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Thermal hazard investigation of cumene hydroperoxide in the first oxidation tower

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Abstract This article studies the thermokinetics and safety parameters of cumene hydroperoxide (CHP) manufactured in the first oxidation tower. Vent sizing package 2 (VSP2), an adiabatic calorimeter, was employed to determine reaction kinetics, the exothermic onset temperature (T_0), reaction order (n), ignition runaway temperature ($T_{C,\ I}$), etc. The n value and activation energy (E_a) of 15 mass% CHP were calculated to be 0.5 and 120.2 kJ mol^{-1}, respectively. The heat generation rate (Q_g) of 15 mass% CHP compared with hS (cooling rate) $= 6.7$ J min^{-1} K^{-1} of heat balance, the $T_{S,E}$ and the critical extinction temperature ($T_{C,\ E}$) under 110 °C of ambient temperature (T_a) were calculated 111 and 207 °C, respectively. The Q_g of 15 mass% CHP compared with $hS = 0.3$ J min^{-1} K^{-1} of heat balance was applied to determine the $T_{C,\ I}$ that was evaluated to be 116 °C. This article describes the best operating conditions when handling CHP, starting from the first oxidation tower.

Keywords Cumene hydroperoxide · Vent sizing package 2 · Reaction order · Ignition runaway temperature · Critical extinction temperature

List of symbols

A	Frequency factor, s^{-1} M^{1-n}
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}
M	Mass of reactant, g
P_{max}	Maximum pressure during overall reaction, psig
Q	Calorific capacity, J g^{-1}
$\dot{Q}$	Heat flow, W g^{-1}
R	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_{A_0}	Initial adjusted temperature, K
T_f	Final temperature, °C
T_M	Final measured temperature, K
T_{max}	Maximum temperature during overall reaction, °C
T_{M_0}	Initial measured temperature, K
T_{NR}	Temperature of no return, °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}
a	Vessel wetted surface area, m^2
k_i	Rate at stage i, s^{-1}
m	Mass of reactor, kg
n	Order of reaction, dimensionless
α	Degree of conversion, dimensionless
β	Heating rate, °C min^{-1}
λ	Heat conductivity, J ms K^{-1}
φ	Thermal inertia, dimensionless
ΔH_d	Heat of decomposition, J g^{-1}
(dT/dt)	Self-heating rate, °C min^{-1}
$(dT/dt)_A$	Actual self-heating rate, °C min^{-1}

Introduction

This article contains the thermokinetics and safety parameters of cumene hydroperoxide (CHP) manufactured

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in the first oxidation tower. Cumene is mixed with oxygen (O_2) or air to yield crude CHP in the oxidation tower [1]. Various CHP concentrations are manufactured in six oxidation towers including 15 mass% (the first oxidation tower), 20 mass% (the second one), 25 mass% (the third one), 30 mass% (the fourth one), 60 mass% (the fifth one), and 80 mass% (the sixth one) CHP [2]. In general, the CHP manufacturing process involves holding the temperature at 110 °C in the first oxidation tower that can generate 15 mass% CHP. CHP has been widely employed to yield phenol and acetone generally by sulfuric acid (H_2SO_4) catalyst. It is also an initiator for the polymerization to produce acrylonitrile–butadiene–styrene (ABS) resin [3], and is an intermediate for the production of dicumyl peroxide (DCPO) [1]. CHP has caused many serious accidents since 1981 [4–6] and a disastrous thermal explosion in the oxidation tower in 2010 in Taiwan [2].

According to accidental investigation report by government, fire was discovered in the first oxidation tower by an employee. The employee has tried to eliminate the fire but failure. Fire and thermal explosion of CHP have caused property damage without any employee injured or passed away that was displayed in Fig. 1. Accidental investigation report displayed that fire and explosion of CHP in the first oxidation tower occurred by piping breakage. A large number of 15 mass% CHP shed at the bottom of the first oxidation tower. This study was applied to analyze the cause of thermal explosion and fire of CHP. By differential scanning calorimetry (DSC), exothermic onset temperatures (T_0) of 80 mass% CHP was previously discovered to be around 110 °C [7]. Thermal runaway reaction and explosion accidents have been studied and analyzed in recent years [8]. In fact, heat generation rate (Q_g) exceeding heat removal rate (Q_r) in an reactor was named runaway reaction by Semenov theory [9]. This study aimed to analyze process safety of CHP in the first oxidation tower. To cope with the runaway, a cooling system or pressure release system must be used. Therefore, process engineers must well known the ability of cooling system and critical situation for disaster prevention and damage control. Critical temperature (T_c), T_0, Q_g, Q_r, and ambient temperature (T_a) are needed to decide if CHP should be temperature governed during processing, transportation, and storage.

