

Thermal Hazard Simulations for Methyl Ethyl Ketone Peroxide Induced by Contaminants

Jo-Ming Tseng*, **Arcady A. Kossoy****, **Yi-Chun Yu***** and **Chi-Min Shu^{*,†}**

*Process Safety and Disaster Prevention Laboratory, Department of Safety, Health and Environmental Engineering, National Yunlin University of Science and Technology, 123 University Rd., Sec. 3, Touliu, Yunlin, Taiwan 640, ROC

**ChemInform Saint Petersburg (CISP), Ltd., 14 Dobrolubov Ave., 197198 St. Petersburg, Russia

***Division of Exhibitions, Institute of Occupational Safety and Health, Council of Labor Affairs, Executive Yuan, 99 Lane 407, Hengke Rd., Shijr, Taipei, Taiwan 221, ROC

[†]To whom correspondence should be addressed.
E-mail: shucm@yuntech.edu.tw (Chi-Min Shu)
Tel.: +886-5-534-2601 ext. 4416
Fax: +886-5-531-2069

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 resulted in 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. Kinetics evaluation was also implemented by means of the methods and software developed by ChemInform St. Petersburg, Ltd. The results indicate that MEKPO was highly hazardous as mixed with any of the above-mentioned contaminants. The hazard of fires and explosions could be effectively controlled to a lesser extent only if safety parameters and thermokinetic parameters are properly imbedded into the manufacture 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 with hydrogen peroxide (H_2O_2), is utilized as a radical source for initiation as a cross-linker during polymerization. In the last four decades, some severe thermal explosions have been recorded and involved with MEKPO in Taiwan, Japan or China as shown in Tables 1, 2 and 3 [Duh et al., 1998]. 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; then, it eventually extended to the victim tank yard. This thermal explosion killed 10 and injured 47 people. 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. 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 prudently 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 .

MEKPO, as regarded as an unstable material, induces micro-self-exothermic decomposition in the ambient atmosphere. If MEKPO is under the 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 unexpected accident. Therefore, if the stored MEKPO has not been well controlled or protected, in chorus, 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.

MEKPO was found to be an inherently 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 the staff to prevent and mitigate the hazards, casualties and the damages from the runaways.

Table 1. Selected thermal explosion incidents caused by MEKPO in Taiwan since 1979 [Duh et al., 1998]

Date	Location	Injuries	Fatalities	Hazard
1979.07.13	Taipei	49	33	Explosion (Storage)
1984.02.18	Taoyuan	55	5	Explosion (Reactor)
1989.09.01	Taoyuan	5	7	Explosion (Tank)
1996.10.07	Taoyuan	47	10	Explosion (Tank)

2001.04. 11	Yunlin	0	0	Explosion (Laboratory)
----------------	--------	---	---	------------------------

Table 2. Selected thermal explosion incidents caused by MEKPO in Japan since 1953

Date	Location	Mass	Injuries	Fatalities
1953.06.29	Tokyo	3 kg	0	3
1953	Hyougo	0.1 kg	0	1
1958	Tokyo	NA	0	0
1958.08	Aichi	0.1 kg	1	0
1958	Nara	8 kg	0	0
1958	Aichi	16 kg	0	0
1958	Osaka	NA	0	0
1958	Osaka	NA	0	0
1960	Tokyo	NA	0	0
1962	Tokyo	0.5 kg	0	0
1964.07.14	Tokyo	3,600 kg	114	19
1964	Tokyo	NA	0	0
1965	Tokyo	NA	0	0
1978.06	Kanagawa	5 kg	0	0

NA: Not Applicable.

Table 3. Selected thermal explosion incidents caused by MEKPO in China since 1980

Date	Location	Injuries	Fatalities
1980	Zhejiang	NA	0
1980	Jiangsu	NA	0
1986	Zhejiang	1	0
1989	Sichuan	NA	0
1990	Hubei	NA	0
1990	Jiangsu	NA	0
1997	Zhejiang	NA	NA
2000	Jiangsu	NA	NA
2001	Guangdong	NA	NA
2001	Jiangsu	2	4
2001	Jiangsu	0	0
2003	Zhejiang	3	5
2003	Jiangsu	0	0

NA: Not Applicable, indicating “many”.

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.

