



Key observations of cumene hydroperoxide concentration on runaway reaction parameters

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ARTICLE INFO

Article history:

Received 19 October 2009

Received in revised form 2 January 2010

Accepted 8 January 2010

Available online 15 January 2010

Keywords:

Reactive chemical

Cumene hydroperoxide

Quantum chemistry method

Runaway reaction

Calorimetry

ABSTRACT

Decomposition of cumene hydroperoxide (CHP) can occur easily and may lead to runaway reactions, which have resulted in fire and explosion incidents in the chemical industry. Therefore, it is important to understand the effects of process conditions on runaway reactions, which is necessary for the development of inherently safer measures to minimize risks associated with the runaway reactions. In this paper, the effects of CHP concentration on runaway reactions were studied using a systematic methodology, a combination of molecular simulation and experimental calorimetric study. Results showed that the concentration of 40 wt% can be regarded as a critical CHP concentration. Below the concentration of 40 wt%, CHP concentration shows significant effect on the parameters representing exothermic behavior of runaway reactions. The dominant reaction pathway associated with the concentration range of 0–40 wt% and some possible explanations of the reaction mechanism for concentration above 40 wt% were proposed. Results can be applied for the development of safer process conditions and other facilities to minimize the risk of runaway reactions.

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1. Introduction

Reactive chemical incidents continue to occur in the process industries and caused many fatalities as well as hundreds of millions of dollars in property and environmental damage. From 1980 to 2001, a total of 167 serious reactive chemical incidents have occurred in the U.S. [1]. Out of all the chemical incidents reported, 35% are resulted from runaway reactions [1]. Runaway reactions occurred because the heat released from a process is not removed efficiently and might present potential hazards to the operation by remaining in the reaction mass and thus raising the process temperature and reaction rate. The deviations are usually due to insufficient cooling, lack of understanding of the kinetics of the desired process, or operating errors. The risk of runaway reaction associated with processes employing reactive chemicals can be reduced by applying Inherently Safer Design (ISD) concept into the process design. One of the key principles of ISD is to minimize the risk by employing less hazardous operating conditions, less hazardous forms of materials or facilities which can minimize the consequences of the runaway reactions [2]. Prior to applying the ISD concept into the process design, it is imperative to understand

the hazards associated with reactive chemicals and the effects of process conditions on reactivity hazards.

Cumene hydroperoxide (CHP) is an unstable reactive chemical due to the weak oxygen–oxygen bond. This bond, shown in Fig. 1, can be easily broken to form radicals and ultimately lead to runaway reactions. CHP is primarily used in the production of acetone and phenol. It is also used as a catalyst for rapid polymerization, a curing agent, an initiator, and a chemical intermediate for the cross-linking agent [3]. Commercial CHP is available in the form of CHP/cumene mixture.

Among other parameters that govern the runaway reactions of CHP, concentration of CHP is of great interest in evaluating the reactivity hazards of CHP. This parameter varies greatly in the production process of CHP: 35 wt% CHP produced in the oxidation reactor was concentrated up to 80 wt% in the condensation unit [4]. Moreover, incident investigations indicate that most incidents related to CHP occurred in the oxidation reactors or condensation units, where the concentration of CHP changes greatly [5,6]. Therefore, there is a need to understand the effects of CHP concentration on runaway reactions.

Previous research in investigating the effects of CHP concentration on runaway reactions has been partially reported. Duh et al. studied runaway reactions in CHP solution at different concentrations. In the concentration range of 12–35 wt%, it was observed that the increase in CHP concentration leads to the decrease of thermal stability of CHP and increases the severity of the runaway reactions [4]. Similarly, in the concentration range of 35–80 wt%,

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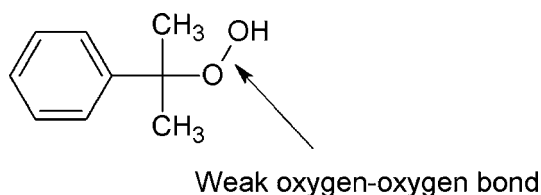


Fig. 1. Chemical structure of cumene hydroperoxide.

further experimental results reveal that higher concentration of CHP resulted in greater heat release rate, thus imposing greater hazards to related processes [7]. In a range of concentration from 10 to 80 wt%, Miyake and O'hamaen further confirmed that higher CHP concentration may lead to greater hazard as demonstrated by the increase in heat release rate of the runaway reactions [8]. The kinetics of CHP decomposition was studied by Somma et al. under different CHP concentrations (30 and 80 wt%) and the decomposition process was determined to be autocatalytic reaction. Based on the reaction scheme proposed, important kinetic parameters such as activation energy were estimated [9].

