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Thermal Hazard Simulations for Methyl Ethyl Ketone Peroxide Induced by Contaminants

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Abstract−Historically, methyl ethyl ketone peroxide (MEKPO), a universal hardener in the rubber industries, has caused many serious explosions and fires in Taiwan, Japan, Korea, and China. This study used certain thermal analytical methods to thoroughly explore both why MEKPO led to these accidents and what happened during the upset conditions. Potential process contaminants, such as H_2SO_4, KOH, and Fe_2O_3, were deliberately selected to mix with MEKPO in various concentrations. Differential scanning calorimetry (DSC) was employed to calculate the thermokinetic parameters. Kinetic evaluation was also implemented by means of the methods and software developed by Chem-Inform St. Petersburg, Ltd. The results indicate that MEKPO is highly hazardous when mixed with any of the above-mentioned contaminants. Fire and explosion hazards can be effectively lessened if safety parameters and thermokinetic parameters are properly imbedded into manufacturing processes.

Key words: Methyl Ethyl Ketone Peroxide, Contaminants, Differential Scanning Calorimetry, Thermokinetic Parameters, Safety Parameters

INTRODUCTION

Methyl ethyl ketone peroxide (MEKPO), a peroxide produced by reacting methyl ethyl ketone (MEK) with hydrogen peroxide (H_2O_2), is used as a radical source for initiation as a cross-linker during polymerization. A chemical reactor, as one of the most important units in the chemical industry, should be paid tremendous attention, especially if containing an unstably reactive chemical, such as MEKPO [Amornchai et al., 2002; Chung et al., 2004; Kim et al., 2002]. In the last four decades, MEKPO has been involved in some severe thermal explosions in Taiwan, Japan or China, as shown in Table 1 [Duh et al., 1998; Jo and Kim, 2001]. When a horizontal layer of fluid is heated from below with a prominent heating rate, the system may become unstable and eventually encounter an expected runaway, causing various types of accidents [Shin and Choi, 1984; Cho et al., 1993; Kim et al., 2003]. MEKPO has become one of the most noxious materials in Asia. In Taiwan, one of the worst accidents occurred in a specialty chemicals plant--the Yung-Hsin explosion in 1996. The initial fire was found to be a mal-controlled oxidation reaction at the process site, which finally extended to the victim tank yard. This thermal explosion killed 10 people and injured 47. In Tokyo, 3,600 kg (8,000 lbm) of MEKPO exploded, killing 19 and injuring 114 in 1964. The direct cost of the damage from this accident totaled 1.25 U.S. million dollars, not to mention its much higher indirect cost. In China, the thermal explosions of MEKPO killed 5 and injured 3 people in 2003. The reasons for these kinds of accidents should be identified, and this study used kinetic theories to calculate the safety parameters, and then manipulated them to evaluate the exothermic reaction hazards for MEKPO while coexisting with any of H_2SO_4, KOH, and Fe_2O_3.

Table 1. Selected severe thermal explosion incidents caused by MEKPO in Taiwan, Japan, Korea, and China [Duh et al., 1998]

Date	Location	Injuries	Fatalities	Hazard
1979	Taiwan (Taipei)	49	33	Explosion (Storage)
1996	Taiwan (Taoyuan)	47	10	Explosion (Tank)
1964	Japan (Tokyo)	114	19	Explosion
1978	Japan (Kanagawa)	0	0	Explosion
2000	Korea (Yosu)	11	3	Explosion
2001	China (Jiangsu)	2	4	Explosion
2003	China (Zhejiang)	3	5	Explosion

MEKPO, regarded as an inherently unstable material, induces micro-self-exothermic decomposition in the ambient atmosphere. If MEKPO is under upset conditions, such as external fire, overheated reactor, failed cooling system, wrong dosing or error feed percentage and so on, and the heat of reaction cannot be adequately removed simultaneously, it may eventually cause an accident [Kim and Ko, 2005; Park and Kim, 2001]. Therefore, if the stored MEKPO has not been well controlled or protected, and when its environment is encompassed by external fire, a serious accident may be triggered in a later stage, such as thermal explosion, fire, toxic releases, or even severe polluting of the environment.

