)
h	convection heat transfer coefficient (J $K^{-1}m^{-2}s^{-1}$)
Q	heat of reaction (J mol^{-3})
R	Universal gas constant (J K^{-1} mol^{-1})
V	volume (m^3)
T	temperature (K)

Greek symbols

ρ	density of reactants, (kg m^{-3})
θ	$=RT/E$, dimensionless temperature
θ_a	$= RT_a/E$, dimensionless ambient temperature
$\phi=(\theta-\theta_a)/\theta_a^2$	dimensionless temperature excess
$\psi = QRC_0VA_n/hSE$	Semenov number
$\psi_f =\psi/\theta_a^2 e^{1/\theta_a}$	Semenov number based on F.K. approximation
$\tau = QC_0RA_nt/\rho c_p E$	dimensionless time
$\tau_f =\tau/\theta_a^2 e^{1/\theta_a}$	dimensionless time based on F.K. approximation

Subscripts and superscripts

a	ambient
i	inflection
o	original (initial)
m	maximum
$*$	critical

cality in Shouman and El-Sayed (1992) is shown in this treatment. The study covers both the Arrhenius rate equation as well as the Frank-kamenetskii approximation for that law. The direct numerical solution for the governing equations with different initial conditions from $\beta = 0$ to $\beta = 1.0$ are introduced. The analytical solutions offered analytical expressions for the critical conditions and the different limits of the solutions are investigated. The treatment showed the effects of low and high exothermicity of the reaction and also the varying of ambient temperature on the critical parameters. The next work will discuss the problem in the temperature-time and concentration-time planes and the induction periods (thermal +kinetics) will also be presented.

2. Mathematical equations and analysis

The equations governing the heat balance (energy) and reaction rate for an exothermic autocatalytic reaction under Semenov conditions and obeys the Arrhenius chemical kinetics. The heat dissipated to the surrounding is only by convection. The rate equation represents the sum of the rates of first order kinetics and first order catalysis. Both equations can be written in the dimensionless form as follows:

$$\frac{d\theta}{d\tau} = (\beta + \beta_0)(1-\beta)e^{-1/\theta}-\frac{(\theta-\theta_a)}{\psi} \qquad (1)$$

and

$$\frac{d\beta}{d\tau} = \frac{1}{B}(\beta + \beta_0)(1-\beta)e^{-1/\theta} \qquad (2)$$

subject to $\theta = \theta_a$ and $\beta = 0$ at $\tau = 0$
Combining Eqs. (1) and (2) gives

$$\frac{d\theta}{d\beta} = B\left[1-\frac{(\theta-\theta_a)e^{1/\theta}}{\psi(\beta + \beta_0)(1-\beta)}\right] \qquad (3)$$

Where $\beta = (C_0 - C)/C_0$ is the degree of conversion or

the fraction of the original substance converted to product and β_0 is the autocatalytic parameter (i.e. a small fractional amount of the product which always must be present to ensure that the reaction can start).

3. Critical conditions in temperature-concentration plane: [A] Analytical solution

One classical definition of critical state in θ - β plane is given as the state where $d^2\theta/d\beta^2 = 0$ and $d\theta/d\beta\langle 0$. Differentiating Eq. (3) with respect to β produces

$$\frac{d^2\theta}{d\beta^2} = \frac{-B}{\psi(\beta + \beta_0)^2(1-\beta)^2}$$
$$\left[(\beta + \beta_0)(1-\beta)\left(\frac{\theta^2-\theta + \theta_a}{\theta^2}\right)e^{1/\theta}\left(\frac{d\theta}{d\beta}\right) - (\theta-\theta_a)\right. \quad (4)$$
$$\left.(1-2\beta-\beta_0)e^{1/\theta}\right]$$

Eq. (4) shows that $d^2\theta/d\beta^2\rangle 0$ when $d\theta/d\beta = 0$. Hence $d\theta/d\beta = 0$ defines the locus of maximum in the θ - β plane giving

$$\beta^2-(1-\beta_0)\beta-\left[\beta_0-\left(\frac{(\theta-\theta_a)e^{1/\theta}}{\psi}\right)\right] = 0 \quad (5)$$

For $\beta_0 \rightarrow 0$, Eq. (5) becomes

$$\beta^2-\beta + \frac{(\theta-\theta_a)e^{1/\theta}}{\psi} = 0 \quad (6)$$

The solution of this quadratic equation gives $\beta_{1,2} = \frac{1}{2}\left[1 \pm \sqrt{1-\frac{4(\theta-\theta_a)e^{1/\theta}}{\psi}}\right]$. For $\theta_m = \theta_a$, then $\beta_m = 0.0$ or 1.0 and for this equation has solution $\frac{(\theta-\theta_a)e^{1/\theta}}{\psi}\langle\frac{1}{4}$ and this depends on the value of ambient temperature θ_a.