This study used three materials of H₂SO₄ (0.5 M), KOH (1.0M) and Fe₂O₃ (solid), as the contaminants, and then added the specific contaminant (0.5–1.0 mg) 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^o). 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].

APPLICATIONS OF SAFETY PARAMETERS WITH THEORETICAL APPROACHES

For the estimation of safety parameters or hazard classifications, the temperature of no return, T_{NR}; the self-accelerating decomposition temperature, T_{SADT}; and time to maximum rate, TMR, are three important parameters. In the literature review, these parameters were acquired to evaluate the related reaction hazards from Townsend [Townsend and Tou, 1980] and Fisher [Fisher and Goetz, 1991]. Besides, this study introduced some theories, which can be utilized in the real conditions.

1. The Definition of Safety Parameters

1.1. Temperature of No Return (T_{NR})

T_{NR} can be calculated via the relationship between heat generating rate and heat removing rate. It will then be applied to design a cooling system and to inform fire fighters of how much time remains to implement a rescue action [Kossov, 2002]. When the maximum self-heating rate compared with the constant of time is the same in the system, then the temperature will up to the T_{NR} in the system. This study used the following equations to calculate the T_{NR}.

$$(T_{NR} + 273.15)^2 = \frac{m \cdot E_a \Delta H \cdot k}{R \cdot U \cdot (1.8) \cdot a} \quad (1)$$

$$= \frac{m \cdot E_a \cdot \Delta H \cdot A \cdot e^{-E_a/R \cdot (T_{NR} + 273.15)}}{R \cdot U \cdot (1.8) \cdot a} \quad (2)$$

1.2. Self-accelerating Decomposition Temperature (T_{SADT})

T_{SADT} is used to estimate whether temperature needs to be controlled during

transportation and storage stages. T_{SADT} is defined as the lowest ambient air temperature at which a self-reactive substance of specified stability (contaminant level, inhibitor concentration, etc.) undergoes an exothermic reaction in a specified commercial package in a period of seven days or less [Fisher and Goetz, 1993]. According to NFPA 43B [NFPA, 1999], a self-reactive substance must be subject to temperature control during transportation if its T_{SADT} is less than or equal to 55°C. Using the method of Willberforce to transmit Eq. (8), and then substituting the T_{NR} into the Eq. (8), the T_{SADT} could be obtained.

$$Q_g = m \cdot \Delta H \cdot A \cdot e^{-E_a/RT} \quad (3)$$

$$Q_1 = U \cdot a \cdot (T - T_0) \quad (4)$$

At boundary condition,

$Q_g = Q_1$, to got the Eq. (5);

$$m \cdot \Delta H \cdot A \cdot e^{-E_a/RT} = U \cdot a \cdot (T - T_0) \quad (5)$$

Differentiating of the Eq. (5);

$$E_a / RT^2 \cdot U \cdot a \cdot (T - T_0) = U \cdot a \quad (6)$$

$$T_0 = T - \frac{RT^2}{E_a} \quad (7)$$

$$T = T_{NR} + 273.15 \text{ (k)}$$

$$T_0 = T_{SADT} + 273.15 \text{ (k)}$$

Sorting the equations above, Eq. (8) can be expressed as follows:

$$T_{SADT} = T_{NR} - \frac{R(T_{NR} + 273.15)^2}{E_a} \quad (8)$$

1.3. Time to Maximum Rate (TMR)

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

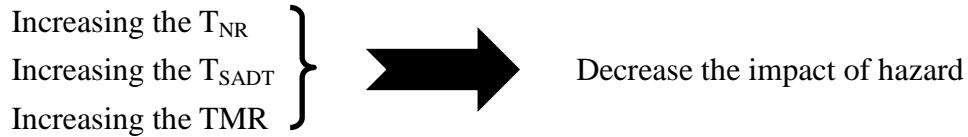
This study used Eq. (9) to calculate the TMR as below:

$$TMR = \frac{RT^2}{A \cdot E_a \cdot \Delta T_{ad}} e^{-E_a/RT} \quad (9)$$

$$\Delta T_{ad} = \frac{Q}{C_p}$$

(10)