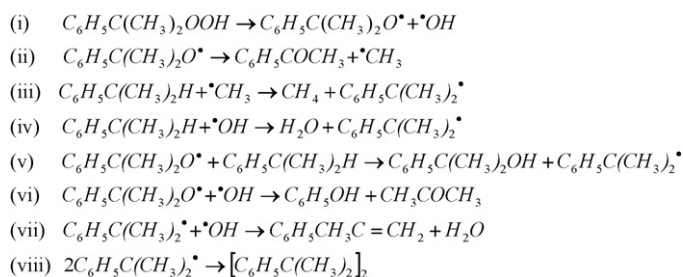
Although previous research had found the relationship between concentration of CHP and its runaway reactions, a comprehensive evaluation of runaway reaction parameters such as maximum temperature, maximum pressure, maximum self-heating rate and maximum pressure rate were not reported. In addition, little is known regarding the reaction pathways of CHP. As noted in the previous research cumene participates in the runaway reaction of CHP [10], thus the change in CHP concentration subsequently changes the mole ratio between reactants and may affect the reaction pathway.

The objective of this paper is to determine and understand the effects of CHP concentration on runaway reactions. In order to overcome the limitations of previous research, runaway reaction of CHP over a broad concentration range of 12–80 wt% was studied using a systematic approach. This approach is based on the combination of molecular simulation, experimental calorimetric analysis and correlations between these two methods, which can be outlined as follows. First, the reaction pathways were analyzed using molecular simulation. Then, the effects of CHP concentration on runaway reactions were evaluated based on the experimental results in conjunction with the results obtained from the molecular simulation of the reaction pathways. Identification of the dominant reaction pathway in combination with the calorimetric study may lead to a better understanding of the mechanism behind the CHP runaway reactions. Results can be used for the development of safer process condition to reduce the occurrence of runaway reactions in the process industries.

2. Materials and methods

2.1. Molecular simulation

Density functional theory (DFT) calculations for the gaseous phase at 298 K and 1 atm were performed using the Gaussian-03 program package [11,12], Becke 3 Lee, Yang, and Parr (B3LYP) [13,14] and the 6-31 G(d) basis set [15,16], including polarization function for angular flexibility [17], were used for frequency calculation and geometry optimization. Molecules were optimized by geometry optimization calculation to find the structures with the lowest energy. The optimized structure was then verified using frequency calculation. Each calculated structure was characterized as a local minimum with no imaginary frequency. The Gibbs free energy and enthalpy of the reaction were calculated by taking the free energies/enthalpies difference between the sum of the products and the sum of the reactants [18].



Scheme 1. The thermal decomposition mechanism of CHP.

Some assumptions were made to simplify the calculation of thermodynamic properties. Since the effects of pressure, mixing and solvent are insignificant compared to the Gibbs free energy and enthalpy of the reaction, these effects can be neglected. Also, considering these thermodynamic parameters were used for relative comparisons of the proposed reactions and were not used for accurate calculations of reaction energy, the data calculated in ideal gas phase can be used for analyzing the reaction occurred in liquid phase [19,20].

2.2. Materials

Cumene 99.9% from Acros Organics Company and CHP 88% from Aldrich Company were used for experimental analysis. CHP was diluted by cumene to different concentrations.

2.3. Calorimeter test

Calorimetric experiments were performed using Reactive System Screening Tool (RSSTTM) manufactured by Fauske & Associates, Inc. Details of this apparatus and the operation mode have been published elsewhere [21,22]. Proper measurement was made to ensure a small deviation of sample level for all tests. The sample was loaded in a 10 ml glass test cell with a thermal inertia factor (φ) of 1.119 ± 0.005 . The deviation of thermal inertia factor for all tests is very small and can be neglected. The scan rate was set at $2^{\circ}C/min$ in the temperature range of 0–90°C. Once the sample temperature exceeded 90°C, the scan rate was changed to $0.5^{\circ}C/min$. Each sample was tested three times to establish reproducibility.

3. Results and discussion

3.1. Reaction pathway analysis

Scheme 1 shows the thermal decomposition mechanism of CHP proposed from the previous experimental study [7]. This mechanism was used as a basis for the reaction pathway analysis.

