Investigation of the decomposition reaction and dust explosion characteristics of crystalline benzoyl peroxides

Kai-Tai Lu [a,*], Ting-Chi Chen [a], Kwan-Hua Hu [b]

[a] *Department of Applied Chemistry & Materials Science, Chung Cheng Institute of Technology, National Defense University, Taoyuan 33509, Taiwan, ROC*
[b] *Department of Occupational Safety and Health, Jen-Teh Junior College of Medicine, Nursing and Management, Miaoli, Taiwan, ROC*

ARTICLE INFO

ABSTRACT

The benzoyl peroxide (BPO) is widely used in the chemical industry. Many catastrophes have been caused by its thermal instability or reactive incompatibility in storage or thermal decomposition reaction. Thus, its hazard characteristics have to be clearly identified. First of all, the differential scanning calorimeter (DSC) is used to measure the heat of decomposition reaction, which can contribute to understanding the reaction characteristics of benzoyl peroxide. The accelerating rate calorimeter (ARC) is used to measure the rates of temperature and pressure rises of decomposition reaction, and then the kinetics parameters are estimated. Furthermore, the MIKE 3 apparatus and the 20-l-Apparatus are used to measure and analyze the dust explosion characteristics of benzoyl peroxide under room temperature and atmospheric pressure. Finally, Semenov's thermal explosion theory is applied to investigate the critical runaway condition and the stability criterion of decomposition reaction, and to build the relationship of critical temperature, convective heat transfer coefficient, heat transfer surface area and ambient temperature. These results contribute to improving the safety in the reaction, transportation and storage processes of benzoyl peroxide.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

In the catastrophes of chemical industry, so many thermal runaway incidents were caused by the organic peroxides owing to their thermal instability. The organic peroxides have an organic (or carbon-containing) molecule attached to at least one side of the oxygen-to-oxygen bond (—O—O—). Their thermal instability is caused by the weak oxygen-to-oxygen bond, which leads to a tendency towards more stable substances. Although their potential energy is low compared to that of conventional explosives, these compounds can be very destructive when stored energy is released. The exothermic threshold temperatures of many organic peroxides are below 120 °C and sometimes even as low as ambient temperature. The National Fire Protection Association (NFPA) divides organic peroxides and their solutions into hazard classes based on reactivity and destructive effects [1]. The United Nations also suggests that the suppliers have to take a precise measurement of the self-accelerating decomposition temperature, T_{SADT}, in dangerous goods before transportation [2].

The benzoyl peroxide (BPO) is a nontoxic, colorless, odourless and tasteless substance, which is widely used in chemical industry. Dry benzoyl peroxide is a crystalline solid and usually contains less than 5% water. Wet benzoyl peroxide is also a crystalline solid; common formulations contain between 50–85% benzoyl peroxide and 15–50% water. Their thermal instability or reactive incompatibility has caused so many incidents in the past [3,4]. The hazard classifications of 98, 75 and 50% crystalline benzoyl peroxides are recognized to be classes I, III and IV organic peroxides, respectively by the NFPA [1]. Unfortunately, their hazardous characteristics are still unknown so far.

Two kinds of experiment methods can be used for measuring the thermal data. One is isothermal reaction temperature by varying removed heat [5]. The other method is where the reaction temperature and heat change throughout the reaction time [6,7]. Both of these methods can be used to evaluate the reaction kinetic parameters. The adiabatic condition is that the heat released due to exothermal reaction raises the temperature of products and container to the final temperature. An isothermal reactor maintains its reaction temperature at a constant value. Adiabatic experiments can fail to detect concentration effects such as autocatalysis, which become important when the reaction is performed under industrial conditions. In these results, thermokinetic parameters are same in adiabatic reaction for both heat capacity constant and heat capac-

* Corresponding author. Tel.: +886 3 3891716; fax: +886 3 3892494.
E-mail address: ktlu@ndu.edu.tw (K.-T. Lu).

Nomenclature

A	pre-exponential factor of Arrhenius equation (min^{-1})
C	concentration (g/cm^3)
C_P	heat capacity (J/g K)
C_0	initial concentration (g/cm^3)
E	activation energy (kJ/mol)
h	overall heat transfer coefficient of ambient medium $(\text{kJ/min m}^2\,\text{K})$
$hS_{(tr)}$	value of hS at transition point (kJ/min K)
ΔH	the measured heat of reaction (J/g)
ΔH_t	the transient released heat of reaction at reaction time t (kJ)
ΔH_{total}	the overall released heat (kJ)
k	reaction rate constant $(\text{M}^{1-n}\,\text{min}^{-1})$
K_{St}	Explosion index (bar m/s)
M_b	mass of the container (g)
M_S	mass of the sample (g)
n	reaction order
P_{max}	maximum pressure of reaction (bar)
q	exothermic heat of reaction (J/g)
Q_g	heat generation rate (kJ/min)
Q_r	heat removal rate by cooling medium (kJ/min)
$-r_b$	chemical reaction rate (mol/l min)
R	universal constant (J/g mol K)
S	external surface area of vessel (m^2)
t	reaction time (min)
T	temperature of reactant (K)
T_a	ambient temperature at cooling medium (K)
$T_{a,tr}$	ambient temperatures at the transition point (K)
T_c	critical ignition or extinction temperature (K)
$T_{C,E}$	critical extinction temperature (K)
$T_{C,I}$	critical ignition temperature (K)
$T_{c,tr}$	transition point of critical ignition and extinction temperatures (K)
T_{max}	final temperature of reaction (K)
ΔT_{max}	the temperature difference between T_0 and T_{max} (K)
T_M	intermediate temperature of intersection point of curves Q_g and Q_r (K)
T_S	temperature at the steady state is the intersection point of curves Q_g and Q_r (K)
$T_{S,E}$	final stable point of extinction temperature (K)
$T_{S,H}$	high stable temperature at steady state (K)
$T_{S,I}$	final stable point of ignition temperature (K)
$T_{S,L}$	low stable temperature at steady state (K)
T_0	initial temperature of reaction (K)
V	volume of reactant (l)
V_c	volume of explosion vessel (m^3)
X_A	fractional conversion

Greek letters

Φ	Phi factor
ρ	density of reactant (g/cm^3)

ity variable, respectively. The evaluated reaction heats have minor differences owing to different values of heat capacity.

Dust explosion characteristics include the minimum ignition energy (MIE), minimum ignition temperature (MIT), the minimum explosion concentration (MEC), the maximum explosion pressure (P_{max}) and the maximum rate of explosion pressure rise ((dP/dt)$_{max}$). The first three items relate to the sensitivity of the combustible dust, and the last two items represent the energy con-

tent and the reactivity of the combustible dust, respectively. In order to classify the relative reactivity of various combustible dusts, and thereby being able to predict the violence of accidental dust explosion in industrial plants, Bartknecht [8] presented a concept of explosion index (K_{St}) and built a cubic law. At present, the K_{St} value is widely used to evaluate the dust explosion class for various combustible dusts.

The batch reaction is a dynamic system whose trajectory depends on various parameters. Parametric sensitivity signifies large change in the reaction trajectory is induced by small changes in parameters across threshold values. This is a form of critical behavior and can lead to runaway conditions. Most of the investigations on parametric sensitivity are based on theoretical analysis or numerical simulation. Semenov's thermal explosion theory was concerned with evaluating the above-mentioned critical temperature [9,10]. Semenov developed a model for thermal explosions, which demonstrated the principles of the thermal ignition phenomenon in a quantitative way. The temperature of the reacting system was assumed to be constant and uniform across the whole volume of the system. Morbidelli and Varma had applied thermal explosion theory to determine a generalized criterion for parametric sensitivity [11]. They determined the variation in the maximum temperature of the non-adiabatic reaction system with respect to different parameters. Eigenberger and Schuler had discussed the concepts of stability and safety in the batch and continuous systems [12]. Villermaux and Geogakis had discussed runaway criteria in terms of time constants for reactions and cooling [13]. However, the various criteria existing in the literatures have been seldom verified.

