Thermal hazard assessment on hydroperoxides－examples on cumene hydroperoxide

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Abstract

Since the nineteenth century, the chemical process industries have developed rapidly not only in terms of degree of complexity and throughput, but also in potential hazards. Such hazards exist when chemicals undergo decomposition, polymerization or other unexpected runaway reactions in various processes. A variety of methods of hazard assessment are used to understand the various possible unexpected reactions in preliminary design stages. These methods include establishing the safety index, reaction hazard index, and safety parameter and assessment procedure, respectively. What is needed is a convenient and cost-effective method for hazard assessment in the process industries. Various factors dictate the accuracy of these methods, such as physical properties of active chemicals, reaction types and thermokinetic parameters. The aim of this study is to introduce and compare some assessment methods with specific examples on Cumene Hydroperoxide, and to elucidate the effects of reaction types and thermokinetic parameters via simulation. The ultimate goal is to develop more useful and practicable methods for hazard assessment for reactively unstable chemicals so that a proactive disaster prevention program can be adequately established.

Key Words : Runaway reactions, Hazard assessment, Reaction types and thermokinetic parameters, Cumene Hydroperoxide

Introduction

Hydroperoxides have been widely utilized since World War II as initiators, hardeners, cross-linking agents, bleaching agents, and drying accelerators, to name a few. In addition, the throughput and demand of hydroperoxides all over the world have increased steadily. However, hydroperoxides are reactively unstable chemicals that have been involved in various industrial accidents in Asia as shown in Table 1 [Ho, et al., 1998].

Hydroperoxides have certain unique characteristic features that are sensitive to thermal and chemical pollutants or even mechanical shock. They are higly exothermic and generate some gases and mists via decomposition reaction. Practically, they could be used in oxidation, also.

For inherently safer process operations, it is necessary to assess thermal hazards of unknown chemicals with reactive natures so that a safer operating environment can be achieved, even under various contingencies. Therefore, because of the amount of

usage and potential hazards of hydroperoxides, the establishment of a useful and practicable procedure of hazards assessment is indispensable. Generally, there is a systemic approach of experimentally assessing thermal hazards of unknown materials. Along with these engineering approaches are other methods such as course of Process Safety Management (PSM), Quantitative Risk Assessment (QRA), safety index and so on, respectively, to evaluate chemicals with potential reaction hazards. As planned, this study focuses on engineering and safety index methods to assess exothermic reaction hazards under various unknown situations for Cumene Hydroperoxide (CHP), as an example.

EXPERIMENTAL

In practice, there are many feasible methods of thermal hazard assessment, depending on real conditions and the impact of hazardous consequences. In order to propose a quick and cost-effective method to estimate safety classes among various industrious processes, the focus should be on methods of engineering approach and safety index that are usually neither implemented on safety management, nor quantified risk assessment.

In 1997, Keller and his associates [Keller et al., 1997] classified runaway reactions via hazard severity, the so-called safety index. Earlier, Townsend and Fisher [Townsend and Tou, 1980; Fisher and Goetz, 1993], respectively, suggested TMR, T_{NR} and T_{SADT} as safety parameters via Semenov's theories. Stull [Stull, 1974] developed a rating system to establish the relatively potential hazards of specific chemicals; the rating is called Reaction Hazard Index (RHI). Hirschler [Hirschler, 1999] used heat release rate to predict self propagating fires that could determine whether it could be hazardous or not. Barton and Rogers [Barton and Rogers, 1997] proposed some procedures for evaluating chemical reaction hazards, and so on. However, the goal is to establish various methods of hazard assessments, with general purpose basis, for recognizing and then preventing potential hazards earlier. These methods could therefore decrease costs of unexpected losses and efficiently assess the hazards in the process industries among all stages.

Based on the above mentioned, the following would examine these methods of examples on CHP. The results could then be used for corrective methods and for suggesting the main varied factors that could affect the assessment effects among assessment procedures.

Safety Index

According to Keller and his associates, who proposed specific experimental steps, a process engineer could obtain the safety index (S_a) of unknown reactive materials so as to determine hazard severity [Keller, et al., 1997]. The following are steps of the entire process to obtain S_a and the flow diagram is shown in Fig. 2:

1. Run scanning experiment via dynamic DSC.

2. Check the samples' experimental values with $\Delta T_{ad} > 50$ K.

3. Identify reaction types and unknown materials' hazard severities by the E_a or $\triangle H_r$ (estimated E_a with dynamic DSC, Jmole^{-1}; heat of reaction, $\triangle H_r$, Jg^{-1}). Then evaluate them separately.

