THERMOKINETIC MODEL SIMULATIONS FOR METHYL ETHYL KETONE PEROXIDE CONTAMINATED WITH H₂SO₄ OR NaOH BY DSC AND VSP2

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In this study, a mixture of methyl ethyl ketone peroxide (MEKPO) with various contaminants, such as H_2SO_4 and NaOH, was prepared in order to elucidate the cause of these accidents and the results of upset conditions. Thermokinetic parameters were acquired by both differential scanning calorimetry (DSC) and vent sizing package 2 (VSP2). In addition, we simulated the thermokinetic parameters and created kinetic models for the specific contaminants. The results indicate that the thermal hazard of MEKPO is less than that of the mixed MEKPO with the above-mentioned contaminants. Consequently, the evaluated parameters could be used to prevent any unexpected exothermic runaway reaction or to alleviate hazards to an acceptable extent, if such a reaction occurs.

Keywords: contaminants, exothermic runaway reaction, kinetic models, methyl ethyl ketone peroxide, thermokinetic parameters

Introduction

Various methods have been used to evaluate the thermal hazards of reactive chemicals, such as iodoform vulcanizate [1], butadiene-acrylonitrile rubber [2], and cyclohexanone [3], but few studies have focused on MEKPO. In the last four decades, many thermal explosions have been caused by MEKPO in Taiwan, Japan, Korea and China, making it as one of the most hazardous materials in Asia, as shown in Tables 1–3 [4]. In Taiwan, one of the worst accidents is the Yung-Hsin explosion in 1996. The initial fire was due to an uncontrollable oxidation reaction at the process site that eventually extended to the tank yard. This accident caused 10 deaths and 47 injuries. In Tokyo, 3 600 kg (8 000 lbm) of MEKPO exploded, killed 19 and injured 114 in 1964. The damages in this period from accidents cost 1.25 million U.S. dollars [5]. In China, thermal explosions killed 5 and injured 3 people in 2003. This study evaluated and simulated the exothermic reaction for MEKPO, along with H_2SO_4 or NaOH by using safety and kinetic parameters.

MEKPO is a typical organic peroxide produced by methyl ethyl ketone (MEK) with hydrogen peroxide (H_2O_2) used as a radical source for initiation and cross-linking agent during polymerization. However, it is very sensitive to thermal and chemical pollutants or even mechanical shock. If a process is under unsafe conditions for a long time, an exothermic runaway will be induced and result in various kinds of hazards, such as fire, explosion, or toxic release. Several methods have been developed concerning the determination of kinetic results from thermal analysis measurements [6]. There is a systematic approach for experimentally assessing thermal hazards of materials with unstably reactive natures. Based upon these engineering approaches, such as process safety management (PSM), quantitative risk assessment (QRA), safety index (SI) and so on, that could be adopted to evaluate a chemical with potential reaction hazards.

This study summarizes the results of the degrees of hazard incurred by MEKPO mixed with either H_2SO_4 or NaOH. In the experiments, DSC, VSP2 and

Table 1 Selected thermal explosion incidents caused by thermal decomposition of MEKPO in Taiwan since 1979 [4]

Year	Location	Injuries	Fatalities	Hazard
1979	Taipei	49	33	explosion storage
1984	Taoyuan	55	5	explosion reactor
1989	Taoyuan	5	7	explosion tank
1996	Taoyuan	47	10	explosion tank
2001	Yunlin	0	0	explosion laboratory

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Table 2 Selected thermal explosion incidents caused by thermal decomposition of MEKPO in Japan since 1953 [7]

Year	Location	Mass/kg	Injuries	Fatalities
1953	Tokyo	3	0	3
1953	Hyougo	0.1	0	1
1958	Tokyo	NA	0	0
1958	Aichi	0.1	1	0
1958	Nara	8	0	0
1958	Aichi	16	0	0
1958	Osaka	NA	0	0
1958	Osaka	NA	0	0
1960	Tokyo	NA	0	0
1962	Tokyo	0.5	0	0
1964	Tokyo	3600	114	19
1964	Tokyo	NA	0	0
1965	Tokyo	NA	0	0
1978	Kanagawa	5	0	0

NA – not applicable

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

Year	Location (province)	Injuries	Fatalities
1980	Zhejiang	NA	0
1980	Jiangsu	NA	0
1986	Zhejiang	I	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 a few

simulative method had been employed to describe and depict the phenomena of exothermic runaway reactions with simulations. The results demonstrate that the hazards to be occurred earlier when MEKPO was mixed with either H_2SO_4 or NaOH.