The slope of the integral curve at the inflection point $(d^2\theta/d\beta^2 = 0)$ is given by

$$\left(\frac{d\theta}{d\beta}\right)^* = \frac{\theta^{*2}(\theta^*-\theta_a)(1-2\beta^*-\beta_0)}{(\beta^* + \beta_0)(1-\beta^*)(\theta^{*2}-\theta^* + \theta_a)} \quad (7)$$

It can be seen that at the end of reaction $\beta^* = 1.0$ or for $\frac{(\theta^*-\theta_a)}{\theta^{*2}} = 1.0$ the slope is infinite. If $\theta^* = \theta_a$ or $\beta^* = \frac{1-\beta_0}{2}$, then $\left(\frac{d\theta}{d\beta}\right)^* = 0$. This equation also shows that $(\theta^*-\theta_a)/\theta^{*2}\rangle 1.0$ since $(d\theta/d\beta)^*\langle 1.0$. Substituting from Eq. (3) into Eq. (7) gives the locus of inflection points $(d^2\theta/d\beta^2 = 0)$ in the $\theta-\beta$ plane by

$$\beta_i^2-\left[(1-\beta_0) + \frac{2\theta_i^2(\theta_i-\theta_a)}{B(\theta_i^2-\theta_i + \theta_a)}\right] \quad (8)$$
$$\beta_i-\left[\beta_0-\frac{\theta_i^2(\theta_i-\theta_a)}{B(\theta_i^2-\theta_i + \theta_a)}\right](1-\beta_0)-\frac{(\theta_i-\theta_a)e^{1/\theta_i}}{\psi} = 0$$

We consider that criticality exists if only one inflection point before the maximum is reached which defines the critical trajectory. So, it can be seen that criticality is defined by the point where $(d^2\theta/d\beta^2 = 0)$, $(d^3\theta/d\beta^3 = 0)$ and $(d\theta/d\beta\rangle 0)$. To determine the critical condition, the differentiation of Eq. (4) with respect to β leads to

$$\frac{d^3\theta}{d\beta^3} = \frac{-B}{\psi(\beta + \beta_0)^4(1-\beta)^4}$$
$$\left\{(\beta + \beta_0)^3(1-\beta)^3\left(\frac{(\theta^2-\theta + \theta_a)e^{1/\theta}}{\theta^2}\right)\left(\frac{d^2\theta}{d\beta^2}\right)\right.$$
$$+ (\beta + \beta_0)^3(1-\beta)^3\left(\frac{(\theta-2\theta\theta_a-\theta_a)e^{1/\theta}}{\theta^4}\right)\left(\frac{d\theta}{d\beta}\right)^2 \quad (9)$$
$$-2(\beta + \beta_0)^2(1-\beta)^2(1-2\beta-\beta_0)\left(\frac{(\theta^2-\theta + \theta_a)e^{1/\theta}}{\theta^2}\right)\left(\frac{d\theta}{d\beta}\right)$$
$$+ 2(\beta + \beta_0)(1-\beta)[(1-2\beta-\beta_0)^2 + (\beta + \beta_0)(1-\beta)]$$
$$\left.(\theta-\theta_a)e^{1/\theta}\right\}$$

Setting $d^2\theta/d\beta^2 = 0$ and $d^3\theta/d\beta^3 = 0$ produces the critical solution in the form

$$(\beta^* + \beta_0)(1-\beta^*) = 0 \therefore \beta^* = 1 \text{ or } \beta^* = \beta_0 \quad (10)$$
$$e^{1/\theta^*} = 0 \therefore \theta^* = \infty \quad (11)$$
$$(\theta^*-\theta_a) = 0 \therefore \theta^* = \theta_a \quad (12)$$
$$\beta_{1,2} = \frac{1}{2}\left[\left(\frac{2Y^* + \beta_0-2Y^*\beta_0-1}{2Y^*-1}\right)\right] \pm \quad (13)$$
$$\sqrt{\left(\frac{2Y^* + \beta_0-2Y\beta_0-1}{2Y^*-1}\right)^2 - \frac{2(Y^* + Y^*\beta_0^2 + 2\beta_0-2Y^*\beta_0)}{(2Y^*-1)}}$$

and

$$Y^* = \frac{(\theta^*-\theta_a)(\theta^*-2\theta^*\theta_a-\theta_a)}{(\theta^{*2}-\theta^* + \theta_a)^2}$$

The solutions $\beta^* = -\beta_0$ and $\theta^* = \infty$ are trivial while the solutions $\beta^* = 1.0$ and $\theta^* = \theta_a$ showed that the criticality occurred at the start or the end of reaction. The fourth solution relates between the critical parameters at the critical point. For $\beta_0 \rightarrow 0$ Eq. (13) becomes

$$\beta_{1,2}^* = \frac{1}{2}\left[1 \pm \sqrt{\frac{1}{1-2Y^*}}\right] \quad (14)$$

or $\beta_{1,2}^* = \frac{1}{2}\left[1 \pm \sqrt{1-\frac{2(\theta^*-\theta_a)^2}{\theta^{*2}\left(1-\frac{\theta^*-\theta_a}{\theta^{*2}}\right)}}\right]$

which means that the solution exists only for $Y^*\langle\frac{1}{2}$. In other words the ambient temperature mainly controls the criticality. If $Y^* = 0$ ($\theta^* = \theta_a$) then $\beta^* = 0$ or 1.0. Referring to Eq. (13), it can be seen that $\beta^* = 1.0$ produces

$Y^* = 0$ which means that $\theta^* = \theta_a$ or $\theta^* = \dfrac{\theta_a}{1-2\theta_a}$ and $\theta_a \langle 1/2$ at critical or $\beta_0 = -1$(rejected). If the critical conditions occurred when the half of the reactants have been consumed $\beta^* = 1/2$ then $\beta_0 = -\dfrac{1}{2Y^* + 1}$ showing that $Y^* \rangle -\dfrac{1}{2}$ and so $\theta^* \rangle \theta_a$.

