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Thermal runaway and shortstopping of esterification in batch stirred reactors

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ABSTRACT

This research deals with the thermal runaway and shortstopping of esterification process in batch stirred reactors. A series of experiments were carried out with RC1e, and an auto-catalytic kinetic model of esterification process was established. The divergence criterion (DIV) which describes the trace of Jacobian matrix of temperature and reactant conversion was used to identify the thermal runaway boundary of esterification. Computational fluid dynamics (CFD) simulation was employed to illustrate the temperature distribution inside the reactor. The cooling temperature and agitation speed significantly affect the esterification runaway. CFD simulation of shortstopping runaway in esterification process with cooling diluent injection was established to study the effect of addition location and quantity of the cold diluent on shortstopping performance.

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1. Introduction

sec-Butyl propionate is a common organic chemical product and plays an important role in fine chemical industry. The esterification of 2-butanol and propionic anhydride is widely used to prepare sec-butyl propionate. This esterification reaction is exothermic, i.e. under certain conditions, the heat generated by reaction may be much more than the heat removed by the cooling system. The surplus heat results in temperature rise and faster rate of reaction, thus accelerates the rate of heat production, which will eventually lead to thermal runaway (Ni et al., 2016).

In order to identify thermal runaway, various runaway criteria have been proposed, such as MV criterion (Morbidelli and Varma, 1982, 1989), VR criterion (Vajda and Rabitz, 1992), DIV criterion (Copelli et al., 2014; Strozzi et al., 1999), boundary diagrams (Maestri and Rota, 2005; Steensma and Westerterp, 1990), temperature diagrams (Maestri and Rota, 2006) and topological criteria (Copelli et al., 2011a,b, 2010). For the esterification reaction at present, some researches focused on the theoretical studies of runaway criterion (Alós et al., 1996; Bosch et al., 2004a,b; Strozzi et al., 1994). For instance, Divergence criterion was applied to detect the runaway initiation of the esterification between 2-propanol and propionic anhydride in a pilot-scale reactor (Bosch

Nomenclature

A	Heat transfer area, m ²
A ₁ & A ₂	Pre-exponential factor, s ⁻¹
C _p	Specific heat capacity, J kg ⁻¹ k ⁻¹
E ₁ & E ₂	Activation energy, kJ/mol
F ₁	Right side of Eq. (6)
F ₂	Right side of Eq. (8)
ΔH _r	Reaction enthalpy, J mol ⁻¹
k ₁ & k ₂	Reaction rates
n ₁₁ , n ₁₂ , n ₁₅ , n ₂₁ , n ₂₂ , n ₂₅	Reaction order
T _r	Reaction temperature, k
T _j	Jacket temperature, k
T _{crit}	A critical parameter between safety reaction and runaway reaction, k
U	Heat transfer coefficient, W m ⁻² k ⁻¹
V	Total liquid reacting volume, m ³
ρ	Density, kg/m ³

et al., 2004a,b). Computational fluid dynamics (CFD) tools have been employed to support the DIV criterion and indicate the temperature gradient in the reactor. Furthermore, CFD-based models were devel-

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oped to estimate the possibility of the global thermal runaway from appearing “hot-spots” (Milewska and Molga, 2007; Rudniak et al., 2004).

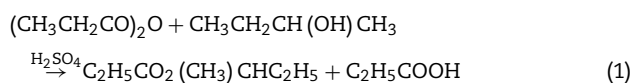
In the past decades, various methods to handle or prevent runaway reaction have been studied (e.g. venting, containment and reaction inhibition). However, the reaction inhibition was rarely discussed because of the prohibitive hazards of actual laboratory experimentation. Dakshinamoorthy et al. (2004, 2006) and Dakshinamoorthy and Louvar (2006) applied the computational fluid dynamics (CFD) to simulate the shortstopping process in a stirred batch reactor. Some measures were studied to enhance effective shortstopping, such as power input, location of adding chemical inhibitor, the quantity of inhibitor and the comparative effect between cold diluent and chemical inhibitor.

In the present research, thermal runaway and shortstopping of esterification of 2-butanol and propionic anhydride with sulfuric acid in batch stirred reactors was studied by experiments and simulations.

2. Experimental

2.1. Reaction pathway

In this paper, the batch synthesis of *sec*-butyl propionate was investigated and the stoichiometric scheme is given in Eq. (1).



2.2. Samples

Reagent: 2-butanol (AR) (Sinopharm Chemical Reagent Co., Ltd, No.20150331), sulfuric acid (AR 98%) (Sinopharm Chemical Reagent Co., Ltd, No.20110210); Propionic anhydride (GC >= 98.5%) (Aladdin Reagent Co., Ltd, P106800).