In this study, the heat of decomposition reaction of crystalline benzoyl peroxide was measured by differential scanning calorimeter (DSC), and the values of the kinetic parameters of a lumped expression were estimated from the measured data using the accelerating rate calorimeter (ARC) apparatus with adiabatic condition. Furthermore, the MIKE 3 apparatus and the 20-l-Apparatus were used to measure and analyze the dust explosion characteristics of benzoyl peroxide under room temperature (around $25\,^\circ$C) and atmospheric pressure. Finally, the calculated kinetic parameters and measured exothermic reaction heat were incorporated into the sufficient and necessary conditions of thermal explosion to determine the critical runaway reaction temperature and stability criterion in the decomposition reaction of benzoyl peroxide. These stability criteria and critical temperatures in the decomposition reaction of benzoyl peroxide can be expressed as a function of kinetic parameters and chemical properties.
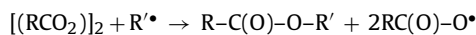
2. The decomposition reaction mechanism of benzoyl peroxide

The thermal decomposition of organic peroxides is comprised of two main elements [14]:
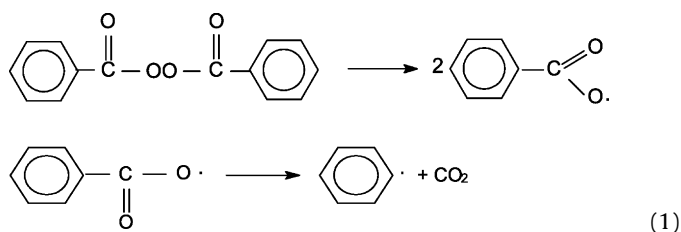
(1) Homolysis of the O—O bond

$$[(RCO_2)]_2 \rightarrow 2RC(O)\text{—}O^\bullet$$
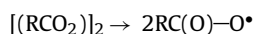
(2) Radical-induced decomposition

$$[(RCO_2)]_2 + R'^\bullet \rightarrow R\text{–}C(O)\text{–}O\text{–}R' + 2RC(O)\text{–}O^\bullet$$

It is not easy to determine how much each of the modes contributes to the overall process of thermal decomposition of any peroxide. Generally speaking, the decomposition reaction

mechanism of benzoyl peroxide can be expressed as below.

$$C_6H_5-\overset{O}{C}-OO-\overset{O}{C}-C_6H_5 \longrightarrow 2\ C_6H_5-C\overset{O}{\underset{O\cdot}{}}$$

$$C_6H_5-\overset{O}{\underset{O}{C}}-O\cdot \longrightarrow C_6H_5\cdot + CO_2 \tag{1}$$

The final products of decomposition of benzoyl peroxide are carbon dioxide and biphenyl, and also smaller amount of phenyl benzoate and benzene are produced.

3. Experimental

3.1. Materials

The experimental chemicals included three kinds of crystalline benzoyl peroxides with weight percentages of 98, 75 and 50%, which were obtained from a commercial supplier. Their densities were 1.32, 1.23 and 1.17 g/cm^3, respectively.

3.2. DSC and ARC measurements

A Mettler-Toledo DSC822 differential scanning calorimeter (DSC) was used to record the non-isothermal exothermic decomposition reaction for the crystalline benzoyl peroxides with various weight percentages. Calibration for the temperature scale was carried out with a pure indium standard on every other run to ensure accuracy and reliability of the data obtained. About 5–10 mg of the test sample was weighted and placed in a sealed stainless steel capsule. Then, the capsule was transferred to the DSC sample holder assembly, which had been set at 25 °C. The sample was heated at a heating rate of 4 °C/min up to 180 °C. This sealed stainless steel capsules can withstand pressure of 100 bar. The characteristic reaction temperature corresponding to the exothermic reaction heat was measured and recorded.

ARC is a bench-scale apparatus, which is designed to operate under almost true adiabatic condition. ARC can be used to characterize a runaway chemical reaction in a closed cell. In this work, 5 g sample was charged into a spherical sample bomb. Then, the sample bomb was positioned inside the calorimeter. ARC operated in the heat-wait-search mode, after heating the sample, the instrument waited for a certain amount of time to allow the system to build thermal equilibrium and started to search for exothermic process. If no exothermic process was detected, the instrument continued heating-searching operation. If an exothermic process was detected, then the instrument started to track this exothermic process. The experimental data of ARC included the transient

temperature profile, the transient pressure profile, the transient temperature variation profile, and the transient pressure variation profile, etc.

3.3. MIKE 3 and 20-l-Apparatus measurements

MIKE 3 is a special equipment for the determination of the MIE of dust [15]. MIE is defined as the lowest energy value of a high-voltage capacitor discharge required to ignite the most ignitable dust. The MIKE 3 has a modified Hartmann tube made of glass with a volume of 1.2 l as the explosion vessel. The dust dispersion system is located at the base of the tube. A blast of compressed air at 7 bar is used to disperse the dust in the glass cylinder where it is ignited by a spark between two electrodes. The MIKE 3 works in an energy region from 1 to 1000 mJ. In this work, the MIE of three crystalline benzoyl peroxides with weight percentage of 98, 75 and 50% was measured. All experiments were carried out under room temperature (around 25 °C) and atmospheric pressure. The relative humidity was to be maintained between 50 and 60%. The inductance and ignition delay time were fixed at 1 mH and 120 ms, respectively. The experimental conditions for the MIE testing are shown in Table 1.

20-l-Apparatus is a standard laboratory equipment, which is designed to measure the maximum explosion pressure and the maximum rate of explosion pressure rise for explosion of combustible gas, steam or dust [16]. The test chamber is a hollow sphere made of stainless steel, with a volume of 20 l. It can withstand a maximum pressure of 40 bar. A water jacket serves to dissipate the heat of explosions or to maintain thermostatically controlled test temperatures. The sample dust is dispersed into the sphere from a pressurized storage chamber. The ignition source is located in the center of the sphere. Pressure is recorded during the test with two independent piezo-electrical pressure transducers. In this work, the ignition delay time and ignition energy were fixed at 60 ms and 10 kJ, respectively. The ignition source was two chemical igniters ($2\times$ 5 kJ). This ignition energy is chosen to determine the explosion indices for industrial practice. All experiments were carried out under room temperature (around 25 °C) and atmospheric pressure. The relative humidity was to be maintained between 50 and 60%. The experimental conditions for the maximum explosion pressure and explosion index testing are shown in Table 2.

4. Analysis of decomposition reaction characteristics

4.1. Heat of reaction

The DSC thermograms of decomposition reaction of three crystalline benzoyl peroxides with weight percentage of 98, 75 and 50% are shown in Fig. 1. These thermograms reveal an endothermic peak around 103 °C due to the vaporization of water and an exothermic peak around 110 °C due to the decomposition of benzoyl peroxide.

Table 1
Experimental conditions for MIE testing

Dust	Particle size (μm)	Dust concentration (g/m^3)	Ignition energy (mJ)
98% crystalline BPO	210–250	300, 600, 900, 1200, 1500, 1800	1, 3, 10
75% crystalline BPO	210–250	300, 600, 900, 1200, 1500, 1800, 2100	1, 3, 10, 30
50% crystalline BPO	210–250	900, 1200, 1500, 1800, 2100, 2400	10, 30, 100, 300

Table 2
Experimental conditions for explosion index and maximum explosion pressure testing

Dust	Particle size (μm)	Dust concentration (g/m^3)	Ignition energy (kJ)
98% crystalline BPO	210–250	600, 900, 1200, 1500	2×5
75% crystalline BPO	210–250	600, 900, 1200, 1500, 1800	2×5
50% crystalline BPO	210–250	1200, 1500, 1800, 2100, 2400	2×5

Fig. 1. DSC thermogram of the decomposition reaction of crystalline BPO at various weight percentages.
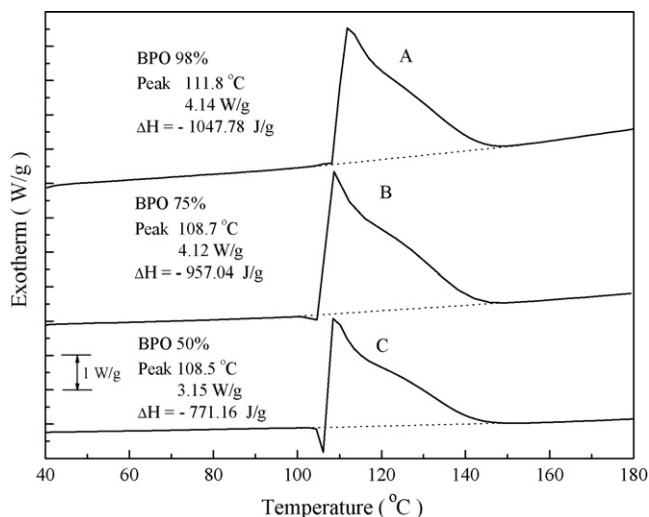

Fig. 3. Measured transient pressure of the decomposition reaction of crystalline BPO with various weight percentages by means of ARC.

