Study of thermal decomposition of methyl ethyl ketone peroxide using DSC and simulation

Jo-Ming Tseng [a], Ying-Yu Chang [b], Teh-Sheng Su [c], Chi-Min Shu [a],*

[a] *Doctoral Program, Graduate School of Engineering Science and Technology, National Yunlin University of Science and Technology (NYUST),*
123 University Road, Sec. 3, Douliu, Yunlin 64002, Taiwan, ROC
[b] *Process Safety and Disaster Prevention Laboratory, Department of Safety, Health, and Environmental Engineering, NYUST,*
123 University Road, Sec. 3, Douliu, Yunlin 64002, Taiwan, ROC
[c] *Department of Safety, Health, and Environmental Engineering, Central Taiwan University of Science and Technology,*
11 Buh-Tzyy Alley, Buh-Tzyy Village, Beei-Twen District, Taichung 406, Taiwan, ROC

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Abstract

Methyl ethyl ketone peroxide (MEKPO) is a typical organic peroxide with thermally unstable nature that has been broadly employed in the manufacturing process of acrylic resins, as a hardening agent for fiberglass-reinforced plastics, and as a curing agent for unsaturated polyester resins.

The aim of this study was to identify the characteristics of MEKPO 31 wt.% while mixing with contaminants, such as H_2SO_4, HCl, and NaCl under runaway conditions. To acquire the thermal runaway data, DSC and a simulation were used for thermal analysis. The results showed that the thermal decomposition of MEKPO and MEKPO + H_2SO_4 follows two stages. The first one can be modeled by using an empirical nth order rate equation. The second stage can be modeled as autocatalytic. MEKPO + HCl and MEKPO + NaCl included two independent autocatalytic reactions. The decomposition of MEKPO in the presence of Cl^- ions (added in MEKPO either in the form of HCl or NaCl) follows a significantly different path, an earlier decomposition "onset" temperature, higher amount of generated thermal power and smaller temperature of no return (T_{NR}) and time to maximum rate (TMR) values. Simulations based on experimental data indicated that the effect of H_2SO_4 was the most dangerous contaminant on MEKPO 31 wt.%. However, the impact of Cl ions was also important. It is therefore recommended that the means of fire fighting employed for this substance to be free of Cl^-.

1. Introduction

In recent years, process accidents have continued to occur around the world. In the past few decades, various serious fire and explosion accidents involving methyl ethyl ketone peroxide (MEKPO) in Asia, as displayed in Table 1 [1–4], were due to its thermal instability or process upsets. In Taiwan, one of the most serious accidents was the Yung-Hsin explosion which occurred in 1996. A fire-induced thermal explosion killed 10 and injured 47 during the fire fighting. In Tokyo, 3600 kg of MEKPO exploded after being heated by a fire in 1964, killing 19, wounding 14, with monetary losses of US$ 1.25 million for that time. In Yuso, Korea, a MEKPO explosion killed 3 and injured 11 in 2000, costing US$ 57,000 [4]. In 2004, the explosion of the Hinhua Chemical plant in Honan, China, killed five, and injured eight, due to improper operation of MEKPO. As seen in the literature, accidents have been induced by unsafe-conditions during the manufacturing process for finishing products, and then the finished products were mixed with the contaminants, which resulted in a thermal explosion. The accidents with MEKPO were mainly ascribed to being induced under thermal runaway and usually occurred during manufacturing, storage, and transportation stages. When MEKPO contacts external heat or various contaminants, such as acids or bases, severe thermal decomposition occurs. Until now, the reaction hazards of its contaminants have not been clearly identified. The critical runaway temperature and unstable reaction criteria for specific systems containing MEKPO need to be evaluated, so that proactive safety measures could be established. These examples of these disasters show the horrors of chemical accidents. Therefore, proactive

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* Corresponding author. Tel.: +886 5 534 2601x4416; fax: +886 5 531 2069.
E-mail address: shucm@yuntech.edu.tw (C.-M. Shu).

Year	Location	Injuries	Fatalities
1964	Tokyo, Japan	114	19
1996	Taoyuan, Taiwan	47	10
2000	Yosu, Korea	11	3
2004	Honan, China	8	5

prevention of thermal runaway of fire and explosion hazards is a critical issue in process safety worldwide. This study discusses the potential hazard-characteristics of MEKPO under various conditions.