Table 1 shows the calculated Gibbs free energy and enthalpy of each reaction in Scheme 1 using the computational quantum chemistry method. It is known that for thermodynamically feasible reactions, the Gibbs free energy of the reaction is negative ($\Delta G < 0$) [20]. Based on the calculation results, all elementary reactions

Table 1
The calculated thermodynamic parameters at B3LYP/6-31G(d) level of theory.

Reaction	ΔG_r (kJ/mol)	ΔH_r (kJ/mol)
(i)	117.2	159.8
(ii)	-45.6	4.2
(iii)	-92.9	-91.2
(iv)	-118.0	-110.0
(v)	-54.8	-49.0
(vi)	-414.2	-399.6
(vii)	-250.6	-256.1
(viii)	-66.1	-142.2

Table 2
Activation energy of CHP decomposition reactions.

Reaction	Intrinsic activation energy E_a^0 (kJ/mol) [24]	Activation energy E_a (kJ/mol)
(i)	4.2	466.1
(ii)	4.2	6.7
(iii)	50.2	15.1
(iv)	50.2	10.0
(v)	50.2	28.9
(vi)	209.2	56.9
(vii)	8.4	369.4
(viii)	4.2	235.1

except the reaction (i) are considered to be thermodynamically feasible in the reference state. For reaction (i), the initiation reaction for CHP decomposition, it does not undertake in the reference state because of the positive Gibbs free energy ($\Delta G > 0$). Once the temperature is elevated to a certain level, this reaction is initiated and the exothermic reaction starts immediately.

Since these elementary reactions are thermodynamically feasible, it is necessary to evaluate its kinetic stability because thermodynamically feasible reactions can be immeasurably slow due to the high activation energy. Efforts have been made to find out the relationship between activation energy and measurable parameters such as enthalpy. An equation was developed by Marcus to address the relationship between activation energy and thermodynamic parameters (Eq. (1)) [23]. Marcus equation was employed here because it is able to address strong exothermic reactions *i.e.*, reactions (vi) and (vii).

$$E_a = \left(1 + \frac{\Delta H_r}{4E_a^0} \right)^2 E_a^0 \quad (1)$$

where E_a is the activation energy, E_a^0 is the intrinsic barrier of reaction, and ΔH_r is the enthalpy of the reaction.

Applying Marcus equation to the reaction mechanism in Scheme 1, the activation energy of each elementary reaction was calculated and presented in Table 2.

As seen in Scheme 1 and Table 2, reaction (i), the initiation step, is the rate-determining step of the overall reaction. The radical $C_6H_5C(CH_3)_2O^\bullet$ produced by the first step could proceed in three routes: (I) decompose further via reaction (ii), (II) react with cumene to produce a new radical via reaction (v), (III) join the termination reaction (vi) to form final products. By comparing the activation energy of these three routes, it was found that the activation energy of route I is much lower than that of routes II and III. Therefore, route I is much more competitive and consumes most of the radicals $C_6H_5C(CH_3)_2O^\bullet$ generated.

For the radical $\bullet OH$ produced by the initiation step, there are also three possible reaction routes: (I) react with cumene via reaction (iv), (II) react with $C_6H_5C(CH_3)_2O^\bullet$ to form acetone and phenol via reaction (vi), (III) follow termination reaction (vii). Based on the activation energy calculation, routes II and III have much higher energy barrier than that of route I. It can be concluded that most radicals $\bullet OH$ react with cumene via route I.

Two termination reactions, reactions (vii) and (viii), share the same reactant $C_6H_5C(CH_3)_2^\bullet$. By comparing the activation energy of these two reactions, it was found that reaction (viii) is much more competitive than reaction (vii). Therefore, reaction (viii) is more dominant than the other reaction.