4. Frank-Kamenetskii approximation to the reaction rate law

In this section, the approximation to the exponential reaction rate $e^{-1/\theta} = e^{\phi}e^{-1/\theta_a}$ is taken into consideration, where $\phi = E(T-T_a)/RT_a^2 = (\theta-\theta_a)/\theta_a^2$ and $\theta_a = RT_a/E$. The governing equations can be rewritten in the form

$$\frac{d\phi}{d\tau_f} = (\beta + \beta_0)(1-\beta)e^{\phi} - \frac{\phi}{\psi_f} \tag{15}$$

and

$$\frac{d\beta}{d\tau_f} = \frac{1}{B_f}(\beta + \beta_0)(1-\beta)e^{\phi} \tag{16}$$

subject to $\phi = 0$ and $\beta = 0$ at $\tau_f = 0$
Combining Eqs. (15) and (16) gives

$$\frac{d\phi}{d\beta} = B_f\left[1 - \frac{\phi e^{-\phi}}{\psi_f(\beta + \beta_0)(1-\beta)}\right] \tag{17}$$

where, $\psi_f = \psi/\theta_a^2 e^{1/\theta_a}$, $\tau_f = \tau/\theta_a^2 e^{1/\theta_a}$ and $B_f = B/\theta_a^2$ subject to the same above initial conditions.

5. Critical conditions in temperature-concentration plane

The locus of maximum can be obtained when $d\phi/d\beta = 0$, giving

$$\beta^2 - (1-\beta_0)\beta - \left[\beta_0 - \frac{\phi e^{-\phi}}{\psi_f}\right] = 0 \tag{18}$$

The two roots of this quadratic equation give the loci of maximum in temperature-concentration plane. It can be seen that for $\beta \rightarrow 0$, Eq. (18) becomes

$$\beta^2 - \beta + \frac{\phi e^{-\phi}}{\psi_f} = 0 \tag{19}$$

giving the solution in the form $\beta_{m1,2} = \dfrac{1}{2}\left[1 \pm \sqrt{1 - \dfrac{4\phi_m e^{-\phi_m}}{\psi_{fm}}}\right]$. It can be seen that for $\phi_m = 0$, $\beta_m = 0$ or 1.0 and the solution of this equation exists if $\dfrac{\phi_m e^{-\phi_m}}{\psi_{fm}} \langle \dfrac{1}{4}$ or $\psi_{fm} \rangle 4\phi_m e^{-\phi_m}$. The slope of the inte-

gral curve at critical point can be obtained when $d^2\phi/d\beta^2 = 0$. Differentiating Eq. (17) with respect to β gives

$$\frac{d^2\phi}{d\beta^2} = \frac{-B_f}{\psi_f(\beta + \beta_0)^2(1-\beta)^2} \tag{20}$$

$$\left[(\beta + \beta_0)(1-\beta)(1-\phi)e^{-\phi}\left(\frac{d\phi}{d\beta}\right) - (1-2\beta-\beta_0)\phi e^{-\phi}\right]$$

Equating Eq. (20) to zero leads to

$$\left(\frac{d\phi}{d\beta}\right)^* = \frac{\phi^*(1-2\beta^*-\beta_0)}{(\beta^* + \beta_0)(1-\beta^*)(1-\phi^*)} \tag{21}$$

It can be seen that for $\phi^* = 1.0$ or $\beta^* = 1.0$, $\left(\dfrac{d\phi}{d\beta}\right)^* = \infty$. Also one can be seen that for $\phi^* = 0$ or $\beta^* = \dfrac{1-\beta_0}{2}$, $\left(\dfrac{d\phi}{d\beta}\right)^* = 0$. The locus of inflection points, which also represents the locus of critical, can be obtained by substituting Eq. (17) into Eq. (21) produces

$$\beta_i^2 - \left[(1-\beta_0) + \frac{2\phi_i}{B_f(1-\phi_i)}\right]\beta_i$$
$$- \left[\beta_0 - \frac{\phi_i}{B_f(1-\phi_i)}(1 \times -\beta_0) - \frac{\phi_i e^{-\phi_i}}{\psi_f}\right] = 0 \tag{22}$$

The two roots of this quadratic equation give the loci of inflection points in the temperature-concentration plane.

To determine the critical solution, differentiating Eq. (20) with respect to β gives

$$\frac{d^3\phi}{d\beta^3} = \frac{-B_f}{\psi_f(\beta + \beta_0)^4(1-\beta)^4}\left\{(\beta + \beta_0)^3(1-\beta)^3(1\right.$$
$$-\phi)e^{-\phi}\left(\frac{d^2\phi}{d\beta^2}\right) + (\beta + \beta_0)^3(1-\beta)^3(\phi-2)e^{-\phi}\left(\frac{d\phi}{d\beta}\right)^2$$
$$-2(\beta + \beta_0)^2(1-\beta)^2(1-2\beta-\beta_0)(1-\phi)e^{-\phi}\left(\frac{d\phi}{d\beta}\right) \tag{23}$$
$$+ 2(\beta + \beta_0)(1-\beta)[(1-2\beta-\beta_0)^2 + (\beta + \beta_0)(1$$
$$\left.-\beta)]\phi e^{-\phi}\right\}$$