2.3. Reaction calorimeter (RC1e)

RC1e (manufactured by METTLER TOLEDO) was used to measure the exothermic condition of reaction. RC1e is an automatic synthesis reaction system. A 2 L vessel was used in the experiment. Specific testing principles can be found in the literature (Lee et al., 2014).

3. Experiment result and kinetic models

3.1. Experiment results

A batch reactor was selected in this experiment. 2-Butanol (2B) and propionic anhydride (PA) were added to the reactor at the beginning. Then the reactions run under constant jacket temperature (T_j). when the reaction temperature reached the jacket temperature. H_2SO_4 was added to the reactor. The reaction began. The molar ratio of 2B to PA was 1:1. The reaction time was 100 min. Specific experiment conditions are shown in Table 1.

The experiment results are shown in Fig. 1 (continuous lines). At the jacket temperature of 296.15 K, the maximum temperature reaches 308.3 K whereas with the jacket temperature of 302.15 K, the maximum temperature climbs to 381.48 K. An increase of jacket temperature by 6 K leads to a change in maximum temperature by about 73.18 K. These experiments indicate how an exothermic reaction can proceed under

Table 1 – Experiment conditions.

$n_{2B}:n_{PA}:n_{\text{H}_2\text{SO}_4}$	Mass _{2B} (g):Mass _{PA} (g):Mass _{H₂SO₄} (g)	T_j (K)
3.88:3.88:0.023	287.6:505:2.28	296.15
3.88:3.88:0.023	287.6:505:2.28	298.15
3.88:3.88:0.023	287.6:505:2.28	300.15
3.88:3.88:0.023	287.6:505:2.28	302.15

Note: n_{PA} , n_{2B} and n_{SA} are the molar mass of PA, 2B and H_2SO_4 , respectively.

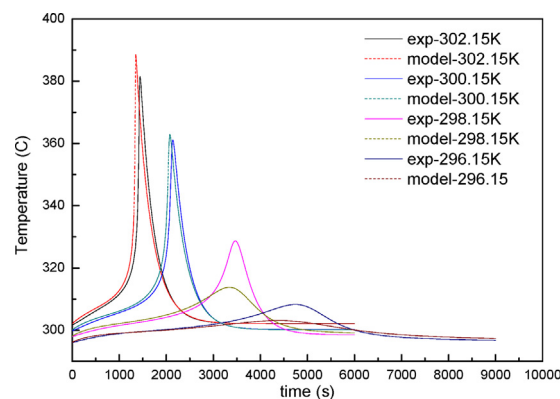


Fig. 1 – Experimental (continuous lines) and simulated (dotted lines) reactor temperature evolution with time under the conditions shown in Table 1.

controlled and runaway conditions with different cooling temperature. Finally, the reaction stops because all reagents are consumed.

3.2. Kinetic modeling

Esterification reaction with sulfuric acid is an autocatalytic reaction based on some previous research (Dhanuka et al., 1977; Galván et al., 1996; Snee et al., 1992). The empirical reaction path can be written as,



Where A is $(\text{CH}_3\text{CH}_2\text{CO})_2\text{O}$, B is $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$, C is $\text{C}_2\text{H}_5\text{CO}_2(\text{CH}_3)\text{CHC}_2\text{H}_5$, D is $\text{C}_2\text{H}_5\text{COOH}$ and E is H_2SO_4 .

Where the reaction rate can be expressed as,

$$r_1 = k_1 C_A^{n_{11}} C_B^{n_{12}} C_E^{n_{15}} \quad (4)$$

$$r_2 = k_2 C_A^{n_{21}} C_B^{n_{22}} C_C^{n_{25}} \quad (5)$$

Where $k_1 = A_1 \exp\left(-\frac{E_1}{RT}\right)$, $k_2 = A_2 \exp\left(-\frac{E_2}{RT}\right)$, A_1 and A_2 are pre-exponential factor, E_1 and E_2 are activation energy, R is ideal gas constant, T is reaction temperature and n_{11} , n_{12} , n_{15} , n_{21} , n_{22} , n_{25} are reaction orders.

Based on the Eqs. (2)–(5), it can be derived that

$$\frac{dC_A}{dt} = -r_1 - r_2 \quad (6)$$

$$\frac{dC_B}{dt} = -r_1 - r_2 \quad (7)$$

$$\rho V C_p \frac{dT_r}{dt} = r_1 (-\Delta H_{r1}) V + r_2 (-\Delta H_{r2}) V - UA (T_r - T_j) \quad (8)$$

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