The total released heats of these three crystalline benzoyl peroxides are equal to 1047.78, 957.04 and 771.16 J/g, respectively. The experimental results reveal that the total released heat and the exothermic peak temperature are raised with the increasing weight percentage of benzoyl peroxide. The increase of total released heat causes the raise of exothermic peak temperature in the reaction system.

Kao and Hu [17] had also used DSC to measure the heat of decomposition reaction of 98% crystalline benzoyl peroxide. They reported the enthalpy change associated with the decomposition process as −1081 J/g. Sun et al. [18] had studied the heat of decomposition reaction of 75% crystalline benzoyl peroxide using C80 apparatus. The measured heat of decomposition reaction was −1010 J/g. The heats of decomposition reaction of these two crystalline benzoyl peroxides obtained from this study are close to those obtained in the literatures.

4.2. Reaction characteristic of adiabatic condition

ARC is a reaction calorimeter system, which is capable of determining rates of temperature and pressure rise for very fast exothermic reaction system in adiabatic condition. Figs. 2 and 3
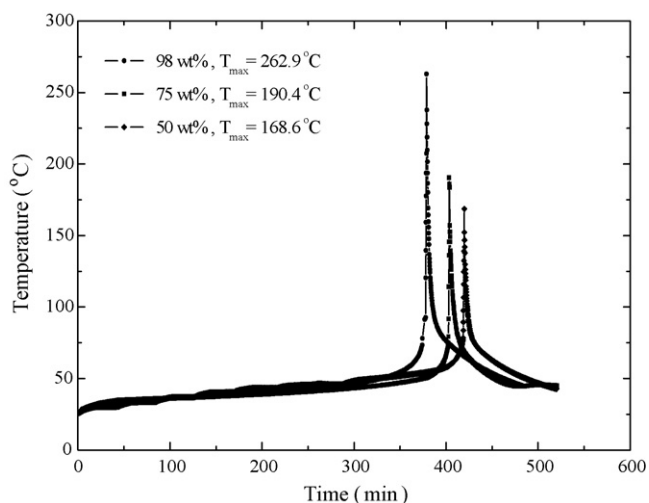

Fig. 2. Measured transient temperature of the decomposition reaction of crystalline BPO with various weight percentages by means of ARC.
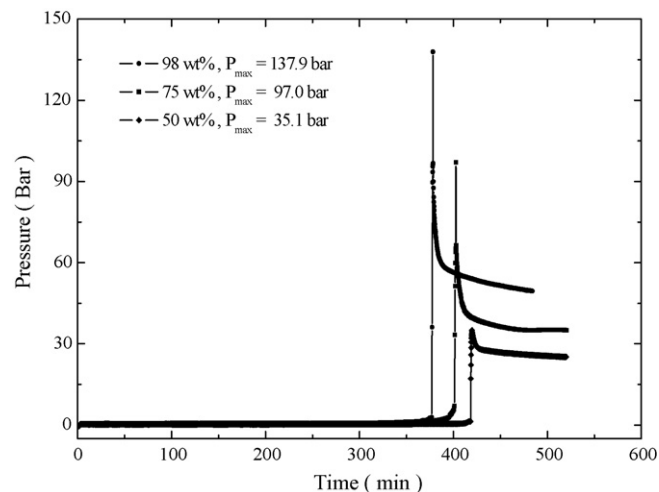
show the transient temperature and pressure profiles for the decomposition reactions of three crystalline benzoyl peroxides with weight percentage of 98, 75 and 50%, respectively. The maximal temperatures T_{max} and pressures P_{max} corresponding to these three weight percentages are equal to 262.9, 190.4, 168.6 °C and 137.9, 97.0, 35.1 bar, respectively. The values of T_{max} are higher than the boiling point temperature of water. The temperature of reaction cannot be tempered by vapor stripping. Therefore, the released heat is largely retained in the reaction system that leads to abrupt temperature rising. Furthermore, the pressure of reaction system contributed from the non-condensable gas and vapor pressure. Therefore, the decomposition reaction of crystalline benzoyl peroxide is a non-tempered hybrid system.

4.3. Evaluation of kinetic parameters

A number of important assumptions are made in order to derive the kinetic parameters of an exothermic reaction from experimental data on the rate of self-heating under adiabatic condition:

(1) The reaction mechanism is assumed to be independent of temperature so that the temperature and concentration dependencies can be treated separately.
(2) The total heat generated is evaluated directly from the adiabatic temperature rise assuming constant heat capacity.
(3) The heat generated is assumed to correspond to changes in concentration such that the rate of change of concentration and the rate of heat generation are directly proportional to the rate of temperature rise under adiabatic condition, with the extent of reaction equal to the temperature increase expressed as a fraction of the total adiabatic temperature rise.
(4) The temperature dependence of the reaction rate constant is assumed to follow the Arrhenius equation.
(5) The dependence of reaction rate on concentration is represented by a single order of reaction with fractional values used so that complex mechanisms can be represented by simple overall kinetic expressions.

In an adiabatic reaction system, the fractional conversion X_A and reaction temperature T at any reaction time t can be correlated with assumption of constant specific heat capacity by the ratio value of ΔH_t to ΔH_{total} at any reaction time t till the end of reaction time t_f

as

$$X_A = \frac{\Delta H_t}{\Delta H_{total}} = \frac{mC_p(T - T_0)}{mC_p(T_{max} - T_0)} = \frac{T - T_0}{T_{max} - T_0} \quad (2)$$

where T_0 and T_{max} are the initial and final temperatures for the overall decomposition reaction of benzoyl peroxide, respectively. ΔH_t and ΔH_{total} are the exothermic reaction heat at temperature T and T_f, respectively. Therefore, reaction concentration can be correlated as

$$C = C_0(1 - X_A) = \frac{C_0(T_{max} - T)}{T_{max} - T_0} = \frac{C_0(T_{max} - T)}{\Delta T_{max}} \quad (3)$$

with C_0 being the initial concentration, C is the concentration at any time t and ΔT_{max} equals to $T_{max} - T_0$. An nth-order rate equation of decomposition reaction for benzoyl peroxide can be expressed as

$$-r_b = -\frac{dC}{dt} = kC^n \quad (4)$$

Substituting Eq. (3) into Eq. (4) and combining with the Arrhenius equation yields

$$k^* = C_0^{n-1}A\exp\left(\frac{-E}{RT}\right) = \frac{dT/dt}{[(T_{max} - T)/\Delta T_{max}]^n \Delta T_{max}} \quad (5)$$

Taking the natural logarithms on both sides of Eq. (5) can obtain

$$\ln k^* = \ln\left\{\frac{dT/dt}{[(T_{max} - T)/\Delta T_{max}]^n \Delta T_{max}}\right\} = \ln(C_0^{n-1}A) - \frac{E}{RT} \quad (6)$$

where dT/dt is the rate of temperature increase between the initial temperature T_0 and the maximum temperature T_{max} in an adiabatic reaction system. The Arrhenius kinetic parameters for the global reaction therefore can be determined from Eq. (6).

The evolved heat during the ARC experiment is absorbed by the sample and sample container. This will attenuate the adiabatic temperature rise and the rate of temperature increase and must be taken into account during data analysis. The Φ (Phi) factor or thermal inertia is defined as $\Phi = 1 + (M_b C_{p,b}/M_s C_{p,s})$ [19], where M_b represents the mass of the container, M_S represents the mass of the sample and C_p represents the heat capacity. The Phi factor is used to adjust the self-heating rate as well as the observed adiabatic temperature rise. Furthermore, the initial data obtained from heat-wait-search processes are unimportant which are excluded in the derivation of the kinetic parameters. The data around runaway condition are also excluded because the reaction system is unstable.

Substituting the modified experimental data from ARC into Eq. (6) and assuming $n = 1$, we can plot $\ln k^*$ vs. $-1000/T$ and obtain a fairly good linear correlation as shown in Figs. 4–6. Therefore, the assumption of $n = 1$ for reaction order is reasonable. The activation energy E and pre-exponential factor A can be obtained from the slope and intersection point at the vertical axis. The measured and evaluated kinetic parameters of decomposition reaction of benzoyl peroxide are listed in Table 3.

