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Applications of reaction calorimetry in reaction kinetics and thermal hazard evaluation

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Abstract

A systematic approach to determination of the kinetics of the exothermic esterification of methanol and acetic anhydride by reaction calorimetry (RC) was addressed in this study. Arrhenius parameters were obtained from isothermal, adiabatic, and temperature-programmed methods. The activation energy, pre-exponential factor, and heat of reaction were determined to be 72.6 ± 0.5 kJ mol^{-1}, $(3.6 \pm 0.6) \times 10^7$ s^{-1} mol^{-1} dm^3, and 67.3 ± 3.0 kJ mol^{-1} respectively. Here, the adiabatic temperature rise of runaway reaction and the critical heat-transfer parameter were obtained using the Mettler RC1 AP01 reactor. A second-order reaction under the condition of excess acetic anhydride was successfully identified and used to simulate adiabatic runaway situations in scale-up quantity. Results in this study demonstrated that combining different calorimeters' features with experimental techniques would create an effective technique capable of obtaining reliable results for both the Arrhenius parameters and thermal hazard assessment.

Keywords: Acetic anhydride; Critical heat transfer; Esterification; Methanol; Reaction calorimetry; Thermal runaway

List of Symbols

A	pre-exponential factor (s^{-1} mol^{-1} dm^3)
E_a	activation energy (kJ mol^{-1})
C_0	initial concentration (M)
C	concentration at time t (M)

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C_{a_0}	initial concentration of reactant A (M)
C_{b_0}	initial concentration of reactant B (M)
k	rate constant (s^{-1} mol^{-1} dm^3)
m	mass of reagent (kg)
S	surface area (m^2)
T_j	jacket temperature (K)
T_r	reactor temperature (K)
T_o	onset temperature (K)
T_f	final temperature (K)
T_a	coolant temperature (K)
U	heat-transfer coefficient (W m^{-2} K^{-1})
V	volume of reactant (dm^{-3})
ΔH_r	heat of reaction (kJ mol^{-1})
dQ/dt	heat generation rate (W)
dT/dt	self-heating rate (°C min^{-1})
$(US/V)_{cr}$	critical heat-transfer parameter (kcal K^{-1} min^{-1} dm^{-1})

Greek letters

α, β	conversion of reagents
ρ	denstiy (g cm^{-3})

1. Introduction

Many runaway incidents are thermally initiated. It is well recognized that an exothermic runaway reaction can occur if the heat generated by the reaction exceeds that removed by the surroundings. Thermodynamic data, kinetic parameters and physical properties of the reactants together with the reactor conditions are required for assessing runaway reaction hazards. These data can be obtained by DSC, accelerating rate calorimetry (ARC), and, recently, by reaction calorimetry (RC) [1]. Emergency relief venting due to runaway reaction has been extensively studied by DIERS (Design Institute of Emergency Relief Systems) of AIChE [2]. Some theoretical models and criteria have been developed for predicting the critical conditions that may lead to runaway [3] based on heat-releasing rate and heat transfer characteristics of the process vessel.

The esterification of acetic anhydride by methanol has been a model reaction in reaction and adiabatic calorimetry for reaction enthalpy and self-heating rate calibrations [4, 5]. The acetic anhydride–methanol system with a mole ratio of 1:2 was chosen and determined to be a pseudo-first-order reaction. The resulting temperature–time profile and self-heating rate, based on the theory of Townsend and Tou [6], were used to determine the reaction kinetics.

In this study, an investigation of the second order reaction of the esterification of acetic anhydride and methanol in different molar ratios was performed and compared with previous studies [7, 8]. Interpretation of small-scale experimental data in scalingup applications is not straightforward and might result in significant uncertainties [9]. A novel approach is also proposed to determine the critical safe condition by using a 2 dm^3 RC flask with the capability of simulating actual reacting process conditions. Finally, both pseudo-first order and second-order reaction schemes were compared and used to simulate the adiabatic runaway temperature versus time curve in scale-up quantity.

2. Experimental

2.1. Chemicals

High purity methanol and acetic anhydride (> 99%) were purchased from Merck.

