

Thermal hazard analysis for cumene hydroperoxide by DSC and TAM

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Abstract

Since the 1980s, hazards arising from reactive chemicals have been investigated with a variety of instruments and even exotic approaches. Among numerous chemicals, considerable attention has been given to unstable mixtures or intermediates used in the chemical industries because of their potential hazards. To reduce any unexpected risks, one must choose appropriate calorimeters to analyze reactive chemicals or their incompatibilities. In principle, calorimeters not only have to have different functions but also be versatile in operation and application. In this study, Cumene Hydroperoxide (CHP), a reactively unstable organic peroxide, was investigated for its inherent hazardous characteristics by two commonly used calorimeters, Differential Scanning Calorimetry (Mettler Toledo 821^o) and Thermal Activity Monitor (2277 Thermal Activity Monitor). Advantages and disadvantages of both calorimeters specifically used for the thermal hazard analysis for CHP were also discussed. Ultimately, the objective is to make extensive and long-term contributions to safer process design as well as to enhance safety technology during the preparation, processing, storage, transportation, or even disposal periods.

Keywords: Reactive chemicals; Cumene hydroperoxide; Differential scanning calorimetry; Thermal activity monitor; Thermal hazard analysis

Introduction

Reactive chemicals are commonly used in the chemical process industries during preparation, sampling, processing, storage, transportation or even disposal periods. During any stage, heat could accumulate via self-accelerating decomposition or polymerization, subject to various upsets or abnormal conditions, such as cooling failure, mischarging, or external fire exposure, to name a few [NFPA 43B, 1999]. The aftermath includes toxic release, uncontrolled runaway reactions, fires and explosions resulting in damage as well as ecological impact. Under certain circumstances, thermal runaways cannot be avoided which are accompanied with calorific capacity and gaseous decomposed materials that would incur different hazards based upon specific physical and chemicals properties as well as various upset scenarios. According to the cause, it is expected that the impact or damage can be alleviated by analyzing the specific chemical with adequate instruments, such as DSC and TAM. Therefore, any possible disaster could be proactively prevented, or if did happen, it could be controlled or mitigated under an acceptable level.

This study compared both DSC and TAM to test and investigate CHP with autocatalytic nature at low temperature conditions, but with nth order reaction behavior under high temperature ranges [Duh, 1997]. Based upon the related thermokinetic parameters, along with

isothermal conditions, prior to the design process stage, safety precautions during storage and transportation as well as preventive measures for runaway reactions must be established. Meanwhile, hazard results from the CHP contaminated by various chemical have been discussed for DSC.

The principal purposes of DSC and TAM are to analyze data from thermokinetic parameters via experimental thermograms. Through these two apparatus, thermal hazards of reactive chemicals under normal or abnormal operating conditions can be determined. According to experimental results and the open literature, the thermal decomposition of CHP and contaminants could be properly measured with a micro-amount of sample [Ho, 1998]. Although sample quantities used in DSC and TAM merely have milligrams or grams, they could be manipulated and extrapolated to commercial use by engineering approaches. They may, in turn, be used in process design to provide safety information and suggestions during storage and transportation for any specifically reactive chemicals such as CHP. This study also compares the principles, functions and structures of DSC and TAM in detail.

Experiment

By design, both DSC and TAM are different in terms of structure, function, capability, and operating steps. In addition, they have different measures in chemical analysis. However, these two instruments could also detect the thermal decomposition temperature of a specific chemical in processing, storage and transportation and then derive related thermokinetic parameters for reactions, such as autocatalytic decomposition. With the above-listed experimental conditions, to obtain the thermal hazard characteristics of CHP, one must evaluate the potential thermal hazards during processing, storage and transportation. Therefore, the complete thermal hazards of reactive chemicals could be determined.

