Effects of stirring rate for thermal runaway reaction in cumene hydroperoxide manufacturing process using calorimetric techniques

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Abstract Oxygen (O_2) or air is widely applied globally to yield cumene hydroperoxide (CHP) in a cumene oxidation tower. In previous studies, CHP has been identified as a thermally hazardous chemical. This study was used to evaluate thermal hazard of CHP in cumene using differential scanning calorimetry and vent sizing package 2 (VSP2). Self-accelerating decomposition temperature (SADT), self-heating rate, exothermic onset temperature (T_0), critical temperature (T_c), time to maximum rate (TMR), activation energy (E_a), etc., were employed to prevent and protect thermal runaway reaction and explosion in the manufacturing process and/or storage area. The reaction order (n) of CHP was evaluated to be 0.5 in this study. The E_a was determined to be 122 kJ mol^{-1} by VSP2. High volume of CHP with 0 rpm of stirring rate by VSP2 was more dangerous than a low one. Control of stirring rate should be a concern in process safety management program. In view of proactive loss prevention, inherently safer handling procedures and storage situations should be maintained in the chemical industries.

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List of symbols

A	Frequency factor (s^{-1} M^{1-n})
A_{tot}	Total peak area (mJ)
C_0	Initial concentration of reaction (M)
C_p	Liquid specific heat at constant pressure (kJ kg^{-1} °C^{-1})
E_a	Activation energy (kJ mol^{-1})
H	The DSC signal deviation from baseline (mW)
HTC	Heat transfer coefficient (W m^{-2} K^{-1})
K	Reaction rate (s^{-1})
k_0	Reaction rate of initiation (s^{-1})
M	Mass of reactant (mg)
M_{cumene}	Mass of cumene (g)
M_{CHP}	Mass of CHP (g)
N	Reaction order (dimensionless)
Q	Calorific capacity (J g^{-1})
R	Ideal gas constant (8.314 J mol^{-1} K^{-1})
$SADT$	Self-accelerating decomposition temperature (°C)
T	Temperature of reaction (°C)
T_0	Exothermic onset temperature (°C)
T_c	Critical temperature (°C)
T_e	Environmental temperature (°C)
T_{max}	Maximum temperature during overall reaction (°C)
T_{NR}	Temperature of no return (°C)
TMR	Time to maximum rate (min, h, day)
T_{wall}	Temperature on the wall (°C)
α	Degree of conversion (dimensionless)
β	Heating rate (°C min^{-1})
ΔH_d	Heat of decomposition (J g^{-1})
λ	Thermal conductivity (J ms K^{-1})

Introduction

Cumene hydroperoxide (CHP) is a typical organic peroxides (OPs) [1] that is identified as type B of OPs by the Globally Harmonized System of Classification and Labeling of Chemicals (GHS) of United Nations (UN) [2].

Cumene is a toxic chemical that is used to mix with oxygen (O_2) or air (21 vol% O_2) in the oxidation tower. The oxidation zone is planned as six of oxidation processes that can be evaluated from low concentration of CHP (15 mass%) to high concentration of CHP (80 mass%) [3]. The oxidation temperature is held at 90–100 °C and the cooling system is operated in the reaction period. A fire and explosion accident in the oxidation area was investigated by the National Fire Agency in Taiwan. The report of the investigation was applied to describe the cause involving a pipeline crack and CHP releasing. Thermal explosions and runaway reactions of CHP in the oxidation tower, reactor, and storage tank have been collected in Table 1 [4].

Eighty mass% CHP was used to produce phenol and acetone by 2,000 ppm of sulfuric acid (H_2SO_4) in the traditional process. H_2SO_4 mixed with 80 mass% CHP can increase heat of decomposition (ΔH_d) and the temperature of reaction. Cooling system failures have caused runaway reactions, fires, and liquid thermal explosions (LTE). Two ways, including sodium hydroxide (NaOH) (as neutralizer) and an amount of water (as latent heat) can be applied to alleviate the temperature of reaction for emergency response by operators [5].