Experimental

Material and methods

MEKPO (31 mass%) was purchased directly from the Fluka Co., and stored in a 4°C refrigerator. Dimethyl phthalate (DMP) was used as a diluted solvent in preparing various MEKPO samples, such as MEKPO 10 mass% for processing this study. NaOH (1 M) and H_2SO_4 (0.5 M) were employed to mix with MEKPO for discussing the mixture hazard phenomenon in the relative manufacturing process or under storage, or transportation period.

Differential scanning calorimetry (DSC)

Temperature-programmed screening and isothermal experiments were performed on a Mettler TA8000 system coupled with a DSC821^e measuring cell that could stand a relatively high pressure of approximately 100 bar. STAR^e software was used for obtaining thermal curves and isothermal traces [8]. For better thermal equilibrium, the scanning rate for the temperature-programmed ramp was 4°C min^{-1} [9].

Vent sizing package 2 (VSP2)

VSP2, which is a PC-controlled adiabatic calorimeter system manufactured by Fauske Associates, Inc. Thermokinetic and thermal hazard data, such as temperature and pressure traces, were measured, related to time [10]. Actually, the low heat capacity of the cell ensures that all the released reaction heat remains within the test sample. Therefore, thermokinetics and pressure behavior in a small vented test cell (116 mL) could be directly tested to the process scale due to the low thermal inertia, about 1.05 to 1.2 [11]. The variable worst case could also be simulated as adiabatic conditions agents, such as cooling failure or external fire conditions had occurred.

Thermal hazard assessment

Applying thermal hazard assessment to a manufacturing process could efficiently lessen the specific degree of hazard. For a quick and cost-effective method to estimate safety classes among various industries' processes, the engineering approaches and safety parameters should be focused on either being implemented in PSM, or applied to QRA.

Stull [12] developed a rating system to establish the relative potential hazards of specific chemicals: the reaction hazard index (RHI). Earlier, Townsend and Fisher [13, 14] proposed TMR (time to maximum rate), T_{NR} (temperature of no return) and SADT (self-accelerating decomposition temperature) as safety parameters via Semenov's theories for evaluating the thermal hazard. In 1997, Keller and his associates [15] classified runaway reactions via hazard severity – the so-called safety index (SI). Barton and Rogers [16] suggested some procedures for evaluat-

Table 4 Calculated kinetic and safety parameters derived from the dynamic scanning experiments by DSC for MEKPO of 10 mass% with H_2SO_4 and NaOH

MEKPO and contaminants	$m/$ mg	$r/$ °C min^{-1}	$T_0/$ °C	$T_{max}/$ °C	$E_a/$ kJ mol^{-1}	$\Delta H/$ J g^{-1}	$A/$ s^{-1}	n	$TMR/$ min	$T_{NR}/$ °C
10 mass% MEKPO	6.1	4	107.98 **95.54**	137.66 **136.58**	117.62 **138.44**	97.62 **98.50**	29.24 **35.51**	* **1.35**	2.40 **11.19**	79.2 **84.5**
10 mass% MEKPO +NaOH (1.0 M)	5.1	4	48.01 **41.29**	59.56 **60.62**	202.89 **200.29**	161.54 **197.86**	69.14 **68.25**	* **1.36**	0.21 **0.77**	26.5 **25.2**
10 mass% MEKPO +H$_2$SO$_4$ (0.5 M)	5.2	4	61.56 **41.30**	95.54 **95.79**	68.64 **88.10**	340.82 **274.55**	16.93 **23.43**	* **1.17**	0.78 **8.75**	11.8 **26.3**

Number which is normal is the first peak of the reaction. Calculated values based on experimental data received from DSC; bolded number are simulated values; *not applicable; all values of T_{NR} were determined by Fisher's approach with fixed conditions [14]

ing chemical reaction hazards. Later, Hirschler [17] used heat release rate to predict self-propagating fires that could determine whether the reactions could be hazardous, and so on. However, our study was initiated with a view to establish various methods of hazard assessments to prevent potential hazards at the initial stage. These methods could be adequately applied for reducing damage in life and property during a process or even at the gestation stage.