Sample

An 80 wt% solution of CHP in cumene purchased directly from the supplier was measured to determine both density and concentration. The sample was then stored in a refrigerator under 4°C conditions. Cumene purchased directly from Merck Co. was used as the dilution solvent in the preparation of various CHP samples. Substances such as H₂SO₄, NaOH, and FeCl₃ were treated as incompatibilities. Contaminants that could be readily encountered in process or storage conditions were chosen to be from 0.1 to 0.5 wt% in DSC experiments. Here, CHP samples of 35 wt% diluted in cumene and 80 wt% were used in DSC tests and TAM tests, respectively [Wang, 2001].

Experimental data acquired from DSC scanning tests for thermal decomposition of CHP 35 wt% and its incompatibilities

With the characteristics imbedded as a micro-calorific scanning analysis in DSC, the experimental temperature can be increased to acquire exothermal phenomena of CHP, associated with its catalytic decomposition reaction with contaminants, such as H₂SO₄, NaOH, and FeCl₃.

Table4 shows results of CHP from contaminating with incompatible chemicals that would increase the probability and impact of a runaway reaction. After contaminants are added, as Fig. 4 indicates, reaction curves of CHP, along with exothermic onset temperature would ahead of time compare CHP 35 wt% runaway without contaminants, and increase the exothermal heat of reaction, too.

Consequently, the results have proven that CHP may demonstrate substantial impacts while potentially incompatible contaminants are encountered during preparation, processing, storage, transportation, or even disposal in which runaway reactions and accompanying hazards cannot be overlooked.

Experimental data acquired from TAM isothermal tests for decomposition of CHP 80 wt%

With isothermal experiments by TAM, data obtained from an autocatalytic runaway

reaction of CHP are shown in Table 5 in which CHP has demonstrated autocatalytic features at a lower temperature environment. After the induction period, the runaway reaction is accelerated until reaching the decay period. Obviously, if CHP reaches an autocatalytic runaway onset temperature during various stages, then any possible catastrophic results cannot be avoided. In this study, there are five different temperature conditions of isothermal experiments, 75°C, 80°C, 83°C, 88°C, and 90°C, of CHP 80 wt% and their thermograms are shown in Fig. 5. Because of the initially exothermal phenomena of CHP, they indicate that the runaway reaction temperature of CHP is below 75°C. Compared with literature values and results of our previous studies, it is actually much lower than the exothermic onset temperature of about 110°C conducted by VSP2 (Vent Sizing Package2) [Wang, 2001; VSP2 Manual, 1997]. Such results demonstrate that CHP, in the process or transportation stage, could slowly accumulate heat to increase its hazard potentials, which may incur any unexpected thermal runaway reaction.

Phenomena analysis for CHP derived from DSC and TAM

From experimental results obtained from both DSC and TAM, two significant results are as follows:

- Contaminants, such as H₂SO₄, NaOH, FeCl₃, with CHP would increase degree of reaction hazards and decrease the exothermic onset temperature.
- After various prolonged induction periods, CHP has demonstrated autocatalytic runaway with autocatalytic behavior at a low temperature environment of 75°C, 80°C, 83°C, 88°C, and 90°C, respectively. This appears to be a novel finding in the literature.

Results and discussion

Application of thermal analysis for CHP derived from DSC and TAM

In this study, CHP has shown unique characteristics with thermally unstable natures and active bonding. Among various process stages, if the characteristics of reactive chemicals are not fully understood with proper calorimeters, it may potentially trigger any unexpected hazards resulting from thermal runaway reactions. According to the above-mentioned experimental phenomena, different types of hazards resulting from CHP could be clearly evaluated at different stages, as stated as follows:

- From Fig. 4 and Table 4, NaOH or FeCl₃ with CHP would produce the most severe thermal runaway reaction that decreases the exothermic onset temperature and have greater heat of reaction than others. CHP contaminated by either OH⁻ or Fe³⁺ could increase the intensity of reaction hazards. Therefore, various incompatibilities with CHP may generate various thermal runaways, corresponding to different reaction pathways.
- CHP contaminated with incompatibilities could result in serious runaways. Foreign objects, such as acids, bases, or dusts could pollute the CHP during preparation, sampling, storage, transportation, processing and even disposal periods. Therefore, it is critically important to avoid contaminants with reactive chemicals during each stage.
- Although CHP is normally stored under ambient environment, a prolonged period reveals a hidden autocatalytic reaction. The thermal runaway reactions of autocatalytic behaviors were conducted in an isothermal environment of 75°C, 80°C, 83°C, 88°C and 90°C. Therefore, it is crucially important that a vessel containing CHP should be controlled to avoid direct heat accumulation by radiation or external fire exposure.
- CHP could slowly initiate a significant thermal runaway reaction at a high temperature environment, as in the prolonged period. CHP hazards detected by the microcalorimeter, TAM, usually could not be sensed by a conventional adiabatic calorimeter, such as the