After excluding those kinetically uncompetitive elementary reactions, a dominant reaction pathway was determined based on five elementary reactions (i), (ii), (iii), (iv), and (viii). The dominant reaction pathway is shown as follows:

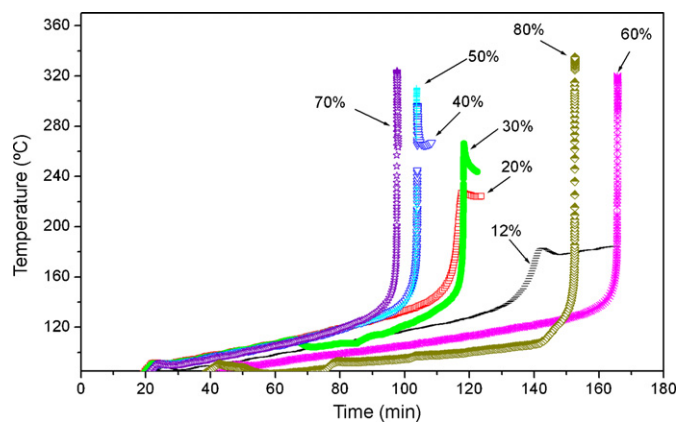
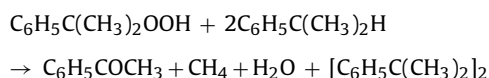


Fig. 2. CHP temperature profiles during the runaway reaction.

The predicted reaction pathway is also in agreement with the available experimental results of methane and acetophenone, which are the major products of CHP decomposition reaction [7]. Using this proposed reaction pathway, the estimation of major products, gas generation, and stoichiometry for CHP decomposition reaction can be made.

3.2. Experimental calorimetric analysis

3.2.1. RSST™ test results

In order to evaluate the reactivity hazards of CHP runaway reactions, RSST™ screening analysis was performed to obtain important parameters such as onset temperature, maximum temperature, maximum pressure, maximum self-heating rate, and maximum pressure rate.

Fig. 2 shows the temperature profiles of CHP at different concentrations during the runaway reactions. Two parameters can be determined from Fig. 2: exothermic onset temperature and maximum temperature reached by the runaway reaction. Such data can be used to assess thermal hazards posed by CHP at different concentrations.

Figs. 3 and 4 show the onset temperature and maximum temperature versus CHP concentration profiles. As seen in Fig. 3, the onset temperature remains above 129 °C in the range of concentration from 12 to 40 wt%. Once CHP concentration exceeds 40 wt%, a slow but observable decrease of onset temperature was detected by RSST™. The onset temperature reached as low as 108.3 °C in 80 wt% CHP solution. Overall, this study implies that the thermal

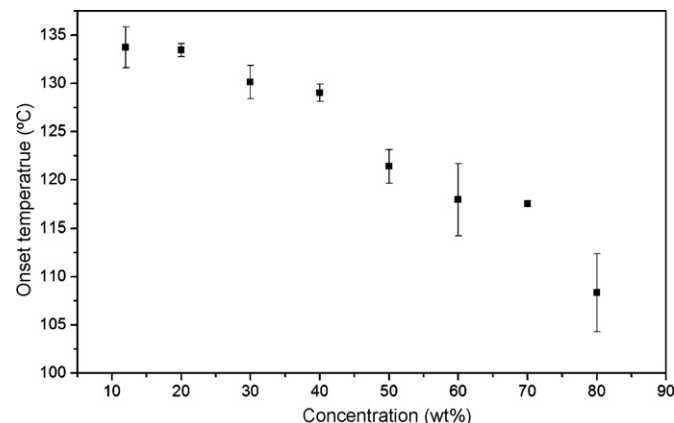


Fig. 3. Effect of CHP concentration on the onset temperature.

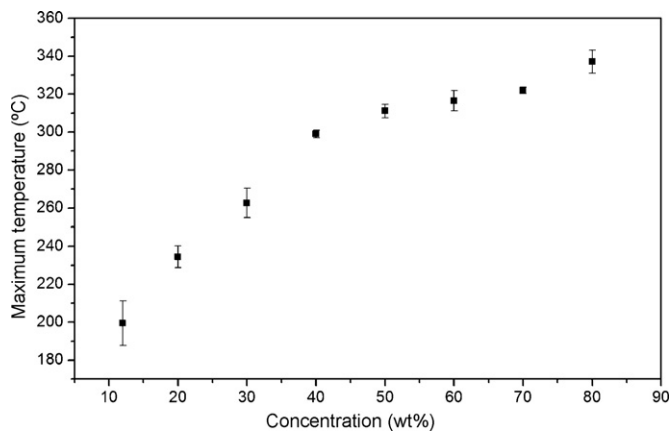


Fig. 4. Effect of CHP concentration on the maximum temperature.

stability of CHP decreases with the increase in CHP concentration, especially in high concentration range.

