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Thermal risk in batch reactors: Theoretical framework for runaway and accident

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ABSTRACT

Thermal safety and risk of accidents are still challenging topics in the case of batch reactors carrying exothermic reactions. In the present paper, the authors develop an integrated framework focusing on defining the governing parameters for the thermal runaway and evaluating the subsequent risk of accident. A relevant set of criteria are identified in order to find the prior conditions for a thermal runaway: failure of the cooling system, critical temperature threshold, successive derivatives of the temperature (first and second namely) vs. time and no detection in due time (reaction time) of the runaway initiation. For illustrative purposes, the synthesis of peracetic acid (PAA) with hydrogen peroxide (HP) and acetic acid (AA) is considered as case study. The critical and threshold values for the runaway accident are identified for selected sets of input data. Under the conditional probability of prior cooling system failure, Monte Carlo simulations are performed in order to estimate the risk of thermal runaway accident in batch reactors. It becomes then possible to predict the ratio of reactors, within an industrial plant, potentially subject to thermal runaway accident.

1. Introduction

Batch reactors are widely used in many fields of industrial production, such as pharmaceuticals, organic synthesis and fine chemical industry (Puxty et al., 2005). The chemical reactions running within these kinds of reactors are usually strongly exothermic (De Filippis et al., 2002; Jiang et al., 2011; Liu and Jiang, 2006). Under given conditions, the heat generated by reaction may be much more than the heat evacuated by the system. Consequently, there will be an important quantity of accumulated heat within the reactor. This may cause thermal runaway.

Usually, safety devices are inserted within the batch reactor in order to avoid this runaway. However, it may happen that the safety devices, such as the external coolers can fail or the emergency discharging system cannot work. If the failure is not detected in due time, thermal runaways may take place and cause a first accident sequence such as explosions. This first sequence can generate blast waves, fragments projection, thermal flux which may damage surrounding facilities (tanks, reactors, lifelines and energy suppliers, trucks, products leakage ...). New sequences of accidents may then be generated and give rise to the so-called domino effect (Mebarki et al., 2009a,b; Zhang and Jiang, 2008). The optimal design of the plant and facilities requires risk analysis for such accidents occurrence and subsequent sequences. It appears then of crucial important to estimate the risk of potential critical thermal runaway. Due to the optimal design or safety analysis which requires relevant probabilistic framework, two main approaches can be considered, in practice:

- Optimal and reliability targeted design by probabilistic methods: Level-3 methods (failure probabilities) or level-2 methods (reliability index, FORM/SORM methods and conventional failure probability) can be used for risk-based

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optimization of utility functions. Such methods have been investigated by several researchers for industrial risks (Anca and Gheorghe, 2012; Maria and Dan, 2012) as well as other scientific fields (Ditlevsen and Madsen, 1996; Mebarki et al., 1990, 1991; Melchers, 1999). These approaches may rely on prior parametric sensitivity analysis in order to identify the most influent governing parameters.

- Risk of industrial accidents and potential domino effects occurrence: It is important to estimate the risk of the first sequences occurrence that may trigger important industrial accidents and their subsequent sequences able to cause domino effect scenario. Experimental feedback from past accidents, industrial hazards modeling as well as theoretical approaches of the accidents occurrence have been also widely investigated, (Abbasi and Abbasi, 2007; Gubinelli and Cozzani, 2009; Pula et al., 2007; Cozzani and Salzano, 2004; Nguyen et al., 2009; Mebarki et al., 2012a,b, 2014). However, accurate prediction of the conditions and the frequency for the first accident occurrence at individual reactor level or at industrial plants scale is still a scientific challenge.

From the collected bibliography, see Table 1, it appears that imminent accident due to thermal runaway is intimately related to so-called critical temperatures (T_{cr}) (Westerterp and Molga, 2006; Strozzi et al., 1999; Nanchen et al., 2009; Abele et al., 2012; Fritzsche and Knorr, 2009; Stoessel, 2009; Copelli et al., 2014). For instance, criticality classes of thermal runaway scenario, caused by cooling failure, have been developed in order to link process thermal safety with the exothermal chemical reactions (Gygax, 1988), see Fig. 1.

