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Isothermal kinetic evaluation of methyl ethyl ketone peroxide mixed with acetone by TAM III tests

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ABSTRACT

Methyl ethyl ketone peroxide (MEKPO), the topic material, has been extensively applied as an initiator and cross-linker during polymerization, but it has also induced many severe accidents on a global scale. Therefore, the purpose of this study was to deeply understanding the basic characteristics of runaway reactions of MEKPO and mixed with acetone. The innovative objective of an isothermal kinetic evaluation is to determine the basic characteristics of reactive chemicals in order to prevent a serious runaway accident. Therefore, we endeavored to demonstrate the reaction model and kinetic parameters, such as activation energy (E_a), frequency factor (A), and so on, by the thermal activity monitor III (TAM III) under three isothermal conditions of 70, 80, and 90 °C, in terms of MEKPO 31 mass% and with acetone 99 mass%. The results showed that MEKPO could liberate a great quantity of heat during exothermic reaction. Moreover, acetone could alleviate the degree of exothermic runaway while being added with MEKPO.

1. Introduction

Methyl ethyl ketone peroxide (MEKPO), which is arguably among the important initiators and cross-linkers used during polymerization, has induced many accidents globally [1], that was the reason of MEKPO had been studied in this text. The development of an accident depends on progress in wrong dosing, temperature-controlled failure, pressure-controlled failure, and so on. The reason for this is simple and straightforward: a runaway reaction is generally an unexpected process that once initiated may cause severe exothermic reactions [2], and the release of heat can also affect other buildings or adjacent equipment. The evaluation of runaway reactions has by necessity become more prevalent for lessening the degree of hazard, because in some cases such accidents may involve fire, explosion, toxic release, etc. From a chemical engineer's viewpoint, MEKPO is treated as dangerous material that is very sensitive to a thermal source. In this study, we made effort to study the basic characteristic phenomena of runaway reactions by isothermal kinetic evaluation, such as activation energy (E_a) and frequency factor (A).

Novel experimental techniques are constantly bringing new insight about evaluating the kinetic parameters for thermally unstable chemicals, such as organic peroxides. Based on these techniques, fundamental concepts related to thermokinetics are being treated as crucial to precisely indicate the basic characteristics for runaway reactions [3–5]. Bunyan et al., apply thermal activity monitor III (TAM III) to evaluate the hazard and identify the safety parameters [6], Briggner et al., employ TAM to detect the phenomenon of crystallinity for lactose monohydrate [7], and this isothermal method has also been extensively applied to evaluate hazardous materials [8,9]. The scope of this study is to describe the exothermic reaction and reaction model of MEKPO 31 mass% and mixed with acetone 99 mass% by the thermal activity monitor III (TAM III), which is likely to play an important role in this field, leading particularly to new methods for evaluating the runaway conditions during processing storage or transportation stage [10].

In this context, we focused attention on three specific isothermal conditions of 70, 80, and 90 °C, for comparing the changes of reactions. All of the results demonstrated that MEKPO is a thermally dangerous material, due to its unstable group of O–O and severe heat released, whereas the addition of acetone could decrease the degree of hazard under mixing conditions. Reaction models, such as nth-order or autocatalytic reactions, are critical for the evaluation process for more precisely realizing the reaction phenomena. In this way, thorough safety information can be provided for plants to instruct their staff on how to protect the plant from an accident during runaway excursions.

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Nomenclature

$C\,dT/dt$	rate of heat accumulation or depletion, kJ/kg min
$f(c)$	kinetic function depends on conversions
g	Seebeck coefficient, V/K
k	constant of reaction rate, 1/s
k_a	heat conductance, W/K
P	thermal power or heat production rate, W = J/s
Q	heat, J
R	gas constant, 8.314 J/mol K
T_o	temperature of surrounding, K
T	temperature of sample, K
t	time, s
U	heat transfer coefficient, kJ/min m^{-2} K
v	rate of change, mol/s, g/s
dC/dt	reaction rate, 1/s
dQ/dt	surrounding temperature, J/K
ΔH	enthalpy change, J/g
Φ	slope of the heat flow time curve, W = J/s
τ	time constant obtained from dynamic calibration, s
ε	calibration constant, W/V

2. Isothermal kinetic evaluation model

Eq. (1) indicates the function of reaction rate, and then the thermal power is obtained by Eqs. (2) and (3) [11]:

$$\frac{dC}{dt} = kf(C) \tag{1}$$

$$P = \frac{dC}{dt}\Delta H \tag{2}$$

$$P = \Delta H k f(c) \tag{3}$$

Here, $dC\,dt^{-1}$ is the reaction rate (1/s); k is the constant of reaction rate; $f(c)$ is the kinetic function depending on conversions; P is the thermal power or heat production rate (W = J/s); ΔH is the enthalpy change (J/g).