Similarly, two patterns can be identified from Fig. 4. At the concentration below 40 wt%, a rapid increase from 200 to 300 °C of maximum temperature can be observed with the increase of CHP concentration. However, when the CHP concentration ranges from 40 to 80 wt%, the increase of maximum temperature is much slower. This trend of maximum temperature over concentration suggests that higher CHP concentration imposes greater thermal hazard. This relationship is significant in the low concentration range of 12–40 wt%, but becomes insignificant in high concentration range of 40–80 wt%.

Fig. 5 shows the pressure generation of CHP runaway reactions at different concentrations. As seen from Fig. 5, the maximum pressure for each trend can be deduced, this build-up of pressure may lead to an explosion. In Fig. 6, a gradual increase of pressure from 2172 to 2468 kPa is observed for the concentration below 40 wt%, whereas a much greater increase in pressure is found when the CHP concentration is above 40 wt%. Here the maximum pressure reached as high as 3516 kPa for the 80 wt% concentration. The tendency of the maximum pressure implies that higher CHP concentration leads to higher pressure hazard.

Fig. 7 depicts the profiles of self-heating rate corresponding to CHP concentration during the runaway reactions. The maximum self-heating rate determined from Fig. 7 is then plotted against CHP concentration in semi-log coordinates in Fig. 8. Similarly, the pressure rate profiles and maximum pressure of CHP runaway reactions are revealed in Figs. 9 and 10, respectively. As indicated in Figs. 8 and 10, the maximum self-heating rate and maximum pres-

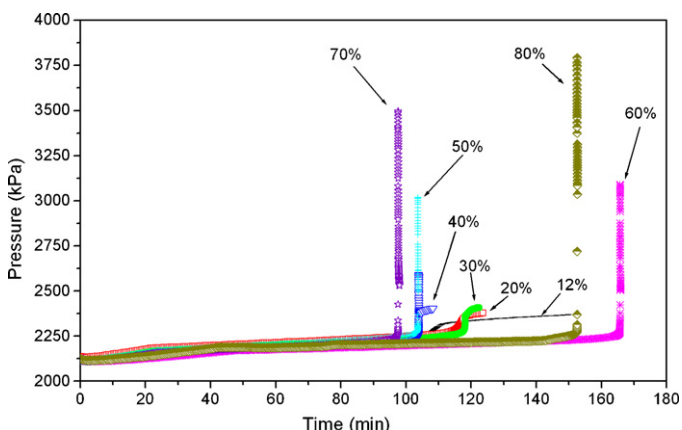


Fig. 5. CHP pressure profiles at different concentrations.

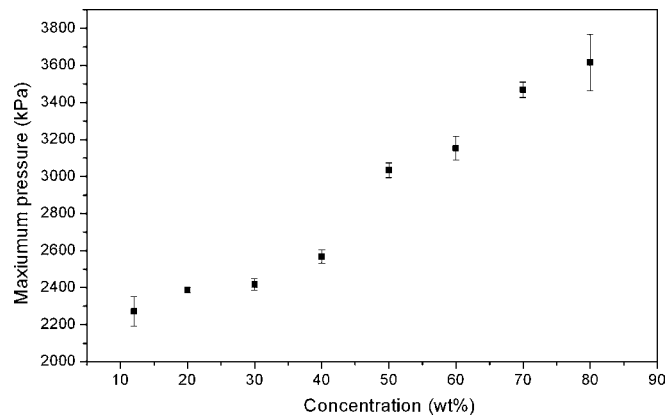


Fig. 6. Effect of CHP concentration on the maximum pressure.

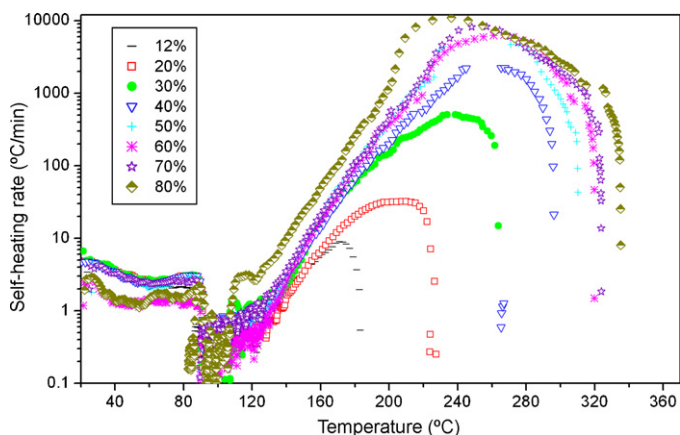


Fig. 7. CHP self-heating rate profiles at different concentrations.

sure rate increase rapidly with the increase of CHP concentration from 12 to 40 wt%. Beyond the 40 wt% concentration, the increase of these two parameters is observable but much slower. The trends of these two parameters indicate that the severity of runaway reaction is significantly affected by CHP concentration, especially in the concentration range of 12–40 wt%.