Based on the above-mentioned investigations, the following would be used to examine MEKPO dimer of 10 mass%. The results could then be used as a corrective measure.

Safety parameters

T_{NR} and SADT are two important parameters for estimating safety parameters or hazard classifications. In previous studies, Townsend [13] and Fisher [14] evaluated the related reaction hazards in order to acquire these parameters. Essentially, T_{NR} could be calculated via the relationship between the heat generating rate and the heat removing rate. It could then be applied to design a cooling system and to inform fire fighters of how much time was remaining to implement a rescue action [18]. SADT is used to estimate whether temperature needs to be controlled during transportation and storage. It is defined as the lowest ambient air temperature at which the specified stability of a self-reactive substance (contaminant level, inhibitor concentration, etc.) undergoes an exothermic reaction at a specified commercial package in a period of seven days or less [14].

According to NFPA 43B [19], a self-reactive substance must be subjected to temperature control during transportation if its SADT is less than or equal to 55°C. Equations (1)–(3) can be used to calculate these two parameters:

$$(T_{NR}+273.15)^2 = \frac{mE_a \Delta H k}{RU(1.8)a} \tag{1}$$

$$= \frac{mE_a \Delta H A e^{-E_a/R(T_{NR}+273.15)}}{RU(1.8)a} \tag{2}$$

$$SADT = T_{NR} - \frac{R(T_{NR}+273.15)^2}{E_a} \tag{3}$$

An example of MEKPO, by using the foregoing theories and thermal calorimeters to calculate these kinetic and safety parameters, was introduced in this study.

Results and discussion

The theories proposed by both Fisher and Townsend were used to precisely calculate the related safety parameters and the kinetic parameters by using DSC and VSP2. In addition, we simulated the kinetic parameters based upon the experimental data acquired by DSC and VSP2 tests. The results are displayed in Tables 4 and 5.

From Figs 1 to 2, MEKPO (10 mass%) was essentially used to calculate the kinetic and safety parameters by VSP2; higher MEKPO concentration, such as 15 mass%, could result in higher pressure, bursting the test cell [7]. Its exothermic onset temperature (T_0), maximum self-heat rate $(dT/dt)_{max}$, and T_{NR} were 101.37°C, 188.65°C min^{-1}, and 93.41°C, respectively. Also demonstrated was that the pressure and temperature corresponding to a mixture of MEKPO with either NaOH or H_2SO_4 had substantially increased the pressure as mixed with NaOH, causing a maximum pressure (P_{max}) of up to 29.31 bar. The $(dT/dt)_{max}$ increased progressively when it was mixed with NaOH (206.80°C min^{-1}) and H_2SO_4 (221.81°C min^{-1}). Figure 3 also shows that the T_0 also tended toward lower temperature when MEKPO was mixed with NaOH toward (48.01°C) and H_2SO_4 toward (61.56°C). The heat of reaction (ΔH) increased when MEKPO was mixed with NaOH to (161.54 J g^{-1}) and H_2SO_4 to (340.82 J g^{-1}). The simulative method was selected to simulate the experimental data, achieving quite consistent results.
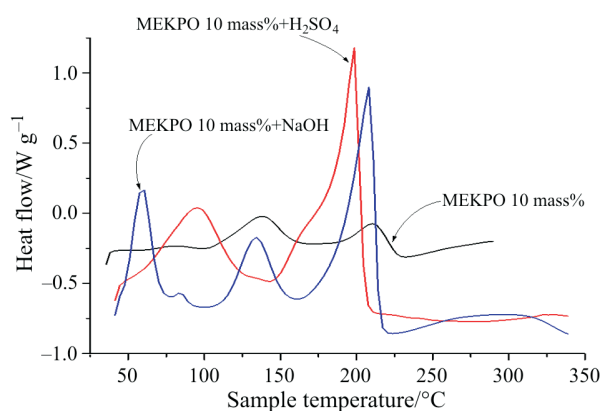
Table 5 Calculated kinetic and safety parameters derived from the adiabatic experiments by VSP2 for MEKPO of 10 mass% with H_2SO_4 and NaOH [20]

