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Screening Test of Evaluation Thermal Hazard for H_2O_2 by DSC

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Abstract. The oxidizing material is substance that can deliver oxygen other substance without the combustion. The hydrogen peroxide (H_2O_2) easily decomposes at ambient temperature. In the present study, it is aimed to thermal hazard of hydrogen peroxide. The thermal data of onset temperature, peak temperature and enthalpy of reaction of hydrogen peroxide at 50% ww^{-1} for commercial grade was tested by differential scanning calorimetry (DSC). The increasing of heating rate in the range of 3-7 $°Cmin^{-1}$ increases the onset temperature from 63.4-86.3 $°C$, respectively. The activation energy of hydrogen peroxide was 77.1 $kJmol^{-1}$. The adiabatic decomposition temperature rise and the time-to-maximum rate were 394.9 K and 21.6 seconds, respectively. It can be described that 50 % ww^{-1} of hydrogen peroxide, themselves is highly oxidizing hazardous material. The storage, transportation and usage must be done very carefully by persons, which have own in chemicals.

1. Introduction

The US Department of Transportation (DOT) classifies the hazardous materials that included explosives, gases, flammable liquids, flammable solids, oxidizing substances and organic peroxides, toxic and infectious substances, radioactive materials, corrosive substances, and miscellaneous dangerous goods/hazardous materials and articles [1]. The tri-nitro toluene ($C_7H_5N_3O_6$), methane (CH_4), methanol (CH_3OH), sodium metal (Na), nitric acid (HNO_3) and cumene hydroperoxide ($C_9H_{12}O_2$), cadmium oxide (CdO) and E coli *(Escherichia coli)*, cobalt 60 (^{60}Co), hydrochloric acid (HCl), and zinc oxide (ZnO) are a little example of hazardous material, respectively.

Consider only the oxidizing substance, it is substance that can deliver oxygen other substance without the need for combustion. It shows in the high risk to occur of fire and explosion [2]. The oxidizing substances have used for many industrials such as ammonium nitrate (NH_4NO_3), calcium chlorate ($Ca(ClO_3)_2$), and hydrogen peroxide (H_2O_2) to use as fertilizer in agricultural, herbicide in plant, and bleaching in pulp and paper industry, respectively.

All of oxidizing agents, we considers only the hydrogen peroxide due to it is used for the chemical reactant in many industries. In addition to the above, hydrogen peroxide is also used as the bleach in the fiber, food or cosmetic industries. It is an oxidizing agent for the production of polymers in the plastics industrial. The control amounts of sludge in wastewater treatment plant. Hydrogen peroxide is a clear liquid which is a boiling point at 150 $°C$. It has a function group of -O-O- which decomposes easily. It is strong oxidizing agent [3]. In general, concentration of hydrogen peroxide greater than 20% which contact with combustible materials, such as methanol or propanone, meth may be caused

fire and explosion. The hydrogen peroxide decomposes to water, oxygen and heat. Another decay of hydrogen peroxide may be cased due to the impurity of metals, such as iron, copper or chromium [4].

Initially the primary guidelines for determining the thermal hazard of hazardous materials for the chemists and the engineering chemistry are the functional groups of explosive and the incompatibility chart of hazardous materials. Both methods were used to evaluate for storage hazardous materials to occur safety. The oxygen balance is calculated to estimate of index the amount of oxygen released from the explosive, oxidizing or organic peroxide materials. The ASTM computer program CHETAH was used to evaluate the heat generated by the decomposition of the hazardous materials. These can be used to assess a single or the chemical reaction of the hazardous materials [5].

The screening test instrument is started from differential Scanning Calorimeter (DSC). It has widely used for quantitative analytical tool of many chemical industrial processes such as plastics, rubbers, electronics, automotive parts, foods and pharmaceutical. The data to obtain from the differential scanning calorimeter has been investigated. They were included melting temperature or glass transition temperature (Tg). The safety data of the thermal hazardous material can be analyzed by differential scanning calorimeter [6]. It consists of onset temperature (T_0), peak temperature (T_P), enthalpy of reaction (ΔH) and mass normalized heat flow rate (q).

Therefore, in the research, we were interested to study the thermal hazards of hydrogen peroxide. It was a high dangerous oxidant. Data were obtained from experiments of differential scanning calorimeter to evaluate for calculation the activation energy (Ea) and risk evaluation of hydrogen peroxide. It is useful for the transportation, storage and usage of hydrogen peroxide to occur safety.

