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Using VSP2 to separate catalytic and self-decomposition reactions for hydrogen peroxide in the presence of hydrochloric acid

Chi-Min Shu*, Yuh-Joang Yang

Process Safety and Disaster Prevention Laboratory, Department of Environmental and Safety Engineering, National Yunlin University of Science and Technology, Yunlin 640, Taiwan, ROC

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Abstract

In the 1980s, the accelerating rate calorimeter (ARC) made an advance in thermal hazard analysis, because it could record temperature and pressure data more accurately within the region of a self-decomposition reaction under approximately adiabatic conditions. Although, ways to keep adiabatic conditions may be similar, test cell (bomb) and sensitivity are not the same in ARC as in other adiabatic calorimeters, such as Vent Sizing Package2 (VSP2). However, the operating procedures—heat–wait–search (H–W–S)—are all the same. In this study, an improved operating procedure was used to find the slow first step catalytic reaction of hydrogen peroxide (H_2O_2) in the presence of hydrochloric acid (HCl). In these two reactions, the HCl concentration decreases with the activation energy of the first catalytic reaction and then increases with the activation energy of the second self-decomposition reaction. The temperature at which the catalytic and self-decomposition reactions intersect in the experiment operated by the improved method is the onset temperature of the experiment operated by the standard operating procedure. By the improved operating procedure, the duration of the first catalytic reaction increases with HCl concentration being decreased. Operating by the improved method, time to maximum heat rate (tmr) can be compensated at lower temperatures (40 °C to onset temperature), which cannot be accomplished by using the standard operating procedure, and the tmr can be modified at higher temperatures.

Keywords: Self-decomposition reaction; Adiabatic calorimeter; Catalytic reaction; Hydrogen peroxide; tmr

1. Introduction

As more and more chemicals are synthesized and used in the modern chemical process industries, their physical, chemical and other useful properties need to be fully understood or unexpected hazards or even disasters could occur while in production, transportation, and storage or disposal stage. In the 1980s, the accelerating rate calorimeter (ARC) made an advance in thermal hazard analysis, because it could record temperature and pressure data more accurately within the region of self-decomposition or polymerization reaction under approximately adiabatic conditions. These data, along with other derived parameters, can be used to determine the parameters of thermodynamics and kinetics, such as heat of reaction (ΔH_r), reaction rate constant (k), temperature rise rate (dT/dt), onset temperature (T_0), pressure rise rate (dP/dt) and time to maximum heat rate (tmr). In turn, these data can be applied in chemical safety assessment during storage, transportation, and processing or even disposal period.

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* Corresponding author. Tel.: +86-886-05-534-2601x4416/4401/4402; fax: +86-886-05-531-2069.
E-mail address: shucm@pine.yuntech.edu.tw (C.-M. Shu).

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Nomenclature

k	rate constant (M^{1-n}/s)
A	fractional factor (min^{-1})
ΔH	heat of reaction (kJ/mol)
T	temperature (K)
T_0	initial exothermic temperature (K)
t	time (min)
dT/dt	self-heating rate (°C/min)
R	rate of reaction (M/s)

Although, ways to keep adiabatic conditions may be similar, test cell (bomb) and sensitivity are not the same in ARC as in other adiabatic calorimeters, such as the Vent Sizing Package2 (VSP2), PHI TECH II and automatic pressure tracking adiabatic calorimeter (APTAC). However, the operating procedures—heat–wait–search (H–W–S)—are all the same. With the experiment of hydrogen peroxide (H_2O_2) in the presence of hydrochloric acid (HCl), anyone using the "traditional" H–W–S operating procedures could just find the rapid final step reaction (self-decomposition reaction), which is the reaction after the onset temperature. In this study, an improved operating procedure was used to find the slow first step catalytic reaction in H_2O_2 in the presence of impurities, contaminants or catalysts such as HCl. After a 60 ml sample was injected into a test cell while the sample was maintained at 40 °C, the main heater was closed and the guard heater opened to keep the sample in this specific adiabatic condition, 40 °C. From temperature and pressure data, the catalytic reaction can be readily compared with the self-decomposition reaction. During a catalytic reaction, the reaction rate is very slow and the reaction duration increases with catalyst, contaminants or impurity being decreased. From a temperature versus tmr plot, the improved operating procedure can plot tmr under lower temperature region (from 40 °C to onset temperature). Therefore, this improved method could compensate for the "gray zone" (between 40 °C and onset temperature) neglected by the traditional approach. The results show that this specific lower temperature, instead of the regular onset temperature, may incur any potential hazards and should not be overlooked.