MEKPO and contaminants	Φ	T_0/°C	E_a/kJ mol^{-1}	A/s^{-1}	P_{max}/bar	$(dT/dt)_{max}$/°C min^{-1}	T_{NR}/°C	SADT/°C
MEKPO 10 mass%, 50 g	1.20	101.37	98.56 **106.02**	25.67 **20.95**	25.61	188.65	93.41	82.07
MEKPO 10 mass%, 50 g+NaOH (1.0 M)	1.19	76.11	112.8 **111.01**	32.36 **33.81**	29.31	206.80	60.01	49.46
MEKPO 10 mass%, 50 g+H_2SO_4 (0.5 M)	1.19	71.84	87.49 **92.12**	24.86 **22.81**	23.69	221.81	71.46	62.71

Normal numbers are calculated values based on experimental data received from VSP2; bolded numbers are simulated values; all values of T_{NR} and SADT were determined by Fisher's approach with fixed conditions [14]
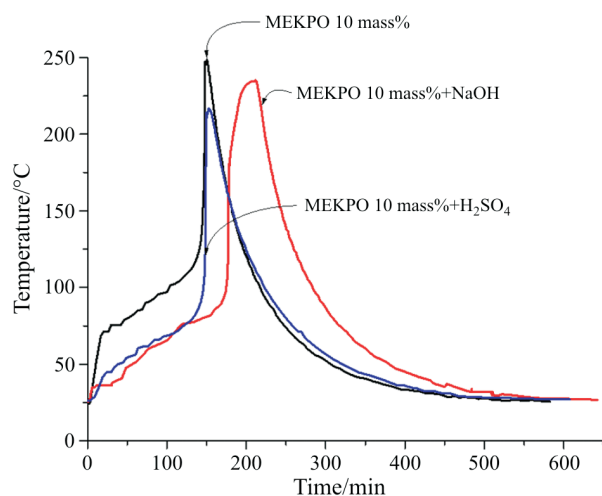
Fig. 1 Temperature *vs.* time for MEKPO of 10 mass% contaminated by H_2SO_4 (0.5 M) or NaOH (1 M)
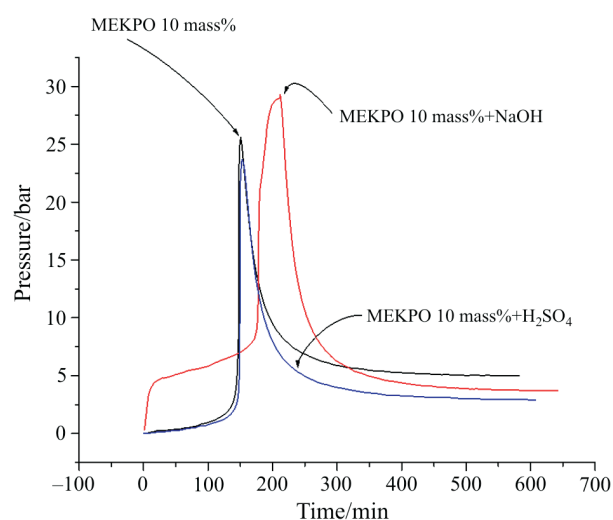
Fig. 2 Pressure *vs.* time for MEKPO of 10 mass% contaminated by H_2SO_4 (0.5 M) or NaOH (1 M)

Fig. 3 Heat flow *vs.* sample temperature for MEKPO of 10 mass% contaminated by H_2SO_4 (0.5 M) or NaOH (1 M)
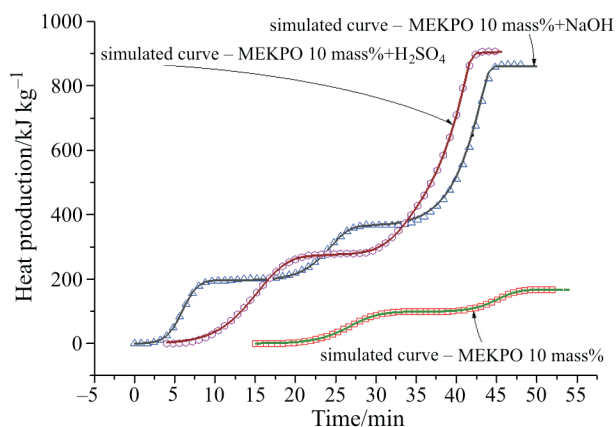
Fig. 4 Simulated heat production *vs.* time for MEKPO of 10 mass% contaminated by H_2SO_4 (0.5 M) or NaOH (1 M). Experimental data: □ – MEKPO 10 mass%; △ – MEKPO 10 mass% +NaOH; ○ – MEKPO 10 mass% + H_2SO_4

This simulative method to find the optimal parameters for the experimental data involved using the Kossoy's methodology [18] – the same method as that used in our earlier studies, as illustrated in Figs 4 and 5.

