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Thermal hazard analyses for the synthesis of benzoyl peroxide

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ABSTRACT

Benzoyl peroxide (BPO), historically, due to its wide applications around the world, has caused many serious fire and explosion accidents. In this paper, in order to prevent such accidents, thermal hazard analyses of synthesis of benzoyl peroxide were studied. Firstly, in order to obtain thermal hazard coefficients, the exothermic processes with different alkaline solutions were studied by RC1e (Reaction Calorimeter). The alkaline solutions are NaOH, NH_4HCO_3 and Na_2CO_3, respectively. Secondly, the thermal decomposition of BPO product was studied by PHI-TECIIto analysis the thermal stability. Finally, the possibility of runaway reactions and thermal risks of synthetic process were evaluated according to the Stoessel criticality diagram. In the first stage, the test results of the reaction heat (ΔH_m), heat release rate (q_r) and adiabatic temperature rise (ΔT_{ad}) with different alkaline solutions were NaOH > Na_2CO_3 > NH_4HCO_3. In the second stage, according to the analysis of experimental data, the heat release rate of reaction with NH_4HCO_3 solution was the slowest, while the Maximum Temperature of the Synthesis Reaction (*MTSR*) and the adiabatic temperature rise (ΔT_{ad}) were lowest when using Na_2CO_3 solution. The time needed to reach the maximum reaction rate under the adiabatic condition (TMR_{ad}) was 0.83 h when using NaOH solution. The temperature was 38.24 °C when TMRad is 24 h (T_{D24}). The evaluation results of the process showed that the risks of reactions with NaOH solution or NH_4HCO_3 solution were not acceptable. Only the risk of the reaction with Na_2CO_3 solution was acceptable. Therefore, the safety level of synthesis of benzoyl peroxide can be significantly improved by using Na_2CO_3 solution. Research in this paper can not only improve the safety level of BPO reaction and storage processes, but also provide technical support for stability criterion of BPO decomposition reaction.

1. Introduction

Benzoyl peroxide (BPO) is a strong oxidizing organic peroxide and easy to decompose under heating. The thermal explosion can be caused by impact, heat, friction, etc (Zhao et al., 2012; Wang et al., 2013; Lee et al., 2014). BPO is widely used as initiator in chemical industries (Zaman et al., 2001). Based on the NFPA standard (National, 2011), the classification level of BPO for flammability and reactivity is 4. In the document of state administration of work safety of China, the synthesis of BPO is a typical high-risk process.

In China, the traditional method for the synthesis of BPO is that benzoyl chloride and hydrogen peroxide are used as main raw material with alkaline solution. Fan Juan (Fan, 2002) found that the decomposition rate of H_2O_2 and hydrolysis rate of BPO are rapid. Although low temperature environment can control the above two side reactions effectively, it can also decrease the main reaction rate. Compared with NaOH and Na_2CO_3, the process of NH_4HCO_3 dissolved in water is an endothermic process. Therefore, the reaction can keep the process temperature without cooling and the reaction time can be shortened (Duan et al., 2003).

Most papers deal with the thermal decomposition of BPO. Dao-Xing Sun et al.(Sun et al., 2012) used C80 calorimetry and accelerating rate calorimetry (ARC) to study the hazardous characteristics of BPO and obtained the pre-exponential factor ($3.61 \times 1019\ s^{-1}$) and activation energy (152.80 kJ mol^{-1}). Liu et al. (2013) analyzed the thermal hazards of BPO with incompatibilities (H_2SO_4, NaOH, and Na_2SO_3) and found that thermal hazard increased prominently when BPO were mixed with H_2SO_4, NaOH, and Na_2SO_3. The thermal

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decomposition of BPP is an autocatalytic reaction. When the BPO was mixed with benzoic acid, benzene or phenol, the hazard significantly increased (Wang et al., 2013; Liu et al., 2015). Acrylic acid and methyl acrylate were identified as catalyst for thermal decomposition of BPO (Huang et al., 2013).

In the first step of synthesis of BPO, the thermal hazard of H_2O_2 mixed with alkaline solutions increased significantly. Chen et al. (2006) used differential scanning calorimetry (DSC) to obtain that the initial decomposition temperature (T_{onset}) of 31mass% H_2O_2 was 40.54 °C by heating rate of 2 °C min^{-1}. Wu et al., (2010) found that the T_{onset} of H_2O_2 mixed with NaOH was close to room temperature.

Many studies have reported the hazards of the decomposition of BPO, but few researches study the hazards of synthesis of BPO mixed with different alkaline solutions. The synthesis of BPO is an exothermic reaction. There is no detailed account of a safety assessment of the synthesis of BPO. In this study, we report the process safety evaluation of the synthesis of BPO mixed with different alkaline solutions. RC1e is used to study the exothermic characteristics for the synthesis of BPO with different alkaline solutions firstly. Secondly, the adiabatic decomposition of raw product is studied by PHI-TECII and the TMR_{ad} and T_{D24} are calculated from the fitting kinetic models. Finally, the risk level of the synthesis of BPO is evaluated based on the Stoessel criticality diagram and the safest process of synthesis of BPO which also has a good yield of BPO can be determined.

