THERMAL STABILITY STUDIES OF BENZOYL PEROXIDE SYSTEMS

A Dissertation

by

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ABSTRACT

Organic Peroxide is one of the common reactive chemical classes. Their unstable O-O bonds make them very useful, but also hazardous due to highly exothermic decomposition, which can result in runaway reactions. Benzoyl peroxide (BPO) is one of the most commonly used organic peroxides in market and the hazards have been revealed in many incidents. To prevent conditions leading to a thermal runaway, it is necessary to understand the kinetics, thermodynamic properties and critical safety parameters of the systems involving reactive chemicals.

In this research, calorimetric experiments were employed to characterize the runaway behavior of BPO in different systems. The aim was the advancement of understanding the thermal risks of BPO under various conditions in a systematic and comprehensive approach. More specifically, BPO was studied in three different systems: 1) solid phase BPO decomposition, 2) BPO decomposition in solvent, and 3) BPO compatibility study in mixtures with selected acids, bases or salts. Chemical reactivity of BPO in different systems were investigated experimentally using screening techniques and adiabatic calorimeter.

Significant differences in thermal behavior and reaction pathways were observed in different systems involving BPO. Solid BPO was tested in pseudo-adiabatic calorimeter to study the condition-dependent BPO decomposition, including the effect of sample size, confinement, and additives. The information was useful in identifying safer operation conditions to avoid exposure of BPO to heat, confined spaces or incompatible materials, and to prevent thermal explosion. BPO-solvent system was evaluated in adiabatic calorimeter. A quantitative assessment of the effects of sample volume and mass fraction on thermal runaway was conducted. The thermal hazards associated with process scaling up and process deviation were revealed. In addition, the effect of dry fire-extinguishing chemicals on BPO stability was assessed. The results showed that sodium bicarbonate and potassium bicarbonate could reduce the “onset” temperature, and reduce the pressure hazard of solid BPO decomposition, and ammonium dihydrogen phosphate had an inhibition effect on BPO decomposition. We anticipate this research to provide useful information in terms of thermal runaway prevention, protection layer design, and developing emergency responding measures in order to safely handle energetic BPO in storage, transportation, manufacturing, production processes, as well as safely tackle BPO-related fires.

DEDICATION

To my mother Yingxian Wang and my father Hao Shen, for their unconditional love and support. To all my family members, for their care and support.

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Contributors

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NOMENCLATURE

ΔH	heat of reaction (J/g)
A	pre-exponential factor of Arrhenius equation (/min)
E_a	activation energy (kJ/mol)
T_o	“onset” temperature (°C)
T_f	final temperature of the reaction (°C)
T_{max}	temperature at the maximum self-heating rate (°C)
$(dT/dt)_{max}$	maximum self-heating rate (°C /min)
P_o	“onset” pressure (psig)
P_f	final pressure of the reaction (psig)
P_{max}	pressure at maximum pressure rise rate (psig)
$(dP/dt)_{max}$	maximum pressure rise rate (psi/min)
P_c	pressure after cooling down (psig)
SADT	self-accelerating decomposition temperature (°C)
T_{NR}	temperature of no return (°C)
TMR_{ad}	adiabatic time to maximum rate (min)
ΔT_{ad}	adiabatic temperature rise (°C)
φ	thermal inertia factor

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CHAPTER I

INTRODUCTION [*]

A variety of products can be manufactured by chemical reactions. However, uncontrolled chemical reactions have led to serious fires, explosions, and toxic emissions posing great threat to personnel, asset and environment. Chemical reactivity can bring significant hazards if not properly understood and controlled. The reactive hazards are related to process parameters involving temperatures, pressures, quantities, and concentrations, as well as other factors such as the presence of other substances or impurities. According to a CSB report [1], three common types of reactive hazards include impact sensitive or thermally sensitive materials, runaway reactions, and chemical incompatibility. The major causes of these reactive chemical incidents include inadequate hazard identification and evaluation, inadequate procedures and training for storage and handling of reactive chemicals, inadequate process design for reactive hazards, inadequate design to prevent human errors, etc. It is required that highly hazardous chemicals and reaction processes should be evaluated in compliance with regulations such as the Occupational Safety and Health Administration (OSHA) Process Safety Management (PSM) Standard (29 CFR 1910.119), and the U.S. Environmental Protection Agency

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[*] Part of this chapter is reprinted with permission from "Thermal decomposition of solid benzoyl peroxide using Advanced Reactive System Screening Tool: Effect of concentration, confinement and selected acids and bases" by Y. Shen, W. Zhu, M. Papadaki, M. S. Mannan, C. V. Mashuga, Z. Cheng, 2019. *Journal of Loss Prevention in the Process Industries*, 60, 28-34, Copyright [2019] by Elsevier.

(EPA) Accidental Release Prevention Requirements: Risk Management Programs (RMP; 40 CFR 68).

Among chemicals involved in reactive incidents, organic peroxide represents a common class. Organic peroxides are generally used as polymerization initiators, curing agent, cross-linking agent, and fuel. The feature of organic peroxide is a weak peroxy (–O–O–) bond, which can break easily and undergo homolytic decomposition generating large amounts of heat and non-condensable gases. A generic O–O bond energy is believed to be 142.2 kJ/mol. O-O bond is the source of energy, and a source of hazards as well. It is a thermally unstable structure and very sensitive to thermal sources. It is very susceptible to contaminants, such as inorganic acids (H_2SO_4, H_3PO_4, HCl, or HNO_3), alkali, Fe_2O_3, and so on. Exothermic decomposition of organic peroxides can result in high temperature and high pressure leading to a fire or explosion if handled improperly. Thermal explosions or runaway reactions caused by organic peroxides resulted in many property losses, injuries and fatalities. For instance, 2017 Arkema plant explosion was caused by organic peroxide decomposition due to failure of refrigeration system, posing great threat to the safety of residents, environment and assets [2]. Therefore, a thorough understanding of thermal risks of organic peroxides decomposition is important to process safety [3-5].

Benzoyl peroxide (BPO) is one of the most commonly used organic peroxides in industry, mainly as initiator for polymerization reactions. BPO is relatively stable at ambient temperature, but it is flammable, explosive, incompatible with various substances, and is sensitive to shock, heat, and friction. Its hazards have been revealed in many incidents in different countries, which has caused extensive loss of property and life [6-

10]. Despite considerable research performed on understanding the decomposition of BPO, incidents are still happening, and this calls for gaining even deeper understanding of its thermal runaway behavior systematically.

Figure 1 shows the application of chemical reactivity evaluation and how it can help prevent incidents from happening and reduce the risks associated with reactive chemicals. It also explains the motivation for this work.

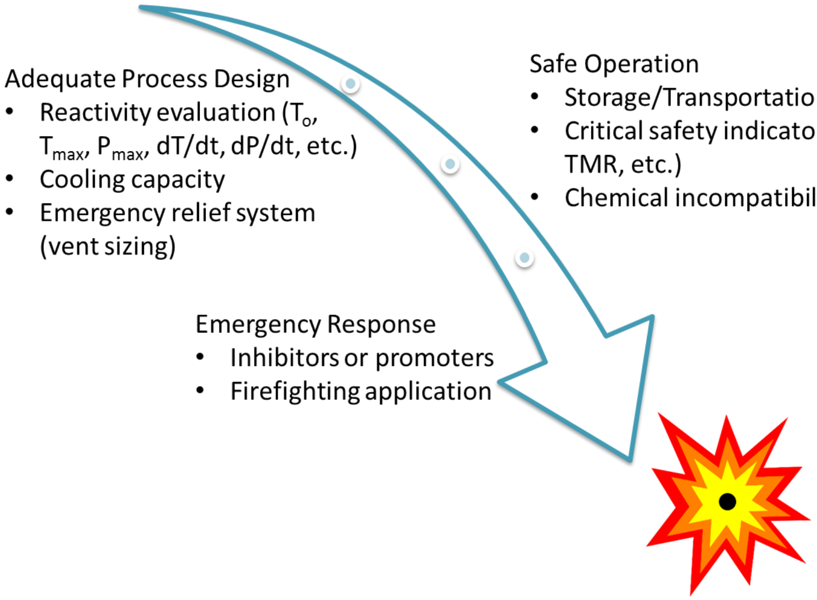

Figure 1 Application of Chemical Reactivity Evaluation

To prevent incidents from happening, at initial stage we are expecting adequate process design to prevent runaway reactions. For example, adequate cooling capacity and emergency relief valve during operation upset. Evaluating the reactivity of these hazardous materials could provide valuable process safety data such as “onset” temperature of exothermic reactions, maximum temperature, maximum pressure, and non-condensable gas generation under intended or unintended conditions. These data would serve as the basis for designing inherently safer process, as well as protection layer such as vent sizing, and methods to control reaction hazards.

Also, we would like to safely handle the reactive chemicals during processing, storage and transportation. Critical safety indicators could ensure safe operation. In addition, a common problem in petrochemical industries is the contamination issue. Contaminants can form potentially hazardous mixtures, leading to unintended thermal decomposition. Therefore, it is desired to establish a complete database of chemical incompatibility to effectively help design safety management measures.

If unfortunately a fire occurs, it is important to understand the safe emergency response. Therefore, it is beneficial to study the effect of fire-extinguishing chemicals and whether it can accelerate or inhibit the thermal decomposition of peroxides. Experimental results could be useful in fire-fighting application to safely handle hazardous chemicals in fire situations.

To select, implement and maintain appropriate safety measures, a risk assessment of the reactive hazards needs to be performed. This research evaluated the reactivity of BPO in solid phase as well as in solvents under various conditions. The experimental results could be useful for vent sizing design, safe storage and transportation of such energetic material. It also investigated the effects of selected contaminants on the thermal decomposition of BPO. The results could be good reference for chemical incompatibility studies. In addition, the effect of dry-fire extinguishing chemicals were also studied to identify potential inhibitors for BPO decomposition, which could provide guidance on implementing emergency response and mitigation approach.

1.1 Dissertation Outline

Chapter I introduces the background and motivation to do this research. It describes the main properties and uses of BPO, incidents related with BPO, thermal decomposition pathways, conditions that affect BPO decomposition, and how calorimeters can be used to study BPO. It also presents a thorough literature review in the field of BPO decomposition and identifies the gaps in this research area.

Chapter II defines the objectives of this research and describes the methodologies used to evaluate chemical reactivity, including equipment and analysis model to achieve the objectives of this work.

Chapter III is dedicated to the experimental study of the thermal decomposition of BPO in solid phase. The effect of various experimental conditions are discussed including sample size, confinement, contaminants, and isothermal testing using the pseudo adiabatic calorimeter Advanced Reactive Systems Screening Tool (ARSST).

Chapter IV is devoted to the thermal runaway study of BPO decomposition in solvents under adiabatic conditions by the Automated Pressure Tracking Adiabatic Calorimeter (APTAC).

Chapter V focuses on the influence of dry fire-extinguishing chemicals on BPO decomposition. The potential inhibition effect of these chemicals on BPO decomposition are reported, providing references when dealing with BPO-related fires.

Chapter VI summarizes the main findings of this dissertation and outlines the recommendations for future work.

1.2 Benzoyl Peroxide Introduction

1.2.1 Properties and Uses

Benzoyl peroxide (BPO is a diacyl peroxide, consisting of two benzoyl groups linked by O–O bond. The molecular structure of BPO is shown in Figure 2. It is one of the most important organic peroxides in terms of applications and the scale of its production. BPO is nontoxic, odorless, and tasteless white granular solid, which has applications in the petrochemical industry to initiate free radical polymerization. It is also applied in food industry as oxidizer to bleach flour or oil, and pharmaceutical industry as antimicrobial agent to cure acne. Given the commercial importance of BPO, it is important to determine the precautions to be observed in handling this organic peroxide [6]. BPO is relatively stable at ambient temperature, but it is flammable under dry conditions and is sensitive to shock, heat, impact and friction [7]. The hazard classifications of 98%, 75% and 50% BPOs are specified as class I, III, and IV, respectively, by the NFPA [11]. BPO is incompatibility with various substances: acids, alkalis, combustible materials, metals. If anything triggers the highly exothermic decomposition of BPO, it could ultimately lead to runaway reactions, and subsequent fires or explosions.

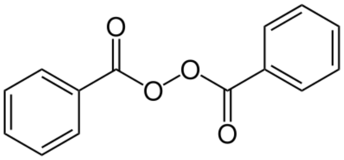

Figure 2 Molecular structure of Benzoyl peroxide (BPO)
(Source: By User Bryan Derksen - Own work, Public Domain, https://commons.wikimedia.org/w/index.php?curid=1557492)

The traditional method for the synthesis of BPO has two steps: firstly, hydrogen peroxide is added to alkaline solution, secondly, benzoyl chloride is added to hydrogen peroxide alkaline solution [12]. In the laboratory, benzoyl peroxide can be synthesized in three steps: 1. Grignard reaction to turn bromobenzene into benzoic acid. 2. Transform the resulting benzoic acid into benzoyl chloride using $SOCl_2$. 3. The addition of H_2O_2/NaOH to the benzoyl chloride to yield benzoyl peroxide. The last step is used in industry to synthesize BPO from benzoyl chloride feedstock [13].

1.2.2 Thermal Decomposition of BPO

The decomposition of BPO is proved to be an autocatalytic reaction that is very sensitive to pressure and temperature change. If handled improperly, the cumulative thermal effect may cause runaway reactions, fires and explosions [6]. Autocatalytic reactions have a low reaction rate at the very beginning. As the reaction proceeds, free radicals are generated and accumulated, and the reaction accelerates until the maximum rate is reached, following the autocatalytic reaction model [14]. For activation energy (E_a) between 220 and 1000 kJ/mol, the decompositions are of autocatalytic nature [15]. The initial reaction is essential for assessing the thermal hazards of the entire decomposition reaction. The autocatalytic reaction results suggest that the hazardous temperature of organic peroxides is significantly lower than the runaway temperature cited in literature [14].

Thermal decomposition reaction of benzoyl peroxide is an exothermic and non-tempered hybrid system because the pressure contributes from both non-condensable gas and vapor pressure. Self-reactive decomposition can develop into a violent explosion at around its melting point 103 °C. Many factors can trigger a decomposition reaction, such as heat, shock and incompatible materials. If any unexpected factors during storage, transportation, manufacturing, and usage cause the process to deviate from the normal operating condition, and the heat generation rate exceeds heat removal rate, a runaway reaction can happen leading to a costly disaster. The first step of its decomposition is an initial dissociation of the oxygen-oxygen bond to produce two benzoate radicals, and then may be followed by carbon dioxide loss to render phenyl radicals. The possible decomposition products include benzoic acid, carbon dioxide, carbon monoxide, benzene, biphenyl, terphenyl, phenyl benzoate [6, 11, 14-16].

The history of the use of BPO is marked by many catastrophes involving explosions and runaway reactions due to inadequate safety precautions. Table 1 shows selected incidents in the past decades. Incidents involving BPO occurred during manufacturing process such as packaging [8] and drying [6], as well as reaction process [9]. Hence, inherently safer design during preparation, manufacturing, transportation, storage and even disposal is critical, and important safety parameters, such as self-accelerating decomposition temperature (SADT), temperature of no return (T_{NR}), adiabatic time to maximum rate (TMR_{ad}) are used to ensure safe operation of organic peroxides [17].

Incidents caused by BPO have occurred as recently as 2017, when three workers at a southeast Arkansas peroxide manufacturing plant were injured in an explosion caused by BPO decomposition [18]. Therefore, its hazardous characteristics should be clearly identified and communicated to obtain reliable safety parameters, to establish optimal process conditions, and to design proper preventive measures. Continuous research needs to be performed to gain deeper understanding on the effect of various conditions on the decomposition of BPO.

Table 1 Selected thermal explosion incidents involving BPOs [6, 7]

Date	Location	Injuries	Fatalities	Hazard	Cause
1990	Daiichi Chemical Industry, Japan	17	9	Explosion	Manufacturing operations violation
1993	Food additives plant, Zhengzhou, China	33	27	Explosion	N/A
2001	Fu-Kao Chemical Plant, Taiwan	112	1	Explosion (reactor)	Runaway polymerization reaction
2003	Catalyst Systems, Inc., USA	1	0	Explosion (dryer)	Thermal decomposition during processing

1.3 Literature Review

A runaway reaction is the direct consequence of overheating in a reaction vessel. A positive feedback mechanism established between the temperature and reaction rate makes large equipment behave similarly to an adiabatic system [19]. A typical runaway trajectory is shown in Figure 3. Curve 1 represents normal operation condition at process temperature T_p, and curve 2 represents a runaway reaction. For curve 2, when the rate of heat generation is greater than rate of heat removal, reaction temperature increases. When the temperature reaches maximum temperature of synthesis reaction (MTSR), secondary reactions can be triggered which may ultimately lead to an uncontrolled runaway. Thermal risk can be evaluated by the probability of runaway and the severity of consequences. The probability can be assessed by parameters such as time to maximum rate (TMR), which gives an estimation of the time available for an emergency system to respond with corrective action to prevent runaway or implement mitigation measures. The severity of consequences can be assessed by parameters such as the adiabatic temperature rise ΔT_{ad}, temperature and pressure increase rate, etc. It should be denoted that a direct consequence of the temperature increase in a vessel is the pressure build up caused by the thermal expansion as well as the vapor pressure of the decomposing substances. In a thermal runaway incident, as the temperature increases, it is the rising pressure that leads to the loss of containment and subsequent fires and explosion. Therefore, pressure is the main hazard that needs to be noted in thermal risk evaluation.

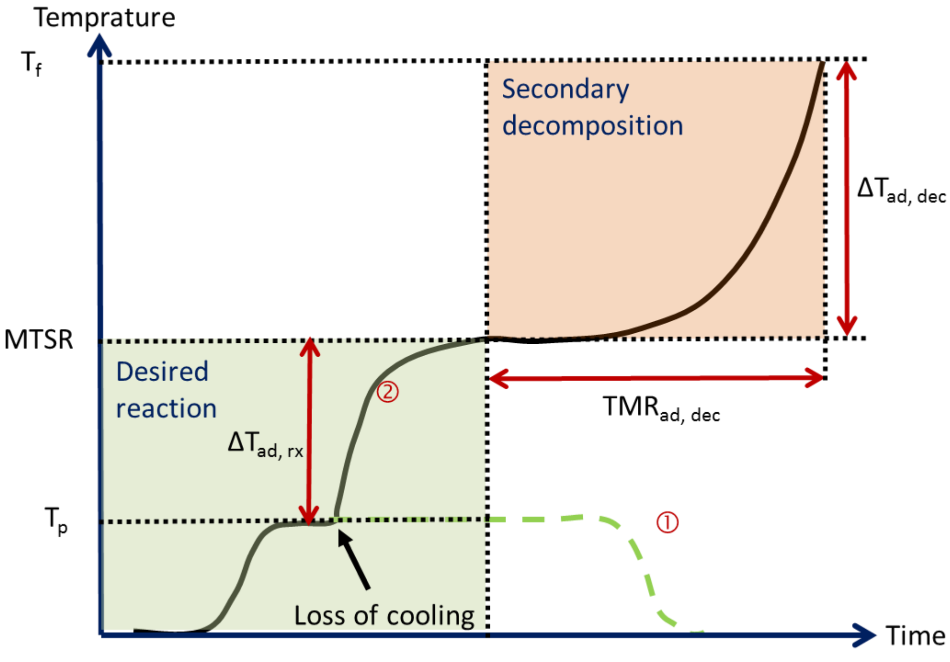

Figure 3 A typical Runaway Trajectory

A variety of reactive hazard identification methods are currently used, including literature searches, expert opinion, computerized tools (CHETAH, The Chemical Reactivity Worksheet, Bretherick's Database of Reactive Chemical Hazards, etc. Theoretical evaluations can determine potential energy of reaction, but they do not determine how fast or slow that energy can be released. The rate of reaction can be the critical factor in determining the severity of the reactive hazard. In addition, theoretical evaluation only provides a qualitative and rough identification and estimation of thermal hazards. Critical safety information needs to be evaluated experimentally in order to design inherently safer process and develop effective protection layers.

One of the major methods to keep balance between productivity and inherently safer design is thermokinetic evaluation through chemical reactivity testing and calorimetric studies. It is possible to quantify thermal runaway risk by following the systematic hazard review procedures along with calorimetric techniques [9, 20]. There are three types of calorimeters including isothermal calorimeter, screening techniques, and adiabatic calorimeter. Each type of calorimeter has different configuration and has its own expertise in terms of evaluation reactivity hazards.

Isothermal calorimeter is designed to study the reaction at the desired conditions. RC1 is a typical example of isothermal calorimeter and is a powerful tool to study optimized process conditions.

Screening techniques are cost-effective, fast, and can provide rough estimation on possible exothermic thermal activities. Differential scanning calorimetry (DSC) is a widely used screening tool for thermal hazards evaluation and decomposition mechanisms investigation of reactive chemicals. Information such as reaction heat, global kinetics can be obtained from a DSC; however, it does not provide pressure data. Another intrinsic drawback of DSC is that it uses very small quantity of sample in the experiments, making it difficult to extrapolate the results to a pilot plant scale. In addition, the onset temperature obtained from DSC cannot be applied directly to determine the practical reaction temperature or storage temperature, and it usually detects an exotherm at temperature much higher than that at pilot and industrial scales, and the heat of decomposition has a relatively large error of 5-10% [21].

Adiabatic calorimeter is employed to study reactions when things go wrong. The most common adiabatic calorimeters are the VSP (Vent Sizing Package), the APTAC (Automatic Pressure Tracking Adiabatic Calorimeter), the ARC (Accelerating Rate Calorimeter) and the PHI-TEC. Adiabatic calorimeter is more expensive and time consuming, but can provide more accurate “onset” and thermal runaway data (e.g. adiabatic temperature rise, rate of reaction, pressure rise in a closed vessel), which are important parameters in reaction scale up. Adiabatic calorimeter tests have been proven to be a more reliable method in evaluation of reactive hazards in bulk quantities under various conditions. Adiabatic experiments might fail to detect concentration effects such as autocatalysis [11], however, has advantage of better simulating real industrial worst case scenarios. The severity of a runaway reaction under an adiabatic environment is usually ranked by the self-heat rate or pressure-rise rate [16].

Among all the safety parameters, the self-accelerating decomposition temperature (SADT) is an important indicator. The SADT is defined as the lowest ambient temperature at which auto-accelerative decomposition of unstable substance occurs. SADT of hazardous chemicals in a container could determine the safe temperature of storage and transportation. The United Nations (UN) transportation regulations recommend that the temperature during the transportation of packaged samples should not exceed the SADT, which should be determined through reliable experimental methods. The SADT is generally determined by one of the following testing methods recommended in the UN orange book: the United States SADT test, the adiabatic storage test (AST), the isothermal storage test (IST), and the heat accumulation storage test (Dewar test) [22]. If the test sample shows vigorous self-accelerating decomposition at 50 °C, it is mandatory to provide controls during the usage, storage, and transportation of this chemical. Appropriate measures include the installation of refrigerating and air conditioning equipment, addition of inhibitors, and improvement of the shape, material, or volume of the container. NFPA 432 specifies the quantity, conditions for storage, solvent for dilution, material for packaging, and type of hazards of commercial organic peroxides [14, 16, 23, 24].

SADT in a full-scale package can be predicted by calculation based on the thermal explosion theory or analytical evaluations using lab-scale measurements with thermal calorimeters. The advantages of calorimeter test include smaller sample quantity and less time and money investment [25]. For liquids in homogeneous systems, the Semenov critical condition can be applied. For solids, the Frank-Kamenetskii model can be used. To evaluate SADT, it is important to understand the mechanism of decomposition reaction and obtain kinetic parameters from isothermal, non-isothermal and adiabatic calorimeters.

The most common instrument for evaluating SADT is the accelerating rate calorimeter (ARC). Fisher and Goetz applied ARC method to obtain SADT values for a variety of reactive substances. SADT of 50% BPO determined by ARC was 44 ºC [26, 27]. Whitmore and Wilberforce proposed to use ARC combined with thermal activity monitor (TAM) to better estimate SADT [28]. Therefore, calorimetry is an important technique to determine important safety parameters like SADT.

To understand the research in the field of BPO decomposition, a thorough literature review has been conducted and summarized in the following sections. The literature review focuses on the calorimeter study of thermal decomposition of benzoyl peroxide in various systems and apparatus. Thermodynamic and kinetic properties, and decomposition characteristics of benzoyl peroxide under different systems and conditions are described and compared, and gaps are identified.

1.3.1 Decomposition of BPO in Solvents

Many studies of benzoyl peroxide diluted in various solvents have been carried out since the 1940s. Studies in early days focused on kinetics, chemistry and mechanism of the decomposition reaction. The decomposition of benzoyl peroxide was shown to involve both unimolecular spontaneous thermal decomposition and bimolecular induced chain decomposition. Induced chain decomposition of benzoyl peroxide was most rapid in ether or amine solutions. Not only the rate, but also the stoichiometry of the decomposition was different in various solvents [29-32].

Nozaki and Bartlett studied the decomposition of benzoyl peroxide in over thirty solvents by heating solution at certain temperature and measuring the percentage of decomposition at given time intervals. Reaction rates varied in the following order: highly halogenated solvents < most aromatics < most aliphatics < ethers, alcohols, monohydric phenols < amines. It was found that the benzoate radicals could attack the solvent. If such attack resulted in more stable free radicals, the effect of the solvent should be to suppress the chain decomposition. If new radicals had similar stability to benzoate radicals, only the products and not the kinetics of the overall reaction should be affected [33, 34].

Benzene is one of the most commonly used solvents in the studies of thermal decomposition of benzoyl peroxide. The thermal decomposition of benzoyl peroxide in benzene has long been an important source of benzoyloxy and phenyl free radicals. Benjamin and William analyzed the kinetics and stoichiometry of benzoyl peroxide decomposition in benzene and investigated the effect of the peroxide concentration on the rate constant [30]. D. J. Brown studied the kinetics of thermal decomposition of benzoyl peroxide in benzene and nitrobenzene. It was also found that light accelerated but did not change the order of the reaction, and changing surface area had no effect [35]. G. B. Gill *et al.* studied the kinetics and products of benzoyl peroxide decomposition in benzene over a range of initial peroxide concentrations (0.01-0.04 M). Reactions of order 1 and 1.5 occurred simultaneously [36]. They also investigated the effect of nitrobenzene on the decomposition of benzoyl peroxide in benzene. The catalytic effect of nitrobenzene on the rate of peroxide decomposition and the change in the distribution of products were discussed [37]. Another study of BPO decomposition in dilute solutions found that when benzene was chosen as solvent, almost all the benzoate radicals generated from benzoyl peroxide lost carbon dioxide before entering into other reactions. Other substances such as styrene or cumene could react with free radicals and decrease the yield of carbon dioxide [38]. G. R. Chalfont *et al.* suggested a mechanistic scheme which rationalized the effect of added nitrobenzene on the nature of the products from the thermal decomposition of benzoyl peroxide in benzene [39]. DeLos F. DeTar *et al.* did a detailed quantitative product study of the thermal decomposition of BPO in benzene to give a definitive account of product distribution as a function of initial peroxide concentration [40].

