



Experimental study on the thermal runaway of hydrogen peroxide with in-/organic impurities by a batch reactor

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ABSTRACT

Hydrogen peroxide, as a very versatile reagent for many industrial processes, has caused many accidents in recent years. Therefore, understanding the thermal hazards of hydrogen peroxide with or without impurities is essential for the prevention of fire and explosion accidents. In this work, batch reactor tests were conducted to study the thermal runaway behavior of hydrogen peroxide under the contaminations of Fe^{3+} ion, formic/acetic acid and ethanol/acetone. Experimental results revealed that the thermal runaway risk of H_2O_2 increased significantly with increasing initial temperature and Fe^{3+} ion concentration. Comparatively, the potential risk of organic impurities on the thermal stability of hydrogen peroxide was found to be much larger, because several violent explosions were measured resulting from a series of rapid and complicated decomposition reactions. The explosion severity of H_2O_2 with organic matters followed acetone > ethanol > formic acid > acetic acid. In addition, a modified runaway scenario characterized as adiabatic temperature increase and time to maximum rate was briefly described to theoretically evaluate the thermal risk of H_2O_2 decomposition. This scenario was found to be valid to estimate thermal runaway hazards. These results improve our understanding of thermal runaway behavior and explosion risk of H_2O_2 with incompatible impurities.

1. Introduction

Hydrogen peroxide, as a multi-functional green oxidizing agent, has been and will continue to be widely used in chemical industry, environmental protection, oil desulphurization, etc., because it has the advantage of producing environmentally benign water and oxygen as its by-product. In general, the normal rate of decomposition for commercially supplied hydrogen peroxide is extremely low, under 1% loss per year (Mackenzie, 1990). However, the violently exothermic decomposition of hydrogen peroxide is well known to incompatible contaminations or high temperatures, including metal ions (Eissen et al., 2003; Eto et al., 2006, 2009; Lu et al., 2006; Liu et al., 2010; Wu et al., 2010), in-/organic acids (Wu et al., 2010; Zang and Qian, 2012; Ni et al., 2016) and other organic matters such as propanone and ethanol (Papadaki et al., 2005; Wu et al., 2010; Chi et al., 2012). If the decomposition is out of control, it releases vast heat and oxygen that may cause fatal fire and explosion accidents. Table 1 lists some accidents caused by H_2O_2 owing to its thermal instability or incompatibility in recent years. It reveals that the accidents of H_2O_2 occurred during its

whole lifecycle including generation, storage and transportation, as well as utilization. The major safety problems of hydrogen peroxide are the potential of rapid pressurization and heat release from catalyzed decomposition, fires due to oxygen release in decomposition and vapor phase explosions. For safety concerns, it is important to understand the thermal hazardous characteristics of hydrogen peroxide and the corresponding influence factors on this process.

The thermal hazard analyses of hydrogen peroxide or other organic peroxides have been experimentally studied with differential scanning calorimetry (DSC) (Chi et al., 2012; Liu et al., 2013; Wu et al., 2009, 2010, 2012; Lv et al., 2014; Gramm et al., 2011), accelerating rate calorimeter (ARC) (Liu et al., 2010; Zang and Qian, 2012) and glass vessel (Eto et al., 2009) or Dewar flask (Eissen et al., 2003), as well as RC1e (Zhang et al., 2016) tests. Eto et al. (2009) studied effects of various ions on the runaway reaction of hydrogen peroxide and concluded that iron, copper and chlorine ions accelerate the runaway reaction, whilst nickel, potassium, sulfate and nitrate ions show an opposite effect. Lu et al. (2006) determined the criteria of critical runaway of hydrogen peroxide in the presence of

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| Nomenclature | | | |
|--------------|--------------------------------------|-------------------|--|
| A | pre-exponential factor, 1/s | T | temperature, K |
| C | molar concentration, mol/L | ΔT_{ad} | adiabatic temperature increase, K |
| c_p | specific heat capacity, J/kg-K | TMR_{ex} | time to maximum rate of experiment, s |
| E_a | apparent activation energy, kJ/mol | TMR_{ad} | time to maximum rate under adiabatic condition, s |
| $f(C)$ | function of concentration, mol/L | ρ | density, kg/L |
| ΔH_d | decomposition enthalpy, J/mol | X | fractional conversion |
| $k(T)$ | first order rate constant, 1/s | <i>Subscripts</i> | |
| m | mass, kg | 0 | initial |
| P | pressure, MPa | C | control |
| \dot{q}_d | specific decomposition power, W/kg | end | final |
| Q_d | specific decomposition heat, kJ/kg | G | gas |
| R | ideal gas constant, J/mol-K | L | liquid |
| r_d | decomposition rate, mol/L-s | max | maximum |
| t | time, s | $T = T_0$ | temperature at the beginning of the decomposition run-away |
| τ | time to peak temperature/pressure, s | | |

