The critical conditions for thermal explosion in a system heated at a constant rate

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A B S T R A C T

We have analyzed the condition needed for thermal explosion to occur in a solid sample when the temperature of the vessel walls is raised at a constant rate. We have developed a dimensionless model that allows its direct comparison with an isoperibolic system (constant vessel wall temperature). We have obtained an analytical expression for the critical condition as a function of the system parameters. Our solution takes into account reactant consumption and covers different geometries: thin film, finite and infinite cylinder. The critical condition has been validated with numerical simulations and experiments. We show that, compared to the isoperibolic system, thermal explosion is a little bit more difficult to achieve under constant heating conditions. Besides, we show that thermal explosion on submicrometric films is nearly impossible.

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1. Introduction

Knowledge of the critical conditions for the occurrence of thermal explosion (sample mass, container geometry, activation energy, thermal conductivity, temperature) allows to determine: a) the chemical risk associated with the storage and transportation of hazardous materials or in running chemical reactors [1–6], b) the conditions for pyrotechnic reactions to occur [7–9], c) munitions cookoff temperatures [10] and d) in general the ignition condition in chemical engineering processes [11,12].

Furthermore, the so-called "combustion synthesis" takes advantage of local heating related to the heat evolved during the chemical reaction to obtain materials at low processing temperature [13,14]. For instance, synthesis of functional metal oxide thin-films via combustion synthesis has attracted great attention because it would allow the use of low-temperature substrates and it would be a promising route towards the development of large-area and low-cost printed electronics [15]. Unfortunately, under isothermal conditions or during slow heating ramps, fast heat dissipation to the substrate hinders thermal explosion by avoiding the local overheating needed for a thermal runaway to occur [16–22]. Several authors have suggested that, during rapid heating ramps, combustion may be achieved in thin films [14,16]. So, the conditions leading to thermal runaway during heating at a constant rate is of interest for many applications.

In [23–28] thermal explosion under dynamic conditions is analysed numerically and theoretically. The parameter range explored numerically is quite limited. Besides, to reduce the original system to an ordinary differential equation (ODE) system, analytical approaches neglect the temperature and transformation degree distribution. As we will see, this approximation is too crude to provide an accurate description of the critical condition. As Boddington et al. [29] noted for the constant heating case: "The development of a realistic model for the ignition experiment is a formidable problem."

The aim of the present work is to provide a thermal runaway condition for a system that is heated uniformly at a constant rate. To be more precise, the reactant is placed in a vessel whose walls are kept at a temperature, T_f, that is raised at a constant rate. We consider a homogeneous solid sample where heat dissipation occurs mainly through heat diffusion towards the vessel walls. We will show that this model correctly describes the observed behavior of one metalorganic precursor. We will use a new dimensionless system of equations that is equivalent to that introduced by Frank-Kamenetskii for an isoperibolic system (a system where T_f remains constant with time) [30,31]. Thus, our approach allows to determine whether thermal runaway during constant heating is easier or not than during an isothermal temperature program. We will obtain a combustion condition that covers different geometries and a wide parameter range that accounts for most practical cases. Finally, we will analyze the possibility of combustion in thin films.
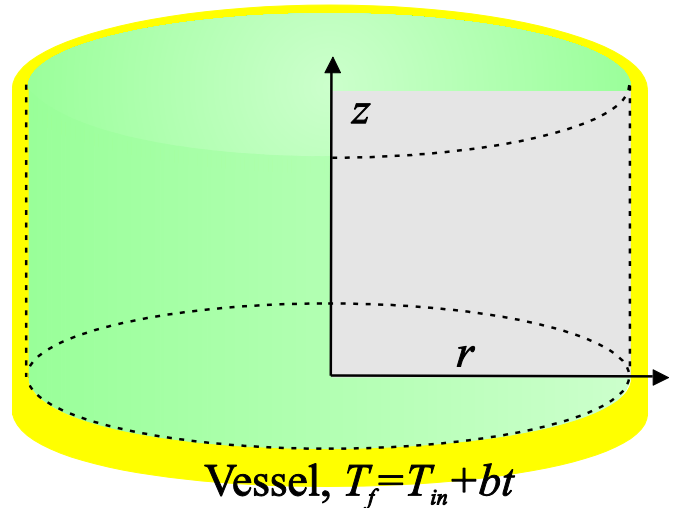
Fig. 1. Geometry analyzed. The sample is placed inside a cylindrical vessel without a cover.

approximations to predict the development of a thermal runaway but are not sufficient to accurately describe the whole reaction course. We also assume a homogeneous medium. The last assumption is also valid for heterogeneous systems provided that the time of heat exchange is much shorter than that of the chemical reaction [36]. For a cylindrical vessel, the evolution of the temperature is described by a two dimensional (2D) partial differential equation (PDE):

$$\rho c \frac{\partial T}{\partial t} = \lambda \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \frac{\partial^2 T}{\partial z^2} \right] + \rho q \frac{\partial \alpha}{\partial t}, \qquad (1)$$

where ρ is density, c is heat capacity, q is the reaction specific heat and λ is thermal conductivity; T is temperature, t is time, z and r are the axial and radial coordinates, respectively (see Fig. 1), and $\alpha(r,z,t)$ is the transformation degree ($\alpha = 0$ untransformed, $\alpha = 1$ totally transformed).

We assume that the initial sample temperature, $T_{in,}$ is uniform and low enough to ensure that the degree of transformation is zero throughout the sample. The boundary conditions are:

$$\left. \frac{\partial T}{\partial r} \right|_{r=0} = 0, \quad T(R, z) = T_f, \quad T(r, 0) = T_f, \quad \left. \frac{\partial T}{\partial z} \right|_{z=H} = 0, \qquad (2)$$

where H is the sample height, R is the vessel's inner radius and T_f is the vessel temperature, that is raised at a constant rate b:

$$T_f = T_{in} + bt. \qquad (3)$$

The last boundary condition states that the heat flux is null at the top of the sample. Actually, if the vessel temperature is below 600°C, the heat lost by radiation is negligible when compared to the heat dissipated by conduction through the crucible walls. As for the heat evolved from the released gases, it is nearly compensated by the loss of heat capacity; so, it has a negligible effect on the heat balance [37]. Finally, due to symmetry, this boundary condition also describes a closed vessel full of reactant provided that H is the vessel half height.

Concerning the reaction, we assume first-order reaction kinetics to account for the reactant consumption and an Arrhenian temperature dependence [38,39]:

$$\frac{\partial \alpha}{\partial t} = A e^{-E_A/R_G T} (1 - \alpha), \qquad (4)$$

where A and E_A are the pre-exponential constant and the activation energy of the reaction rate constant, respectively, and R_G is the universal gas constant.

2. The model

The model is based on the classical theory for ignition and front propagation in solid samples [11,21,30,32–35]. The heat balance is the result of two opposite effects: heat generation by chemical reaction and heat removal through thermal conduction. We neglect the effect of reactive gas depletion or the evolution of the system parameters during the reaction. These are reasonable