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MEKPO was found to be an extremely dangerous material, especially when mixed with the above-mentioned contaminants in a process. By combining differential scanning calorimetry (DSC) with simulative programming method to describe and depict the phenomena of exothermic reactions, we could provide a way for a staff to prevent and mitigate the hazards, casualties and the damages from the runaways. In this study, we used kinetic theories to calculate the safety operation parameters, and then manipulated them to evaluate the heat of exothermic reaction for MEKPO while it coexists with any of H_2SO_4, KOH, and Fe_2O_3 in process.

EXPERIMENTAL SETUP

1. Sample Preparations

MEKPO 31 wt% was purchased directly from the Fluka Co., and then stored in a refrigerator at 4 °C. Dimethyl phthalate (DMP) was used as the diluent solvent in preparing various concentration MEKPO samples.

Three specific concentrations of different contaminants were used in this study, of H_2SO_4 (0.5 M), KOH (1.0 M) and Fe_2O_3 (solid), as the contaminants, and then the specific contaminant (0.5-1.0 mg) was added into the measuring cell mixed with MEKPO 31 wt% (about 5.0 mg).

2. Differential Scanning Calorimetry (DSC)

Temperature-programmed screening and isothermal experiments were performed (Mettler TA8000 system) and coupled with a measuring cell that can withstand relatively high pressure to approximately 100 bar (DSC 821^e). STAR^e software was used to obtain thermograms and isothermal traces [Mettler, 1998]. For better thermal equilibrium, the scanning rate chosen for the temperature-programmed ramp was 4 °Cmin^{-1} [Hou et al., 2001]. The range of temperature rise was chosen from 30 to 350 °C for each condition of experiments. This apparatus could precisely calculate the kinetic parameters and then evaluate the n-order reaction in the complex reactions.

APPLICATIONS OF TMR WITH THEORETICAL APPROACHES

For the estimation of safety parameters in kinetics, the time to maximum rate (TMR) is an important approach to tabulate the hazardous scenarios for runaway reaction. In the literature review, TMR was acquired to evaluate the related reaction hazards from Townsend [Townsend and Tou, 1980; Kang et al., 2001] for the purpose of evaluating and preparing the emergency response measures. To determine the possibility of multiple steady states in a complex reaction network of high deficiency, one efficient method is to study its subnetworks [Chuang et al., 2004]. Moreover, this study introduced theories for promising applications in real conditions.

1. The Definition of Time to Maximum Rate (TMR)

TMR is a very important safety parameter in a manufacturing process or upset conditions. It is used to investigate the degree of safety, degree of threat, and so on. TMR means that the reaction is very imminent. Calculating the TMR in the runaway reaction can provide the firefighter information about how much time is left to salvage, or instruct workers on how to curtail the degree of hazard.

This study used Eq. (1) to calculate the TMR as below:

$$\mathrm{TMR}=\frac{\mathrm{RT}^2}{\mathrm{AE}_a\Delta\mathrm{T}_{ad}}\mathrm{e}^{-E_a/RT} \tag{1}$$

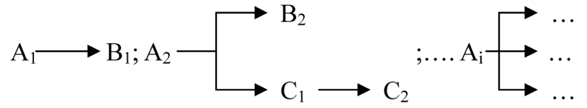
$$\Delta\mathrm{T}_{ad}=\frac{\mathrm{Q}}{\mathrm{C}_p} \tag{2}$$

According to the calculated results for safety parameters, if the TMR is increased, the impact of hazard will decrease.