Vent sizing package 2 (VSP2) is an adiabatic calorimeter that can be used to determine thermokinetics and safety parameters. This study was used to investigate thermal hazard and process safety management of CHP in the first oxidation that can be provided the employee, operator, user for safety use, transportation, etc. Cooling system efficiency, the Q_g, the Q_r, etc., are provided by Semenov theory model in this study. The heat generation rate (Q_g) of 15 mass% CHP compared with hS (cooling rate) $= 6.7$ J min^{-1} K^{-1} of heat balance, the $T_{S,E}$ and the critical extinction temperature ($T_{C,\ E}$) under 110 °C of ambient temperature (T_a) were calculated as 111 and 207 °C, respectively. The Q_g of 15 mass% CHP compared with $hS = 0.3$ J min^{-1} K^{-1} of heat balance was applied to determine the $T_{C,\ I}$ that was evaluated to be 116 °C. This article describes the best operating conditions when handling CHP, starting from the first oxidation tower.

Experimental method

Samples

Eighty mass% CHP and 99 mass% cumene were directly purchased from the Fluka Co. and both density and concentration were measured. Thermal hazard studies were made with 15 mass% CHP (with 85 mass% cumene). This study was used to determine the thermal reactive behaviors of 15 mass% CHP in the first oxidation tower.

Vent sizing package 2

VSP2 is an adiabatic calorimeter that can handle various stirring rates, volume of reactants, concentration of reactants, material of test cells, heat-wait-search (H-W-S) models, dosing rates, relief rates, etc., to determine the


(a) (b)

Fig. 1 **a**, **b** Thermal explosion of CHP in 2010 in Taiwan. **a** Damage and loss by CHP explosion and **b** fire and explosion by CHP

Table 1 Thermokinetics data of 15 mass% CHP ($C_0 = 0.81$ M) by VSP2 using various volumes

Volume/mL	T_0/°C	T_{max}/°C	P_{max}/bar	$(dT/dt)_{max}$/°C min^{-1}	$(dP/dt)_{max}$/bar min^{-1}	E_a/kJ mol^{-1}	A/s^{-1}
20 (10 rpm)	153	167	4.9	1.521	0.0337	120.2	3.4×10^{12}
30 (10 rpm)	151	172	7.5	1.687	0.1687	120.2	3.4×10^{12}
20 (0 rpm)	150	170	6.0	0.588	0.1098	120.2	3.4×10^{12}
30 (0 rpm)	145	173	6.9	0.667	0.1254	120.2	3.4×10^{12}
						$y = 14.459x + 28.875$	

effect of thermal runaway and explosion. The VSP2, a PC-controlled adiabatic calorimeter manufactured by Fauske & Associates, Inc. [10], was used to acquire thermokinetics and thermal hazard data, such as temperature and pressure traces versus time. Reaction rate (k) was evaluated by the Arrhenius law that can be described as Eq. 1:

$$k = Ae^{-\frac{E_a}{RT}} \tag{1}$$

The kinetic parameters of the nth order reaction can be evaluated from the equation derived by Townsend and Tou for an adiabatic process [10]:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{2}$$

$$\ln k = \ln \frac{\frac{dT}{dt}}{C_0^{n-1}\left(\frac{T_f - T}{T_f - T_0}\right)^n (T_f - T_0)} \tag{3}$$

Substituting the experimental thermal data from VSP2 into Eq. 3 and assuming that $n = 0.5$, we can plot ln k versus $-1000/T$ and obtain a very good straight line.

