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HAZARD EVALUATION FOR REDOX SYSTEM OF CUMENE HYDROPEROXIDE MIXED WITH INORGANIC ALKALINE SOLUTIONS

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In petrochemistry, dicumyl peroxide (DCPO) is used in various resins for improving physical properties, which was produced by cumene hydroperoxide (CHP) with oxidization reaction, redox reaction, and dehydration reaction. The reactant, CHP, is a typical organic hydroperoxide and has been intrinsically unstable and reactive due to its bivalent –O–O– structure which can be broken readily with bond-dissociation energy. This sequence on sensitive study aimed at the thermal hazard evaluation for the reactive and incompatible characteristics of CHP mixed with various inorganic alkaline solutions. Differential scanning calorimetry (DSC) and vent sizing package 2 (VSP2) were used to analyze the thermal hazards and runaway reaction of redox system, such as decomposition of CHP in cumene solution and CHP react with inorganic alkaline solutions, exothermic onset temperature, peak power, heat of decomposition of dynamic scanning tests, adiabatic self-heating rate, pressure rise rate, maximum temperature, maximum pressure of reaction system, etc. The results of the tests have proven helpful in establishing safe handling, storage, transportation, and disposal guidelines.

Keywords: *incompatible characteristics, inorganic alkaline, organic hydroperoxide, redox system, thermal hazard*

Introduction

Cumene hydroperoxide (CHP) is widely used in many industrial fields as an initiator or curing agent of radical polymerisation process with unsaturated monomers. Actually, the typical manufacturing process for CHP to produce phenol and acetone in the acid-catalyzed process, and product of dimethylphenyl carbinol (DMPC, also called α-cumyl alcohol, CA) and dicumyl peroxide (DCPO) in the base-catalyzed process, which were listed as Fig. 1. However, a pivotal factor of potential hazards for which CHP is a typical organic hydroperoxide, and sensitive to thermal source and incompatible with many materials due to its reactive and unstable characteristic. The decomposition is exothermic reaction involves the splitting of the peroxide bond with a huge heat release and gas product, that may cause a fire or thermal explosion under an uncontrollable situation. Runaway incidents can occur in oxidation reactors, vacuum condensation reactors, or transportation and storage tanks [1, 2]. The other potential hazards may exist due to its autocatalytic behavior. The exothermic temperature of CHP was detected at 75°C under isothermal condition [3], that indicated the variable and complex reactive behaviors of CHP which are prone to violent decomposition reaction, initiated by thermal source, mechanical shock, or friction, especially in the presence of certain catalysts.

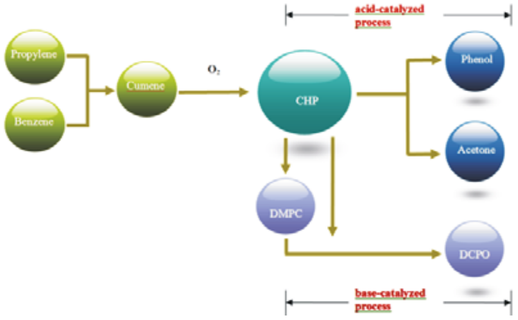

Fig. 1 Manufacturing process for CHP

Many studies were performed to clarify the basic thermal runaway hazards and kinetics of CHP decomposition properties [3–7] and the incompatable reaction in the presence of a catalyst [8–11], strong mineral acids, base, and metals that will initiate a rapid decomposition at lower onset temperature. However, the incompatable characteristics of CHP have not been clearly identified yet, alkaline solution was used as a catalyst during base-catalyzed process to form the economically valuable product, CA, but it

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also effected the reactive temperature of reaction or storage even as lower as ambient temperature.

In this study, the base-catalyst of CHP reaction system was evaluated by thermal analysis techniques, dynamic scanning calorimetry and adabatic calorimetry. The hazard evaluation of incompatibilities was carried out and compared to each other. Runaway traces of the tests have proven helpful in establishing safe handling, storage, transportation, and disposal guidelines.