A booming amount of research was developed related to the decomposition of benzoyl peroxide in various solvents focusing on kinetics and mechanism analysis. For example, the decomposition of benzoyl peroxide in the presence of iodine in solvents such as benzene, chlorobenzene and carbon tetrachloride solution were reported [41, 42]. Paul F. Hartman *et al*. measured the reaction rates and the apparent activation energies of benzoyl peroxide decomposition in dilute solutions of five hydrocarbons (benzene, t-butylbenzene, cyclohexane, methylcyclohexane, n-octane), and discussed about the decomposition mechanism [43]. Bailey *et al*. found that benzoyl peroxide in cumene decomposed by concurrent first and three-halves order reactions in 45-80 °C [44]. A mechanism study of the induced decomposition of BPO in a mixture of diethyl ether and sodium hydride. These results indicated that in the induced decomposition of benzoyl peroxide in ether the α-ethoxyethyl radical attacked predominantly on one of the oxygens of the peroxide link [45]. Benzophenone ketyl radical induced decomposition of benzoyl peroxide in benzene at 25 °C. The results showed that the rate determining step was the hydrogen abstraction from alcohol, and the transition state for the induced decomposition probably involved a partial hydrogen transfer from the ketyl radical to one of the peroxide oxygen atoms [46]. Foster *et al*. studied the decomposition reaction of benzoyl peroxide with isopropylbenzene, ethylbenzene, and p-xylene over a range of initial peroxide concentrations. A mechanism for the reaction of benzoyl peroxide with alkylbenzenes was suggested [47]. Simone Vidal *et al*. investigated the decomposition kinetics of benzoyl peroxide in pyridine and in pyridine-benzene in the presence and absence of inhibitor and found that pyridine could induce the decomposition of benzoyl peroxide to give pyridine N-oxide and benzoic anhydride [48]. Other solvents such as chlorobenzene, bromobenzene, as well as hydric solvents including ethanol, propylene glycol, and PEG 400, were also reported [49, 50]. Early study by differential scanning calorimetry was reported by decomposing benzoyl peroxide in di-n-butylphthalate and proved that DSC could become a standard method for thermal studies [51, 52].

The effect of other factors such as pressure and type of gas were also considered in previous literature. Nicholson *et al.* studied the rates of decomposition of benzoyl peroxide in carbon tetrachloride at temperatures of 60 °C and 70 °C in the pressure range 0 to 3000 kg/cm^2. The results showed that high pressures did not change the decomposition mechanism, and the effect of pressure was to decrease the rate of the unimolecular decomposition but to increase the rate of the chain decomposition [53]. Cheves Walling *et al.* found that the rate of decomposition of BPO in acetophenone at 80 °C was retarded 22% by a pressure of 1500 kg/cm^2. They also found that the decomposition of BPO in cumene/styrene solution was significantly accelerated by mercury at atmospheric pressure [54]. Russell investigated the effect of oxygen on the decomposition of initiators in aromatic solvents and the results showed that the overall rate of decomposition of benzoyl peroxide in cumene at 100 °C was retarded by oxygen [55]. K. Tokumaru *et al.* decomposed benzoyl peroxide in benzene in the presence of oxygen at various temperatures and found that phenyl radicals reacted with oxygen with a greater activation energy than with benzene [56]. The decomposition of benzoyl peroxide was conducted under CO pressure in benzene, cyclohexane and carbon tetrachloride solution reaction to demonstrate the reaction of phenyl radicals with carbon monoxide [57].

Staring from recent years, a few studies further investigated benzoyl peroxide decomposition in solvent using more advanced calorimeters. For example, Federica Barontini *et al*. reported the thermal hazard analysis of BPO in toluene solution by Phi-Tec II adiabatic calorimetry. Simultaneous thermogravimetric (TG)-differential scanning calorimetry (DSC)-Fourier Transformed InfraRed (FTIR) analysis was used to obtain the “onset” temperature, decomposition heat, and decomposition products. The results showed that the concentration of BPO in the solution strongly affected the decomposition rate [58]. A thorough literature review revealed that very few studies focused on the more concentrated BPO-solution system, which represents the mischarging scenario in industrial practices. Mischarging of initiators is one of the most possible mal-operation scenarios in polymer production process and its hazards have not been fully understood. Moreover, reactions under adiabatic conditions have attracted less attention and more effort is needed to quantify the thermal risks of BPO-solution system using more advanced calorimeter, which can provide useful information on inherent safer design.

1.3.2 Decomposition of Solid BPO

In early research, kinetic studies of benzoyl peroxide were limited to the decomposition in solvents. Later studies provided information on the kinetics and mechanism of thermal decomposition in pure state. Explosion hazard of benzoyl peroxide has been revealed in literature [59], and its high explosion hazard is connected with its high sensitivity to heating and high intensity of thermal explosion. Therefore, it is more difficult to deal with solid BPO sample because the decomposition reaction is explosive and more violent. This section introduces the chronicle of research effort that has been done in this field.

In 1964, P.C. Bowes studied isothermal decomposition of 98% benzoyl peroxide in the solid phase at atmospheric pressure in temperature range of 70 to 95 °C. The rate of decomposition was found to depend on the dimensions of the sample and partial vapor pressures of volatile decomposition products such as benzoic acid, diphenyl and phenyl benzoate [60]. The thermal decomposition of benzoyl peroxide pastes with plasticizers dimethyl phthalate and tritolyl phosphate were also investigated. The kinetics and thermal explosion risks were discussed and compared with dry benzoyl peroxide [61].

In 1967, D. H. Fine and Peter Gray investigated the decomposition of benzoyl peroxide (15 to 40 mg) in the temperature range of 105 to 140 °C. Their experiments showed that above 50 mm of mercury, the type of gas (argon, carbon dioxide, nitrogen and oxygen) and its pressure had no impact on the explosion delay time. However, small amount of oxygen could inhibit the decomposition in solution. The overall activation energy was 29±3 kcal/mole [62].

In 1968, P.C. Bowes examined dry solid (98% purity) BPO and paste BPO with plasticizer (65% peroxide, 35% dimethyl phthalate). The isothermal decomposition of 98% BPO, at temperatures below the melting point of the peroxide, had an autocatalytic character, while the paste had a relatively high initial rate and followed zero order. Explosion studies of dry peroxide were made with 30 g paste peroxide up to 800 g. Critical explosion data are consistent with isothermal decomposition data when compared in terms of the generalized Frank-Kamenetskii model of thermal explosion [63].

In 2009, Kai-Tai Lu *et al*. studied dust explosion characteristics of benzoyl peroxide with the MIKE 3 apparatus and the 20-l-Apparatus at room temperature and atmospheric pressure. 98% and 75% BPO had minimum ignition energy (MIE) values lower than 1 mJ, while 50% BPO had a MIE between 10 and 30 mJ, indicating that 98% and 75% BPO were more sensitive to static discharge. The maximum K_{St} (explosion index) values of 98%, 75% and 50% BPO were 245, 226 and 143 bar m/s respectively. In addition, Semenov's thermal explosion theory was applied to investigate the critical runaway condition and the stability criterion of decomposition reaction [11].

In recent years, more advanced calorimeters have been utilized for thermal hazard analysis. The commonly used techniques can be summarized into categories below:

Table 2 Thermal Hazard Analysis Techniques [14]

Thermal Analysis Technology	DSC, DTA
Isothermal Calorimetric Technology	TAM III
Adiabatic Calorimetric Technology	VSP2, ARC, APTAC, PHI-TEC
Reaction Calorimetric Technology	RC1, C80
Emergency Relief Control Technology	VSP2, RSST

Two kinds of experimental methods can be used for measuring the thermal data: isothermal and non-isothermal. Both can be used to evaluate the reaction kinetic parameters. Isothermal test methods use fewer experimental variables in a single measurement, so that the scope for ambiguity in the interpretation of experimental data is reduced, thus data interpretation is simpler and kinetic data is more reliable and of wider applicability [14]. Isothermal approach can simulate unit operations such as the storage, transportation, drying, or distillation process, during which a material is exposed to a constant temperature for an extended time that may cause the violent self-reaction and runaway reaction [64].

In 1984, F. Severini and R. Gallo studied the thermal decompositions of benzoyl peroxide with DSC and reported the half-lifetime and time required to decompose the entire peroxide. At 104.85 °C, BPO decomposition had a ΔH value relatively lower than that observed in dynamic measurements. This could be explained by a "cage effect", which should promote the recombination of primary radicals. In dynamic tests "cage effect" can be weakened, because the temperature will be gradually higher than the melting point and promotes the rapid migration of the radicals as well as the decomposition reaction. In addition, they studied the decomposition of BPO and 2,2'-azobisisobutyronitrile (AIBN) mixtures in the absence of a solvent. The mixtures decomposed without induction times and the DSC curves showed only one peak. At 79.85 °C and 89.85 °C, radicals generated by AIBN decomposition had a possible induced decomposition effect on BPO. At 104.85 °C mixtures showed a higher heat of decomposition than pure compounds alone [65, 66].

In 2001, F. Zaman *et al*. evaluated the degradation of BPO over a low temperature range of 20–45 °C using isothermal micro calorimetry and reported an activation energy of 137.8 kJ/mol. Arrhenius equation could satisfactorily estimate the values of the rate constant at significantly lower temperatures. In addition, solution phase degradation of 1.33 g BPO was conducted using UV-visible spectrophotometry. The activation energy obtained from UV-visible spectrophotometry at 55, 70 and 90 °C was 112.7 kJ/mol [67].

In 2005, Xin-Rui Li *et al*. reported an analytical procedure to characterize the decomposition reactions and analyze kinetics for BPO by means of isothermal method using a thermal activity monitor (TAM). Self-accelerating decomposition temperature (SADT) was evaluated under the assumptions of Frank-Kamenetskii thermal explosion model in a 500 ml Dewar vessel test and in a USA SADT test. The evaluated SADT was 72 °C in Dewar and 73.5 °C in 25 kg package [23].

In 2011, Dao-Xing Sun *et al*. studied thermal kinetics of benzoyl peroxide by accelerating rate calorimeter (ARC) and C80. The C80 micro calorimeter is a heat-flow calorimeter. In the C80 tests, 0.1990 g 99% BPO was heated at a rate of 0.1 °C/min from room temperature to 300 °C, and the detected "onset" temperature of BPO was 90.1°C. The reaction heat and E_a value obtained from C80 were -219.3 kJ/mol and 104.36 kJ/mol. In ARC tests, 1.9970 g BPO was heated from 60 °C to 400 °C; in this case, the "onset" temperature was determined to be 92.39 °C. They speculated that C80 data could obtain more reliable kinetic parameters of BPO than ARC method [7].

In 2013, Jiayu Lv *et al*. studied decomposition mechanism of benzoyl peroxide experimentally and theoretically. Differential scanning calorimeter, thermal scanning unit and accelerating rate calorimeter were used to record the temperature histories and pressure rise during BPO's decomposition. DSC dynamic tests showed there was a sharp endothermic peak followed by a sudden temperature rise, indicating that decomposition of BPO overlapped with its fusion, therefore, the exothermic onset temperature was unable to be accurately determined. DSC isothermal tests showed that higher temperature resulted in shorter induction period. Furthermore, DSC obtained symmetrical and bell-shaped curves at 88 °C and 90 ºC, proving that BPO decomposition was autocatalytic reaction. 0.4 g 98% BPO was tested in TSU with heating rate of 0.5 °C/min. The "onset" temperature was determined to be 90 °C and maximum temperature rise rate $(dT/dt)_{max}$ was 220 °C/min. TSU results showed that the decomposition of BPO can cause a very rapid pressure rise, indicating a high possibility of explosion once the runaway reaction occurs. In ARC tests, 0.32 g 98% BPO was used; and the "onset" temperature was found to be 94.3 °C. Quantum chemistry method was applied to study reaction mechanism and calculate thermodynamic energies of BPO molecule in gas phase [15].

Thermogravimetry (TG) was also applied to study the thermal stability of BPO. TG is widely used to investigate the kinetics of thermal decomposition at different stages of a runaway reaction. The advantage of dynamic TG over isothermal method is that mass change is measured as a function of increasing temperature, and one mass-loss curve equals a large number of isothermal mass-loss curves. Ming-Hsun Lee *et al*. employed 14.8-27.4 mg samples and heated samples at rates of 0.5, 1.0, 2.0, 4.0, and 10.0 °C/min with oxygen flow rate of 20.0 mL/min. Freeman and Carroll method was used to calculate the activation energy and the value was found to be 146.87 kJ/mol [6].

In 2019, An-Chi Huang *et al*. examined the thermal stability parameters of BPO under low concentrations (1.0, 2.5, 5.0, and 10.0 mass%.) using DSC, TG, and TAM III and compared the results of various linear regression models. Two stages of reaction were discovered in their multiple linear regression analysis, including an autocatalytic reaction and an n-order reaction. According to their results, ASTM E698 method was the optimal kinetic model to calculate thermokinetic parameters of BPO at various concentrations. In addition, BPO at different concentrations had different SADT values. They concluded that there might be risk of thermal runaway even at low concentrations of BPO during transportation [68].

In recent years, a green, precise and cost-effective approach including experiment and simulation has been established for energy reduction in thermal decomposition and explosion property study and thermal hazard assessment [4]. Research focusing on safety aspects of solid BPO decomposition reaction has attracted more attention and more work is needed to better understand its explosion hazard.

1.3.3 Decomposition of BPO with Other Substances

1.3.3.1 Polymerization Related Research

Polymerization is a very complicated process with thousands of products and recipes. Polymerization process has risks of thermal runaway under abnormal conditions, such as a wrong dose in a reactor, or contamination of vessel, leading to deviation from normal operating conditions and runaway reactions. A study of runaway reaction incidents for the year range from 1988 to 2013 showed that most of the incidents occurred in polymerization and decomposition processes. Although the number of incidents was reduced, the number of fatalities and injuries has increased by ~300% [69]. Factors (such as monomers, solvents, and inhibitors, etc.) that affect polymerization reaction can also influence the thermal stability of initiators. Numerous studies have been conducted to investigate the effect of various factors or the combination of these factors on initiator degradation. This literature survey covers a comprehensive but not exhaustive review of these studies with a focus on BPO decomposition. Undoubtedly, understanding the thermal behavior of BPO under various conditions could be a basis for improving the safety of polymerization.

Decomposition of benzoyl peroxide is widely used to initiate polymerization reactions and it is important to understand the kinetics of thermal decomposition of initiators in monomers. It is to be expected that the rates of decomposition of benzoyl peroxide in different solvents and monomers may influence the kinetics of the polymerization reaction [70]. For example, the decomposition of BPO in monomer allyl acetate as solvent at 80 °C was studied and the rate constant was determined under various initial peroxide concentrations [71]. It was found that the rates of BPO decomposition in solutions containing monomers were generally increased over those in the non-polymerizing solvent alone [72]. A mechanism for the decomposition of BPO at 91 °C in cyclohexane solution containing styrene was proposed. Styrene was not effective in capturing benzoate radicals in cyclohexane solution, but could compete against cyclohexane for phenyl radicals [73].

There were studies of the effect of metal ion on the thermal decomposition of benzoyl peroxide in solvents. For example, the effect of ferrous ion on the decomposition of benzoyl peroxide was studied in various solvents (methanol, ethanol, n-propanol and n-butanol) by thermal analysis method. The apparent rates were of first order and rate constants and activation energies were reported [74, 75]. The ferrocene - benzoyl peroxide initiating system is widely used in the processes of polymerization of olefins. The kinetic features and pathways of benzoyl peroxide decomposition in the presence of ferrocene were investigated [76-78]. The effect of copper salts on the thermal decomposition of benzoyl peroxide in benzene and chlorobenzene was also studied together with mechanism analysis [79].

Free radical initiators can be used as crosslinking of polymers. The decomposition characteristics of the crosslinking agent need to be investigated to select efficient operating conditions for a crosslinking process. Therefore, thermal decomposition of BPO in polymer is also worth studying. For example, the efficiency of BPO as crosslinking agent for polyethylene was studied as a function of concentration and temperature in relation with the resin melt flow index and particle size [80]. Kinetic regularities of decomposition of BPO in polystyrene medium [22, 81-84], polyethylene [85], polyisobutylene and polypropylene were also studied. Makarov *et al*. found that thermal decomposition of benzoyl peroxide in polyamide caused decomposition of polymer macromolecules. Chain decomposition of benzoyl peroxide was induced by polymer macromolecules and the order of the reaction was 1/2 [86]. They also studied the effects of ionol and oxygen on the thermal decomposition of the benzoyl peroxide in polyamide. The ionol could suppress the BPO chain decomposition and reduce the rate of polymer degradation initiated by BPO. The rate of BPO decomposition was slower in oxygen than that in an inert atmosphere [87]. The effect of oxygen and inhibitors (2,6-di-tert-butyl-4-methylphenol and 2,4,6-tri-tert-butylphenol) on kinetics of thermal decomposition of BPO in polyamide was also been investigated [88]. The non-isothermal degradation kinetics of cured polymer samples of bisphenol A diglycidyl ether diacrylate /BPO system was investigated in DSC and thermogravimetric (TG) and mechanism was discussed [89].

The natural mineral fillers used in polymer synthesis contain small amounts of metal oxides and can influence the polymerization process. Therefore, the thermal decomposition of benzoyl peroxide on surface of dispersed minerals such as oxides of iron (Fe_2O_3), chromium (Cr_2O_3) and vanadium (V_2O_5) in styrene solution was also investigated. The results showed that introduction of dispersed oxides increased the decomposition rate of peroxide [90].

Other organic peroxides were mixed with BPO to evaluate the thermal hazards. For example, tert-butyl peroxy-3,5,5-trimethylhexanoate (TBPTMH) was mixed with BPO and tested in DSC. It was determined that the degree of thermal safety of TBPTMH mixed with BPO was better than tert-butyl peroxybenzoate (TBPB) mixed with BPO due to higher T_o and lower ΔH_d [91, 92]. The rates of decomposition of benzoyl peroxide in presence of Lewis acids such as aluminum chloride and antimony pentachloride were also examined in order to investigate the initiation of copolymerization [93].

The complexity and diversity of research involving BPO decomposition is related to the tremendous numbers of polymerization systems, together with their complicated reaction conditions. Therefore, it requires a lot of effort to study its decomposition under various systems and conditions and it is crucial to understand its thermal behavior to make the reaction system safe and effective.

1.3.3.2 Study of Incompatible Materials

In the petrochemical industries, incompatible materials such as acid or alkaline solutions, metal ions and rust, are a common problem in both upstream and downstream production processes. Incompatible substances not only affect the yield and quality of the final products but also have impact on process safety. For incompatible contaminants, even a small amount of impurities could have catalytic effect and potentially accelerate the decomposition reaction. Barton and Nolan [94] analyzed 189 thermal runaway incidents in the period 1962-1987 and reported that 9% of the incidents were related to the raw materials quality control. According to CSB data [1], approximately 36% of the reactive chemical incidents in the US from 1980 to 2001 were related to chemical incompatibility. Sales *et al.* [95] studied 132 incidents occurred in Europe included in Major Accident Reporting System (MARS) database and found that about 11% of them were caused by the presence of impurities/contaminants.

There is a lot of research to investigate the thermal decomposition of BPO in the presence of other materials. Some substances only dilute the system, but others may participate in the radical chain process or trigger the thermal runaway. There are studies of thermal decomposition of solid benzoyl peroxide in the presence of solid admixtures. The course of thermal decomposition of benzoyl peroxide in four types of solid media was investigated by DSC. The decomposition reactions in dilute solid media remained autocatalytic, but the induction times were shortened in the presence of different admixtures [96, 97]. Other solid media were also investigated, including various kinds of carbon blacks, activated charcoal and colloid silica. Effects of surface area, chain structure, free-spin concentration, BPO concentration and mixing time were discussed [98, 99]. The thermal characteristics of BPO mixed with carbazole and its derivatives were also studied using DSC. The results indicated that the hazard increased with lower activity energy and exothermic peak when mixing with electron-rich conjugated systems such as carbazole and N-alkyl carbazole [100].

Contaminants can form potentially hazardous mixtures in storage tanks or bulk-shipping tanks which can result in thermal decomposition. Acids (such as nitric acid, sulfuric acid, phosphoric acid, and hydrochloric acid), and bases (such as sodium hydroxide and potassium hydroxide) are widely used as catalysts and reactants in chemical industries. Both could be potential contaminants during process or storage.

Yih-Shing Duh *et al*. evaluated hazards of nine organic peroxides, including benzoyl peroxide, with DSC, vent sizing package 2 (VSP2) and ARC. They recommend that if a contaminant added to the peroxide system lowers the onset temperature more than 25 °C or increases the heat of decomposition more than 25%, the chemical is classified as incompatible. They found that strong acid did not change the “onset” temperature too much, but the thermogram became broader. However, 6N NaOH reduced the “onset” temperature of BPO decomposition significantly, revealing great incompatibility [16]. Jo-Ming Tseng *et al*. assessed thermokinetic parameters and safety indices of BPO decomposition contaminated with sulfuric acid and sodium hydroxide using thermal activity monitor III (TAM III). They found that the stability of BPO mixed with NaOH was greater than the original BPO and that mixed with H_2SO_4. Simulations of a 0.5 L Dewar vessel and 25 kg commercial package in green thermal analysis technology were performed [24]. Lung-Chang Tsai *et al.* studied exothermic decomposition of three solid organic peroxides by DSC and VSP2. The results showed that when 75 mass% BPO was mixed with 6 N H_2SO_4, the ΔH_d was increased from 1045 to 1229 J/g and the degree of hazard increased when BPO was mixed with incompatible solutions [101]. S. H. Liu *et al*. evaluated thermal runaway hazards of three organic peroxides (CHP, BPO, and DCPO) contaminated by acids and alkaline using DSC, VSP2 and TAM III. They concluded that the degree of hazard prominently increased when these peroxides mixed with H_2SO_4, or NaOH, or Na_2SO_3 [64]. Sheng-Hung Wu *et al*. measured several organic peroxides with DSC and VSP2. The "onset" temperature of BPO was determined to be 103 °C, with reaction order of 0.9, reaction heat of 1000 J/g and activation energy of 188 kJ/mol. SADT was calculated to be 70 °C and T_{NR} was determined to be 63.9 °C. When HCl was added to BPO solution, ΔH_d of BPO/HCl increased tremendously, therefore, HCl was proved to be incompatible with BPO [5]. Thermal behavior of BPO mixed with NaOH solution was studied by DSC and the reaction was demonstrated to be a multi-step reaction by model-based method. SADT was predicted to be -1 °C and BPO with NaOH solution was more hazardous than BPO alone [102].

As can be seen from the above, the findings of different research groups were not consistent and often contradictory; hence, more research is needed to identify the effects of contaminants on BPO thermal decomposition.

There are studies of BPO decomposition mixed with its own decomposition products. Tien-Szu Wang *et al*. proved that BPO decomposition was an autocatalytic reaction when mixed with benzoic acid by TAM III. The obtained thermal runaway data such as TMR_{iso}, ΔH_d and Q_{max} can be fully exploited for thermal hazard evaluation and emergency planning [103]. S. H. Liu *et al*. evaluated the thermal hazard of autocatalytic reaction for benzoyl peroxide mixed with benzoic acid, benzene, and phenol by DSC and TAM III [8]. Bin Laiwang *et al*. studied thermal hazards of BPO mixed with its derived products (benzoic acid, biphenyl, methyl benzoate, and benzene) through calorimetric technologies and thermodynamic assessment. The results showed that BPO mixed with its by-products caused the degree of thermal hazard to be much higher with lower T_o, lower E_a, and advanced TMR_{iso}, especially for biphenyl [104]. Hua-bo Li *et al*. analyzed thermal risk of benzoyl peroxide in the presence of phenol through experimental and simulation approach. The DSC results indicated that the phenol significantly reduced the thermal stability of BPO and the Benito-Perez model was credible to describe the reaction kinetics. The simulation results predicted that the explosion could take place even at the 40 °C for 50 kg packaging sample [105].

Impurities or contaminants caused by incompatible materials can not only affect the quality of raw material, but also become a great threat to the safety of the process. Certain precautions must be taken in the production process, for instance, incompatible materials should not be stored together; the residual of incompatible chemicals in a batch reactor should be thoroughly removed, etc. It is desired to establish a complete database of incompatible materials to assist reactive hazard management. This research focuses on the selected acids, bases and salts and endeavor to evaluate the compatibility of these materials with benzoyl peroxide.

Selected previous works are summarized in Tables 3-6. The gaps identified from literature review are discussed below:

- Most of the studies were based on screening techniques, which has relatively small scale and large heat loss. They are used as initial screening test for hazard identification, but are not capable of analyzing risk for real industrial scenarios.
- There is a lack of quantitative risk assessment of the thermal decomposition of BPO under runaway conditions. To identify and assess its thermal hazard and pressure hazard, it is necessary to perform a comprehensive experimental study on the influence of different parameters on the runaway severity.
- The results and conclusions are inconsistent regarding the effect of commonly used acids and bases on the thermal stability of BPO. It is important to clarify the discrepancies reported in the literature to facilitate a better understand of the influence of impurities or contaminants on such reactive organic peroxide.
- Few study investigate the effect of water and dry fire-extinguishing chemicals on thermal stability of BPO. The knowledge is of great importance in firefighting application and risk mitigation.