The n value of sample can be predicted using Eq. 4. The dT/dt of sample can be calculated from VSP2 data, but we do not know the n value of specific chemical. Therefore, Eq. 4 [11] is applied to determine the value of the dT/dt using various n values. We can use the predicted data of dT/dt to fit the experiment of dT/dt and to identify the true n value of a chemical.

$$\frac{dT}{dt} = k\frac{(T_f - T_0)^n}{(C_0)^n}(T_f - T)^n \tag{4}$$

In a reactor with an exothermic reaction, it is very easy to accumulate energy and temperature when the Q_g exceeds the Q_r by Semenov theory. Equations 5–10 are defined to assess the critical situation in Semenov model.

$$Q_g = qVr_b \tag{5}$$

where Q_g was employed to depict thermal development in a reactor of interest.

$$Q_r = hS(T - T_a) \tag{6}$$

where Q_r is called the Newton Cooling Law.

$$r_b = kC_0^n \tag{7}$$

where r_b is the reaction rate

$$r_b = kC_0^n = Ae^{-E_a/RT}C_0^n \tag{8}$$

Equation 5 was compared with Eq. 8 to evaluate the Q_g that was shown in Eq. 9.

$$Q_g = qVAe^{-E_a/RT}C_0^n \tag{9}$$

$$Q_{acc} = Q_g - Q_r = qVAe^{-E_a/RT}C_0^n - hS(T - T_a) \tag{10}$$

where Q_{acc} is heat of accumulation used to investigate the critical development in three cooling system circumstances. This study was applied to calculate the Q_g using

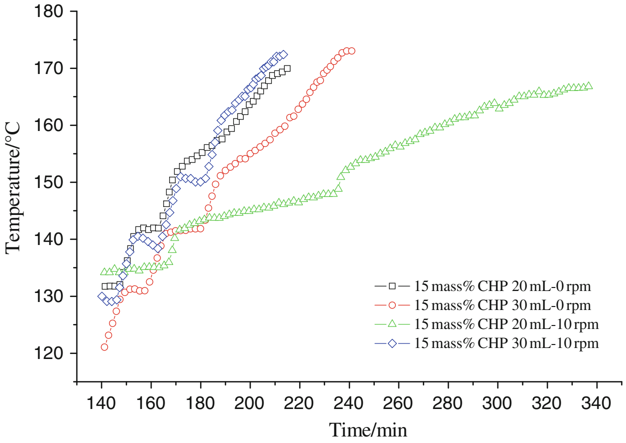

Fig. 2 Temperature vs. time for thermal decomposition of 15 mass% CHP with various volumes and stirring rates by VSP2

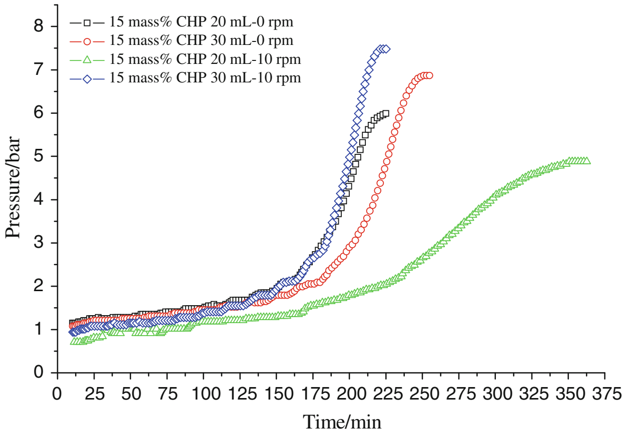

Fig. 3 Pressure vs. time for thermal decomposition of 15 mass% CHP with various volumes and stirring rates by VSP2

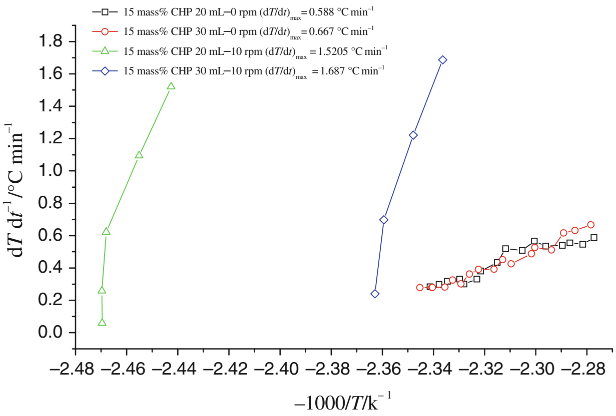

Fig. 4 Dependence of self-heating rate (dT/dt) on temperature from VSP2 experimental data for 15 mass% CHP with various volumes and stirring rates