Dynamic correction is also a very critical procedure in precisely evaluating the kinetic parameters applied in this study by Tian's equation shown in Eq. (4) [12]:

$$P = \phi + \tau\frac{d\phi}{dt} \tag{4}$$

where Φ is the slope of the heat flow time curve and τ is a time constant obtained from dynamic calibration.

Eqs. (5)–(7) are the heat balance equation in terms of temperature, where P is obtained by adding heat flow and rate of heat accumulation or depletion; k_a is the heat conductance (W/K); dQ/dt depends on the surrounding temperature, which can be monitored by a thermopile. Eq. (8) can be used to improve Eqs. (5)–(7) for stability, where dQ/dt does not depend on the surrounding temperature:

$$P = \Phi + C\frac{dT}{dt} \tag{5}$$

$$\Phi = k_a(T - T_o) \tag{6}$$

$$\frac{dQ}{dt} = k_a(T - T_o) + C\frac{dT}{dt} \tag{7}$$

$$P = k_a(T_S - T_R) + C\frac{d(T_S - T_R)}{dt} \tag{8}$$

Eqs. (9) and (10) indicate the heat balance equation in terms of voltage (V), and Eq. (10) is adopted to dynamically correct calibration data [11]:

$$\Phi = k_a(T - T_o) = \frac{k_a}{g}U \Rightarrow T = \frac{U}{g} + T_o \Rightarrow \frac{dT}{dt} = \frac{1}{g}\frac{dU}{dt} \tag{9}$$

$$P = \frac{k_a}{g}U + \frac{C}{g}\frac{dU}{dt} = \frac{k_a}{g}\left(V + \frac{C}{k_a}\frac{dU}{dt}\right) = \varepsilon\left(V + \tau\frac{dU}{dt}\right) \tag{10}$$

Fig. 1. Structure of thermal activity monitor III [13].

3. Experimental setup

3.1. Preparation of MEKPO 31 mass% and acetone 99 mass%

MEKPO 31 mass%, which was directly purchased from Aldrich Co., was stored in a refrigerator at 4 °C. Acetone 99 mass%, employed as a diluent and also was stored in a refrigerator at 4 °C. After these two materials were mixed, we applied TAM III to evaluate the kinetic parameters based on the experimental data.

3.2. Thermal activity monitor III (TAM III)

TAM III was used to investigate the runaway reaction under temperatures of 70, 80, and 90 °C, as shown in Figs. 1 and 2 [13]. Absolute temperature could be adjusted to within 0.02 K, while operating in isothermal mode, the bath mean temperature fluctuations were within 10^{-5} K. A maximum scanning rate is ±2 K/h for chemical and physical equilibrium. We used the software of TAM III assistant to control the thermostat. The thermostat liquid is mineral oil with a total volume of 22 L, and the temperature range of the thermostat is 15–150 °C when mineral oil is employed [13].

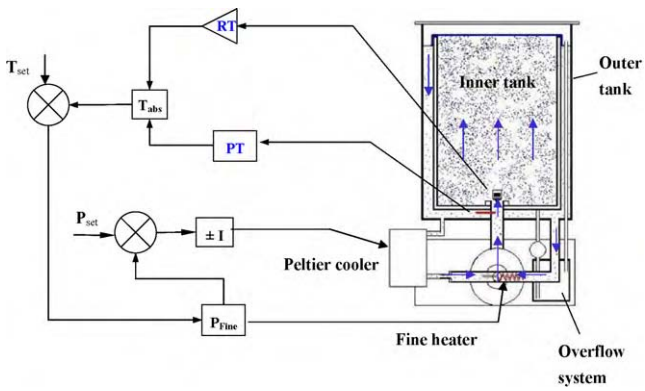

Fig. 2. TAM III thermostat principle [13].

Table 1
Experimental data by TAM III tests for MEKPO 31 mass% and with acetone 99 mass%.