Table 3 BPO decomposition by DSC

System	Temperature (°C)	Scan Rate (°C/min)	T_o (°C)	T_{max} (°C)	-ΔH (J/g)	Ea (kJ/mol)	Ref
BPO	94.85 99.85 104.85				674.9 806.0 801.1		[65]
	49.85-279.85	10			1602		
BPO		10 K/min	113		369 cal/g		[21]
BPO			108		438 cal/g		
75% BPO	20, 25, 30, 40, 45					137.8	[67]
98%, 75%, 50% BPO	25-180	4	110	111.8 108.7 108.5	1047.78 957.04 771.16		[11]
98% BPO	88, 90, 92, 94, 96					191	[15]
	30-200	1 2 4 8		101.52 102.85 104.07 109.16	1184.4 1226.1 1386.6 1094.5	637	
75% BPO	30-300	0.5 1 2 4 10	73 94 95 98 150	101.5 103.5 103.6 107 210	1016 1165 1112 990 989	239 229	[106]
75% BPO	30-300	1 2 4 10	100 102 106 108	101.0 104.0 109.0 118.0	742 789 1178 1130	146.9	[6]
75% BPO	30-300	4	105	108	736		[8]
75% BPO	30-300	0.5 1 2 4	100 101 103 104	100 102 104 107	758 875 845 1045	130	[4]
75% BPO	30-500	5	108.5		1260		[58]

Table 4 BPO decomposition with additives by DSC

System	Scan Rate (°C/min)	T_o (°C)	T_{max} (°C)	$-\Delta H$ (J/g)	Ref
BPO	4	105		1034	[16]
BPO+6N HCl		104		2448	
BPO+6N NaOH		60		1436	
75% BPO	4	102	107	1045	[101]
75% BPO+ 6N H_2SO_4		104	107	1229	
75% BPO+ 6N NaOH		105	108	975	
75% BPO	4	102	107	1047	[64]
75% BPO+1N H_2SO_4		104	107	1229	
75% BPO+1N NaOH		105	108	975	
BPO	4	103	111	1332	[5]
BPO+H_2SO_4		103	110	239	
BPO+ HCl		118	118	2390	
BPO+ NaOH		105	108	140	
75% BPO+95% benzene		105	109	770	[8]
75% BPO+98% benzoic acid		96	119	799	
75% BPO+97% phenol		98	128	869	
BPO + carbon blacks/charcoal/colloid silica	32K/min				[98]

Table 5 BPO decomposition by thermal activity monitor (TAM)

System	Temperature (°C)	Scan Rate	TMR_{iso} (h)	-ΔH (J/g)	Ea (kJ/mol)	Ref
75% BPO+ 99.7% toluene	80 90 100		25.4 15.5 0.5		182.3	[6]
75% BPO+ 98% benzoic acid/ 95% benzene/ 97% phenol	70 80 90 100	2 K/h	0.08-251	389-1140		[8]
75% BPO	85 90 95		14.8 4.71 1.31			[14]
75% BPO+ 99% benzoic acid	70 80 90	2 K/h	0.25-332.68	888.1-1068.5		[103]
75% BPO, 75% BPO+6N H_2SO_4/NaOH	80 90	2 K/h	28.6 25.6 31.1	1085 1031 921		[64]
75% BPO+10 mass% 6N H_2SO_4/NaOH	80	2 K/h		996.56 854.17 792.42	100.16 84.27 110.84	[24]
75% BPO	65 70 72 75				188.6	[23]
98% BPO	70-95					[60]

Table 6 BPO decomposition by adiabatic calorimeter

System	Equipment	Sample Size	T_o (°C)	T_{max} (°C)	P_{max}	$(dT/dt)_{max}$	$(dP/dt)_{max}$	Ref
75mass% BPO + toluene	VSP2	20, 30, 40 mL 20mass % BPO				2.7 °C /min	10.19 psig/min	[106]
98% BPO (N_2 purging 30mL/min)	ARC	0.32 g	94.3			150 °C/min	16 bar/min	[15]
75% BPO, 75% BPO + 6N H_2SO_4/ NaOH	VSP2	5 g BPO+ 0.25 g H_2SO_4/ NaOH	94 87 89	316 300 311	326 291 302 psig	12354 13452 13612 °C /min	7084 15781 21664 psig/min	[64]
75% BPO, 75% BPO + 6N H_2SO_4/ NaOH	VSP2	5 g BPO +2.5 g H_2SO_4/ NaOH	94 88 89	316 300 310	23 21 22 bar	12354 16451 13612 °C /min	490 1089 1495 bar/min	[101]
99% BPO	ARC	1.997 g	92.4	138.75		80.38 °C /min		[7]
98% 75% 50% BPO	ARC	5 g	70.6 73.4 78.4	262.9 190.4 168.6	137.9 97.0 35.1 bar	178.75 120.34 87.08 K/min		[11]
Synthesized BPO	PHI-TECII	1.01 g	67.6	199.24	3.967 Mpa	4598.3 °C /min		[12]
20%, 25%, 30%, 40% by weight BPO + toluene	PHI-TECII	6 mL	78.6 72.1 70.5 70.7	118.3 139.8 173.5 222.0	11.4 15.2 21.6 30.0 bar	0.61 5.41 112.0 609.1 °C /min	0.13 1.09 29.2 127.8 bar/min	[58]

CHAPTER II

OBJECTIVES AND METHODOLOGY

2.1 Objectives

The objective of this study is the advancement of understanding the thermal decomposition of BPO under various conditions to mitigate the risks during storage, transportation and production processes involving BPO. More specifically, BPO was studied in three different systems: 1) solid phase BPO decomposition, 2) BPO decomposition in solvent, and 3) BPO compatibility study mixed with selected acids, bases or salts. Chemical reactivity of BPO in different systems were investigated experimentally using screening techniques and adiabatic calorimeter, aiming to: (1) assess the influence of various experimental conditions at lab-scale, (2) understand the behavior of thermal decomposition of BPO under runaway conditions, (3) evaluate the compatibility of selected additives with BPO to mitigate the thermal risks associated with its decomposition. The obtained critical safety indicators, thermodynamic and kinetic parameters can be useful in safely handling energetic organic peroxide in terms of thermal runaway prevention, protection layer design, and developing emergency responding measures. Below are various sub-objectives of this research.

1. To study the thermal decomposition of BPO in solid phase under various environmental conditions to help understand the hazards and reduce the risks of BPO during storage and transportation.

- Evaluate the thermal stability of pure BPO using pseudo-adiabatic calorimetry to determine its runaway behavior and parameters associated with its decomposition
- Assess condition-dependent thermal decomposition of BPO, including the effect of concentration, sample size, confinement, and isothermal testing to provide a better understanding of explosion hazards of BPO
- Evaluate the effect of selected acids and bases (NaOH, HCl, H_2SO_4, HNO_3, H_3PO_4), which are commonly used in chemical industry and have potential of contaminating BPO system during production processes to close the gaps or clarify discrepancies in literature.

2. To study the thermal stability of BPO in alkylbenzene solvent under adiabatic conditions to determine its runaway behavior and parameters.
    - Characterize the physical, thermodynamic and kinetic behavior of BPO hybrid system when diluted in solvent using an advanced adiabatic calorimeter to provide a more realistic assessment of the runaway features at industrial scale
    - Identify the influence of experimental conditions (solvent, sample concentration, sample volume) on the severity of the runaway decomposition
    - Analyze the mechanisms of decomposition of BPO in alkylbenzene solvent.
3. To study the effect of dry fire-extinguishing chemicals on the thermal stability of BPO.
    - Investigate the effect of dry fire extinguishing chemicals ($NH_4H_2PO_4$, $NaHCO_3$, $KHCO_3$) on BPO decomposition to identify inhibitors that could potentially mitigate the risk of BPO decomposition.

2.2 Methodology

In this research, calorimetric measurements using Advanced Reactive System Screening Tool (ARSST) and Automated Pressure Tracking Adiabatic Calorimeter (APTAC) were used to complement previous studies on BPO using other calorimetric techniques.

2.2.1 Advanced Reactive System Screening Tool (ARSST)

The ARSST is a pseudo-adiabatic calorimeter manufactured by Fauske and Associates. It can screen reactive chemical systems for pressures up to 500 psig and temperatures up to 700 °C. The standard containment vessel is 350 ml with a 10 ml open glass test cell. In this apparatus only the test cell is heated, while the containment vessel remains at ambient temperature. The ARSST can handle larger quantities of BPO compared to the Differential Scanning Calorimeter (DSC) which uses only several milligrams of sample. As mentioned before, DSC data can assess thermal hazard by providing heat generation information for small sample quantities, but are not enough to adequately assess the reaction hazards at industrial scales under worst-case scenarios. Compare to DSC, another advantage of ARSST is that it can obtain pressure data. A sample is usually heated at a constant rate, which could vary from 0.5 °C/min to 30 °C/min, attempting to simulate fire or explosion scenarios. In this study, single ramp-polynomial control mode was used. This method provides constant power to the sample and can heat the sample smoothly. The heat-up rates for each experiment can differ, however, due to variation in heat capacity and sample volumes. As a result, samples can experience various power rates [107]. A simplified schematic diagram of the ARSST is shown in Figure 4. The ARSST is often used as a screening tool, and combined with other instruments, like adiabatic calorimeters, to obtain more precise results and quantitative analysis.

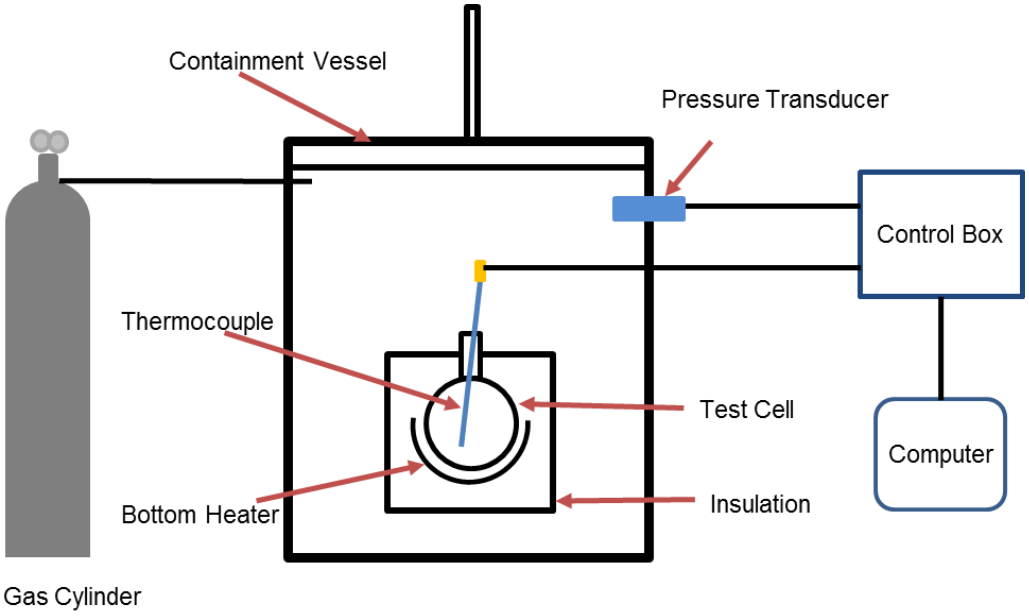

Figure 4 Simplified diagram of the ARSST

Temperature and pressure data are recorded and the plots are drawn including temperature vs. time, pressure vs. time, self-heating rate vs. temperature, and pressure rate vs. temperature. The key parameters are obtained from these plots, including the "onset" temperature, "onset" pressure, maximum self-heating rate, maximum pressure-rise rate, maximum temperature, temperature at maximum self-heating rate, and final temperature, etc.

Figure 5 Photograph of ARSST calorimeter

2.2.2 Automatic Pressure Tracking Adiabatic Calorimeter (APTAC)

The APTAC was developed by Arthur D. Little and commercialized by Netzsch. The APTAC is a closed cell system and can be operated at temperatures up to 500 °C and pressures up to 2000 psi in a batch process. It enables the use of a relatively large sample size and maintains the sample at near adiabatic conditions by minimalizing the temperature and pressure difference in and out of the test cell. Heat losses are minimized by measuring the temperatures of sample, test cell wall, and nitrogen surroundings with type-N thermocouples, and keeping the temperature surrounding the sample as close as possible to that of the sample with heaters. Nitrogen is injected into the containment vessel at a rate of up to 20000 psi min^{-1} to prevent the test cell from bursting due to internal pressure generation, ensuring the pressure difference across the wall of the test cell is less than 10 psi. The reaction vessel or test cell is a spherical flask, which can be constructed of various materials including glass, titanium, and stainless steel. Figure 6 shows a simplified diagram of the APTAC. The test cell is placed inside a containment vessel and the containment vessel is sealed with two safety clamps [108].

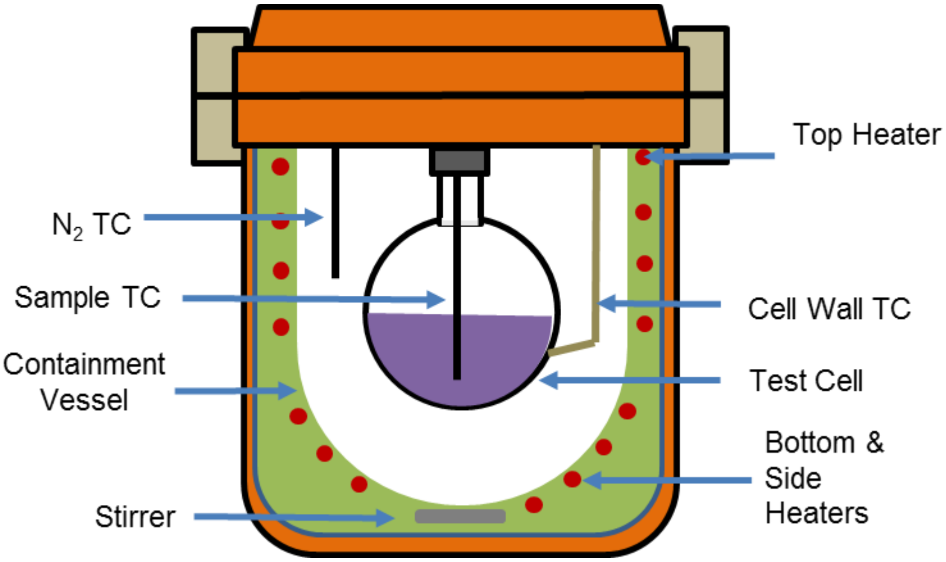

Figure 6 Simplified diagram of the APTAC

In this work, operating mode of Heat-Wait-Search (HWS) was used. In HWS mode, the sample is heated up to the preset temperature, and then the system temperature stabilizes and stays constant for a while, and then the equipment searches for an exotherm. An exotherm means that the self-heating rate of the sample is greater than the pre-determined threshold (determined as 0.05 °C/min in this study). If an exotherm is not identified, the sample is heated up by a certain temperature increment and continues the cycle until an exotherm is detected. When an exotherm is discovered, the APTAC automatically shifts to adiabatic mode until the reaction completes or the shutdown criteria is met. Figure 7 shows a typical HWS track. The "onset" temperature is defined as the temperature at which the exotherm is first detected. Other important safety parameters can also be determined from the plotted data, such as maximum temperature, temperature at maximum rate, time to maximum rate (TMR), etc.

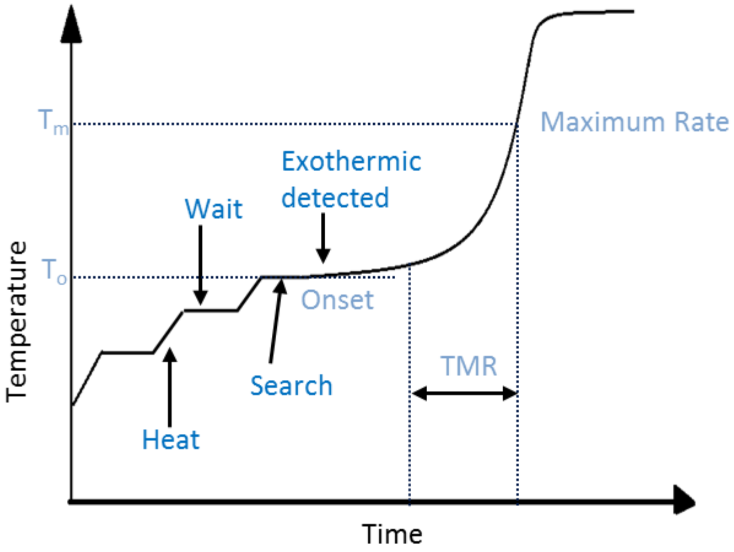

Figure 7 "H-W-S" mode of the APTAC

2.2.3 Analysis of Thermodynamic and Kinetic Parameters

Basically, there are two kinds of models to use for the thermal decomposition of BPO, nth order model and autocatalytic model [4] [14]:

Nth-order reaction:

$$\frac{d\alpha}{dt} = k_0 e^{-\frac{E_a}{RT}}(1-\alpha)^n \qquad \text{Equation 1}$$

Autocatalytic reaction:

$$\frac{d\alpha}{dt} = k_0 e^{-\frac{E_a}{RT}}(1-\alpha)^{n1}(\alpha^{n2} + z) \qquad \text{Equation 2}$$

where E_a is the activation energy, k_0 is the pre-exponential factor, z is the autocatalytic constant, and n1 and n2 are the reaction orders of a specific stage.

For non-isothermal tests, there are several analytical approaches to calculate the thermokinetic parameters, such as Ozawa, Friedman, and Freeman and Carroll method. Ozawa and Friedman methods require experiments of different heating rates:

$$\frac{2.15d[\log(\beta)]}{d(\frac{1}{T_{max}})} = -\frac{E_a}{R} \qquad \text{Equation 3}$$

where E_a can be calculated from the slope of the plot of log (β) again $T^{-1}{}_{max}$ [109]. Freeman and Carroll is a difference-differential method using mass loss with respect to temperature change between two adjacent points [6].

For isothermal tests, Li and Koseki describe the kinetic calculation method depending on various isothermal temperatures:

$$\frac{q_m}{D_0} = -\Delta H \beta k \alpha_m^{1-x}(1-\alpha_m)^{1-y} = A\exp(-\frac{E_\alpha}{RT}) \qquad \text{Equation 4}$$

where q_m is the value of heat flow when the rate of the reaction is maximum. D_0 is defined as the amount of sample at the time t = 0. β is defined as the fraction of the peroxide which ultimately react. Thus, a plot of $\ln(q_m/(D_0\Delta H\beta k))$ against 1/RT will be linear and have a slope of $-E_a$ [23].

In an adiabatic reaction system, the following assumptions are made in order to derive the kinetic parameters of an exothermic reaction from experimental data [11]:

(1) The reaction mechanism is assumed to be independent of temperature.

(2) Single reaction, with nth order global kinetics.

(3) The reaction rate constant, k, follows the Arrhenius equation.

(4) The total heat generated is evaluated from the adiabatic temperature rise assuming constant heat capacity.

(5) The conversion of concentration (or the extent of reaction) can be expressed in terms of temperature increase as a fraction of the total adiabatic temperature rise.

For adiabatic reaction process, kinetic parameters can be evaluated from equation derived by Townsend and Tou [17]:

$$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} = \ln \frac{dT/dt}{T_f - T} \qquad \text{Equation 5}$$

Reaction kinetics can be determined from the experimental data based on the following equations [7]. According to the heating rate Equation 6:

$$M_T = \Delta T_{ad}\, k \left(\frac{T_f - T}{\Delta T_{ad}}\right)^n \qquad \text{Equation 6}$$

Equation 7 can be obtained:

$$k = \frac{M_T}{\Delta T_{ad}\left(\frac{T_f - T}{\Delta T_{ad}}\right)^n} \qquad \text{Equation 7}$$

Combining the Arrhenius law Equation 8:

$$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \qquad \text{Equation 8}$$

Equation 9 can be obtained:

$$\ln \frac{M_T}{\Delta T_{ad}\left(\frac{T_f - T}{\Delta T_{ad}}\right)^n} = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \qquad \text{Equation 9}$$

Using the adiabatic data obtained in experiment, a multiple linear regression can be performed to calculate n. If the calculated n is accurate, the plot of lnk vs 1/T is linear. Then the kinetic parameters E_a and A can be calculated.

For real calorimeters, a portion of heat generated by heaters will be consumed by the sample cell, therefore, temperature of sample is not able to represent the heat absorbed by the sample and the cell. To deal with this problem, a thermal inertia factor, φ, is introduced to correct temperature data. The φ factor is defined as Equation 10.

$$\varphi = 1 + \frac{m_c \cdot c_{p,c}}{m_s \cdot c_{p,s}} \qquad \text{Equation 10}$$

where m is the mass, c_p is the heat capacity, and subscript s and c stand for the sample and the cell respectively.

The heat of reaction, ΔH_d, can be estimated by Equation 11, assuming that c_p is not a function of temperature [110].

$$-\Delta H_d = \frac{m \cdot c_p \cdot \varphi \cdot \Delta T_{ad}^{mes}}{n} \qquad \text{Equation 11}$$

In this equation, m is the sample mass, n is the moles of material reacted, c_p is the heat capacity of the sample, ΔT_{ad}^{mes} is the measured adiabatic temperature rise and defined as Equation 12:

$$\Delta T_{ad}^{mes} = (T_f - T_o) \qquad \text{Equation 12}$$

where T_o is the “onset” temperature and T_f is the final temperature of the reaction.

CHAPTER III

THERMAL DECOMPOSITION OF SOLID BENZOYL PEROXIDE UNDER VARIOUS CONDITIONS*

3.1 Synopsis

In this chapter, the experimental study of thermal decomposition of solid benzoyl peroxide (BPO) was conducted using the Advanced Reactive System Screening Tool (ARSST) and results are compared with the literature. ARSST provides thermal stability information such as the "onset" decomposition temperature, maximum temperature and pressure, maximum pressure rate and self-heat rate. Compared with other screening tools such as DSC, ARSST is superior because it analyzes a greater number of samples. The results reveal hazards during storage, transportation and handling of BPO, and can be useful in the design safety measures to avoid runaway reactions. The detected "onset" temperature highly depends on the sensitivity and accuracy limits of the calorimeters. The "onset" temperatures of 75% BPO and 98% BPO were determined to be 98 °C and 79 °C. The confinement tests showed that adding initial pressure can decrease the "onset" temperature, as well as increase the maximum self-heating rate, maximum pressure rise rate, and maximum temperature. Isothermal aging tests were conducted to study the effect

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* This Chapter contains material reprinted with permission from "Thermal decomposition of solid benzoyl peroxide using Advanced Reactive System Screening Tool: Effect of concentration, confinement and selected acids and bases" by Y. Shen, W. Zhu, M. Papadaki, M. S. Mannan, C. V. Mashuga, Z. Cheng, 2019. *Journal of Loss Prevention in the Process Industries*, 60, 28-34, Copyright [2019] by Elsevier.

of induction. A higher isothermal temperature shortened the induction time. The results showed that BPO can decompose at 75 °C if held at this temperature for a period of time, and the “onset” temperature in isothermal tests can be much lower than that measured in dynamic screening tests. In addition, effect of selected acids and bases on BPO thermal decomposition were investigated. All the additives had little impact on the BPO decomposition reaction under the tested conditions. Further experiments are needed to investigate the thermal hazards of mixtures. Our research is the first in the literature to study BPO decomposition using ARSST and the results provide useful information to characterize hazardous decomposition, and design safe measures during drying, storage, and transportation of BPO.

3.2 Materials and Methods

75% benzoyl peroxide (Sigma Aldrich, Luperox® A75, 75%, remainder water) and 98% benzoyl peroxide (Sigma Aldrich, Luperox® A98, reagent grade, ≥98%) were used without further purification. Nitrogen was used to purge and pressurize the ARSST pressure containment vessel before each experiment. Additives examined in this study include: hydrochloric acid solution (Sigma Aldrich, 1.0 N and 6 N), sulfuric acid solution (Sigma Aldrich, 1.0 N and 5 N), nitric acid solution (Sigma Aldrich, 1.0 N and 10 N), phosphoric acid solution (Sigma Aldrich, 85 wt %), and sodium hydroxide solution (Sigma Aldrich, 1.0 N).

In a typical experiment, solid BPO was weighed and loaded into the 10 ml glass test cell. When an additive was included, the additive was weighed and mixed with the BPO by shaking for 1 min. Since the additive amount is relatively small and the mixture is relatively stable at room temperature, any partial reaction during mixing stage cannot be detected and can be neglected. To study the effect of confinement, 0.5 g of solid BPO sample was tested under various initial pressures, including 80 psig, 150 psig, and 200 psig. Before each test, nitrogen was applied to the containment vessel including the test cell, to the initial back pressure. All measurements were preceded by nitrogen purging. A polynomial heating ramp was used with a heating rate of 2 °C/min. The shutdown temperature and pressure limits were set to 400 °C and 400 psig, respectively.

3.3 Results and Discussion

In this work, the "onset" temperature T_o is defined from the self-heating rate profile. This parameter is estimated as being the intersection between the tangent of the fast ascending self-heating rate and the horizontal baseline. $(dT/dt)_{max}$ is the maximum temperature-rise rate during the entire reaction process; it is determined from the self-heating rate data. $(dP/dt)_{max}$ is the maximum pressure-rise rate determined in a similar fashion. T_{max} is defined as the temperature at maximum self-heating rate $(dT/dt)_{max}$. T_f is defined as the temperature when the reaction completes and represents the temperature when the self-heating rate equals to zero. P_f is defined in similar way, which is the highest pressure during the reaction. P_c is the pressure after cooling down.

3.3.1 Thermal Scanning of Pure Solid BPO

The thermal decomposition of 0.5 g 75% BPO and 0.3 g 98% BPO was evaluated under ambient pressure. The test cell broke when increasing 98% BPO to 0.5 g, so 0.3 g was chosen for decomposition tests. The temperature history, pressure history, self-heating rate and pressure rise rate profiles are shown in Figure 8 for all three replicate tests. More detailed data for each experiment are summarized in Table 7. This research is the first to report results of BPO tests under various conditions with ARSST.

Table 7 Experimental data for pure BPO under ambient pressure

Chemical	T_o (°C)	P_o (psig)	T_{max} (°C)	T_f (°C)	P_f (psig)
75% BPO	97.6(±3.5)	5.6(±0.3)	104.4(±3.1)	120.5(±2.5)	12.0(±0.5)
98% BPO	78.9(±2.6)	2.7(±2.0)	87.8(±8.3)	109.5(±21.7)	9.4(±0.2)

As can be seen from Figure 8, the three replicate tests for BPO are not identical. The time to "onset" was different, but the "onset" temperatures obtained were relatively close. This is commonly the case in measurements involving solid reactants because ARSST has only one thermocouple which is located at the center of the test cell. For solids, the heating rate, the heat transport and the temperature distribution within the sample is not expected to be homogeneous which could lead to differences in time to "onset". However, the overall trends and the measured critical parameters were very similar.

The average "onset" temperature of 75% BPO was around 98 °C, which is similar to literature data [106]. The maximum self-heating rate average value was 6366 °C/min and the maximum pressure rate had an average of 6484 psi/min, showing that decomposition of solid BPO can generate heat and gas very rapidly. The average "onset" temperature for 98% BPO was measured to be 79 °C and was approximately 20 °C lower than that of 75% BPO. The average value of the maximum self-heating rate was 6946 °C/min, and the maximum pressure rate average was 4939 psi/min.