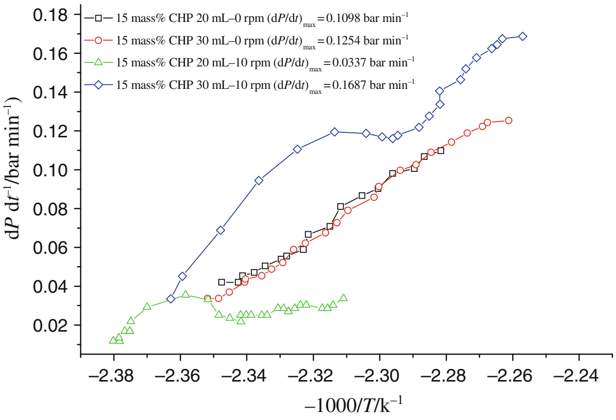

Fig. 5 Dependence of pressure rise rate (dP/dt) on temperature from VSP2 experimental data for 15 mass% CHP with various volumes and stirring rates

Eq. 11 method and thermokinetics of CHP by VSP2. Therefore, the Q_g can be described as follows [3]:

$$Q_g = qVAe^{-E_a/RT}\left(C_0\left(\frac{T_f - T}{\Delta T_{max}}\right)\right)^n \qquad (11)$$

Comparing with Eqs. 6 and 11, we can predict the hS (cooling rate) and ambient temperature (T_a) of industrial applications.

Results and discussion

Thermokinetics determination by VSP2

The T_0 of 20 and 30 mL of 15 mass% CHP by VSP2 under 0 rpm of stirring rate were calculated to be 150 and 145 °C (Table 1). The corresponding T_{max} of 15 mass% CHP (30 mL) is higher than the 15 mass% CHP (20 mL) (Fig. 2). Similarly, the P_{max} of 15 mass% CHP (30 mL) was determined to be 6.87 bar (Fig. 3). Table 1, Figs. 4 and 5 shows the dT/dt and the dP/dt of 15 mass% CHP by VSP2. According to those data, from the constants of stirring rate and concentration, it discovered that the volume is more important for thermal runaway reaction of CHP in the oxidation tower or batch reactor.

The T_0 of 20, 30, and 40 mL (reactant volume) of 15 mass% CHP by VSP2 under 10 rpm of stirring rate were calculated to be 152, 150, and 82 °C. The T_{max} of 15 mass% CHP (40 mL) under 10 rpm of stirring rate was higher than the 15 mass% CHP (20 and 30 mL). The P_{max} of 15 mass% CHP under 10 rpm of stirring rate (40 mL) was determined to be 18.52 bar. The activation energy (E_a) was calculated to be 120.2 kJ mol^{-1}. Equation 4 was applied to simulate the reaction order (n) of 15 mass% CHP. This study was applied to predict the n value using 0.5, 1, and 1.5. Results showed that the n was analyzed to be 0.5 that was assessed in Table 2. Therefore, the n of CHP was calculated to be 0.5 by Huang et al. [6] and Chen et al. [12].

Cooling system efficiency analyses

In practice, cumene mixed with air or pure O_2 was applied to yield CHP under 110 °C in traditional process. Heat balance between the Q_g and Q_r of 15 mass% CHP was determined using Eqs. 6 and 11 that were shown in Figs. 6 and 7, respectively. The reaction rates are affected by the 15 mass% CHP. According to Q_g of 15 mass% CHP compared with $hS = 6.7$ J min^{-1} K^{-1} of heat balance, the $T_{S,\ E}$ and the critical extinction temperature ($T_{C,\ E}$) under 110 °C (383 K) (reaction temperature of first oxidation

Table 2 The n order calculation and thermokinetics of 15 mass% CHP ($C_0 = 0.81$ M)

Volume/mL	Stirring rate/rpm	T_0/°C	T_{max}/°C	(dP/dt)$_{max}$/ bar min^{-1}	(dT/dt)$_{max}$/ °C min^{-1}	(dT/dt)$^a_{max}$ $n = 0.5$/°C min^{-1}	(dT/dt)$^a_{max}$ $n = 1.0$/°C min^{-1}	(dT/dt)$^a_{max}$ $n = 1.5$/°C min^{-1}
20	10	153	163	0.0034	0.2630	0.2630	3	40
30	10	150	156	0.1687	1.6870	1.6870	13	100
20	0	153	204	0.1098	0.5880	0.5880	37	5,373
30	0	153	165	0.1254	0.6670	0.6670	10	140