2. Literature review

In a closed system, the exothermic reaction of H_2O_2 in the presence of HCl will produce oxygen, which will rapidly raise the temperature and pressure due to its non-condensable property. To prevent the higher pressure from crushing vessels, it is necessary to design a safe venting system. Crowley and Block [1], referring to the experimental results of Livingston and Bray [2] and Budge [3], mixed 12N HCl with 30% H_2O_2 for different volume ratios from 1:15 to 1:2 to investigate the vapor–liquid behavior and venting systems. However, in computer chip manufacturing processes, these materials are often stored at the same place. Any negligence happening during various stages that leave minute amounts of HCl in the H_2O_2 vessel may incur an unacceptable explosion. In this case, the HCl concentration should be kept as low as possible. Therefore, this study uses a new method, the so-called "improved operating procedure", on H_2O_2 to analyze the first slow catalytic reaction, distinguishing it from the second rapid self-decomposition reaction while in the presence of HCl.

3. Experimental apparatus

VSP2 was developed by Fauske and Associates Inc. (FAI) [4]. Its detectable temperature range is from room temperature to 400 °C, and maximum detectable sensitivity is 0.05 °C/min. Normally, two common test cell types are made from Hastelloy C and 316 stainless. The standard operating procedure is repeated by automatic H–W–S mode. Under heating conditions, the main heater will turn on to heat the sample to the pre-set temperature, then turn on a guard heater to keep in an adiabatic environment. Under waiting conditions, stirring will make the sample temperature more uniform. Under searching conditions, it is considered that the reaction has started into the self-decomposition reaction as the sample temperature rise rate is more than apparatus sensitivity (0.05 °C/min). VSP2 can turn on the guard heater to maintain the sample in an adiabatic condition and record reaction temperature and pressure data, to the corresponding time. Essentially, it is a highly sensitive calorimeter that can analyze data to obtain thermodynamic and kinetic variables under an adiabatic condition. Not only could it help plant personnel to clearly understand unexpected reactions, but it could also apply basic data for the prevention and control of runaway reactions.

4. Dynamics of thermal hazard analysis

From the Arrhenius equation:

$$k = A\exp\left(-\frac{E_a}{RT}\right) \tag{1}$$

where k is the rate constant at temperature T, A the frequency factor and R the gas constant. For a single, irreversible and nth order reaction [5]:

$$-\frac{dC}{dt} = kC^n \tag{2}$$

and

$$C = \frac{T_f - T}{T_f - T_0}C_0 \tag{3}$$

where C_0 is the sample initial concentration, T_0 onset temperature of runaway reaction, C the sample concentration at temperature T and T_f the final temperature of the reaction.

Therefore,

$$\frac{dC}{dT} = -\frac{C_0}{T_f - T_0} \tag{4}$$

and

$$\frac{dT}{dt} = \frac{dT}{dC}\frac{dC}{dt} \tag{5}$$

Inserting Eqs. (2) and (4) into Eq. (5) yields

$$\frac{dT}{dt} = k\left(\frac{T_f - T}{T_f - T_0}\right)^n (T_f - T_0)C_0^{n-1} \tag{6}$$

$$\Rightarrow \text{tmr} = t_m - t = \int_t^{t_m} dt$$

$$= \int_T^{T_m} \frac{dT}{k(T_f - T/T_f - T_0)^n (T_f - T_0)C_0^{n-1}} \tag{7}$$

Let

$$\Delta T_{AB} = T_f - T_0 \tag{8}$$

$$\ln(\text{tmr}) = \ln\frac{RT^2}{C_0^{n-1}(T_f - T/\Delta T_{AB})\Delta T_{AB}E_a} - \ln A + \frac{E_a}{R}\left(\frac{1}{T}\right) \tag{9}$$

where dT/dt is rate of temperature rise, which under adiabatic conditions is called "self-heat rate". If this reaction is under a broader temperature range, along with a higher activation energy, then,