VSP2.

- By the dynamic scanning of DSC, a thermal runaway reaction of CHP under fire exposure could be adequately simulated. Because of thermal radiation by fire exposure around a vessel containing CHP, the temperature rise rate, dT/dt , is greater than the one by its own thermal decomposition. Without knowing the temperature of no return (T_{NR}) of CHP under specific dangerous conditions, safe and conservative emergency rescue could not be accomplished.

Comparison of thermokinetic parameters for CHP derived from DSC and TAM

Reactions such as polymerization, decomposition, oxidation, physical property changes, crystallization, and so forth, could be properly manipulated and observed via kinetic models. A kinetic model for a decomposition reaction could accurately depict any process hazards which are, in turn, used to simulate the degree of hazard corresponding to abnormal process conditions. Furthermore, it could also evaluate potential hazards of reactive materials during various stages, even as early as the conceptual design stage.

The quick pressure rise with thermal decomposition by itself or contaminants can lead to serious injuries, fatalities and costly property damages resulting from CHP under fire or explosion. Therefore, the application of different calorimeters, such as DSC and TAM, is more than adequate to calculate and elucidate thermokinetic parameters which can be verified by scanning and isothermal conditions, as shown in Table 6. From experimental results, the real situations during processing, transportation or storage period can be clearly and thoroughly realized, especially for mitigation of runaway reaction and strategies on emergency response. Additionally, the application of these devices is anticipated to cope with any unexpected CHP runaway reaction and proactively predict or prevent the process from any hazards during early stages of the development and operation.

Conclusions

In most thermal hazard analysis, one usually cannot merely rely on a single instrument to judge the actual degree of hazards for chemicals of interest. Therefore, evaluation and analysis for related thermal hazards by available instruments will play key roles in the chemical process industries. According to the above studies, the thermal hazard characteristics of CHP, along with its incompatibilities, could be clearly covered by DSC and TAM. Experimental results that reveal the degree of hazard of CHP, not to mention its compatibilities, should therefore not be overlooked. With the new approach comparing the advantages and disadvantages of DSC and TAM, the results also show that there is no perfect calorimeter, only strictly depending on applications corresponding to specific conditions.

In principle, physical and chemical properties of hazardous materials could be adequately analyzed by calorimeters with various features, such as stability, sensitivity, materials of test cell, and range of operating temperature, and so on. To choose a calorimeter economically, prudently and sensibly for chemicals of interest with reactive natures, one could properly demonstrate hazardous properties of materials being analyzed.

With proper calorimeters, the best parameters can be provided to the process industries for the chemicals they use. Therefore, thermokinetics and potential hazards of reactive chemicals could be clearly understood. By the new approach with suitable calorimeters, they could not only acquire properties of hazardous chemicals, but also effectively reduce the probability and extent of hazards generated during upset conditions among all the process stages. Finally, the results of this study could be used to ameliorate any unexpected disasters by realizing the inherent chemical hazard via proper calorimeters.