The changes of exothermic onset temperature (T_o) and apparent activation energy (E_a) demonstrated that hazardous conditions of MEKPO in the presence of contaminants could be much more dangerous than the pure one, as seen in Figs 1–5. Therefore, on the basis of the calculated values of safety parameters, T_{NR}, SADT, and TMR, as presented in Tables 4 and 5,
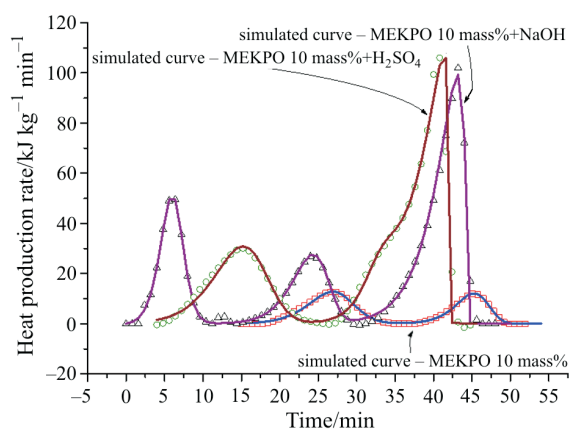
Fig. 5 Simulated heat production rate *vs.* time for MEKPO of 10 mass% contaminated by H_2SO_4 (0.5 M) or NaOH (1 M). Experimental data: □ – MEKPO 10 mass%; △ – MEKPO 10 mass% +NaOH; ○ – MEKPO 10 mass% + H_2SO_4

k	rate constant/s^{-1} M^{1-n}
m	mass of reactant/g
n	reaction order, dimensionless
P_{max}	maximum pressure/bar
r	scanning rate/°C min^{-1}
R	gas constant/8.314 J mol^{-1} K^{-1}
T_{max}	maximum temperature during overall reaction/°C
TMR	time to maximum rate at adiabatic conditions/min
T_{NR}	temperature of no return/°C
T_o	exothermic onset temperature/°C
SADT	self-accelerating decomposition temperature/°C
U	heat transfer coefficient/kJ min^{-1} m^{-2} K^{-1}
(dT/dt)	self-heat rate/°C min^{-1}
$(dT/dt)_{max}$	maximum self-heat rate/°C min^{-1}
ΔH	heat of reaction/J g^{-1}
ϕ	thermal inertial, dimensionless

MEKPO became much more dangerous under dynamic scanning conditions (DSC experiments) than in an adiabatic environment (VSP2 experiments).

In addition, according to the mathematical calculations of safety parameters, the potential hazards of 10 mass% MEKPO combined with contaminants indicated a greater degree of impact in terms of hazards than the pure one.

Conclusions

This study employed a simulated method to establish the kinetic parameters (E_a, A, ΔH) and then compared with the parameters obtained from experiments, as used to estimate the safety parameters (TMR, T_{NR}, SADT). From the simulated results, we precisely simulated the kinetic parameters adopted by experimental values, and then used its mathematical function to predict abnormal situations that might trigger runaway reactions. Furthermore, since the simulation process displayed inaccuracy to some degree when the base-line was cut off, it should be established prudently.

In summary, the kinetic and safety parameters of mathematical values indicated that the MEKPO dimer was safer by itself without specific contaminants, either NaOH or H_2SO_4. The safety parameters could also provide essential and reliable information to realize the inherent hazards of MEKPO to a deeper extent, regardless of its different structures, such as monomer, dimer, or even its contaminants.

Nomenclature

a	vessel wetted surface area/m^2
A	frequency factor/s^{-1}
E_a	apparent activation energy/kJ mol^{-1}

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