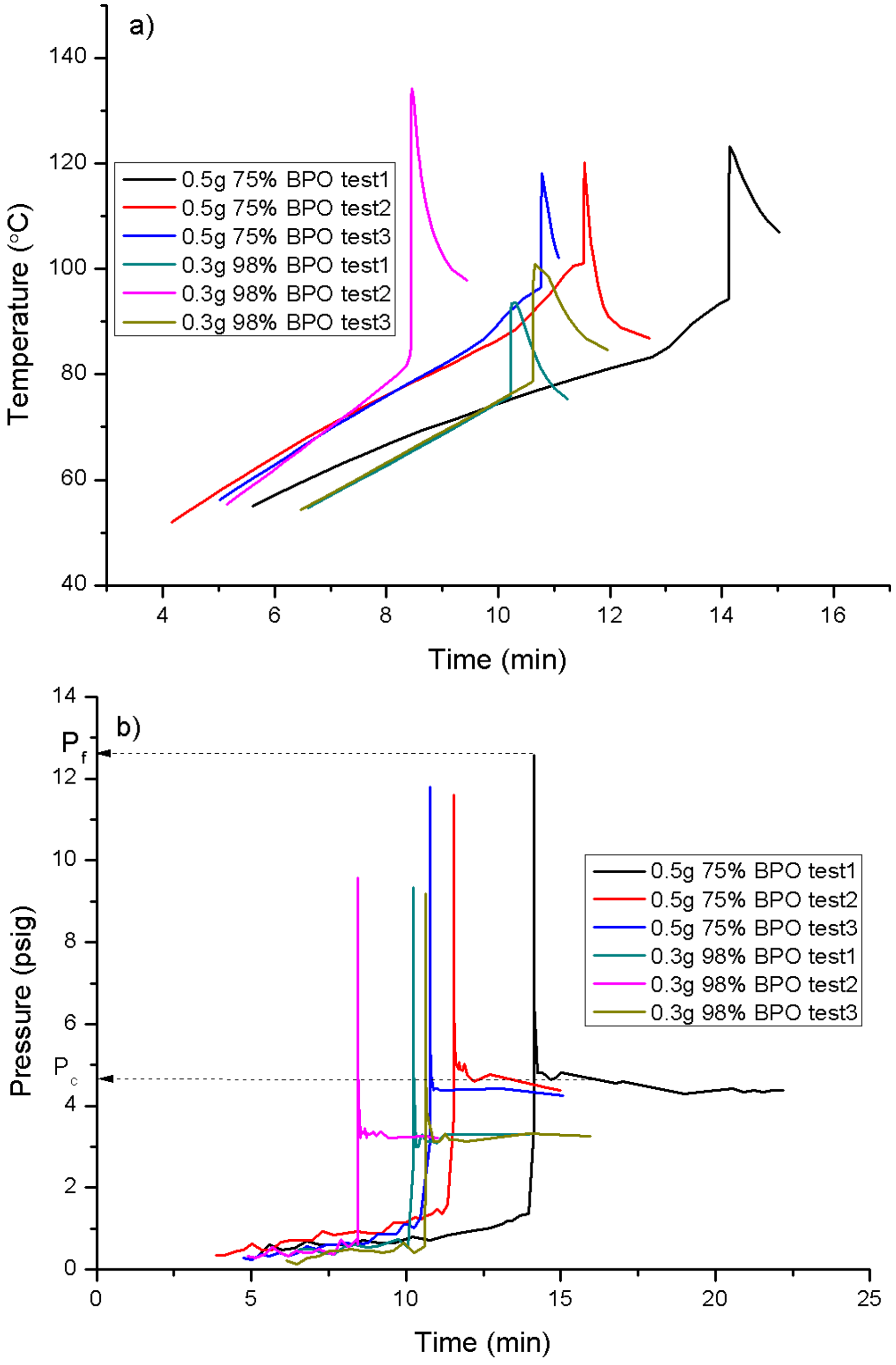


Figure 8 Pure BPO under ambient pressure a) Temperature history; b) Pressure history; c) Self-heat rate profile; d) Pressure rate profile

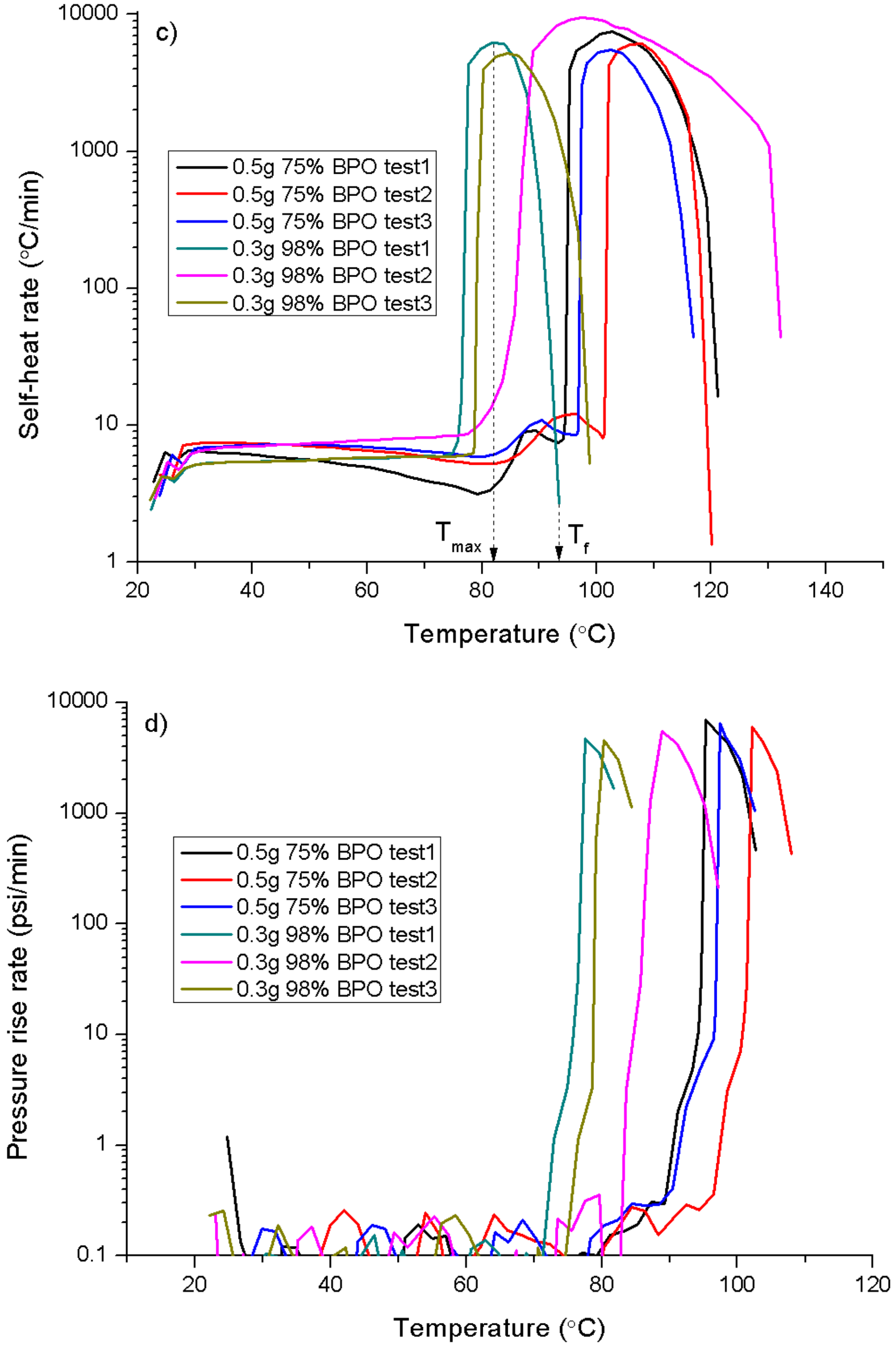


Figure 8 Continued

It is known that autocatalytic reactions have a low reaction rate at the very beginning. As the reaction proceeds, free radicals are generated and accumulated, and the reaction accelerates until the maximum rate is reached [14]. From the figure we can see that the decomposition reaction of pure solid BPO also showed an autocatalytic feature, hence the initial decomposition was difficult to detect and the reaction accelerated rapidly after the “onset”. Therefore, temperature alarm as a design of protection layer will not be effective because the temperature remains stable during induction period, and suddenly increases after the “onset”, hence, there is little time for emergency response. The explosive decomposition was observed from experiment, revealing the hazard of thermal explosion of solid BPO sample. It is clear that more concentrated benzoyl peroxide (98% BPO) was more prone to thermal decomposition. From another point of view, increasing the moisture content could reduce the thermal hazard to certain extent.

After cooling down, the pressure was greater than initial pressure, indicating that non-condensable gases were generated during the reaction. During reactions under ambient pressure, there was significant mass loss due to violent gas generation. Less mass loss was measured when initial backpressure was added. Experiments under pressure are discussed in the following section.

3.3.2 Effect of Confinement

To study the effect of confinement, 0.5 g of solid BPO samples were tested under various initial pressures, including 80 psig, 150 psig, and 200 psig. Another test without pressurization was conducted to compare BPO behavior under ambient pressure with high-pressure conditions. Important parameters are summarized in Table 8, and the results are shown in Figure 9.

As shown in Table 8, when the initial pressure in the cell was 80 psig, the “onset” temperature decreased to around 90 °C. T_o decreased to 87 °C with higher initial pressures. T_{max} showed a decreasing trend, indicating that the maximum self-heating rate could be achieved at a lower temperature. Hence, time to “onset” or time to maximum rate could be reduced. From Figure 9, it can also be seen that the thermal explosion time was shortened when increasing initial back pressure. The reason could be that the rate of radical propagation increased by increasing the pressure to a certain amount, resulting in faster overall reaction consequently the time to reach the maximum self-heating rate was much shorter at higher pressures.

With increasing initial pressure, T_f had an increasing trend, $(dT/dt)_{max}$ and $(dP/dt)_{max}$ increased significantly, and the maximum pressure increase, P_f -P_1, also increased. The severity of thermal explosion increased with more confinement.

Assuming the gases in the experiments follow ideal gas law, PV=nRT, the generated moles of gas can be calculated as $n_{generate} = n_2 - n_1 = P_{final} \times V/R \times T_{final} - P_{initial} \times V/R \times T_{initial}$. n_1 represents total moles of gas in the containment vessel before the reaction; n_2, the moles of gas after the reaction; V, the volume of the containment vessel ($3.5 \cdot 10^{-4}$ m^3); and R, the gas constant (8.3145 J/mol/K). The net pressure rise is defined as $P_{rise} = P_c - P_1$. The calculated values are shown in Table 8. The results showed that an increase in initial pressure did not affect the amount of gas generation; however, higher initial pressures resulted in higher maximum pressure rise and higher maximum pressure rate, making the reaction more hazardous. The larger amount of nitrogen employed to achieve a higher back pressure may account for the increase of maximum pressure rise and maximum pressure rate during the reaction.

Table 8 Experimental data for 75% BPO under various levels of confinement

P_1 (psig)	T_o (°C)	T_{max} (°C)	T_f (°C)	$(dT/dt)_{max}$ (°C /min)	$(dP/dt)_{max}$ (psig/min)	$P_f - P_1$ (psig)	P_{rise} (psig)	$n_{generate}$ (mol)
200	87.2 (±1.5)	98.5 (±1.2)	167.3 (±6.0)	10069 (±590)	16579 (±913)	29.7 (±2.2)	4.4 (±0.2)	0.0030
150	87.4 (±0.7)	99.7 (±3.7)	168.0 (±8.3)	10620 (±1407)	16647 (±969)	29.9 (±1.3)	4.2 (±0.3)	0.0033
80	90.3 (±1.0)	106.0 (±1.7)	157.4 (±13.6)	9068 (±447)	14227 (±419)	24.6 (±0.6	3.8 (±0.5)	0.0024
Ambient	97.6 (±3.5)	104.4 (±3.1)	120.5 (±2.5)	6366 (±1047)	6484 (±491)	11.9 (±0.5)	3.3 (±0.2)	0.0031

It is concluded that confinement could decrease the “onset” temperature of solid BPO by 10 °C. However, T_o decreased slightly with further increasing of initial pressure. Time to thermal explosion was shortened under confinement, but further increment of initial pressure had little effect on the time to “onset”. The severity of thermal decomposition increased due to dramatic increase of maximum temperature rate and maximum pressure rate. The maximum temperature and maximum pressure rise also showed an increasing trend. There was non-condensable gas generation but the amount of gas generation was not affected by the initial confinement. It is obvious that confinement is dangerous to BPO, which should be avoided in BPO storage and transportation.

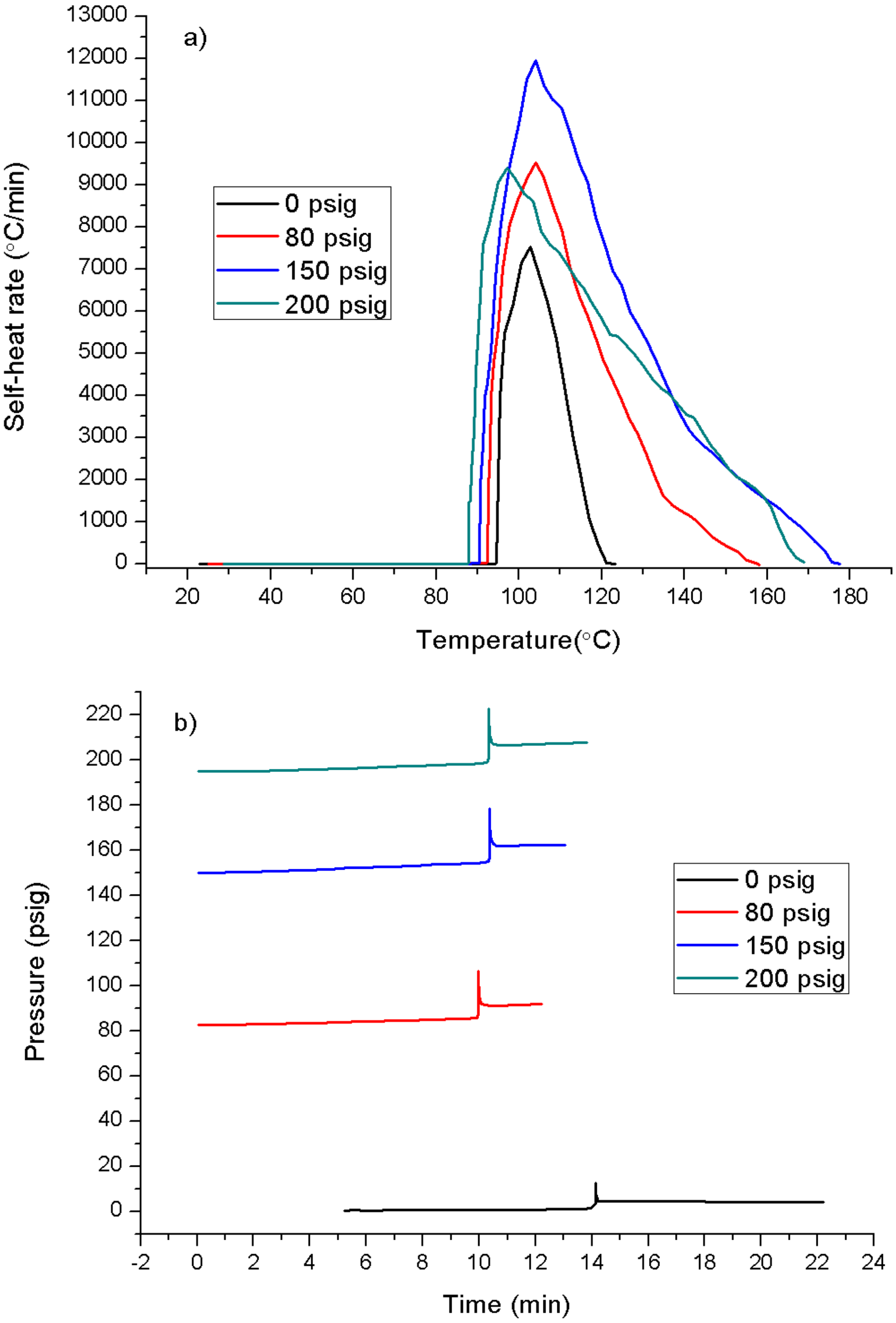


Figure 9 0.5g 75% BPO under various initial pressures a) Self-heat rate profile; b) Pressure profile

3.3.3 Isothermal Tests

After the dynamic heating decomposition studies, isothermal tests were conducted. Measurements were performed using 0.5 g of 75% BPO in each isothermal test. In three tests, the samples were heated at an identical rate (2 °C/min) up to 75 °C, 80 °C, and 85 °C, where they remained for 1440 minutes. Figure 10 shows the temperature and pressure profiles for the three isothermal experiments. After heating up to 75 °C, decomposition occurred in about 129 minutes. At higher temperatures the reaction "started" earlier. Decomposition occurred almost immediately after heating up to 85 °C. Therefore, higher isothermal temperature could result in shorter induction time.

Both 75% BPO and 98% BPO were tested under 70°C. No significant temperature change was recorded; however, a small portion of sample became yellow after the isothermal tests, indicating that a reaction of some kind took place. Therefore, as expected and as the isothermal tests indicated, the "onset" temperature can be much lower than the one measured during dynamic screening tests.

In literature, SADTs of BPO was estimated using various calorimetry techniques and kinetic models. For instance, kinetic data obtained from isothermal heat flux reaction calorimeter (C80D) combined with Semenov model was used to evaluate SADT and this method proved to be more accurate than ARC method. The calculated SADT for 75% BPO was 80 ºC for 25 kg package [111]. A simulated decomposition kinetic method considering the mass of the reactant as a variation with temperature was proposed to predict SADT of organic peroxides based on non-isothermal decomposition in C80D. The predicted SADT of 75% BPO for UN 25 kg package test was 76.3 ºC [112]. Li and Koseki used TAM to determine the kinetics of autocatalytic decomposition reaction of solid 75% BPO and applied Frank-Kamenetskii model to estimate SADT in full-scale packages. The evaluated SADT in 25 kg package was 73.5 ºC [23]. Yang-Fan Cheng *et al*. simulated SADTs of 75% BPO in a 24 kg cubic box package and a 400 kg barrel reactor with data from DSC non-isothermal tests, and obtained SADTs of 65 ºC and 61 ºC respectively [4]. It can be seen that the estimated SADT of 75% BPO range from 61 ºC to 80 ºC. Our work proved that BPO could decompose at temperature as low as 70 ºC. Although no explosive decomposition was observed at 70 ºC, the thermal explosion is highly possible at industrial scale due to large sample quantity and the heat accumulation inside sample. It is highly recommended to provide temperature controls during the usage, storage, and transportation of BPO. The quantity of sample or volume of the container should be specified, and appropriate measures include the installation of refrigerating and air conditioning equipment should be implemented.

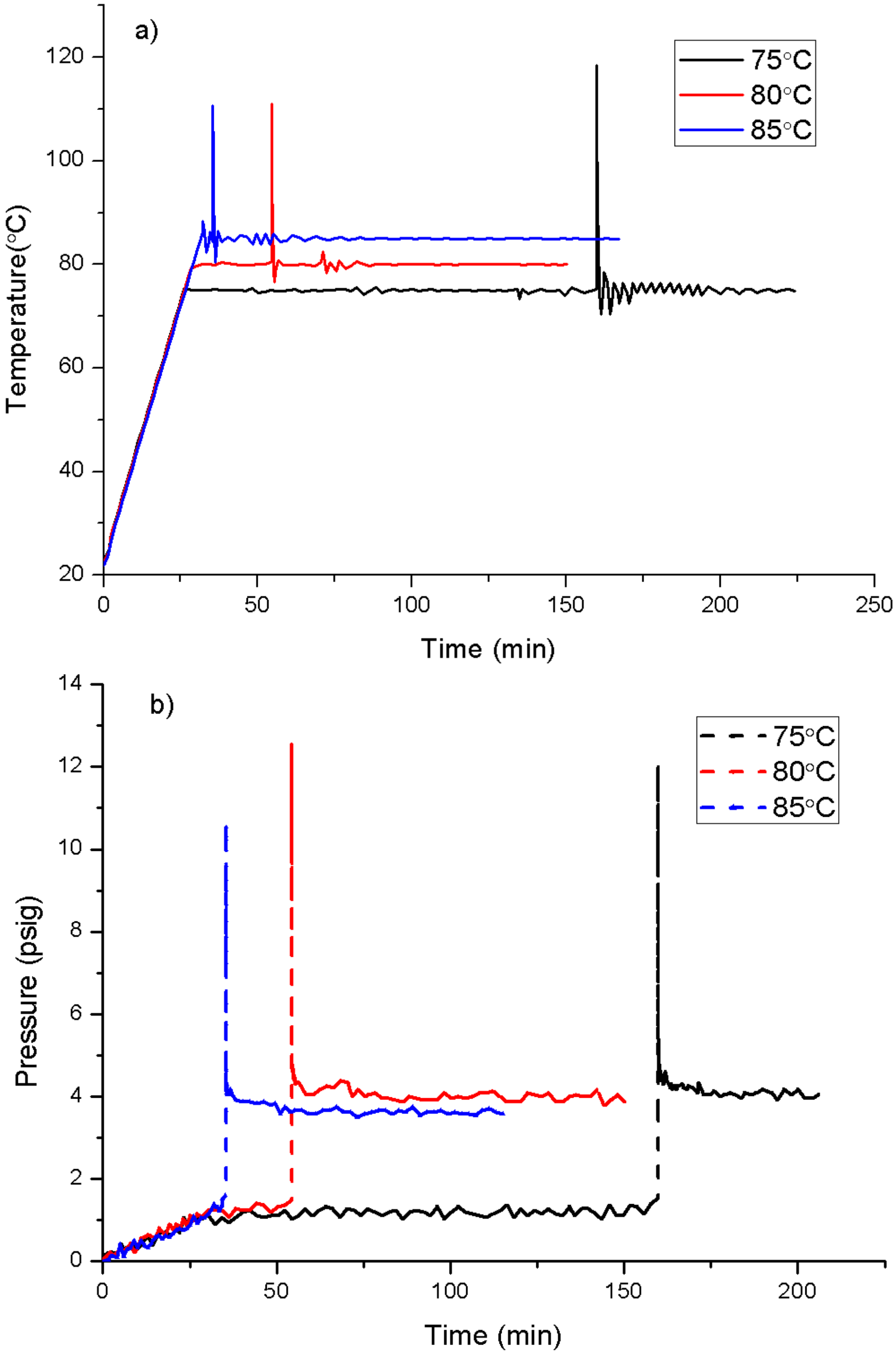


Figure 10 0.5 g 75% BPO isothermal tests under ambient pressure a) Temperature history; b) Pressure history

3.3.4 Effect of Acids and Bases

The decomposition reaction was also examined in the presence of additives. More specifically, approximately 0.1 g of hydrochloric acid (1N and 6N), sulfuric acid (1N and 5N), nitric acid (1N and 5N), phosphoric acid (1N and 6N), and sodium hydroxide (1N) were tested individually, with solid 75% BPO (0.5 g). Each test was repeated three times. The temperature versus time profiles and the self-heating rate versus temperature profiles of the decomposition of the mixtures are reported in Figure 11 and 12, and pure BPO experimental data is provided as a reference in each figure. The parameters are summarized in Table 9, which also reports the averaged T_o, $(dT/dt)_{max}$, T_{max}, and T_f for pure BPO under ambient pressure.

The results showed that there was little change in T_o, T_{max} and T_f after incorporation of the additives mentioned above, except that after adding 1N HNO_3, the final temperature slightly decreased. Therefore, in contrast to results of other published work, these additives were not found to influence the stability of the BPO under the conditions studied here. The disagreement with other researchers' work could be attributed to the following reasons. First, mixing of the solid BPO with the liquid acid or alkaline solution is difficult. Second, the sample quantities employed were not large enough to ensure that observed differences can be attributed to the presence of the additive. This could be the reason why researchers who employed much smaller samples than the ones employed here found contradictory results, as discussed in the introduction. Moreover, the effect of water in the contaminants might contribute to the delay of "onset" or offset the effect of impurities. More work is needed to understand the reasons behind it.