2. Simulation Methods

2-1. Kinetic Models

In an ordinary single reaction, the effect is only by external mass transfer, because the surface concentration of a reaction is never thicker than that in the bulk under isothermal conditions due to diffusional resistance [Sei and Won, 1985; Song et al., 2002]. In a non-isothermal process, the explanation of the phenomenon around the catalyst particles is quite sophisticated since the reaction rate is simultaneously susceptible to both the concentration gradient and the temperature gradient [Won, 1986; Yu et al., 2003]. Formal models can represent complex multi-stage reactions that may include several independent, parallel, and consecutive stages [Kossoy and Hofelich, 2003].



2-2. Formal Models

There are three kinds of reaction mechanisms that could be expressed as follows:

(1) Simple single-stage reaction:

$A \rightarrow B$

$$\frac{\mathrm{d}\alpha}{\mathrm{dt}}=\mathrm{Ae}^{-E_a/RT}\mathrm{f}(\alpha);\ \text{where } \alpha \text{ is the conversion of the reactant A} \tag{3}$$

$$\mathrm{f}(\alpha)=\begin{cases}(1-\alpha)^n\text{-n-order reaction}\\(1-\alpha)^{n_1}(\alpha^{n_2}+\mathrm{z})\text{-autocatalytic reaction}\end{cases}$$

(2) Reaction including two consecutive stages:

$A \rightarrow B \rightarrow C$

$$\frac{\mathrm{d}\alpha}{\mathrm{dt}}=\mathrm{Ae}^{-E_1/RT}(1-\alpha)^{n_1};\ \frac{\mathrm{d}\gamma}{\mathrm{dt}}=\mathrm{A}_2\mathrm{e}^{-E_2/RT}(\alpha-\gamma)^{n_2} \tag{4}$$

where α and γ are conversions of the reactant A and product C, respectively.

(3) Two parallel reactions:

$A \rightarrow B+\ldots$----initiation stage

$A+B \rightarrow 2B^+\ldots$----autocatalytic reaction

The above equations represent a very useful model of full autocatalysis:

$$\frac{\mathrm{d}\alpha}{\mathrm{dt}}=\mathrm{K}_1(\alpha)+\mathrm{K}_2(\alpha) \tag{5}$$

$$\mathrm{K}_1(\alpha)=\mathrm{k}_1(\mathrm{T})(1-\alpha)^{n_1} \tag{6}$$

$$\mathrm{K}_2(\alpha)=\mathrm{k}_2(\mathrm{T})\alpha^{n_2}(1-\alpha)^{n_3} \tag{7}$$

2-3. Complex Models

Like esterification reactions, they could be characterized by self-

Table 2. Calculated thermokinetic and safety parameters derived from the dynamic scanning experiments of MEKPO 31 wt% and its contaminants for the first peak of the reaction by DSC (MEKPO 31 wt%–n-order; MEKPO 31 wt%+H_2SO_4–n-order; MEKPO 31 wt%+KOH–autocatalytic; MEKPO 31 wt%+Fe_2O_3–autocatalytic) [Chang, 2003]

MEKPO and contaminants	m (mg)	r (°Cmin^{-1})	T_{max} (°C)	T_0 (°C)	E_a (kJmol^{-1})	n_1	n_2	A (sec^{-1}M^{1-n})	ΔH (Jg^{-1})
MEKPO 31 wt%	5.5	4	130.08	96.22	70.46	0.55	*	15.33	351.07
				98.91	**80.33**	**0.69**	*	**18.45**	**345.37**
MEKPO 31 wt%+H_2SO_4 (0.5 M)	4.8	4	100.87	79.33	92.70	1.18	*	24.42	374.87
				78.02	**86.74**	**1.15**	*	**22.49**	**408.93**
MEKPO 31 wt%+KOH (1.0 M)	4.5	4	45.73	38.70	269.37	1.76	*	97.71	34.55
				36.37	**50.35**	**0.91**	**0.64**	**14.79**	**54.09**
MEKPO 31 wt%+Fe_2O_3 (solid)	5.0	4	59.70	45.11	115.22	1.26	*	36.74	76.07
				42.79	**68.25**	**1.00**	**0.45**	**20.01**	**79.61**

---The first peak of the reaction.