As far as loss prevention for MEKPO is concerned, its contaminants reaction hazards have not been clearly identified, and the critical runaway temperature and unstable reaction criterion for specific systems are still unknown. To acquire the thermal runaway data, differential scanning calorimetry (DSC) and simulation were employed for thermal analysis. Their kinetic model and safety parameters were estimated, and then provided to the manufacturing process for lessening the degree of hazard.

2. Literature review

In 2004, the annual quantity of MEKPO usage was 250 tonnes in Taiwan and 13,000 tonnes in China. Most Taiwanese chemical industries have their own supply of MEKPO, but a few rely on imports [5]. MEKPO, which has been broadly used in the process industries, as initiator and hardener for curing of the unsaturated polyester resins, is generalized as the two typical structures shown in Fig. 1.

MEKPO is a kind of oily liquid; its boiling point is below $-20\,°C$, and its flash point is $52–93\,°C$. If it is not controlled properly, while contacting heat or various contaminants, such as acids or bases, severe thermal decompositions will be induced immediately. According to the National Fire Protection Association (NFPA), the thermal decomposition of MEKPO might occur at $40\,°C$. If MEKPO is inadvertently contacted with contaminants (such as rags or rust), this might occur at even below $30\,°C$. In a typical container, its active oxygen (AO) is 5.5–9.0 wt.%. Its transport concentration limit value is 60 wt.%, and AO must be less than 9 wt.% [6]. For safe maintenance during various stages, MEKPO has been usually diluted by dimethyl phthalate (DMP).

Many chemical incidents have been caused by organic peroxide whose peroxy functional group –O–O– is inherently unstable and active. According to NFPA 43B, the degree of hazard for MEKPO has been classified as class III or IV [6].
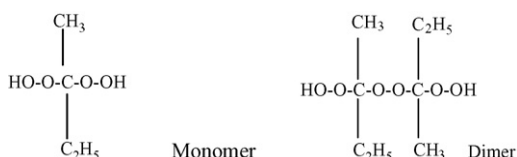
This study was undertaken with a view of identifying the characteristic behavior of contaminants with MEKPO under runaway conditions. Dynamic DSC tests and then simulations were employed on MEKPO to mix with H_2SO_4, HCl, and NaCl for thermal analyses in order to acquire tests.

3. Experimental setup

3.1. Sample

MEKPO dimer of 31 wt.% in DMP was purchased from the Fluka Co., and then stored in a $4\,°C$ freezer to avoid any runaway under ambient conditions.

3.2. Contaminants

Three types of contaminants were employed for testing the mixing conditions, such as H_2SO_4 (0.5 M), HCl (1.0 M) and NaCl (1.0 M), as the contaminants, and then the quantitative-specific contaminant (0.4–0.5 mg) was added into the measuring cell and mixed with MEKPO 31 wt.% (about 4.5 mg). We deliberately selected compounds of H^+, such as HCl, H_2SO_4. Furthermore, by comparing the effects of Na^+ and Cl^- on MEKPO, NaCl was used as another contaminant for other comparisons.

3.3. 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 [7]. The sample and reference were connected with a low resistance heat-flow path (a metal disc). The changes for enthalpy or heat capacity in the sample caused a temperature difference relative to the reference for comparison. The resulting heat flow was small, compared with differential thermal analysis, because the sample and reference were in good thermal contact. The temperature difference was recorded and related to enthalpy change in the sample by using calibration experiments. The scanning rate chosen for the temperature-programmed ramp was $4\,°C/min$ to maintain better thermal equilibrium. The tests were conducted between 35 and $350\,°C$ with a series of various contaminants.

