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Thermal risk in batch reactors: Case of peracetic acid synthesis

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ABSTRACT

The present paper deals with accidents risk in batch reactors. It identifies the conditions for the occurrence of a thermal runaway and develops a probabilistic approach to assess the relevant risk. It investigates also the conditions for optimal synthesis of peracetic acid (PAA) with hydrogen peroxide (HP) and acetic acid (AA). The kinetic model of reversible reaction and side reaction of PAA synthesis is used to predict reactor temperature and molar ratio of PAA by ASPEN PLUS software. A sensitivity analysis is performed under different conditions such as constant temperature or adiabatic process with different concentrations of sulfuric acid. Assuming a prior cooling system failure, the conditions for reaction runaway triggering a thermal accident are identified in the case of PAA synthesis. Monte Carlo simulations are used in order to calculate the conditional probability of accident and optimize the synthesis of PAA.

1. Introduction

Peracetic acid (PAA) is a strong oxidant, widely used in disinfection, bleaching of textiles and pulps, oxidation of organic synthesis, for instance (Zhao et al., 2007). However, peracetic acid shows great instability, suffers easy decomposition under normal temperature and may cause explosions under high temperature. Mainly, two preparation methods exist for PAA:

- the most widely used method results from synthesis of hydrogen peroxide (HP) and acetic acid (AA): $CH_3COOH + H_2O_2 \xleftarrow{H_2SO_4} CH_3COOOH + H_2O$.
- the second method results from the oxidation of acetaldehyde (Dul Neva and Moskvin, 2005).

Currently, many researches on PAA synthesis focus on the mechanism of its formation (Sawaki and Ogata, 1965; YuanNi and Van Heiningen, 1997; Dul Neva and Moskvin, 2005; RubioRamírez-Galicia and López-Nava, 2005). Being synthesis of PAA with HP and AA catalyzed by SA a reversible and exothermic reaction, thermal safety assessment is of crucial importance.

Cooling failure scenario and process thermal safety have already been partly investigated for exothermal reactions (Gygax, 1988) and critical classes have been proposed (Nanchen et al., 2009). These critical classes have also been used to evaluate the thermal safety of the peroxyformic acid synthesis from formic acid and hydrogen peroxide (Leveneur et al., 2012). However, it is still a scientific challenge of crucial important to investigate and estimate the risk of critical thermal runaway. Actually, this can cause a first sequence of accidents (fire, explosion or leakage) (Nguyen et al., 2009; Mebarki et al., 2012) followed by a domino effect with (Mebarki et al., 2014) subsequent accidents in the surrounding facilities.

Many experiments have been carried out to investigate thermal runaway reactions and find the optimal process conditions. They are cost and time consuming and some experiments can, under critical conditions, even be hazardous.

It becomes thus worth to use thermal runaway reactions

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simulations. For this purpose, numeric models have already been developed for some specific commercial polymerizations (Balchan et al., 1999). Also, Aspen Dynamics has been used to predict different accidental scenarios that may occur in CSTR and tubular reactors (Luyben, 2012). MATLAB has been also used in order to simulate the synthesis of 4-Chloro-3-nitrobenzotrifluoride under cooling system failure condition (Copelli et al., 2014). In the present paper, numeric models and simulations are proposed and run in order to study thermal runaway reactions. It focuses on peracetic acid (PAA) synthesis with hydrogen peroxide (HP) and acetic acid (AA). The critical accident conditions and the risk of synthesis of PAA as well as the optimal process conditions are investigated.

2. The detail flow of thermal safety assessment and risk of accidents for synthesis of PAA with HP and AA

The thermal safety and risk assessment of accidents due to synthesis of PAA with HP and AA require various steps (see Fig. 1).

- Define the initial conditions of PAA synthesis in a batch reactor,
- Identify the critical values of thermal runaway for PAA synthesis,
- Use numeric simulation of chemical reactions,
- Chose probabilistic distributions of the governing parameters and derive the conditional probability of thermal runaway,