More studies concerning CHP were focused on reactive hazard and runaway reaction [6–8]. This study was used to analyze the effect of stirring rate for a runaway reaction in a batch reactor. Differential scanning calorimetry (DSC) (non-isothermal calorimeter) and vent sizing package 2 (VSP2) (adiabatic calorimeter) were used to evaluate the reaction behavior of CHP under various stirring rates. Stirring rate, self-accelerating decomposition temperature (SADT), exothermal onset temperature (T_0), time to

maximum rate (TMR), maximum temperature (T_{max}), maximum pressure (P_{max}), ΔH_d, activation energy (E_a), maximum self-heating rate ($(dT\ dt^{-1})_{max}$), and maximum pressure rise rate ($(dP\ dt^{-1})_{max}$) can be provided to operators, engineers, and designers for loss prevention.

Reaction order (n) of a chemical is an important index widely used as a parameter for thermal explosion simulation or reaction rate calculation of reactant. Consequently, the n of CHP is calculated to be 0.5 by VSP2 in this study. Our aim was to calculate the E_a of 25 mass% CHP by VSP2 that can be determined to be 122 kJ mol^{-1}. Frequency factor (A) was evaluated to be 1.07×10^{13}.

Experimental setup

Samples

Eighty mass% CHP and 99 mass% cumene (diluent) were purchased from the Fluka Co. and both density and concentration were measured. CHP is a liquid and was stored at 4 °C. To prevent thermal hazard for operators in the laboratory and to protect the experimental equipment, less than 30 mass% CHP was used to detect thermal hazard using an adiabatic calorimeter. Twenty-five mass% (in 75 mass% cumene) CHP (Table 2) was analyzed by DSC and VSP2.

Differential scanning calorimetry (DSC)

Dynamic scanning experiments were conducted on a Mettler TA8000 system coupled with a DSC 821^e measuring test crucible (Mettler ME-26732), which is the essential part of the experiment. It was used to perform experiments for withstanding relatively high pressure to approximate 100 bar.

Temperature-programmed screening experiments were performed with DSC. The heating rates (β) selected for the temperature-programmed ramp were 4 and 10 °C min^{-1}. The range of temperature by DSC was chosen from 30 to 300 °C for CHP. The initial temperature of DSC was selected to be 30 °C (the lowest temperature of DSC without cooling system). Final temperature of reaction was selected to be 300 °C because the reaction of CHP was developed completely.

Table 1 Selected thermal explosion accidents caused by CHP in Taiwan [4]

Year	Chemical	Deaths/injuries	Hazard
1981	CHP	1/3	Explosion
1986	CHP	0/0	Explosion
1999	DCPO	0/0	Explosion
2003	CHP/DCPO	0/2	Explosion
2005	DCPO	0/0	Explosion
2008	DCPO	0/0	Explosion
2009	CHP	0/0	Explosion
2010	CHP	0/0	Explosion

DCPO dicumyl peroxide

Table 2 Concentration information of CHP

Conc./mass%	M_{CHP}/g	M_{cumene}/g	Total sample volume/mL	C_0/M
20	16.45	68.96	100	1.082
25	20.56	64.65	100	1.353

DSC was used to detect the temperature change between the sample and reference for determining the heat change, time, and temperature. Roughly 3–8 mg of the sample was used for acquiring the experimental data. The test cell was sealed manually by a special tool equipped with Mettler's DSC, and we conducted dynamic scanning by starting the programmed setting. The DSC test was established as follows.

The E_a can be calculated by using the built-in model of DSC that can be described as Eqs. 1 and 2. The nth-order model equation compared with the Arrhenius method of the temperature function of the reaction rate constant is [9]:

$$\frac{d\alpha}{dt} = k_0 \exp\left(-\frac{E_a}{RT}\right)(1-\alpha)^n \quad (1)$$

$$\frac{d\alpha}{dt} = \frac{H}{A_{tot}} \quad (2)$$

where H is the DSC signal deviation from baseline and A_{tot} is total peak area [9].