4. Results and discussion

4.1. Thermal hazard analysis

Fig. 2 illustrates the results of heat flow versus sample temperature of MEKPO 31 wt.% with contaminants from dynamic DSC tests. Figs. 3 and 4 show the proposed decomposition mechanism of MEKPO and heat production rate versus temperature on MEKPO with the compounds of various contaminants, respectively. From Fig. 2, two distinct exothermic peaks obtained from MEKPO 31 wt.% test indicated that the reaction was very complex. In Table 2, the onset temperature (T_o) of the first reaction region detected by DSC was about $98.91\,°C$, and its peak tem-

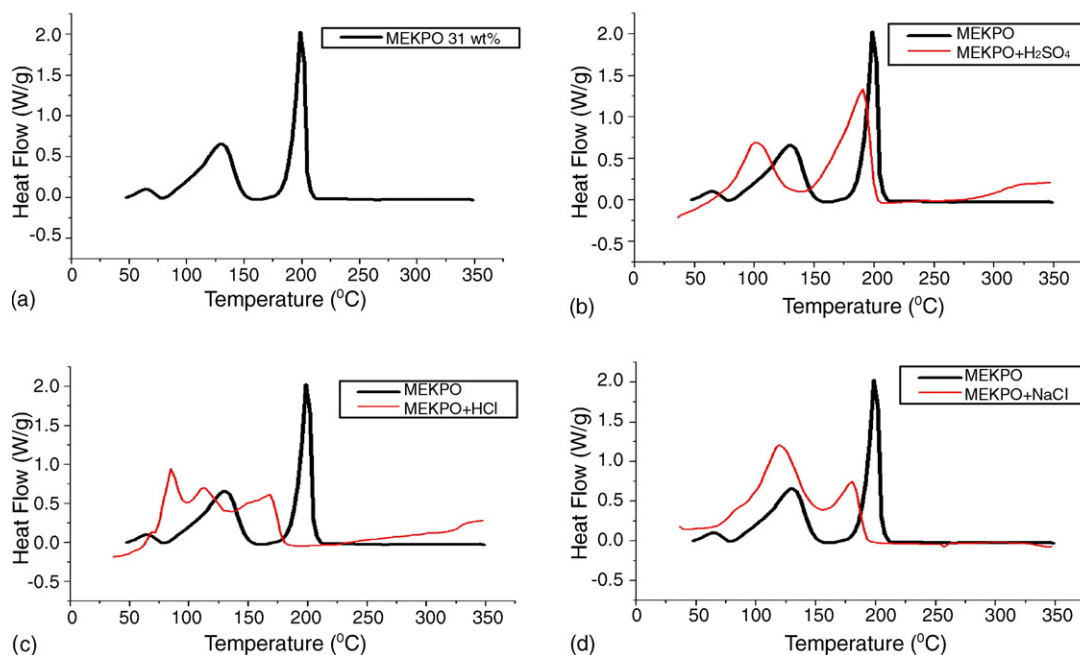

Fig. 1. Two typical forms of MEKPO.

Fig. 2. Heat flow vs. temperature of MEKPO 31 wt.% mixed with its contaminants from DSC tests. (a) MEKPO 31 wt.%, (b) MEKPO 31 wt.% mixed with 0.5 M H_2SO_4, (c) MEKPO 31 wt.% mixed with 1.0 M HCl and (d) MEKPO 31 wt.% mixed with 1.0 M NaCl.
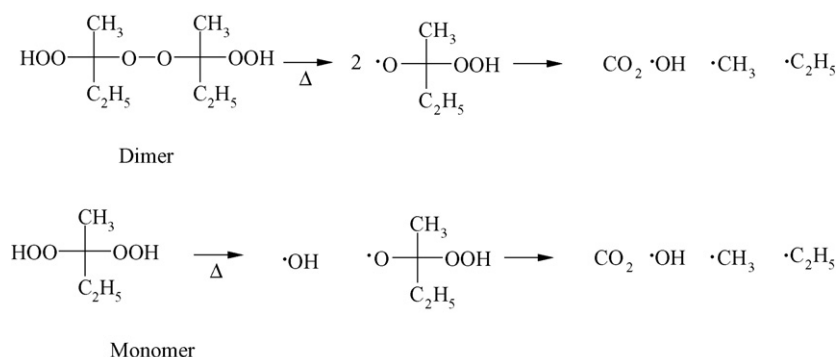

Fig. 3. Proposed decomposition mechanism of MEKPO.

perature was 130.08 °C. Tables 2 and 3 summarize the data of the related kinetic parameters, such as activation energy (E_a), frequency factor (k_0), reaction order (n), and heat of reaction (ΔH).

