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Evaluation of adiabatic runaway reaction of methyl ethyl ketone peroxide by DSC and VSP2

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Abstract Methyl ethyl ketone peroxide (MEKPO) is generally applied to manufacturing in the polymerization processes. Due to thermal instability and high exothermic behaviors of MEKPO, if any operation is undertaken recklessly or some environmental effect is produced suddenly during the processes, fires and explosions may inevitably occur. In this study, thermal analysis was evaluated for MEKPO by differential scanning calorimetry (DSC) test. Vent sizing package 2 (VSP2) was used to analyze the thermal hazard of MEKPO under various stirring rates in a batch reactor. Thermokinetic and safety parameters, including exothermic onset temperature (T_0), maximum temperature (T_{max}), maximum pressure (P_{max}), self-heating rate ($dT\,dt^{-1}$), pressure rise rate ($dP\,dt^{-1}$), and so on, were discovered to identify the safe handling situation. The stirring rates of reactor were confirmed to affect runaway and thermal hazard characteristics in the batch reactor. If the stirring rate was out of control, it could soon cause a thermal hazard in the reactor.

Keywords Batch reactor · Differential scanning calorimetry (DSC) · Methyl ethyl ketone peroxide (MEKPO) · Stirring rates · Thermokinetic and safety parameters · Vent sizing package 2 (VSP2)

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List of symbols

$dP\,dt^{-1}$	Pressure rise rate (psig min^{-1})
$(dP\,dt^{-1})_{max}$	Maximum pressure rise rate (psig min^{-1})
$dT\,dt^{-1}$	Self-heating rate (°C min^{-1})
$(dT\,dt^{-1})_{max}$	Maximum self-heating rate (°C min^{-1})
P_{max}	Maximum pressure (psig)
T_0	Exothermic onset temperature (°C)
T_{max}	Maximum temperature (°C)
$T_{p1\ max}$	Maximum temperature of first peak (°C)
$T_{p2\ max}$	Maximum temperature of second peak (°C)
β	Scanning rate (°C min^{-1})
ΔH_d	Heat of decomposition (J g^{-1})
Φ	Thermal inertia (dimensionless)

Introduction

Modern life has greatly benefitted from the convenience offered by the evolution of industry, but hazards often accompany such progress. Chemical industries use organic peroxides (OPs) including methyl ethyl ketone peroxide (MEKPO), di-tert-butyl peroxide (DTBP), tert-butyl peroxybenzoate (TBPB), cumene hydroperoxide (CHP), tert-butyl hydroperoxide (TBHP), lauroyl peroxide (LPO), benzoyl peroxide (BPO), and dicumyl peroxide (DCPO), etc. The important reason for accidents of OPs is due to the peroxy group (–O–O–), because of its thermal instability and high sensitivity to thermal sources [1, 2]. When encountering thermal sources or high atmospheric temperature, OPs can decompose and incur exothermic reactions during preparation, use, transportation, storage, and even disposal [3]. They may cause various hazards, such as fire, explosion, toxic release, and other serious destruction of the environment [3, 4].

The MEKPO is a reactive substance that is applied as an initiator of polymerization and a curing agent for unsaturated polyester resins in the manufacture of acrylic resins [3, 5]. Industrial MEKPO can be made of methyl ethyl ketone (MEK), adding acidified hydrogen peroxide (H_2O_2) slowly in a vigorously stirred reactor to control the reaction rate and heat release by dosage, stirring rate, temperature, and pressure [6], then diluted with dimethyl phthalate (DMP) [7]. MEKPO has led to many incidents that are attributed to poor training, human error, stirring rates getting out of control, incorrect operative assumptions, and inadequate protection in the manufacturing process [1] or mixed with incompatible contaminants like NaOH, KOH, H_2SO_4, HCl, HNO_3, etc. [8–11]. For these reasons, MEKPO has resulted in much hazardous behavior and runaway reaction [12]. In the past, many thermal hazard incidents were caused by MEKPO in Asia, as shown in the selected serious accidents concerning MEKPO in Table 1 [13, 14]. In Taiwan, the most representative accidents are displayed in Table 2. In recent years, the most serious accident was the Yung-Hsin corporation explosion in 1996 that killed ten people including six firemen [15]. Accidents also had been caused by MEKPO around the world as recorded by the Major Hazard Incident Data Service (MHIDAS) [1, 16].

