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EVALUATION OF THERMAL HAZARDS FOR DICUMYL PEROXIDE BY DSC AND VSP2

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Organic peroxides (OPs) have caused many momentous explosions and runaway reactions, resulting from thermal instability, chemical pollutants, and even mechanical shock. In Taiwan, dicumyl peroxide (DCPO), due to its unstable reactive nature, has caused two thermal explosions and runaway reaction incidents in the manufacturing process. To evaluate thermal hazards of DCPO in a batch reactor, we studied thermokinetic parameters, such as heat of decomposition (ΔH_d), exothermic onset temperature (T_0), maximum temperature rise ($(dT/dt)_{max}$), maximum pressure rise ($(dP/dt)_{max}$), self-heating rate (dT/dt), etc., via differential scanning calorimetry (DSC) and vent sizing package 2 (VSP2).

Keywords: *dicumyl peroxide (DCPO), DSC, runaway reaction, thermokinetic parameters, vent sizing package 2 (VSP2)*

Introduction

Accidents often are very complicated, involving human error, insufficient chemical knowledge, incorrect dosing, poor training of operators, and so on, as shown in Fig. 1. Calorimetric and related methodologies for preventing thermal hazards of organic peroxides (OPs) have been widely developed by the Design Institute for Emergency Relief System (DIERS) technology, which has also been applied for safe venting of runaway reactions incurred by OPs in the early stages of a runaway excursion [1]. Chemical catastrophes are a serious problem in the process industries. From 1962 to 1987 [2, 3], about 134 runaway accidents occurred in the United Kingdom involving chemical incidents in a batch reactor. OPs which exothermically decompose require inherently safer design during manufacturing, transportation, storage, and even disposal, whereas they can release large amounts of thermal energy and spark off high pressure during runaway excursion, resulting in fires or explosions. Thermal explosions or runaway reaction accidents occasioned by OPs, such as cumene hydroperoxide (CHP), dicumyl peroxide (DCPO), methyl ethyl ketone peroxide (MEKPO) and so forth have also been an important issue in the past four decades in Taiwan, as displayed in Table 1 [4–7].

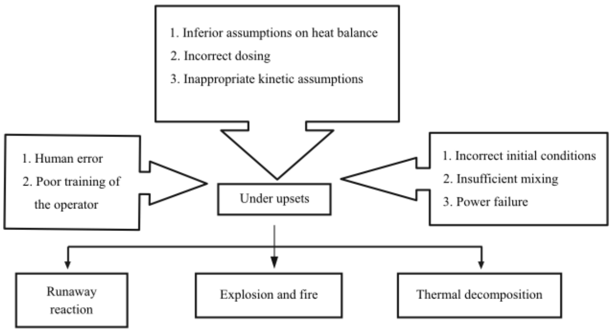

Fig. 1 Runaway reaction and thermal explosion development scheme

In addition, DCPO is applied for various resins to enhance physical properties in architectural materials, decorations, electronics, electrical insulators, plastic foams, composite parts, footwares, and so on. The aim of this study was to determine the thermal hazard characteristics of DCPO in the manufacturing process. We used differential scanning calorimetry (DSC) and vent sizing package 2 (VSP2) to quan-

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Table 1 Selected thermal explosion accidents caused by OPs in Taiwan [4–7]

Year	Chemical	Deaths/injuries	Hazard behavior
1979	MEKPO	33/49	explosion
1981	CHP	1/3	explosion
1984	MEKPO	5/55	explosion
1986	CHP	0/0	explosion
1989	MEKPO	7/5	fire and explosion
1999	DCPO	0/0	explosion
2001	MEKPO	0/1	explosion
2003	CHP/DCPO	0/2	explosion

tify the thermokinetic parameters of DCPO, such as exothermic onset temperature (T_0), heat of decomposition (ΔH_d), maximum pressure (P_{max}), and maximum temperature (T_{max}), activation energy (E_a), maximum temperature rise ($(dT/dt)_{max}$), maximum pressure rise rate ($(dP/dt)_{max}$), and the like.