Experimental

DSC (differential scanning calorimeter)

DSC experiments were carried out with Mettler DSC controlled by the TA 8000 thermal analysis. The HP crucible can withstand pressure up to 100 bar and temperature up to 600°C. Calibration of the temperature and heat flow measurements with the DSC was carried out by using high-purity metals indium and zinc.

Analysis were presented which illustrate methods for scanning test data to practical hazards evaluations at different sampling method.

Method 1

Injected CHP and incompatibilities into DSC821^e measuring cell individually, and then sealed and performed on a Mettler TA8000 system. For better thermal equilibrium purpose, the scanning rate chosen for the temperature-programmed ramp was chosen to be 4°C min^{-1}.

Method 2

Mixed the sample and incompatibilities in the proportion, and then shook to break the equilibrium of homogeneous mixture of two liquids. Finally, took out the upper and oil layer of mixture for DSC dynamic screening experiments.

VSP2 (Vent Sizing Package 2)

VSP2 is developed by Fauske & Associates Inc. (FAI) and could be used to detect the temperature range from ambient temperature to 400°C, and its maximum detectable sensitivity is 0.02°C min^{-1}.

Results and discussion

DSC

From reactive incompatible experiments, CHP in cumene solution with impurities of aqueous hydroxides were revealed the undissolvable phenomenon between oil and water interface during mixing procedure. However, shook to support the energy to break the equilibrium condition, the mixture of CHP and aqueous hydroxides from clear to turbid, such as Fig. 2, which was attributed to the existence of 'critical opalescence' during the influence between two different phases coexist [12]. The heat release rate *vs.* temperature for the thermal decomposition of 80 mass% CHP in cumene solution with various hydroxides, NaOH, t-BuONa, KOH, LiOH, and $NH_{3(aq)}$, were summarized in Figs 3 and 4. The onset temperature (T_o) and heat of decomposition (ΔH_d) were reported in Tables 1 and 2.

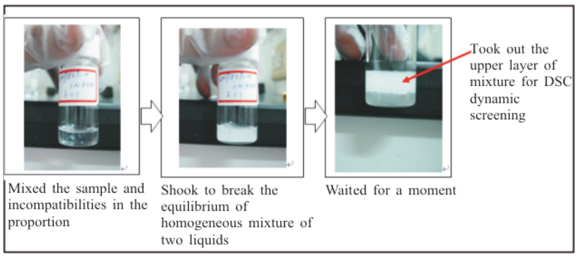

Fig. 2 Sampling procedure of Method 2 on DSC runs

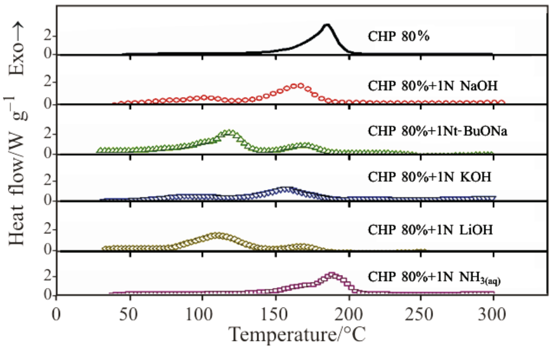

Fig. 3 Thermal decomposition of CHP with various alkalines compared to CHP itself in cumene solution by DSC tests (Method 1)

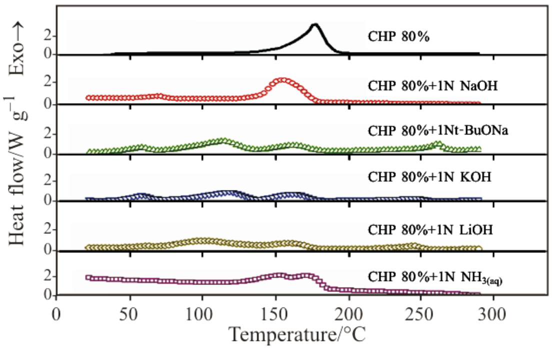

Fig. 4 Thermal decomposition of CHP with various alkalines compared to CHP itself in cumene solution by DSC tests (Method 2)

Table 1 Heat of decomposition and initial exothermic temperature of CHP with various alkalines (Method 1)