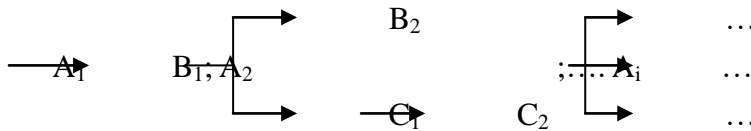
According to the calculated results for safety parameters, this study sorted the relationship between the safety parameters and impact as follows:



2. Simulation Methods

2.1. Kinetic Models

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 which could be expressed as follows:

(1) Simple single-stage reaction:

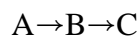


$$\frac{d\alpha}{dt} = A \cdot e^{-E_a/RT} f(\alpha); \text{ where } \alpha \text{ is the conversion of the reactant A}$$

(11)

$$\left\{ \begin{array}{l} (1-\alpha)^n \text{-n-order reaction} \\ f(\alpha) = (1-\alpha)^{n_1} (\alpha^{n_2} + z) \text{-autocatalytic reaction} \end{array} \right.$$

(2) Reaction including two consecutive stages:



$$\frac{d\alpha}{dt} = A \cdot e^{-E_1/RT} (1-\alpha)^{n_1}; \quad \frac{d\gamma}{dt} = A_2 \cdot e^{-E_2/RT} (\alpha - \gamma)^{n_2}$$

(12)

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

(3) Two parallel reactions:

$A \rightarrow B + \dots$ —initiation stage

$A + B \rightarrow 2B + \dots$ —autocatalytic reaction

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

$$\frac{d\alpha}{dt} = K_1(\alpha) + K_2(\alpha)$$

(13)

$$K_1(\alpha) = k_1(T)(1 - \alpha)^{n_1}$$

(14)

$$K_2(\alpha) = k_2(T)\alpha^{n_2}(1 - \alpha)^{n_3}$$

(15)

RESULTS AND DISCUSSION

1. Results of Experiments and Simulations

This study thoroughly conducted analytical experiments with simulated methods by the aid of DSC. Operating conditions, in coordination with the theories of Townsend [Townsend and Tou, 1980] and Fisher [Fisher and Goetz, 1991], 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 4, 5 and Figures 1–6 are shown as follows.

Table 4. 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 ($^{\circ}\text{Cmin}^{-1}$)	T_{\max} ($^{\circ}\text{C}$)	T_0 ($^{\circ}\text{C}$)	E_a (kJmol^{-1})	n_1	n_2	A ($\text{sec}^{-1}\text{M}^{1-n}$)	ΔH (Jg^{-1})	T_{NR} ($^{\circ}\text{C}$)	T_{SADT} ($^{\circ}\text{C}$)
MEKPO 31 wt%	5.5	4	130.08	96.22	70.46	0.55	*	15.33	351.07	37.8	26.39
				98.91	80.33	0.69	*	18.45	345.37	44.4	33.96
MEKPO 31 wt% + H_2SO_4 (0.5 M)	4.8	4	100.87	79.33	92.70	1.18	*	24.42	374.87	30.4	22.14
				78.02	86.74	1.15	*	22.49	408.93	26.2	17.61
MEKPO 31 wt% + KOH (1.0 M)	4.5	4	45.73	38.70	269.37	1.76	*	97.71	34.55	24.8	22.06
				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	16.9	10.83
				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 5. 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 ($^{\circ}\text{Cmin}^{-1}$)	E_a (kJmol^{-1})	n_1	n_2	z	A ($\text{sec}^{-1}\text{M}^{1-n}$)	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 [Kossov and Hofelich, 2003].

* : Not applicable.