Setting $d^2\phi/d\beta^2 = 0$ and $d^3\phi/d\beta^3 = 0$ produces the critical solutions in the form

$$(\beta^* + \beta_0)(1-\beta^*) = 0 \therefore \beta^* = 1 \text{ or } \beta^* = -\beta_0 \tag{24}$$

$$e^{-\phi^*} = 0 \therefore \phi^* = \infty \tag{25}$$

$$\phi^* = 0 \tag{26}$$

$$\beta_{1,2}^* = \tag{27}$$

$$\frac{1}{2}\left[(1-\beta_0) \pm \sqrt{(1-\beta_0) - 2\left(\frac{Y^*(1-2\beta_0 + \beta_0^2) + 2\beta_0}{(2Y^*-1)}\right)}\right]$$

and

$$Y^* = \frac{\phi^*(\phi^*-2)}{(1-\phi^*)^2}$$

It can be seen that the solutions $\beta^* = -\beta_0$ and $\phi^* = \infty$ are trivial. The solutions $\phi^* = 0$ and $\beta^* = 1.0$ showed that criticality may be occurred at the beginning or the end of the reaction. Now we will examine the limits of the fourth solution, as $\beta_0 \rightarrow 0$, Eq. (27) gives

$$\beta^*_{1,2} = \frac{1}{2}\left[1 \pm \sqrt{\frac{1}{1-2Y^*}}\right] \qquad (28)$$

$$= \frac{1}{2}\left[1 \pm \sqrt{\frac{(1-\phi^*)}{(1 + 2\phi^* - \phi^{*2})}}\right]$$

It can be seen that for $\phi^* = 1.0$, $\beta^* = 1/2$ and the solution exists only for $Y^* \langle \frac{1}{2}$ or $\phi^* \langle 2.414$. From Eq. (27), if $Y^* = 0(\phi^* = 2.0)$ then $\beta^*1,2 = [(1-\beta_0) \pm \sqrt{(1 + 2\beta_0 + 4\beta^*)}]$ and if $Y^* = \infty$ this means that $\phi^* = 1.0$ and $\beta^* = \frac{(1-\beta_0)}{2}$. If the critical conditions occurred when the half of the reactants have been consumed $\beta^* = 1/2$ then $Y^* = -\frac{(1 + \beta_0)}{2\beta_0^2}$ showing that $\phi^* \langle 2.0$.

6. Numerical solution and results

Eqs. (3) and (17) can be solved directly by using what we call the marching Taylor series method which are demonstrated for both equations as follows:
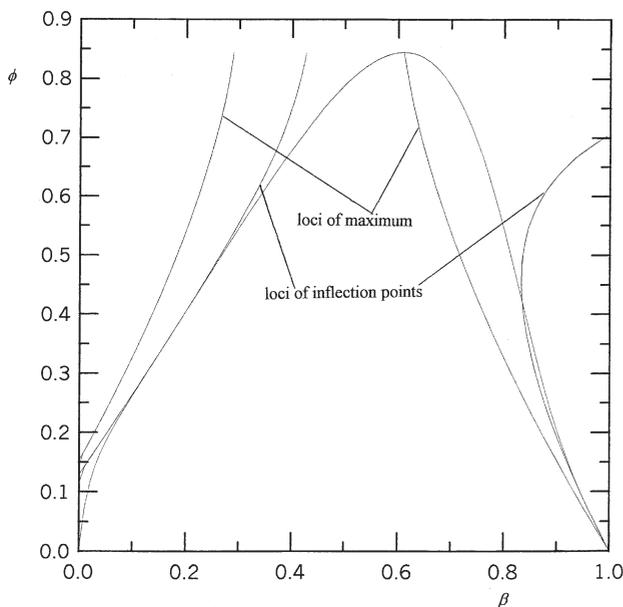
Fig. 1.   The loci of maximum, inflection points and the integral curve for $\psi_f^* = 1.3117$, $B_f = 10.0$ and $\beta_0 = 0.1$
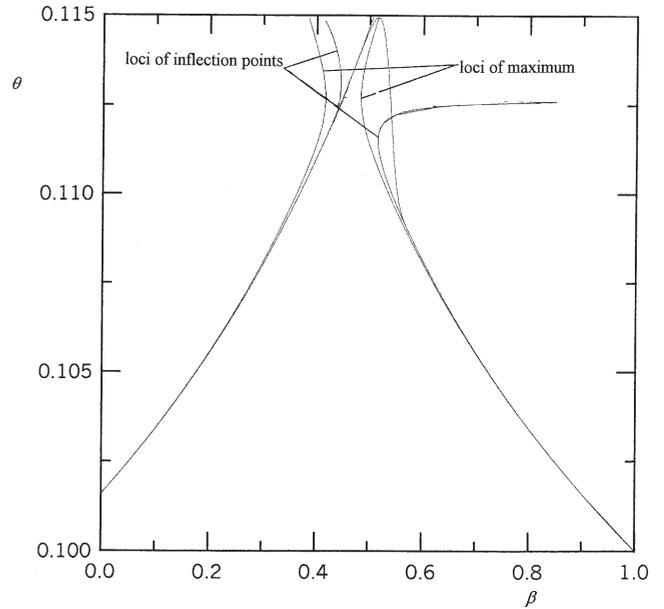

