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SELF-ACCELERATING DECOMPOSITION TEMPERATURE (SADT) CALCULATION OF METHYL ETHYL KETONE PEROXIDE USING AN ADIABATIC CALORIMETER AND MODEL

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The highly reactive and unstable exothermal features of methyl ethyl ketone peroxide (MEKPO) have led to a large number of thermal explosions and runaway reaction accidents in the manufacturing process. To evaluate the self-accelerating decomposition temperature (SADT) of MEKPO in various storage vessels, we used differential scanning calorimetry (DSC) and vent sizing package 2 (VSP2). The thermokinetic parameters were, in turn, used to calculate the SADT from theoretical equations based on the Semenov model.

This study aimed at the SADT prediction value of various storage vessels in Taiwan compared with the UN 25 kg package and UN 0.51 L Dewar vessel. An important index, such as SADT, temperature of no return (T_{NR}) and adiabatic time maximum rate (TMR_{ad}), was necessary and useful to ensure safe storage or transportation for self-reactive substances in the process industries.

Keywords: *DSC, methyl ethyl ketone peroxide (MEKPO), self-accelerating decomposition temperature (SADT), Semenov model, vent sizing package 2 (VSP2)*

Introduction

Organic peroxides are self-reactive chemical materials widely employed as initiators and cross-linking agents for polymerization reactions, since they typically form free radicals upon decomposition [1]. This free radical formation can induce further decomposition by autocatalysis and thus a runaway reaction hazard can exist with insufficient heat removal. Organic peroxides when exothermically decomposed require inherently safer design during preparation, manufacturing, transportation, storage and even disposal. They can release large amounts of thermal energy and result in high pressure during runaway excursion, leading to a fire or explosion accident.

Important parameters, such as self-accelerating decomposition temperature (SADT), temperature of no return (T_{NR}), adiabatic time to maximum rate (TMR_{ad}) and so on, are applied to dictate vessel temperature for transportation and storage.

According to ‘Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria’ (TDG) of the United Nations (UN), the SADT is defined as the lowest ambient temperature at which self-accelerating decomposition may occur in organic peroxides or self-reactive substances in the packaging for transportation purposes [2]. SADT is the lowest environmental temperature at which the temperature increase of a chemical substance is at least 6°C in a specified commercial package during a period of seven days or less [2].

The UN committee recommends four-test methods for determination of the SADT, as displayed in Table 1, which involve a storage test either at a fixed external temperature or under near-adiabatic conditions. The test method selected should be such that it is appropriate for the size and material of the actual package, as the SADT varies according to package size and material [2]. We applied the H2 test that is based on lab-scale experiments which use a few reactive materials to significantly alleviate explosive and dangerous impacts.

In general, methyl ethyl ketone peroxide (MEKPO) is used as initiator and cross-linking agent for the resin polymerization process. Many thermal explosions and runaway reactions have caused a great number of deaths and injuries by MEKPO globally, as indicated in Table 2 [3–10]. From Table 2, we find three accidents

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Table 1 Test methods for test series in TDG of UN [2]

Test code	Name of test
H1	The United States SADT test (US SADT test)
H2	Adiabatic storage test (AST)
H3	Isothermal storage test (IST)
H4	Heat accelerating storage test (Dewar test)

for MEKPO in Australia and the UK by the Major Hazard Incident Data Service (MHIDAS) [10].

This study aimed to calculate the SADT of MEKPO in various vessels, such as UN 25 kg package, UN 0.51 L Dewar vessel, 55 gallon drum, storage tank and so on.

First, we used differential scanning calorimetry (DSC) to determine the fundamental thermal hazard and the essential parameters, such as exothermic onset temperature (T_0), heat of decomposition (ΔH_d) and maximum temperature (T_{max}). According to the UN suggestions, vent sizing package 2 (VSP2) (adiabatic H2 test) was employed to investigate and evaluate thermokinetics, such as activation energy (E_a), frequency factor (A), ΔH_d, maximum temperature rise ($(dT/dt)_{max}$), maximum pressure rise ($(dP/dt)_{max}$) and so on. Finally, we applied all of the thermokinetics from experiments, combined with the Semenov model, to determine the SADT of MEKPO in various vessels.