hydrochloric acid and estimated the kinetic parameters of decomposition reaction via reactive system screening tool (RSST) apparatus. Liu et al. (2010) used ARC to investigate the effect of micro amount of Fe^{3+} on thermal explosion of hydrogen peroxide and found that the presence of Fe^{3+} leads to a lower decomposition temperature of H_2O_2 with decreasing apparent activation energy (E_a). Chi et al. (2012) adopted DSC and vent sizing package 2 (VSP 2) to analyze the reactive characteristics of H_2O_2 with propanone for acquiring thermal runaway data such as adiabatic temperature (ΔT_{ad}) and adiabatic time to maximum rate (TMR_{ad}). In addition, Eissen et al. (2003) proposed an adiabatic model to theoretically investigate the runaway scenario and an experiment of H_2O_2 with potassium iodide was conducted in a Dewar flask to verify the theoretical assessment. Raines et al. (2006) examined the chemical reactivity of hydrogen peroxide at two different temperatures both with and without contamination by using the fast-thermal activity interpreter (FTAI) instrument. They (Raines et al., 2006) found that the reaction rate of 50% H_2O_2 increased by almost a factor of 4 when the initial temperature increased from 30 °C to 40 °C, while the reaction rate increased by a factor of 50 with the contamination of a small amount of rust at 30 °C.

In this paper, we experimentally studied the thermal characteristics of H_2O_2 under the contaminations of Fe^{3+} ion, formic/acetic acid and ethanol/acetone through a batch reactor. By varying the initial temperature and the concentration of Fe^{3+} ion, as well as the impurity type, we determined and compared the maximum temperature/pressure, the time to the maximum temperature and reaction mechanism. The aim of this work is to improve the understanding of the runaway behaviors of H_2O_2 under contaminations.

Table 1
Selected incidents of H_2O_2 due to thermal runaway reactions.

| Date | Location | Casualty | Explosion occurrence |
|------------|------------------------------|----------|----------------------|
| 09/05/1987 | Taiwan (Wu et al., 2009) | 20 | utilization |
| 10/29/1999 | Tokyo (Kumasaki, 2006) | 23 | transportation |
| 04/22/2004 | Ningbo (Liu et al., 2010) | 6 | production |
| 11/24/2005 | Chongqing | 6 | utilization |
| 06/15/2006 | Longquan | 3 | production |
| 07/28/2006 | Shanghai | 4 | production |
| 06/02/2007 | Luzhai (Guan, 2007) | 0 | transportation |
| 09/06/2007 | Wuyi | 0 | transportation |
| 01/07/2009 | Jiaozhou | 4 | storage |
| 09/15/2010 | Jinzhou | 19 | transportation |
| 06/09/2010 | Dalian (Zang and Qian, 2012) | 0 | utilization |
| 07/23/2011 | Taiyuan | 0 | storage |

2. Experimental apparatus and procedure

2.1. Experimental samples

In this work, 30% H_2O_2 (mass fraction, hereinafter the same) was selected as the reagent. The average values of its properties are following: specific heat capacity c_p (3.72 kJ/kg-K), density ρ (1110 g/L) and decomposition enthalpy ΔH_d (-98 kJ/mol). Considering the accidents of H_2O_2 during storage and transportation as summarized in Table 1, iron rust (Fe^{3+} ion in Fe_2O_3) as typical metal impurities was reported in Eto et al. (2006, 2009), Liu et al. (2010) and Kumasaki (2006), thus a substitution Fe^{3+} ion in ferric sulfate $Fe_2(SO_4)_3$ ($\geq 99.0\%$) was selected. Formic acid and acetic acid as catalysts were widely used with the H_2O_2 on the oxidative desulphurization (Zang and Qian, 2012; Filippis et al., 2002), thus we chose formic acid HCOOH ($\geq 88.0\%$) and acetic acid ($\geq 99.5\%$) as the organic impurities in this work. Furthermore, ethanol and acetone as the common reagents in laboratories may be mishandled and mixed with H_2O_2 by accident, therefore ethanol C_2H_5OH ($\geq 99.7\%$) and propanone/acetone CH_3COCH_3 ($\geq 99.5\%$) were taken for thermal risk analyses. All the experimental samples were purchased from Beijing Chemical Reagent Co., Ltd.

2.2. Batch reactor test

An agitated batch reactor was adopted to determine the thermal decomposition reaction behavior of hydrogen peroxide in this work as illustrated in Fig. 1. This reactor provides a maximum temperature of 600 °C and a maximum pressure of 50 MPa. A 400-mL stainless steel cylinder vessel was built-in the center of the reactor and surrounded by the thermal insulation materials. The temperature (T_C) of the vessel was controlled by an electrical heating system and stabilized within ± 1 °C. A magnetic stirrer was installed on the top of the reactor to keep the liquid reaction homogenous and its rotate speed ranged from 5 to 1400 rpm (200 rpm was used for all the tests in this work). Two extra thermocouples were placed inside of the vessel to monitor the liquid phase temperature (T_l) and gas phase temperature (T_g), respectively. Meanwhile the pressure inside of the vessel was measured by a pressure transducer with a maximum pressure of 50 MPa. The vessel was flushed by deionized water and dried prior to each experiment. When the test started, the desired sample of H_2O_2 with or without impurities was placed in the vessel that was immediately closed after feeding the sample, and the sample was heated to an expected initial temperature. Once the temperature was heated to the desired temperature, the heating system was switched off. The pressure transducer and all the thermocouples were recorded simultaneously every 1/4 s. To verify the

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