4. Calculate TMR$_{dyn}$ for the unknown material reactions by dynamic DSC.

5. Confirm the ones with TMR$_{dyn}$ less than 24 hrs and evaluate these values separately.

6. Conduct adiabatic VSP2 experiment or search literature values to determine TMR$_{adi}$.

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7. Compute $S_a = \dfrac{TMR_{dyn}}{TMR_{adi}}$

If S_a is less than one (< 1.0), then it safe; otherwise the system is judged as unsafe [Lees, 1996; Keller, et al., 1997; Shu, et al., 1999; Hou, et al., 2001; Grewer, 1994; Fisher and Goetz, 1993; Barton and Rogers, 1997].

Experimental values: $S_{a,CHP} = \dfrac{TMR_{dyn}}{TMR_{adi}} = \dfrac{0.03}{0.0411} = 0.730$ (safe)

Simulated values: $S_{a,CHP} = \dfrac{TMR_{dyn}}{TMR_{adi}} = \dfrac{0.04}{0.0446} = 0.897$ (safe)

Therefore, according to CHP safety properties, it is on the safe side.

If the vessel is inadvertently mixed with contaminants, the safety properties of CHP could be shown as follows [Keller, et al., 1997; Frank-Kamenetskii, 1969; Peng, et al., 2001]:

(Acid: H_2SO_4)

Experimental values: $S_{a,CHP+H_2SO_4} = \dfrac{TMR_{dyn}}{TMR_{adi}} = \dfrac{0.089}{0.0617} = 1.442$ (unsafe)

Simulated values: $S_{a,CHP+H_2SO_4} = \dfrac{TMR_{dyn}}{TMR_{adi}} = \dfrac{0.068}{0.0563} = 1.208$ (unsafe)

(Acid: HCl)

Experimental values: $S_{a,CHP+HCl} = \dfrac{TMR_{dyn}}{TMR_{adi}} = \dfrac{4.117}{0.1444} = 28.511$ (unsafe)

Simulated values: $S_{a,CHP+HCl} = \dfrac{TMR_{dyn}}{TMR_{adi}} = \dfrac{4.464}{0.1466} = 30.451$ (unsafe)

According to the above calculations, tables received from experimental data for CHP with contaminants significantly illustrate a higher degree of hazard severity than the pure one. Therefore, from these cases, this method is validated to be quite useful for safety evaluation, in terms of degree of hazard severity.

Safety Parameter

Among the estimation of safety parameters or hazard classifications, T_{NR} and T_{SADT} are also two important parameters. Based upon the previous theories, the related reaction hazards are mostly evaluated from Townsend [Townsend and Tou, 1980] and Fisher [Fisher and Goetz, 1993] to acquire these parameters. Basically, T_{NR} could be calculated via the relationship between heat generating rate and heat removing rate. It would then be used to design a cooling system and to inform fire fighters on how much time remains to conduct a rescue action [Kossoy, 2002]. Contrasted to T_{NR}, T_{SADT} is used to estimate whether temperature needs to be controlled during transportation or not. T_{SADT} is defined as the lowest ambient air temperature at which a self-reactive substance of specified stability (contaminant level, inhibitor concentration, etc.) undergoes an exothermic reaction in a specified commercial package in a period of seven days or less [Fisher and Goetz, 1993]. According to NFPA code (NFPA 49, 1999), a self-reactive substance must be subject to temperature control during transportation if its T_{SADT} is less than or equal to 55℃. In practice, Eqs. (1) and (3) could be used to calculate these two parameters:

$$\left(T_{NR} + 273.15\right)^2 = \frac{m \cdot E_a \Delta H \cdot k}{R \cdot U \cdot (1.8) \cdot a} \tag{1}$$

$$= \frac{m \cdot E_a \cdot \Delta H \cdot A \cdot e^{-E_a/R \cdot (T_{NR} + 273.15)}}{R \cdot U \cdot (1.8) \cdot a} \tag{2}$$

$$T_{SADT} = T_{NR} - \frac{R\left(T_{NR} + 273.15\right)^2}{E_a} \tag{3}$$

This study introduces an example of CHP by using the foregoing theories and thermal calorimeters to calculate these kinetic parameters and safety parameters. Duh, et al. have studied the runaway hazard and decomposition kinetics for various conditions [Duh, et al., 1997; Duh, et al., 1998]. The final experimental and mathematical calculation results are summarized in Tables 2 and 3.