2.2. Reaction calorimetry (RC)

The reaction calorimeter used to study the exothermic esterification of methanol and acetic anhydride was a 2 dm^3 AP01 glass reactor (RC1) from Mettler [10]. This instrument comprises a computer-controlled jacketed reactor provided with an agitator, electrical immersion calibration heater, thermocouple, and dosing-controlled system. Thermostatted silicone oil is circulated through the jacket of the vessel. This heat transfer fluid can be maintained at a constant temperature (isoperibolic mode) or the jacket temperature can be controlled to maintain the reactor contents at a constant temperature (isothermal mode), constant temperature scanning (temperature-programmed mode), or adiabatic mode. The RC1 works according to the heat flow principle: the temperature difference $\Delta T = T_r - T_j$ between the jacket (T_j) and the reactor (T_r) is continually measured. The heat transfer coefficient U was determined by calibration using an electrical immersion heater; the heat transfer surface area, S, can be determined once the reactor geometry and the stir speed is given. Reaction heat can thus be calculated by the following equation:

$$\Delta H_r = US\Delta T \tag{1}$$

Different quantities of methanol (16 g and 32 g) were added to the reactor containing a large quantity (756 g) of acetic anhydride. Isothermal testing was carried out at 30, 40, 50, 60, and 70°C. A 0.47°C min^{-1} temperature scanning rate from 20 to 112°C was performed in the temperature-programmed mode which is similar to the DSC method. To use the adiabatic mode the heat transfer between reactor and jacket must be minimized. The adiabatic slope and offset parameter at reacting temperature (T_r) was determined prior to simulating an adiabatic runaway reaction in the RC1. The slope and offset were determined to be -0.012 and -0.11°C respectively. A linear ramp function was then utilized to define the adiabatic control algorithm in the RC1 once the slope and offset had been determined. The adiabatic temperature rise (ΔT_{ad}) can be calculated using the following equation provided that the heat capacity (C_p) and reaction mass (m) of the reaction solution are known:

$$\Delta H_r = US\Delta T = mC_p\Delta T_{ad} \tag{2}$$

C_p was determined by RC using the temperature-programmed mode, usually with a 5°C increase over a 10-min period prior to and after the reaction was complete. This is similar to the conventional DSC method assuming no exothermic or endothermic reactions in the testing temperature range. The severity of the runaway reaction is usually indicated by the adiabatic temperature rise, ΔT_{ad}.

3. Reaction theory

3.1. Homogeneous reaction

The exothermic esterification reaction of acetic anhydride and methanol is

$$(\mathrm{CH_3CO})_2\mathrm{O} + \mathrm{CH_3OH} \rightarrow \mathrm{CH_3COOCH_3} + \mathrm{CH_3COOH} \tag{3}$$

Beretta and Janelli [11] stated that this acetylation of methanol was a normal bimolecular reaction as the concentration of the methanol approached zero. However, a pseudo-first-order reaction model along with its reaction enthalpy and Arrhenius parameters has been extensively used as a reference for calorimeter calibration purposes. Hydrolysis of acetic anhydride in dilute solution has been studied by Glasser and Williams [12] and determined to be pseudo-first-order in the presence of excess water.

Typically, reaction rate is a function of temperature, T, as well as the concentrations of acetic anhydride ($C_{\mathrm{a_o}}$) and methanol ($C_{\mathrm{b_o}}$) it follows that:

$$\dot{q} = \mathrm{d}Q/\mathrm{d}t = Ae^{-E_a/RT}\Delta H_{\mathrm{r}} V[C_{\mathrm{a_o}}(1-\alpha)][C_{\mathrm{b_o}}(1-\beta)] \tag{4}$$

A pseudo-first-order reaction was chosen under the condition of excess methanol ($C_{\mathrm{a_o}} < < C_{\mathrm{b_o}}$). In this study, a second order reaction was proposed under the condition of excess acetic anhydride ($C_{\mathrm{a_o}} > > C_{\mathrm{b_o}}$) and verified by RC calorimetry.

Arrhenius parameters E_{a} and A and reaction order were determined from the equation:

$$\ln\left[\frac{(\mathrm{d}Q/\mathrm{d}t)}{\Delta H_{\mathrm{r}} V[C_{\mathrm{a_o}}(1-\alpha)][C_{\mathrm{b_o}}(1-\beta)]}\right] = \ln A - \frac{E_{\mathrm{a}}}{RT} \tag{5}$$

using the appropriate plot.