Experimental

Samples

31 mass% MEKPO in dimethyl phthalate (DMP) was directly purchased from the Fluka Co. and both density and concentration were measured. Then, MEKPO was stored in a refrigerator at 4°C. In addition, to avoid bursting the test cell and losing all of the exothermic data, the VSP2 tests were run with 10–20 mass% MEKPO.

Differential scanning calorimetry (DSC)

Dynamic scanning experiments were performed on a Mettler TA8000 system coupled with a DSC 821^e measuring test crucible (Mettler ME-26732) that could withstand relatively high pressure of about 100 bar. STAR^e software was employed for acquiring thermal curves. For the sake of better thermal equilibrium, a variety of heating rates (β) were chosen, such as 1, 2, 4 and 10°C min^{-1}. About 1 to 10 mg of the sample was selected for acquiring the experimental data. The test cell was sealed manually by a special tool equipped with Mettler DSC and we conducted dynamic scanning by starting the programmed setting [11–13].

DSC is regarded as a useful tool for evaluating thermal hazards and investigating decomposition mechanisms of reactive chemicals if the experiments are carried out carefully. The experimental conditions were as follows:

- Heating rates: 1, 2, 4, 10°C min^{-1}.
- Materials mass: 1–10 mg.
- Temperature range: 30–300°C
- Test cell: These gold-plated high-pressure crucibles, which can be pressed together, have proven to be very useful for safety investigation, but they can only be used for one measurement with a maximum pressure of 15 MPa. The lid is pressed into the crucible with a pressure of about a ton so that the seal tightens the crucible. A toggle press is used to close the crucible.

Vent sizing package 2 (VSP2)

VSP2, a PC-controlled adiabatic calorimeter manufactured by Fauske & Associates, Inc. [14], was used to obtain thermokinetic and thermal hazard data, such as temperature and pressure traces *vs*. time. The low heat capacity of the cell ensured that all the reaction heat released remained within the tested sample. Thermokinetic and pressure behavior in the same test cell (112 mL) usually could be tested without any difficult extrapolation to the process scale due to the low thermal inertia factor (Φ) of about 1.05 to 1.32 [15].

Table 2 Thermal explosion accidents caused by MEKPO globally

Year	Nation	Frequency	Injuries	Fatalities	Worst case
1953–1978	Japan	14	115	23	114 (I) 19 (F) in Tokyo
1980–2004	China	14	13	14	8 (I) 5 (F) in Honan
1984–2001	Taiwan	5	156	55	49 (I) 33 (F) in Taipei
2000	Korea	1	11	3	11 (I) 3 (F) in Yosu
1973–1986	Australia*	2	0	0	NA
1962	UK*	1	0	0	NA

*Data from MHIDAS [10] NA: Not applicable

The low Φ allows for bench scale simulation of the worst credible case, such as wrong dosing, cooling failure, or external fire conditions.

Semenov model

According to the Semenov model [16], the rate of uniform temperature rise in a system is established by the difference between the rate of heat generation for the system and the rate of heat transfer to the environment by the following equations:

$$C_p M_0 \frac{dT}{dt} = \Delta H M_0^n A \exp(-E_a/RT) - US(T-T_0) \quad (1)$$

$$B_1 \exp(-E_a/RT_{NR}) - B_2(T_{NR}-T_0)=0 \quad (2)$$

$$\frac{B_1 E_a}{RT_{NR}^2} \exp(-E_a/RT_{NR}) - B_2 = 0 \quad (3)$$

where

$$B_1 = \Delta HAM_0^{n-1}/C_p \quad (4)$$

$$B_2 = US/(C_p M_0) \quad (5)$$

According to Eqs (3)–(5), the following equations are given:

$$\frac{E_a}{RT_{NR}} - 2\ln(1/T_{NR}) + \ln(USR/M_0^n \Delta HAE_a) = 0 \quad (6)$$

$$\frac{E_a}{R} - T_{NR}^2/(T_{NR}-T_0) \quad (7)$$

$$\mathrm{SADT} = T_{NR}/(RT_{NR}^2 - E_a) \quad (8)$$

$$\mathrm{SADT} = T_{NR} - R(T_{NR}+273.15)^2/E_a \quad (9)$$

where

$$(T_{NR}+273.15)^2 = \frac{mE_a \Delta Hk}{RU(1.8)a} \quad (10)$$

$$= \frac{mE_a \Delta HAe^{-E_a / R(T_{NR}+273.15)}}{RU(1.8)a} \quad (11)$$

Townsend and Tou [17] and Fisher and Goetz [18] support the Semenov model from Eq. (11).