---Calculated values based on experimental data from DSC tests.

---Simulated values.

*Not applicable.

Table 3. Calculated thermokinetic and safety parameters derived from the dynamic scanning experiments of MEKPO 31 wt% and its contaminants for the second peak of the reaction by DSC (MEKPO 31 wt%–autocatalytic; MEKPO 31 wt%+H_2SO_4–autocatalytic; MEKPO 31 wt%+KOH–autocatalytic; MEKPO 31 wt%+Fe_2O_3–n-order)

MEKPO and contaminants	m (mg)	r (°Cmin^{-1})	E_a (kJmol^{-1})	n_1	n_2	z	A (sec^{-1}M^{1-n})	ΔH (Jg^{-1})
MEKPO 31 wt%	5.5	4	96.22	0.85	1.41	0.0335	20.68	438.46
MEKPO 31 wt%+H_2SO_4 (0.5 M)	4.8	4	100.16	0.54	0.21	0.0994	20.66	593.78
MEKPO 31 wt%+KOH (1.0 M)	4.5	4	72.19	0.41	0.43	0.0115	19.61	21.49
MEKPO 31 wt%+Fe_2O_3 (solid)	5.0	4	91.94	1.03	*	*	22.05	344.20

---The second peak of the reaction.

---Calculated values based on experimental data from DSC tests.

---Simulated values.

---z: Autocatalytic constant [Kossoy and Hofelich, 2003].

*: Not applicable.

acceleration. Therefore, the two-stage concentration-based descriptive model that describes the autocatalytic effect of an acid reaction product has been chosen for kinetics evaluation [Kossoy and Akhmetshin, 2005]:

$\mathrm{I+P} \xrightarrow{b_1} \mathrm{IP+PA}$----initiation stage

$\mathrm{I+P+PA} \xrightarrow{b_2} \mathrm{IP+2\cdot DPA}$----catalyzed interaction

$$b_1=k_1[I]^{n_{11}}[P]^{n_{12}} \tag{8}$$

$$b_2=k_2[I]^{n_{21}}[P]^{n_{22}}[PA]^{n_{23}} \tag{9}$$

$$\frac{d[I]}{dt}=\frac{d[P]}{dt}=-b_1-b_2 \tag{10}$$

$$\frac{d[IP]}{dt}=\frac{d[PA]}{dt}=b_1+b_2 \tag{11}$$

$$k_i=k_{0i}e^{-E_i/RT} \tag{12}$$

$$\frac{dQ}{dt}=Q_1b_1+Q_2b_2 \tag{13}$$

RESULTS AND DISCUSSION

1. Results of Experiments and Simulations

This study conducted thorough analytical experiments with simulated methods by the aid of DSC. Operating conditions, in coordination with the theories of Townsend [Townsend and Tou, 1980],

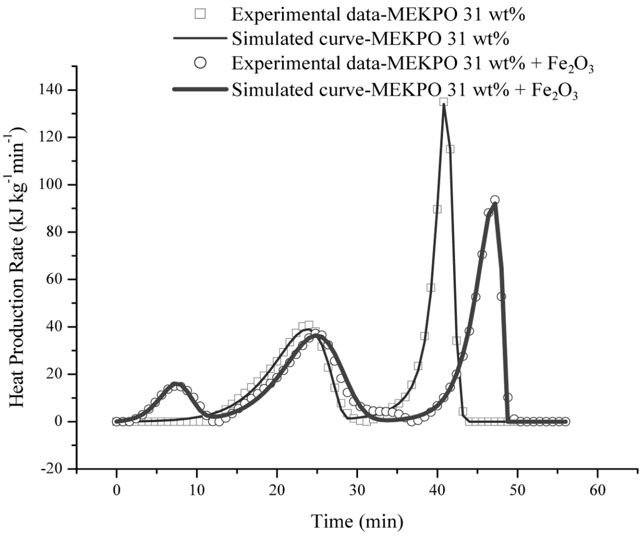


Fig. 1. Simulated heat production rate vs. time by the DSC experiments for MEKPO 31 wt% mixed with Fe_2O_3.