3.2. Kinetic analysis

The application of RC1 adiabatic mode in the determination of kinetic parameters was established by Shatynski and Hanesian [13]. For a constant-volume batch reactor, the energy balance equation was determined as

$$(-\Delta H_{\mathrm{r}})\left(\frac{-\mathrm{d}C_{\mathrm{a}}}{\mathrm{d}t}\right)V\mathrm{d}t + Q_{\mathrm{stirrer}}\mathrm{d}t = mC_p\mathrm{d}T + UA(\Delta T)\mathrm{d}t \tag{6}$$

For an adiabatic system, no heat is transferred between reactants and coolant. No energy was produced by the stirrer. The concentration of the reactant can be approximately related to the temperature of the system

$$-\int_{C_{a0}}^{C_a} \mathrm{d}C_a = \frac{mC_p}{-\Delta H_r V}\int_{T_0}^{T} \mathrm{d}T \tag{7}$$

$$C_a = C_{a_0} + \frac{mC_p}{\Delta H_r V}(T - T_0) \tag{8}$$

The total temperature change can be related to the initial concentration of reactant A for complete conversion in an adiabatic calorimeter.

$$-\Delta H_r = \frac{mC_p}{C_{a_0} V}(T_f - T_0) \tag{9}$$

For a second-order reaction (A + B → P), the mass balance can be represented by

$$C_{a_0} - C_a = \alpha C_{a_0} = \beta C_{b_0} = C_{b_0} - C_b \tag{10}$$

$$C_b = C_{b_0} - (C_{a_0} - C_a) \tag{11}$$

The rate equation can be written as

$$\frac{mC_p}{-\Delta H_r V}\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right) = kC_aC_b$$

$$= k\left[C_{a_0} + \frac{mC_p}{\Delta H_r V}(T - T_0)\right] \times \left[C_{b_0} + \frac{mC_p}{\Delta H_r V}(T - T_0)\right] \tag{12}$$

The self-heating rate or temperature vs. time curve can be given by:

$$\mathrm{d}T/\mathrm{d}t = \frac{kC_{a_0}}{(T_f - T_0)}(T_f - T)\left[\frac{C_{b_0}}{C_{a_0}}(T_f - T_0) + (T_0 - T)\right] \tag{13}$$

For a large excess of methanol ($C_{b_0} >> C_{a_0}$), an approximate pseudo-first-order analysis produces the following equation

$$\mathrm{d}T/\mathrm{d}t = k(T_f - T)[C_{b_0}] \tag{14}$$

Arrhenius parameters can be determined from the plot of ln (dT/dt) against the reciprocal of temperature.

4. Results and discussion

4.1. Heat reaction and exothermic onset temperature

The heats of reaction and onset temperature determined using the RC1 along with DSC and ARC are listed in Table 1. The experimental data correlate well with those found in other studies [4, 5, 7, 8, 14, 15]. The exothermic heat of esterification measured by the RC1 was 67.3 ± 3.0 kJ mol^{-1}. The onset temperature of the exothermic reactions depends on the sensitivity of the instrument. The minimum exothermic temperature detected by ARC was 16.6°C.

Table 1
Comparison of reaction heat and exothermic onset temperature obtained by different tests

	DSC	ARC	RC1
Onset temp/°C	19	16.6	19
Reaction heat/(kJ mol^{-1})	65.8 ± 2.7	67.3 ± 0.9	67.3 ± 3.0

4.2. Kinetic analysis

The reaction rate constant is here assumed to follow the Arrhenius rate law. The time-dependent isothermal trace at 60°C recorded using the RC1 is shown in Fig. 1 along with curve-fitted data. The Arrhenius parameters were determined as A (frequency factor) = $3.65 \times 10^7 s^{-1} mol^{-1} dm^3$, E_a (activation energy) = 72.2 kJ mol^{-1}, and n (reaction order) = 2. Those results were verified by repeated isothermal runs.

Temperature-programmed tracing using the RC1, similar to the DSC dynamic temperature scanning method, was performed. The heat evolution curve is shown in Fig. 2; its integration was determined to be 66.30 kJ mol^{-1}. The temperature-dependent reaction rate plot is shown in Fig. 3, from which A, E_a and n determined in the linear region were $4.25 \times 10^7 s^{-1} mol^{-1} dm^3$, 73.1 kJ mol^{-1} and 2, respectively.

Table 2 summarizes the overall Arrhenius parameters measured using the RC1 and by other methods.

