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Comparison of criteria for prediction of runaway reactions in the sulphuric acid catalyzed esterification of acetic anhydride and methanol

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ABSTRACT

Loss of temperature control is one of the major reasons that can lead to runaway reaction. This occurrence is commonly named thermal runway. The aim of this paper is the application of thermal runaway criteria in order to predict the onset of runaway phenomena and define the range of stability related to operating conditions in the reactor, with specific reference to the esterification of acetic anhydride and methanol catalysed by sulphuric acid tested in isoperibolic conditions. The isoperibolic calorimeter has also been used to obtain thermodynamic, kinetic and physical chemistry data necessary to develop a model for the reaction. Some runaway criteria applied in this work require a model for the process, so a model for the analyzed system been developed.

Because of the modest reaction enthalpy and low activation energy this reacting system provide a severe test to the runaway criteria.

In this work, various runaway criteria have been applied to the experimental and simulated data and the results obtained have been compared.

1. Introduction

The uncontrolled self-heating in a chemical reactor can generate the occurrence of a "runaway reaction" or "thermal explosion". In many cases, accidents are generated because of inadequate provision for heat removal when increasing plant size from laboratory scale to production scale. Indeed, it has been remarked that in many cases the exothermicity of a process is under estimated when conducted on a laboratory scale (Bowes, 1984). Eventually, the loss of temperature control is possibly the major reason that can lead to thermal explosion. This occurrence has been named thermal runaway.

A study of Barton and Nolan (1987) about thermal runaway incidents gave chemical processes as being responsible for most incidents over the period 1962–1987. Maschio et al. (1992) examined some case histories of incidents that occurred in polymerization reactors. A general conclusion derived from their analysis is that in many cases the development of incidents is due to:

- lack of understanding of the process chemistry and thermo dynamics,
- inadequate reactor design (heat transfer devices, agitation, scale-up),
- inadequate control and safety devices,
- inadequate operating procedures and operator training.

All the above cited causes may be avoided by defining runway boundaries for the analysed process.

Runaway reactions have the potential to inflict considerable damage if appropriate emergency measures are not in place. So the majority of accidents involving runaway reactions are associated either with the failure of controls and safe-guards or with human error. There are different ways of handling runaway reactions: venting, containment, venting with containment, and reaction inhibition. The first three alternatives were studied widely. Reaction inhibition involves injecting small amounts of a particular substance into the reactor at an early stage of the runaway. In spite of their apparent suitability, inhibition systems are rarely used in industrial processes. The main disadvantages are: problems of mixing, position of the injector and choice of the method for the early detection of the onset of runaway (McIntosh & Nolan, 2001). In order to apply this prevention system, robust on-line early warning detection system (EWDS) must be developed to identify situations that can lead to runaway reactions.

The EWDS should be supported by theoretical criteria for the prediction of the onset of runaway reactions.

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Many studies about the detection of runaway boundary have been performed, for example Westerterp and Molga (2004 and 2006), Varma, Morbidelli, and Wu (1999), Strozzi, Zaldívar, Kronberg, and Westerterp (1999), Zaldívar et al. (2003), Zaldívar, Bosch, Strozzi, and Zbilut (2005), Maestri and Rota (2005a,b).

An EWDS, based on the divergence theory developed by Zaldívar and Strozzi, has been extensively applied at several reacting systems characterized by a high exothermicity during the course of the EC AWARD project (Advance Warning and Runaway Disposal – AWARD – GROWTH Project G1RD-CT-2001-00499 Final Report, 2005).

In this work, various runaway criteria have been applied to the experimental and simulated data related to the esterification of acetic anhydride and methanol catalysed by sulphuric acid in order to test various criteria with a reacting system characterized by a not large reaction enthalpy and low activation energy.

2. Runaway criteria

Literature shows several criteria for the prediction of the onset of runaway phenomena. The existing different approaches can be classified as geometry and sensitivity based. In the first case thermal explosion is related to some geometrical features of the system; the second approach is related to the parametric sensitivity of the system and is very suitable for practical application. This work is focused on testing different criteria belonging to both categories as they are formulated in the fundamental work of Varma et al. (1999), and in particular:

- geometry based (Semenov, Bowes and Thomas, Adler and Enig, van Welsenaere and Froment, Barkelew);
- sensitivity based (Hub and Jones, Strozzi and Zaldivar).