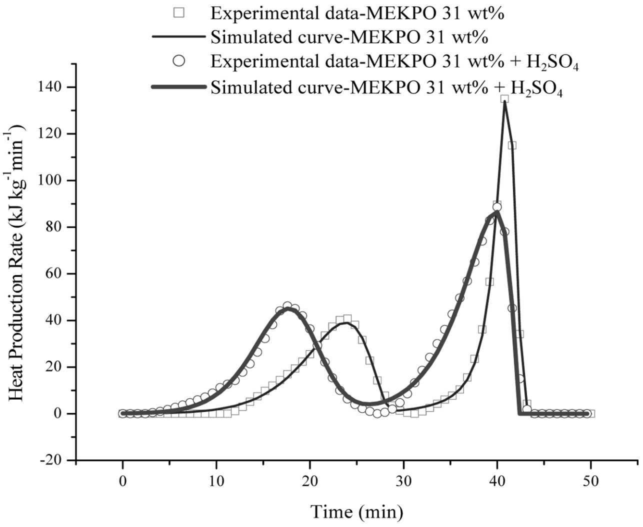


Fig. 2. Simulated heat production rate vs. time by the DSC experiments for MEKPO 31 wt% mixed with H_2SO_4.

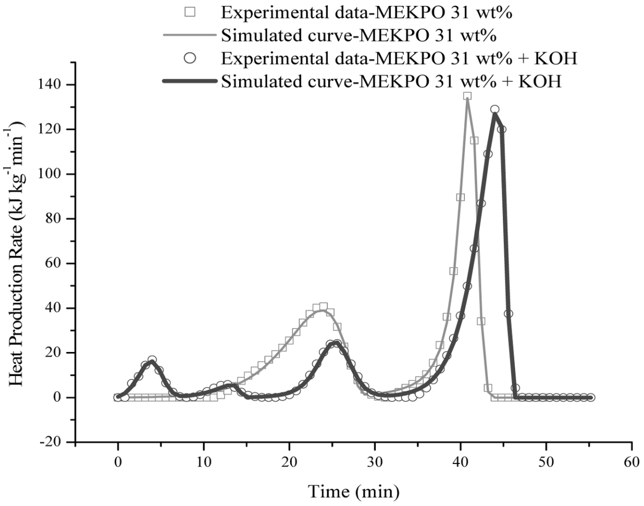


Fig. 3. Simulated heat production rate vs. time by the DSC experiments for MEKPO 31 wt% mixed with KOH.

led to the results which could be used to evaluate the hazard of reactions.

Sulfuric acid (H_2SO_4), potassium hydroxide (KOH) and iron sesquioxide (Fe_2O_3) were used as the contaminants, mixed with MEKPO 31 wt%. In summary, Tables 2, 3 and Figs. 1-6 are shown as follows.

2. Experimental Analyses

In experiments tested by DSC, H^+ (H_2SO_4), OH^- (KOH) and Fe^{3+} (Fe_2O_3) were used as the contaminants of interest. In general, the added contaminants all increased the degree of hazard, in terms of lower T_0, higher ΔH and A.

Chemicals like Fe^{3+} (Fe_2O_3) and OH^- (KOH) affected the exothermic onset temperature (T_0) significantly, both of which induced the exothermic reaction to form earlier. In comparison, pure MEKPO displayed two peaks. After the Fe^{3+} (Fe_2O_3) or OH^- (KOH) was added to MEKPO, it formed different peaks on the exothermic reactions, and changed its configuration, as disclosed in Figs. 1 and 3.