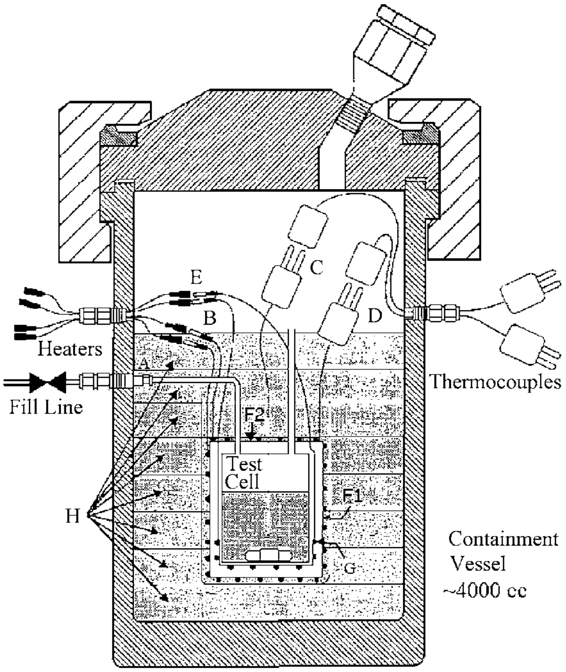
$$\ln(\text{tmr}) = \frac{E_a}{R}\left(\frac{1}{T}\right) - \ln A \tag{10}$$

$$\ln(\text{tmr}) = -\ln k \tag{11}$$

$$\text{tmr} = \frac{1}{k} \tag{12}$$

5. Experimental program

Fundamentally, VSP2 is one of the adiabatic calorimeters (shown in Fig. 1). The standard operating procedure is H–W–S cycle to find the onset temperature of a specific runaway reaction whose heat rate is



A-Fill Line Attachment
B-Guard Heater Plugs
C-Test Cell Temperature (TC)
D-Guard Heater Temperature (TC)
E-Test Cell Heater Plugs
F1-Guard Heater Bottom
F2-Guard Heater Lid
G-Test Cell Heater
H-Insulation Disks

Fig. 1. The schematic of VSP2 [4].

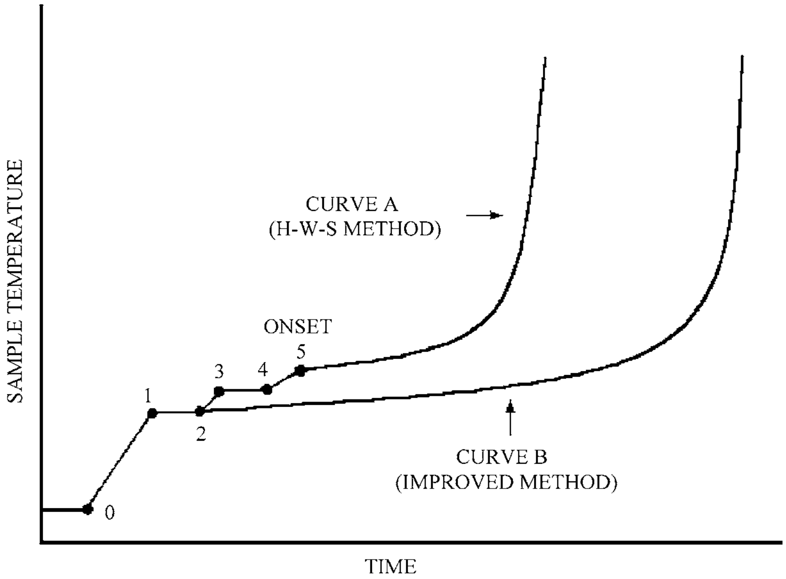


Fig. 2. The relation of time and temperature with standard and improved operating procedures.

equal to or greater than 0.05 °C/min. It can be plotted as curve A shown in Fig. 2. It can be manipulated to heat a sample from room temperature (point 0) to the pre-set temperature (point 1), then the main heater is turned off and the guard heater turned on to keep the sample in adiabatic condition. After a pre-set waiting period, such as 10 or 20 min (point 2), if the sample temperature rise rate is lower than the apparatus sensitivity (0.05 °C/min for VSP2), the main heater will turn on again and heat sample temperature to the next pre-set temperature (point 3). This cycle will not stop until the sample temperature rise rate is equal to or greater than 0.05 °C/min. Instead of using the conventional H–W–S operating procedure, this research used an improved method to operate VSP2. The sample was injected into the test cell, then the main heater was turned on to heat the sample to 40 °C. At 40 °C, the main heater was turned off and the guard heater was turned on to maintain the adiabatic condition and record all the temperature and pressure data. The relation between temperature and time is shown in curve B in Fig. 2.

Experiments in this study use a mixed 20 wt.% H_2O_2 with HCl in 3:1 volume ratio, and the total sample volume is 60 ml. HCl concentrations are 0.1, 0.5, 1, 5 and 10N, respectively as shown in Fig. 10. Both, 35 wt.% H_2O_2 and 37 wt.% HCl are produced by RdH Laborchemikalien GmbH & Co.