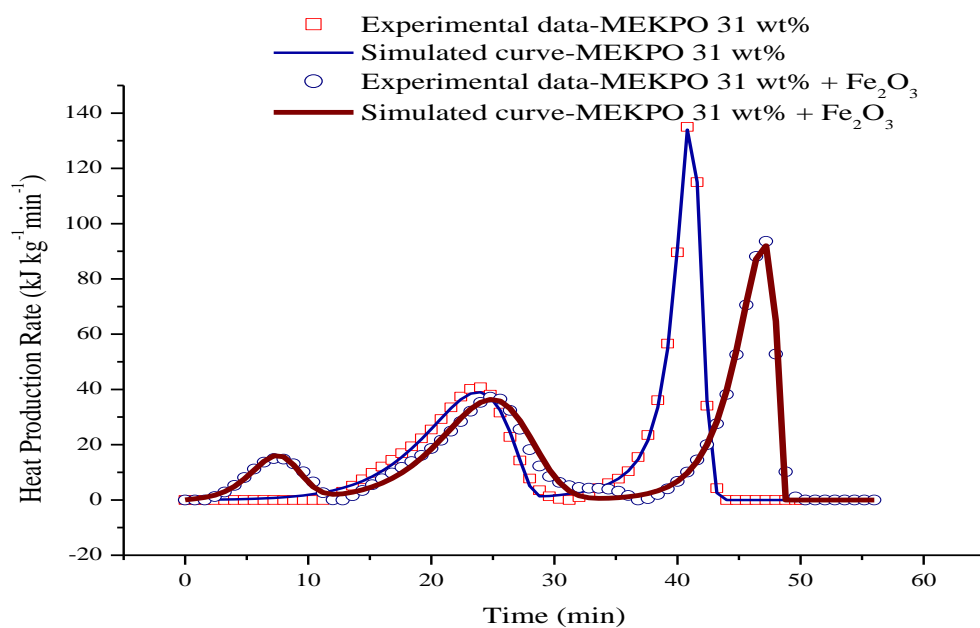


Fig. 1. Simulated heat production rate vs. time by the DSC experiments for MEKPO 31 wt% mixed with Fe_2O_3 .

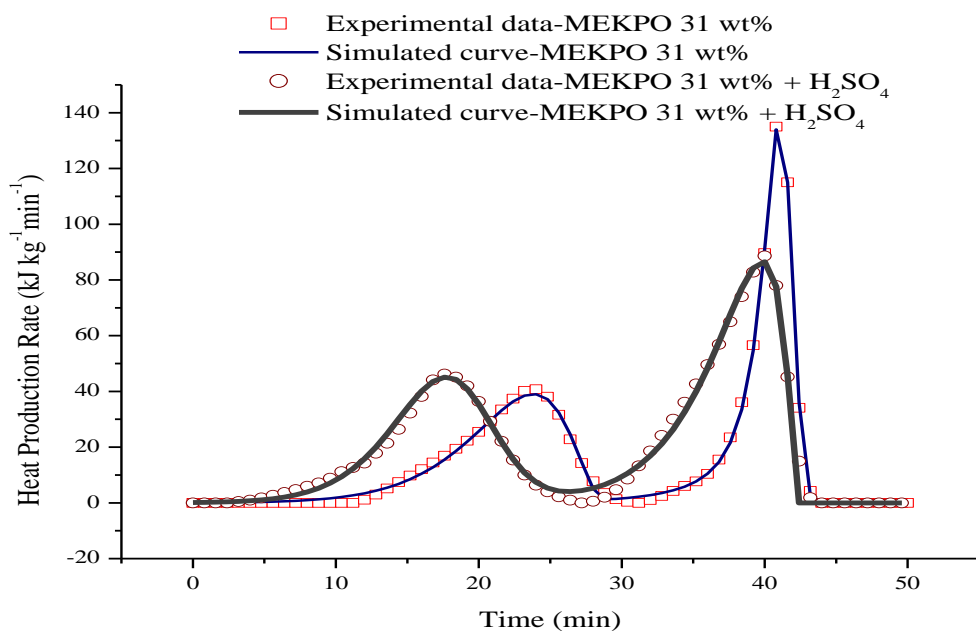


Fig. 2. Simulated heat production rate vs. time by the DSC experiments for MEKPO 31 wt% mixed with H_2SO_4 .