[a] The (dT/dt)$_{max}$ prediction with various n values

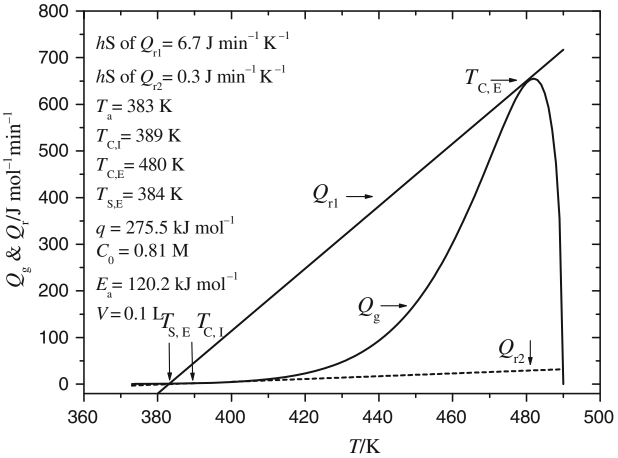

Fig. 6 The Q_g and Q_r calculations under 383 K of environmental temperature for 15 mass% CHP reaction at $C_0 = 0.81$ M

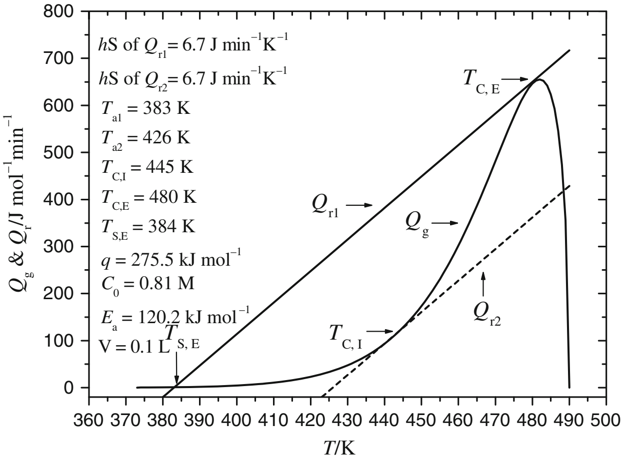

Fig. 7 The Q_g and Q_r calculations under 6.7 J min^{-1} K^{-1} of hS for 15 mass% CHP reaction at $C_0 = 0.81$ M

tower) of T_a were calculated as 111 °C (384 K) and 207 °C (480 K), respectively.

Therefore, Q_g of 15 mass% CHP compared with $hS = 0.3$ J min^{-1} K^{-1} of heat balance was applied to determine the ignition runaway temperature ($T_{C,\ I}$) that was evaluated to be 116 °C (389 K). In Fig. 7, the $T_{C,\ I}$ of $hS = 6.7$ J min^{-1} K^{-1} compared with Q_g was calculated to be 172 °C (445 K). Equation 6 was applied to evaluate the values of hS which are the overall heat transfer coefficients multiplied by the external surface of the reactor. This study was used to predict the hS using Eqs. 6 and 11 under 110 °C (383 K) of T_a. Differential T_a can be simulated at various the hS and $T_{C,\ I}$ in the batch reactor or oxidation tower. In that case, two values of hS were calculated at the same T_a. If the heat removed from 110 °C (383 K) of T_a in the reactor, the hS was determined to be 0.3 J min^{-1} K^{-1} and the $T_{C,\ I}$ was calculated to be 116 °C (389 K) for thermal runaway reaction.

Conclusions

The T_0 of CHP was determined to be about 110 °C. According to those data, from the constants of stirring rate and concentration, it was discovered that the volume is more important for thermal runaway reaction of CHP in the oxidation tower or batch reactor.

The n of CHP was identified to be 0.5 using the VSP2 approach in this study. According to thermal curve, stirring rate, the volume of chemical, and the concentration of material in the oxidation tower were identified as more important parameters. Process engineers must take care of those indicators for thermal runaway reaction of CHP. The reaction rates are affected by the 15 mass% CHP. The T_a are set at 110 °C (383 K) (cooling temperature of first oxidation tower) in these two plots of heat balance. The $T_{C,\ E}$ and $T_{C,\ I}$ were calculated to be 207 °C (480 K) and 116 °C (389 K), respectively. The $T_{S,\ E}$ between the curves Q_g and Q_r was determined to be 111 °C (384 K).

Differential T_a can be simulated by various hS and $T_{C,\ I}$ in the batch reactor or oxidation tower. In that case, two values of hS were calculated at the same T_a. If the heat removed from 110 °C (383 K) of T_a in the first oxidation tower, the hS was determined to be 0.3 J min^{-1} K^{-1} and the $T_{C,\ I}$ was calculated to be 116 °C (389 K) for thermal runaway reaction.

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