Table 3
The kinetic parameters for the decomposition reactions of crystalline BPOs

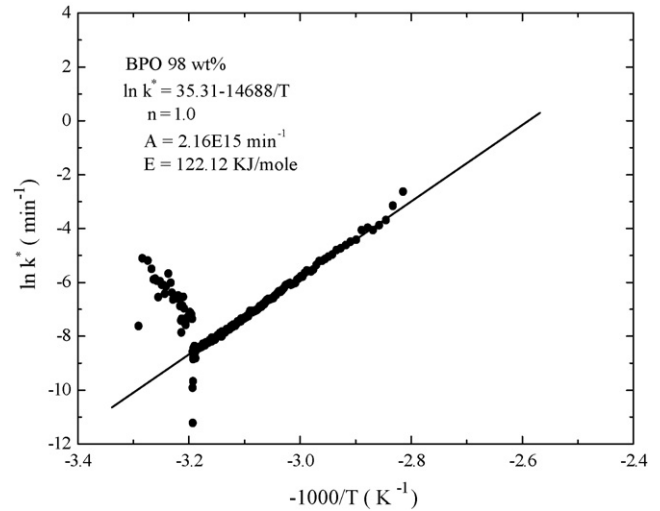| Parameters	BPO (wt.%)		
	98%	75%	50%
C_0 (g/cm^3)	1.32	1.25	1.17
T_0 (K)	343.75	346.55	351.55
T_{max} (K)	536.05	463.55	441.75
ΔT_{max} (K)	192.3	117.0	90.2
$(dT/dt)_{max}$ (K/min)	178.75	120.34	87.08
q (J/g)	1048.78	957.04	771.16
n	1	1	1
A (min^{-1})	2.16×10^{15}	8.26×10^{16}	1.90×10^{18}
E (kJ/mol)	122.12	131.22	144.29

Fig. 4. The correlation of overall rate constant k^* and temperature T for the decomposition reaction of 98% crystalline BPO.
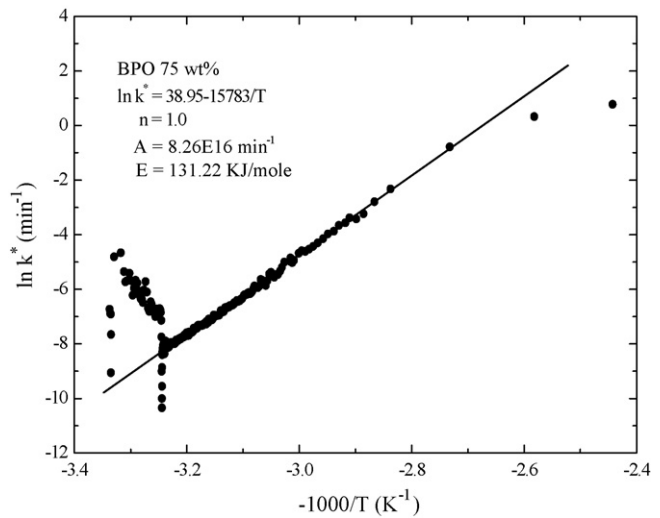

Fig. 5. The correlation of overall rate constant k^* and temperature T for the decomposition reaction of 75% crystalline BPO.
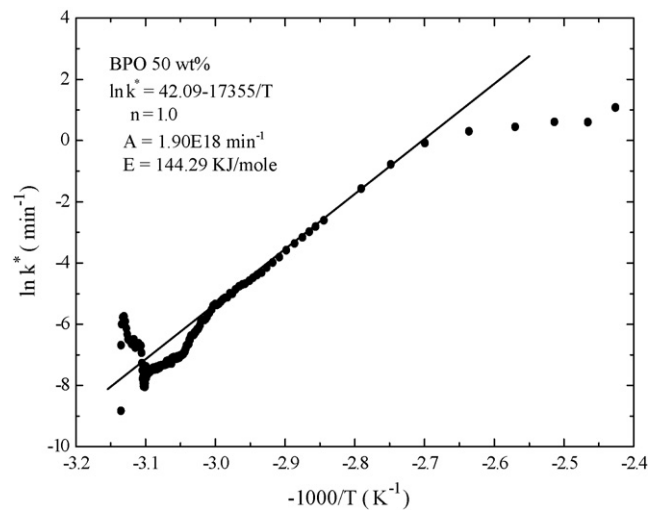

Fig. 6. The correlation of overall rate constant k^* and temperature T for the decomposition reaction of 50% crystalline BPO.

Zaman et al. [20] had used the isothermal microcalorimetry to study the kinetic parameters of decomposition reaction of 75% crystalline benzoyl peroxide. Their research indicated that the decomposition reaction of 75% crystalline benzoyl peroxide was a first order reaction, with activation energy of $137.8 \pm 6.6 \, \mathrm{kJ \, mol^{-1}}$, and the pre-exponential factor was calculated as $(4.7 \pm 13.7) \times 10^{15} \, \mathrm{s^{-1}}$. These kinetic parameters obtained from Zaman et al.'s study are very close to those obtained in this study. Unfortunately the kinetic parameters of decomposition reaction of 98 and 50% crystalline benzoyl peroxides have not been reported in the related literatures.

5. Analysis of dust explosion characteristics under room temperature and atmospheric pressure

5.1. Minimum ignition energy

The MIE experiments were carried out using a MIKE 3 apparatus. Figs. 7–9 show the results of MIE testing for 98, 75 and 50% crystalline benzoyl peroxides, respectively. The solid squares indicate ignition and the hollow squares represent no ignition in 10 trials. The curve is an estimated border between ignition and no ignition in each figure, indicating the lowest ignition energy as a function
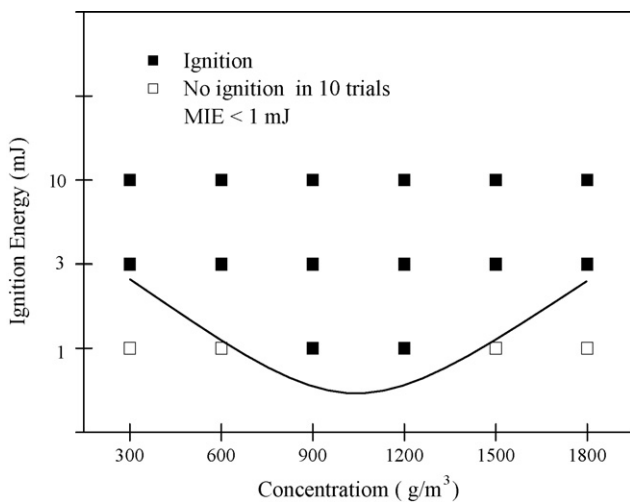

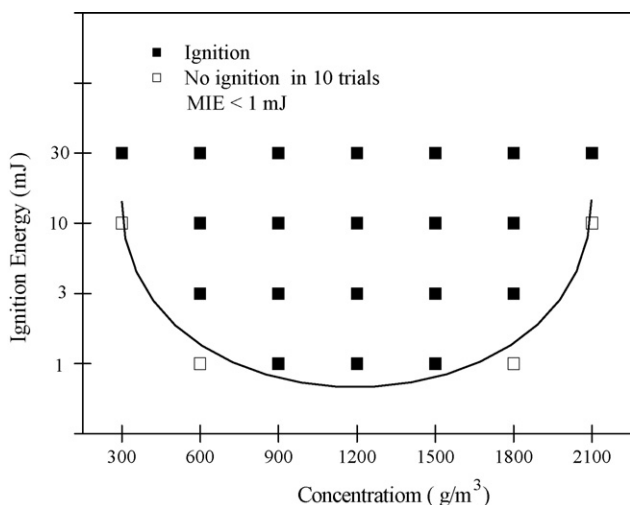**Fig. 7.** The result of the MIE testing for 98% crystalline benzoyl peroxide.