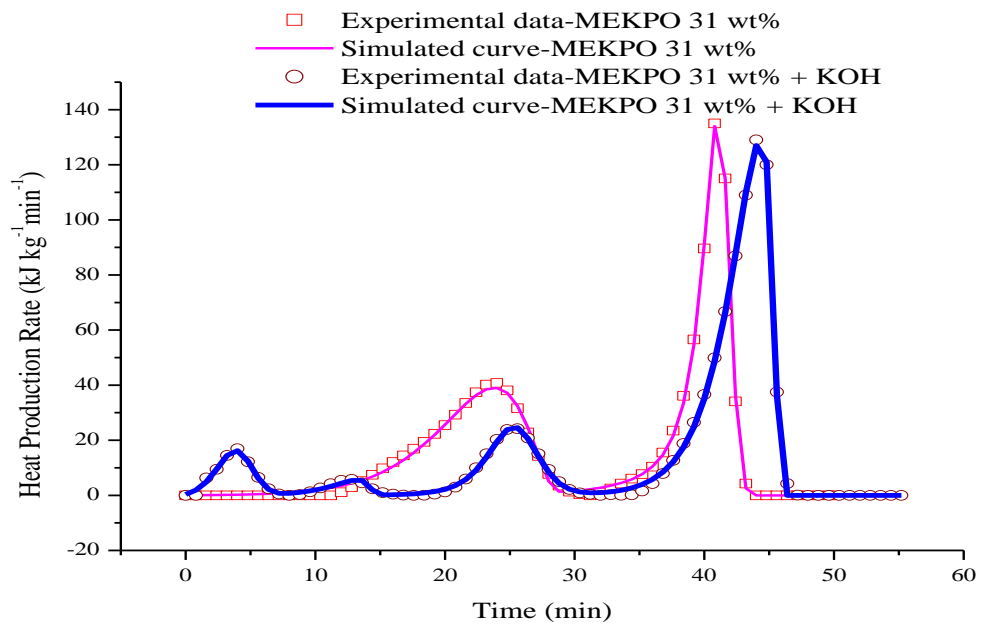


Fig. 3. Simulated heat production rate vs. time by the DSC experiments for MEKPO 31 wt% mixed with KOH.

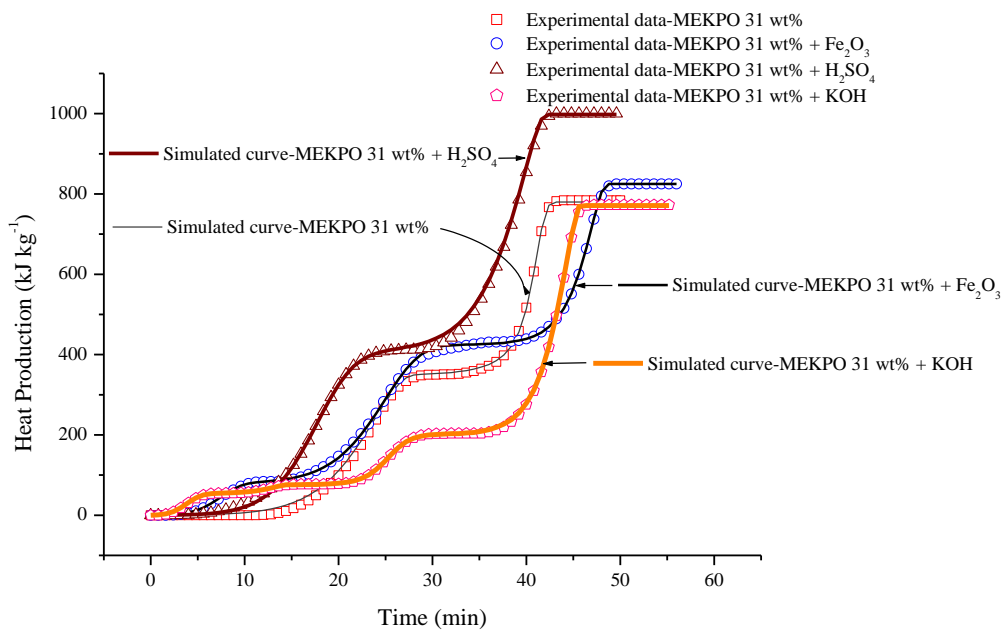


Fig. 4. Simulated heat production vs. time by the DSC experiments for MEKPO 31 wt% with its contaminants.