Table 1 Select serious accidents caused by MEKPO in Japan, Taiwan, Korea, and China since 1964 [13, 14]

Year	Location	Injuries	Fatalities
1964	Tokyo, Japan	114	19
1979	Taipei, Taiwan	49	33
2000	Yosu, Korea	11	3
2004	Henan, China	8	5

Table 2 Thermal explosion accidents involving thermal decomposition of MEKPO in Taiwan since 1979 [15]

Date	Location	Injuries	Fatalities	Hazards
July 13, 1979	Taipei	49	33	Explosion (storage)
February 18, 1984	Taoyuan	55	5	Explosion (reactor)
September 1, 1989	Taoyuan	5	7	Explosion (tank)
October 7, 1996	Taoyuan	47	10	Explosion (tank)

Because of the inherent hazards of MEKPO, many regulations have been established as basis of manipulation during use, transportation, storage, and disposal, such as the Department of Transportation (DOT) 49 CFR, National Fire Protection Association (NFPA) 43B, OSHA (Occupational Safety and Health Administration) 29 CFR 1910.119, North American Emergency Response Guidebook (NAERG), and so on [8].

In this study, we obtained the thermokinetic and safety parameters including exothermic onset temperature (T_0), heat of decomposition (ΔH_d), maximum temperature (T_{max}), maximum pressure (P_{max}), self-heating rate ($dT\ dt^{-1}$), pressure rise rate ($dP\ dt^{-1}$), etc., by using differential scanning calorimetry (DSC) and vent sizing package 2 (VSP2). When varying the stirring rate, the concentration of reactive chemical and the amount of reactive chemical, we identified the factors that affect runaway and thermal hazard characteristics in the batch reactor.

Experimental setup

Sample preparations

The MEKPO 31 mass% was purchased directly from the Fluka Co., and was stored at 4 °C in the refrigerator, that avoided potential thermal decomposition and runaway reaction. DMP was used as a diluted solvent in preparing the sample of MEKPO 15 mass% to perform this study.

DSC

Dynamic temperature-programmed scanning and isothermal detecting experiments can be performed on DSC. Mettler DSC821[e] is the calorimetry that includes the TA8000 system, a sensor with 56 thermocouples and a measuring cell which can sustain rather high pressure to nearly 100 bar. The sensor is used to detect the different changes of heat flow between sample and reference. After the detection, we can get the thermokinetic parameters by evaluation of the system. In this study, STAR[e] software was used to obtain thermal traces [17, 18]. To maintain better thermal equilibrium, the experiments were chosen of scanning characters at the rates of 0.5, 1, 2, and 4 °C min^{-1} [19]. The thermal analyses were investigated from 30 to 300 °C.

VSP2

The VSP2 is an adiabatic reaction calorimeter system manufactured by Fauske and Associates, Inc. It is capable of determining thermal hazard data for very fast exothermic reactions. Automatic heat-wait-search (AHWS) has been selected to confirm an initial temperature of exothermic reaction for VSP2 [20]. The behavior of temperature and pressure rise in a vented test cell (112 mL) could be definitively tested due to the low thermal inertia (Φ), about 1.05–1.20 [21]. According to Yeh et al. [15], the generation of pressure easily exceeded the limitation of the test cell by using MEKPO 15 mass% 15 mL. Therefore, we used a small amount of less than 15 mL of MEKPO 15 mass% to avoid bursting the test cell and leading to errors in the data. When varying the stirring rate from non-stirred (0 rpm) to high speed (500.0 ± 5 rpm), we detected the parameters of runaway and thermal hazard characteristics in the batch reactor, such as T_0, T_{max}, P_{max}, $dT\ dt^{-1}$, and $dP\ dt^{-1}$.

Results and discussion

Thermal analysis by DSC for MEKPO 15 mass%

By using DSC, when MEKPO 15 mass% was programmed scanning at four different scanning rates, we listed the experimental results of thermoanalytical parameters as summarized in Table 3. The heat flow versus temperature curve for MEKPO 15 mass% is displayed in Fig. 1. There were two apparent exothermic peaks in each scanning rate. The heat flow rising was invariably accompanied with the advancement of scanning rate in this study.