6. Results

To prove the possibility for using an improved operating method by VSP2, 60 ml distilled water was injected into the test cell, then the main heater and guard heater were turned on to heat the distilled water to 40 °C. When the distilled water was kept at 40 °C, the main heater was turned off. After the distilled water was maintained at adiabatic condition for 367 min, the temperature of distilled water decreased from 41.09 to 39.54 °C. The temperature decrease rate is −0.0042 °C/min, which is far less than the sensitivity of VSP2 (0.05 °C/min). Apparently, the heat loss is small enough to be assumed that the improved operating procedure is an adequate way to operate VS for this study.

The onset temperature of 20 wt.% H_2O_2 and 10N HCl mixture solution is 30 °C, which is less than 40 °C, this mixture concentration of HCl and H_2O_2 solution is not suitable for the improved method operated by VSP2. All experimental results can be readily seen in Table 1 for both operating methods.

Table 1
Summary of experimental results by two operating methods

HCl concentration (N)	Operating method	E_{ac} (cal/mol)	E_{ad} (cal/mol)	P_{max} (psig)	T_{max} (°C)	$(dP/dt)_{max}$ (psig/min)	$(dT/dt)_{max}$ (°C/min)	tmr at 40 °C (min)	tmr at onset temperature (min)	Onset temperature (°C)
10.0	40 °C hold	NA	NA	NA	NA	NA	NA	NA	NA	30
10.0	H–W–S	NA	20665.9	1114.7	139.1	1339	226	NA	45.6	30
5.0	40 °C hold	8687.7	22091.6	1213.4	158.3	810	78	113.23	113.2	40
5.0	H–W–S	NA	22774.7	1136.8	133.7	443.5	36	NA	119.3	40
1.0	40 °C hold	7446.6	24859.8	1235.4	153.4	1000	95	124.76	32.8	55
1.0	H–W–S	NA	26041.3	1131.4	160.7	1119	94	NA	69.2	55
0.5	40 °C hold	3357.9	31249.9	1214.6	147.6	580	52	334.25	66.5	55
0.5	H–W–S	NA	29284.1	1112.1	150.0	2393	229	NA	87.8	55
0.1	40 °C hold	4025.2	46244.5	1229.3	139.7	600	50	656.834	114.4	60
0.1	H–W–S	NA	32391.8	1113.4	145.2	499.7	52	NA	120.8	60

E_{ac}: the activation energy in catalytic reaction; E_{ad}: the activation energy in self-decomposition reaction; NA: not applicable.

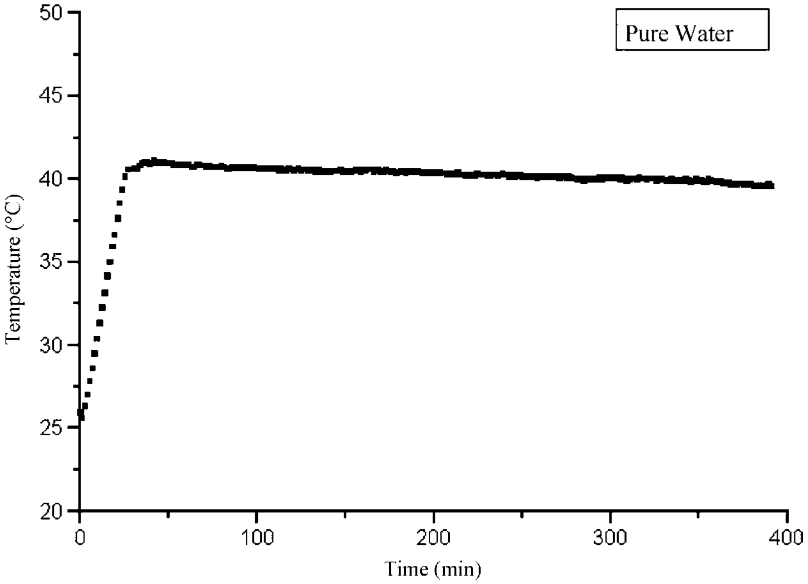


Fig. 3. The time vs. temperature relation of 60 ml distilled water at 40 °C adiabatic condition.

Table 2
Relations of activation energy and HCl concentration summary

Operating method	Improved operating method		H–W–S operating method
Reaction type	Catalytic reaction	Self-decomposition reaction	Self-decomposition reaction
Fitting curve	$y = 1335.1 \ln x + 6342.1$	$y = -6266.7 \ln x + 28940$	$y = -2567.6 \ln x + 26702$
R^2-value	0.6986	0.8869	0.9868

x: the hydrochloric acid concentration (N); y: activation energy (cal/mol).