Results and discussion

Thermal decomposition analysis for DSC

Figure 1 demonstrates a comparison of thermal curves of decomposition of 31 mass% MEKPO with four types of β (β=1, 2, 4 and 10°C min^{-1}) by DSC. When the β was lower, the reaction could be detected at a lower temperature; on the other hand, if the β was higher, the T_0 determined could be delayed and the T_{max} was high.

As a result, if β increases we could reach the following phenomena [19]:

- The temperature at which reaction begins increases with β.
- The exothermic T_{max} increases β.
- The temperature at which the completion of the curve reaction occurs increases with β.
- The size of a T_{max} increases with β.

Table 3 summarizes the thermodynamic data by the STAR^e program for the runaway assessment. MEKPO could decompose slowly at 30–32°C, as indicated by our previous study for monomer [3]. We surveyed MEKPO decomposing at 30°C, as disclosed in Fig. 1. We used various scanning rates by DSC to survey the initial decomposition circumstances. Under a heating rate of 10°C min^{-1} situation, the T_0 was measured at

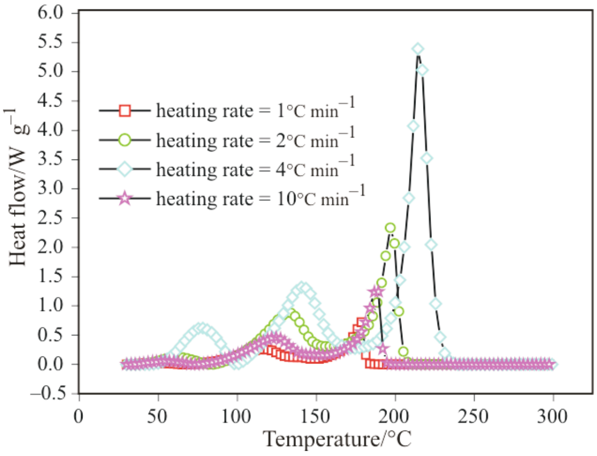

Fig. 1 Heat flow *vs.* temperature of MEKPO 31 mass% under dynamic various heating rates by DSC

Table 3 Thermokinetics and safety parameters of 31 mass% MEKPO by DSC under various scanning rates

β/ °C min^{-1}	Mass/ mg	Initial decomposition		Mainly thermal decomposition						ΔH_{total}/J g^{-1}
		1st peak		2nd peak			3rd peak			
		T_1/°C	ΔH_d/J g^{-1}	T_2/°C	T_{max}/°C	ΔH_d/J g^{-1}	T_3/°C	T_{max}/°C	ΔH_d/J g^{-1}	
1	4.00	30	30	70	115	382	142	180	825	1.238
2	3.72	35	36	75	125	324	152	187	768	1.128
4	4.00	42	41	83	135	304	160	200	768	1.113
10	4.90	47	96	100	140	250	175	220	584	931

Table 4 Parameters of MEKPO by VSP2 with various concentrations

Concentration/ mass%	T_0/°C	T_{max}/°C	P_{max}/bar	$(dT/dt)_{max}$/ °C min^{-1}	$(dP/dt)_{max}$/ bar min^{-1}	A/s^{-1}	E_a/kJ mol^{-1}
10	103	207	16	14	2.3	$4.82\cdot10^{12}$	108.4
15	100	219	25	75	125		
20	90	263	34	83	134		
Liaw *et al.*,	[24] used PHI-TEC II (adiabatic calorimeter) to calculate the E_a and A of 50 mass% MEKPO					$6.38\cdot10^{11}$	116.7