Fig. 2.   The loci of maximum, inflection points and the integral curve for $\psi^* = 214$, B=10.0 and $\beta_0 = 0.1$
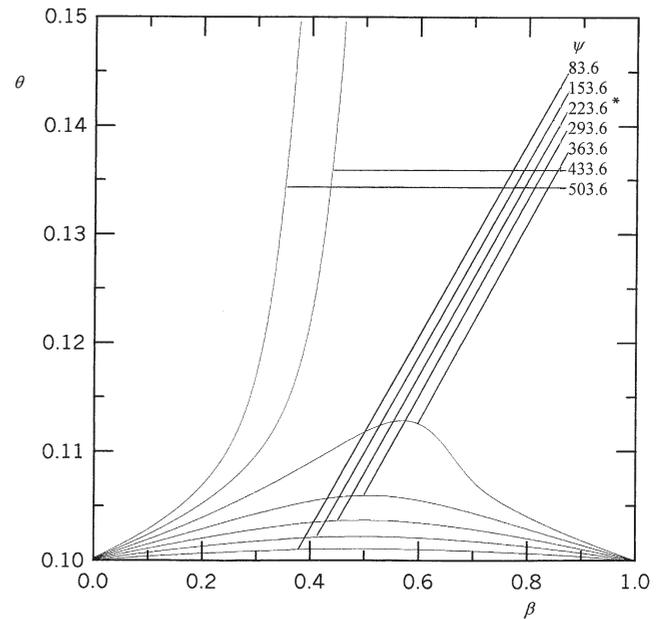

Fig. 3. $\theta - \beta$ trajectories for $B = 1.0$, $\beta_0 = 0.01$, and $\theta_a = 0.1$.

$$\Delta\theta = \frac{d\theta}{d\beta}\Delta\beta + \frac{d^2\theta(\Delta\beta)^2}{d\beta^2\ 2!} + \frac{d^3\theta(\Delta\beta)^3}{d\beta^3\ 3!} + ... \qquad (29)$$

and

$$\Delta\phi = \frac{d\phi}{d\beta}\Delta\beta + \frac{d^2\phi(\Delta\beta)^2}{d\beta^2\ 2!} + \frac{d^3\phi(\Delta\beta)^3}{d\beta^3\ 3!} + ... \qquad (30)$$

where all derivatives were obtained before and at least the first and second derivatives are used to eliminate any difficulties with singular points which do not exist in this problem. The effect of the number of terms and the size
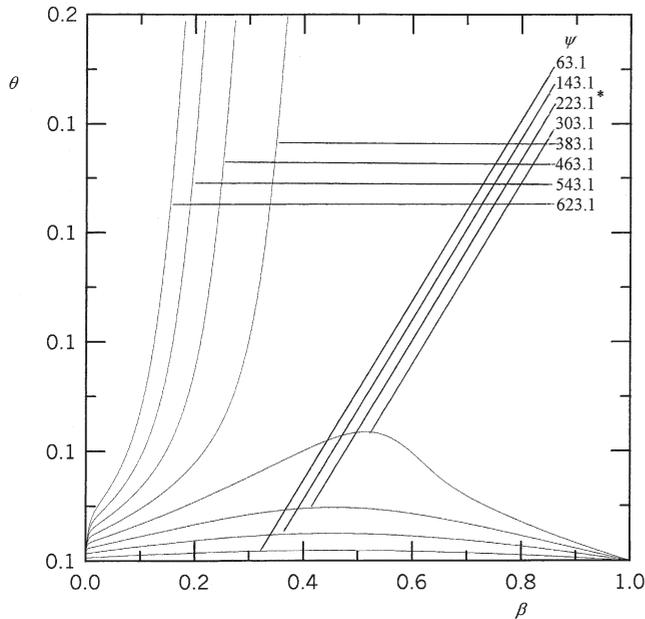
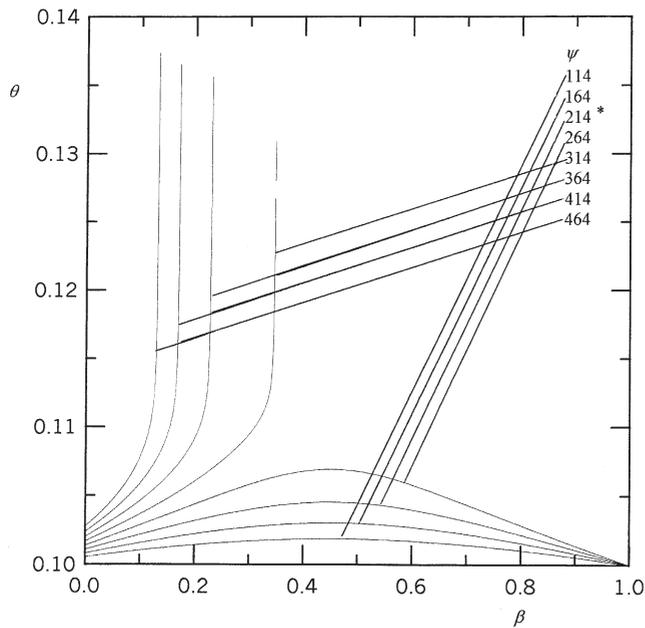Fig. 4. $\theta - \beta$ trajectories for $B=1.0$, $\beta_0 = 0.1$, and $\theta_a = 0.1$.