Experimental

Samples

DCPO is a white crystalline solid substance. When used to link with other chemicals, such as polyethylene (PE), ethylene vinyl acetate (EVA) copolymer, and ethylene propylene terpolymer (EPT), it is a potent initiator which can readily be an oxidizer and react with reducing agents [8, 9]. Experimental techniques using DSC and VSP2 are proposed in this study. Based on the experimental techniques applied, we could find the thermal hazards and the characteristics of adding cumene, CHP, cumyl alcohol (CA), H_2SO_4, HCl, and H_3PO_4, etc., and then, the substances mentioned were all stored at 4°C in a refrigerator.

Methods

DSC

Dynamic scanning experiments were performed on a Mettler TA8000 system coupled with a DSC 821^e measuring test crucible (Mettler ME-26732) that is the essential part of the experiment. It was used to perform experiments for withstanding relatively high pressure to approximately 100 bar. Temperature-programmed screening experiments were performed with DSC [10]. The scanning rate (β) selected for the temperature- programmed ramp was 1, 2, 4 and 10°C min^{-1}. The range of temperature rise was chosen from 30 to 300°C for DCPO 99.3 mass%. DSC was employed to detect the temperature change between the sample and reference for determining the heat change, time and temperature. About 3 to 8 mg of the sample was used for acquiring the experimental data. The test cell was sealed manually by a special tool equipped with Mettler's DSC, and we conducted dynamic scanning by starting the programmed setting [11, 12].

VSP2 (Vent sizing package 2)

A PC-dedicated adiabatic calorimeter system,VSP2 manufactured by Fauske Associates, Inc. [13], was employed to measure the thermokinetics and thermal hazard data such as temperature and pressure traces with respect to time. Essentially, the low heat capacity of the cell ensures that all the reaction heat released remains within the test sample. Thermokinetic and pressure behavior in the same test cell (112 mL) usually could be tested, without any difficult extrapolation to the process scale due to the low thermal inertia factor (Φ) of about 1.05 and 1.32 [13]. The low Φ allows for bench scale simulation of the worst credible case, such as incorrect dosing, cooling failure, or external fire conditions. The low Φ-factor test cell (typically 35 g) constructed of 304 or 316 stainless steel, Hastelloy C, or titanium is situated in a 4 L pressure vessel (~1900 psig rating). Test cells are two inches in diameter with a capacity of 112 mL. In addition, to avoid bursting the test cell and missing all the exothermic data, the VSP2 tests were run with low concentration (25 mass% DCPO in 75 mass% cumene thinner) or smaller amount of reactants.

Information available from a VSP2 test includes [13]:

- heat of reaction (ΔH)
- total adiabatic temperature rise (ΔT_{ad})
- adiabatic kinetics parameters (1st order)
- rates of temperature and pressure rise (dT/dt and dP/dt)
- reaction onset temperature (T_0)
- system vapor pressure *vs*. temperature
- adiabatic time to maximum rate (TMR_{ad})
- maximum temperature and pressure (T_{max} and P_{max})
- two-phase flow regime
- temperature of no return (T_{NR})
- resident incubation time to decomposition

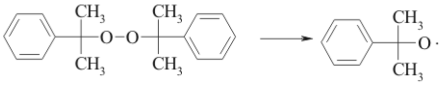
Thermal safety software (TSS)

Experimental data and kinetic evaluation were carried out by applying the thermal decomposition program (TDPro) and ForK software developed by CISP, Ltd. The method was entirely described for creation of a kinetic model and algorithms that are utilized in ForK [14].

Results and discussion

Reaction mechanisms

According to Eq. (1), we find a significant phenomenon. At the vulcanization temperature, DCPO decomposes homiletically in nonacid medium, it will yield cumyloxy radicals. In the meantime, these radicals are very unstable; therefore, they may decompose to the bottom on Eq. (2) to form a methyl radical and acetophenone. The extent of this decomposition relies on specific reaction conditions. Either the cumyloxy radical or the methyl radical abstracts a hydrogen atom from the polymer, mainly from the carbon atom indicated [15, 16].



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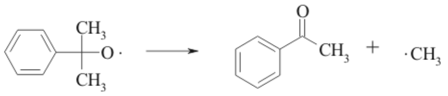

(2)

Thermal analysis by DSC

In this study, we used DSC under various β to estimate the thermal hazard of 99.3 mass% DCPO and determine thermokinetics, as shown in Fig. 2. Figure 2 shows thermal curves of decomposition of 99.3 mass% DCPO with various types of β (β=1, 2, 4 and 10°C min^{-1}) by DSC. From Fig. 2, we determined that the initial reaction of DCPO was endothermic when temperature approached 40°C, which caused a phase change on the instant and the ΔH_d was about 78 J g^{-1}. When the β became lower, the ΔH_d could be detected at a lower temperature. In other words, if the β was higher, the T_0 determined could delay decomposition and the T_{max} was relatively higher. Differential β has a disparity in sensitivity and resolution.