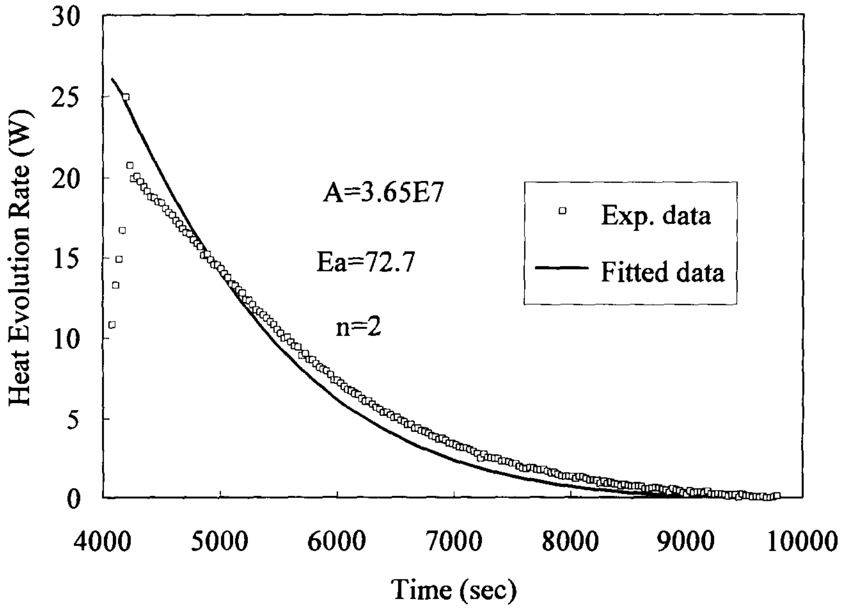

Fig. 1. Isothermal exothermic reaction at 60°C.

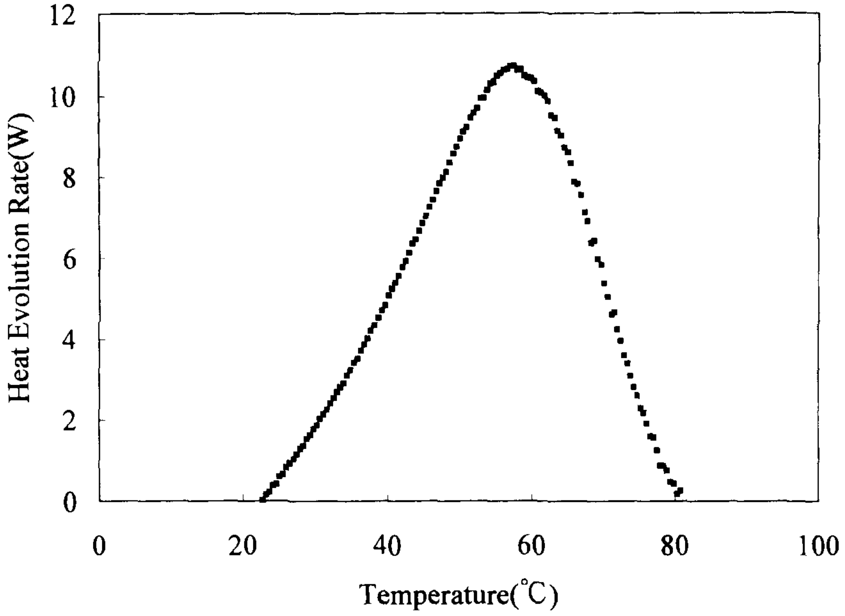

Fig. 2. Dynamic scanning of esterification reaction.