Thermal analysis by Method 1								
Items	CHP 80 mass%/ mg	Incompatibility			Total mass/mg	CHP/ contaminant ratio	T_o/°C	Heat of reaction/ J g^{-1}
		Substance	Mass/mg	pH values				
1	4.6	–	–	–	4.6	–	110	1.207
2	5.0	1N NaOH	1.5	13.44	6.5	3.3:1	58	1.126
3	3.6	1N t-BuONa	1.2	12.9	4.8	3:1	46	1.247
4	6.4	1N KOH	2.28	13.4	8.68	2.8:1	55	1.077
5	3.6	1N LiOH	1.1	11.4	4.7	3.3:1	55	1.172
6	5.8	1N $NH_{3(aq)}$	2.0	11.5	7.8	2.9:1	54	1.132

Table 2 Heat of decomposition and initial exothermic temperature of CHP with various alkalines (Method 2)

Thermal analysis by Method 2						
Items	Sample	Incompatibility	Mass/mg	CHP/ contaminant ratio	T_o/°C	Heat of reaction/J g^{-1}
1	CHP 80mass%	–		–	110	1.207
2		1N NaOH	4.80	3:1	51	1.189
3		1N t-BuONa	4.24	3:1	35	1.268
4		1N KOH	5.30	3:1	38	1.087
5		1N LiOH	4.81	3:1	41	1.128
6		1N $NH_{3(aq)}$	3.96	3:1	62	1.135

According to the results of the DSC measurements, the exothermic onset temperature conspicuously decreased and impelled the reaction process to be complicated. No matter what kind of aqueous hydroxides, when mixed with hydroxide ions, CHP will be more hazardous and unstable because of lower exothermic onset temperatures behaviors that will exacerbate the thermal hazard or enhance the hazardous risk of handing CHP. From the tests, the exothermic onset of the first peak was lower than 62°C and also had a large heat of reaction about 1.150±75 J g^{-1}. The thermal curves became complex due to the sample dealt with beforehand, the exothermic peak probable changed from twin (Method 1) to three peaks (Method 2), such as CHP decomposed by t-BuONa, KOH and LiOH catalyzed which was evident different to CHP itself. The hydroxide ions reduced the onset decomposition of first peak from 110 to around 50°C, which increase the thermal hazard in the case of inadvertent mixing and will lead to the worst exothermic accident. That is, the homolysis –O–O– linkage of CHP initiates the decomposition process and to form the unstable intermediate peroxy anions, ROO^-, and alkoxy anions, RO^- [13, 14].

The comparison between various sampling methods reveal the similar hazards and heat of decomposition, the most difference was the peak of thermal curves. The sample which sampling by Method 2 had two nonuniform phases and exist more unstable intermediaries in the form of peroxy anions and alkoxy anions at the initial period. Thermal curves show the complicated reaction pathway and decomposition mechanisms, the thermal sharps of CHP decomposition from one to two, even became three peaks, while CHP reacts with alkoxy anions.

Adiabatic tests by VSP2

The thermal runaway tests conducted by adiabatic calorimeter with lower heat capacity of the test cells to acquire the pressure rise rate and self-heating rate traces *vs.* temperature. Small values of ϕ bring the experimental condition nearer to real process condition and simplify extrapolated the reaction hazard. Followed the dynamic scanning tests, the experimental results of CHP 15 mass% by Heat–Wait–Search procedure in VSP2 disclosed the initial self-accelerating decomposition temperature (SADT) was about 125°C the maximum self-heating rate and maximum pressure rise rate were 2.7°C min^{-1} and 10.19 psig min^{-1}. The adiabatic runaway curves were summarized in Fig. 5. The deliberately chosen lower concentration of CHP could avoid the damage of instrument and assure the operation safety. However, it could also stand for the character of sample hazard.