Some runaway criteria applied in this work require a model for the reaction in which energy and mass balance for the system are usually expressed in terms of dimensionless variables and parameters.

Because of this a model for a first order reaction such as the one studied in this work in an isoperibolic reactor has been developed.

Consider the mass balance as shown in Eqn. (1):

$$\frac{dX}{dt} = k\cdot(1-X) \tag{1}$$

expressed here for a first order reaction kinetics, and the energy balance for the isoperibolic system:

$$\frac{\mathrm{d}T_r}{\mathrm{d}t} = -n^i\cdot\Delta_r H\cdot\frac{dX}{dt} + \frac{UA\cdot(T_j - T_r)}{C} \tag{2}$$

where the conversion, X, is defined by Eqn. (3):

$$X = \frac{n^i - n}{n^i} \tag{3}$$

In order to have a homogeneous formulation of the criteria, the following definitions are used here according to Varma et al. (1999).

The dimensionless temperature (θ) is defined as:

$$\theta = \frac{(T_r - T_i)}{T_i}\cdot\gamma \tag{4}$$

where the Arrhenius number (γ) is defined as

$$\gamma = \frac{b_1}{T_i} \tag{5}$$

T_i is the initial temperature of the reaction mixture and b_1 is the kinetic parameter showing the dependence on temperature of the catalyzed reaction rate. It represents the dimensionless activation energy for the reaction considered.

The dimensionless time (τ) for a first order kinetics reaction is:

$$\tau = t\cdot k(T_i) \tag{6}$$

The Semenov number (ψ) is defined here as

$$\Psi = \frac{-\Delta_r H\cdot k(T_i)\cdot n^i\cdot\gamma}{UA\cdot T_i} \tag{7}$$

and the dimensionless heat of reaction or dimensionless adiabatic temperature rise (B) as:

$$B = \frac{-\Delta_r H\cdot n^i\cdot\gamma}{C_p\cdot T_i} \tag{8}$$

The Semenov criterion (S) is based on the hypothesis of negligible reactant consumption, this represents a limit in its applicability, even if this criterion is still a good approximation for a number of real systems, in particular for thermal runaway occurring at the very early stages of the process when the conversion is nearly zero and also the reactant consumption.

The critical dimensionless temperature for runway for the Semenov is given by

$$\theta_C = 0.5\gamma\cdot\left((\gamma-2) - \sqrt{\gamma\cdot(\gamma-4) - 4\theta_j}\right) \tag{9}$$

and the critical Semenov number by

$$\Psi_C^S = (\theta_C - \theta_j)\cdot\exp\left(\frac{-\theta_C}{1+\frac{\theta_C}{\gamma}}\right) \tag{10}$$

According to S criterion runaway occurs when $\psi > \psi_c^S$, which physically means that the heat generation rate is increasing or the heat removal rate is decreasing in the system, leading to loss of thermal control and so runaway conditions.

When the consumption of the reagent has to be taken into consideration, Semenov criterion becomes too conservative (Varma et al., 1999). Alternative approaches have been proposed by different authors, that still based their criteria on geometric features of the temperature profile (in conversion or in time). Here Bowes and Thomas (BT), Alder and Eining (AE), Van Welsenaere and Froment (VF) and Barkelew (Bw) have been applied.

The Bowes and Thomas criterion states that runaway occurs when in the θ vs. τ plane, the second order derivative becomes positive before the temperature hot-spot:

$$\frac{d^2\theta}{d\tau_2} = 0 \text{ and } \frac{d^3\theta}{d\tau^3} = 0 \tag{11}$$

In the dimensionless temperature trajectory, the inflexion in the region where the reactor temperature is increasing represents the boundary between runaway and non-runaway condition.

The Adler and Enig criterion (Adler and Enig, 1964 and Varma et al., 1999) is formulated in the θ vs. X plane and the critical conditions is similar to the BT criterion:

$$\frac{d^2\theta}{dX^2} = 0 \text{ and } \frac{d^3\theta}{dX^3} = 0 \tag{12}$$

Another geometric based criterion here considered is the van Welsenaere and Froment (Van Welsenaere and Froment, 1970 and Strozzi et al., 1999). It is a very algebraically simple criterion to apply to first order kinetics reaction, that gives the boundary for runaway according to Eqn. (13):