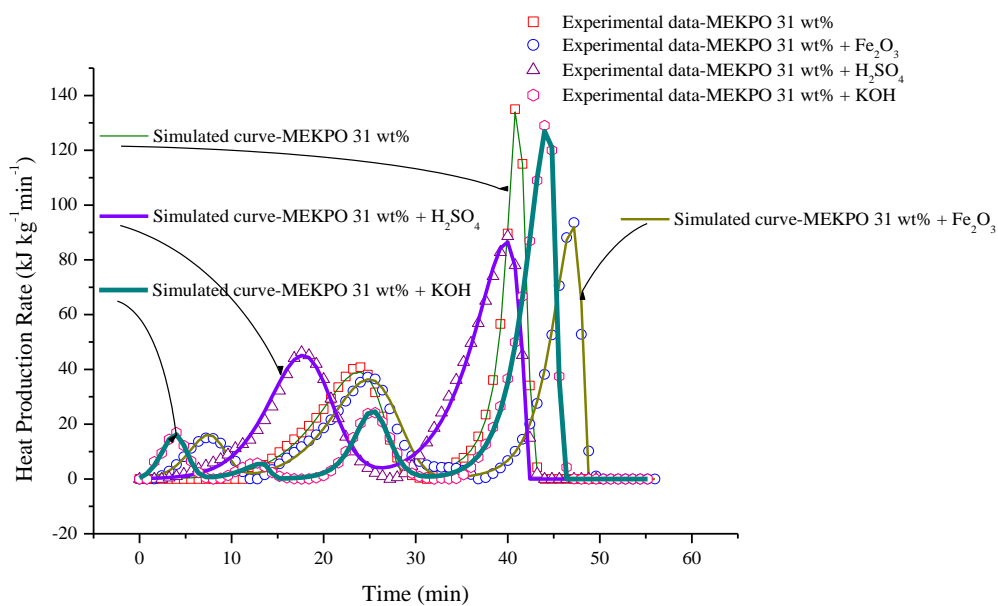


Fig. 5. Simulated heat production rate vs. time by the DSC experiments for MEKPO 31 wt% with its contaminants.

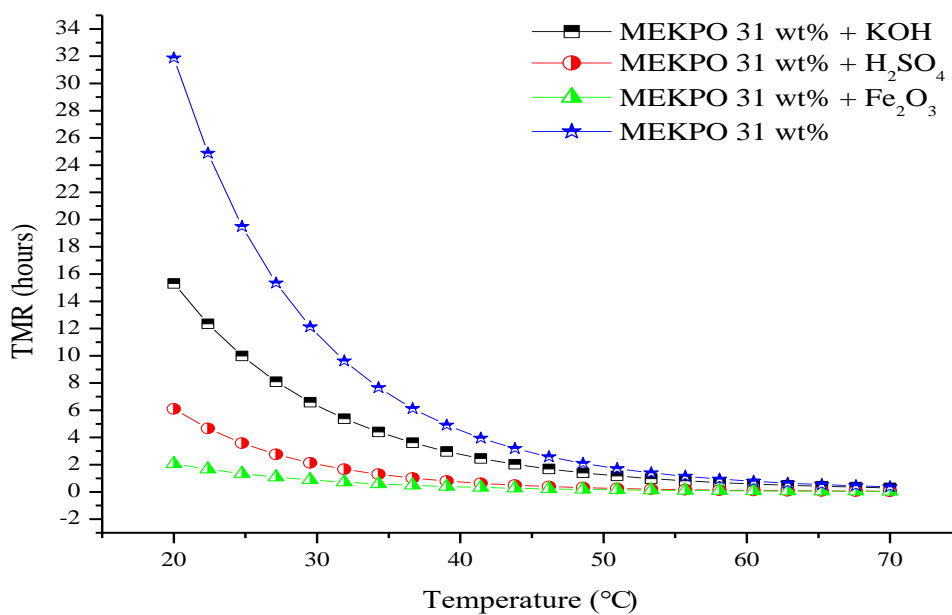


Fig. 6. Simulated time to maximum rate (TMR) vs. temperature by the DSC experiments for MEKPO 31 wt% with its contaminants.

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 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). It, however, 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 the 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.

3. Simulative Analyses

The simulative method was employed to deal with the experimental data. It can not only calculate the n-order reaction but also calculate the autocatalytic reaction. From Table 4, MEKPO 31 wt%, when mixed with KOH and Fe_2O_3 , shows a great of diversity in apparent activation energy (E_a) and frequency factor (A), because the n-order reactions were considered in STAR^e software. Actually, 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 mixing experimental process. From Table 5, 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.

Figure 6 discloses 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 time to maximum rate

(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 the accident in the manufacturing processes.