Fig. 8. The result of the MIE testing for 75% crystalline benzoyl peroxide.
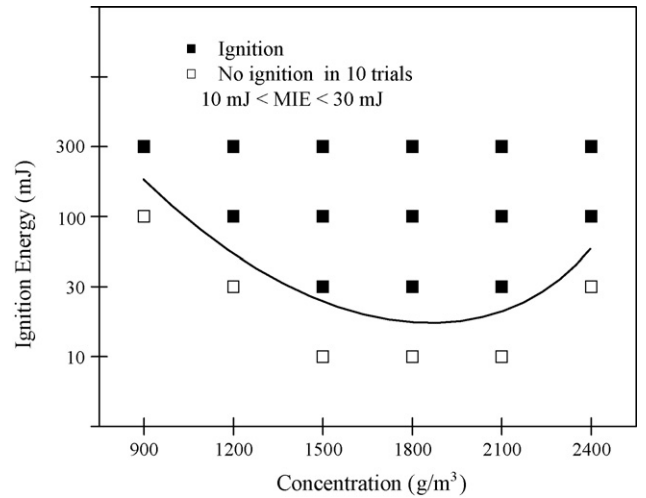

Fig. 9. The result of the MIE testing for 50% crystalline benzoyl peroxide.

of dust concentration. The MIEs of 98 and 75% crystalline benzoyl peroxides are lower than 1 mJ, which indicates that they are very sensitive to static discharge. The 50% crystalline benzoyl peroxide has a MIE between 10 and 30 mJ, therefore, its sensitivity is lower than the sensitivity of 98 and 75% crystalline benzoyl peroxides. The experimental results also indicate that the MIE has an increasing tendency when increasing the water content of crystalline benzoyl peroxide.

5.2. Explosion index and maximum explosion pressure

K_{St} (explosion index) is the maximum rate of explosion pressure rise normalized to a $1.0 \, \mathrm{m^3}$ volume of explosion chamber. It is defined according to the following equation [21]:

$$K_{St} = \left(\frac{dP}{dt} \right)_{max} V_c^{1/3} \tag{7}$$

where $(dP/dt)_{max}$ is the maximum rate of explosion pressure rise and V_c is the volume of test chamber. The relationship between K_{St} and explosion classes is shown in Table 4. 20-l-Apparatus is used to measure the maximum explosion pressure and the maximum rate of explosion pressure rise for 98, 75 and 50% crystalline benzoyl peroxides at studied experimental conditions. According to the results of explosion tests, the 98% crystalline benzoyl peroxide has a maximum K_{St} value around 245 bar m/s with concentration of $900 \, \mathrm{g/m^3}$ as shown in Fig. 10, the maximum explosion pressure and the maximum rate of explosion pressure rise for 98% BPO are 7.3 bar and 902 bar/s, respectively. As for 75 and 50% crystalline benzoyl peroxides, the maximum K_{St} values are 226 and 143 bar m/s at the concentrations of 1200 and $1500 \, \mathrm{g/m^3}$, respectively. Their maximum explosion pressure and maximum rate of explosion pressure rise are shown in Figs. 11 and 12. Furthermore, the explosion classes of 98 and 75% crystalline benzoyl peroxides are St-2, which indicates that their explosibility are strong. The explosion class of 50% crystalline benzoyl peroxide is St-1, therefore, its explosibility is weaker than the explosibility of 98 and 75% crystalline benzoyl peroxides.

Table 4
The relationship between K_{St} and explosion classes

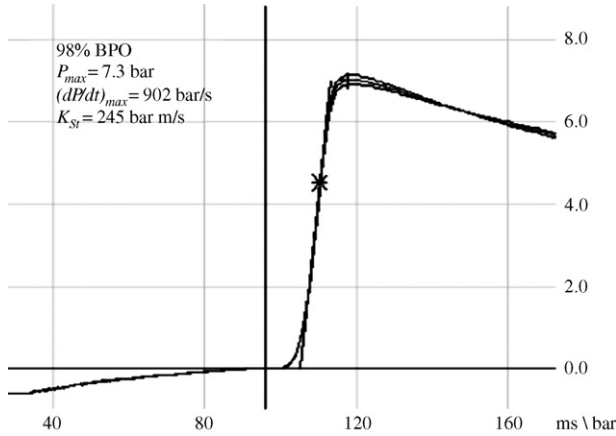| K_{St} (bar m/s)	Explosion classes (St)	Explosibility
$0 < K_{St} < 200$	St-1	Weak
$200 < K_{St} < 300$	St-2	Strong
$300 < K_{St}$	St-3	Very strong

Fig. 10. The result of the explosion characteristic testing for 98% crystalline benzoyl peroxide with dust concentration of 900 g/m^3.
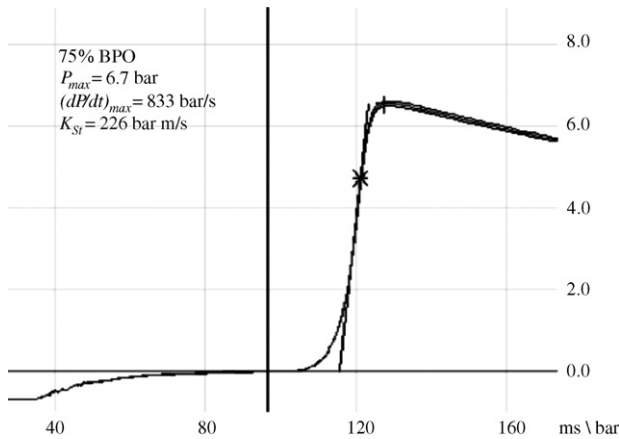

Fig. 11. The result of the explosion characteristic testing for 75% crystalline benzoyl peroxide with dust concentration of 1200 g/m^3.
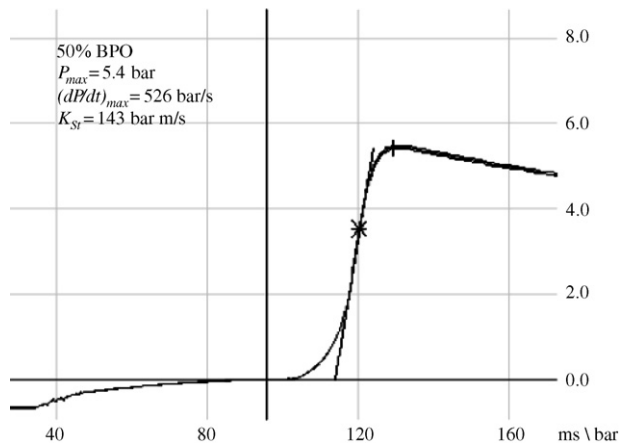

Fig. 12. The result of the explosion characteristic testing for 50% crystalline benzoyl peroxide with dust concentration of 1500 g/m^3.

6. The stability criterion and critical runaway temperature for the decomposition reaction of crystalline benzoyl peroxide

Semenov [9] assumed a uniform temperature distribution within the reaction system. This assumption is very close to the case of homogeneous system in a vessel. The general formula of heat generation rate owing to the reaction in a control volume V is expressed as

$$Q_g = qV(-r_b) \tag{8}$$

where q is the exothermic heat of reaction and $-r_b$ is its reaction rate. Expressing the reaction rate in Arrhenius form and substituting it into Eq. (8), the heat generation rate can be expressed as

$$Q_g = qVAC^n \exp\left(\frac{-E}{RT}\right) \tag{9}$$

The heat removal rate from the vessel to the ambient cooling medium is expressed as

$$Q_r = hS(T - T_a) \tag{10}$$

where h is the convective heat transfer coefficient of the ambient medium and S is the external surface area of the vessel. T and T_a are the temperatures in the vessel and of ambient cooling medium, respectively.

The overall energy balance in the control volume is that the rate of heat accumulation is equal to the rate of heat generation minus the rate of heat removal, which is

$$\rho VC_P \left(\frac{dT}{dt}\right) = Q_g - Q_r \tag{11}$$

The first term on the right-hand side represents the heat generation rate for an exothermic reaction and the second term is the heat removal rate from this reaction system. Combining Eqs. (9)–(11), the overall energy balance can be expressed as

$$\rho VC_P \left(\frac{dT}{dt}\right) = qVAC^n \exp\left(\frac{-E}{RT}\right) - hS(T - T_a) \tag{12}$$

It is assumed that the overall reaction order of decomposition reaction of benzoyl peroxide, n, is equal to unity. Thus, substituting Eq. (3) into Eq. (12) with $n = 1$, this equation can be rewritten as

$$\rho VC_P \left(\frac{dT}{dt}\right) = qVAC_0 \left[\frac{T_{max} - T}{T_{max} - T_0}\right] \exp\left(\frac{-E}{RT}\right) - hS(T - T_a) \tag{13}$$

At steady state, i.e. $(dT/dt) = 0$, Semenov's sufficient and necessary conditions for critical situation of the reaction system are

$$Q_g|_{T=T_c} = Q_r|_{T=T_c} \tag{14}$$

and

$$\left.\frac{dQ_g}{dT}\right|_{T=T_c} = \left.\frac{dQ_r}{dT}\right|_{T=T_c} \tag{15}$$

Eq. (14) also represents the reaction system in the condition of steady state, i.e. $(dT/dt) = 0$, when the rate of heat generation of the system is equal to the rate of heat removal. If Q_g is greater than Q_r, then $(dT/dt) > 0$. In such case, heat accumulation can lead to the runaway of the system.