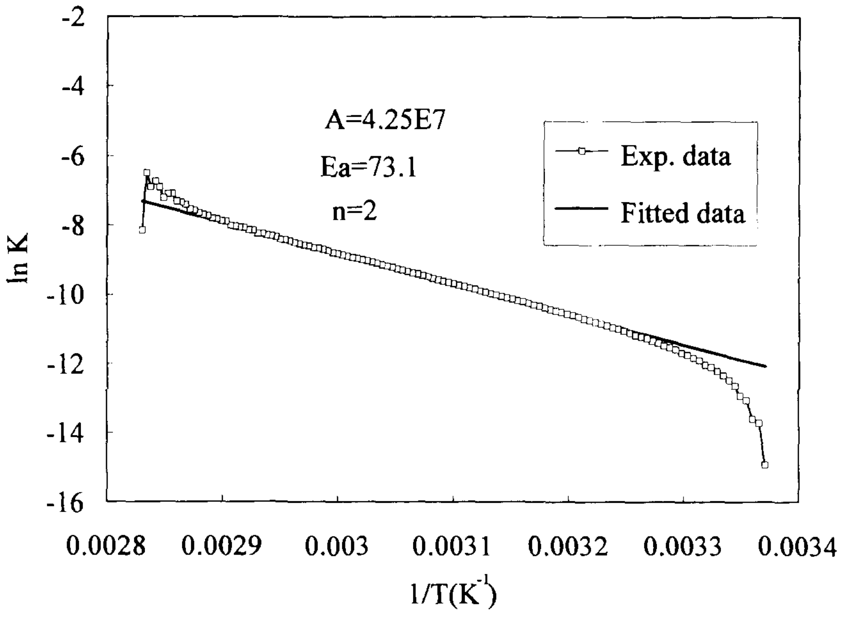

Fig. 3. Arrhenius plot of dynamic scanning of esterification reaction.

Table 2
Comparison of Arrhenius parameters and reaction enthalpy obtained by different tests

	ΔH_r/(kJ mol^{-1})	E_a/(kJ mol^{-1})	A/(s^{-1} mol^{-1} dm^3)
RC1 test	67.3 ± 3.0	72.6 ± 0.5	$(3.6 \pm 0.6) \times 10^7$
ITRI ARC test (Ref. [15])	67.9 ± 0.9	71.4 ± 0.6	$(2.4 \pm 0.5) \times 10^7$
FAI round-robin test (Ref. [5])	64.85	69.45	2.47×10^7
ICI dewar test (Ref. [5])	63.18	71.55	3.94×10^7
FAI RSST test (Ref. [5])	61.9	68.20	1.8×10^7
Monsanto ARC test (Ref. [5])	62.76	71.55	5.48×10^7
HEL PHI-TEC test (Ref. [14])	66.3	71.55	4.67×10^7
VSP test (Ref. [8])	64.9	73.75	8.97×10^6
Dewar test (Ref. [7])	64.4	73.22	1.05×10^7

4.3. Adiabatic runaway measured using the RC1

A safe runaway experiment was performed by adding 16 g methanol to a large quantity of acetic anhydride (756 g) such that the heat evolution was adequately controlled. The adiabatic temperature rise (ΔT_{ad}) was 28°C and the heat of reaction was calculated to be 70 kJ mol^{-1}. The experimental self-heating and adiabatic temperature rising curves are shown in Figs. 4 and 5, respectively. The kinetic parameters in this second-order reaction were obtained by fitting the theoretical curve to the experimen-

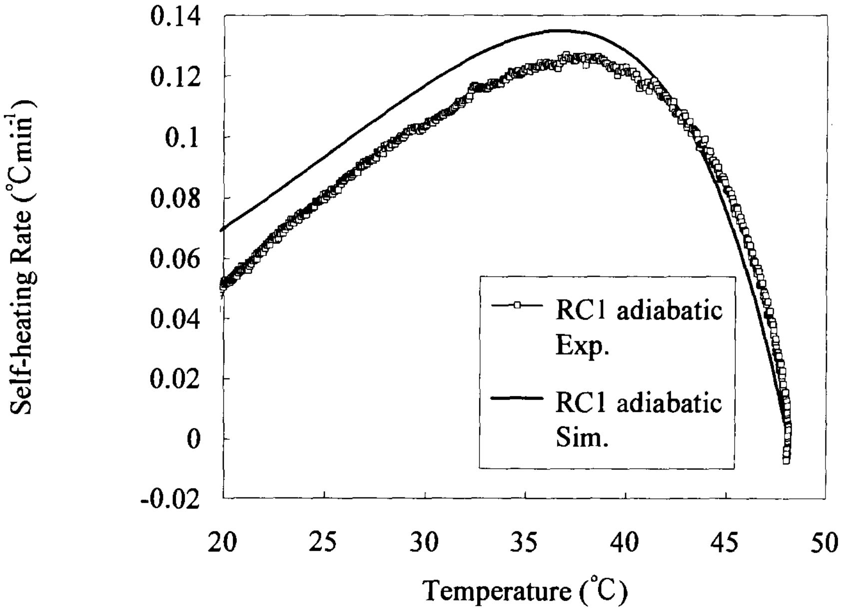

Fig. 4. Self-heating rate of adiabatic runaway reaction.