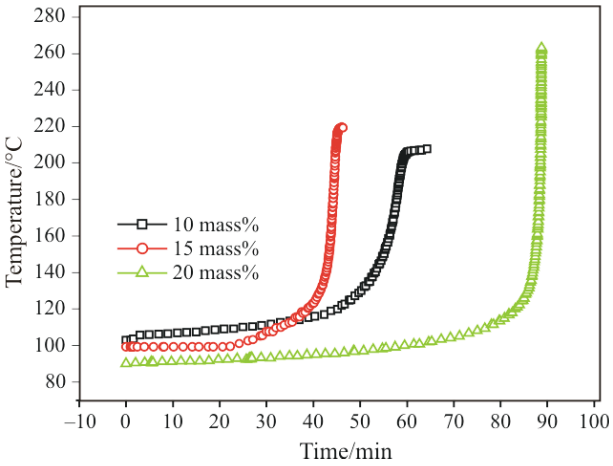

Fig. 2 Temperature *vs*. time for thermal decomposition of MEKPO with various concentrations by VSP2

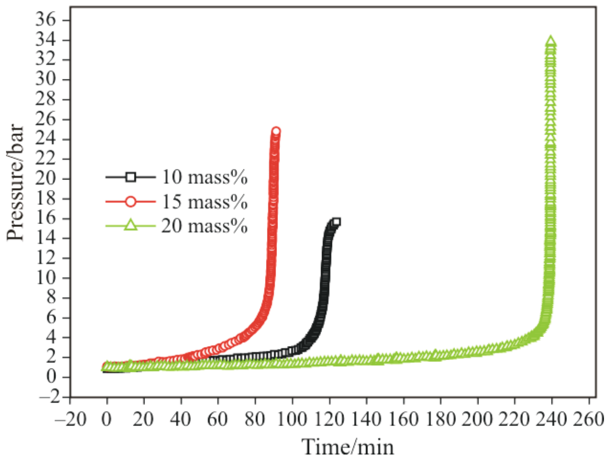

Fig. 3 Pressure *vs*. time for thermal decomposition of MEKPO under various concentrations by VSP2

about 47°C and ΔH_d of the first peak was evaluated at about 96.87 J g^{-1}. As a result, a quick temperature rise may cause violent initial decomposition (the first peak) of MEKPO under external fire condition. Table 3 shows thermokinetic parameters, such as T_0, ΔH_d, T_{max}, of 31 mass% MEKPO by DSC under various scanning rates. The initial decomposition peak usually releases little thermal energy, so it is often disregarded. The T_0 of mainly decomposition was about 80°C. The total heat of reaction was about 1200 J g^{-1}.

Thermal decomposition analysis for VSP2

Table 4 indicates T_0, T_{max}, P_{max}, $((dT/dt)_{max})$ and $((dP/dt)_{max})$ for various concentrations of MEKPO by VSP2. Figure 2 displays temperature *vs*. time by VSP2 with various concentrations. The pressure *vs*. time by VSP2 under disparity concentrations is displayed in Fig. 3. 20 mass% MEKPO by VSP2 was more dangerous than the other concentrations in Fig. 4 because it began self-heating at 90°C and T_{max} reached 263°C. Figure 5 displays the self-pressure rise rate of various MEKPO concentrations by VSP2.

The kinetic parameters of a single reaction can be evaluated from the equation derived by Townsend and Tou for an adiabatic process:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{12}$$

$$= \ln \frac{\frac{dT}{dt}}{C_0^{n-1}\left(\frac{T_f - T}{T_f - T_0}\right)^n (T_f - T_0)} \tag{13}$$

$$= \ln \frac{\frac{dT}{dt}}{1\left[\frac{T_f - T}{T_f - T_0}\right]^1 (T_f - T_0)} \tag{14}$$

$$= \ln \frac{\frac{dT}{dt}}{(T_f - T)} \tag{15}$$

where the rate constant is represented by the Arrhenius law:

$$k = Ae^{-\frac{E_a}{RT}} \tag{16}$$

Substituting the experimental thermal data from VSP2 into Eq. (13) and assuming that n=1, we can plot ln$k$ *vs*. $-1000/T$ and obtain a very good straight line as in Fig. 6. The estimated kinetic parameters A and E_a for adiabatic reaction are summarized in Table 4.