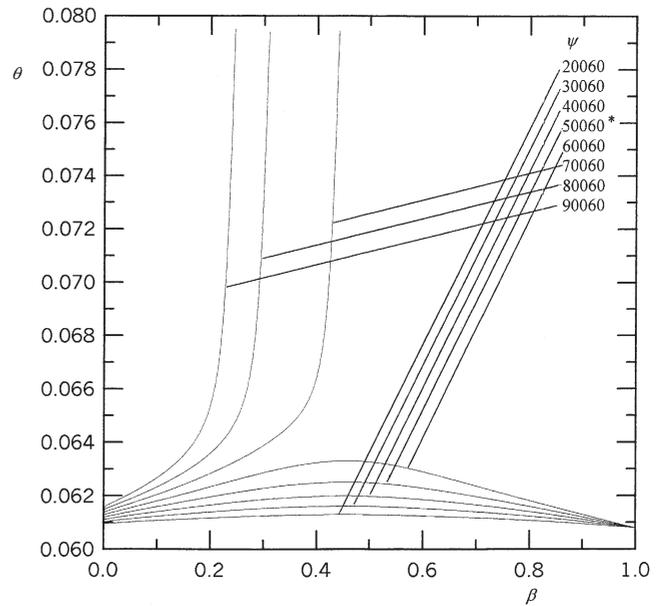Fig. 6. $\theta - \beta$ trajectories for $B=1.0$, $\beta_0 = 0.1$, and $\theta_a = 0.0608$.

Fig. 5. $\theta - \beta$ trajectories for $B=50.0$, $\beta_0 = 0.1$, and $\theta_a = 0.1$.
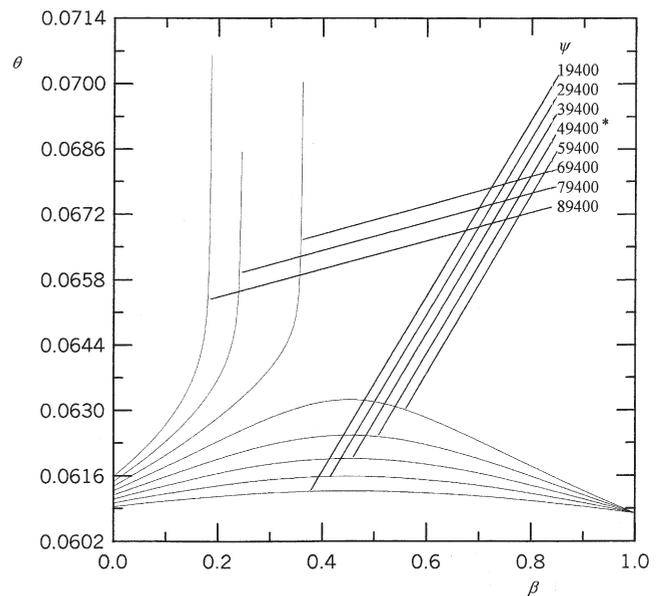

Fig. 7. $\theta - \beta$ trajectories for $B=1.0$, $\beta_0 = 0.1$, and $\theta_a = 0.0608$.

of the increments on the results can be calculated since the series is absolutely convergent. The calculations are done with increment $\Delta\beta = 10^{-6}$.

The numerical solution obtained covers the whole range from the initial conditions $\beta = 0$ to the completion of the reaction $\beta = 1.0$. The numerical calculations confirm the previously analytical solutions. Figs. 1 and 2 show samples of the critical trajectory from numerical solution in the $\phi - \beta$ and $\theta - \beta$ planes for $B = 1.0$ and 10.0 with $\theta_a = 0.1$, and $\beta_0 = 0.1$ to clarify the behavior of the critical trajectory line. Superimposed on the fig-