2. Materials and methods

2.1. Sample
Hydrogen peroxide (concentration 50 % ww^{-1}, commercial grade) was purchased from Union Chemical 1986 Co., Ltd. to use as the risk assessment and the thermal hazard potential. The CAS number, chemical formula, molecular weight and the density of hydrogen peroxide was 7722-84-1, H_2O_2, 34.01 $gmol^{-1}$ and 1.19 gcm^{-3} at 20 ℃, respectively.

2.2. DSC tests
Amount 4 mg of hydrogen peroxide was sucked and put by micropipette into the high pressure capsule which was made from stainless steel. The capsule was covered by the metal seal sheet. Then the capsule and metal sheet was screwed by the capsule lid for close all system. Then it was inducted to the differential scanning calorimeter (TA Instrument, model Q10) and used the condition of experiment for temperature in the range 30-200 ℃, the heating rate at 3, 5 and 7 ℃min^{-1}. The onset temperature, peak temperature, enthalpy of reaction and mass normalized heat flow rate was evaluated from the TRIOS data analysis.
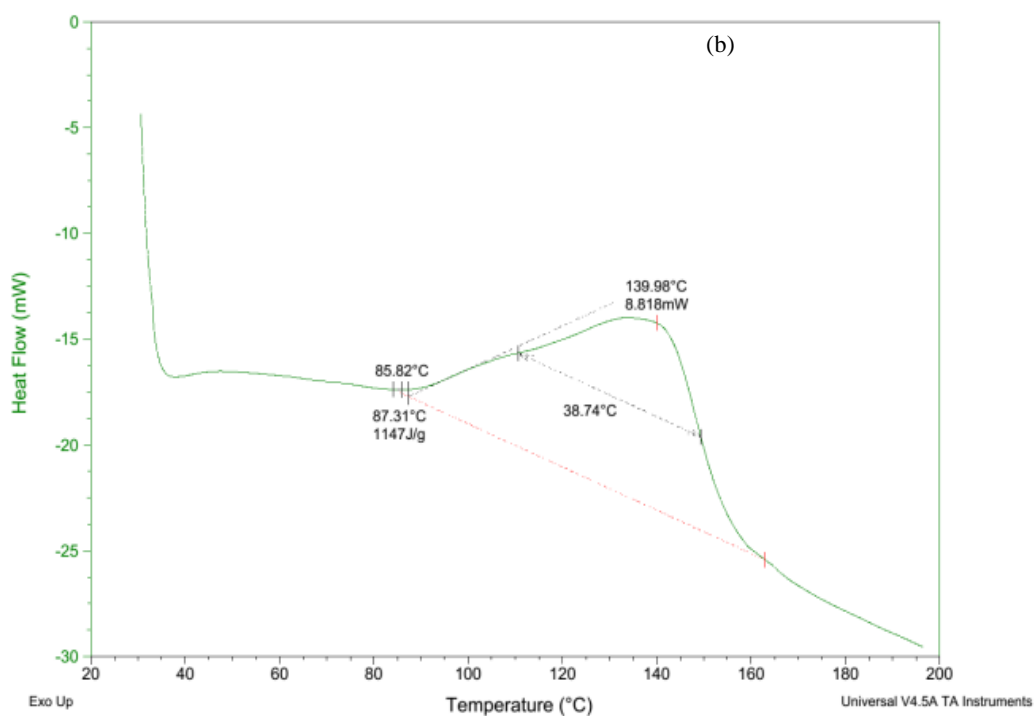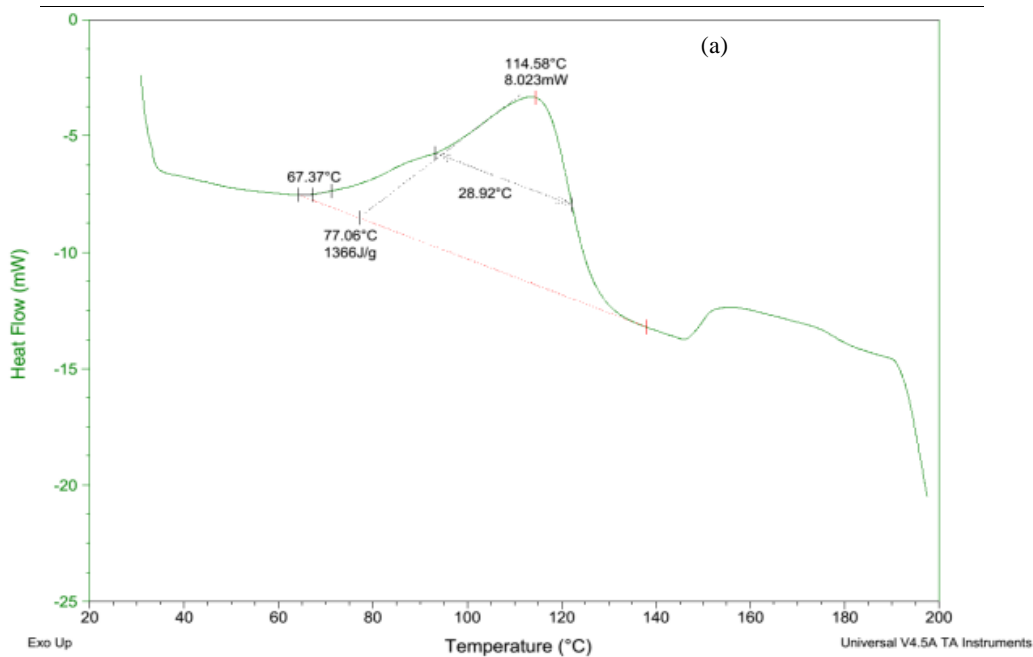
3. Results and discussion