From Fig. 2, DCPO decomposed at about 110°C. In Table 2, the thermokinetic parameters of 99.3 mass% DCPO were determined by STAR^e program of DSC. The first peak was an endothermic reaction that about phase changes (solid to liquid) by DSC curve. The second peak was an exothermic reaction. Activation energy (E_a) of DCPO exothermic reaction was determined to be above 135 kJ mol^{-1}. The E_a, A and others were employed to calculate a useful index, such as self-accelerating decomposition temperature (SADT), temperature of no reaction (T_{NR}), critical temperature (T_c) and control temperature (CT), etc. The DCPO manufacturing process uses various chemicals, such as cumene, CHP, CA, catalyst acid (CATA), and so on in a batch reactor. Table 3 summarizes the fundamental exothermic index of various reactants in a batch reactor by DSC tests. First, 88 mass% CHP was used compared with CA, cumene, and CATA to produce lesser concentration of DCPO. In parallel, a small amount DCPO could be produced in a batch reactor when CHP was mixed along with CA. So, many chemicals, such as DCPO, CHP, CA and cumene may exist at the same time. From Table 3, the ΔH_d of CA, cumene and CATA was determined to be an exothermic phenomenon near zero by DSC. Accordingly, CA, cumene and CATA were not exothermic reactions. According to Fig. 3, CHP and DCPO produced a great deal of heat. The ΔH_d for DCPO was 737 J g^{-1} and ΔH_d for 88 mass% CHP was 1.513 J g^{-1} by DSC (β=4°C min^{-1}). The T_0 of CHP was about 105°C. 88 mass% CHP must be kept at a small amount in a blend with CA to avoid heat being generated swiftly in a batch reactor. There are three thermometers in a

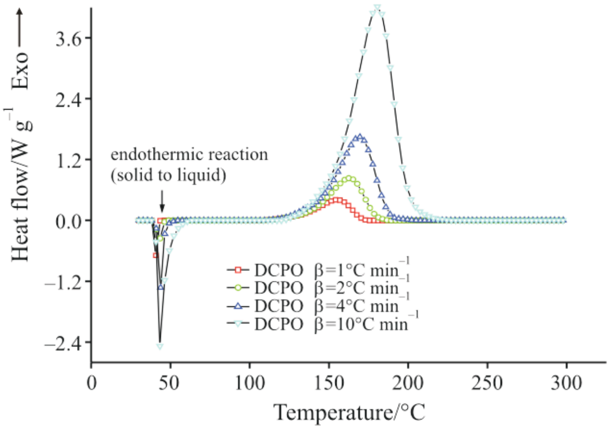

Fig. 2 Thermal decomposition of 99.3 mass% DCPO under various dynamic scanning tests (β=1, 2, 4 and 10°C min^{-1}) by DSC

Table 2 Thermokinetics and safety parameters of 99.3 mass% DCPO by DSC tests

β/ °C min^{-1}	Mass/ mg	Endothermic reaction		Exothermic reaction					
		T_{01}/ °C	ΔH/ J g^{-1}	T_{02}/ °C	T_{max}/ °C	ΔH_d/ J g^{-1}	E_a/ kJ mol^{-1}	A/ s^{-1}	n-order/ J g^{-1}
1	5.52	38	76	107	155	666	132	30.7	0.85
2	5.64	39	77	110	162	704	139	32.6	0.94
4	5.47	40	78	112	169	737	130	30.2	0.88
10	5.18	40	89	100	181	813	137	32.0	1.00

Table 3 Exothermic onset temperature and heat of decomposition of different mixtures in a batch reactor by DSC tests

Sample	Mass/mg	T_0/°C	ΔH_d/J g^{-1}
DCPO	5.47	111	169
CA	4.07	–	–
Cumene	3.70	–	–
CHP	4.50	105	175
CATA	4.67	–	–