ures the loci of maximum and inflection points. It is shown that the critical trajectory follows the locus of maximum temperature as β approaches 1.0. It is also demonstrated that there is only one inflection point before the maximum point is reached. Examining the loci of maximum and inflection point with help of Eqs. (3) and (17), it can be seen that at the beginning of reaction $\theta = \theta_a$ and $\beta = 0$, $\frac{d\theta}{d\beta}\rangle 0$ and $\frac{d^2\theta}{d\beta^2}\langle 0$ and as θ increases $\frac{d\theta}{d\beta}$ decreases and $\frac{d^2\theta}{d\beta^2}$ decreases reaching to the first inflection where $\frac{d\theta}{d\beta}\rangle 0$, $\frac{d^2\theta}{d\beta^2} = 0$ and $\frac{d^3\theta}{d\beta^3} = 0$. As reactant
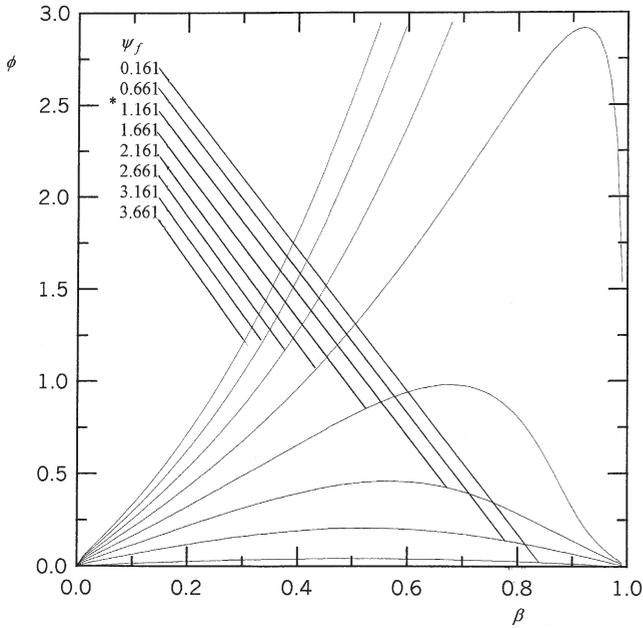
Fig. 8. $\phi-\beta$ trajectories for B_f =10.0, and β_0 = 0.01.
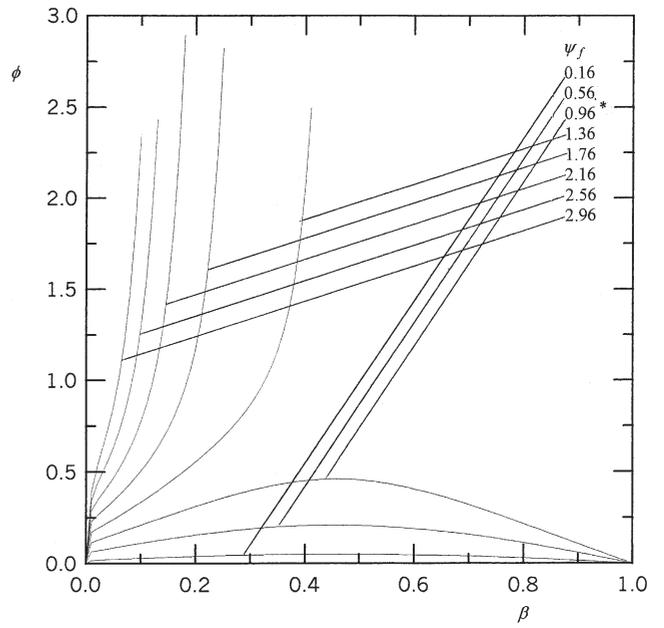
Fig. 10. $\phi-\beta$ trajectories for B_f =100.0, and β_0 = 0.1.
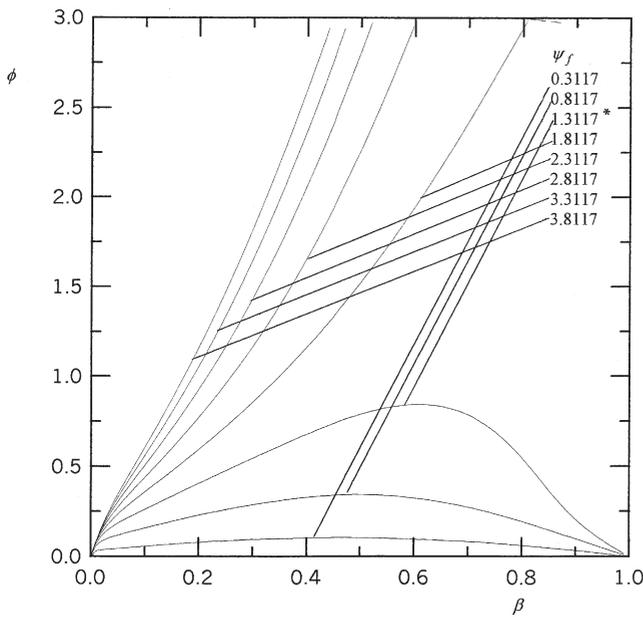

Fig. 9. $\phi-\beta$ trajectories for B_f =10.0, and β_0 = 0.1.

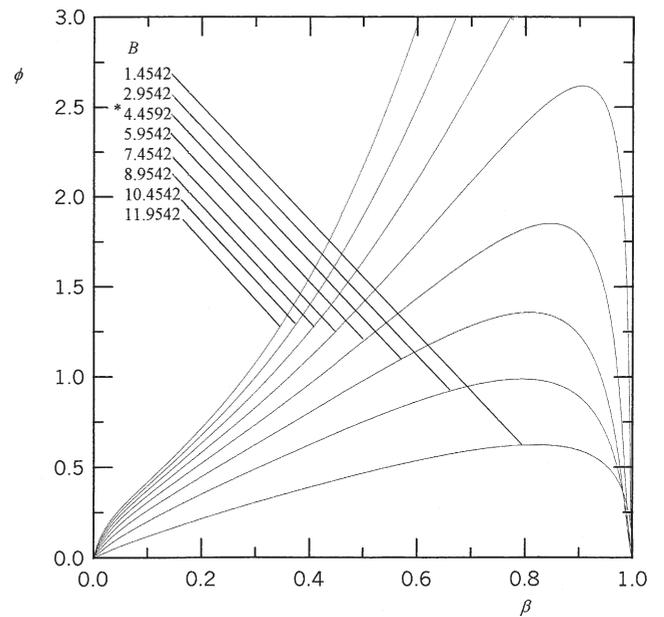Fig. 11. $\phi-\beta$ trajectories for ψ_f = 2.0, and β_0 = 0.1.

depletion increases, θ increases until reaches the maximum where $\frac{d\theta}{d\beta} = 0$ and $\frac{d^2\theta}{d\beta^2}\langle 0$. As β increases, θ decreases until the second inflection point where $\frac{d\theta}{d\beta}\langle 0$ and $\frac{d^2\theta}{d\beta^2} = 0$ is reached. At the end of reaction $\frac{d\theta}{d\beta}\langle 0$ and $\frac{d^2\theta}{d\beta^2}\rangle 0$. Now we can see that criticality obtained when a first inflection before maximum in the integral curve is obtained.