From DSC thermal curves, pure MEKPO 31 wt.% had two peaks, which revealed it was more complicated than other per-

oxides, such as cumene hydroperoxide (CHP) [8]. After the above-mentioned contaminants were mixed in the experiment, the configuration of the peaks was varied, and more than two peaks were induced. In addition, mixing with contaminants that would promote the reaction advanced (all of the T_0 had been decreased) and exacerbated the thermal hazard of the first reac-

Table 2
Calculated thermokinetic parameters derived from the dynamic scanning experiments of MEKPO 31 wt.% and its contaminants for the first peak of the reaction by DSC tests

MEKPO and contaminants	Parameters							
	m (mg)	T_{max} (°C)	T_0 (°C)	E_a (kJ/mol)	n_1	n_2	k_0	ΔH (J/g)
MEKPO 31 wt.%	5.5	130.08	98.91	80.33	0.69	[a]	18.45	345.37
MEKPO 31 wt.% + H_2SO_4 (0.5 M)	5.3	100.87	78.02	86.74	1.15	[a]	22.49	246.89
MEKPO 31 wt.% + HCl (1.0 M)	4.6	90.77	68.43	92.57	1.80	0.44	25.49	563.43
MEKPO 31 wt.% + NaCl (1.0 M)	5.3	119.44	77.97	67.75	0.96	0.31	14.23	580.67

[a] Not applicable.

Table 3
Calculated thermokinetic parameters derived from the dynamic scanning experiments of MEKPO 31 wt.% and its contaminants for the second peak of the reaction by DSC tests

MEKPO and contaminants	Parameters						
	m (mg)	E_a (kJ/mol)	n_1	n_2	z	k_0	ΔH (J/g)
MEKPO 31 wt.%	5.5	96.22	0.85	1.41	0.034	20.68	438.46
MEKPO 31 wt.% + H$_2$SO$_4$ (0.5 M)	5.3	100.26	0.54	0.21	0.099	20.66	593.79
MEKPO 31 wt.% + HCl (1.0 M)	4.6	111.54	0.88	0.81	0.152	26.26	237.13
MEKPO 31 wt.% + NaCl (1.0 M)	5.3	124.23	0.95	0.54	0.003	28.49	187.32

z: autocatalytic constant.

tion region; especially, the Cl$^-$ ions extracted from HCl and NaCl had induced T_0 earlier to occur at the temperature of 68.43 and 77.97 °C separately. Accordingly, their Cl$^-$ compound is assumed to be potentially hazardous.

4.2. Kinetic analysis

4.2.1. Kinetic analysis for MEKPO 31 wt.%

By inferring that the decomposition mechanism of MEKPO could be expressed as in Fig. 3.

However, the decomposition mechanism of MEKPO with contaminants has not yet been established. In the past, there was a problem with the thermal safety analysis software—STAR^e, in that it can only calculate an nth order reaction. Therefore, we tried to use the simulation function with kinetic models to assess the decomposition of MEKPO and its contaminants. For every stage of a kinetic model in simulation functions, the rate of the stage should be defined as a function of temperature and degree of conversion: $r = k(t)f(\alpha)$. The simulation function is based on the usual assumption that temperature dependency of a reaction rate follows the Arrhenius law, i.e. $k = k_0 \exp(-E_{ai}/RT)$ (where k_{0i} and E_{ai} denote the frequency factor and activation energy of the ith stage). R is the gas constant (=8.314 J/mol/K).

As delineated in Fig. 4, the curve of MEKPO 31 wt.% contains two distinct exothermic peaks. The decomposition behavior of MEKPO 31 wt.% could be properly described by a model

Fig. 4. Calculated and experimental reaction rate of heat production vs. time curves at different contaminants mixed with MEKPO 31 wt.%.

of competitive reactions. Further, this scheme results in two independent reactions:

$$A \xrightarrow{\alpha_1} B \quad \text{(1st peak)} \tag{1}$$

$$E \xrightarrow{\alpha_2} F \quad \text{(2nd peak)} \tag{2}$$

where the first initial reaction is a single stage of the nth order, and the second single stage reaction is an autocatalytic one.