3.1. Thermal decomposition of hydrogen peroxide
The thermal decomposition of hydrogen peroxide for 50% ww^{-1} under heating rates of 3, 5 and 7 ℃min^{-1} were shown in Figures 1 (a)-(c), respectively. The results showed that it appeared the initial onset temperature at 67.4, 85.8 and 86.3 ℃, respectively. The peak temperature of decomposition occurred at temperature 114.6, 139.9 and 134.7 ℃, respectively. The enthalpy of reaction displayed at 1366, 1147 and 1192 Jg^{-1}, respectively which all the numeral from experiment were appeared again in Table 1. The onset temperature of hydrogen peroxide was coincident increases when increased the heating rate. At the low temperature of heating rate, the onset temperature could be clearly observed. The heating rate was increased. The onset temperature was delayed and shipped to a higher temperature. The transition shifted to a higher temperature when heated at a higher heating rate with less time of exposure of the sample.

Table 1. Thermal decomposition data of H_2O_2 from DSC

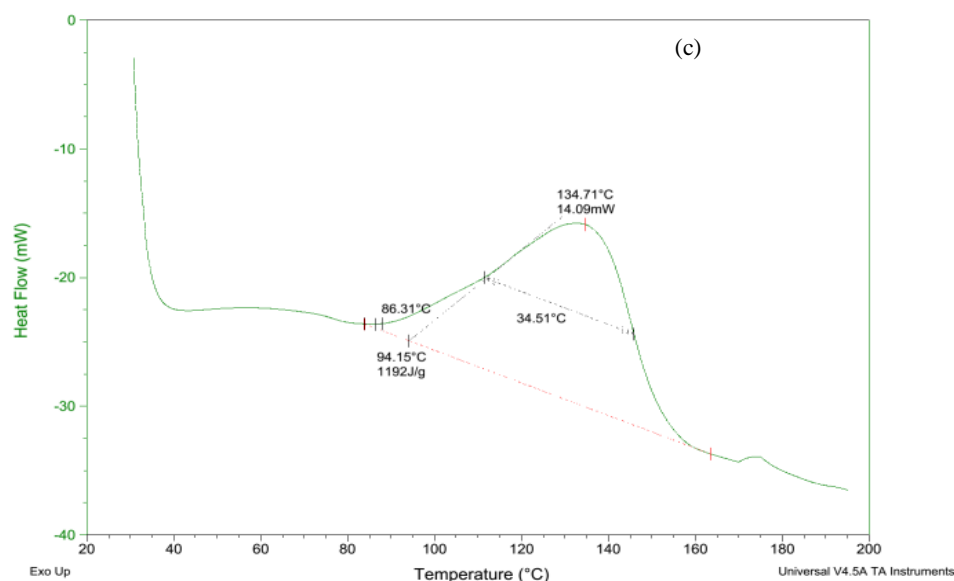| H_2O_2 (% ww^{-1})	Heating rate (°Cmin^{-1})	T_o (°C)	T_P (°C)	Peak of power (mW)	ΔH (Jg^{-1})
	3	63.4	114.6	8.0	1366
50	5	85.8	139.9	8.8	1147
	7	86.3	134.7	14.1	1192

Figure 1. Thermal decomposition of H_2O_2 by DSC at heating rate (a) 3, (b) 5 and (c) 7 $^\circ Cmin^{-1}$

The enthalpy of reaction has showed high value in all experiments. The exothermic reaction of hazardous material is higher than 250 Jg^{-1} indicated that it was the potentially hazardous substance [7]. From experimental of all heating rates, the enthalpy of reaction of hydrogen peroxide is higher than 250 Jg^{-1}. It noticed that the hydrogen peroxide was an inorganic peroxide hazardous material which easily decomposed due to the weak bond of peroxide (-O-O-) functional group in the structure.

