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Thermal hazards evaluation of cumene hydroperoxide mixed with its derivatives

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Abstract Over 90% of the cumene hydroperoxide (CHP) produced in the world is applied in the production of phenol and acetone. The additional applications were used as a catalyst, a curing agent, and as an initiator for polymerization. Many previous studies from open literature have verified and employed various aspects of the thermal decomposition and thermokinetics of CHP reactions. An isothermal microcalorimeter (thermal activity monitor III, TAM III), and a thermal dynamic calorimetry (differential scanning calorimetry, DSC) were used to resolve the exothermic behaviors, such as exothermic onset temperature (T_0), heat power, heat of decomposition (ΔH_d), self-heating rate, peak temperature of reaction system, time to maximum rate (TMR), etc. Furthermore, Fourier transform infrared (FT-IR) spectrometry was used to analyze the CHP products with its derivatives at 150 °C. This study will assess and validate the thermal hazards of CHP and incompatible reactions of CHP mixed with its derivatives, such as acetonphenone (AP), and dimethylphenyl carbinol (DMPC), that are essential to process safety design.

Keywords Cumene hydroperoxide (CHP) · Fourier transform infrared (FT-IR) spectrometry · Phenol · Isothermal microcalorimeter (thermal activity monitor III, TAM III) · Thermal dynamic calorimetry (differential scanning calorimetry, DSC)

Introduction

Phenol, formerly recognized as carbolic acid, is a pivotal material in the chemical industry that is also used in the production of drugs, weed killers, and synthetic resins [1]. In view of the history of the phenol market, it has been examined in detail with much discussion regarding product usage, emerging markets, and process economics over the past 10–20 years [2]. With more than 90% of the world's phenol production, the technology is currently based on the cumene hydroperoxide (CHP) route (see Fig. 1) [3]. However, CHP is a typical organic peroxide that may cause severe fire and explosion incidents because of its thermal instability and reactive incompatibilities during transport, storage, or processing and also with its derivatives [4, 5]. Consequently, we focused on the thermal hazards of phenol added into CHP in this study.

A thermal dynamic calorimetry (differential scanning calorimetry, DSC) and isothermal microcalorimeter (thermal activity monitor III, TAM III) were, respectively, used to observe the exothermic behaviors, such as exothermic onset temperature (T_0), peak temperature (T_p), and heat of decomposition (ΔH_d) [6–8] and then obtain the thermokinetic parameters by the Arrhenius Law [9, 10]. IR probe

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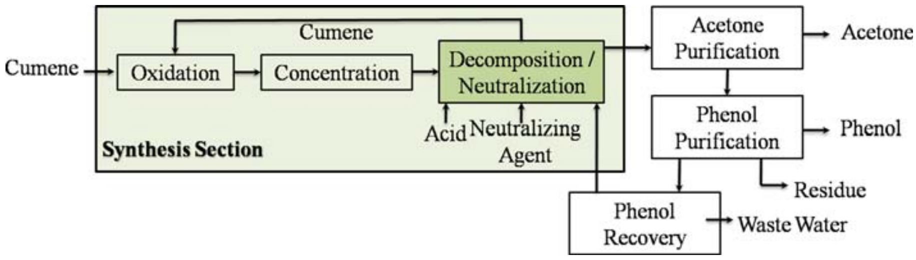

Fig. 1 Sunoco/UOP Phenol process [2]

experiments are perfectly suited for the analysis of the unusual exothermic reaction.

Method and materials

Samples

CHP of 80 mass% and its thinner cumene of 90 mass% was directly purchased from the Aldrich Co., and then stored in a refrigerator at 4 °C. Phenol was 99.5 mass% under solid state in room temperature that was purchased from the Riedel-deHaën Co. Therefore, we heated it to 50 °C to assure good mixing with CHP in the liquid state.

DSC

The preliminary thermal analysis was achieved on a Mettler TA8000 system DSC821^e. The test cell (Mettler ME-26732) was sealed manually with a special tool equipped with Mettler's DSC, that could resist high pressure until about 100 bar. STAR^e software was used to obtain exothermic curves and calculate kinetic parameters. Scanning rate chosen for the temperature-programmed ramp was at about 4 °C min^{-1} in order to have a better access to thermal equilibrium. To obtain the experimental data, about 4 to 6 mg of the testing sample was used. Dynamic scanning of the test cell was initiated by starting the programmed setting [10].