As shown in Figs. 1 to 3, the MEKPO, along with its contaminants, is discussed separately as follows. When MEKPO mixed with Fe_2O_3, it caused the first peak to form in advance and increased the exothermic capacity (greater ΔH). However, it decreased the exothermic reaction of the second peak distinctly. This reaction induced more than two peaks, which indicated that Fe^{3+} might play a crucial role on MEKPO runaway. When mixed with H_2SO_4, it affected the T_0 unclearly and did not induce very furious reactions. But, it still had potential hazard due to the mixing conditions. When mixed with KOH, it had more than two reactions and changed the configuration of the first peak. The potential reactions were induced by OH^- and then the T_0 occurred earlier in the range of 35-40 °C, whereas the second peak was not affected clearly.

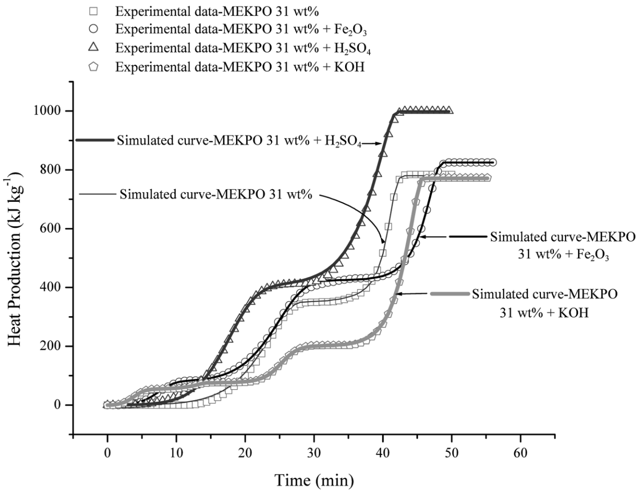


Fig. 4. Simulated heat production vs. time by the DSC experiments for MEKPO 31 wt% with its contaminants.

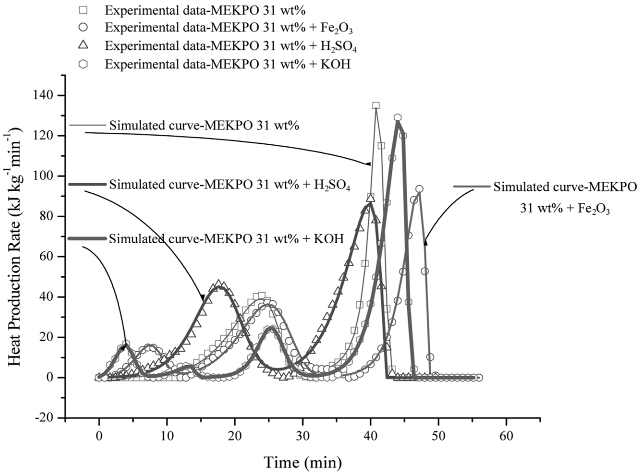


Fig. 5. Simulated heat production rate vs. time by the DSC experiments for MEKPO 31 wt% with its contaminants.

3. Simulative Analyses

The simulative method was employed to deal with the experimental data. Not only can it calculate the n-order reaction, but also calculate the autocatalytic reaction. From Table 2, MEKPO 31 wt%, when mixed with KOH and Fe_2O_3, shows a great diversity in apparent activation energy (E_a) and frequency factor (A), because only the n-order reactions were considered in the STAR^e software. Actu-