3.2. Activation energy of hydrogen peroxide
The data of the heating rate and the peak temperature at 50% ww^{-1} of hydrogen peroxide were brought to use for the calculation of the activation energy. The activation energy (Ea) was used to describe the chemical safety processes. There are two possible explanations. The first described the minimum energy required for a chemical reaction. The hazardous material with low activation energy can be described as easily decomposable. The second described the reactivity of the chemical reaction rate when the temperature occurred changing. The hazardous material showed high value of activation energy. It occurred from the decomposition of chemical [8]. The decomposition of hydrogen peroxide is written in Eq. (1).

$$2H_2O_2 \text{ (aq)} \rightarrow 2H_2O \text{ (aq)} + O_2 \text{ (g)} \qquad (1)$$

The kinetics parameter approach was based on the variable program rate method of ASTM E698 [9] which used heating rates 3, 5 and 7 $^\circ Cmin^{-1}$ to determine the activation energy of reaction for differential scanning calorimeter is written in Eq. (2).

$$\frac{dT}{dt}\frac{d\alpha}{dt} = Ze^{-\frac{E_a}{RT}} \qquad (2)$$

Where dT/dt is heating rate ($^\circ Cmin^{-1}$), dα/dt is reaction rate (sec^{-1}), t is time (sec), T is temperature (K), Z is pre-exponential factor (sec^{-1}) Ea is activation energy ($Jmol^{-1}$) and R is gas constant (8.314 $Jmol^{-1}K^{-1}$)

Rearrange Eq. (2) and new writing followed in Eq. (3)

$$ln\left(\frac{dT}{dt}\right) + ln\left(\frac{d\alpha}{dt}\right) = ln(Z) - \frac{E_a}{RT} \qquad (3)$$

In peak temperature, dα/dt is zero. The activation energy can be calculated by an Arrhenius plot by taking the natural logarithm on the both sides of Eq. (3), the linear form of Eq. (3) is written in Eq. (4).

$$ln\left(\frac{dT}{dt}\right) = ln(Z) - \frac{E_a}{RT_P} \tag{4}$$

Where T_P is peak temperature (K)

The plot of ln heating rate against $1/T_P$ gives a straight line which is shown as in Figure. 2. It was found that a slope of the Eq. (4) was $-E_a/R$. The determination of the activation energy was 77.1 kJmol^{-1}. While an intercept of the same straight line indicates of ln (Z) and the calculation of the pre-exponential factor equals 1.1×10^7 sec^{-1}. Sweeney et al. reporting the activation energy of hydrogen peroxide was 76 kJmol^{-1} [10]. Comparing the activation energy from out experimental and Sweeney et al. it was found that value differed about 1.4 percent.
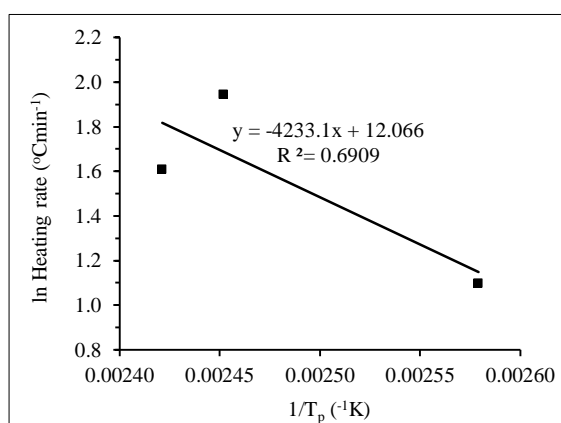

Figure 2. Linear regression according to the Arrhenius plot for 50% ww^{-1} H$_2$O$_2$

3.3. Risk evaluation

The application of activation energy has been bring to use evaluation of thermal hazard materials. The adiabatic decomposition temperature rise (ΔT_d) displays the impact of decomposition, while the time-to-maximum rate (TMR$_d$) indicates the probability of runaway reaction in the case of cooling failure [8]. The adiabatic decomposition temperature rise and the time-to-maximum rate were defined according to Eq. (5) and Eq. (6), respectively.