In the experimental data, the T_0 of the reaction for MEKPO 15 mass% was about 80 °C, and it was retarded when the scanning rate was increased with permissible range. The T_{max} in two stages of exothermic reaction were both advanced when the scanning rate was increased from 0.5 to 4.0 °C min^{-1}. The heat of reaction in the first peak was higher than the second peak for all scanning rates. When the complete decomposition was reacted, for $\beta = 2.0$ °C min^{-1} especially, the heat of decomposition for MEKPO 15 mass% was between 550 and 680 J g^{-1}.

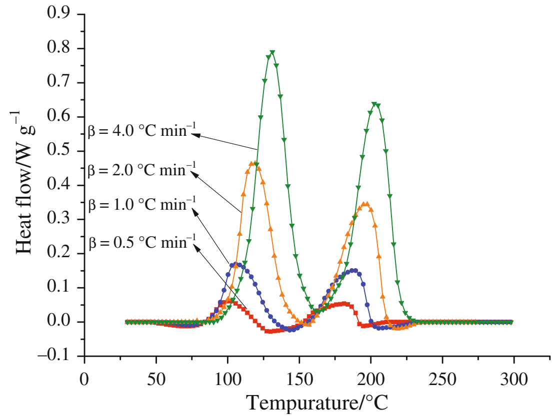

Fig. 1 Heat flow versus temperature curve for MEKPO 15 mass% by DSC test

Hazard analysis by VSP2 for MEKPO 15 mass%

The parameters of runaway characteristics and thermal hazards for MEKPO 15 mass% with various stirring rates by VSP2 are summarized in Table 4, such as T_0, T_{max}, P_{max}, maximum self-heating rate $[(dT\ dt^{-1})_{max}]$, and maximum pressure rise rate $[(dP\ dt^{-1})_{max}]$. Figure 2 indicates the temperature versus time curve with various stirring rates. The pressure versus time plot with various stirring rates is presented in Fig. 3. Figure 4 displays the self-heating rate with various stirring rates for MEKPO 15 mass%. The pressure rise rate with various stirring rates for MEKPO 15 mass% is shown in Fig. 5.

In Figs. 2 and 3, the lowest T_0 occurred in the reaction with 0 rpm of stirring rate. The T_{max} and the P_{max} were about 354.7 °C and 317.9 psig, respectively, for 0 rpm of stirring rate. According to Fig. 4, the most unstable self-heating reaction was detected at 0 rpm of stirring rate, but the $(dT\ dt^{-1})_{max}$ with the 50 rpm of stirring rate was higher than the others. The pressure was produced more violently for 0 rpm of stirring rate than others in Fig. 5. Especially, the $(dP\ dt^{-1})_{max}$ reached 977.9 psig min^{-1} for 0 rpm of stirring rate.

Table 3 Thermoanalytical parameters were obtained by using DSC for MEKPO 15 mass% at different scanning rates

Sample	Scanning rate, β/°C min^{-1}	Thermoanalytical parameters			
MEKPO 15 mass%/mg		T_0/°C	$T_{p1\ max}$/°C	$T_{p2\ max}$/°C	ΔH_d/J g^{-1}
3.44	0.5	80.77	101.50	181.21	329.74
3.71	1.0	80.32	105.16	186.63	550.61
3.60	2.0	102.78	118.13	197.47	679.24
3.90	4.0	91.14	130.81	202.34	576.03

Table 4 Parameters of runaway characteristics and thermal hazards for MEKPO 15 mass% with various stirring rates by VSP2

Sample	Stirring rate/rpm	Thermoanalytical parameters				
MEKPO 15 mass%/mL		T_0/°C	T_{max}/°C	P_{max}/psig	$(dT\ dt^{-1})_{max}$/°C min^{-1}	$(dP\ dt^{-1})_{max}$/psig min^{-1}
10.0	0	76.0	354.7	317.9	98.9	977.9
10.0	50.0 ± 2	76.7	252.6	203.1	240.0	426.7
10.0	500.0 ± 5	91.2	201.3	189.0	51.5	140.2

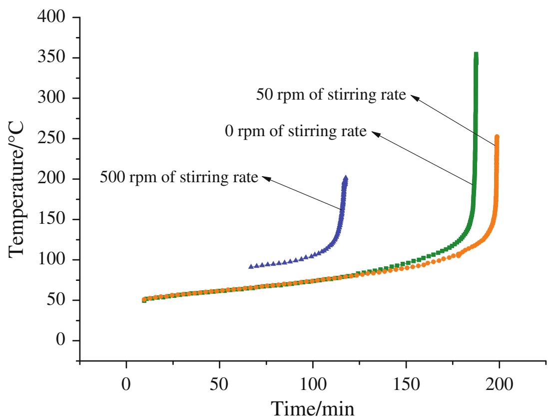

Fig. 2 Temperature versus time curve with various stirring rates for MEKPO 15 mass% by VSP2 test