TAM III

The microisothermal calorimeter (TAM III, Thermometric AB, Jarfalla, Sweden) designed for monitor a wide range of chemical and biological reactions was able to operate between 20 and 150 °C, the working temperature range. Constant temperature was maintained within $\pm 2 \times 10^{-4}$ °C, which allowed heat flow in fractions of a micro Watt (μW) to be gauged. The test samples were dispensed into disposable calorimetric glass ampoules, capped and then placed in the measuring and reference chambers, respectively. The temperature of the oil bath was set isothermally at 100 °C for a higher temperature than a practical process, which is typically 82–90 °C [3, 7, 11].

Fourier transform infrared spectrometry (FT-IR)

The different decomposition products were identified between CHP and CHP/phenol mixture by FT-IR spectrometry, Perkin Elmer SPECTRUM 100 series, of which the resolution of detection was set as 2 cm^{-1}. For complete decomposition, the products of CHP/phenol (5:1 in mass) mixtures were acquired in the ampoules under an isothermal oven temperature of 150 °C after 8 h [12].

Results and discussion

DSC tests

The T_0 observe the reaction characteristics and rudimentary thermal hazards. From DSC tests, CHP in cumene solution were revealed it as a hazardous material which has recommendation need to concern the safe transport in order to avoid incidents. As a low concentration of phenol mixed with the CHP, the incompatible reactions were revealed the unexpected worst exothermic behaviors which were summarized in Fig. 2. Although the exothermic peaks were increased and centralized with the systematic increasing of the concentration of phenol, the exothermic peaks were displayed a singular phenomenon. Therefore, it is considered to have relatively little influence on the thermal analysis data which are presented in Table 1. Both T_0 and ΔH_d were changed slightly, and revealed the reactive pathway might be the same with the CHP. Furthermore, the peak of CHP mixed with phenol was higher than itself, so the phenol might play a key role as catalyst in this incompatible reaction. Furthermore, we proposed that the heat flow was diffused when the higher ratio of phenol was added. The induction period might be too short to acquire the integral free radical reaction under the heating condition.

TAM III tests

Isothermal temperature is also important to have thermal hazard information. Not only did the glass ampoule have a bigger volume than the test cell, but it also had the detected limit with greater precision. Figure 3 shows the results of various concentrations of phenol mixed with CHP. It is

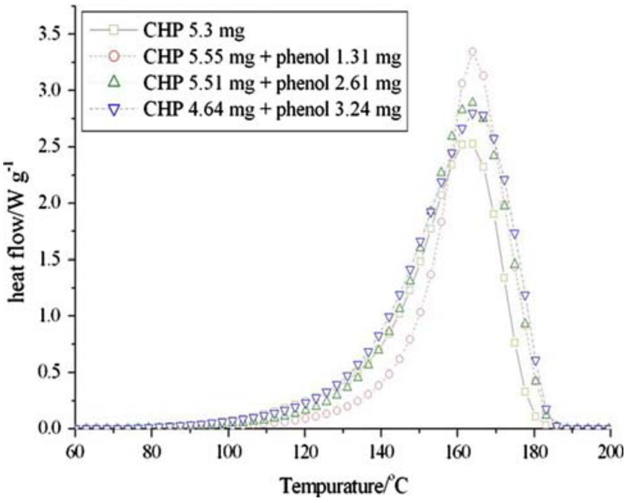

Fig. 2 Thermal curves of various ratios of CHP mixed with phenol by DSC under 4 °C min^{-1}

Table 1 The kinetic parameters of CHP with various ratios of phenol from DSC curves

80 mass% CHP/mg	99.5 mass% phenol/mg	CHP/ phenol ratio	T_0/°C	Peak heat flow /Wg^{-1}	ΔH_d/ Wg^{-1}
5.30	–	–	103.61	2.53	1112.14
5.55	1.31	4/1	101.03	3.35	1133.92
5.51	2.61	2/1	98.25	2.89	1272.41
4.64	3.24	1.4/1	98.14	2.80	1369.78

clear that the exothermic peak was steeper and sharper, and the exothermic interval was shifted earlier, when the concentration of phenol increased. Table 2 displays the experimental results for making out the relationship between phenol dosed and exothermic reaction.