CONCLUSIONS

By the simulated kinetic parameters (E_a , A , ΔH , n), the results were compared with the parameters obtained from experiments, as used to estimate the safety parameters (T_{NR} , T_{SADT} , 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, these safety parameters could provide valuable information to prevent an operating process from incurring any runaways.

Various discrepancies may arise from the process of experiments and simulations. To increase the degree of accuracy on 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 on curve fitting, and thereby gain accurate data for coping with any runaway reactions in real manufacturing processes.

ACKNOWLEDGEMENT

The authors are indebted to Dr. Y. S. Duh at Jen–Teh Junior College of Medicine, Nursing and Management, Taiwan, ROC for his valuable suggestions on this study.

NOMENCLATURE

A	: frequency factor [$\text{sec}^{-1}\text{M}^{1-n}$]
a	: vessel wetted surface area [m^2]
C_p	: specific heat capacity [$\text{Jg}^{-1}\text{K}^{-1}$]
E_a	: apparent activation energy [kJmole^{-1}]
k	: rate constant [$\text{sec}^{-1}\text{M}^{1-n}$]
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_l	: calorific capacity from measuring cell to the environment [Jg^{-1}]
r	: scanning rate [$^{\circ}\text{Cmin}^{-1}$]
R	: gas constant [$8.314 \text{ Jmol}^{-1}\text{K}^{-1}$]
T	: temperature [$^{\circ}\text{C}$]
T_0	: exothermic onset temperature [$^{\circ}\text{C}$]

T_{\max} : maximum temperature during overall reaction [$^{\circ}\text{C}$]
 TMR : time to maximum rate [hr]
 T_{NR} : temperature of no return [$^{\circ}\text{C}$]
 T_{SADT} : self-accelerating decomposition temperature [$^{\circ}\text{C}$]
 U : heat transfer coefficient [$\text{kJmin}^{-1}\text{m}^{-2}\text{K}^{-1}$]
 z : autocatalytic constant
 (dT/dt) : self-heating rate [$^{\circ}\text{Cmin}^{-1}$]
 $(dT/dt)_{\max}$: maximum self-heating rate [$^{\circ}\text{Cmin}^{-1}$]
 ΔH : heat of reaction [Jg^{-1}]
 ΔT_{ad} : adiabatic temperature raise [$^{\circ}\text{C}$]
 Φ : thermal inertial, dimensionless
 α : degree of conversion, dimensionless
 γ : degree of conversion, dimensionless

REFERENCES

- Chang, R. H., "Thermal Runaway Hazard Analysis on Methyl Ethyl Ketone Peroxide with Incompatible Substances", *MS Thesis*, Taiwan, ROC (2003).
- "Code for the Storage of Organic Peroxide Formulations", *NFPA 43B; National Fire Protection Association*, Quincy, MA, USA (1999).
- Duh, Y. S., Kao, C. S., Hwang, H. H. and Lee, W. L., "Thermal Decomposition Kinetics of Cumene Hydroperoxide", *Trans. Inst. Chem. Eng.*, **76B** (1998).
- Fisher, H. G. and Goetz, D. D., "Determination of Self-Accelerating Decomposition Temperatures for Self-Reactive Substances", *J. Loss Prev. Process Ind.*, **6** (1991).
- Hou, H. Y., Shu, C. M. and Duh, Y. S., "Exothermic Decomposition of Cumene Hydroperoxide at Low Temperature Conditions", *AIChE J.*, **47** (2001).
- Kosoy, A. A., "Proceedings for Inherently Safer and Assessment of Reaction Hazards Technology Workshop", Taiwan, ROC (2002).
- Kosoy, A. A. and Hofelich, T., "Methodology and Software for Assessing Reactivity Ratings of Chemical Systems", *Pro. Saf. Prog.*, (2003).
- "Safe Storage and Handling of Reactive Materials", *Published by Center for Chemical Process Safety of the AIChE*, New York, USA (1995).
- "STAR^o Software with Solars Operating System", *Operating Instructions*, Mettler Toledo, Sweden (1998).
- Townsend, D. I. and Tou, J. C., "Thermal Hazard Evaluation by An Accelerating Rate Calorimeter", *Thermochim. Acta*, **37** (1980).