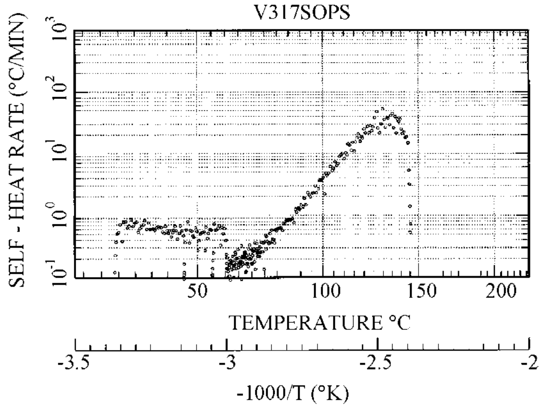


Fig. 4. The experimental results of 20 wt.% H_2O_2 and 0.1N HCl mixture solution operated by standard operating procedure.

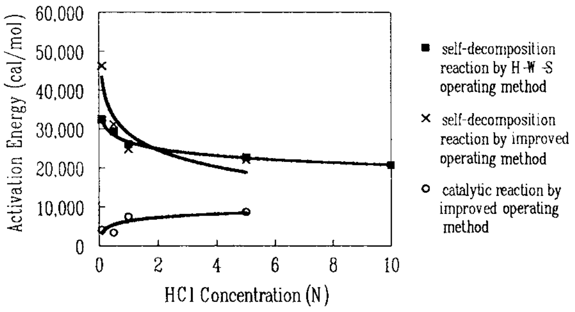


Fig. 5. The relation of activation energy and hydrochloric acid concentration.

The H–W–S operating method can only show the self-decomposition reaction, which is clearly seen in Figs. 3–5. Figs. 6–9 demonstrate that when HCl concentration decreases, the first catalytic reaction can be readily differentiated from the following second self-decomposition reaction. This second reaction can transparently distinguish itself from the catalytic reaction. From Figs. 5–9, Table 2, it can be seen that when HCl concentration decreases, the activation energy of the first catalytic reaction decreases, but the second self-decomposition reaction increases. This relation can be clearly seen in Fig. 5 that it shows opposed phenomenon. It could be surmised that the catalytic reaction does not follow the Arrhenius equation because the activation energy increases when HCl concentration increases in the first slow catalytic reaction. The temperature at which the catalytic and self-decomposition reactions intersect in Fig. 5 is roughly the onset temperature in Fig. 4. When HCl concentration decreases, the duration of the catalytic reaction increases, as shown in Figs. 10–12. The final pressures of the four HCl concentrations are almost all at 1200 psig so that different HCl concentrations do not affect the final reaction pressure that the HCl in both catalytic and self-composition reactions is considered to merely act as a catalyst and not a reactant.

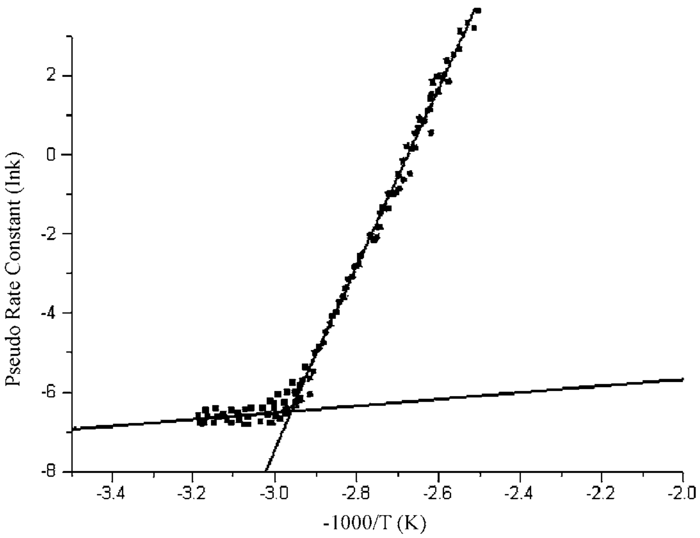


Fig. 6. The experimental results of 20 wt.% H_2O_2 and 0.1N HCl mixture solution operated by improved operating procedure.