2. Experiments

2.1. Reaction path

There are two steps for the synthesis of Benzoyl peroxide. Firstly, Hydrogen peroxide (H_2O_2) is added to alkaline solution to prepare the hydrogen peroxide alkaline solution. Secondly, benzoyl chloride is added to hydrogen peroxide alkaline solution. See Fig. 1.

2.2. Experiment reagent and instrument

2.2.1. Experiment reagent and sample

(1) Reagent: H_2O_2 (AR 30 wt%), NaOH (AR), Na_2CO_3 (AR), NH_4HCO_3 (AR), benzoyl chloride (AR), sodium dodecyl sulfate (SDS, CP), Sinopharm Chemical Reagent Co., Ltd; deionized water.
(2) Sample1 is the product of the synthesis of BPO which is produced by RC1e and then liquid-solid separation. Sample 2 is the product of sample1 being washed and dried.

In order to study the adiabatic decomposition condition of BPO effectively, Sample 1 is used as the sample of adiabatic experiment. Sample 2 is used for product analysis.

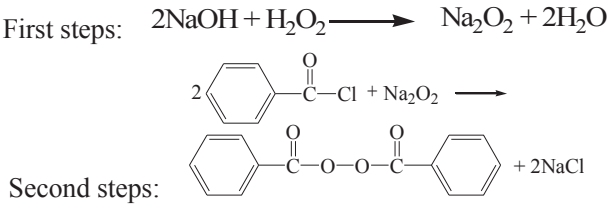

Fig. 1. Flow chart of the synthesis process of BPO.

2.2.2. Reaction calorimeter (RC1e)

(1) RC1e is manufactured by METTLER TOLEDO and used to measure the exothermic condition of reaction. RC1e is an automatic synthesis reaction system. A 2 L reactor is used in our experiment. Specific testing principle can be found in the literature (Lee et al., 2014).
(2) Experiment conditions: reaction temperature is 10 °C. Stirring speed is 100 r•min^{-1}. Feed rate is 13.59 g s^{-1} (H_2O_2) and 13.52 g s^{-1} (benzoyl chloride). Solution concentration is 3.93 mol L^{-1}. Alkali solutes are NaOH, NH_4HCO_3 and Na_2CO_3.

2.2.3. Nuclear magnetic resonance spectrometer (Bruker AV500 MHz NMR)

(1) Bruker AV500 MHz NMR is used to analyze the molecular structure and determinate the material content.
(2) Experiment reagent is Sample 2 and solvent is $CDCl_3$.

2.2.4. PHI-TECII

(1) PHI-TECII is a quasi-adiabatic calorimeter manufactured by HEL. PHI-TECII is used to obtain the thermal hazard parameters, such as temperature versus time, pressure versus time, self-heating rate and pressure-rising rate. The heat-wait-search (H-W-S) mode for detecting the self-heating rate is adopted for PHI-TEC II (Townsend and Tou, 1980; Sun et al., 2004). The volume of sample ranges from 0.5 to 100 ml. The experimental equipment is shown in Fig. 2.
(2) Experiment conditions: the mass of sample 1 is 1.01 g. The volume of test is 10 ml. The temperature range is 60–300 °C. Heating step is 5 °C. The criterion for no self-heating is 0.02 °C min^{-1}.

3. The experiment results and analysis of RC1e

3.1. The experiment results of first step

Because both the adiabatic temperature rise (ΔT_{ad}) and the calculated MTSR are small in first step. Therefore, the worst conditions for the whole process corresponding to either reactions under adiabatic conditions or cooling system failure event are considered in this paper. $T_{max} = \Delta T_{ad} + T_p$. The exothermic

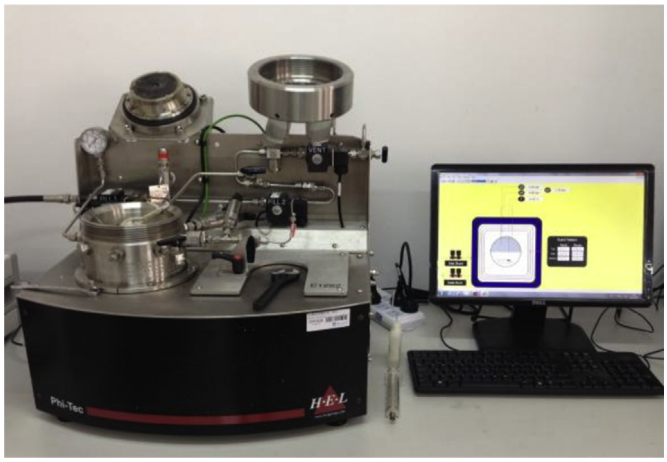

Fig. 2. Schematic diagram of PHI-TECII.