Figure 4 shows the concentration of phenol versus TMR at 100 °C. It implies the catalyst of phenol was linear by the similar TMR and thermal curves when the ratio of phenol exceeded 11.35 mass%. Therefore we could realize that although the CHP is more hazardous by the appropriate presence of phenol, the limited effect is capable of evaluation. On the other hand, the worst-case could be quantified by risk assessment.

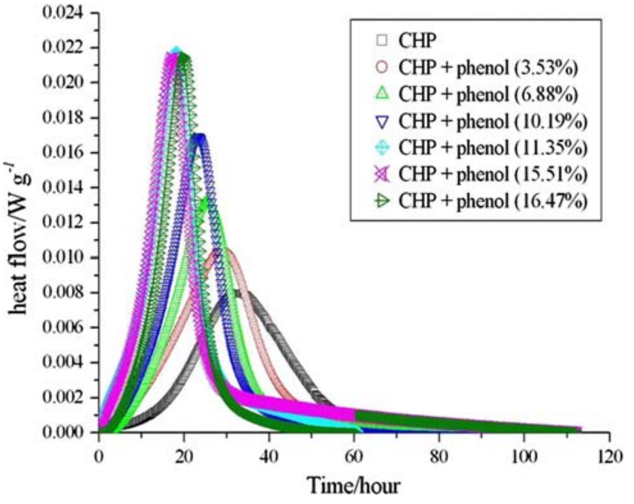

Fig. 3 Thermal curves of various ratios of CHP mixed with phenol under isothermal condition at 100 °C

Table 2 The detail of experimental results of CHP with various ratios of Phenol from TAM III curves

80 mass% CHP/mg	99.5 mass% phenol/mg	The ratio of phenol/CHP	Peak/Wg^{-1}
30.16	–	0	0.00797
30.58	1.08	35.3	0.01041
30.40	2.09	6.88	0.01322
31.03	3.16	10.19	0.01693
30.10	3.42	11.35	0.02177
30.31	4.70	15.51	0.02143
36.31	6.00	16.47	0.02150

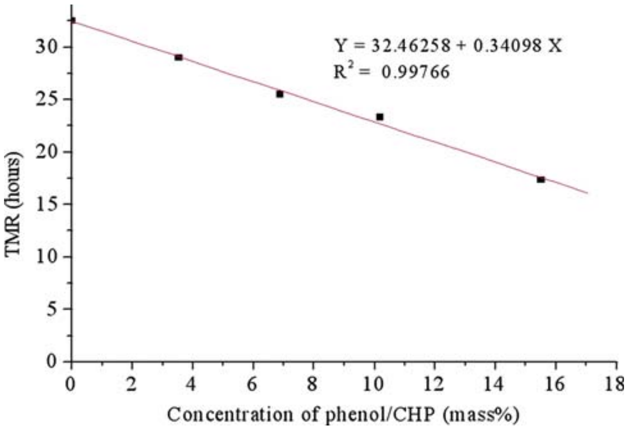

Fig. 4 TMR versus various ratios of CHP mixed with phenol at 100 °C

Spectroscopic analyses of the products after decomposition

In order to elucidate the final products of CHP mixed with its decomposition derivative, phenol, the analytic results were carried out by IR and compared the final products in Fig. 5. The exhibited reactivity were significantly affected by the reactive incompatibility. In addition, the peaks became neither stronger nor weaker when phenol was augmented, as can be seen in Fig. 6. It indicated that the quantity of functional groups may be not transformed for