Eq. (14) can also be written as

$$qVAC_0 \left[\frac{T_{max} - T_c}{T_{max} - T_0}\right] \exp\left(\frac{-E}{RT_c}\right) = hS(T_c - T_a) \tag{16}$$

Applying the condition of Eq. (15) can obtain

$$qVAC_0 \exp\left(\frac{-E}{RT_c}\right) \frac{-1 + (E(T_{max} - T_c)/RT_c^2)}{T_{max} - T_0} = hS \tag{17}$$

After dividing Eq. (17) by Eq. (16) and rearranging, the critical temperature in the reaction system can be obtained from the following equation:

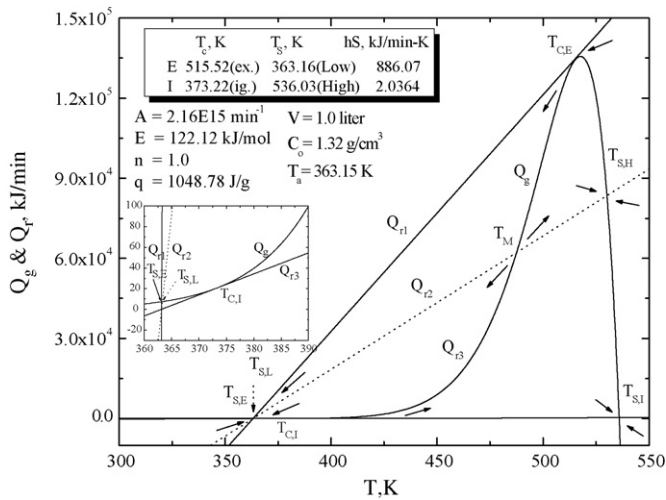$$\frac{E}{RT_c^2} = \frac{1}{T_c - T_a} + \frac{1}{T_{max} - T_c} \tag{18}$$

Fig. 13. The balance diagram of heat generation rate Q_g and heat removal rate Q_r for the decomposition reaction of 98% crystalline benzoyl peroxide.

The critical temperature, T_c, can be solved as

$$T_c = \frac{(T_{max} + T_a) \pm \sqrt{(T_{max} + T_a)^2 - 4[1 + R(T_{max} - T_a)/E]T_{max}T_a}}{2[1 + R(T_{max} - T_a)/E]}$$

(19)

Eq. (19) means the critical temperature is a function of the activation energy (E), the temperature of the cooling medium (T_a) and the final temperature of the reaction system in adiabatic condition (T_{max}).

Fig. 13 shows an example of calculating critical temperatures for the decomposition reaction of 98% crystalline benzoyl peroxide. The value of T_a is set as 363.15 K and the values of experimental T_{max} and E are listed in Table 3, respectively. Two critical temperature points of T_c can be obtained from the diagram of heat generation rate and theoretical critical heat removal rate vs. temperature. One is the critical extinction temperature $T_{C,E} = 515.52$ K and the other is the critical ignition temperature $T_{C,I} = 373.22$ K, which are calculated from Eq. (19). Substituting these two values of T_c into Eq. (17), the values of hS can be obtained, which are the overall heat transfer coefficient multiplied by the external surface of the vessel. The calculated values of hS from this equation are equal to 886.07 and 2.0364 kJ/min K, which correspond to $T_{C,E}$ and $T_{C,I}$, respectively. By substituting the values of hS into Eq. (16) and iteration one can obtain another set of temperature, which are denoted as $T_{S,E}$ and $T_{S,I}$. These $T_{S,E}$ and $T_{S,I}$ are the intersection points of the curve Q_g with curves Q_{r1} and Q_{r3} instead of tangent points, respectively. These two points, $T_{S,E}$ and $T_{S,I}$, can also be obtained from the intersection points of Q_g and Q_r graphically when the values of hS are equal to 886.07 and 2.0364 kJ/min K, respectively. Consequently, it is found that the value of $T_{S,I}$ is equal to 536.03 K and the value of $T_{S,E}$ is equal to 363.16 K in this case. As $hS = 886.07$ kJ/min K and the temperature in the reaction system is greater than 515.52 K, i.e. $T > T_{C,E}$, then the heat removal rate Q_{r1} is greater than the heat generation rate Q_g. Therefore, the temperature in the reaction system decreases continually and moves toward point $T_{C,E}$. Finally, it terminates at this point. When the temperature in the reaction system is in the range of $T_{S,E} < T < T_{C,E}$. Similarly the heat removal rate Q_{r1} is again greater than the heat generation rate Q_g. Thus, the temperature of reaction system approaches and stops at point $T_{S,E}$. When the temperature is lower than $T_{S,E}$, the heat removal rate Q_{r1} becomes less than the heat generation rate Q_g. As a result, temperature of the reaction system increases and goes back to point $T_{S,E}$ at the end. Points $T_{C,E}$ and $T_{S,E}$ are called the critical extinction temperature and the final

stable extinction temperature, respectively. These two points also represent the temperature that never goes up and the temperature that never drops down at $hS = 886.07$ kJ/min K, respectively.

Another calculated results using the minus sign in Eqs. (19) and (17) gives the values of $T_{C,I}$ and hS equal to 373.22 K and 2.0364 kJ/min K, respectively. The intersection point of curves Q_g and Q_{r3} at this calculation is $T_{S,I} = 536.03$ K. When the temperature in the reaction system is smaller than 373.22 K, i.e. $T < T_{C,I}$, the heat removal rate Q_{r3} is smaller than heat generation rate Q_g. Therefore, the temperature in the reaction system increases and moves towards to $T_{C,I}$. When the temperature of the reaction system is in the range of $T_{C,I} < T < T_{S,I}$, the heat removal rate Q_{r3} is again less than the heat generation rate Q_g, which leads to the temperature of the reaction system increasing from point $T_{C,I}$ forward to point $T_{S,I}$. Once the temperature is higher than $T_{S,I}$, the heat removal rate Q_{r3} is now larger than the heat generation rate Q_g, which leads to the temperature of the reaction system going back to point $T_{S,I}$. Points $T_{C,I}$ and $T_{S,I}$ are the critical ignition temperature and the final stable ignition temperature, respectively. These two points also represent the temperature that never drop down and the temperature of no return at $hS = 2.0364$ kJ/min K. When the value of hS is in the range of $2.0364 < hS < 886.07$ kJ/min K, three intersection points can be obtained between curves Q_{r2} and Q_g. These three points are denoted as $T_{S,L}$, T_M and $T_{S,H}$, and represent the steady-state temperatures at the low, intermediate and high points, respectively. The curve Q_{r2} is expressed as a dashed line. As in previous analysis, it is difficult to reach the intermediate point T_M because this point is unstable. Suppose it is possible to start this reaction system exactly at the temperature T_M; then if some slight perturbation in the operating conditions is to take the reaction system away from this steady state, it will not go back to T_M but will finish up either at the low or the high temperature at steady state, $T_{S,L}$ or $T_{S,H}$, respectively. Hence, a slight increase in temperature produces a net heat generation that can drive the temperature even higher. Conversely, a slight drop of temperature induces a net heat removal, which will cause the temperature to fall even more. In this sense, the intermediate steady-state temperature T_M is unstable. By contrast, the steady-state temperatures $T_{S,L}$ and $T_{S,H}$ are stable, if the state is perturbed away from one of them, it will return there naturally.