3.2.2. RSSTTM test results analysis

Important parameters such as activation energy and heat of reaction of CHP decomposition reaction can be derived from the RSSTTM experimental data. These parameters can be used to

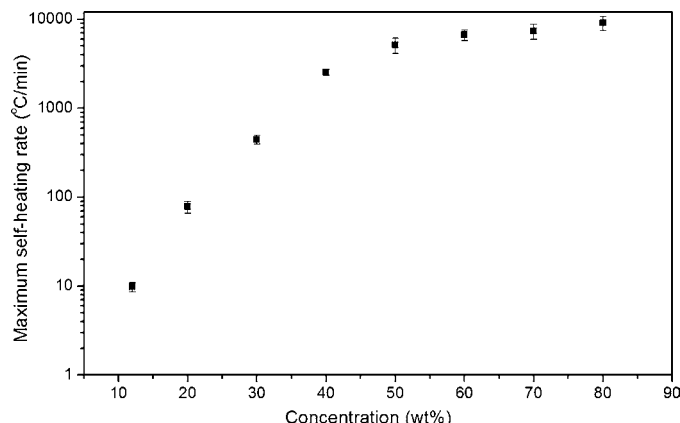


Fig. 8. Effect of CHP concentration on the maximum self-heating rate.

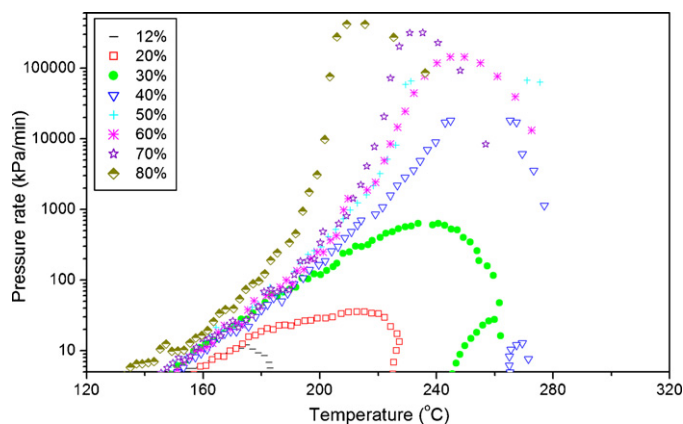


Fig. 9. CHP pressure rate profiles at different concentrations.

quantitatively evaluate the effects of CHP concentration on runaway reactions.

Assuming that the overall reaction of CHP decomposition can be represented by the reaction order of 0.5 [4], the pseudo reaction rate constant, k^* , of the CHP decomposition reaction can be calculated using the following equation [4,7,25].

$$k^* = kC_0^{n-1} = \frac{dT}{dt} \frac{(T_{\max} - T_0)^{n-1}}{(T_{\max} - T)^n} \quad (2)$$

where k is the reaction rate constant, C_0 is the initial concentration of CHP, dT/dt is the self-heating rate, n is the order of reaction, T_{\max} is the maximum temperature reached by the reaction, and T_0 is the onset temperature.

Eq. (2) can be correlated to the Arrhenius equation and is given as:

$$\ln k^* = \ln C_0^{n-1} + \ln A - \frac{E_a}{R} \frac{1}{T} \quad (3)$$

where A is the pre-exponential factor, and R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

By plotting $\ln k^*$ versus $-1/T$, a straight line can be obtained and the activation energy of the decomposition reaction can be estimated using the slope of the plot. In this work, the plot of $\ln k^*$ versus $-1/T$ yielded a linear fitting with a high R^2 value for all CHP concentrations, indicating the order of the reaction was chosen correctly (not shown here). The activation energy of CHP decomposition reaction under different concentrations was calculated and listed in Table 3.