Sample	Temperature (°C)	Sample mass (mg)	Cell	Reaction time (day)	ΔH_d (J/g)
MEKPO 31 mass%	70	101.29	Glass ampoule	16.2	1002.17
	80	102.34	Glass ampoule	9.8	1206.18
	90	104.18	Glass ampoule	3.7	1135.92
MEKPO 31 mass% + acetone 99 mass%	70	MEKPO (102.25) + acetone (13.22)	Glass ampoule	16.2	810.42
	80	MEKPO (105.18) + acetone (13.95)	Glass ampoule	9.8	976.41
	90	MEKPO (102.59) + acetone (15.70)	Glass ampoule	3.7	937.02

Table 2
Time to maximum rate at three temperatures for MEKPO 31 mass% and with acetone 99 mass%.

Sample	Temperature (°C)	*TMR* (day)
MEKPO 31 mass%	70	6.7
	80	3.3
	90	0.9
MEKPO 31 mass% + acetone 99 mass%	70	8.1
	80	3.6
	90	1.0

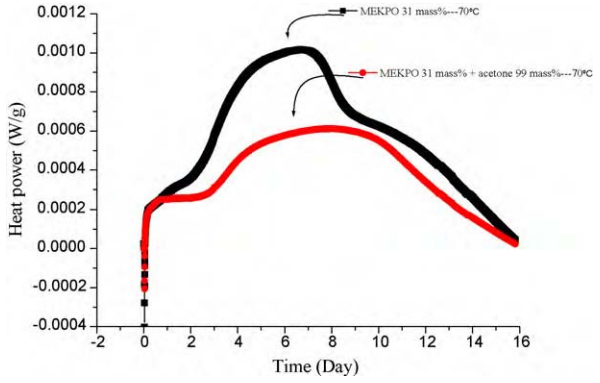

Fig. 3. Heat power *vs.* time for the thermal decomposition of 31 mass% MEKPO along and with acetone 99 mass% at 70 °C.

4. Results and discussion

Experimental results by TAM III tests are shown in Tables 1 and 2 and Figs. 3–7. All of the results detected under three isothermal conditions of 70, 80, and 90 °C indicated that the heat of reaction for MEKPO could be significantly lessened with addition of acetone.

Figs. 3–5 depict the result of the measurements on MEKPO 31 mass% and mixed with acetone 99 mass% under three isothermal conditions of 70, 80, and 90 °C. From these peaks it can be observed that the spread of the results between both conditions of MEKPO alone and with acetone is very clear. While acetone was being added into the glass ampoule with MEKPO, the heat of reaction lessened significantly from 1000–1200 to 810–976 J/g, respectively, under three different temperatures. When these two materials are

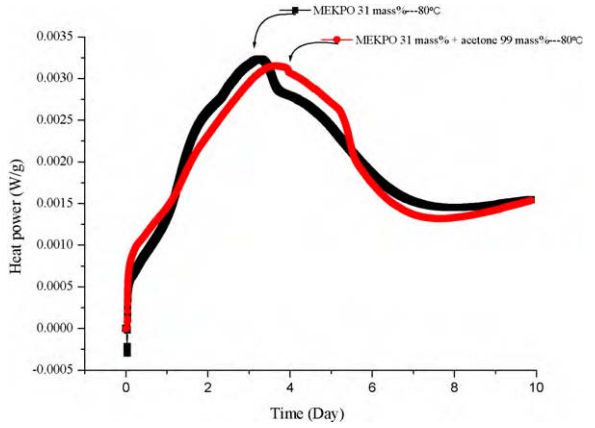

Fig. 4. Heat power *vs.* time for the thermal decomposition of 31 mass% MEKPO along and with acetone 99 mass% at 80 °C.

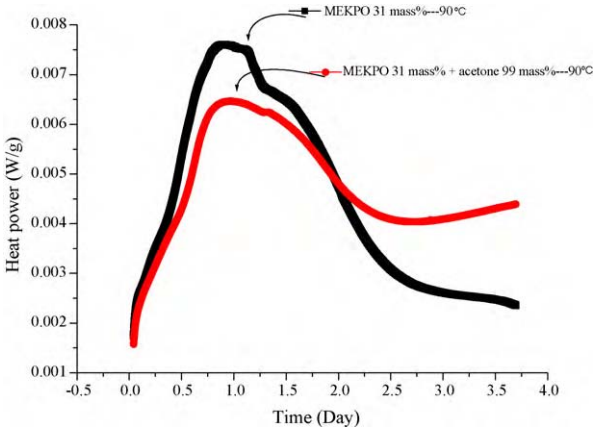

Fig. 5. Heat power *vs.* time for the thermal decomposition of 31 mass% MEKPO alone and with acetone 99 mass% at 90 °C.