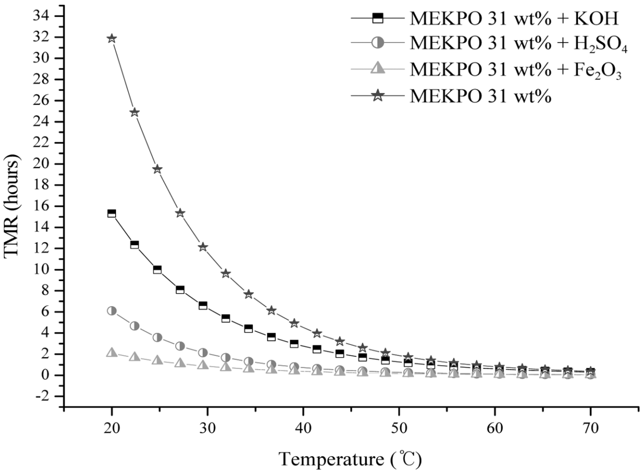


Fig. 6. Simulated time to maximum rate (TMR) vs. temperature by the DSC experiments for MEKPO 31 wt% with its contaminants.

ally, the reactions may include various conditions, such as self-accelerating reactions, consecutive reactions, n-order reactions and autocatalytic reactions. Consequently, the simulative method was chosen to calculate the reactions, which were determined as autocatalytic reactions for the experimental mixing process. From Table 3, the second peak of MEKPO, mixed with contaminants, was simulated. The simulative parameters were aimed at the E_a, A, n, and ΔH. This method was applied to test and corroborate the experimental results with the adds of the meaning of complex reactions.

Fig. 6 shows that MEKPO, when mixed with contaminants, such as H_2SO_4, KOH, and Fe_2O_3, might increase the degree of hazard by lessening the TMR. Especially, while mixed with Fe_2O_3, MEKPO not only changed its innate character but also greatly dropped the TMR, and triggered unexpected runaway reactions, such as decomposition, fire, explosion, and so on. This study used the T_0 to confer the exothermic decomposition. Then, by evaluating the evaluated ΔH could be discussed as to the degree of hazard for curtailing accidents in manufacturing processes.

CONCLUSIONS

With the simulated kinetic parameters (E_a, A, ΔH, n), the results were compared with the parameters obtained from experiments, as used to estimate safety parameters such as TMR. The simulations could precisely optimize the kinetic parameters from the experimental values in the simulated results, and then the mathematical function could be fully exploited to estimate upset situations which might induce runaway reactions.

The thermokinetic and safety parameters of mathematical values indicate that the MEKPO dimer is safer by itself than when mixed with contaminants. Consequently, the safety parameter could provide valuable information to prevent an operating process from incurring any runaways.

Various discrepancies may arise from the experiments and simulations. To increase the degree of accuracy in curve fitting, many methods can be employed, such as tightly sealing the measuring cell, avoiding churning in the experiment, exactly placing the materials for measurement, making frequent modifications, and so forth. By utilizing the DSC and simulative method, one can achieve a good degree of accuracy in curve fitting, and thereby gain accurate data for coping with any runaway reactions in real manufacturing processes.

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NOMENCLATURE

A : frequency factor [sec^{-1}M^{1-n}]
b_i : rate of the ith stage
C_p : specific heat capacity [Jg^{-1}K^{-1}]
E_a : apparent activation energy [kJmole^{-1}]
k : rate constant [sec^{-1}M^{1-n}]
K : rate of a stage [Ms^{-1}]
m : mass of reactant [g]
n : reaction order, dimensionless
P_{max} : maximum pressure [psig]
Q_g : calorific capacity of measuring cell from exothermic substances [Jg^{-1}]
Q_i : heat of a reaction of the ith stage; in formal models [kJkg^{-1}] and in concentration-based descriptive models [kJmol^{-1}]
Q_l : calorific capacity from measuring cell to the environment [Jg^{-1}]
r : scanning rate [°Cmin^{-1}]
R : gas constant [8.314 Jmol^{-1}K^{-1}]
T : temperature [°C]
T_{max} : maximum temperature during overall reaction [°C]
TMR : time to maximum rate [hr]
T_0 : exothermic onset temperature [°C]
z : autocatalytic constant, dimensionless
ΔH : heat of reaction [Jg^{-1}]
ΔT_{ad} : adiabatic temperature rise [°C]
α : degree of conversion, dimensionless
γ : degree of conversion, dimensionless

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