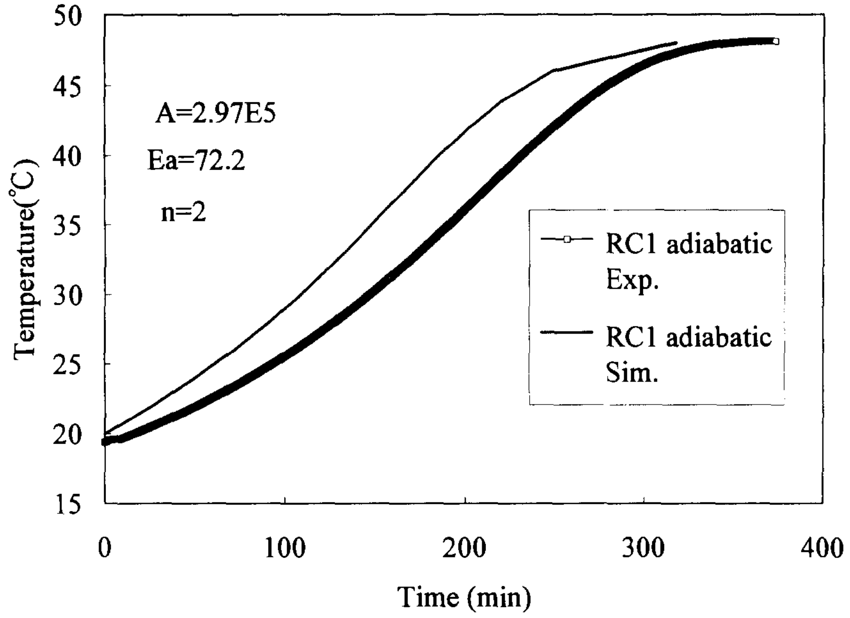

Fig. 5. Experimental and simulated adiabatic runaway reaction in RC1 reactor.

tal data. Notably, the adiabatic temperature rising curve from the RC1 experiment, due to some heat loss, was somewhat behind the theoretical model. Results are shown in Fig. 5 with $A = 2.97 \times 10^7\,\mathrm{s^{-1}\,mol^{-1}\,dm^3}$ and $E_a = 72.2\,\mathrm{kJ\,mol^{-1}}$. The adiabatic self-heating rate (dT/dt) was modeled successfully by Eq. (13), which is that for a second-order reaction.

Adiabatic runaway of acetic anhydride–methanol in the molar ratio 1:2 ($C_{a_0} < C_{b_0}$) was simulated by Eq. (14) with the final temperature (T_f) given by:

$$T_f = T_0 + C_{a_0} \times V \times (\beta/\alpha) \times \Delta H_r/mC_p \tag{15}$$

The experimental and simulated results are shown in Fig. 6. Simulated results based on first-order reaction mechanism correlate well with calorimetry results. Other adiabatic runaway simulations of different molar ratios were also performed. Data and results are displayed in Table 3 and Fig. 7.

4.4. Identification of the critical condition

The heat of reaction, the temperature-dependence of the reaction rate, the concentration, the thermal conductivity, the heat transfer coefficient, the reactor volume, and the heat transfer area are data essential for defining a safe critical condition. A pseudo-zero-order reaction model, which represents the most dangerous exothermic conditions, is employed for safety considerations. This principle is applied and extended to a reaction vessel with its own heat-transfer characteristics. The rate of heat removal is assumed