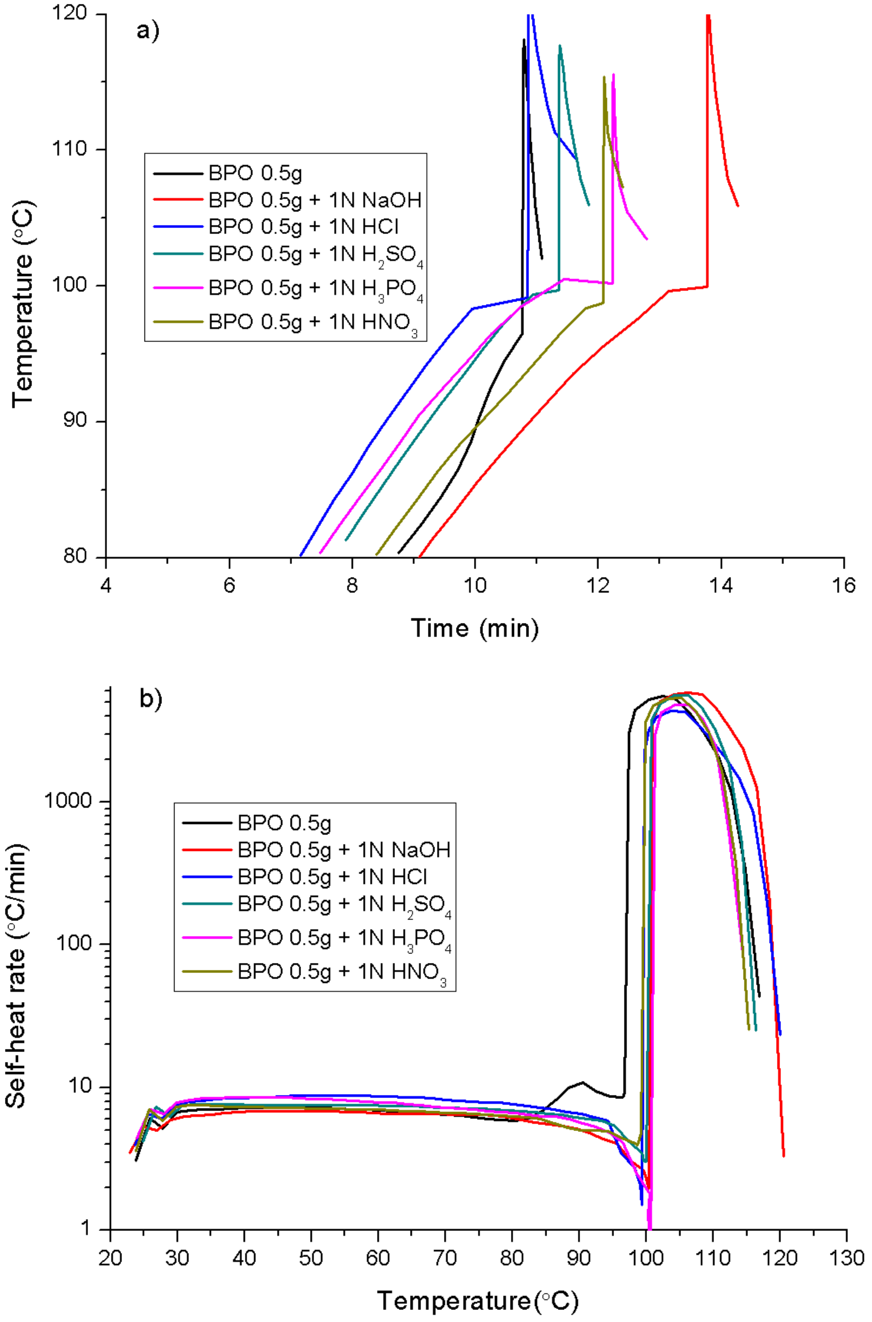


Figure 11 0.5 g 75% BPO mixed with less concentrated additives a) Temperature profile; b) Self-heat rate profile

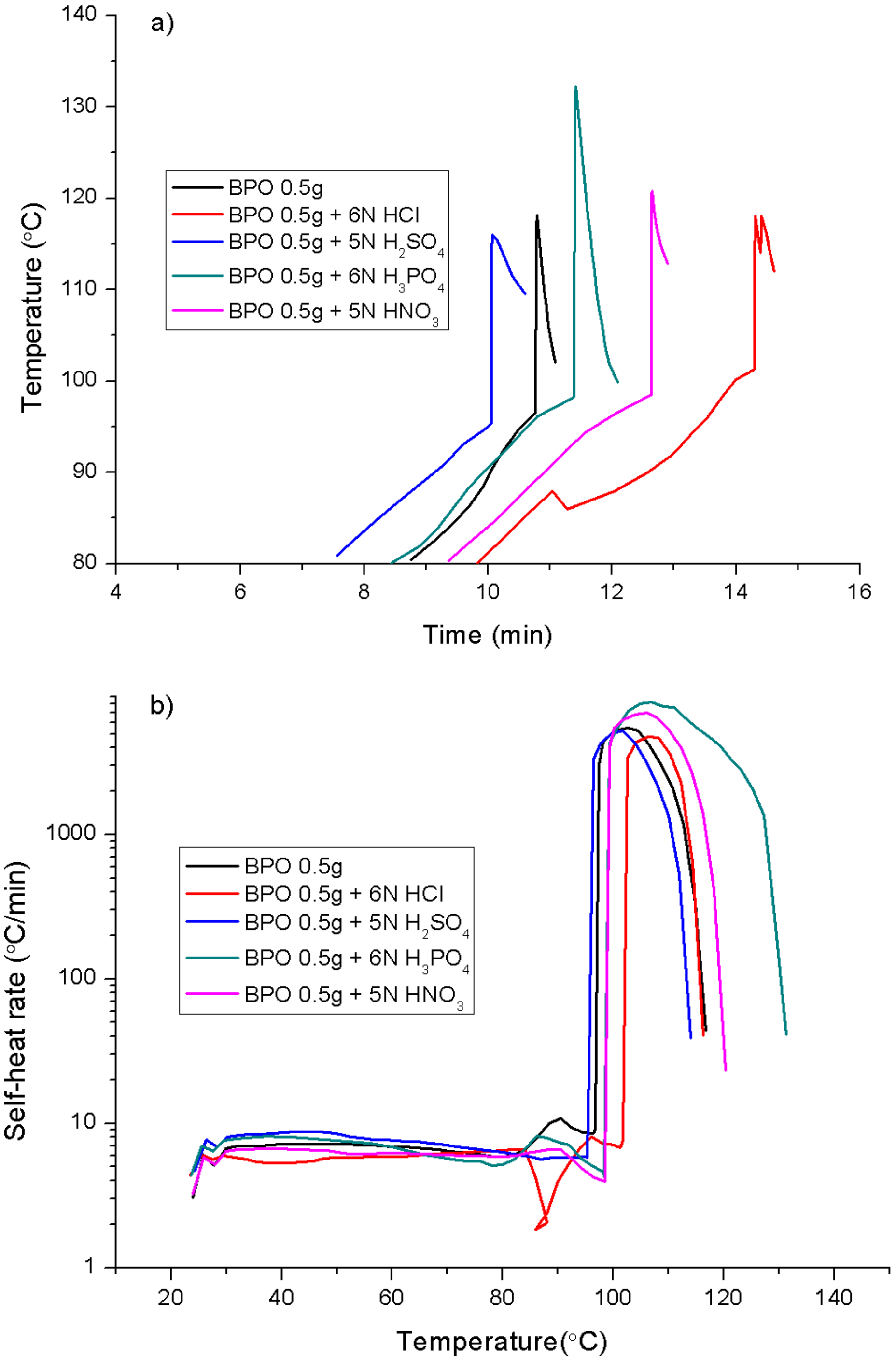


Figure 12 0.5 g 75% BPO mixed with more concentrated additives a) Temperature profile; b) Self-heat rate profile

Table 9 Effect of additives on BPO decomposition (mass ratio of 75% BPO and additives is 5:1)

Additives	T_o (°C)	$(dT/dt)_{max}$ (°C/min)	T_{max} (°C)	T_f (°C)
1N HNO_3	99.6(±0.4)	5423.3(±317.6)	105.1(±0.6)	114.9(±1.2)
5N HNO_3	98.5(±0.4)	6844.7(±1560.2)	104.9(±1.5)	121.7(±2.8)
1N HCl	100.1(±0.6)	4871.5(±875.2)	105.5(±1.6)	120.2(±1.1)
6N HCl	101.9(±0.6)	4893.9(±776.2)	106.4(±1.8)	118.0(±2.2)
1N NaOH	101.5(±3.1)	4204.5(±1454.0)	105.6(±2.7)	116.2(±3.9)
1N H_2SO_4	101.4(±4.8)	5119.0(±1409.1)	105.7(±7.2)	117.9(±10.4)
5N H_2SO_4	99.1(±3.0)	4827.3(±1677.9)	104.4(±3.0)	117.9(±3.5)
1N H_3PO_4	100.1(±0.5)	5038.7 (±550.3)	104.4(±1.3)	116.4(±3.2)
6N H_3PO_4	97.5(±2.7)	6714.5(±1689.2)	104.5(±2.3)	121.5(±10.4)
Pure BPO	97.6(±3.5)	6366.0(±1047.1)	104.4(±3.1)	120.5(±2.5)

3.4 Conclusions

In this work, ARSST was used to study the runaway behavior of solid BPO. The “onset” temperatures of 75% BPO and 98% BPO were determined to be around 98 °C and 79 °C, respectively. The “onset” temperature, therefore, is lower with higher concentration or purity. The confinement tests showed that increase of the initial back pressure resulted in decreased “onset” temperature, increased maximum temperature rate, and maximum pressure rate. The increasing amount of nitrogen may cause the increase of maximum pressure rise and maximum pressure rate during the reaction. Back pressure had little effect on the amount of non-condensable gas. Isothermal tests were conducted to investigate the effect of induction. When the isothermal temperature increased from 75 °C to 85 °C, time to maximum rate decreased from 129 minutes to 3 minutes. The “onset” temperature of pure BPO was found to be much lower during isothermal experiments compared with that obtained during the dynamic screening tests. The selected additives (HNO_3, HCl, NaOH, H_2SO_4, H_3PO_4) had little influence on the “onset” temperature of

BPO decomposition under the studied conditions. More work is needed to investigate the thermal hazards of contaminated BPO under different conditions. The ARSST used in this study is a screening tool which can give qualitative information about the principle safety parameters. It has the advantage of using relatively larger quantities of samples, and the results are more reliable than other screening techniques; however, more work needs to be done using more precise instruments, such as automatic pressure tracking adiabatic calorimeter (APTAC) to obtain quantitative results and further validate the above findings.

CHAPTER IV

THERMAL HAZARD ASSESSMENT OF BENZOYL PEROXIDE IN SOLVENTS

4.1 Synopsis

Benzoyl peroxide is mainly used as an initiator in free-radical polymerization reactions. It is usually mixed with monomers to produce polymers in various solvents. Unintended decomposition of benzoyl peroxide would result in highly exothermic runaway reactions, explosive polymerization, and subsequent fire or explosion due to its exothermic and auto-accelerating nature. Therefore, it is critical to understand the thermal behavior of initiator in solvents to prevent runaway reactions from happening. This study aimed at investigating the runaway hazard of BPO decomposition in alkylbenzene solvent through calorimetry studies and providing quantitative assessment of the effect of mass fraction and sample size on BPO thermal decomposition. Automatic Pressure Tracking Adiabatic Calorimeter (APTAC) was used to evaluate the thermal runaway behaviors of BPO on a relatively large scale. Adiabatic tests were conducted under various concentrations (20.0%, 22.5%, and 25.0% by weight) and sample volumes (15 ml, 20 ml, and 25 ml). The experiments showed that the “onset” temperature of BPO decomposition in solvent was about 71°C. The overall heat of reaction increased with the BPO mass fraction. The maximum temperature, maximum pressure, maximum temperature rate and maximum pressure rate increased with the BPO mass fraction and sample volume, but not linearly. Townsend and Tou kinetic model was used to calculate thermodynamic and kinetic parameters. A 1st order reaction assumption could adequately describe the decomposition reaction under the studied system. The data generated serves as a useful guidance for designing limits of operation, controls and safeguards of processes where BPO is involved.

4.2 Materials and Methods

75% benzoyl peroxide (Sigma Aldrich, Luperox® A75, 75%, remainder water), 98% benzoyl peroxide (Sigma Aldrich, Luperox® A98, reagent grade, ≥98%), toluene

As the thermal decomposition of pure solid BPO can exert pressure on the test cell at very rapidly increasing rates, it may not be possible to obtain meaningful adiabatic experimental data for concentrated sample in closed cell configuration. In this study, in order to make the reaction milder and protect the equipment, toluene was used to dissolve and dilute the 98% BPO sample to mass concentrations of 20.0%, 22.5%, and 25.0%. Toluene was chosen as a solvent due to 1) it has the simplest structure in alkylbenzene family and 2) to have a comparable set of experiments with data reported in literature [58, 106]. Since BPO was not fully dissolved in toluene under the selected concentrations, agitation was needed to improve the heat and mass transfer in the heterogeneous mixture. Sample mixture of various volumes (15ml, 20ml, and 25ml) were loaded to a 50 ml glass spherical flask, and stirred by a magnetic stirrer bar. Initial pressure of 300 psi was used to reduce the vaporization of solvent. Solutions were first quickly heated to 60 °C, and then the equipment was programmed to start operating in the heat-wait-search mode with temperature increment of 5°C, a heating rate of 2°C/min, and a 30 min waiting period between heating steps. APTAC entered adiabatic mode once the self-heating rate exceeded

0.05°C/min. Temperature and pressure, as well as the rate of self-heating and pressure-rise, were measured and recorded throughout the experiment.

4.3 Results and Discussion

The runaway behavior of BPO-solvent system was characterized under adiabatic conditions using one of the best instruments for such studies, which can mimic the real reaction vessel. The influence of the experimental variables including sample size and mass fraction on the runaway severity of the BPO decomposition from a process safety perspective were addressed based on the following parameters:

- T_o (°C): detected "onset" temperature, defined as the lowest temperature at which the calorimeter first detects the exothermic reaction and changes into adiabatic mode. This parameter depends strongly on the sensitivity of the instrument.
- T_f (°C): final temperature of the exothermic reaction, which is also the maximum temperature achieved during the entire reaction course under adiabatic conditions.
- ΔT_{ad} (°C): true adiabatic temperature rise, calculated as the difference between T_f and T_o, multiplied by the phi factor of the experiment: $\Delta \mathrm{T}_{ad} = \varphi(T_f - T_o)$
- ΔP (psi): maximum pressure rise, calculated as the difference between the maximum pressure achieved during the reaction and the initial pressure.
- dT/dt_{max} (°C/min) and dP/dt_{max} (kPa/min): maximum self-heating rate and maximum pressure rise rate.
- TMR_{ad} (min): time to maximum rate under adiabatic conditions, defined as the time interval between the "onset" temperature and the temperature at maximum rate
- ΔH: enthalpy of reaction. Calculated as:

$$-\Delta H = \frac{m_s \cdot C_{p,s} \cdot \varphi \cdot (T_f - T_o)}{m_{BPO}} \qquad \text{Equation 13}$$

where $c_{p,s}$ denotes heat capacity of sample solution, and calculated by Equation 14:

$$C_{p,s} = C_{p,BPO}\text{BPO mass\%} + C_{p,solvent}(1 - \text{BPO mass\%}) \qquad \text{Equation 14}$$

4.3.1 Effect of Sample Volumes

20 mass% BPO at three different sample volumes (15, 20, 25 ml) were tested and the results of the measurements were summarized in Table 10. Each condition was repeated twice. The temperature and pressure profile, self-heating rate *vs*. temperature, and pressure rise rate *vs*. temperature were shown in Figure 13. These key hazard indicators obtained from adiabatic tests were plotted in Figure 14.

The “onset” temperature of the adiabatic reaction was taken as the temperature when the detected self-heating rate exceeded 0.05°C/min and the APTAC changed into the adiabatic mode. The “onset” temperature of the thermal decomposition of BPO in solvent was detected at around 71°C, which was much lower compared to its solid state decomposition with an “onset” temperature of 98 °C. The effect of solvent was significant. Several possible reasons could provide explanations to the phenomena: 1) BPO was diluted in solvent and the reaction was much milder, therefore, it was easier for the exotherm to be detected in a slower reaction at an early stage; 2) solvent reduced the “cage effect” of the radicals generated during the decomposition and changed the mass transfer and heat transfer of radicals, so less energy would be required to break the O-O bond; 3) the thermal insulation and sensitivity of APTAC was superior to screening tool, therefore, the “onset” occurred at a lower temperature. The results also showed that T_o was not influenced by the sample volume, which demonstrated that it was determined by the resolution of the equipment rather than by the phi factor.

Soon after the “onset”, a steep temperature rise of more than 150 °C was observed within short time. Such rapid, explosive-like reaction behavior indicated the severity of uncontrolled thermal decomposition of BPO in toluene. Correspondingly, the pressure inside the test cell increased by more than 1860 kPa (270 psi), posing a great threat to reaction vessels and relief valves during runaway. From the temperature or pressure profile, it can be seen that as sample volume increased, the curve became steeper and shifted left. This was probably because the φ factor was greatly affected by the sample size and it decreased from 2.4 to 1.8 when increasing sample fill level from 15 ml to 25 ml. As the φ factor became lower, the reaction vessel was more adiabatic. The heat inside the vessel accumulated faster and accelerated the decomposition resulting in an earlier and more violent reaction. As expected, the final temperature at the end of exothermic reaction increased when increasing sample volume. The adiabatic temperature rise obtained in this study was around 154°C at the lowest φ factor.

The maximum pressure rise (ΔP) can be calculated by subtracting the initial pressure from the peak pressure. As shown in Table 10 and Figure 14, the maximum pressure rise increased monotonically with increasing sample volume. The pressure rise primarily consisted of three parts: (1) no non-condensable gas production during this reaction, which might include carbon monoxide and carbon dioxide, (2) the vapor pressure of volatile components, which was also a function of temperature, and (3) the expansion of pad gas at higher temperature, which was nitrogen in this case. When dissolved in solvent, BPO-toluene system can be classified as hybrid system, in which both gas and vapor are generated simultaneously to contribute to the total pressure build-up. From a safety point of view, it is crucial to understand whether the system will temper during the operation of pressure relief, and it requires the knowledge of both temperature rise rate and pressure build-up rate for vent sizing for a hybrid system [113].

The maximum self-heating rate $((dT/dt))_{max}$ and maximum pressure rise rate $((dP/dt))_{max}$ are displayed in Table 10 and Figure 14. The log scale of the data had a linear increasing trend, indicating that the maximum pressure-rising rate and the maximum self-heating rate during the runaway both raised exponentially with respect to sample volume.

The time-to-maximum rate (TMR) is the time needed for the reaction to reach its maximum self-heating rate after reaching the “onset” temperature. When the sample volume was 15 ml, it took 102-127 min for the adiabatic reaction to reach its maximum self-heating rate. As φ factor became lower with increasing sample volume, TMR showed a trend of decreasing and it shortened to 75-80 min for sample with volume of 25ml.

The estimated kinetic parameters A and E_a for adiabatic reaction are also summarized in Table 10. They were calculated based on Townsend and Tou model assuming n=1 using the experiment data after the “onset” temperature. A good linear fitting was obtained when plotting lnk vs 1/T. A simple linear regression could adequately describe the relationship between the observed outcomes and the observed predictor values with the coefficient of determination R^2 being almost 1. Therefore the assumption of 1^{st} order type kinetics was justified, at least over the range of test variables that were studied. The activation energy was about 132 kJ/mol, which is similar to literature data of 124 kJ/mol [106]. The total heat of reaction was about 1200 J/g.

Table 10 Experimental data for 20 mass% BPO with various sample volumes

Solvent volume (ml)	T_f (°C)	ΔP (psi)	$(dT/dt)_{max}$ (°C min^{-1})	$(dP/dt)_{max}$ (kPa min^{-1})	-ΔH (J g^{-1})	Ea (kJ mol^{-1})	A (s^{-1})
15	142.69 (±4.84)	269.49 (±7.55)	12.55 (±5.90)	329.91 (±131.06)	1271.28 (±63.24)	133.19 (±0.50)	2.82×10^{15} (±0.54)
20	152.24 (±1.58)	321.07 (±4.46)	28.71 (±4.21)	819.01 (±68.24)	1253.13 (±21.33)	132.05 (±0.16)	2.00×10^{15} (±0.08)
25	158.04 (±0.25)	365.06 (±26.71)	47.27 (±0.69)	1477.37 (±9.65)	1172.54 (±2.82)	131.11 (±0.34)	1.47×10^{15} (±0.16)

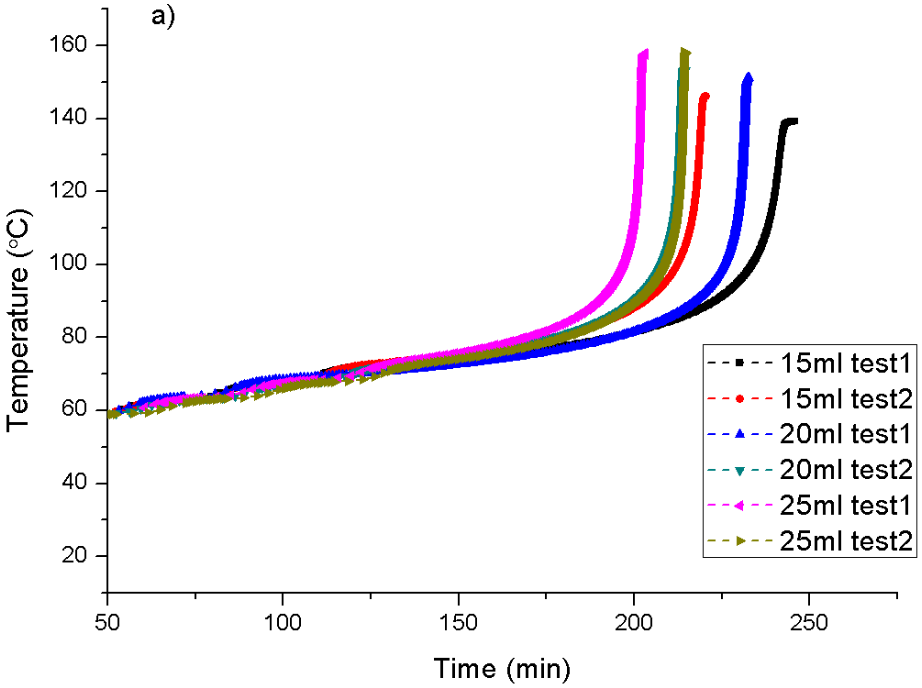
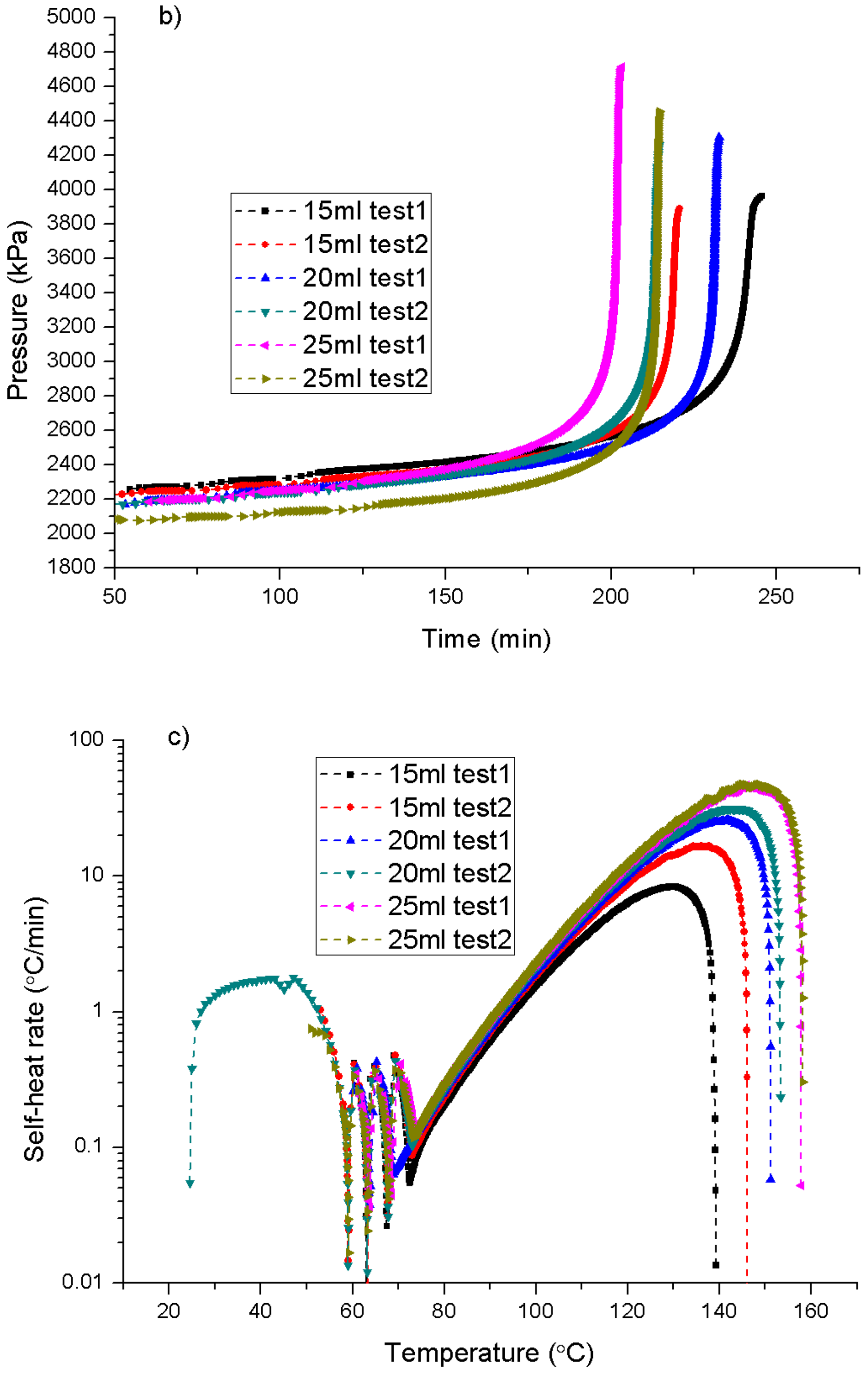


Figure 13 15 ml, 20 ml, 25 ml 20 mass% BPO in toluene a) temperature *vs*. time; b) pressure *vs*. time; c) self-heating rate *vs*. temperature; d) pressure rise rate *vs*. temperature



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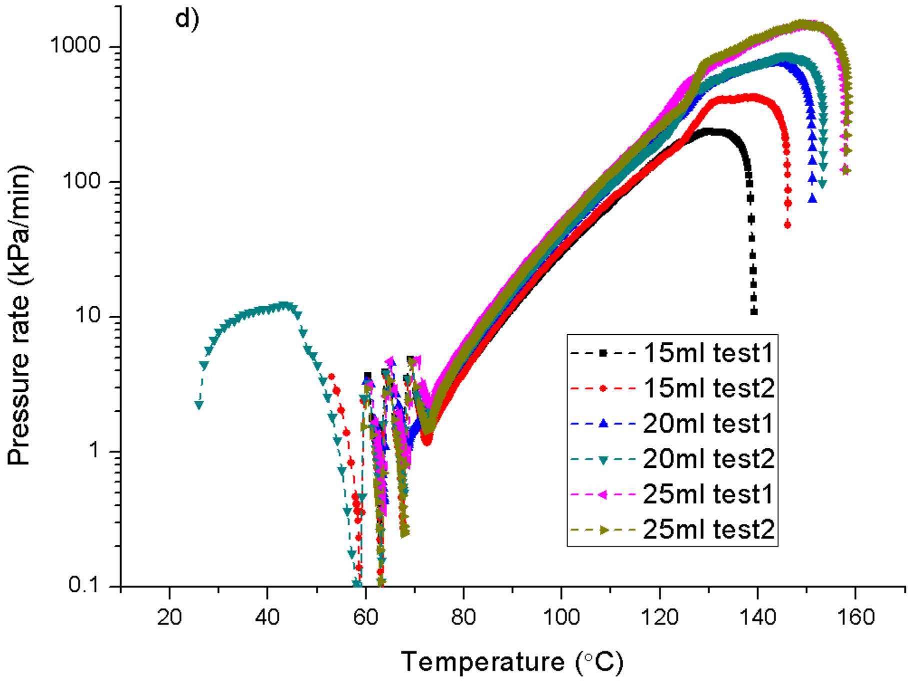

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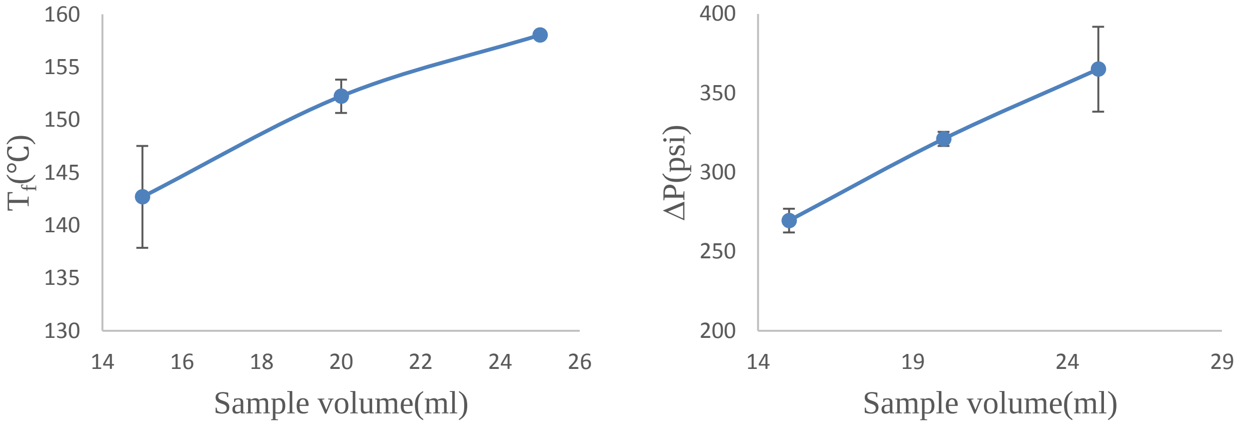


Figure 14 Effect of sample volume on T_f, ΔP, $(dT/dt)_{max}$, $(dP/dt)_{max}$

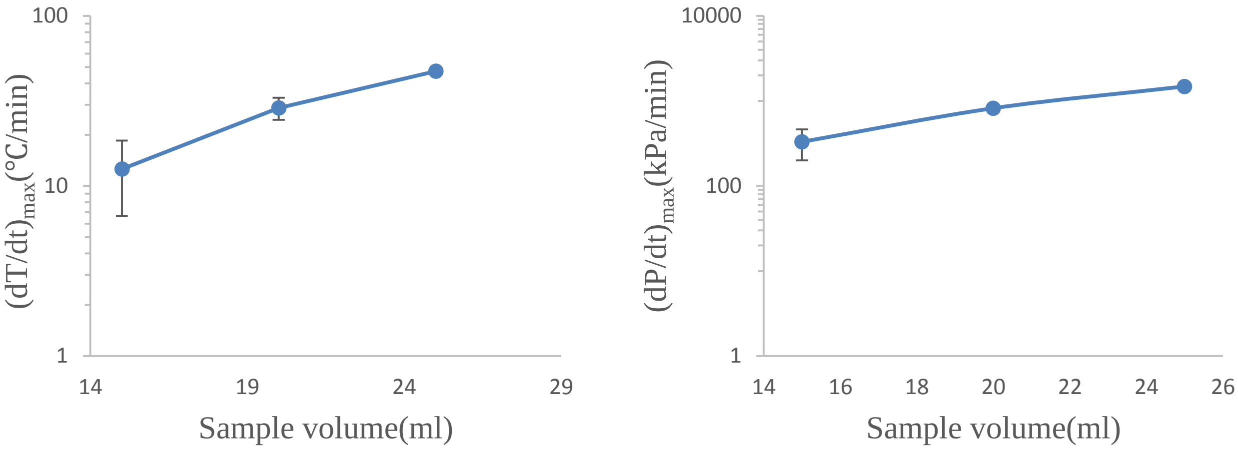


Figure 14 Continued

4.3.2 Effect of Mass Fractions

20 ml BPO-toluene solution at three different mass fractions (20.0%, 22.5%, and 25.0%) were tested and the results of the measurements were summarized in Table 11. Each condition was repeated twice. Figure 15 displays temperature *vs*. time, pressure *vs*. time, self-heating rate *vs*. temperature, and pressure rise rate *vs*. temperature of BPO at three different mass concentrations. These key hazard indicators obtained from adiabatic tests were plotted in Figure 16.