Vent sizing package 2 (VSP2)

VSP2, a PC-controlled adiabatic calorimeter manufactured by Fauske and Associates, Inc. [10], was used to obtain thermokinetic and thermal hazard data, such as temperature and pressure traces versus time. The heat-wait-search (H–W–S) mode for detecting the self-heating rate was adopted for VSP2 tests. If the self-heating rate is larger than 0.1 °C min^{-1}, the H–W–S and main heater will be immediately terminated for measuring the original phenomenon of self-exothermicity. Thermal runaway reaction evaluation by VSP2 is displayed in Fig. 1. T_1 is the temperature of the test cell and T_2 is the temperature of the heater in Fig. 1. If the temperature of the sample rises, the temperature of the sample will be detected by thermocouple linking the sensor of the computer, and the T_2 will be increased until a stable situation ($\Delta T = 0$) by the control box. P_1 is the pressure of the sample and P_2 is the pressure of the holding cell. If P_1 rises by T_1, nitrogen (N$_2$) will be purged into the holding cell. At the same time, P_2 will be held at the stable condition that was described as P_1 equaling to P_2 ($\Delta P = 0$) [11].

Information available by VSP2 test includes:

- Heat of decomposition (ΔH_d),
- Total adiabatic temperature rise (ΔT_{ad}),
- Adiabatic kinetics parameters,
- Rates of temperature and pressure rise (dT dt^{-1} and dP dt^{-1}),
- Exothermic onset temperature (T_0),
- System vapor pressure versus temperature,
- Adiabatic time to maximum rate (TMR_{ad}),
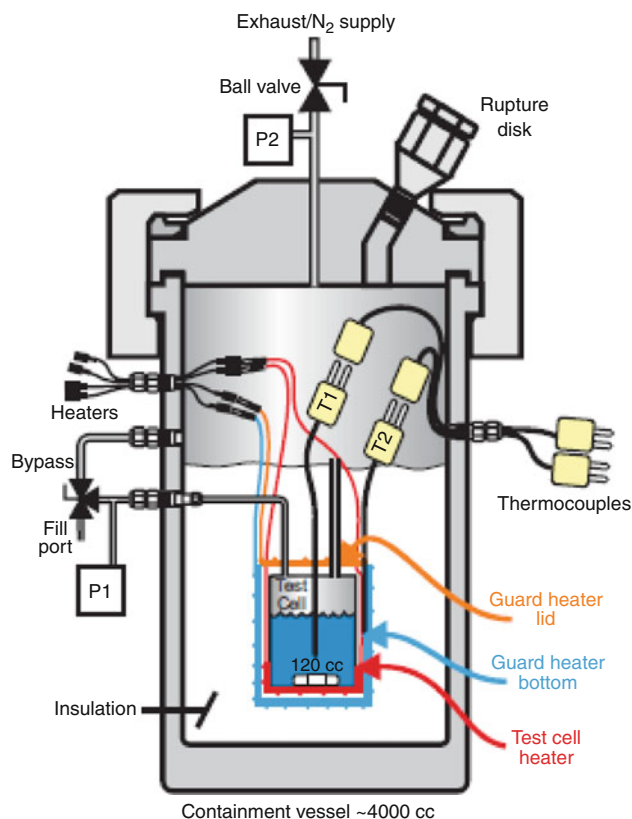- Maximum temperature and pressure,

Fig. 1 Thermal runaway evaluation equipment for VSP2 [14]

- Two-phase flow regime,
- Temperature of no return (T_{NR}),
- Resident incubation time to decomposition [11].

The E_a investigation using adiabatic calorimeter

The kinetic parameters of a single reaction can be evaluated from the equation derived by Townsend and Tou for an adiabatic process [2]:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (3)$$

$$= \ln \frac{\frac{dT}{dt}}{C_0^{n-1}\left(\frac{T_f - T}{T_f - T_0}\right)^n (T_f - T_0)} \quad (4)$$

where the rate constant is represented by the Arrhenius law:

$$k = A e^{-\frac{E_a}{RT}} \quad (5)$$

Substituting the experimental thermal data from VSP2 into Eq. 4, the figure can plot $\ln k$ versus $-1000/T$ in a very good straight line.