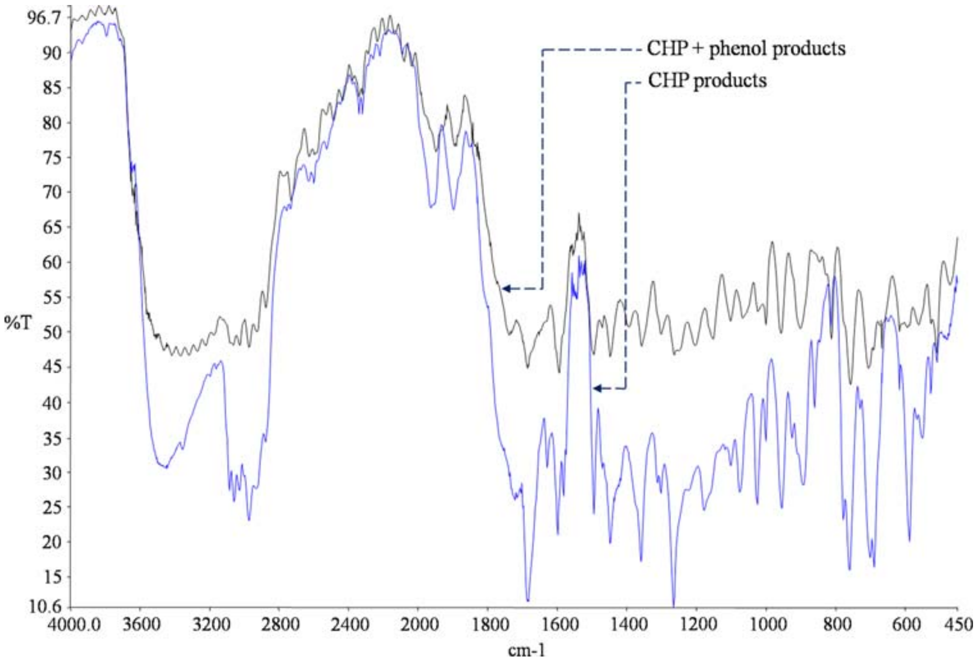

Fig. 5 The comparison of final products between CHP and CHP/phenol mixture under the isothermal oven temperature of 200 °C after 8 h

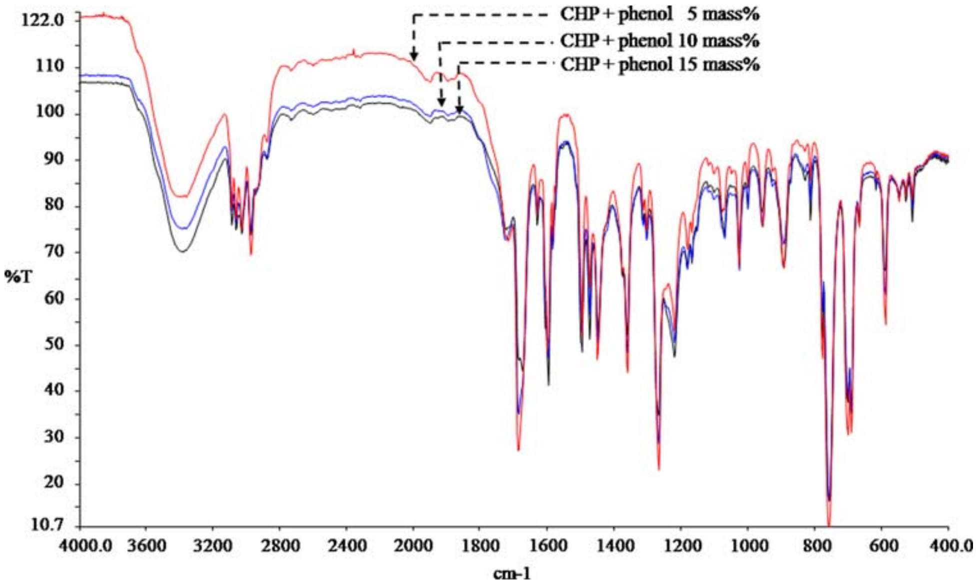

Fig. 6 Comparisons of final products between CHP/phenol mixtures under the isothermal oven temperature of 200 °C after 8 h

the same IR absorptivity. Finally, we analyzed the functional group of final products by standard sample and referred articles. The results are in Fig. 7. We could speculate that the products corresponded to the documents reviewed. We conjectured that the mostly functional groups were not altered by the presence of peaks, and then phenol was confirmed as an activator in thermal decomposition of CHP. Furthermore, the peaks of products of CHP decomposition were more specifically prominent than CHP/phenol mixture by the intensity of peaks. We could also propose that the decomposition of CHP was completely by free radical reaction.