The “onset” temperature T_o was detected at around 71 °C and slightly dropped to 67 °C as mass fraction increased. The adiabatic temperature rise ΔT_{ad} was calculated and plotted in Figure 16. It showed a positive correlation with mass concentration. A linear behavior of the ΔT_{ad} with concentration corroborated that the assumption of a single reaction was reasonable [113]. The corrected adiabatic temperature rise could reach more than 230 °C after “onset” temperature.

The pressure data showed that the system pressure reached its peak and gradually decreased afterward. The pressure after cooling down was higher than the initial pad pressure. This demonstrated that the total pressure buildup was contributed by nitrogen gas expansion, volatile substances of solution, and non-condensable gases generated during the decomposition. However, this work was not able to quantify the amount of each factor. Figure 16 displays the pressure buildup of the reaction as a function of BPO concentration. As expected, there was a higher maximum pressure buildup ΔP as the mass of BPO increased. The peak pressure P_{max} and pressure difference ΔP did not change linearly with the mass content. There are two possible explanations: 1) the large variance of the middle point data, 2) at higher concentrations, more non-condensable gases were produced, however, in a closed cell environment, the head space was fixed for the same fill level and therefore more gases were forced to dissolve in the solvent. A significant pressure buildup was not observed at higher concentration.

The maximum self-heating rate $(dT/dt)_{max}$ and the maximum pressure rise rate $(dP/dt)_{max}$ increased significantly with sample concentration. From Table 11, it can be seen that when mass concentration increased from 20.0% to 25.0%, $(dT/dt)_{max}$ increased from 29 °C/min to 368 °C/min, and $(dP/dt)_{max}$ increased from 819 kPa/min to 9141 kPa/min. It should be noted that the upper limit of temperature rate of APTAC is 400 °C/min. If self-heating rates exceed the equipment tracking specification, heaters may start failing to maintain the adiabatic conditions of the sample and heat losses from the cell may increase. Therefore, self-heating rates and self-pressurization rates should be carefully analyzed as they could transform to unreliable data [113]. In this study, 25.0% BPO sample did not exceed the equipment tracking capability, however, the adiabatic performance is very likely to be affected if the mass concentration of BPO continues to increase. This shows the challenging aspect of conducting adiabatic experiments of thermal decomposition of energetic materials, and it will be more difficult to increase the BPO concentration at lab scale. The sensitivity analysis in Figure 16 showed that the maximum pressure build-up rate and maximum temperature rate increased exponentially with mass fraction. The results indicated that a small increase in peroxide concentration could result in much more severe consequence. Federica Barontini *et al*. reported the thermal hazard analysis of BPO in toluene solution by Phi-Tec II adiabatic calorimetry. Their results also showed that the concentration of BPO in the solution strongly affects the decomposition rate [58]. Our conclusion is consistent with literature data.

As BPO mass fraction decreased, heat generated by the reaction was either absorbed by the solvent or dissipated into the environment, a significant delay and mitigation of thermal decomposition was expected. However, there was no obvious pattern between mass fraction and TMR or time to “onset” temperature. The “onset” time was not consistent within repeated tests. The reason could be that BPO was not fully dissolved in solvent, therefore, the mass and heat transfer of the system was not ideally uniform although there was stirring and mixing throughout the reaction. As a result, time to “onset” and time needed for the reaction to be fully developed varied in each experiment.

Heat of reaction ΔH was determined to be more than 1200 J/g, and increased with mass concentration of BPO, indicating that increase of peroxide mass fraction can increase the overall thermal hazards. The concentration of the peroxide did not display an influence on the activation energy. E_a was calculated to be 130 kJ/mol and was similar to literature data.

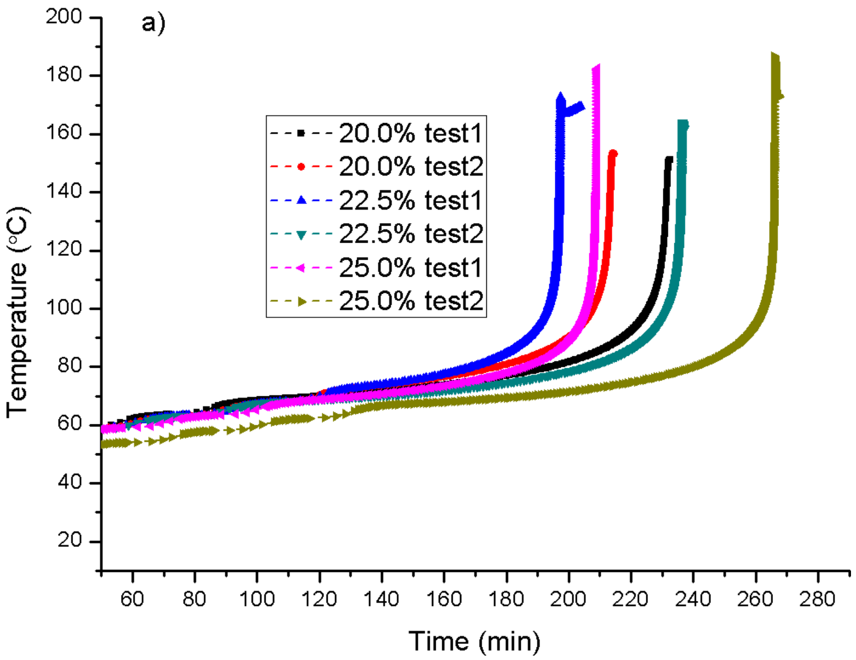
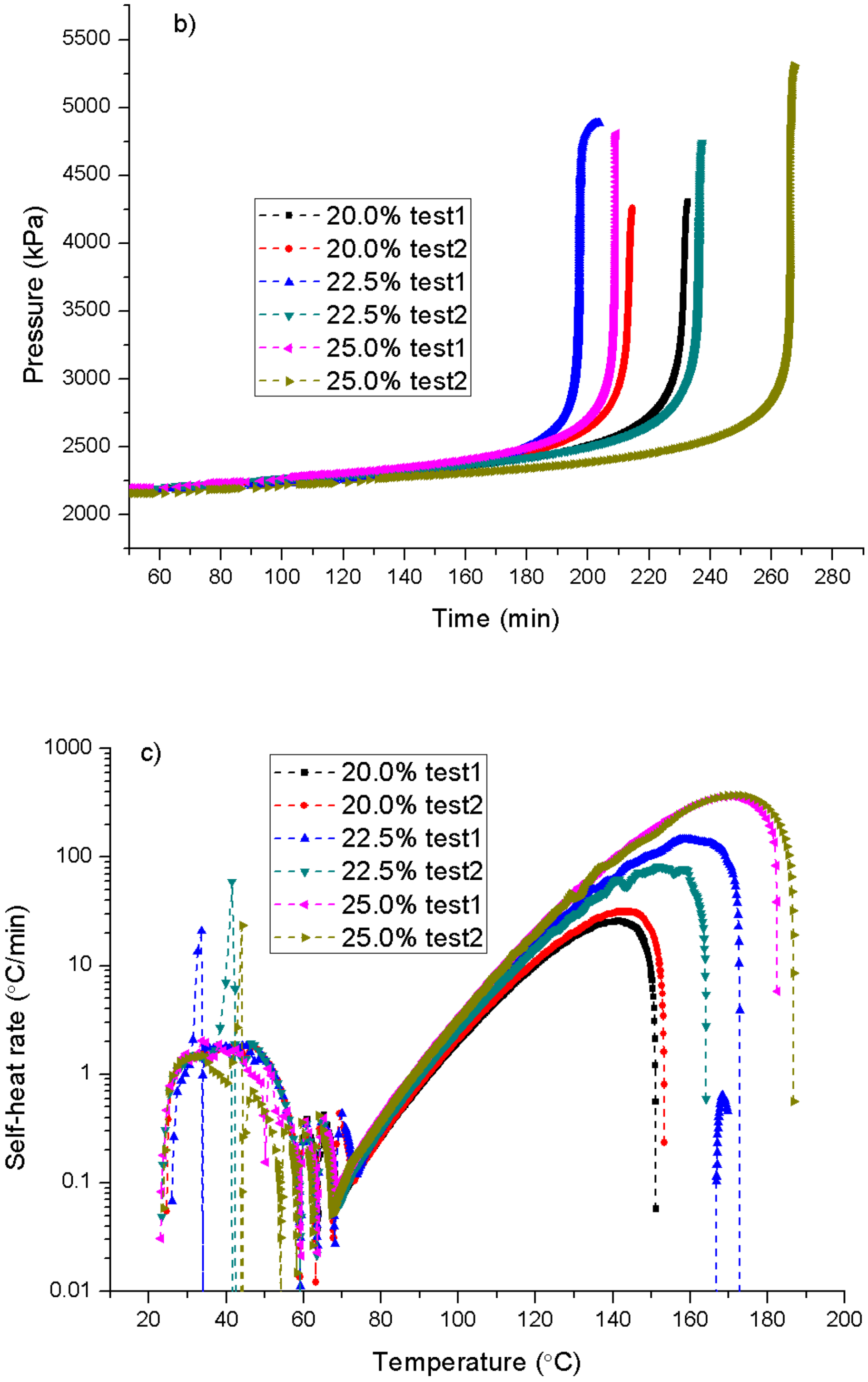


Figure 15 20 ml 20%, 22.5%, 25% BPO by weight in toluene a) temperature *vs*. time; b) pressure *vs*. time; c) self-heating rate *vs*. temperature; d) pressure rise rate *vs*. temperature



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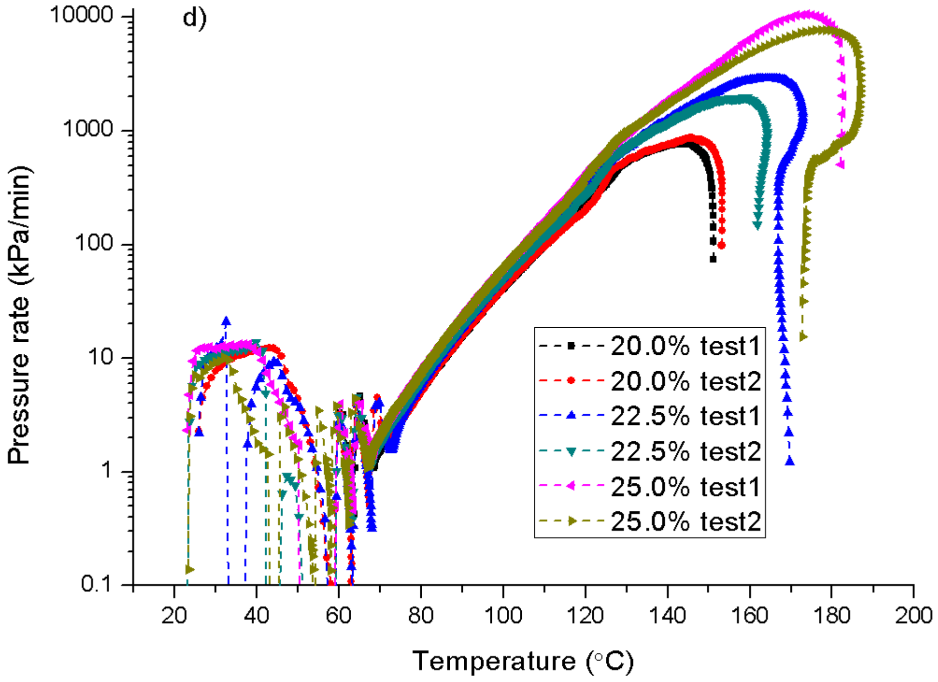


Figure 15 Continued

Table 11 Experimental data for 20 ml BPO with various mass concentrations

Mass Fraction	ΔT_{ad} (°C)	ΔP (psi)	$(dT/dt)_{max}$ (°C /min)	$(dP/dt)_{max}$ (kPa/min)	$-\Delta H$ (J/g)	Ea (kJ/mol)	A (s^{-1})
20.0%	166.36 (±3.00)	321.07 (±4.46)	28.71 (±4.21)	819.01 (±68.24)	1253.13 (±21.33)	132.05 (±0.16)	2.00×10^{15} (±0.08)
22.5%	197.74 (±5.20)	398.45 (±14.70)	114.54 (±45.30)	2440.08 (±664.63)	1312.75 (±28.56)	131.75 (±2.05)	1.93×10^{15} (±1.20)
25.0%	234.05 (±7.87)	396.79 (±1.51)	367.54 (±7.57)	9140.66 (±2006.06)	1381.34 (±46.46)	130.46 (±1.66)	1.24×10^{15} (±0.74)

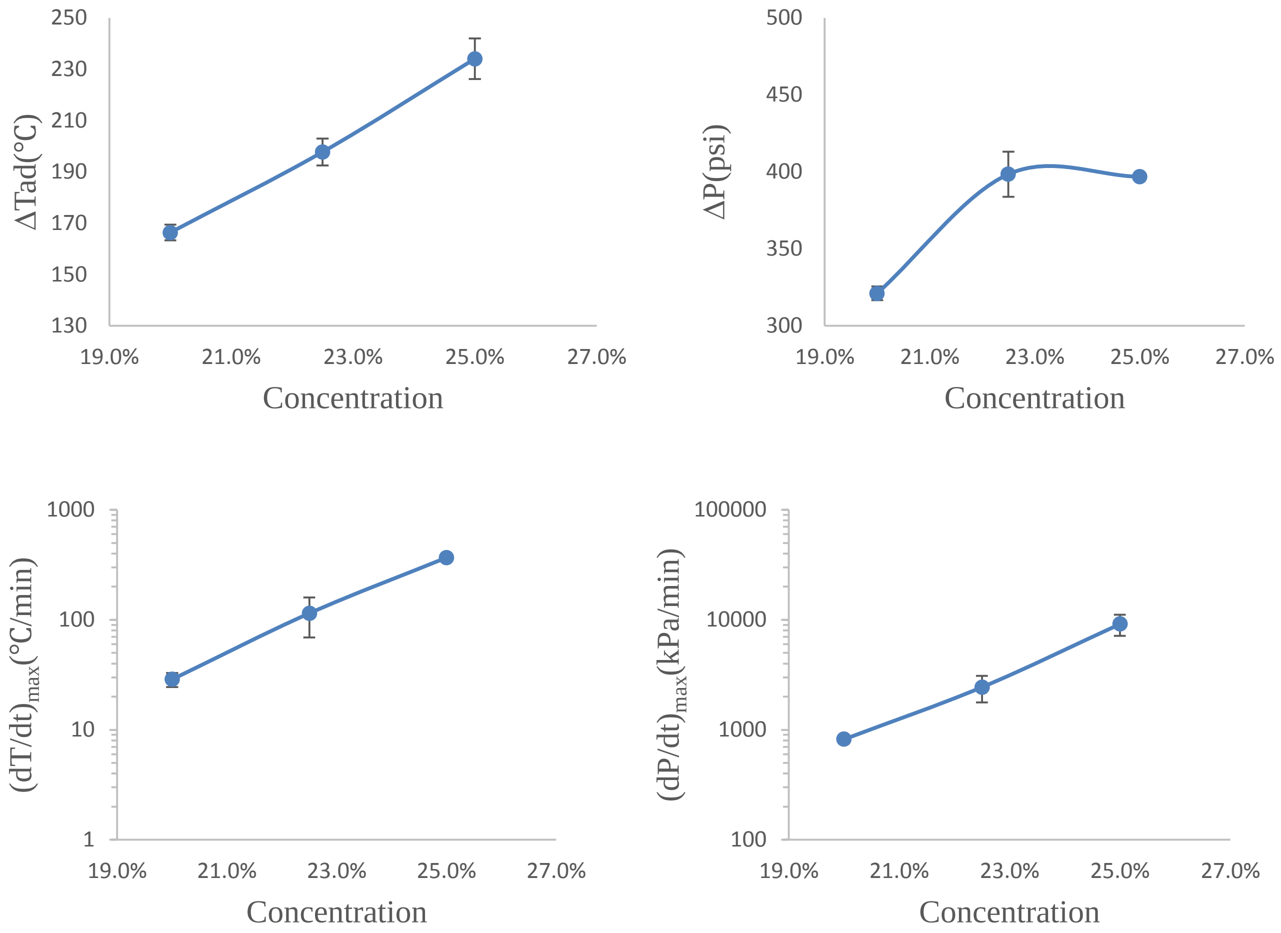


Figure 16 Effect of mass concentration on ΔT_{ad}, ΔP, $(dT/dt)_{max}$, $(dP/dt)_{max}$

4.3.2 Decomposition Mechanism

The alkylbenzenes are suitable for investigating the reaction mechanism of organic peroxide because benzyl-type "solvent radicals" are formed from them by hydrogen-abstraction from their side-chains, and these benzyl-type radicals undergo dimerization to give easily identified products. The kinetics and mechanism of BPO decomposition in alkylbenzenes, including ethylbenzene, p-xylene, and isopropylbenzene, were studied extensively. A scheme for the decomposition of benzoyl peroxide in alkylbenzenes was proposed by W. R. Foster and Gareth H. Williams as shown below [47].

(a) $P \longrightarrow 2R\cdot$

(b) $R\cdot + Ar\cdot CR_2H \longrightarrow Ar\cdot CR_2\cdot + RH$

(c) $R\cdot + Ar\cdot CR_2H \longrightarrow \sigma\cdot$

(d) $Ar\cdot CR_2\cdot + P \longrightarrow \text{Products} + R\cdot$

(e) $\sigma\cdot + P \longrightarrow \text{Products} + R\cdot$

(f) $R\cdot + P \longrightarrow \text{Products} + R\cdot$

(g) $2Ar\cdot CR_2\cdot \longrightarrow \text{Products}$

(h) $2\sigma\cdot \longrightarrow \text{Products}$

Reaction (a) represents the unimolecular dissociation of peroxide to generate radicals ($R\cdot$). Reaction (b) represents the α-hydrogen-abstraction from alkylbenzene ($Ar\cdot CR_2H$) by the radicals $R\cdot$ and generate benzyl type radical ($Ar\cdot CR_2\cdot$). In reaction (c), $\sigma\cdot$ is the σ-complex formed by the addition of a phenyl or benzoyloxy radical to the nucleus of the alkylbenzene. Reactions (d) to (f) represent the induced decomposition of the peroxide by solvent radicals, σ-complex, phenyl radicals and benzoyloxy radicals. Reactions (g) and (h) are termination steps.

Based on the proposed reaction scheme, the possible decomposition products include benzoic acid, benzene, biphenyl, benzyl benzoate, etc. Benzoic acid can be formed from attack on solvent by benzoate radicals, and benzene can be formed from attack on solvent by phenyl radicals generated from spontaneous decomposition of benzoate radicals. Benzyl benzoate can be formed from induced decomposition of benzoyl peroxide by benzyl radicals. Biphenyl can be formed by recombination of incompletely separated radicals. Other biaryls and esters can also be formed from chain reactions. However, gaseous products such as carbon dioxide or carbon monoxide are not considered in the simplified scheme. It is found in literature that the type of solvent might affect the amount of carbon dioxide generation. When benzene was chosen as solvent in dilute solutions, almost all the benzoate radicals generated from benzoyl peroxide lost carbon dioxide before entering into other reactions. Other solvents such as styrene or cumene could react with free radicals and decrease the yield of carbon dioxide [38]. In this work, the mass of the sample mixture after reaction decreased, hence, there was a mass loss due to non-condensable gas generation. Product analysis by analytical tool is needed in the future to gain a better understanding of the decomposition mechanism.

4.4 Conclusions

In runaway reactions, the hazard does not vary linearly with the amount of reactant. Thus, it is of paramount importance to evaluate reactive hazards with various sample sizes and to determine if the reaction follows a trend upon scale-up. In this work, thermal risk of BPO-toluene system was evaluated at different concentrations and fill volumes using adiabatic calorimeter APTAC.

The “onset” temperature was detected at around 71 °C and was not affected by the sample volume. The increase in sample volume resulted in earlier decomposition and more severe consequences with higher maximum temperature and maximum pressure rise. The maximum self-heating rate and maximum pressure rise rate increased exponentially indicating the potential challenge in process scale up. In addition, the probability of runaway increased as TMR was shortened significantly due to sample volume increase. Heat of reaction was determined to be more than 1200 J/g. It was determined that a 1st order kinetic model was sufficient for the BPO decomposition reaction under the tested conditions. The activation energy E_a was calculated to be 130 kJ/mol, which was similar to literature data.

As expected, the data obtained and analyzed showed that the severity of BPO runaway increased when increasing the concentration of the peroxide. As mass fraction increased, the “onset” temperature slightly dropped from 71°C to 67 °C. The adiabatic temperature rise had a positive linear correlation with mass concentration. The maximum pressure rise also showed an increasing trend with respect to peroxide fraction. It was worth noting that the $(dP/dt)_{max}$ and $(dT/dt)_{max}$ increased exponentially with mass fraction. Even a small increase in BPO mass content could result in much more severe hazard. From another aspect, it proved that dilution with solvent is an effective measure to moderate thermal hazards of reactive organic peroxide. From a safety perspective, although diluting the peroxide helps slow down the explosive decomposition of BPO, the toxic and flammable solvent may bring another type of hazard to the system. In addition, the elevated vapor pressure in a closed system due to volatile components may pose another safety concern. The real hazard of an uncontrolled reaction is the pressure when the pressure build up exceeds the design strength of the vessel or the pressure rate is too high resulting in loss of containment. Therefore, optimum process design should be based on a systematic and comprehensive risk assessment of various hazards and worst case scenarios by evaluating the thermal hazard and pressure hazard of the system thoroughly.

CHAPTER V

THERMAL DECOMPOSITION OF BENZOYL PEROXIDE MIXED WITH DRY FIRE-EXTINGUISHING CHEMICALS

5.1 Synopsis

The main objective of this chapter is to study the effect of dry-fire extinguishing chemicals including ammonium dihydrogen phosphate ($NH_4H_2PO_4$), sodium bicarbonate ($NaHCO_3$) and potassium bicarbonate ($KHCO_3$) on the thermal decomposition of benzoyl peroxide (BPO). Advanced Reactive Systems Screening Tool (ARSST) was used for reactivity and compatibility evaluation, and Automatic Pressure Tracking Adiabatic Calorimeter (APTAC) was employed to analyze reaction kinetics under adiabatic conditions. The results showed that sodium bicarbonate and potassium bicarbonate could lower the "onset" temperature, and the decomposition occurred earlier. However, the addition of sodium bicarbonate or potassium bicarbonate reduced the pressure hazard of solid BPO decomposition. The effect of ammonium dihydrogen phosphate on BPO decomposition was also analyzed using APTAC. The results showed that ammonium dihydrogen phosphate had an inhibition effect on BPO decomposition. The "onset" temperature was not affected, but decomposition was delayed. The maximum temperature, maximum self-heating rate, and heat of reaction showed a decreasing trend. The pressure rate was reduced significantly. It is important to understand the potential hazard when employing fire-extinguishing agents to deal with fires and explosions caused by organic peroxide decomposition. The findings from this work could be useful for firefighting application and emergency response.

5.2 Introduction

Fires and explosions caused by organic peroxides occur time and time again, and present a serious threat to the chemical process industry and the community with devastating consequences. Emergency response, such as firefighting, is critical to mitigate the risks associated with such incidents. Usually, water and dry fire-extinguishing chemicals are used to eliminate fires. Extinguishing agents are divided into four main categories: ABC powder (containing ammonium dihydrogen phosphate), XBC powder (containing potassium chloride), BC powder (containing sodium bicarbonate), and KBC powder (potassium bicarbonate). Many studies have evaluated the hazards of organic peroxides, but few research focus on organic peroxides combined with fire-extinguishing agents. However, it is crucial to understand whether the fire-extinguishing agents can decrease the thermal hazards of organic peroxides or not.