As seen in Table 3, the activation energies are almost the same values in the concentration range of 12–40 and 50–80 wt%, respec-

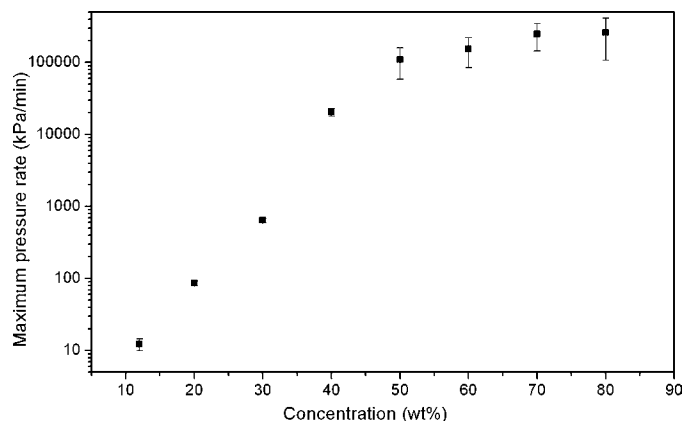


Fig. 10. Effect of CHP concentration on the maximum pressure rate.

Table 3
Activation energy of CHP decomposition reaction at different CHP concentrations.

Concentration (wt%)	E_a (kJ/mol)
12	111.4 ± 5.4
20	108.6 ± 7.2
30	109.7 ± 1.4
40	113.4 ± 2.9
50	136.6 ± 8.2
60	136.4 ± 5.3
70	138.3 ± 7.5
80	138.7 ± 5.4

tively. An obvious difference in activation energy was observed between these two concentration ranges. The change of activation energy indicates that the reaction mechanism changes when the CHP concentration exceeds 40 wt%.

Furthermore, the heat of reaction can be calculated using the following equation [22]:

$$\Delta H_r = \phi C_p \frac{T_{\max} - T_0}{x} \quad (4)$$

where ϕ is the thermal inertia factor, x is the weight fraction of CHP, and C_p is the heat capacity of CHP solution and is assumed to be independent of temperature. The heat capacity of CHP solution, $C_{p \text{ mix}}$ can be estimated using the following equation [26]:

$$C_{p \text{ mix}} = C_{p1}x_1 + C_{p2}x_2 \quad (5)$$

where C_{p1} and C_{p2} respectively are the heat capacities of cumene ($1.72 \text{ J g}^{-1} \text{ K}^{-1}$) and CHP ($1.88 \text{ J g}^{-1} \text{ K}^{-1}$) obtained from Cameo Chemicals Database [27].

The calculated heat of reaction was plotted against CHP concentration in Fig. 11. As seen in Fig. 11, the heat of reaction keeps on decreasing with the increase of CHP concentration. The heat of reaction in 80 wt% CHP solution is only half of that in 12 wt% CHP solution. Detailed explanation of this finding is provided in Section 4.

4. Discussion

Through the analysis of the experimental data (Figs. 2–10), it was found that the concentration of 40 wt% can be regarded as a critical CHP concentration due to the tendencies of runaway reaction parameters over CHP concentration across this point. Below the concentration of 40 wt%, CHP concentration shows significant effect on the parameters representing exothermic behavior of runaway reactions. However, the effects of CHP concentration on runaway reactions become much less significant once the CHP concentration

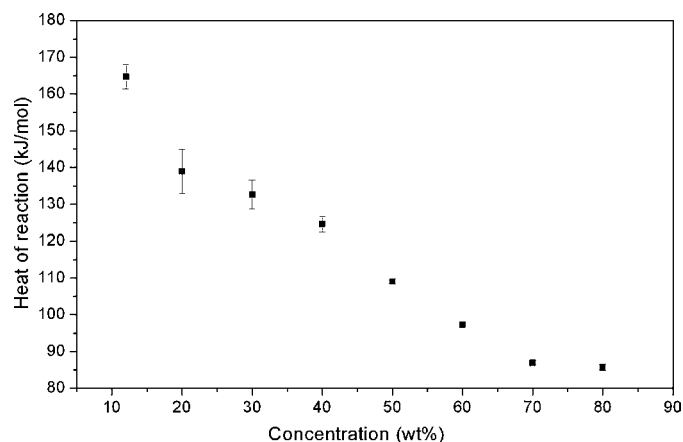


Fig. 11. Effect of CHP concentration on the heat of reaction.

exceeds 40 wt%. These findings are also in agreement with the previous works and imply that the increase of CHP concentration can lead to exponential increase of severity of runaway reactions, indicated by data of maximum heat flow rate, maximum self-heating rate and maximum pressure rate [4,8].