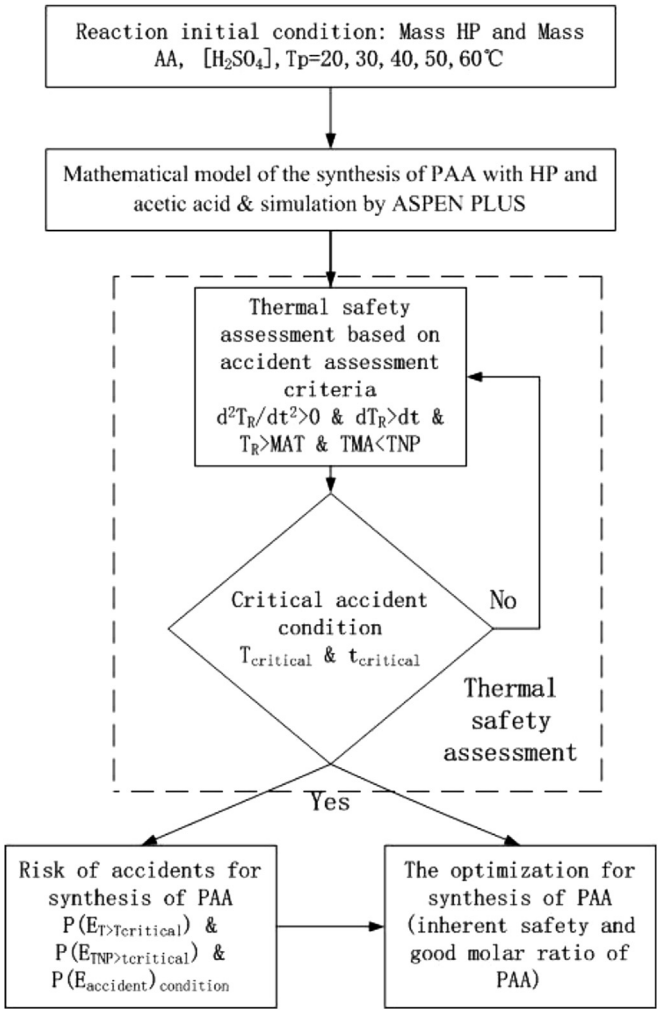

Fig. 1. The flowchart of thermal safety assessment and risk of accidents for synthesis of PAA with HP and AA.

- Evaluate the failure risk and find the optimal and safest process of PAA synthesis.

3. Chemical model of PAA synthesis with HP and AA

The synthesis mechanism of PAA with HP and AA, (Zhao et al., 2008), is discussed in the present paper. Because the energy for break of O–O bond of HP in the liquid phase is relatively high (~51 kcal/mol), the thermal decomposition of HP in the PAA synthesis is not easy to reach since the critical temperature for HP decomposition in PAA synthesis is larger than 120 °C (F. and H-m. 2001). The PAA synthesis reactions are:

$$CH_3COOH(A) + H_2O_2(B) \underset{k_{2obs}}{\overset{H_2SO_4, k_{1obs}}{\rightleftharpoons}} CH_3COOOH(C) + H_2O(D) \quad (1)$$

$$2CH_3COOOH \xrightarrow{k_{3obs}} 2CH_3COOH + O_2 \quad (2)$$

where: k_{1obs}, k_{2obs} and k_{3obs} are constants for reactions rate (L mol^{-1} h^{-1}).

The reaction rates are defined as:

$$\frac{dC_A}{dt} = k_{2obs}C_C C_D - k_{1obs}C_A C_B + k_{3obs}C_C^2 \quad (3)$$

$$\frac{dC_B}{dt} = k_{2obs}C_C C_D - k_{1obs}C_A C_B \quad (4)$$

$$\frac{dC_C}{dt} = k_{1obs}C_A C_B - k_{2obs}C_C C_D - k_{3obs}C_C^2 \quad (5)$$

$$\frac{dC_D}{dt} = k_{1obs}C_A C_B - k_{2obs}C_C C_D \quad (6)$$

where: C_A, C_B, C_C and C_D are the concentrations of CH_3COOH, H_2O_2, CH_3COOOH and H_2O respectively.

The kinetic constants k_{1obs}, k_{2obs} and k_{3obs} collected from existing literature (Zhao et al., 2008) are:

$$k_{1obs} = \left[H^+\right] \times 6.83 \times 10^8 \times \exp\left(-\frac{57846.15}{RT}\right) \quad (7)$$

$$k_{2obs} = \left[H^+\right] \times 6.73 \times 10^8 \times \exp\left(-\frac{60407.78}{RT}\right) \quad (8)$$

$$k_{3obs} = \frac{2.72 \times 10^{19} \times \exp(-118529.37/RT)\left[H^+\right]}{\left\{1 + 2.528 \times 10^6 \times \exp(-30151.55/RT)\left[H^+\right]\right\}^2} \quad (9)$$

where: $[H^+]$ is H^+ concentration (mol L^{-1}); R is gas constant; T is temperature.

In order to simplify the simulation of batch reaction, several assumptions are adopted:

(1) The reaction mass is perfectly mixed;
(2) Heat generation effects are due to the chemical reactions only;
(3) Heat removal effects are only related to cooling system;
(4) Ideal gas behavior;
(5) The H^+ concentration results from sulfuric acid dissociation.

Based on these assumptions, the energy equation is then