In literature, there are a few studies of thermal decomposition of organic peroxides mixed with water or fire extinguishing chemicals. S.-H. Wu *et al.* investigated thermal runaway reactions of cumene hydroperoxide (CHP), methyl ethyl ketone peroxide (MEKPO), and tert-butyl peroxide (TBPO) with H_2O or $NH_4H_2PO_4$ powder by differential scanning calorimetery (DSC). They found that the activation energy (E_a) of organic peroxides/ABC powder was higher than pure organic peroxides or organic peroxides/water mixtures, and heat of decomposition (ΔH_d) was lower, hence ABC powder is an effective inhibitor in chemical reaction. Water caused organic peroxides decomposition at lower “onset” temperature and reduced the ΔH_d. However, the E_a of CHP mixed with water was low and reaction rate was rapid, therefore, CHP should not be mixed with water in an external fire situation [114]. Ang-Cian Li *et al.* evaluated the thermal runaway reaction of MEKPO and CHP mixed with H_2O or dry fire-extinguishing chemicals by differential scanning calorimetry and vent sizing package 2 (VSP2). The results indicated that MEKPO and CHP were highly hazardous when mixed with H_2O or some dry fire-extinguishing chemicals. They found that ABC, BC, and XBC dry chemicals lowered the “onset” temperature of MEKPO decomposition, and H_2O caused the ΔH_d of MEKPO to become higher. Therefore, the decomposition behaviors of MEKPO mixed with H_2O, ABC, BC, and XBC dry fire-extinguishing chemicals were more dangerous than MEKPO alone. In addition, the decomposition behaviors of CHP mixed with water, XBC, and KBC dry fire-extinguishing chemical were more dangerous than CHP alone [115]. Sheng-Hung Wu *et al.* evaluated effects of various fire-extinguishing reagents on thermal hazard of triacetone triperoxide (TATP) by DSC and thermogravimetric analyzer (TG). The results showed that “onset” temperature was increased and heat of decomposition was decreased when mixed with water, ABC, BC, XBC, and KBC fire-extinguishing reagents, indicating that they are useful reagents for TATP fire [116]. C.H. Su *et al.* analyzed safety parameters of 1,1,-Di(tert-butylperoxy) cyclohexane (CH 70% mass) mixed with monoammonium phosphate (MAP) by DSC and found the E_a was about 154-184 kJ/mol [117]. The influence of water on the thermal explosion of benzoyl peroxide was evaluated by adiabatic accelerating rate calorimeter

(ARC). It was concluded that the addition of water could raise the SADT of BPO, and inhibit the thermal explosion of benzoyl peroxide [118].

From previous studies we can see that different fire extinguishing agents have different effects on thermal decomposition of organic peroxides, and there are conflicts in results from different studies. Therefore, it is important to understand the thermal hazard of various organic peroxides mixed with different fire-extinguishing chemicals. However, there is no report on the effect of dry fire-extinguishing chemicals on BPO decomposition. This study aims to carry out a quantitative assessment of the thermal decomposition of BPO in the presence of commonly used dry fire extinguishing chemicals including ammonium dihydrogen phosphate ($NH_4H_2PO_4$), sodium bicarbonate ($NaHCO_3$) and potassium bicarbonate ($KHCO_3$) in calorimeters. Thermal hazards were evaluated experimentally by determining the critical safety parameters including the “onset” temperature of exothermic activity, the overall heat generation, activation energy, and the rate of temperature and pressure increment, using Advanced Reactive Systems Screening Tool (ARSST) and Automatic Pressure Tracking Adiabatic Calorimeter (APTAC). This information is essential in terms of developing emergency response measures and mitigation measures for runaway reactions. The results from this study can provide useful information for fire-related agencies when dealing with fires caused by thermal decomposition of benzoyl peroxide.

5.3 Materials and Methods

75% benzoyl peroxide (Sigma Aldrich, Luperox® A75, 75%, remainder water), 98% benzoyl peroxide (Sigma Aldrich, Luperox® A98, reagent grade, ≥98%), ammonium dihydrogen phosphate (Aldrich, 99.999% trace metals basis), sodium bicarbonate (Sigald, ACS Reagent, ≥99.7%), and potassium bicarbonate (Sigald, ACS Reagnet, 99.7%, powder, crystals or granules) were used without further purification.

In a typical ARSST experiment, 0.5 g of solid 75% BPO was weighed and loaded into the test cell. To study the effect of different fire extinguishing chemicals, 0.5 g of granular BPO was mixed with various amounts of the additives. The mixture was heated up with a single ramp-polynomial control program from room temperature to the end of the exothermic reaction with a heating rate of 2 °C/min. All measurements were preceded by nitrogen purging. Each experiment was repeated at least twice.

In APTAC study, toluene was used to dissolve and dilute the 98% BPO sample to 20% mass concentration, in order to make the reaction milder and protect the equipment. 20 ml sample mixture was loaded to a 50 ml glass spherical flask, and stirred by a magnetic stirrer bar. Initial pressure of 300 psi was provided with nitrogen to reduce the vaporization of solvent. A heat-wait-search operating mode was chosen to study the decomposition under adiabatic condition.

5.4 Results and Discussion

5.4.1 Effect of Sodium Bicarbonate in ARSST

In order to study the effect of $NaHCO_3$, 75% BPO (0.50 g) was mixed with $NaHCO_3$ under molar ratios of 1:1 and 1:2, as shown in Table 12. The profiles of temperature, pressure, temperature rate and pressure rate were plotted in Figure 17.

T_o is the temperature when the decomposition reaction is detected. This paratemer highly depends on the resolution of equipment. Our results indicated that the “onset” temperature of mixture was lower than BPO alone. The reason could be that sodium bicarbonate can decompose at its melting point around 50°C. Therefore, we can see from temperature profile Figure 17(a) that the decomposition of mixture occurred earlier and at a lower temperature compared with pure BPO. From this aspect, it seemed that the likelihood of thermal risk increased due to the shortened TMR and a lowered “onset” temperature.

T_{max} is the temperature when the maximum self-heating rate is achieved. It also showed a decreasing trend with the addition of sodium bicarbonate, indicating that maximum temperature rate could be reached at a lower temperature. Moreover, the maximum temperature rise rate was slightly reduced as shown in Figure 17(c).

T_f is defined as the final temperature, which is also the maximum temperature during the entire reaction. As can be seen from Table 12 that with addition of sodium bicarbonate, T_f showed a slight increase and then dropped. It seemed that the molar ratio of organic peroxide and dry fire extinguishing chemical played an important role in the thermal behavior of the mixture. But due to the large error at molar ratio 1:1, experimental data was not statistically significant to draw conclusion. Therefore, more evidence is needed to validate the results and it is recommended to evaluate the thermal activity in other calorimeters, such as DSC, to characterize the detailed thermal activity of the mixture and facilitate a better understanding of the thermal hazard.

It is interesting to see from Figure 17(b) that the maximum pressure in the reaction course was lowered after adding sodium bicarbonate. In addition, the maximum pressure rise rate $(dP/dt)_{max}$ was significantly reduced by introducing sodium bicarbonate into the system, as shown in Figure 17(d). As a result, pressure hazard was suppressed, and the severity of thermal explosion was reduced. It is possible that the carbon dioxide generated from melting and decomposition of sodium bicarbonate inhibited the gas generation from benzoyl peroxide decomposition, and reduced the pressure hazard of BPO decomposition to certain extent. The mechanism behind the phenomena needs further analysis.

Table 12 BPO mixture with $NaHCO_3$ at various molar ratios

Chemicals	Molar ratio	Sample Mass (g)	T_o (°C)	T_{max} (°C)	T_f (°C)
BPO		0.50	98 (±4)	104 (±3)	120 (±3)
BPO: $NaHCO_3$	1:1	0.50 : 0.13	85 (±1)	90 (±1)	129 (±26)
BPO: $NaHCO_3$	1:2	0.50 : 0.26	88 (±4)	94 (±5)	103(±4)

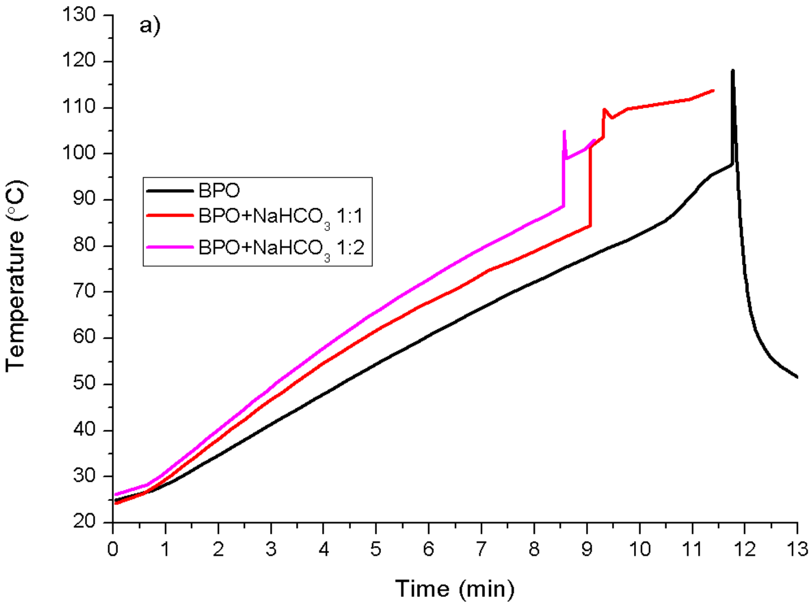
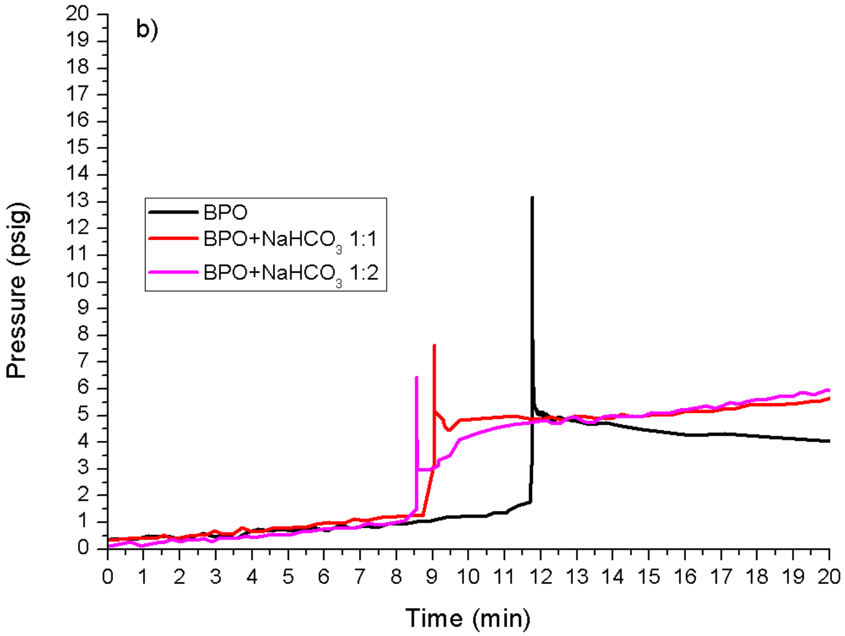


Figure 17 Thermal decomposition of BPO mixed with $NaHCO_3$ (a) Temperature profile (b) Pressure profile (c) Self-heating rate (d) Pressure rate



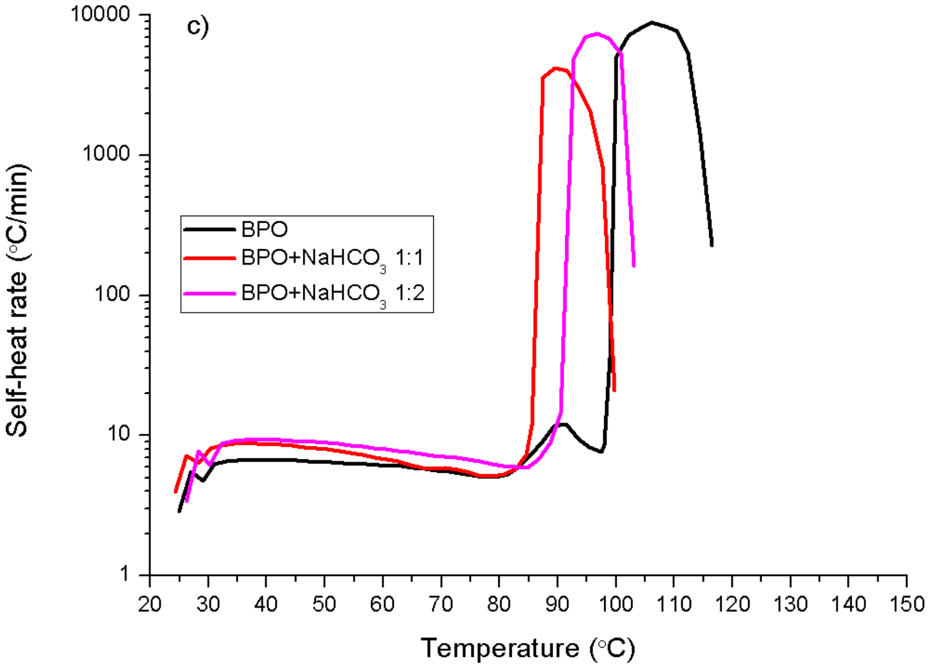


Figure 17 Continued

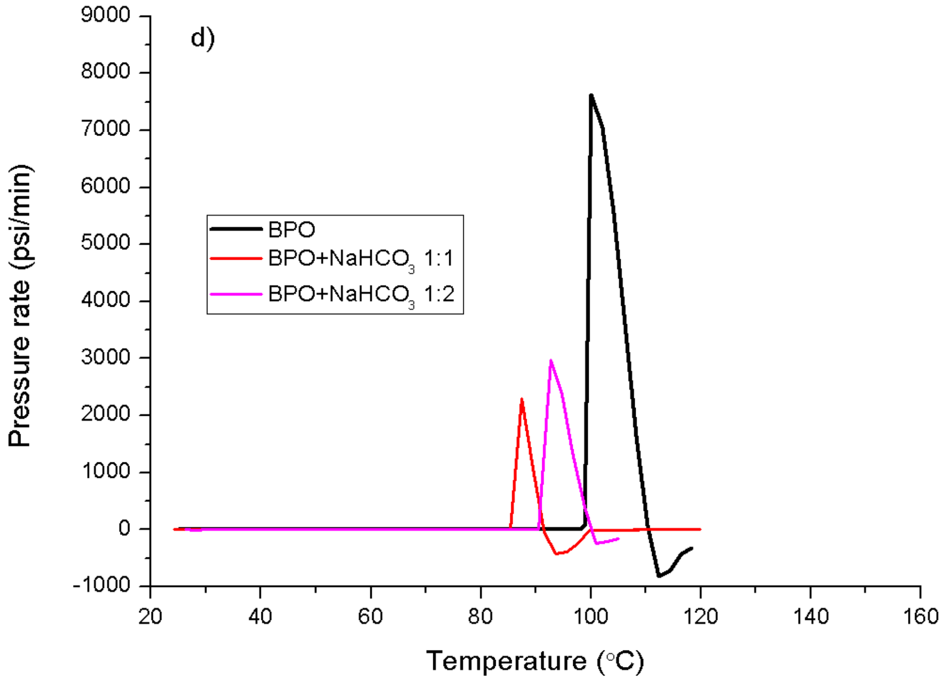


Figure 17 Continued

5.4.2 Effect of Potassium Bicarbonate in ARSST

In order to study the effect of $KHCO_3$, 75% BPO (0.50 g) was mixed with $KHCO_3$ under molar ratios of 1:1 and 1:2, and results are summarized in Table 13. The experimental data was plotted in Figure 18.

Similar to sodium bicarbonate, the "onset" temperature of mixture was lowered after adding potassium bicarbonate. The decomposition of potassium bicarbonate occurs at 100°C, which is about the same decomposition temperature of 75% BPO. However, the "onset" temperature of mixture decreased by around 10°C, and the decomposition occurred earlier as shown in Figure 18(a). The T_{max}, T_f and maximum self-heating rate had a decreasing trend. Again, ARSST can provide a rough estimation of thermal behavior, and it is strongly encouraged to further the thermal hazard assessment of mixture in more sophisticated calorimeters.

The pressure data obtained from ARSST could provide useful information. As can be seen from Figure 18(b) and 18(d), the maximum pressure and maximum pressure rise rate were reduced significantly, revealing the potential inhibition effect of the decomposition reaction.

In a simplified reaction, 1 mol of BPO can decompose and generate benzoate radicals, then benzoate radicals could further decompose completely to generate 2 mol of carbon dioxide and phenyl radicals, as shown in Equation 15. It is the main reaction when the temperature is relatively low. However, when the temperature is higher, another pathway involving asymmetrical homolytic cleavage of peroxide might take place to form free radical $C_6H_5C(O)\cdot$ and oxygen, as shown in Equation 16, even further to produce the phenyl radical and carbon monoxide [119]. Therefore, when temperature is very high under external fire situation, it is possible that BPO can decompose to generate carbon dioxide, oxygen, and carbon monoxide. After introducing bicarbonate salt ($NaHCO_3$ or $KHCO_3$) into the system, it may react with benzoic acid and produce sodium benzoate or potassium benzoate. A possible overall reaction is proposed as shown in Equation 17. The hypothesis needs further investigation of gas product analysis in order to be able to understand the decomposition mechanism.

$1\ (C_6H_5CO)_2O_2 \rightharpoonup 2\ (C_6H_5CO)O\cdot \rightharpoonup 2\ (C_6H_5)\cdot + 2\ CO_2$ Equation 15

$1\ (C_6H_5CO)_2O_2 \rightharpoonup C_6H_5COOO\cdot + C_6H_5C(O)\cdot \rightharpoonup 2\ C_6H_5C(O)\cdot + O_2$ Equation 16

$1\ (C_6H_5CO)_2O_2 + 2\ KHCO_3 \rightharpoonup 2\ C_6H_5CO_2K + CO_2 + CO + O_2 + H_2O$ Equation 17

Table 13 BPO mixture with $KHCO_3$ at various molar ratios

Chemicals	Molar ratio	Sample Mass (g)	T_o (°C)	T_{max} (°C)	T_f (°C)
BPO		0.50	98 (±4)	104 (±3)	120 (±3)
BPO: $KHCO_3$	1:1	0.50 : 0.15	87 (±2)	92 (±1)	127 (±6)
BPO: $KHCO_3$	1:2	0.50 : 0.31	84 (±3)	90 (±4)	110 (±5)

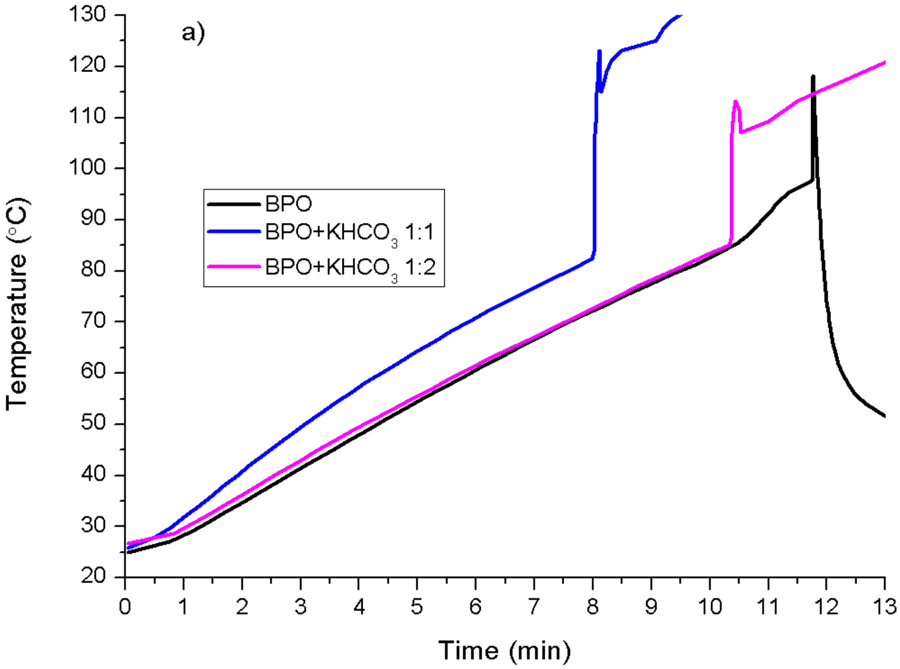


Figure 18 Thermal decomposition of BPO mixed with $KHCO_3$ (a) Temperature profile (b) Pressure profile (c) Self-heating rate (d) Pressure rate

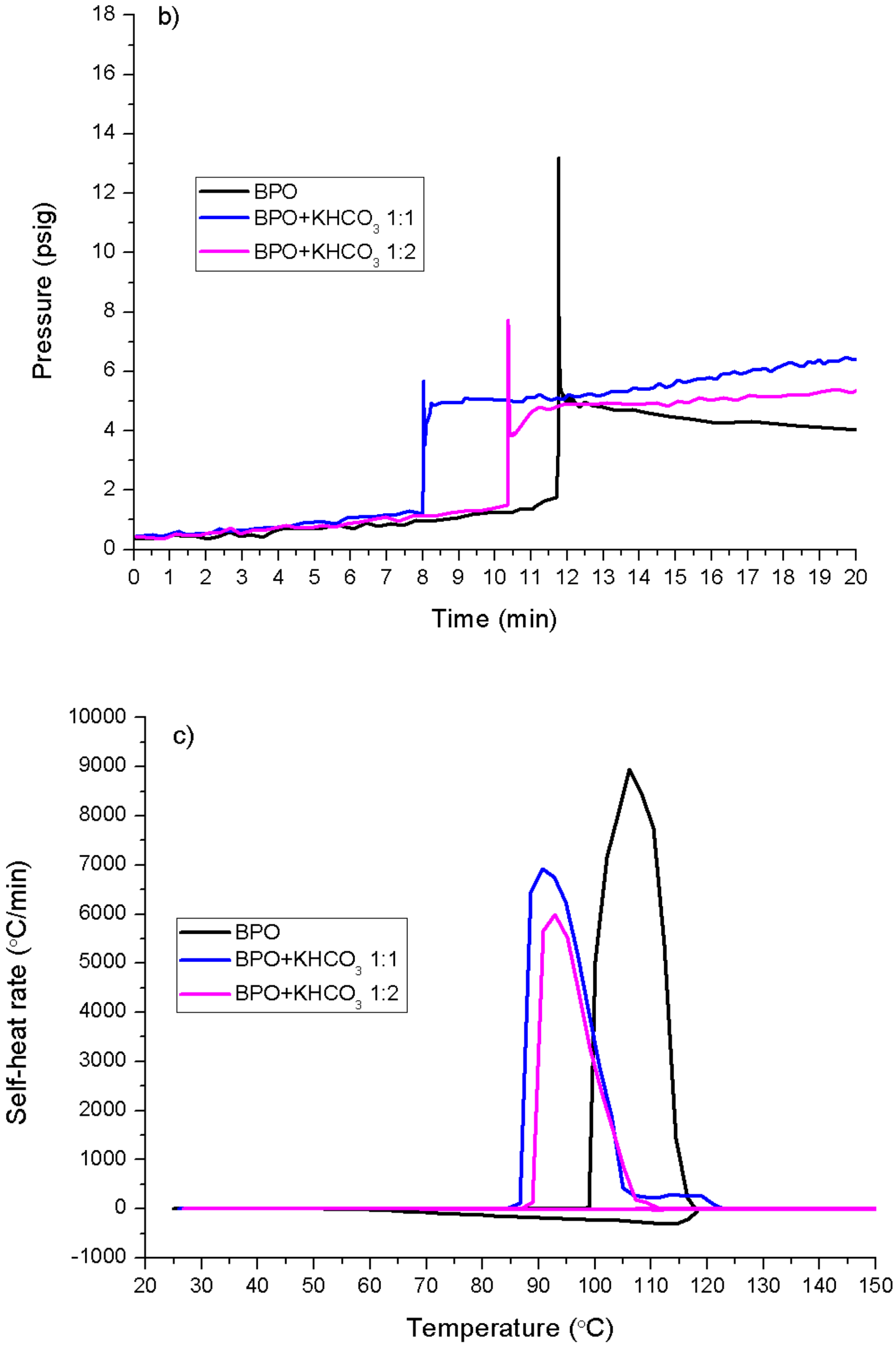


Figure 18 Continued

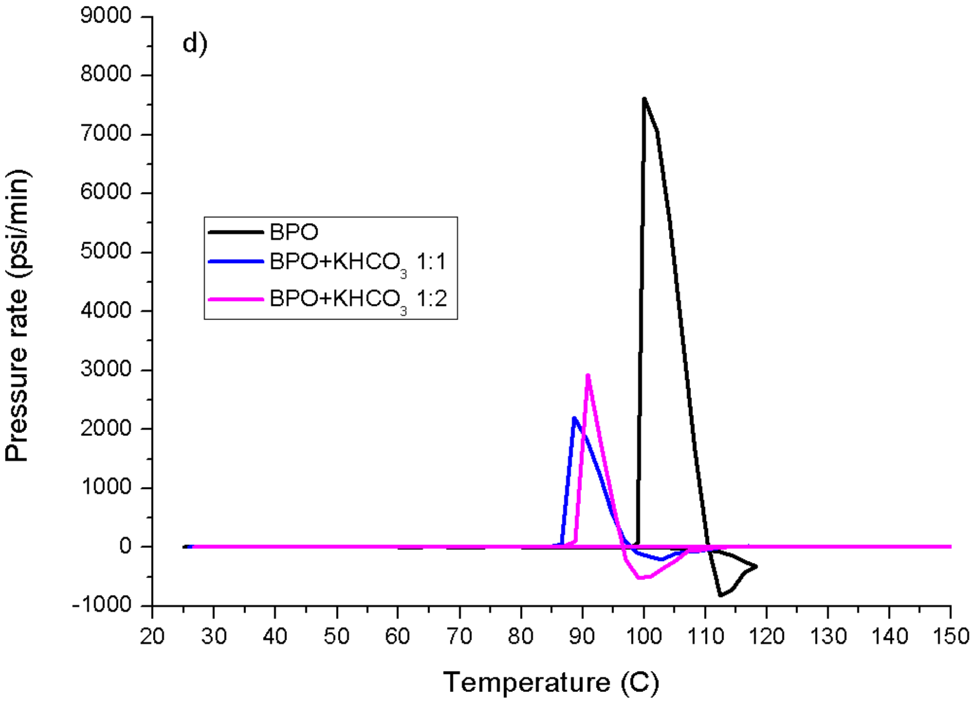


Figure 18 Continued

5.4.3 Effect of Ammonium Dihydrogen Phosphate in ARSST

In order to study the effect of $NH_4H_2PO_4$, 75% BPO (0.50 g) was mixed with $NH_4H_2PO_4$ with various molar ratios, including 2:1, 1:1, 1:2, as shown in Table 14.

Table 14 BPO mixture with $NH_4H_2PO_4$ at various molar ratios

Chemicals	Molar ratio	Sample Mass (g)	T_o (°C)	T_{max} (°C)	T_f (°C)
BPO		0.50	98 (±4)	104 (±3)	120 (±3)
BPO: $NH_4H_2PO_4$	2:1	0.50: 0.09	96 (±11)	102 (±11)	116 (±13)
BPO: $NH_4H_2PO_4$	1:1	0.50: 0.18	96 (±1)	107 (±1)	131 (±4)
BPO: $NH_4H_2PO_4$	1:2	0.50: 0.36	100 (±2)	107 (±6)	126 (±15)

From Table 14 and Figure 19, we can see that adding ammonium dihydrogen phosphate did not influence the “onset” temperature of decomposition reaction. It is known that the “onset” temperature depends on factors such as the sensitivity of thermocouple, adiabatic conditions, and heat capacity of sample and cell [120]. Therefore, it is recommended to conduct tests in more advanced adiabatic calorimeter to better characterize the “onset” temperature. T_{max} and T_f were also determined and summarized in Table 14. The results showed that T_{max} and T_f increased slightly but not statistically significant. From pressure profile we can see that pressure could increase suddenly and rapidly due to thermal decomposition, but the maximum pressure was not changed significantly by adding $NH_4H_2PO_4$. It is shown from our previous study [121] that solid 75% BPO decomposition is a violent reaction, therefore, it is difficult for the apparatus to precisely record the maximum temperature or pressure or maximum rate. Therefore, in order to characterize the reaction course and analyze reaction kinetics, we decided to dilute the concentrated sample to slow down the reaction and study the decomposition in a more advanced adiabatic calorimeter APTAC. Details about APTAC tests are discussed in the following section.