The n of sample can be predicted by using Eqs. 3 and 5. The dT dt^{-1} of sample can be calculated from VSP2 data, but we do not know the n of the chemical. Therefore, Eq. 6 [12] is applied to determine the value of the dT dt^{-1} using various n values. One can use the predicted data of dT dt^{-1}

to fit the experiment of $dT\,dt^{-1}$ and to identify the true n of a chemical of interest.

$$\frac{dT}{dt} = k\frac{(T_f - T_0)^n}{(C_0)^n}(T_f - T)^n \tag{6}$$

Results and discussion

Thermal hazard evaluation by DSC

Figure 2 shows the reactive behavior of 25 mass% CHP by DSC under 4 and 10 °C min^{-1} of β. The ΔH_d of 25 mass% CHP by DSC under 4 and 10 °C min^{-1} of β were determined to be 354 and 313 J g^{-1} ($n = 0.5$, $E_a = 93$ kJ mol^{-1}). Two significant peaks were found in 25 mass% CHP solutions. In fact, the cumene usually affects the thermal decomposition of CHP. Process engineers must exercise much care about thermal generation and thermal removal rate in a batch reactor. This behavior can be discovered at the first and second oxidation towers in the CHP oxidation process. An exothermic reaction of CHP was discovered exceeding 100 °C by DSC. The T_0 of 25 mass% CHP was determined to be 100 °C. SADT of CHP was noted at 80 °C [13]. Chen et al. [3] use a LTE simulation model to simulate a storage tank ($H = 1.2$ m and

$r = 0.4$ m) and 50 gallon drum of 88 mass% CHP. Emergency response time for a storage tank ($H = 1.2$ m and $r = 0.4$ m) and 50 gallon drum of 88 mass% CHP was determined to be 80 and 100 min, respectively. T_0 of 80 mass% CHP was determined to be 110 °C [3]. Roughly more than 90% of CHP produced in the world is applied in the production of phenol and acetone.
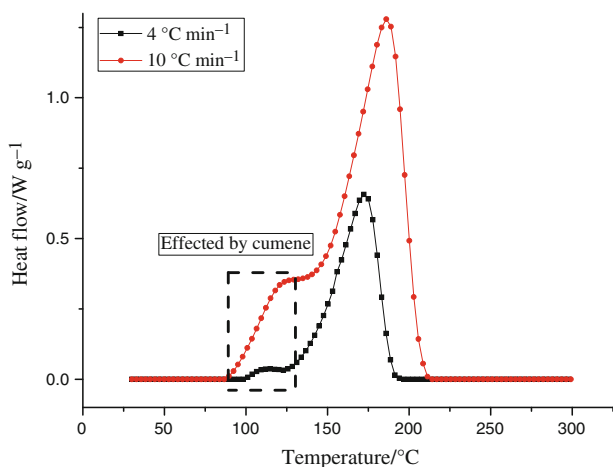

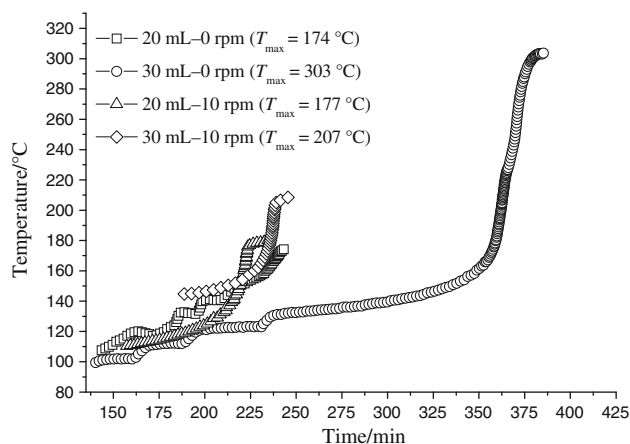**Fig. 3** Temperature vs. time for thermal decomposition of 25 mass% CHP with various volumes and stirring rates by VSP2
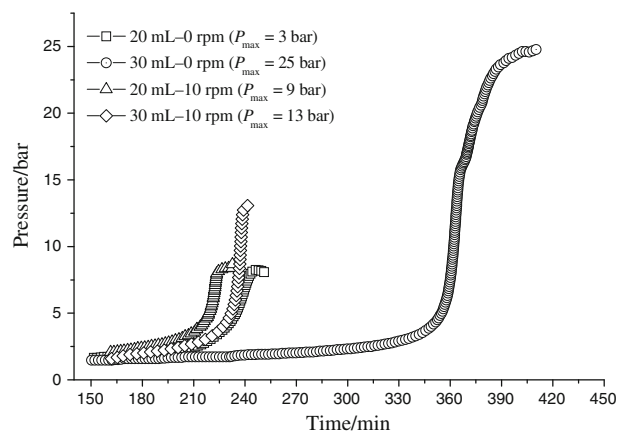