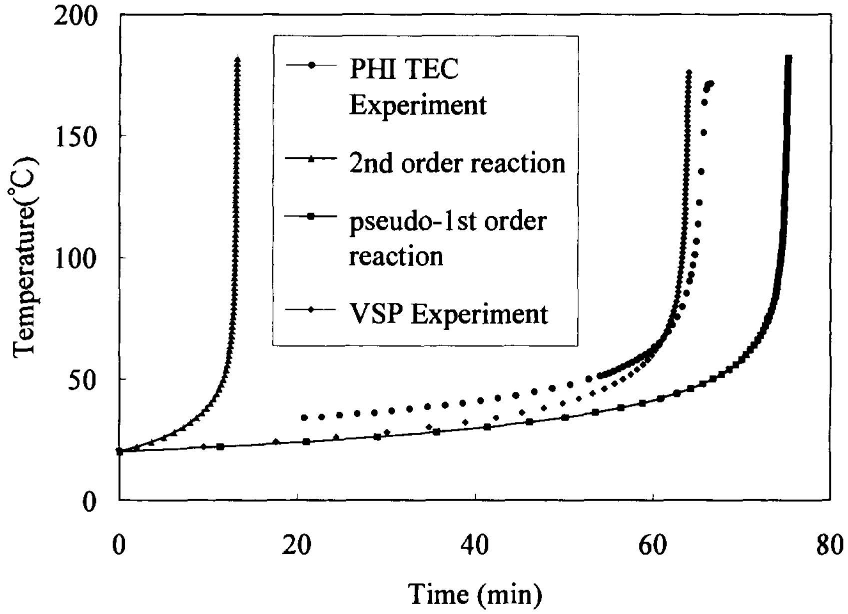

Fig. 6. Experimental and simulated adiabatic runaway reaction in VSP and PHI-TEC equipment.

Table 3
Comparison of adiabatic temperature rise for different molar ratios

	Case 1	Case 2
Reactor volume/m^3	7	7
Mass of methanol/kg	1600	3200
Mass of acetic anhydride/kg	2550	2550
Molar ratio of methanol–acetic anhydride	2	4
Adiabatic temperature rise/°C	164	137

here to be governed by Newtonian cooling, i.e., linearly dependent on the temperature difference between the system temperature and the coolant temperature (T_a). The critical heat-transfer parameter, $(US/V)_{cr}$, can be calculated from the following equation with known values for the kinetic parameters and reaction enthalpy:

$$(US/V)_{cr} = e\{\Delta H_r \rho E_a A\,[\exp(-E_a/RT_a)]/RT_a^2\} \tag{16}$$

Safe (thermal stability) and unsafe (thermal instability) regions can be determined in Fig. 8 by the area either to the left or right of the critical heat transfer parameter curve. Utilizing the data in Table 4, the critical temperature (T_{cr}) was determined as shown in Fig. 9 where T_{cr} is defined by the tangential contact of the heat generation and heat

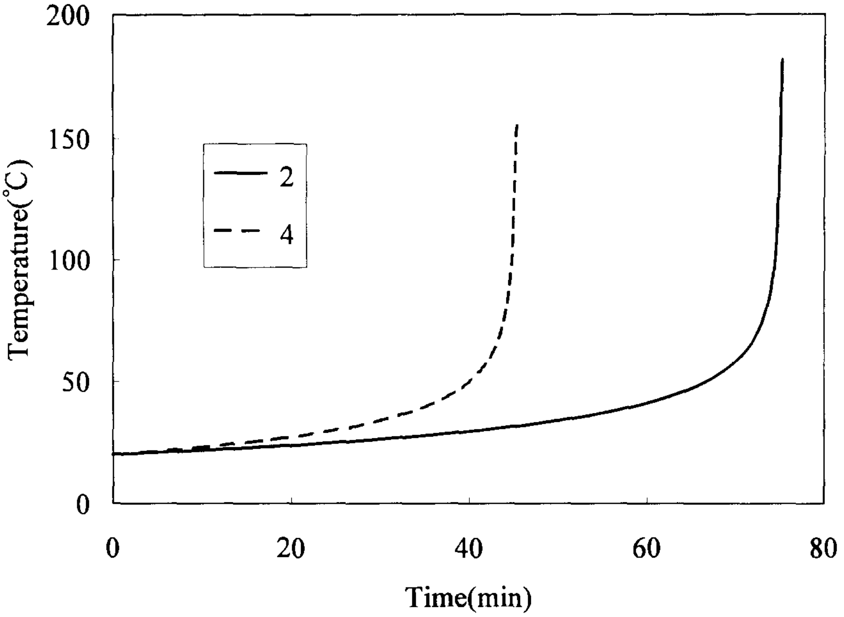

Fig. 7. Simulation of adiabatic runaway reaction for different molar ratios (2 and 4) of methanol–acetic anhydride.