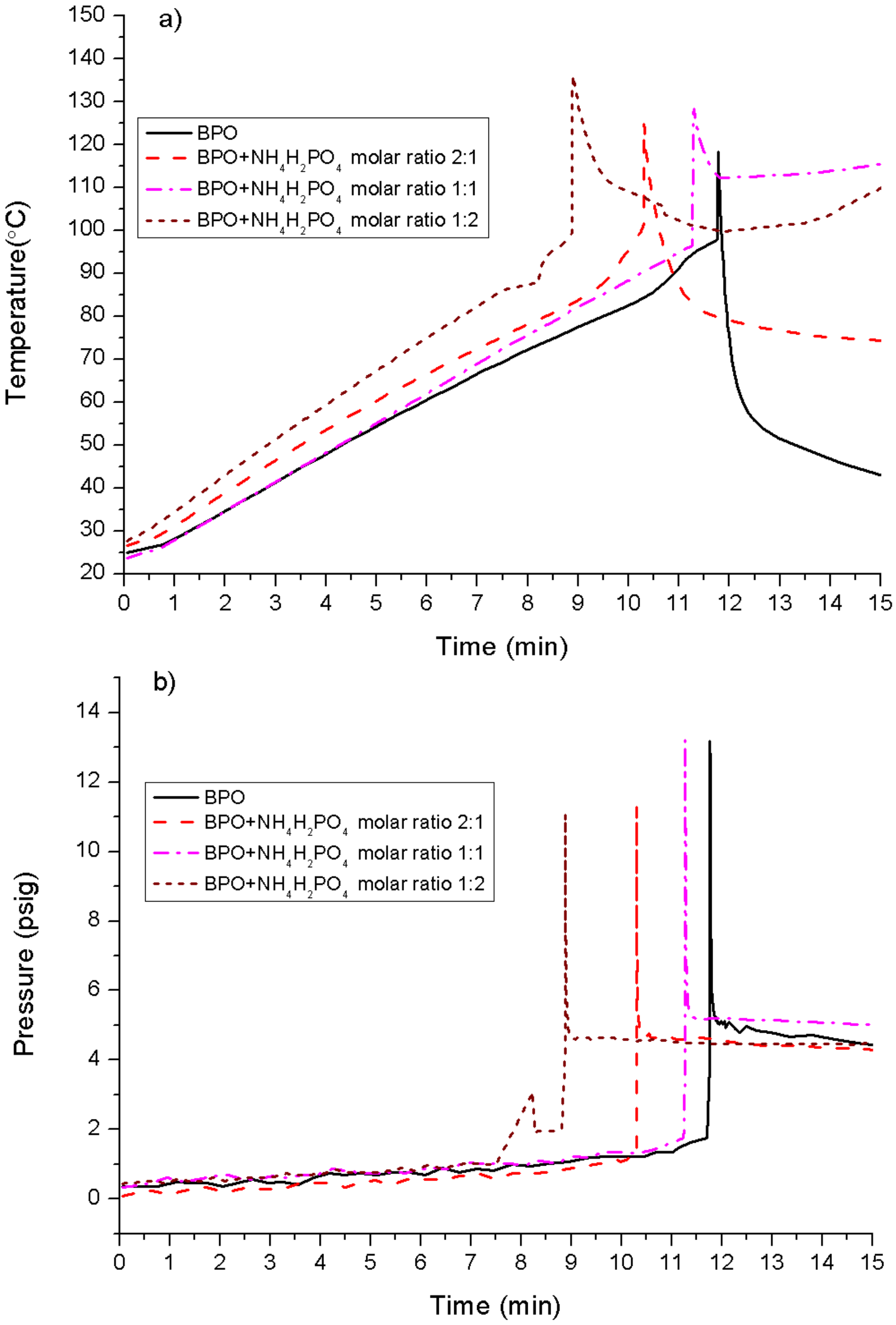


Figure 19 Thermal decomposition of BPO mixed with $NH_4H_2PO_4$ (a) Temperature profile (b) Pressure profile (c) Self-heating rate (d) Pressure rate

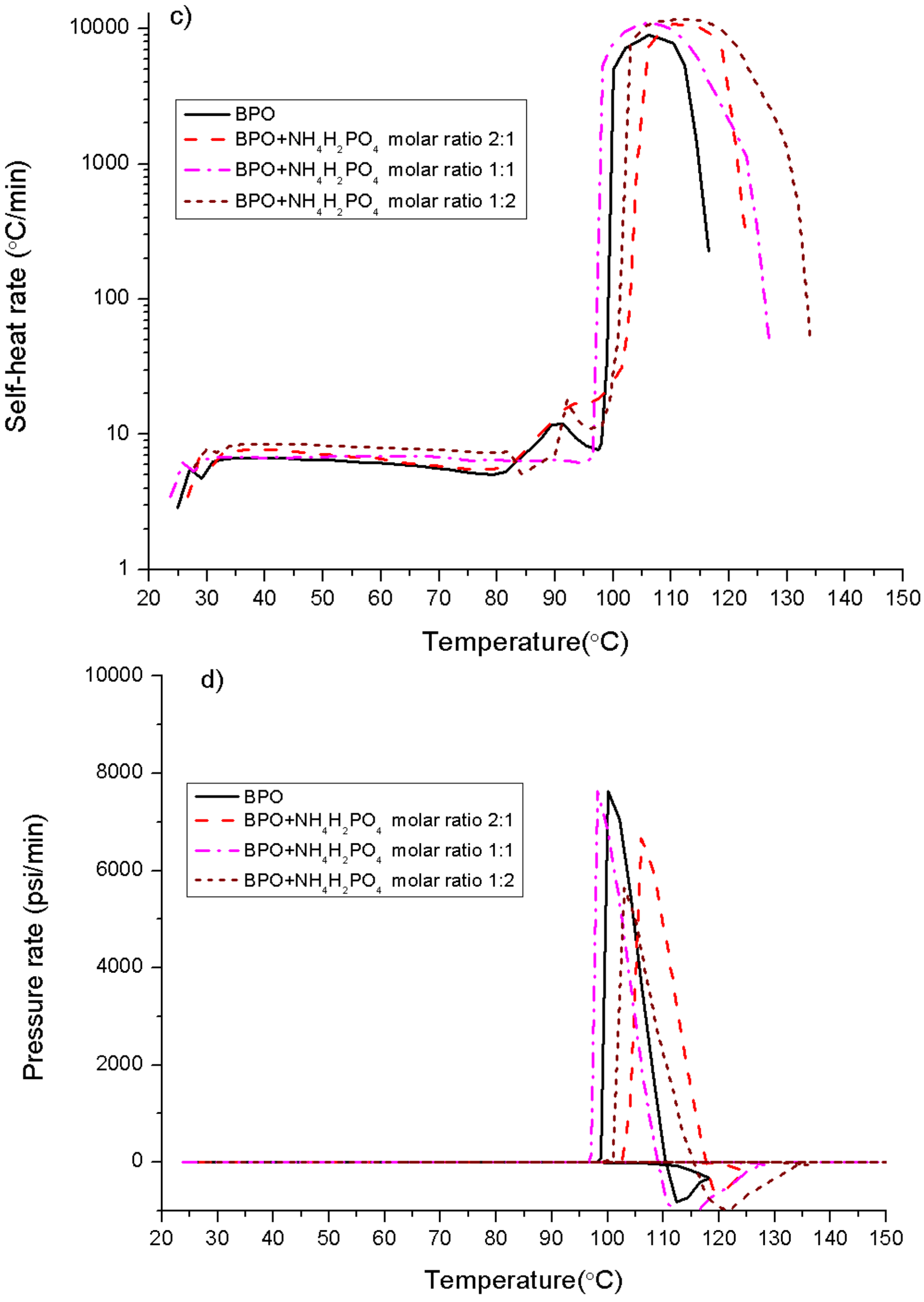


Figure 19 Continued

5.4.4 Effect of Ammonium Dihydrogen Phosphate in APTAC

The effect of ammonium dihydrogen phosphate on BPO thermal decomposition was also evaluated in APTAC. In this study, toluene was used to dissolve and dilute the 98% BPO sample to 20% mass concentration. 20 ml sample mixture was loaded to a 50 ml glass spherical flask, and stirred by a magnetic stirrer bar. Initial pressure of 300 psi was used to reduce the vaporization of solvent. Each test used 4.34 g 98% BPO mixed with $NH_4H_2PO_4$ with mass ratios of 10:1, 5:1 and 3:1. The experimental data are summarized in Table 15.

Compared with ARSST study, the “onset” temperature detected in APTAC was much lower. The effect of solvent was significant. The “onset” temperature of solid BPO was determined to be around 98 °C, but after dissolving and diluting with toluene solvent, the “onset” temperature decreased to 71 °C. The possible reasons were provided in previous chapter: 1) the reaction was slowed down after diluting the sample in solvent, therefore, it was easier for the calorimeter to detect the “onset” at the early stage of an autocatalytic reaction and record the entire reaction course.; 2) solvent enhanced the mass and heat transfer of radicals, resulting in easier decomposition; 3) the sensitivity of APTAC is superior to screening tool. As shown in Figure 21(a), with increasing amount of $NH_4H_2PO_4$, the “onset” temperature of BPO decomposition did not change, however, time to the “onset” was delayed, denoting an inhibition effect. From Figure 21(c) and 21(d), we can see that the maximum temperature rate and maximum pressure rate were decreased significantly when adding increasing amount of $NH_4H_2PO_4$ to the system, indicating that the severity of thermal runaway was reduced.

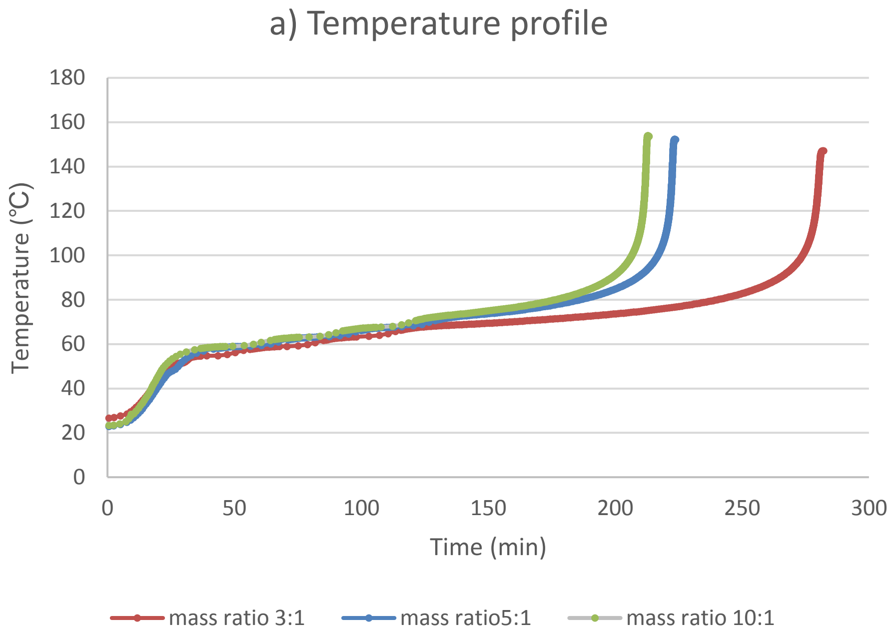
Table 15 20% BPO mixed with $NH_4H_2PO_4$ at various mass ratios in 20 ml toluene

Mass ratio ($BPO:NH_4H_2PO_4$)	$NH_4H_2PO_4$ mass (g)	T_o (°C)	T_f (°C)	$(dT/dt)_{max}$ (°C/min)	P_f (kPa)	$(dP/dt)_{max}$ (kPa/min)	ΔH_d (J/g)	E_a (kJ/ mol)
10:1	0.41	71	154	34	4354	890	1192	130
5:1	0.87	71	152	30	4059	790	1074	132
3:1	1.45	67	147	19	4092	523	967	131

From Table 15, we can see that the final temperature of the reaction also showed a trend of decreasing. In addition, ΔH_d was also decreased, indicating that $NH_4H_2PO_4$ could potentially reduce the thermal hazard of BPO decomposition.

According to literature, when the ammonium dihydrogen phosphate was heated, it would decompose into the phosphorus species (PO_2, HOPO, $HOPO_2$, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}). That phosphorus-containing radicals HOPO and $HOPO_2$ could catalyze the recombination of radicals, resulting in the decrease in concentration of radicals [117]. This provides a possible explanation for the inhibition effect of $NH_4H_2PO_4$ on BPO decomposition.

Figure 20 Photograph of sample after reaction in APTAC



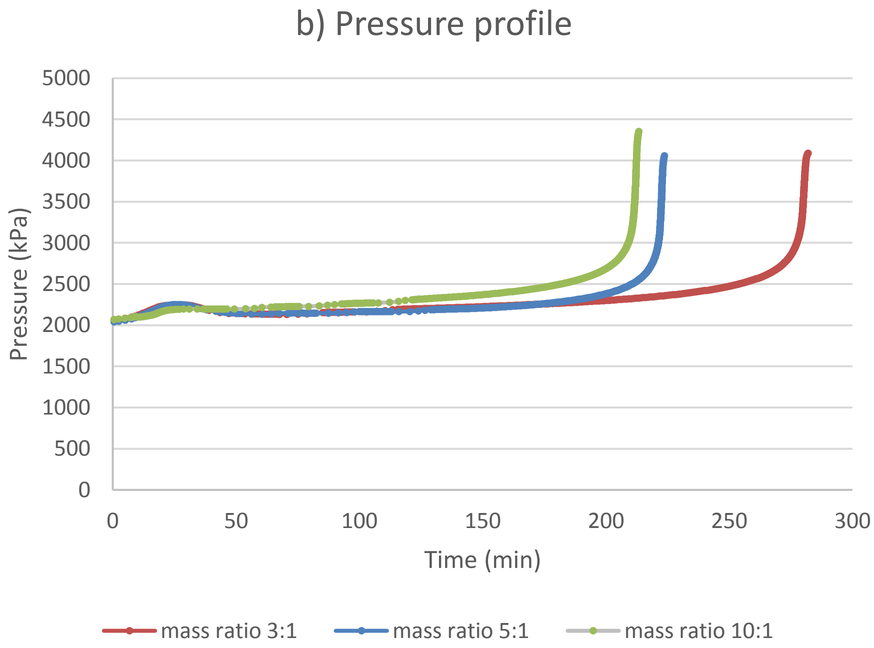
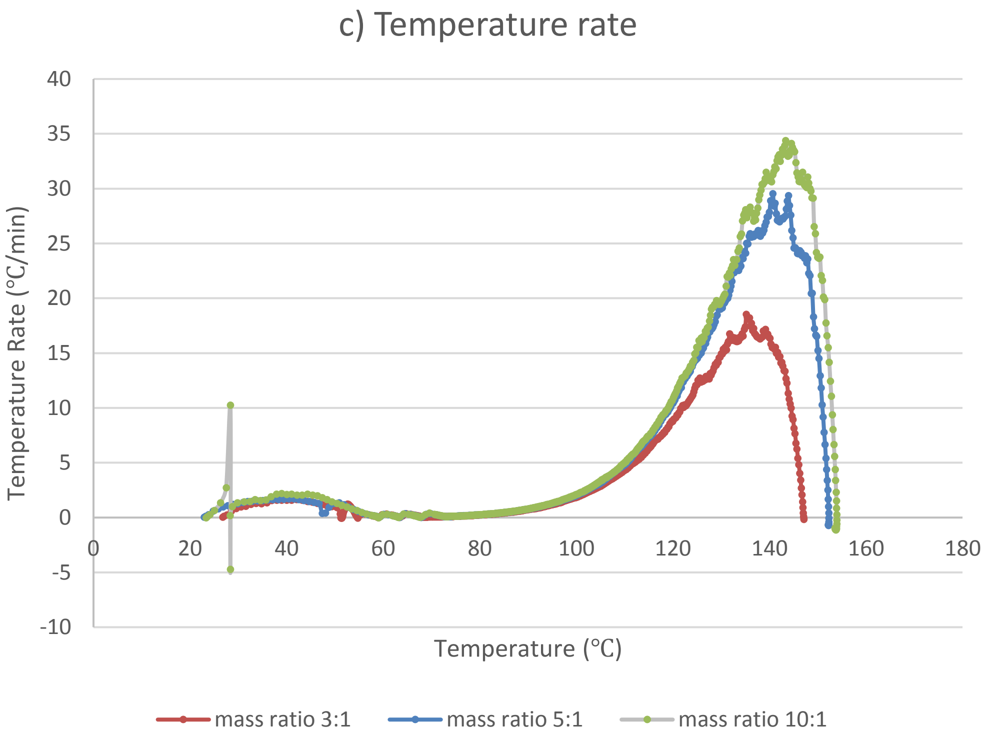


Figure 21 Thermal decomposition of BPO mixed with $NH_4H_2PO_4$ in APTAC (a) Temperature profile (b) Pressure profile (c) Self-heating rate (d) Pressure rate



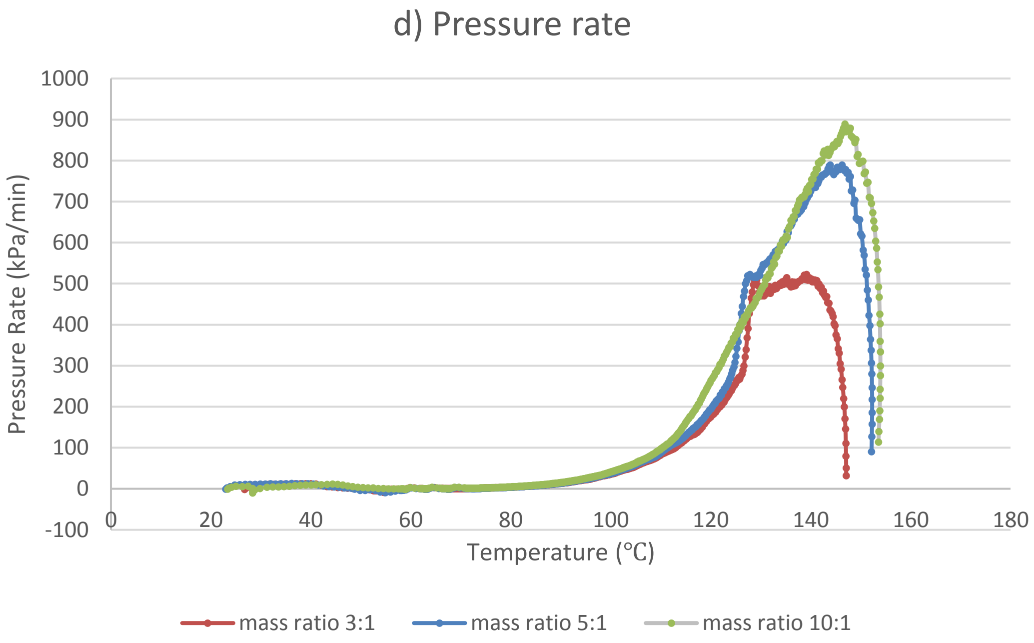


Figure 21 Continued

5.5 Conclusions

In this chapter, the effects of sodium bicarbonate, potassium bicarbonate, and ammonium dihydrogen phosphate on benzoyl peroxide decomposition were evaluated using screening technique and adiabatic calorimeter.

The compatibility of mixture was studied in solid phase in ARSST. The results showed that sodium bicarbonate and potassium bicarbonate could lower the “onset” temperature of BPO, and the decomposition of mixture occurred earlier, indicating that the TMR or emergency response time was shortened. However, the pressure hazard of solid BPO was mitigated after adding sodium bicarbonate or potassium bicarbonate, as the maximum pressure and maximum pressure rate were reduced significantly. The maximum temperature and maximum self-heating rate also showed a decreasing trend. More detailed calorimetry analysis is needed to evaluate the thermal activity of mixtures.

The effect of ammonium dihydrogen phosphate on BPO thermal stability was further investigated in APTAC. The results obtained from adiabatic calorimeter showed that ammonium dihydrogen phosphate had an inhibition effect on thermal decomposition of BPO. Ammonium dihydrogen phosphate did not change the “onset” temperature, but the “onset” was delayed. The maximum temperature, maximum self-heating rate and maximum pressure rate were decreased, indicating that the severity of thermal runaway was reduced with the addition of ammonium dihydrogen phosphate.

This work gave a preliminary investigation of the effect of three dry fire-extinguishing chemicals on the thermal decomposition of BPO. Although sodium bicarbonate and potassium bicarbonate showed an inhibition effect on the pressure hazard of BPO thermal explosion, they could cause the mixture to decompose earlier and at a lower temperature. Ammonium dihydrogen phosphate could be an ideal inhibitor during organic peroxide decomposition, as shown in this work as well as other studies in literature. The information of this work could be a useful reference for firefighting of organic peroxide.

CHAPTER VI

CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

This research involved calorimetry study of thermal decomposition of benzoyl peroxide under different conditions. The main conclusions of this dissertation are summarized as follows.

The condition-dependent benzoyl peroxide decomposition in solid phase was investigated using pseudo-adiabatic calorimetry ARSST. The effects of sample concentration, confinement, isothermal temperature, and selected acids and bases were evaluated to identify the potential hazards and provide guidance during the storage, transportation and handling of solid BPO. The results showed that the “onset” temperatures of 75% BPO and 98% BPO were 98 °C and 79 °C. The explosive like reaction revealed the hazard of thermal explosion of solid BPO. The effect of confinement was tested by observing BPO decomposition under various initial back pressures varying from ambient pressure to 200 psig. With increasing initial pressure, the “onset” temperature decreased slightly, the maximum temperature rate and the maximum pressure-rise rate increased dramatically. The thermal explosion occurred earlier under confinement with higher maximum temperature and maximum pressure rise. It is concluded that pressure accumulation is hazardous to BPO and confinement should be avoided for BPO storage and transportation. Isothermal tests demonstrated that higher isothermal temperature resulted in shorter induction time, and the decomposition of BPO could occur at 70 °C. It is recommended to implement adequate temperature control measures to prevent heat accumulation and BPO thermal decomposition. The effects of selected acids and bases on BPO stability were evaluated in ARSST. However, the results showed that these water-based impurities did not influence the thermal behavior of BPO under the tested conditions. More work is needed to investigate the incompatibility hazards of these contaminants.

The thermal runaway behavior of benzoyl peroxide in alkylbenzne solvent was studied employing adiabatic calorimetry APTAC, which simulates better worst case scenario on a large-scale. The experimental work allowed characterizing the physical behavior, thermodynamic and kinetic parameters of the runaway decomposition of benzoyl peroxide. The influence of experimental factors including sample volume and mass fraction on the runaway severity was assessed by performing a sensitivity analysis. Self-heating rates and self-pressurization rates depicted an exponential increase with sample size and mass concentration.

The thermal decomposition of benzoyl peroxide in the presence of dry fire-extinguishing chemicals was characterized in calorimeters. The compatibility of dry fire-extinguishing chemicals with BPO was evaluated and potential inhibitors for BPO decomposition was identified. Sodium bicarbonate and potassium bicarbonate decreased the “onset” temperature of BPO and shortened the time to “onset”, denoting the potential of reducing the emergency response time. However, they could mitigate the severity of thermal decomposition of BPO by decreasing the maximum temperature, maximum self-heating rate, maximum pressure, and maximum pressure rate significantly. Ammonium dihydrogen phosphate had an inhibition effect on BPO decomposition. Although it did not influence the “onset” temperature much, it could delay the occurrence of decomposition, and decrease the maximum temperature, maximum self-heating rate, heat of reaction, and maximum pressure rate.

Overall, this research applies calorimetry techniques to investigate thermal hazards of benzoyl peroxide in different systems, and serves as a foundation to further the understanding of BPO under various conditions. This work demonstrates the complexity when handling organic peroxide in various scenarios including storage, transportation, and reaction processes. In addition, the evaluation of the effect of dry fire extinguishing chemicals on BPO decomposition could provide useful information for mitigating the risks of BPO related fires. The systematic approach of this research can be used to study other reactive chemicals of interest.

6.2 Future Work

For solid BPO system, the fast pressure rise and fast temperature increase during BPO decompositions could burst the test cell, as observed in open cell pseudo-adiabatic experiments. Therefore, it is quite challenging to obtain meaningful adiabatic experimental data without damaging the equipment or exceeding the adiabatic tracking limit. To obtain reliable thermal activity data, the recommended testing is to be done in equipment different than the ones used during this research, for example in a differential scanning calorimeter (DSC) or in a micro-calorimeter. When scaling up in closed cell adiabatic tests, it is recommended to mix BPO with other inert materials to increase the sample size and reduce its explosivity. But the mixture could result in other concerns, like the results are not for pure BPO and the repeatability of solid mixtures. So when testing BPO using closed cell adiabatic calorimeter in the future, the choice of diluents and the testing methodology must be careful. Other factors such as the effects of surrounding gas atmosphere, heating rate, thermal history or preheat can also be considered in future work. It is beneficial to use Design of Experiments methods to systematically study these factors.

For BPO-solution system, deeper investigation and a wider concentration range and higher initial fill level should be done. It is important to determine the effect of the amount of sample on the thermal runaway of organic peroxide and propose a scale-up methodology to predict larger-scale BPO decomposition behaviors. Other types of solvent should be studied, which will allow gaining a better understanding of the role of different solvents in the thermal decomposition of BPO under runaway conditions. Other factors such as stirring rate, initial back pressure are worth studying in the future. Calculation of gas production rate including non-condensable gases and volatile components could help with better understanding of runaway behavior and accurate vent sizing.

The incongruences of the effect of acids and bases need further clarification. More additives or impurities apart from what have been reported in literature and this dissertation could be studied to gain a more thorough understanding of BPO in the presence of additives. The effects of water and dry-fire extinguishing chemicals need more investigation. It is important to understand their mechanism and further explore their properties for mitigation of explosion potentials of BPO.

The analytical techniques such as Gas Chromatography (GC), Mass Spectrometry (MS) and/or High-performance liquid chromatography (HPLC) can be coupled with calorimetry study in order to perform a product distribution analysis and verify the mechanisms proposed in literature and in this work.

Theoretical analysis such as molecular simulation could be used to identify potential pathways and understand decomposition mechanism. Molecular simulation using Gaussian software could be conducted to understand BPO and its interaction with solvents and additives from a more fundamental point of view. This could facilitate the interpretation of experimental data, or fill the gap when testing is costly and improbable.

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