Based on kinetics of runaway reaction, the maximum temperature reached by the runaway reaction should be proportional to the initial concentration of CHP (Eq. (6)).

$$T_{\max} \propto \Delta H_r(C_0V_0 - C_fV_f) \propto C_0 \quad (6)$$

where C_0 is the initial concentration of CHP, C_f is the final concentration of CHP, V_0 is the initial volume of the reaction system, V_f is the final volume of the reaction system.

According to kinetics of runaway reaction and previous research, the trends of these parameters should be consistent over the whole concentration range. Because the trends of these parameters change for the concentration of 40 wt% as shown in Figs. 4–10, it is reasonable to speculate that a different decomposition reaction pathway might present when CHP concentration exceeds 40 wt%. This speculation is also supported by the quantitative analysis of activation energy, which shows obvious change when the CHP concentration is greater than 40 wt% as shown in Table 3.

By converting weight fraction into mole fraction, it was found that at 40 wt%, the mole ratio between cumene and CHP is 1.9:1, which is quite close to the ratio of 2:1 predicted by the dominant reaction pathway. Therefore, it is speculated that the shift of reaction mechanism might be the major cause for the change of exothermic behavior beyond 40 wt%. When the CHP concentration is lower than 40 wt%, the reaction follows proposed reaction pathway since cumene is sufficient in the reaction system. Once the concentration exceeds this critical point, some of the CHP follows a different reaction pathway: reactions (iii), (iv) and (v) in the dominant pathway are no longer kinetically competitive because of lack of cumene; reactions (vi) and (vii) become active because radicals •OH need to be consumed. With the increase of concentration in the range from 40 to 80 wt%, the percentage of CHP following the different reaction pathway should increase.

It is postulated that this different reaction pathway might not be as exothermic as the proposed dominant reaction pathway, which can be an explanation for the slow increase of maximum temperature, maximum self-heating rate, and maximum pressure rate when the CHP concentration is above 40 wt%. This postulation agrees with the analysis of heat of reaction, which shows significant decrease with the increase of CHP concentration when CHP concentration is above 40 wt%. However, the decrease of heat of reaction in the concentration range of 12–40 wt% is unexpected because the decomposition reaction of CHP maintains the same reaction mechanism. This unexpected tendency may be caused by the assumption made in the equation, *i.e.*, the change of heat capacity during the decomposition reaction is negligible. In order to further investigate the effects of CHP concentration on heat of reaction, the use of direct heat measurement apparatus such as Differential Scanning Calorimeter (DSC) is recommended.

Another speculation on this reaction pathway is that more gas generation such as methane or other kinds of gases might be involved in this different reaction pathway. This assumption will need to be further studied to explain the reason why the maximum pressure increases more dramatically in relation to the increase of CHP concentration once the CHP concentration is above 40 wt%.

Furthermore, the onset temperature of CHP shows only a slight change for concentrations below 40 wt%, but decreases significantly above 40 wt%. This is important for CHP condensation processes wherein CHP concentration varied within high concentration ranges (35–80 wt%). Therefore, it is necessary to consider this critical transition in the prevention of runaway reactions.

5. Conclusions

In this work, the effects of CHP concentration on runaway reactions were evaluated using the systematic approach. A dominant reaction pathway was proposed when the CHP concentration is below 40 wt%. The CHP concentration profile was also plotted against the runaway reaction parameters such as onset temperature, maximum temperature, maximum self-heating rate, and maximum pressure rate to observe the trends of CHP concentration below 40 wt% and greater than 40 wt%. Moreover, the activation energy analysis from the RSSTTM test results confirms that 40 wt% is a critical CHP concentration where the reaction mechanism begins to change. The change of the reaction mechanism causes the increase in the activation energy of the decomposition reaction. Some possible explanations of the reaction pathway are also proposed for the concentration above 40 wt%. This change of the reaction pathway affects the relationship between CHP concentration and runaway reactions and influences the associated hazards resulting from the runaway reactions.

The findings of the reaction pathway of CHP and associated hazards over concentration are important for developing an inherently safer process where CHP is employed. In these processes, safer CHP concentration range or operating temperature can be adopted based on this study. Results can also be applied to the design of mitigation systems such as emergency relief system to reduce the risk associated with CHP in chemical processes.

Acknowledgements

This research was funded by the Mary Kay O'Connor Process Safety Center at Texas A&M University. We thank the Laboratory for Molecular Simulation in the Department of Chemistry at Texas A&M University for software and support.

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