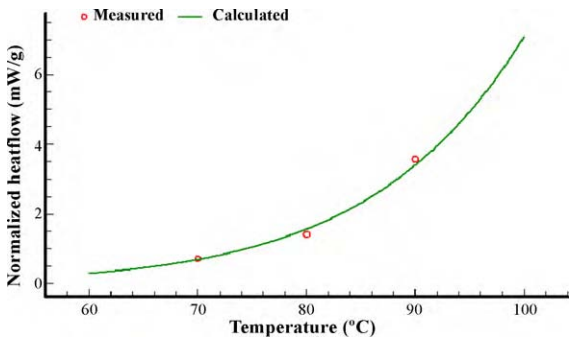

Fig. 6. Temperature *vs.* normalized heat flow for evaluating E_a of 31 mass% MEKPO at 70, 80, and 90 °C (E_a = 82.8 ± 6.0 kJ/mol).

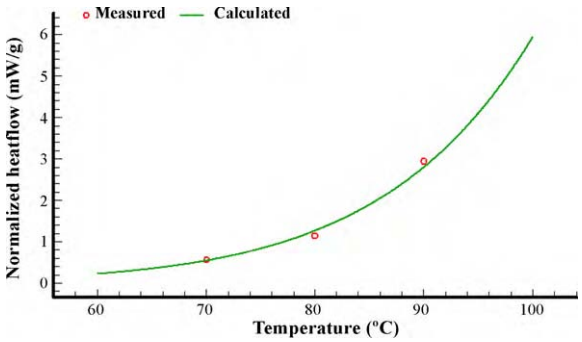

Fig. 7. Temperature *vs.* normalized heat flow for evaluating E_a of 31 mass% MEKPO with 99 mass% acetone at 70, 80, and 90 °C (E_a = 84.9 ± 6.2 kJ/mol).

being mixed, free radicals produced by MEKPO can be transformed to more stable enol radicals [14]. Figs. 6 and 7 show the evaluation results of activation energy for MEKPO and with acetone by employing the Arrhenius equation, as shown in Eq. (11):

$$k_i(T) = A \exp\left(-\frac{E_a}{RT}\right) \tag{11}$$

where A, E_a, and R represent, respectively, the frequency factor, the activation energy of the stage, and the gas constant ($R = 8.314$ J/mol K). The E_a was about 82.8 ± 6.0 kJ/mol for pure MEKPO, and $E_a = 84.9 \pm 6.2$ kJ/mol for MEKPO mixed with acetone. Both results demonstrate that the exothermic reaction tended to lessen when acetone was added, and the MEKPO is a thermally unstable material because of the weak O–O bond [15]. In terms of the time to maximum rate (*TMR*), which could be applied to evaluate the degree of hazard during storage or transportation, *TMR* is also one of the safety parameters [14,16] prevailingly used in plants. While acetone was added into a glass ampoule with MEKPO, the *TMR* was increased about 1.4, 0.3, and 0.1 days under isothermal conditions of 70, 80, and 90 °C, respectively. Therefore, the degree of hazard was lessened under mixture conditions. By this point, we could significantly realize a tendency that the *TMR* had clearly increased with lower isothermal temperature.

Note that it is also possible to observe runaway reactions under a lower isothermal temperature, as per the extension of the reaction time. It can also be seen that TAM III is an excellent instrument for the study of discussing runway reactions. For storage and transportation measurements, an isothermal calorimeter, such as the TAM III has been demonstrated to be a better instrument than a non-isothermal calorimeter.

5. Conclusions

We employed TAM III to evaluate the basic characteristics of MEKPO 31 mass% and with acetone 99 mass%, in terms of runaway reactions. *TMR* is a quick and effective safety parameter to precisely evaluate the degree of hazard under isothermal conditions. As revealed in this study, acetone alleviated the heat of reaction and also increased the *TMR* while mixed with pure MEKPO. It could also be treated as the degree of hazard was decreased. Therefore, all of the safety information generated by this study will be provided to the relevant plants for mitigating the loss of property and human life.

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