Table 3 Adiabatic data of incompatibilities of CHP 15 mass% and mixed with aqueous NaOH solution

Sample		Incompatibility		ϕ	T_0/ °C	T_{max}/ °C	P_{max}/ psig	$(dT/dt)_{max}$/ °C min^{-1}	$(dP/dt)_0$/ psig min^{-1}
		Material	Volume/ mL						
CHP 15 mass%	50 mL	–	–	1.13	127.1	197.8	219.9	2.7	10.2
		1N NaOH	2.5	1.13	57.2	188.8	327.2	0.9	5.4

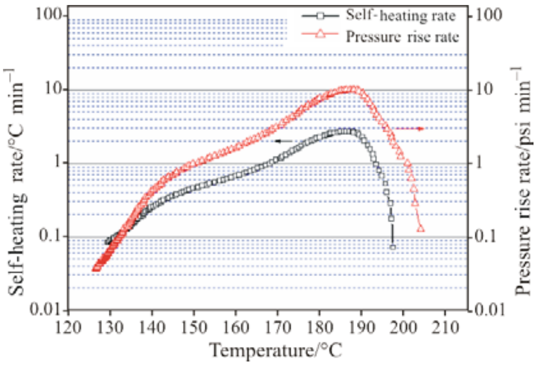

Fig. 5 Self-heating rate and pressure rise rate *vs.* temperature for thermal decomposition of CHP 15 mass%

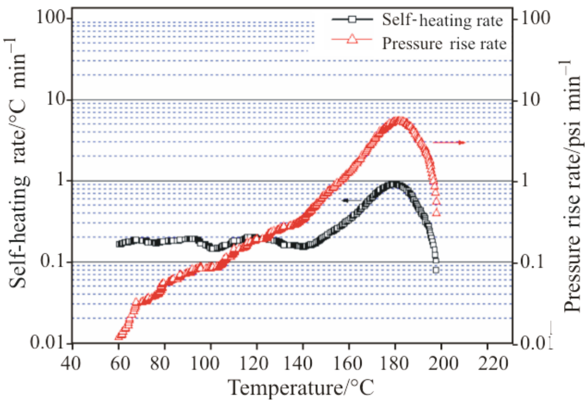

Fig. 6 Self-heating rate and pressure rise rate *vs.* temperature for thermal decomposition of CHP 15 mass% with 1N NaOH

The curves of self-heating rate and pressure rise rate *vs.* temperature for mixture of CHP with less than 5% NaOH are shown in Fig. 6. Data of experimental conditions and decomposition hazard were summarized in Table 3. The exothermic onset temperature and exothermic traces were conspicuously changed. Furthermore, the incompatible hazard and initial induced reaction was in good agreement with dynamic scanning tests. From the data of self-heating rate versus temperature, the onset temperature was lower than 60°C and the self-accelerating decomposition reaction showed that three exothermic peaks in incompatible thermal curve. The reaction performed in aqueous solution of CHP/NaOH mixtures, salts were generated and CHP transformed into an unstable intermediate in the form of peroxy anions and alkoxy anions [15, 16]. The free radicals promoted the initial thermal decomposition and presumably induced the main exothermic sharp.

In fact, the onset temperature conspicuously decreased. The self-heating rate, pressure rise rate and the maximum temperature of reaction became mild while the reactant CHP mixing with NaOH. However, the incompatible decomposition behaviors, the maximum pressure of reaction, and the range of decomposition temperature all transformed into more complication and danger. The temperature range from 57 to 189°C since initial exothermic rate is 0.1°C min^{-1}, and the maximum pressure of decomposition is 327 psig. In the petrochemical industries, a mixture of sodium hydroxide or sodium sulfite and CHP is reacted to generate DMPC by the redox reaction, and then used to produce DCPO. The reactant CHP was recognized to be flammable by NFPA and cleavage has highly exothermic features [17]. In addition, the CHP base-catalyzed decomposition revealed a mild and continuous process, but lower SADT which will lead to the worst exothermic hazard in the case of inadvertent mixing.

Conclusions

This study identified that CHP must be cautiously during handling, storing, and operating. Incompatibly reaction of CHP mixed with aqueous hydroxides generate unstable intermedia that could lead to a lower SADT, complicated reaction pathway, and then trigger a thermal runaway hazard. Additionally, identification of the incompatibly decomposition and induced reaction conducted by thermal scanning calorimeter and adiabatic calorimeter is crucial, since this study addressed a systematic approach for thermal analysis of incompatibilities.

Acknowledgements

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