Figs. 14–16 show the correlation of evaluated temperatures $T_{C,I}$, $T_{C,E}$, $T_{S,I}$ and $T_{S,E}$ vs. ambient temperature T_a using the above calculation technique for the decomposition reactions of 98, 75 and 50% crystalline benzoyl peroxides, respectively. These temperatures are
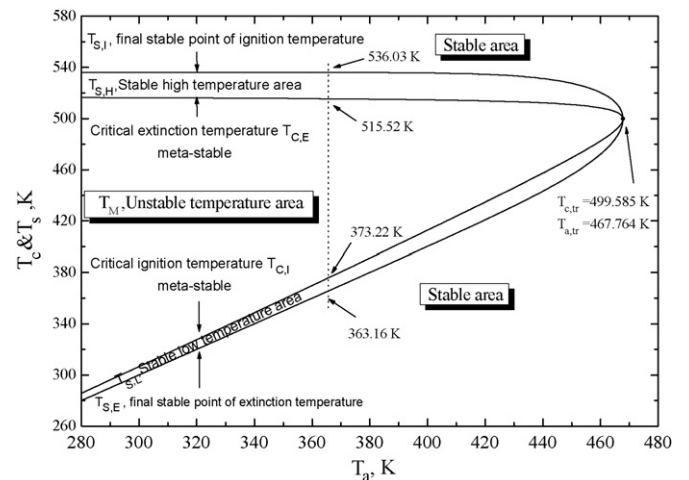

Fig. 14. The correlation of evaluated temperatures $T_{C,I}$, $T_{C,E}$, $T_{S,I}$ and $T_{S,E}$ vs. ambient temperature T_a and the temperature of transition point for the decomposition reaction of 98% crystalline BPO.
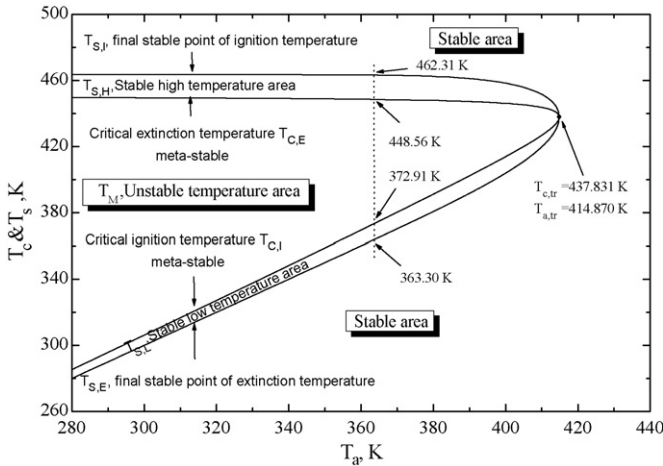
Fig. 15. The correlation of evaluated temperatures $T_{C,I}$, $T_{C,E}$, $T_{S,I}$ and $T_{S,E}$ vs. ambient temperature T_a and the temperature of transition point for the decomposition reaction of 75% crystalline BPO.

in the order of $T_{S,I} > T_{C,E} > T_{C,I} > T_{S,E}$. Both $T_{S,I}$ and $T_{C,E}$ decrease and both $T_{C,I}$ and $T_{S,E}$ increase gradually with increasing T_a. As soon as the ambient temperature T_a increases to the transition point $T_{a,tr}$, all four of these temperature curves coinciding at a transition point $T_{c,tr}$. The temperatures of transition point can be determined from the following equations:

$$T_{a,tr} = \frac{ET_{max}}{E + 4RT_{max}} \tag{20}$$

and

$$T_{c,tr} = \frac{ET_{max}}{E + 2RT_{max}} \tag{21}$$

To obtain the stable and unstable criteria in the reaction system, the heat generation and removal diagram does not allow us to conclude stability when

$$\frac{dQ_g}{dT} < \frac{dQ_r}{dT} \tag{22}$$

This equation is only a necessary, but not sufficient condition for stability. However, it does allow us to say the state will be unstable
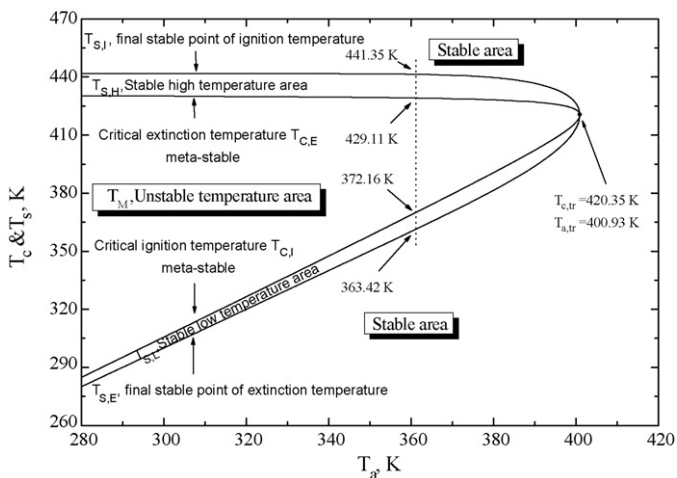
when

$$\frac{dQ_g}{dT} > \frac{dQ_r}{dT} \tag{23}$$

If T_S is defined as a stable temperature in a reaction system at the state of $Q_g = Q_r$ and a small temperature perturbation as $\delta T = T - T_s$ at this state, the reaction system is stable under the following conditions:

$$
\begin{aligned}
&\text{if} \quad \delta T > 0, \quad Q_g < Q_r \quad \text{or,} \\
&\text{if} \quad \delta T < 0, \quad Q_g > Q_r
\end{aligned}
\tag{24}
$$

Eq. (24) is the sufficient and necessary conditions for a stable reaction system. This criterion of stability had been analyzed by Lu et al. [6,7].

From the above definitions and energy–mass balance equations, the stable and unstable criteria in this decomposition reaction of benzoyl peroxide can be determined. When the temperature of the reaction system is higher than the curve of $T_{S,I}$ or lower than the curve of $T_{S,E}$, the system is stable. The temperature in the reaction system would return to these two curves eventually. When the reaction temperature is enclosed by the curves of $T_{C,I}$ and $T_{C,E}$, the system is unstable. Furthermore, there are two stable areas, $T_{S,L}$ and $T_{S,H}$, lying between two narrow areas of $T_{S,E} < T_{S,L} < T_{C,I}$ and $T_{C,E} < T_{S,H} < T_{S,I}$, respectively. When the value of T_a is increased, the values of $T_{S,I}$ and $T_{C,E}$ temperature curves decrease but the values of $T_{C,I}$ and $T_{S,E}$ temperature curves increase at same time. Therefore, when the value of T_a increases, these four temperature curves move closer and closer. As soon as the values of T_a are higher than 467.764, 414.870 and 400.930 K, for the 98, 75 and 50% crystalline benzoyl peroxides, respectively, the phenomenon of criticality disappears. These temperature curves corresponding to the three kinds of crystalline benzoyl peroxides coincide to three transition points. The values of three different transition points $T_{c,tr}$ corresponding to above three $T_{a,tr}$ are 499.685, 437.831 and 420.350 K, respectively.

The required values of hS at critical runaway and stable temperatures can be evaluated by using either Eqs. (16) or (17) after the value of T_c is determined from Eq. (19). The calculated results of T_a vs. hS at the critical runaway and stable temperatures for the decomposition reactions of 98, 75 and 50% crystalline benzoyl peroxides are shown in Fig. 17. There are three bull-horn shaped areas on this plot. The solid curves of hS denote the critical
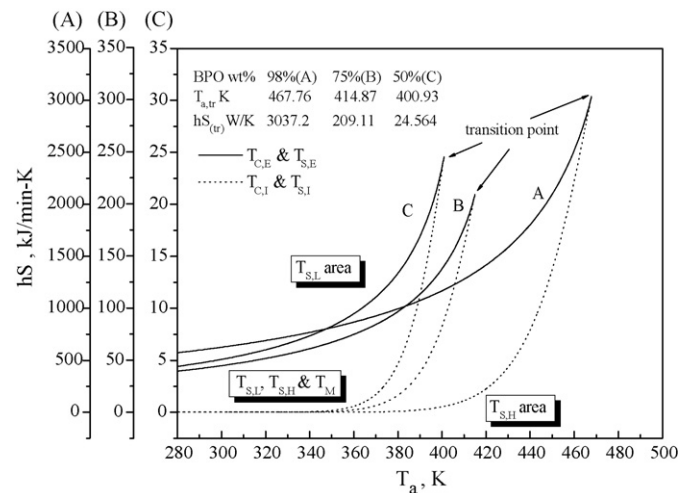

Fig. 16. The correlation of evaluated temperatures $T_{C,I}$, $T_{C,E}$, $T_{S,I}$ and $T_{S,E}$ vs. ambient temperature T_a and the temperature of transition point for the decomposition reaction of 50% crystalline BPO.