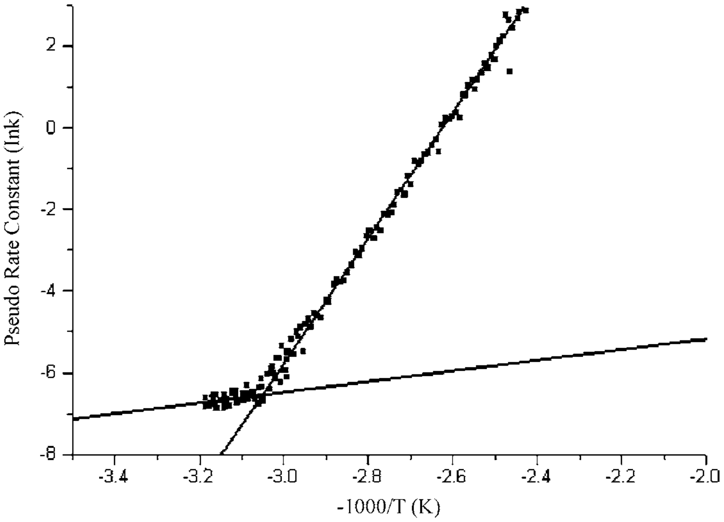


Fig. 7. The experimental results of 20 wt.% H_2O_2 and 0.5N HCl mixture solution operated by improved operating procedure.

Not only can the improved operating procedure separate the catalytic and self-decomposition but it can also compensate for the tmr. It can provide the tmr at lower temperatures (from 40 °C to onset temperature) and then correct tmr at higher temperatures. In Fig. 13, the curve AB (from 40 to 60 °C) can compensate for the shortage in Fig. 12. Nevertheless, the curve BC in Figs. 12 and 13 are almost the same. In the experiment with operating procedure, the tmr at higher (curve after point C) is relatively less than one with the improved operating procedure. For example, with a 20 wt.% H_2O_2 and 0.1N HCl at 115 °C, the tmr from the standard operating procedure is 4.1 min and the tmr by improved operating procedure is 9.0 min (both are point D in Figs. 12 and 13). In Table 1, the tmr at the onset temperatures

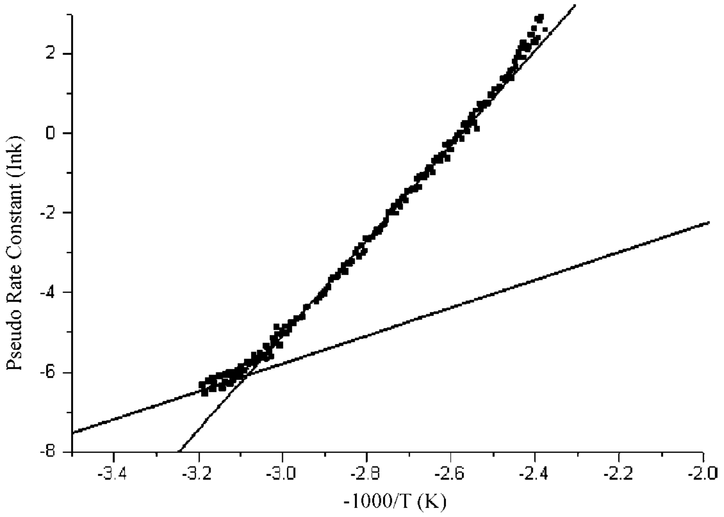


Fig. 8. The experimental results of 20 wt.% H_2O_2 and 1N HCl mixture solution operated by improved operating procedure.

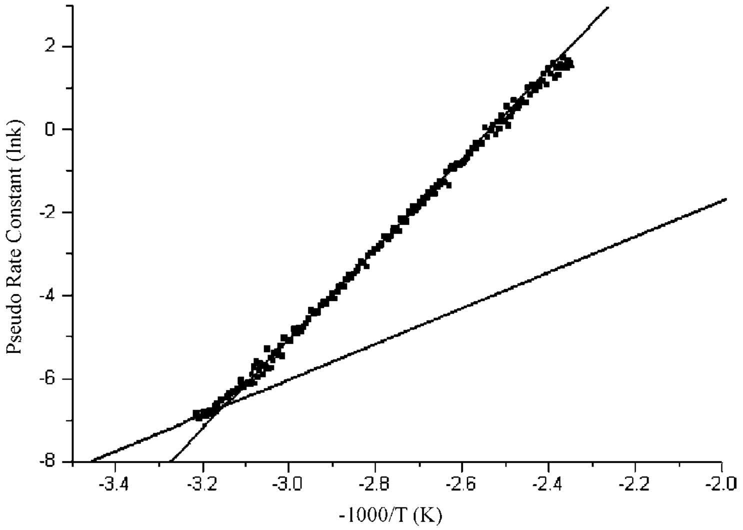


Fig. 9. The experimental results of 20 wt.% H_2O_2 and 5N HCl mixture solution operated by improved operating procedure.