Table 5 Parameters of SADT equation by various situations

Vessel type	m/kg	U/kJ min^{-1} m^{-2} K^{-1}	S/m^2	T_{NR}/°C	SADT/°C	A/s^{-1}	E_a/kJ mol^{-1}
5 gallon drum	15.2	11.3	0.137	78.0	72.0	$4.82\cdot10^{12}$	108.4
55 gallon drum	167.4	11.3	1.51	97.9	84.5	$4.82\cdot10^{12}$	108.4
UN 25 kg package	20.1	0.17	0.4812	62.7	54.2	$4.82\cdot10^{12}$	108.4
0.51 L Dessel vessel	1.21	0.087	0.0303	55.0	50.0	$4.82\cdot10^{12}$	108.4

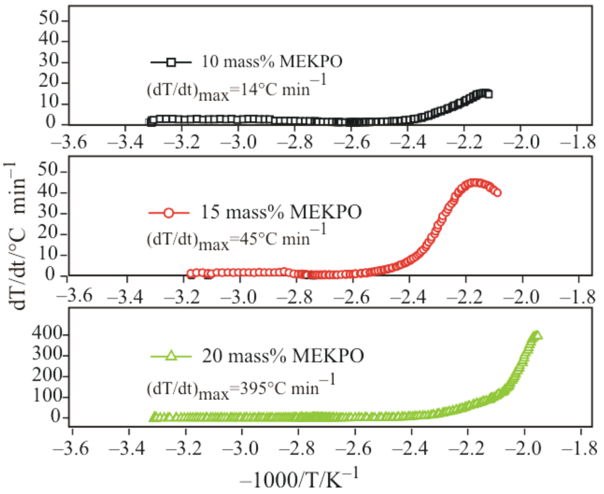

Fig. 4 Dependence of self-heating rate (dT/dt) on temperature from VSP2 experimental data for MEKPO under various concentrations

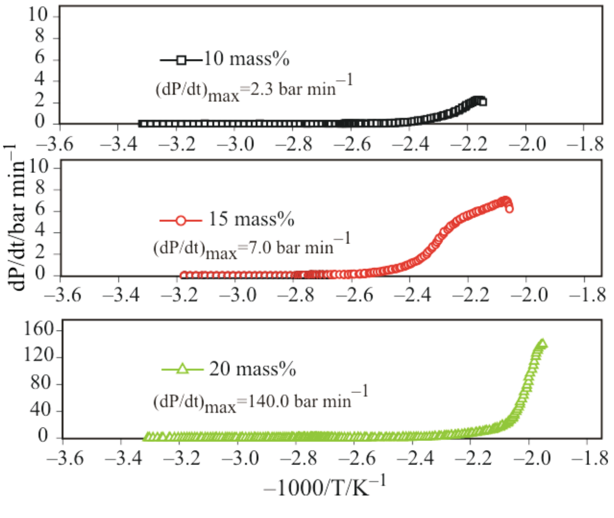

Fig. 5 Dependence of pressure rise rate (dP/dt) on temperature from VSP2 experimental data for MEKPO under various concentrations

Evaluation of safety parameters

We used VSP2 parameters, including E_a, A and ΔH_d, to set up the Semenov equation as illustrated in Table 5. SADT for a 25 kg package was calculated by using a wetted surface area (S), S=0.48124 m^2 and heat transfer coefficient (U), U=1.7034 10^{-1} kJ m^{-2} °C^{-1} min^{-1} refer to [17–19]. SADT for a 0.51 Dewar vessel was evaluated as S=0.0303 m^2 and U=8.7402 10^{-2} kJ m^{-2} °C^{-1} min^{-1} refer to [20–22].