The corresponding kinetic model is expressed by a system of ordinary differential equations, as Eqs. (3)–(5) [9,10]:

$$\frac{d\alpha}{dt} = kf(\alpha);$$

$$\text{where } f(\alpha) = \begin{cases} [C_0(1-\alpha)]^n, & \text{Case 1 : } n\text{th order reaction} \\ (1-\alpha)(\alpha+z), & \text{Case 2 : autocatalytic reaction} \end{cases} \tag{3}$$

where the degree of conversion is defined as (initial concentration, C_0 − current concentration, C)/C_0. As a result $f(\alpha)$ should be equal to $[C_0(1-\alpha)]^n$ for nth order reaction:

$$r = \frac{d\alpha}{dt} = k_1(T)(1-\alpha)^{n_1} + k_2(T)(1-\alpha)^{n_1}(z+\alpha^{n_2}) \tag{4}$$

$$\frac{\Delta H}{dt} = \Delta H_i^\infty r_i \tag{5}$$

where $z = -k_1/k_2 = (k_{01}/k_{02}) \exp(-(E_{a1} - E_{a2})/RT)$, α_1 and α_2 are the degree of conversions of species A, and E, respectively; r_1 and ΔH_i^∞ represent reaction rate and heat effect of the ith stage, $i = 1$ and 2; $d\Delta H/dt$ is the overall rate of heat production.

4.2.2. Kinetic analysis for MEKPO 31 wt.% mixed with contaminants

According to the above statements on the reaction kinetic models, this study attempted to analyze the conditions of contaminants with MEKPO 31 wt.% at the same conditions. Furthermore, their scheme results in two independent reactions like MEKPO 31 wt.%. However, there was a difference between the first initial reactions, and the second one was both a single stage reaction of the autocatalytic type, except that MEKPO 31 wt.% mixed with H$_2$SO$_4$. Similarly, the corresponding kinetic model is represented by a system of ordinary differential equations as follows [9,10]—MEKPO 31 wt.% + HCl (1.0 M), MEKPO
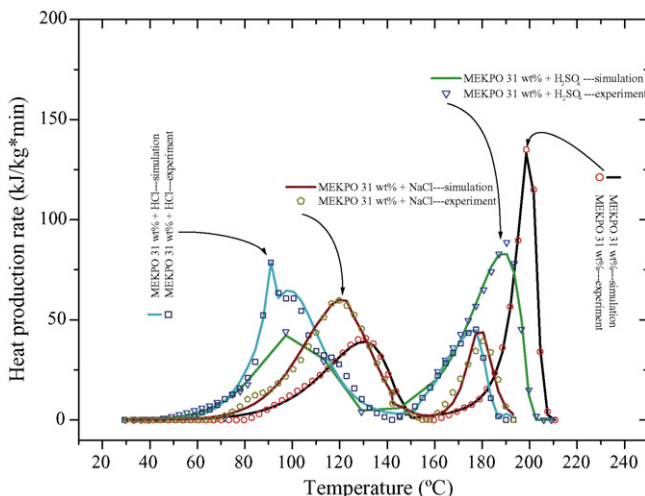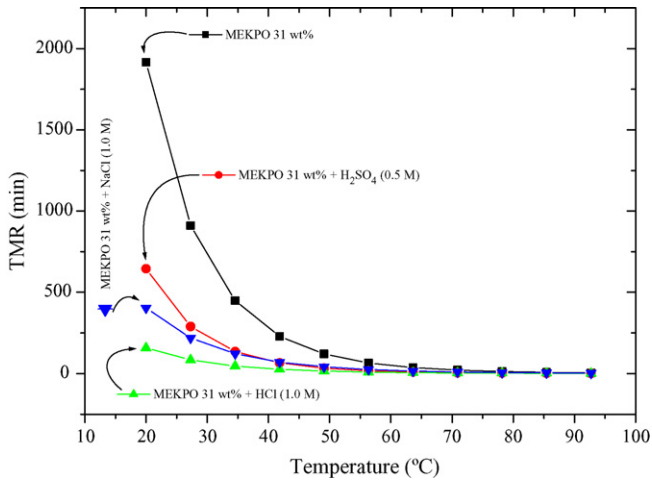
Fig. 5. A plot of TMR vs. temperature curves at different contaminants mixed with MEKPO 31 wt.%.