from the improved operating method is all lower than the tmr at onset temperature from the standard operating method in various HCl concentrations. The most important point here is that the tmr at the onset temperature are much higher than the tmr at 40 °C by the improved operating method. This means that the "traditional operating procedure"—H–W–S operating procedure—cannot produce the real results when peroxide is in the presence of catalyst. It could only be applied to model the fire case but not used in the catalytic reaction starting from the ambient temperature. The reactions in

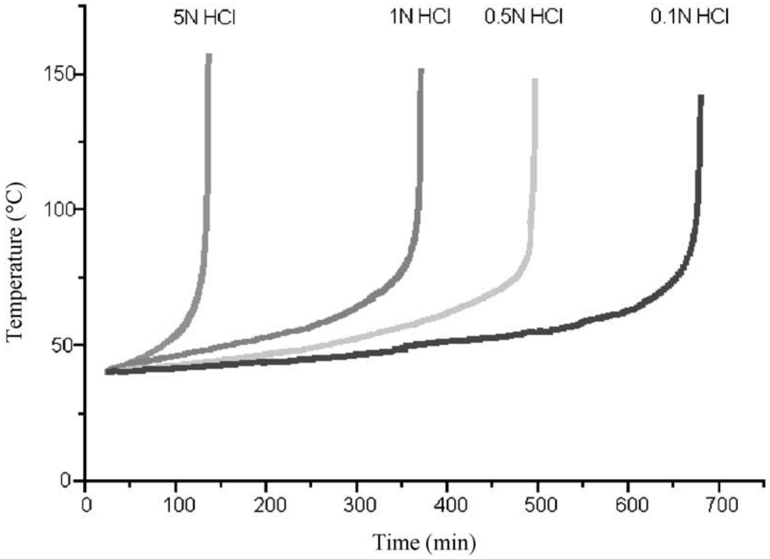


Fig. 10. The temperature vs. time operated by the improved operating procedure for 20 wt.% H_2O_2 with 0.1, 0.5, 1 and 5N HCl.

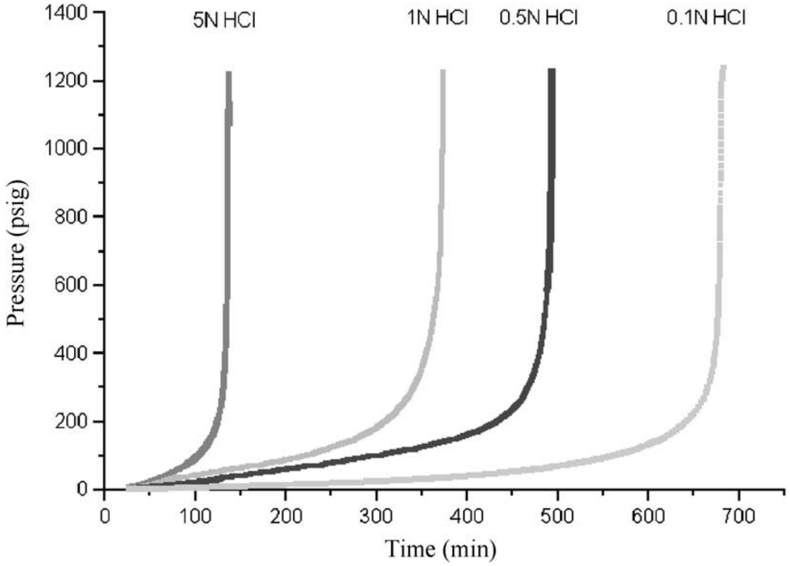


Fig. 11. The pressure vs. time operated by the improved operating procedures for 20 wt.% H_2O_2 with 0.1, 0.5, 1 and 5N HCl.