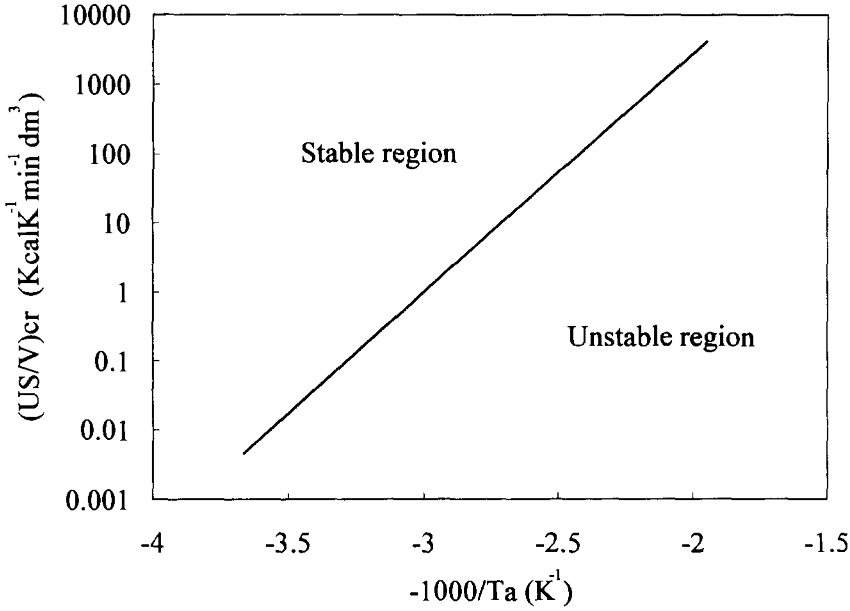

Fig. 8. Critical heat-transfer parameter curve as a function of coolant temperature.

Table 4
Data for calculation of critical heat-transfer parameter

Parameter	Value
Activation energy/(kJ mol^{-1})	72.6
Frequency factor/s^{-1}	3.6×10^7
Reaction enthalpy/(kJ mol^{-1})	66.3
Density/(g cm^{-3})	1.07
Heat transfer coefficient/(W K^{-1})	6.44

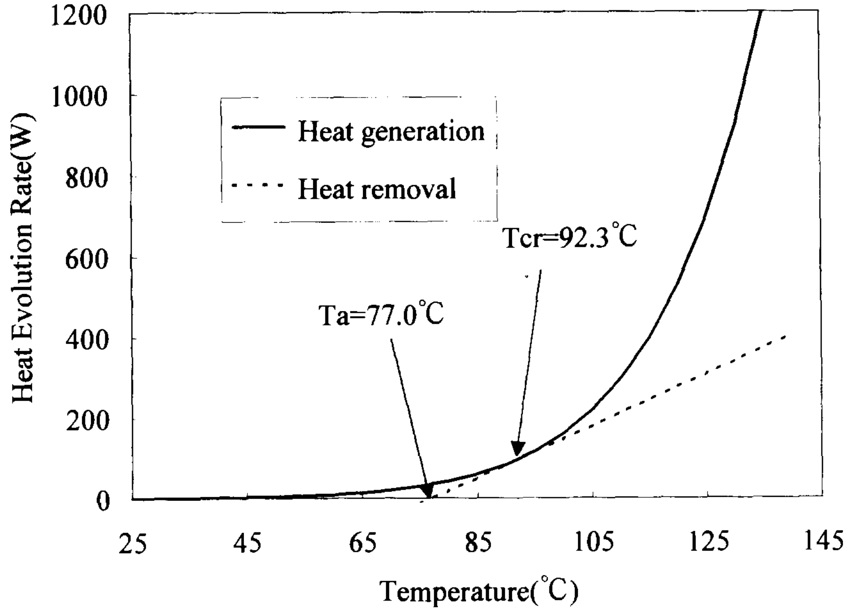

Fig. 9. Tangential point of heat generation and heat removal curves in RC1 reactor.

removal curves. Temperatures higher than T_{cr} cause an increase of temperature and an accelerating runaway will eventually occur.

5. Conclusions

The application of reaction calorimetry (RC) to determination of the kinetics of the reaction between methanol and acetic anhydride can be achieved by utilizing temperature vs. time data under isothermal, temperature-programmed, and adiabatic conditions. The reaction is second order when acetic anhydride is in excess. The activation energy, pre exponential factor, and heat of reaction were determined to be

72.6 ± 0.5 kJ mol^{-1}, $(3.6 \pm 0.6) \times 10^7$ s^{-1} mol^{-1} dm^3, and 67.3 ± 3.0, kJ mol^{-1}, respectively.

Critical safety conditions can be determined using the RC1 reactor and successfully scaled to satisfy actual plant vessel conditions. The experimental data from thermal calorimeters can provide fundamental safety characteristics and can be utilized to prevent the occurrence of thermal runaway reactions.

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