In Tables 2 and 3, experimental results, mathematical calculation results, kinetic parameters, and safety parameters all are obtained from DSC and VSP2 for pure CHP and its contaminants [Wang, et al., 2001]. Changes of T_o and E_a demonstrate that hazards of CHP with contaminants could be more dangerous than the pure one (as can be seen Figs. 1 and 2). Therefore, based upon the calculation values of safety parameters T_{NR} and T_{SADT} as shown as Tables 2 and 3, CHP is more dangerous under dynamic scanning conditions (DSC experiments) than an adiabatic environment (VSP2 experiments). In addition, according to the mathematical and simulated values of safety parameters, the potential hazards of CHP joined with contaminants also show as more hazardous than a pure one. In summary, safety parameters of mathematical and simulated values indicate the CHP joined with contaminants are dangerous as the same with experimental results, but the determination under various experimental conditions could be different. Therefore, to obtain correct assessment results it is very important to determine the reactive chemicals under the particular kind of environment.

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Table 1. Selected thermal explosion accidents caused by hydroperoxides in Japan and Taiwan since 1964 [Ho, et al., 1998; Shu, et al., 1999]

Year	Chemical	Deaths/Injures	Hazard	Cause
1964	MEKPO[1] (Japan)	19/114	Explosion	Thermal Decomposition
1979	MEKPO (Taiwan)	33/49	Explosion (Storage)	Thermal Decomposition
1981	CHP (Taiwan)	1/3	Explosion (Condensation)	Thermal Decomposition
1984	MEKPO (Taiwan)	5/55	Explosion (Reactor)	Thermal Decomposition
1986	CHP (Taiwan)	0/0	Explosion (Reactor)	Thermal Decomposition
1987	H_2O_2 (Taiwan)	0/20	Explosion (Storage Tank)	Incompatibilities
1988	TBHP[2] (Taiwan)	0/19	Fire & Explosion (Storage Tank)	Cooling Failure
1989	MEKPO (Taiwan)	7/5	Explosion (Storage Tank)	Unsuitable Storage
1996	MEKPO (Taiwan)	10/47	Explosion (Storage)	Thermal Decomposition

1: MEKPO: Methyl Ethyl Ketone Peroxide
2: TBHP: Tert-Butyl Hydroperoxide

Table 2 Calculated kinetic and safety parameters derived from the kinetic scanning experiments of CHP and contaminants by DSC [Wang, et al., 2001; Duh, et al., 1998]

Data CHP and contaminants	Sample mass (mg)	Scanning rate, r ($°C \min^{-1}$)	T_0 ($°C$)	T_{max} ($°C$)	E_a ($kJmol^{-1}$)	ΔH_r (Jg^{-1})	TMR_{dyn} (min)	T_{NR} ($°C$)	T_{SADT} ($°C$)
35 wt% CHP	6.15	4	135	192.6	112.80	607.3	0.03	76	67.01
			136	**191.8**	**113.00**	**630.5**	**0.04**	**59.85**	**51.73**
35 wt% CHP + H$_2$SO$_4$ (1N)	4.33 + 1.05	4	90	167.3	77.59	667.3	0.089	11	2.35
			96	**166.9**	**78.00**	**526.1**	**0.068**	**12.85**	**4.13**
35 wt% CHP + HCl (1N)	4.68 + 0.74	4	85	171.9	138.59	715.7	4.117	64	57.18
			85	**169.7**	**141.97**	**601.3**	**4.464**	**46.45**	**40.47**

---Calculated values based on experimental data

---Simulated values based on CISP software

＊ All values of T_{NR} and T_{SADT} were determined by Fisher's approach with fixed conditions (Fisher and Goetz, 1993)

Table 3 Calculated kinetic and safety parameters derived from the adiabatic experiments of CHP and contaminants by VSP2 [Wang, et al., 2001; Duh, et al., 1997]

Data CHP and contaminants	Conc. & mass	Φ	T_0 ($°C$)	T_{max} ($°C$)	E_a ($kJmol^{-1}$)	$(dT/dt)_0$ ($°C \min^{-1}$)	TMR_{adi} (min)	T_{NR} ($°C$)	T_{SADT} ($°C$)
35 wt% CHP	16 g	1.45	140.93	248.72	119.75	0.70	0.0411	92.34	83.07
			146.85	**249.85**	**120.43**	**0.65**	**0.0446**	**94.12**	**84.81**
35 wt% CHP + H$_2$SO$_4$	(0.5 M, 1 g)	1.45	121.01	241.42	118.06	0.45	0.0617	87.86	76.85
			125.11	**249.63**	**117.53**	**0.52**	**0.0563**	**82.76**	**71.99**
35 wt% CHP + HCl	(1 M, 1 g)	1.45	131.15	259.64	155.22	0.15	0.1444	103.40	95.81
			137.56	**256.56**	**155.21**	**0.16**	**0.1466**	**101.64**	**94.12**