Fig. 2 Thermal hazard evaluation of 25 mass% CHP by DSC using two heating rates

Fig. 4 Pressure vs. time for thermal decomposition of 25 mass% CHP with various volumes and stirring rates by VSP2

Table 3 Thermokinetics of 25 mass% CHP using VSP2

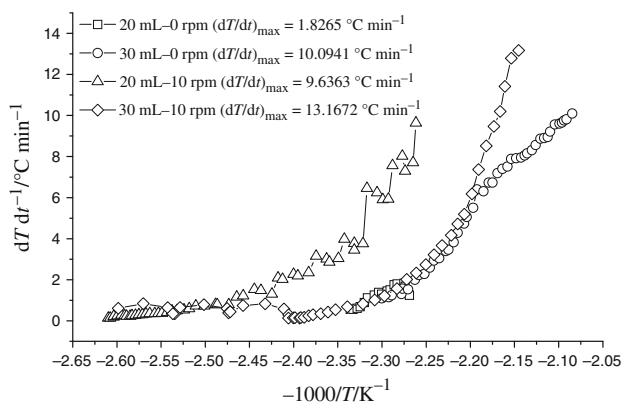|	T_0/°C	T_{max}/°C	P_{max}/bar	$(dT\,dt^{-1})_{max}$/°C min^{-1}	$(dP\,dt^{-1})_{max}$/bar min^{-1}	E_a/kJ mol^{-1}	A/s^{-1}
20 mL—0 rpm	142	174	3.0	1.8265	0.4155	122.3	1.07×10^{13}
30 mL—0 rpm	130	303	25.0	10.0941	1.8412	122.3	1.07×10^{13}
20 mL—10 rpm	110	177	9.0	9.6363	1.1345	122.3	1.07×10^{13}
30 mL—10 rpm	145	207	13.1	13.1672	2.8776	122.3	1.07×10^{13}

$y = 14.712x + 30.00$

Fig. 5 Dependence of self-heating rate $(dT \; dt^{-1})$ on temperature from VSP2 experimental data for 25 mass% CHP with various volumes and stirring rates
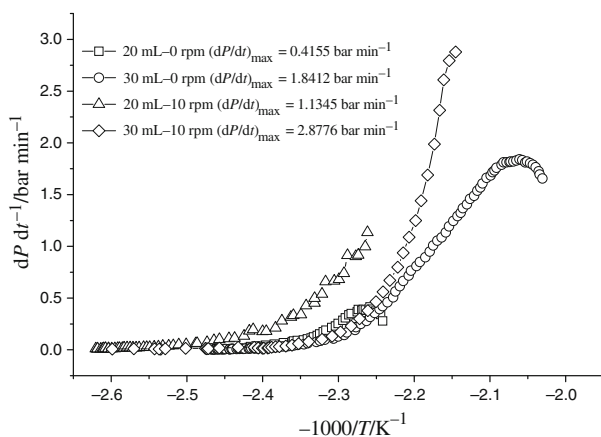

Fig. 6 Dependence of pressure rise rate $(dP \; dt^{-1})$ on temperature from VSP2 experimental data for 25 mass% CHP with various volumes and stirring rates

Stirring rate analyses and runaway reaction calculations by VSP2

A large number of chemicals can generate pressure and temperature. In this study, the T_0 of 20 and 30 mL of 25 mass% CHP by VSP2 under 0 rpm of stirring rate was calculated to be 142 and 130 °C (Table 3), respectively. According to those data, 30 mL of 25 mass% CHP can be

accumulated to exothermic initial temperature easily but it can generate high temperature. The T_{max} of 25 mass% CHP (30 mL) is higher than the 25 mass% CHP (20 mL) (in Fig. 3). The P_{max} of 25 mass% CHP (30 mL) was analyzed to be 25 bar (Fig. 4). The $(dT \; dt^{-1})_{max}$ of 25 mass% CHP (30 mL) under 0 rpm of stirring rate was calculated to be 1.84 bar min^{-1}. According to those data, from the constants of stirring rate and concentration it was discovered that the volume is an important indicator for thermal runaway reaction of CHP in the batch reactor.