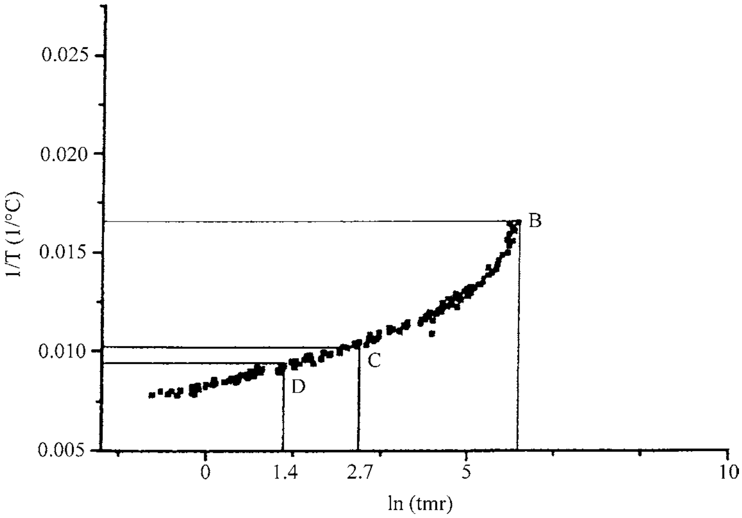


Fig. 12. The tmr vs. temperature of 20 wt.% H_2O_2 and 0.1 N HCl mixture solution operated by the standard procedure.

H_2O_2 and HCl mixed solution can be separately expressed as catalytic and self-deposition reactions. The catalytic reaction occurs at a lower temperature as following [2]:

$$2H^+ + 2Cl^- + H_2O_2 \rightarrow Cl_2 + 2H_2O$$

$$Cl_2 + H_2O_2 \rightarrow O_2 + 2Cl^- + 2H^+$$

The self-decomposition reaction happens at a higher temperature as the following:

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2$$

For the improved operating procedure, the experimental results (as can be seen from Figs. 6–9) show that an

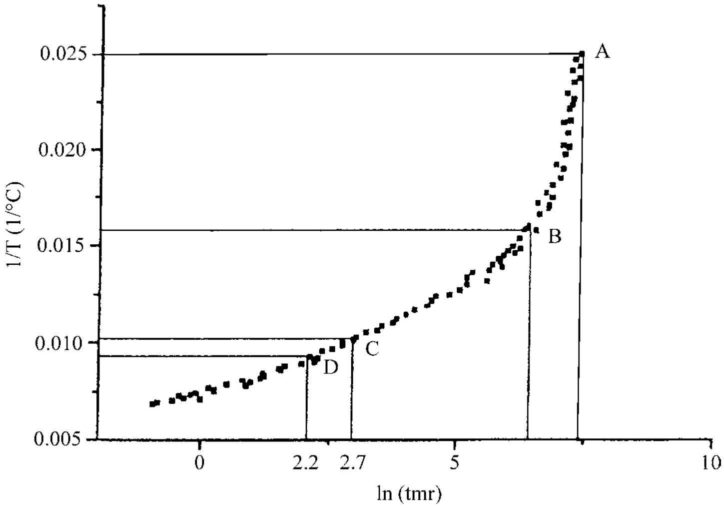


Fig. 13. The tmr vs. temperature of 20 wt.% H_2O_2 and 0.1 N HCl mixture solution operated by the improved procedure.

adiabatic calorimeter (such as VSP2 in this study) can clearly separate the first slow catalytic reaction from the second fast self-decomposition reaction. However, with the standard operating procedure, it cannot separate the catalytic and self-decomposition reactions (such as shown in Fig. 4).

7. Conclusions

This research adopted an improved operating procedure on VSP2 for 20 wt.% H_2O_2 mixed with 0.1, 0.5, 1 and 5N HCl to separate the catalytic reaction from the prevailing self-decomposition reaction. The results can be summarized as follows:

1. VSP2 is adequate for separating the slow catalytic reaction from the fast self-decomposition reaction of H_2O_2 and HCl mixture solution at 40 °C under adiabatic conditions.
2. In these two reactions, the HCl concentration decreases with the activation energy of the first catalytic reaction and then increases with the activation energy of the second self-decomposition reaction.
3. The temperature at which the catalytic and self-decomposition reactions intersect in the experiment operated by the improved method is roughly the onset temperature of the experiment operated by the standard operating procedure.
4. By the improved operating procedure, the duration of the first catalytic reaction increases with HCl concentration being decreased.
5. It is proved that different HCl concentrations act as a catalyst but not as a reactant.
6. Operating by the improved method can compensate tmr at the lower temperature (40 °C to onset temperature), which cannot be accomplished by using the standard operating procedure, and can modify the tmr at higher temperature.

8. Recommendations

With higher concentrations of HCl, such as 10N, the thermal activity monitor (TAM), which can be conducted at lower temperatures, is recommended. Using more catalysts, such as ferric ion (Fe^{3+}) and base, is also recommended.

Acknowledgements

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