–: Not detectable

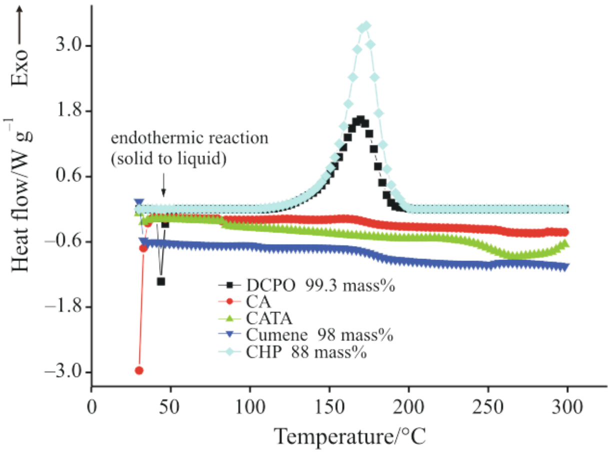

Fig. 3 Thermal decomposition of various materials in a batch reactor under 4°C min^{-1} dynamic scanning test by DSC

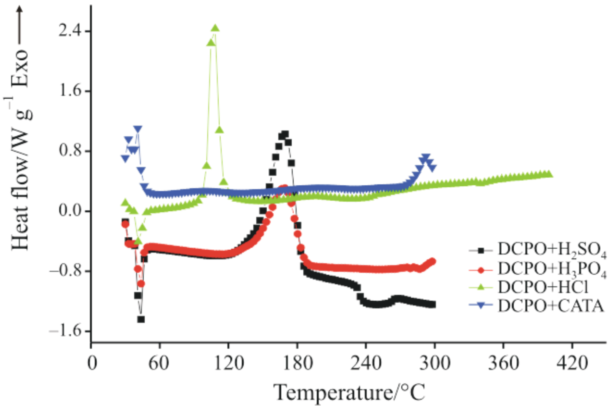

Fig. 4 Thermal decomposition of DCPO compared with various acids under 4°C min^{-1} by DSC tests

batch reactor to monitor temperature of reaction: on top, side and bottom in a batch reactor. However, a broken thermometer may make it difficult to become aware of the temperature rise, leading to thermal runaway reaction development.

Figure 4 diagrams heat production for different temperatures for thermal decomposition of DCPO compared with various acids, such a sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), hydrochloric acid (HCl) and CATA by DSC tests. The ratio of DCPO compared with various acids is about 2:1. This study investigated four acids compared with DCPO to assess safety reactants in the DCPO manufacturing process. CATA reactant from industry was employed to produce DCPO. From Fig. 4, only CATA with DCPO has not released a great deal of ΔH. From Fig. 4, the beginning of CATA scanning curve was a heat balance between sample and reference. Thus, this phenomenon was established as a reasonable circumstance. CATA is defined as a safety reactant and stable material for the DCPO manufacturing process. Thus, another acid caused DCPO to release heat at low temperature. The thermokinetics of DCPO compared with various acids for incompatibility test is illustrated in Table 4. The T_0 of DCPO compared with HCl for incompatibility test was determined at 80°C by DSC. The T_0 of DCPO compared with H_3PO_4 for incompatibility test was determined about 100°C by DSC. But, the ΔH_d was decreased to 445 J g^{-1}. The T_0 of DCPO compared ith H_2SO_4 for incompatibility test was determined to be about 110°C by DSC. To avoid an intermediate product DCPO mixed with acids from producing a great deal of heat in a batch reactor, the DCPO manufacturing process should decide on the CATA to mix with CHP and CA.

By experimental results, the reaction model was identified as an *n*-order reaction. The average value of

Table 4 Exothermic onset temperature, heat of decomposition and T_{max} of different reactants in a batch reactor by DSC tests under 4°C min^{-1} scanning rate

Sample ratio=2:1	Mass/ mg	T_0/ °C	ΔH_d/ J g^{-1}	T_{max}/ °C
DCPO+H_2SO_4	5.38	110	769	169
DCPO+H_3PO_4	8.00	100	445	168
DCPO+HCl	6.80	80	380	108
DCPO+CATA	7.78	–	–	–