The T_0 of 25 mass% CHP (20 and 30 mL) by VSP2 under 10 rpm of stirring rate was calculated to be 110 and 145 °C (Table 3), respectively. For a high volume of CHP in the batch there exists a high risk of thermal hazard because it can release a large amount of heat and pressure. According to the thermal curve by VSP2 tests, 0 rpm of stirring rate is more dangerous than 10 rpm of stirring rate because of thermal accumulation in the batch. When temperature rises to the T_0 of runaway reaction under 0 rpm stirring rate condition, the system will decompose totally. This study was used to calculate the E_a of 25 mass% CHP by VSP2 that can be determined to be 122 kJ mol^{-1}. Figure 5 displays the $dT \; dt^{-1}$ of 25 mass% CHP by VSP2. Therefore, the $dP \; dt^{-1}$ is described in Fig. 6.

To determine the n value of CHP, Eq. 6 was used to predict the n value with VSP2 data. The 0.5, 1, and 1.5 of n were applied to calculate the $dT \; dt^{-1}$ by Eq. 6. Predicting data using various n values can be applied to fit the VSP2 data. The n of CHP was calculated to be 0.5. The $dT \; dt^{-1}$ by VSP2 is fitted well with $n = 0.5$ of predicting model (Table 4). Seventy minutes of TMR of 25 mass% CHP (20 mL) was evaluated by VSP2 under 10 rpm of stirring rate. At the same situation, the TMR of 25 mass% CHP (30 mL) was calculated to 60 min. Under the same stirring rate, volume of CHP is the key condition for a runaway reaction. TMR is a useful indicator that can be used as emergency response time for operators in the chemical industries. Therefore, the TMR under 0 rpm of stirring rate using 25 mass% CHP (20 mL) by VSP2 was investigated to be 30 min. The TMR of 25 mass% CHP (30 mL) under 0 rpm of stirring rate by VSP2 was evaluated to be 140 min. Thermal accumulation effect can be analyzed

Table 4 The n order calculation of 25 mass% CHP by VSP2

	T_0/°C	T_{max}/°C	P_{max}/bar	VSP2 $(dT \; dt^{-1})_{max}$ (experiment)/°C min^{-1}	Prediction $(dT \; dt^{-1})_{max}$ $n = 0.5$/°C min^{-1}	Prediction $(dT \; dt^{-1})_{max}$ $n = 1.0$/°C min^{-1}	Prediction $(dT \; dt^{-1})_{max}$ $n = 1.5$/°C min^{-1}
20 mL—0 rpm	142	174	3.0	1.9415	1.9415	27	390
30 mL—0 rpm	130	207	25.0	10.2010	10.2010	560	31020
20 mL—10 rpm	110	177	9.0	9.6363	9.6363	337	14660
30 mL—10 rpm	145	207	13.1	13.1672	13.1672	150	17470

under 0 rpm of stirring rate by VSP2. This situation is more dangerous than 10 rpm of stirring rate.

Conclusions

A stirring rate of 0 rpm is more dangerous than 10 rpm because of thermal accumulation of CHP in the batch reactor. When temperature rises to the T_0 of runaway reaction under 0 rpm of stirring rate, the system will be decomposed totally. High volume of CHP in the reactor is high risk for the process because it can yield a large amount of heat and pressure. In CHP industries, the engineers, operators, and designers should be concerned with the effect of the stirring rate, volume of reactant, concentration of reactant, and effect of cooling system for loss prevention. The n of CHP was calculated to be 0.5 in this study. This study was employed to calculate the E_a of 25 mass% CHP by VSP2 that can be determined to be 122 kJ mol^{-1}.

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