$$\Delta T_d = \frac{\Delta H}{C_P} \tag{5}$$

$$TMR_d = \frac{C_P R T_P^2}{E_a q} \tag{6}$$

Where ΔT_d is adiabatic decomposition temperature rise (K), TMR$_d$ is time to maximum rate (sec), ΔH is enthalpy of reaction (Jg^{-1}), C_P is specific heat capacity (3.6 Jg^{-1}K^{-1} for hydrogen peroxide) and q is mass normalized heat flow rate (Wg^{-1})

Table 2 shows a classification of an adiabatic decomposition temperature rise. The medium and high ($\Delta T_d > 50$ K) of an adiabatic decomposition temperature rise must be evaluated to consider to the probability of runaway reaction. Table 3 lists the probability of runaway reaction [8]. The mean value of an enthalpy of reaction was 1235 Jg^{-1}. The adiabatic decomposition temperature rise calculated for Eq. (5) for hydrogen peroxide at 50% ww^{-1} was 373.3 K which is displayed in Table 4. Classification from Table 2, the impact of hydrogen peroxide for this concentration is regarded as being high impact. In the future, the probability of hydrogen peroxide for 50% ww^{-1} is necessary to perform.

The mean value of a mass normalized heat flow rate was 10.31 Wg^{-1}. The time-to-maximum rate can be calculation from Eq. (6). The time-to-maximum rate of hydrogen peroxide for 50% ww^{-1} was 21.6 sec it is appeared in Table 4. Classification from Table 3 described that it is highly thermal runaway reaction. The incompatibility of hydrogen peroxide includes metals of copper, chromium, iron and metals or their salts. Beside several of the organic solvents such as acetone, methanol or

ethanol were incompatible of hydrogen peroxide [11]. Thus the transportation, storage and usage of hydrogen peroxide in both laboratory and industry must be act carefully by knowledge person of chemicals.

Table 2. Classification of an adiabatic decomposition temperature rise

ΔT_d (K)	Impact
>200	High
50-200	Medium
< 50	Low

Table 3. Classification of time-to-maximum rate

TMR_d (hr)	Probability
< 8	High
8-24	Medium
> 24	Low

Table 4. The activation energy, ΔT_d and TMR_d for 50% ww^{-1} H_2O_2

H_2O_2 (ww^{-1})	E_a ($kJmol^{-1}$)	ΔT_d (K)	TMR_d (sec)
50%	77.1	373.3	21.6

4. Conclusion

An increasing of heating rate increases the rate of energy release which leading the thermal runaway of hydrogen peroxide occurs at low temperature. The activation energy of hydrogen peroxide for 50% ww^{-1} was 77.1 $kJmol^{-1}$. The adiabatic decomposition temperature rise and the time-to-maximum rate were 373.3 K and 21.6 sec, respectively. It confirmed that hydrogen peroxide for 50% ww^{-1} is the highly oxidizer chemical. There are many advantages of screening test by DSC that included it uses less sample as the operator is highly security. The time for analysis is short as a result reduces cost to operate. The present of the thermal hazard primary test from DSC of hydrogen peroxide is very useful in transportation, storage and usage in the laboratory and the industrial factory.

References
[1]   Torretta V, Rada E C, Schiavon M and Viotti P 2017 Saf. Sci. **92** 1
[2]   Yang X W,Zhang X Y,Guo Z C, Bai W S, Hao L and Wei H Y 2013 Thermochim. Acta. **559** 76
[3]   Romantsova O V and Ulybin V B 2015 Acta Astronaut. **109** 231
[4]   Garc ía M A G, Dobrosz-G ómez I and Toro J C O 2017 Process. Saf. Environ. Prot. **109** 46
[5]   Pasturenzi C, Dellavedova M, Gigante L, Lunghi A, Canavese M, Sala Cattaneo C and Copelli S 2014 J. Loss Prevent. Process. Ind. **28** 79
[6]   Tseng C P and Lin C P 2011 Ind. Eng. Chem. Res. **50** 9487
[7]   Gibson N, Rogers R L, and Wright T K 1987 IChemE Symposium Series **102** 61
[8]   Stoessel F 2008 *Thermal safety of chemical processes: risk assessment and process design* (Basel: Wiley-VCH)
[9]   ASTM E698-11 2011 (ASTM: West Conshohocken)
[10]   Sweeney W, Lee J, Abid N and DeMeo S 2014 J. Chem. Educ. **91** 1216
[11]   Chi J H, Wu S H, Charpentier J C, I Y P and Shu C M 2012 J. Loss Prevent. Process. Ind. **25** 142