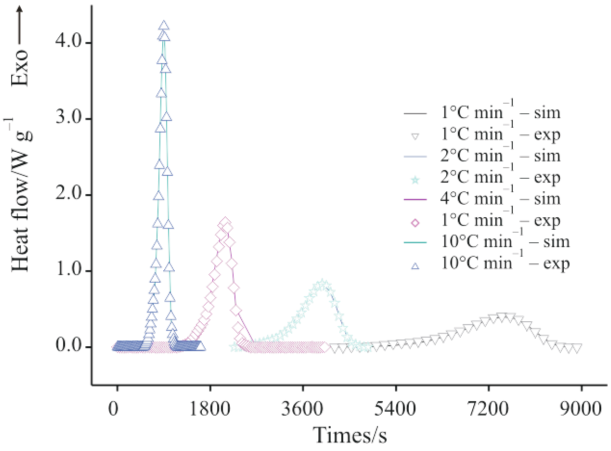

Fig. 5 Simulated heat production *vs.* time by DSC tests for 99.3 mass% DCPO (β=1, 2, 4 and 10°C min^{-1})

Table 5 ForK simulation data compared with DSC experimental results of 99.3 mass% DCPO

β/ °C min^{-1}	Mass/ mg	Experimental		Simulation	
		T_0/ °C	ΔH_d/ J g^{-1}	T_0/ °C	ΔH_d/ J g^{-1}
1	5.52	107	666	104	679
2	5.64	110	704	108	698
4	5.47	111	737	110	735
10	5.18	120	813	116	800

E_a was calculated at about 135 kJ mol^{-1} with the STAR^e program. By DSC trials, Fig. 5 depicts the simulated *n*-order model based on ForK. Table 5 shows ForK simulation data compared with DSC experimental results of 99.3 mass% DCPO. Also from Table 5, simulation results are near the experimental data. Subsequently, we used the simulation to mimic the thermal hazard of various concentrations under normal ambient circumstances.

Thermal decomposition analysis for VSP2

Table 6 lists T_0, T_{max}, P_{max}, (($dT/dt)_{max}$), (($dP/dt)_{max}$) of 25 mass% DCPO by VSP2. Figure 6 shows the temperature *vs.* time for thermal decomposition of 25 mass% DCPO by VSP2. Meanwhile, pressure *vs.* time by VSP2 under various concentrations is shown in Fig. 7. For 25 mass%, as in Fig. 6, T_{max} reached 175°C. The $(dT/dt)_{max}$ and $(dP/dt)_{max}$ of 25 mass% were about 1.61°C min^{-1} and 0.6 bar min^{-1}, respectively, as in Figs 8 and 9. A lower concentration of DCPO in an adiabatic runaway reaction test would

