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Criteria of thermal stability of exothermically reacting systems. Second order reactions

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Abstract

The method of thermal explosion (TE) critical condition calculation for any type of exothermic reactions was proposed. The method is a generalization of the TE classical theory and it is based on the fact that the values of temperature and conversion level are very sensitive to the change in parameters at the limit of ignition. The universal algebraic equation of critical conditions for any kind of kinetic function was obtained. The application of the method to the calculation of the second order exothermic reactions allows to determine the TE degeneration conditions and to define the regions of critical conditions. The difference between the algebraic results obtained and results of numerical calculation is several percent up to TE degeneration.

Keywords: Thermal explosion; Parametric sensitivity; Maximum temperature; Conversion depth; Crirical conditions

1. Introduction

Currently, the mathematical theory of thermal explosion is a well-studied branch of combustion science. However, a number of problems related to the critical ignition conditions determination remain uninvestigated. Indeed, the classical TE theory [1–3] is applicable to the systems with high values of thermal effect when the self-heating process occurs much faster than the reaction product formation. In this context, the currently existing methods of critical conditions calculation for systems with reactants consumption are based on the determination of small correction to the classical criteria of TE (the methods of integral manifolds) [4–7]. Obviously, these methods can give erroneous results in the case when the deviation from the classical values of critical parameters is significant [8]. However, classes of exothermically reacting systems are very broad and diverse. There are exothermic reactions which are characterized by relatively low rate of heat release (smoldering modes of reaction). The existing methods are not applicable for the calculation of such systems. Thus, the problem of the determination of TE parametric boundaries in the case of significant reactant consumption influence remains uninvestigated. On this basis, methods which would allow to determine the critical conditions in a broader range of parameters are required.

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In the present work, a generalized criterion of critical condition determination is proposed. This method is an alternative to the method of integral manifolds and it is based on the successive approximation techniques. The main feature of ignition phenomenon is the high sensitivity of the temperature and conversion level to the change of parameters in a certain range. Mathematically, it should be determined by the values of derivatives of parameters with respect to temperature (or conversion level). Also, the characteristic temperature of an exothermic reaction (taking into account the reactant consumption) is the maximum temperature. This temperature can be considered as an additional parameter of the model along with the Todes parameter and the Semenov parameter.

1.1. The basic equations

The generalized set of self-heating dynamics and product formation kinetics equations can be written in the dimensionless form as follows [4–6]:

$$\begin{aligned} d\theta/d\tau &= w + \varphi(y)\exp[\theta/(1+\beta\theta)] - \delta\theta \\ dy/d\tau &= \gamma\varphi(y)\exp[\theta/(1+\beta\theta)] \end{aligned} \tag{1}$$

The initial conditions are: $\tau = 0,\ \theta = 0,\ y = y_0$. Here, $\theta = (E/RT_0^2)(T - T_0)$is the dimensionless temperature, $0 \le y \le 1$ is the conversion level (fraction transformed), $\varphi(y)$ is the kinetic function, γ is the Todes parameter (the ratio of the characteristic time of heat release to the characteristic time of chemical reaction), δ is the Semenov parameter (the ratio of the characteristic time of heat release to the characteristic time of heat removal), T_0 is the initial temperature, E is the activation energy. $w = W/W_0$ is the ratio of the external heating power to the heating power of the chemical reaction at $T = T_0$, $\beta = RT_0/E$ is the Arrhenius parameter. The forms of parameters γ and δ depend on the specificity of the exothermic reaction.

The basic approximation of the classical theory is $\gamma << 1,\ \beta << 1,\ y \approx y_0$. As a consequence, the following conditions are valid at a stationary solution:

$$\varphi(y) \approx \varphi(y_0), \quad \delta \approx \exp\theta/\theta \tag{2}$$

However, the stationary modes are impossible when the characteristic times of heat release and product formation are comparable. Thus, the ignition phenomenon can be considered as a fast transition to a high temperature mode at small changes of parameters. In this case, the values of θ and $y$change continuously without any jump or points of discontinuity. This does not allow identifying the characteristic point of transition to the high temperature mode. However, the classical condition of TE can be considered from another viewpoint. Namely, the asymptotic condition $d\delta/d\theta = 0$ for Eq. (2) leads to well-known conditions of TE: $\theta = 1,\ \delta = e$., where $e \approx 2.71828$ is Napier's constant. This means that the critical TE condition can be considered as the point of infinite sensitivity of parameter δ to the change of temperature. In this relation, the question arises whether we can use this asymptotic criterion for critical conditions calculation taking into accounts the reactants consumption ($\gamma \neq 0$)?

2. Maximum temperature equation

As follows from Eq. (1), the phase trajectory equation for any exothermic reaction has the form:

$$\gamma d\theta/dy = 1 + \varphi^{-1}(y)(w - \delta\theta)\exp[-\theta/(1+\beta\theta)] \tag{3}$$

with initial conditions: $\theta = 0,\ y = y_0$. It should be noted that we can consider an arbitrary continuous function $\varphi(y)$ which determines some kinetic law. For example:

$$\varphi(y) = (1-y)^n \tag{4}$$

$$\varphi(y) = (3/2)[(1-y)^{-1/3} - 1]^{-1} \tag{5}$$

where Eq. (4) corresponds to homogeneous reactions, Eq. (5) corresponds to heterogeneous reactions (Ginstling–Brounshtein law [9]).

As follows from Eq. (3), the maximum temperature condition has the form:

$$\varphi(y_m) = (\delta\theta_m - w)\exp[-\theta_m/(1+\beta\theta_m)] \tag{6}$$

where θ_m is the maximum temperature of the reaction, y_m is the corresponding conversion level:

$$y_m = \varphi^{-1}\{(\delta\theta_m - w)\exp[-\theta_m/(1+\beta\theta_m)]\} \tag{7}$$

where φ^{-1} is the inverse function of phi.

Let us integrate Eq. (3) with respect to y between the limits $y = y_0$ and y:

$$\gamma\theta = y - y_0 + \int_{F_0}^{F} (w - \delta\theta)\exp[-\theta/(1+\beta\theta)]dF \tag{8}$$

where the function $F(y)$ is determined by integral:

$$F(y) = \int_{y_0}^{y} dy/\varphi(y) \tag{9}$$

Let us integrate Eq. (8) by the parts and consider the integration with respect to θ:

$$\begin{aligned} \gamma\theta = {} & y - y_0 + F(y)(w - \delta\theta)\exp[-\theta/(1+\beta\theta)] \\ & - F(y_0)w \\ & - \int_0^{\theta} F(y)d\{(w - \delta\theta)\exp[-\theta/(1+\beta\theta)]\} \end{aligned} \tag{10}$$