Figs. 3 and 4 show the effect of β_o on the critical conditions for the same $B = 1.0$ and $\theta_a = 0.1$. It was found that criticality for β_0=0.01 occurred at lower values of critical parameters $\beta*$ and $\theta*$ than those for $\beta_0 = 0.1$ although $\psi^*$is slightly changed. The effect of high exothermicity of reaction $B = 50.0$ for the same $\theta_a = 0.1$ and $\beta_o = 0.1$ on the critical conditions is shown in Fig. 5. It can be seen that criticality obtained at lower values of $\psi^*$and so β^*as compared with $B = 1.0$ case. It was also found that increasing B decreases both the values of the critical temperature and maximum tem-
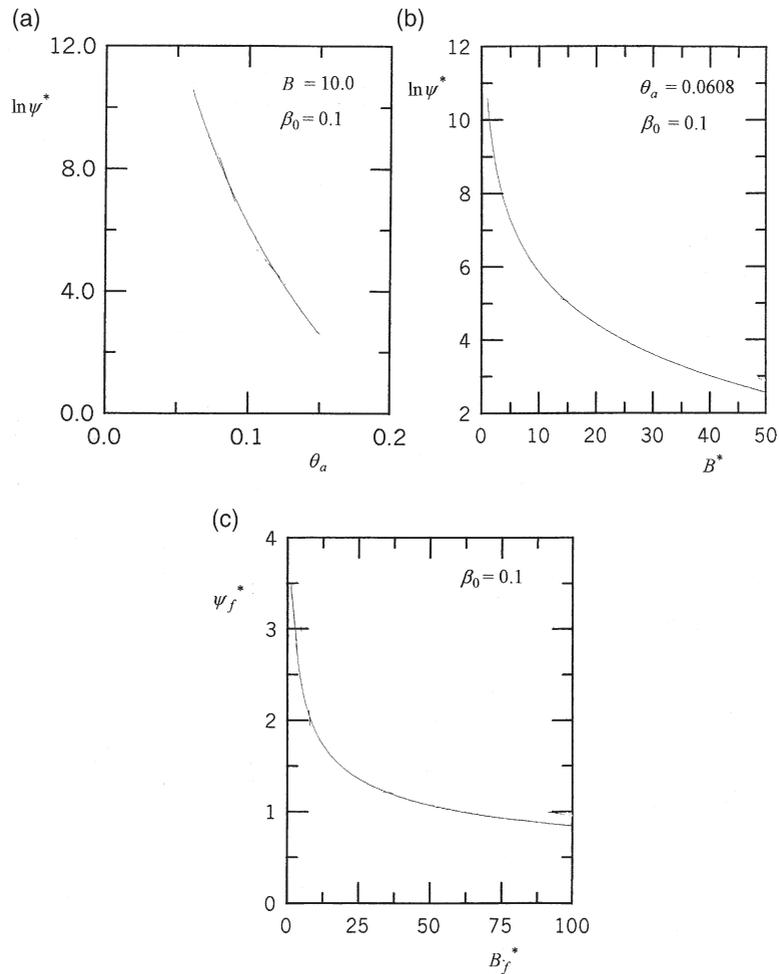
(a)

(b)

(c)

Fig. 12.   a. $\ln \psi^*$ versus θ_a. b. $\ln \psi^*$ versus B^*. c. ψ_f^* versus B_f^*.

perature. High exothermicity of reaction means early ignition where low consumption of reactants exists. Figs. 6 and 7 shows the effect of reducing ambient temperature to $\theta_a = 0.0608$ with $B = 1.0$ and 10.0. It can be seen that the critical value of ψ becomes so high as compared with $\theta_a = 0.1$. No significant difference in the trajectories is noticeable. It can be seen that logically increasing the value of B leads to a decrease in the values of ψ^* and so β^* and θ^*.

Regarding to the Frank-Kamenetskii approximation case, Figs. 8 and 9 show the effect of β_0 on the critical conditions for small value of $B_f = 10.0$. It can be seen that increasing the value of β_0 from 0.01 to 0.1 leads to an increase in the values of the critical parameters. This confirms that the lower the values of β_0 the pronounced the explosion of the autocatalytic reaction. Fig. 10 shows the effect of high value of $B_f = 100$ on the critical conditions. It can be seen that there is a difference in the trajectories and the values of critical parameters becomes lower. For certain ψ_f the critical value of B_f can be obtained from the numerical solution as shown in Fig. 11. It can be seen that there is a continuous change from subcritical to critical then to supercritical trajectories.

7. Conclusions

1. It was shown that as $\beta \rightarrow 0$, the thermal explosion of autocatalytic reaction tends to occur with low values of critical parameters.
2. It was found that the critical parameters for high exothermicity (B) are lower than that for low (B).
3. The effect of ambient temperature on criticality is shown. It was presented that the ambient temperature affects the critical parameters for ignition.
4. The analytical solutions presented analytical expressions which relate between the different critical parameters. A complete picture of solutions for both Arrhenius reaction rate and F.K. approximation with the different limits of solutions are presented.
5. The numerical solutions showed that the critical trajectory has only one inflection point before the maximum. The boundaries between the subcritical and supercritical states are presented.
6. The relationship between the critical parameters ψ^* or ψ_f^*, B^* or B_f^* and θ_a are shown in Fig. 12 for certain initial parameters.

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