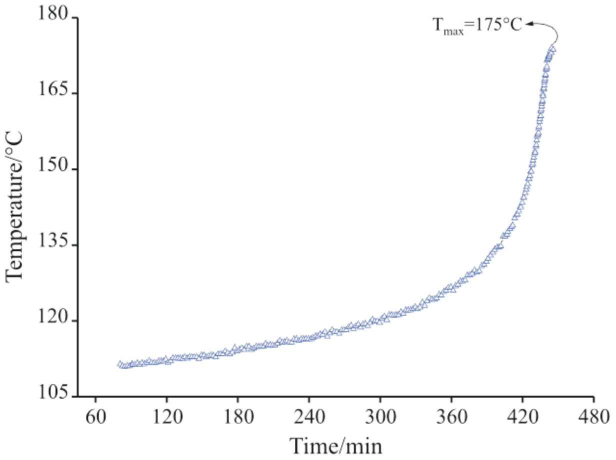

Fig. 6 Temperature *vs.* time for thermal decomposition of 25 mass% DCPO by VSP2

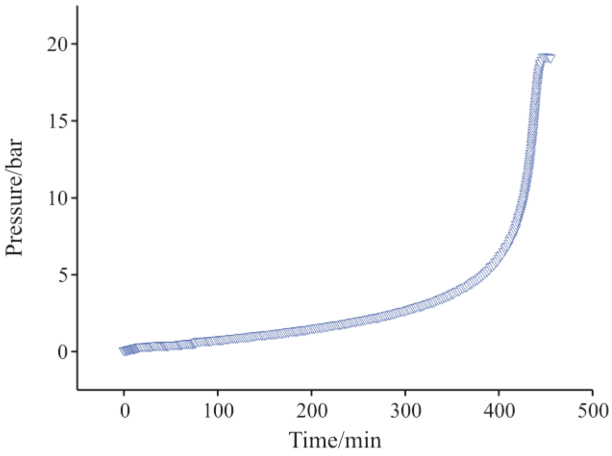

Fig. 7 Pressure *vs.* time for thermal decomposition of 25 mass% DCPO by VSP2

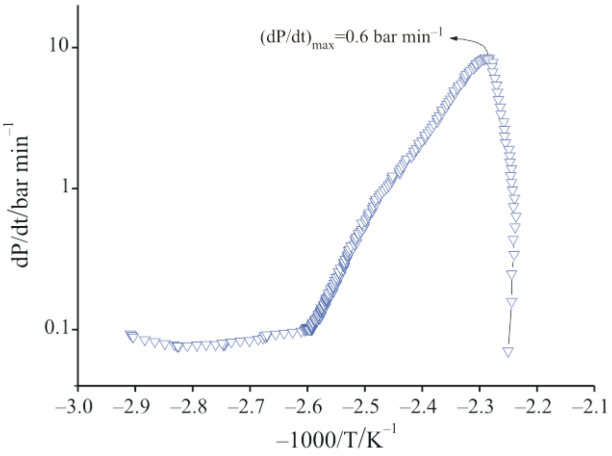

Fig. 8 Dependence of pressure rise rate on temperature from VSP2 experimental data for 25 mass% DCPO

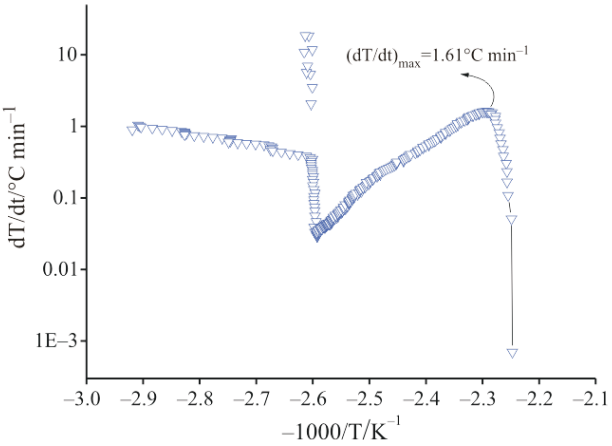

Fig. 9 Dependence of self-heating rate temperature increase on temperature from VSP2 experimental data for 25 mass% DCPO

Table 6 Thermokinetics of 25 mass% of DCPO by adiabatic VSP2 test

Concentration/mass%	T_0/°C	T_{max}/°C	P_{max}/bar	$(dT/dt)_{max}$/°C min^{-1}	$(dP/dt)_{max}$/bar min^{-1}	Φ
25	110	175	20	1.61	0.6	1.10

not cause violent thermal decomposition and release substantial amount of gas, resulting in high pressure by VSP2 tests. In the future, this study will test a higher concentration of DCPO in an adiabatic runaway reaction test. During a chemical process in a batch reactor, one should prudently take care of temperature control or external thermal hazard. In practice, an inherently safer design for DCPO operation is necessary for avoiding runaway incidents. Furthermore, understanding the thermokinetic characteristics and basic chemical or physical properties of DCPO via calorimetries could provide adequate information for minimizing industrial disasters.

Conclusions

According to the data and evidence collected in this study, when DCPO is transported or handled, extra precaution should be taken to avoid contamination and mixing with incompatible materials that may incur explosions and fires. Thermokinetics determined from the thermal curves can be used to assess the thermal explosion hazard of OP and to determine safety parameters, such as T_0, SADT, T_{NR}, and adiabatic time to maximum rate (TMR_{ad}).

If the DCPO product, a white crystalline solid, is properly maintained at low temperature during transportation and storage, it will not initiate any prominent runaway reaction, unless it goes through the melting stage under higher temperature. However, it is likely to result in accidents in a chemical process under higher temperature, incompatible substances, improper temperature control, human error, and so forth. CHP and DCPO are important reactive reactants in the DCPO manufacturing process. The DCPO manufacturing process uses low concentration or a small amount of CHP compared with CA and acids in a batch reactor. The DCPO process should dictate temperature under T_0 of CHP. In practice, these data are necessary for safe application, storage, and transportation of a chemical product. Future studies will focus on reaction mechanism analysis in a batch reactor.

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