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

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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.

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-

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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 (kJ/min m^2 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 (M^{1-n} 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 content 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 °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

$$[(RCO_2)]_2 \rightarrow 2RC(O)—O^{\bullet}$$

(2) Radical-induced decomposition

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

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