31 wt.% + NaCl (1.0 M):

$$\frac{d\alpha}{dt} = kf(\alpha);$$

where $f(\alpha) = \begin{cases} (1-\alpha)(\alpha+z), & \text{Case 1 : autocatalytic reaction} \\ (1-\alpha)(\alpha+z), & \text{Case 2 : autocatalytic reaction} \end{cases}$ (6)

$$r = \frac{d\alpha}{dt} = k_1(T)(1-\alpha)^{n_1}(z+\alpha^{n_2}) + k_2(T)(1-\alpha)^{n_2}(z+\alpha^{n_3})$$ (7)

$$\frac{d\Delta H}{dt} = \Delta H_i^{\infty} r_i$$ (8)

As shown in Fig. 4, there is a delayed term in the second peak of the MEKPO reaction. It is assumed to be related to the autocatalytic reaction, and this was corroborated from the simulation. The assumption was, in turn, proved from the simulation. As given in Tables 2 and 3, the heat production of MEKPO 31 wt.% + H$_2$SO$_4$ and MEKPO 31 wt.% was higher than the other ones. Fig. 5 shows that time to maximum rate (TMR) of MEKPO 31 wt.% + H$_2$SO$_4$ and MEKPO 31 wt.% was longer than the others'.

We had evidence to evaluate that their first peak was nth order. After dosing with HCl and NaCl, the heat production of their first peaks was lower than the others'.

4.3. Safety assessment during storage and transportation stages

T_{NR} (temperature of no return) is an important parameter, among parameters or hazard classifications. In previous studies, Townsend and Tou [11] and Fisher and Goetz [12] applied the methods to a variety of self-reactive substances and have advanced its usage capabilities. Basically, by calculating the relationship between the heat generation rate and the heat removal rate, T_{NR} could be obtained. It would then be applied

Table 4
Calculated T_{NR} for MEKPO 31 wt.% with its contaminants

MEKPO and contaminants	T_{NR} (°C)
MEKPO 31 wt.%	44.0
MEKPO 31 wt.% + H$_2$SO$_4$ (0.5 M)	31.0
MEKPO 31% + HCl (1.0 M)	17.6
MEKPO 31% + NaCl (1.0 M)	32.6

to design a cooling system and to inform fire fighters on how much time remained to conduct a rescue action [13].

In contrast, T_{NR} is used to estimate whether temperature needs to be controlled during transportation and storage stages [14,15].

In practice, Eqs. (9) and (10) could be used to calculate the safety parameters of T_{NR} [4]:

$$(T_{NR} + 273.15)^2 = \frac{mE_a \Delta Hk}{RU(1.8)a}$$ (9)

$$= \frac{mE_a \Delta Hk_0 \exp(-E_a/R(T_{NR} + 273.15))}{RU(1.8)a}$$ (10)

In this study, the system was assumed as the standard test, and its capacity was 150.88 kg (55 gallons). As seen in the above equations, where internal area, $a = 1.51$ m^2, thermal transfer coefficient, $U = 11.34$ J/m^2/k, gas constant, $R = 8.314$ J/g/mol/K and sample weight, $m = 150.88$ kg (55 gallons). The calculated T_{NR} for MEKPO 31 wt.% and its contaminants are summarized in Table 4.

The results showed that T_{NR} of MEKPO 31 wt.% and its contaminants was MEKPO < MEKPO + NaCl < MEKPO + H$_2$SO$_4$ < MEKPO + HCl. In conclusion, dosing contaminants in MEKPO would enhance the potential hazard on a reactive system, and curtail the emergency response time for the cooling and fire extinguishing. As seen in Fig. 5, TMR had been reduced after MEKPO mixed with contaminants. Therefore, after dosing, contaminants would decrease the emergency time for MEKPO disaster and also increase its potential hazard.

5. Conclusions

Runaway reactions by employing the simulations for this study were obtained from the kinetic models of MEKPO 31 wt.% and mixed with contaminants. We found that the MEKPO 31 wt.% had two independent reactions: nth order and autocatalytic reaction. After dosing of the contaminants, such as H$_2$SO$_4$, HCl, or NaCl into MEKPO 31 wt.%, these two independent reactions were changed to two autocatalytic reactions (except MEKPO 31 wt.% + H$_2$SO$_4$). The results indicated that while H$_2$SO$_4$ was mixed with MEKPO 31 wt.%, the runaway reaction that was triggered was more dangerous than other situations during the experimental process. In addition, Cl$^-$ ions also played an important role in mixing conditions, from which it was recommended that the use of a fire extinguisher that contains Cl$^-$ (such as halogenated hydrocarbons) or NaCl (dry chemical) must be prohibited.

Acknowledgments

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