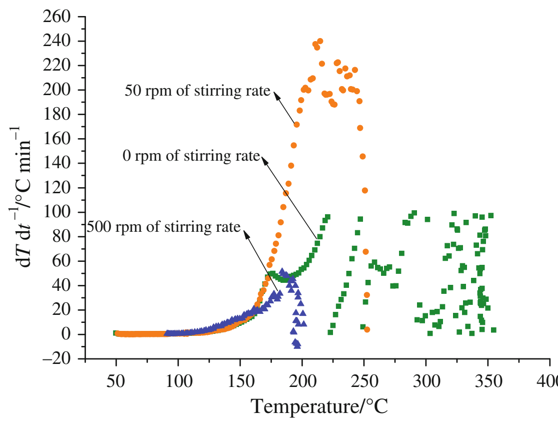

Fig. 4 Self-heating rate on temperature with various stirring rates for MEKPO 15 mass% by VSP2 test

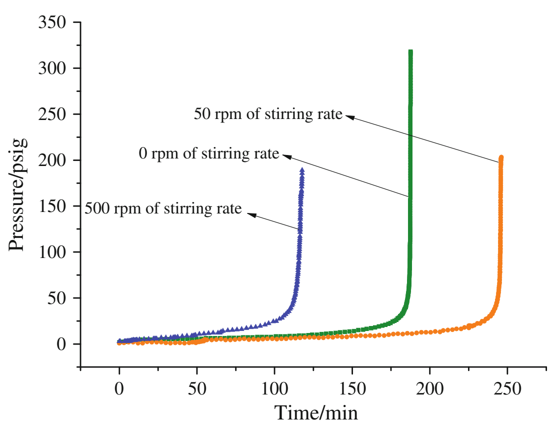

Fig. 3 Pressure versus time curve with various stirring rates for MEKPO 15 mass% by VSP2 test

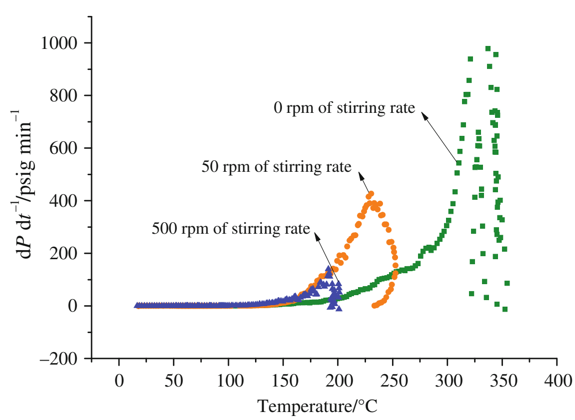

Fig. 5 Pressure rise rate on temperature with various stirring rates for MEKPO 15 mass% by VSP2 test

Conclusions

According to the results, the stirring rate played an important role in affecting a runaway and thermal hazard for decomposition of MEKPO. In this study, the stirring rate was controlled as a factor to simulate the process within a batch reactor. The bases of hazardous characteristics were the experimental data in this research. When investigating by VSP2 test, 0 rpm of stirring rate was much more dangerous than others, including 50 and 500 rpm. Though the highest $(dT\ dt^{-1})_{max}$ was detected at 50 rpm of stirring rate, it was just transient. Because the automatic pressure tracking system injected huge gas continually into the vessel to balance the pressure, it caused the reaction to heat loss for 0 rpm of stirring rate. Due to irregular reaction, the pressure rise was continuously accumulated a huge volume for 0 rpm of stirring rate. Because of thermal accumulation in the reactor, the hazards of thermal decomposition obviously occurred in the reaction. When evaluating MEKPO with 0 rpm of stirring rate, it led to a runaway reaction of temperature and pressure more easily and seriously than the others.

The MEKPO is widely applied to manufacturing; the reactor stirring rate was evaluated to affect runaway and thermal hazards in this study. In terms of the results, the stirring rate was one of the most important parameters that affected the safety in the reactor. When MEKPO was applied in the process, a poor stirring rate should be avoided during the stirring apparatus shutdown.

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