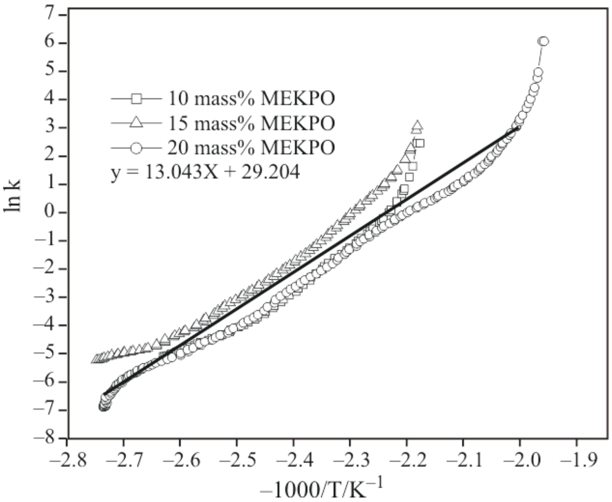

Fig. 6 The correlation of overall rate constant (k) and temperature (T) for 10–20 mass% MEKPO by VSP2

The SADT for a 5 and 55 gallon drum was evaluated as S=0.137 and 1.51 m^2, respectively and U=11.34 J m^{-2} °C^{-1} refer to [6, 23]. The SADT of various vessels was determined as demonstrated in Table 5.

Conclusions

According to DSC experimental data, MEKPO decomposes at 30–40°C. If the β is high, the initial exothermic temperature could be delayed and ΔH_d causes its temperature to rise quickly. Under an external fire circumstance, MEKPO can decompose quickly and cause a runaway reaction and thermal explosion. On the other hand, for 20 mass% MEKPO by VSP2, the maximum temperature (T_{max}) and pressure (P_{max}) were about 263°C and 34.7 bar, respectively. Under 20 mass% MEKPO by VSP2 test, the ((dT/dt)$_{max}$) and ((dP/dt)$_{max}$) were about 394.7°C min^{-1} and 140.0 bar min^{-1}, respectively.

During storage and transportation, a low concentration (<40 mass%) and a small amount of MEKPO should be controlled. Under various storage and transportation vessels, for the SADT there was a disparity. This study, with a view of predicting the SADT of a 220 L drum in Taiwan, came up with a value of about 85°C.

Thermokinetics determined by autocatalytic thermal curve could be used to assess the thermal explosion hazard for organic peroxides and to determine useful parameters such as T_0, SADT, temperature of no return (T_{NR}) and adiabatic time to maximum rate (TMR$_{ad}$). In practice, these data are necessary for the proper choice of safe conditions of application, storage and transportation in terms of chemical products.

In view of loss prevention and employee understanding, MEKPO must be supposed as type B of organic peroxide by Globally Harmonized System (GHS). Material safety data sheets (MSDS) must be used to note the symbol on storage vessel or drum as follows:

Nomenclature

A	frequency factor, s^{-1} M^{1-n}
a	vessel wetted surface area, m^2
C_p	liquid specific heat at constant pressure, kJ kg^{-1} °C^{-1}
C_0	initial concentration, mol L^{-1}
E_a	activation energy, kJ mol^{-1}
K	pre-exponential factor, s^{-1}
k_i	rate at stage i, s^{-1}
M	mass of reactant, g
m	mass of reactor, kg
n	order of reaction
P_{max}	maximum pressure during overall reaction, bar
$Q^{\bullet}$	heat flow, W g^{-1}
Q	calorific capacity, J g^{-1}
R	ideal gas constant, 8.314 J mol^{-1} K^{-1}
S	wetted surface area, m^2
SADT	self-accelerating decomposition temperature, °C
T	temperature, °C
T_A	final adjusted temperature, K
T_{A0}	initial adjusted temperature, K
T_f	final temperature, °C
T_M	final measured temperature, K
T_0	exothermic onset temperature, °C
T_{M0}	initial measured temperature, K
T_{NR}	temperature of no return, °C
T_{max}	maximum temperature during overall reaction, °C
T_{wall}	temperature on the wall, °C
TMR$_{ad}$	time to maximum rate under adiabatic system, min, h
U	heat transfer coefficient, kJ min^{-1} m^{-2} K^{-1}
ϕ	thermal inertia
dT/dt	self-heating rate, °C min^{-1}
$(dT/dt)_A$	actual self-heating rate, °C min^{-1}
α	degree of conversion
β	heating rate, °C min^{-1}
ΔH_d	heat of decomposition, J kg^{-1}
λ	heat conductivity, J ms K^{-1}

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