Fig. 17. The relationship between T_a and hS at critical ignition and extinction temperatures for the decomposition reaction of crystalline BPO at various weight percentages.

extinction temperature $T_{C,E}$ and final stable extinction temperature $T_{S,E}$, while the other three solid curves with dot points inside denote the curves of hS at critical ignition temperature $T_{C,I}$ and final stable ignition temperature $T_{S,I}$. Between these two curves is a bull-horn shaped area which contains one unstable temperature T_M and two stable temperatures $T_{S,L}$ and $T_{S,H}$. When the temperatures $T_{C,E}$, $T_{S,E}$, $T_{C,I}$ and $T_{S,I}$ are equal, the values of hS coincide to one transition point which is expressed as $hS_{(tr)}$. The values of $hS_{(tr)}$ are equal to 3037.2, 209.11 and 24.564 kJ/min K which corresponding to the decomposition reactions of 98, 75 and 50% crystalline benzoyl peroxides, respectively. The values of $hS_{(tr)}$ can be calculated from Eq. (25), which is obtained by combining Eqs. (17), (20) and (21):

$$hS_{(tr)} = \frac{qVAC_0}{T_{max} - T_0} \left(1 + \frac{4RT_{max}}{E}\right) \exp\left[-\left(2 + \frac{E}{RT_{max}}\right)\right] \qquad (25)$$

Beyond these bull-horn shaped diagrams, the area contains the temperatures $T_{S,L}$ and $T_{S,H}$, which are distributed above and below this diagram. From these figure, we see that the required value of hS in the decomposition reactions of crystalline benzoyl peroxide are strongly affected by variation of the ambient temperature T_a. Once the value of T_a is given, the required value of hS, the critical ignition temperature $T_{C,I}$ and extinction temperature $T_{C,E}$ can be estimated from the reaction kinetic parameters and Eqs. (16)–(19) mentioned before.

7. Prevention of runaway decomposition reaction and dust explosion

The hazards of benzoyl peroxide are well known and documented. A number of important recommendations are given for safe handling, storage, and manufacture of benzoyl peroxide.

(1) The self-accelerating decomposition temperature of benzoyl peroxide is around 70 °C. The benzoyl peroxide may decompose violently when exposed to excessive heat, and produces a large amount of gas, hence safeguards should be in place to avoid overheating benzoyl peroxide. Additionally, precautions should be also taken to avoid contamination, which may initiate the decomposition reaction.
(2) Safeguards should be in place to protect against the possibility of exposing benzoyl peroxide to ignition sources, friction, and shock. Electrical equipment in areas with open containers of benzoyl peroxide should be classified and all equipment should be adequately grounded.
(3) The benzoyl peroxide is used in a number of industrial processes, particularly in manufacturing plastics. Equipment uses to heat benzoyl peroxide should be isolated from storage areas, other equipment, and work areas. The decomposition reaction of benzoyl peroxide generates a large amount of gas, which should not be confined for the prevention of explosion. Buildings that house manufacturing equipment should be built with fire- and explosion-resistant walls with adequate capabilities to vent pressure.

8. Conclusions

(1) The heats of decomposition reaction of 98, 75 and 50% crystalline benzoyl peroxides are equal to 1047.78, 957.04 and 771.16 J/g, respectively, which were measured by means of DSC. The experimental results revealed that the total released heat is increased with the increasing weight percentage of benzoyl peroxide.
(2) The kinetic parameters of decomposition reaction of 98, 75 and 50% crystalline benzoyl peroxides are listed in Table 3. They

were determined from the experimental results of ARC. It was found that the decomposition reaction of crystalline benzoyl peroxide is a non-tempered hybrid system.
(3) The MIEs of 98 and 75% crystalline benzoyl peroxides are lower than 1 mJ, which indicates that they are very sensitive to static discharge. The 50% crystalline benzoyl peroxide has a MIE between 10 and 30 mJ, its sensitivity is lower than the sensitivity of 98 and 75% crystalline benzoyl peroxides. These experimental results were measured by means of the MIKE 3 apparatus.
(4) The maximum K_{St} values of 98, 75 and 50% crystalline benzoyl peroxides are 245, 226 and 143 bar m/s under room temperature and atmospheric pressure, respectively. These experimental results were measured by means of the 20-l-Apparatus. Furthermore, the explosion classes of 98 and 75% crystalline benzoyl peroxides are St-2, which indicates that their explosibility are strong. The explosion class of 50% crystalline benzoyl peroxide is St-1, therefore, its explosibility is weaker than the explosibility of 98 and 75% crystalline benzoyl peroxides.
(5) The unstable temperature area of decomposition reaction of 98, 75 and 50% crystalline benzoyl peroxides is enclosed by the curves $T_{C,I}$ and $T_{C,E}$ in Figs. 14–17. The reaction system is stable outside this unstable area.

References

[1] National Fire Protection Association, Code for the Storage of Organic Peroxide Formulations, NFPA Standard, Quincy, Massachusetts, 2002.
[2] United Nations, Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria of UN, 4th ed., New York, 2003, pp. 249–260.
[3] Catalyst Systems Inc., Fire and explosion: hazards of benzoyl peroxide, Case Study, Chemical Safety and Hazard Investigation Board, NO. 2003-03-C-OH, 2003, pp. 1–20.
[4] M. Wakakura, I. Yoshiaki, Trends in chemical hazards in Japan, J. Loss Prev. Process Ind. 12 (1) (1999) 79–84.
[5] F. Zaman, A.E. Beezer, J.C. Mitchell, Q. Clarkson, J. Elliot, M. Nisbet, A.F. Davis, The stability of benzoyl peroxide formulations determined from isothermal microcalorimetric studies, Int. J. Pharm. 225 (2001) 135–143.
[6] K.T. Lu, C.C. Yang, P.C. Lin, The criteria of critical runaway and stable temperatures of catalytic decomposition of hydrogen peroxide in the presence of hydrochloric acid, J. Hazard. Mater. B135 (2006) 319–327.
[7] K.T. Lu, K.M. Luo, S.H. Lin, S.H. Su, K.H. Hu, The acid-catalyzed phenol–formaldehyde reaction critical runaway conditions and stability criterion, Process Saf. Environ. 82 (B1) (2004) 37–47.
[8] W. Bartknecht, Explosions: Course, Prevention, and Protection, Springer, New York, 1981.
[9] N.N. Semenov, The calculation of critical temperatures of thermal explosion, Z. Phys. Chem. 48 (1928) 571–582.
[10] N.N. Semenov, Thermal theory of combustion and explosion, Usp. Fiz. Nauk 23 (1940) 4–17.
[11] M. Morbidelli, A. Varma, A generalized criterion for parametric sensitivity application to thermal explosion theory, Chem. Eng. Sci. 43 (1988) 91–98.
[12] G. Eigenberger, H. Schuler, Reaction stability and safe reaction engineering, Int. Chem. Eng. 29 (1989) 12–19.
[13] J. Villermaux, C. Georgakis, Current problems concerning batch reactors, Int. Chem. Eng. 31 (3) (1991) 434–441.
[14] X.R. Li, H. Koseki, SADT prediction of autocatalytic material using isothermal calorimetry analysis, Thermochim. Acta 431 (2005) 113–116.
[15] Ch. Cesana, R. Siwek, MIKE 3 Minimum Ignition Energy 3.3, Adolf Kuhner AG, Birsfelden, Switzerland, 2007.
[16] Ch. Cesana, R. Siwek, Operating Instructions 20-l-Apparatus 6.0, Adolf Kuhner AG, Birsfelden, Switzerland, 2007.
[17] C.S. Kao, K.H. Hu, Acrylic reactor runaway and explosion accident analysis, J. Loss Prev. Process Ind. 15 (2002) 213–222.

[18] J. Sun, Y. Li, K. Hasegawa, A study of self-accelerating decomposition temperature (SADT) using reaction calorimetry, J. Loss Prev. Process Ind. 14 (2001) 331–336.

[19] H.T. Kohlbrand, The use of SimuSolv in the modeling of ARC (accelerating rate calorimeter) data, in: Proceedings of the International Symposium on Runaway reactions, 1989, pp. 86–111.

[20] F. Zaman, A.E. Beeze, J.C. Mitchel, Q. Clarkson, J. Elliot, A.F. Davis, R.J. Willson, The stability of benzoyl peroxide by isothermal microcalorimetry, Int. J. Pharm. 277 (2001) 133–137.

[21] A.S.T.M. E1226-88, Standard Test Method for Pressure and Rate of Pressure Rise for Combustible Dusts, American Society for Testing and Materials, Philadelphia, USA, 1988.