Conclusions

From a series tests, the catalyst reaction of CHP, with phenol added, was performed by various tests of thermal decomposition. Since the induction period might have been insufficient, we could derive that ΔH_d was increased slightly. In addition, through DSC tests the exothermic peaks were increased and were centralized by adding phenol. TMR was calculated be also shorter when phenol was mixed with CHP at 100 °C by TAM III tests. The final products were also analyzed by FT-IR. Phenol is a worldwide economic product, and CHP is also a primary material for producing phenol

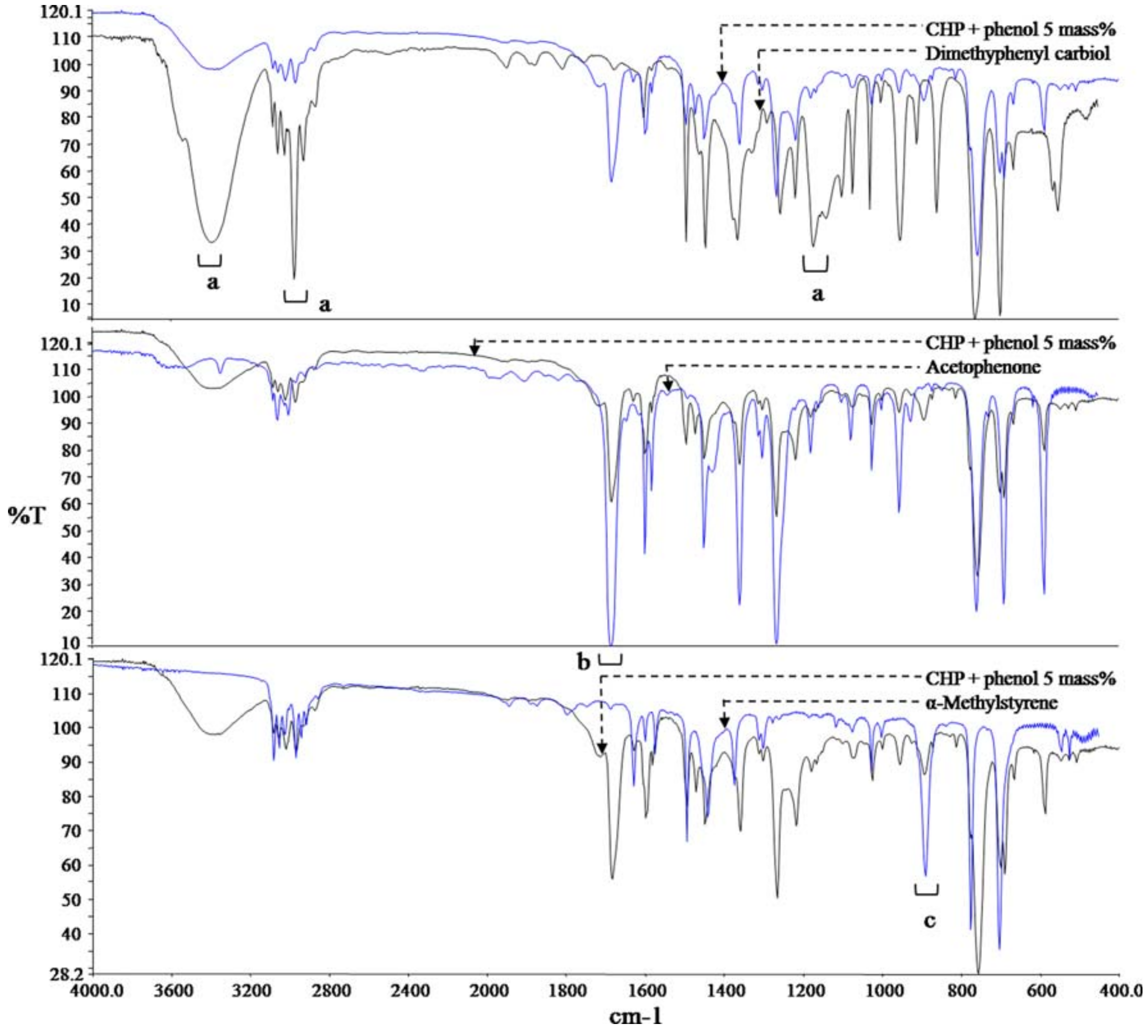

Fig. 7 Comparisons of final products between CHP/phenol and (**a**) DMPC; (**b**) AP; (**c**)AMS under the isothermal oven temperature of 200 °C after 8 h

nowadays. If CHP had been polluted by phenol in a real process, a worse unforeseen reaction might have been perceived in this study. Obviously, phenol is an important factor which should be paid attention when CHP and phenol coexist in a reactor, without mentioning the effects of acid or base.

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