---Calculated values based on experimental data

---Simulated values based on CISP software

＊ All values of T_{NR} and T_{SADT} were determined by Fisher's approach with fixed conditions [Fisher and Goetz, 1993]
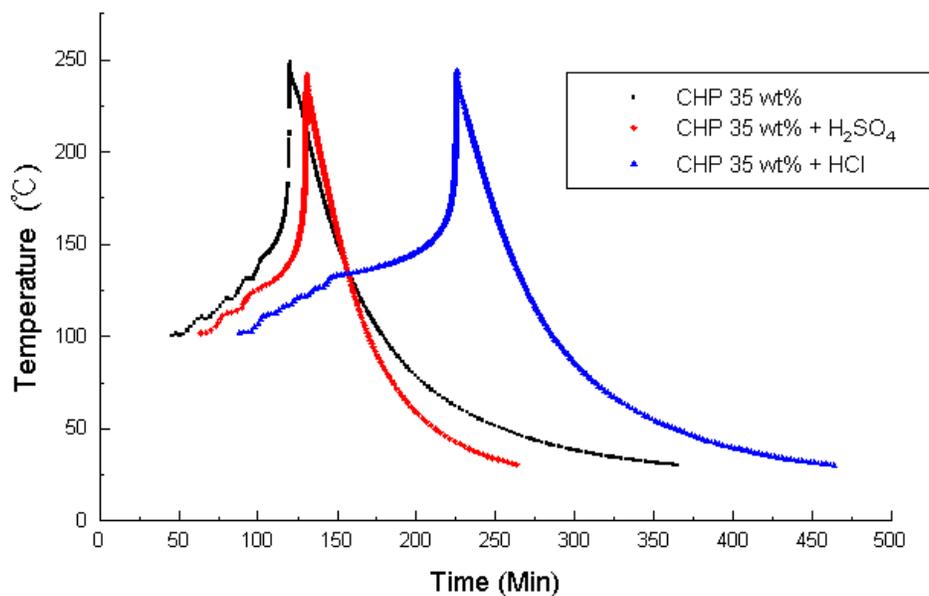
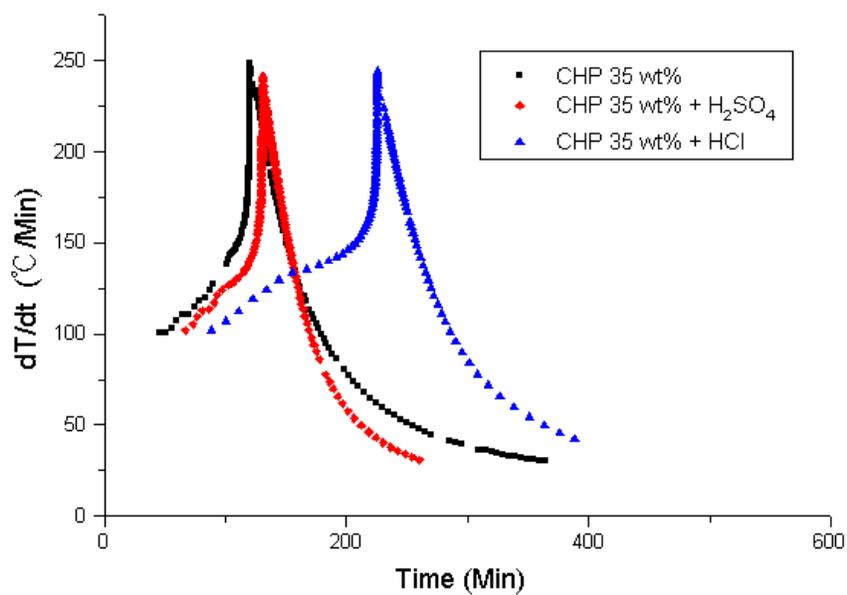Fig. 1 Temperature versus time of CHP 35 wt% and its contaminants by VSP2.

Fig. 2 Self-heating rate versus time of CHP 35 wt% and its contaminants by VSP2.