In the present paper, batch reactors are analyzed and an integrated probabilistic framework is developed for the evaluation of risk occurrence of the first accident sequence triggered by thermal runaway. It focuses on the indicators or precursors of imminent accident which may cause fire or explosion as first accident sequence. The paper investigates the adequate set of criteria governing batch reactors thermal safety and determines the risk of accidents.

2. General framework for thermal safety assessment and risk of accidents in batch reactors

The proposed general framework requires successive steps, see Fig. 2:

- First, define the initial conditions and chemical components for the reaction supposed to take place within the batch reactor,
- Then, identify the governing indicators and their critical values for the thermal runaway occurrence,
- Validate these criteria by comparison between simulation results and experiments,
- Express therefore the theoretical probability of accident due to thermal runaway,
- Evaluate the failure risk and define the utility function to use for the layout optimization.

Table 1
Criticality classes of thermal runaway scenario (Nanchen et al., 2009).

Classes	Temperature thresholds
1	$T_p < T_{MTSR} < T_{MTT} < T_{D24}$
2	$T_p < T_{MTSR} < T_{D24} < T_{MTT}$
3	$T_p < T_{MTT} < T_{MTSR} < T_{D24}$
4	$T_p < T_{MTT} < T_{D24} < T_{MTSR}$
5	$T_p < T_{D24} < T_{MTSR} < T_{MTT}$

Note: T_p = normal process temperature; T_{MTSR} = maximum temperature of the synthesis reaction; T_{D24} = temperature at which the time to maximum rate under adiabatic conditions equals 24 h; and T_{MTT} = maximal temperature for technical reasons.

3. Mathematical model of batch reactor

The chemical models describing the synthesis are briefly summarized for batch reactors case. For illustration purposes, an exothermic liquid-liquid reaction is considered:

$$\upsilon_A A + \upsilon_B B \xrightarrow{catalyst, r_1} \nu_C C + \nu_D D \tag{1}$$

where: component C is the product.

The decomposition of the product may correspond to:

$$\upsilon_m C \xrightarrow{r_2} \upsilon_e E + \upsilon_f F \tag{2}$$

where: r_1 and r_2 are the reaction rate; $\upsilon_A, \upsilon_B, \nu_C, \nu_D, \upsilon_m, \upsilon_e$ *and* υ_f are the stoichiometric numbers of component A, B, C, D, E and F respectively.

In order to simplify the batch reaction model, the following assumptions are stated:

(1) The reaction mass is perfectly mixed and the reaction is homogenous reaction system;
(2) Heat generation effects are due to the chemical reactions only;
(3) Heat removal effects are only related to cooling condition;
(4) Ideal gas behavior.

The reaction rate r_1 and r_2 are defined as:

$$r_1 = k_1 C_A^n C_B^m [catalyst]^y \tag{3}$$

$$r_2 = k_2 C_C^W \tag{4}$$

where: k_1 and k_2 are the rate constants; [*catalyst*] is the concentration of catalyst; n, m, w and y are the reaction order. If there is no catalyst in the reactor, $[catalyst]^y$ is substituted with 1.

Based on these assumptions, the energy equation becomes:

$$\rho V C_P' \frac{dT_R}{dt} = \sum_{j=1}^{2} r_j(-\Delta H_{rj})V - UA(T_R - T_j) \tag{5}$$

where: T_R is temperature of reaction; T_J is jacket temperature; ρ is density; V is total liquid reacting volume; C_P' is specific heat capacity; U is heat transfer coefficient; A is heat transfer area; and ΔH_{rj} is the reaction enthalpy of *j-th* reaction.

4. Accident assessment criteria

As shown in Fig. 1, three main stages take place during a thermal runaway scenario, i.e.: normal process progress, cooling failure and secondary reaction, this later being the runaway sequence. During the secondary reaction, the temperature of reaction can become higher than the maximum allowable temperature (T_{MAT}) and may give rise to an accident.

Several researchers have studied the batch reactors and investigated the conditions for thermal runaway. For example, TB criterion states that runaway occurs when the temperature second