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Table 4

Experimental data of decomposition of CHP 35 wt% and contaminants conducted by DSC tests

Sample Weight of CHP 35 wt% (mg)	Contaminants		T ₀ (°C)	Δ H (Jg ⁻¹)	TMR (°C min ⁻¹)
	Substances	Dosage (mg)			
6.15	-	-	135	607.3	192.6
4.33	H ₂ SO ₄ (1N)	1.05	90	667.3	167.3
5.09	NaOH (1N)	0.4	55	768.7	147.9
5.20	FeCl ₃ (1M)	0.81	40	768.7	144.6

Table 5

Experimental data of autocatalytic reaction of CHP 80 wt% conducted by TAM tests

Isothermal temperature (°C)	Sample weight (g)	Reaction course (days)	1 st peak		2 nd peak	
			Time (hours)	Δ H (Jg ⁻¹)	Time (days)	Δ H (Jg ⁻¹)
75	0.505	42.7	27.6	5.28	20.9	1,082.51
80	1.020	20.0	20.8	4.05	13.0	980.98
83	0.510	22.0	13.3	6.29	9.7	1,128.86
88	0.504	16.5	8.30	4.46	6.5	1,181.65
90	0.506	14.1	7.55	2.61	4.9	1,248.45

Table 6

Comparisons of kinetic parameters of CHP 80 wt% derived from DSC and TAM tests

Calorimeters	T_0 (°C)	n	E_a (kJmole ⁻¹)	A (min ⁻¹)	k (min ⁻¹)
DSC	100	0.45	141.13	9.26×10^{13}	4.5×10^{-7}
TAM	70	0.5	95.02	9.064×10^9	1.61810^{-4}

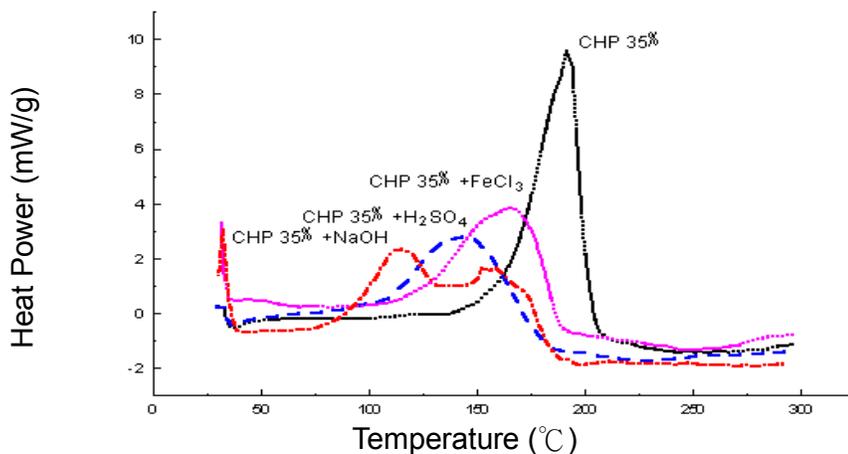


Fig. 4. Comparisons with heat power vs. temperature for CHP 35 wt% and contaminants obtained from DSC tests.

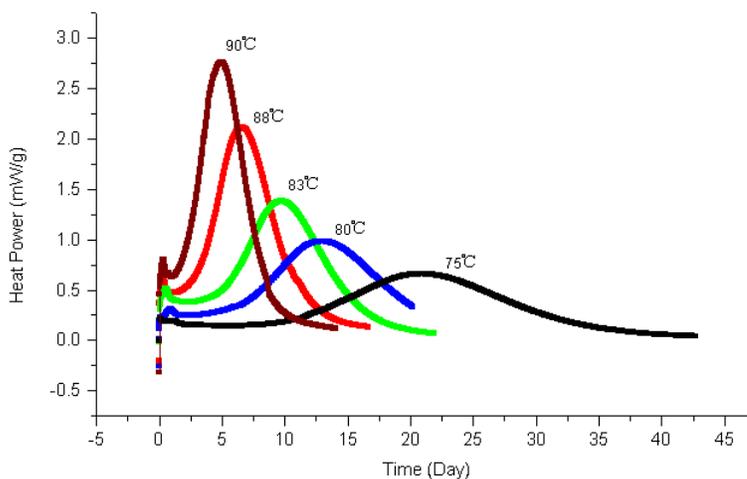


Fig. 5. Comparisons with heat power vs. time of CHP 80 wt% under different isothermal temperatures obtained from TAM tests.