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Chemical Engineering Journal 88 (2002) 215–223

Chemical Engineering Journal

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Catalytic decomposition process of cumene hydroperoxide using sulfonic resins as catalyst

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Received 29 October 2001; accepted 21 January 2002

Abstract

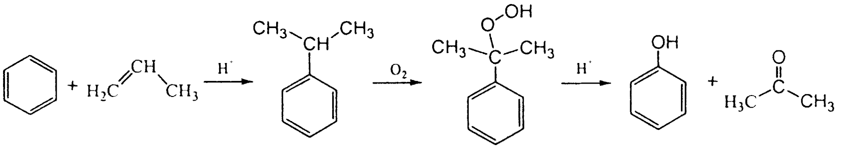
A new catalytic process for cumene hydroperoxide (CHP) decomposition using sulfonic resins is developed. A macroporous sulfonic resin entitled TH-02 is selected as the catalyst. A novel three-phase circulating fluidized bed (TPCFB) reactor in which the geometry and the particular flow regime resolve the conflict between heat transfer and resin fragmentation is used for this process. RTD results show that this reactor approximates a CSTR, and solids and liquid are distributed uniformly in it. Under the optimal reaction conditions, which are a volumetric ratio of CHP to acetone 1:2–1:3, temperature 75–85 °C preferably 80 °C, solid holdup 1–1.5 wt.% and WHSV of CHP 30–40 h^{-1}, the conversion and product selectivity of CHP can be over 99 and 98%, respectively.

Keywords: Catalytic decomposition process; Cumene hydroperoxide; Sulfonic resins

1. Introduction

Phenol is one of the important basic chemicals in the organic chemical industry. It can be used for broad purposes, e.g., manufacturing phenol aldehyde resins, aminocaprolactam, alkyl phenol, preparing pesticide and medicine, etc. Furthermore, with the rapid increase of synthetic materials, the demand for phenol has increased. Acetone is also one of the important chemicals in the chemical industry. It can be used for manufacturing methyl methacrylate, bisphenol A and other chemicals such as ketene, methyl vinyl ketone, isopropyl amino, isophorone, β-irisone, etc. In addition, acetone plays a very important role in the chemical and other industries as a favorable solvent.

At present, about 94.5% of phenol in the chemical market is manufactured by cumene decomposition [1], which was developed in the 1950s. The process consists of the following three steps: (a) cumene synthesis from benzene and propylene catalyzed by certain acid catalysts, (b) cumene oxidization by air to cumene hydroperoxide (CHP) and (c) decomposition of CHP into phenol and acetone catalyzed by acid catalysts. The following reaction equation shows this process:



(1)

In industry, the third step of this process, CHP decomposition, is carried out in a continuous stirred or back-mixed reactor and is catalyzed by sulfuric acid. CHP decomposition is a strong exothermic reaction with a reaction heat of 1457.6 kJ mol^{-1} corresponding to the heat of evaporation of 2.7 kg acetone; hence, it is a sensitive and even dangerous reaction if sulfuric acid is used as the catalyst. Further disadvantages of using this liquid acid catalyst include [2] the need for an efficient means of separating the phenol and acetone products from the acid, the need to neutralize the acid and the disposal of salts generated by the neutralization. Therefore, it is of great importance and significance to develop new catalysts and new processes for phenol and acetone production.

Six types of catalysts that can be used for CHP decomposition have been reported in the literature [3]. These are

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PII: S1385-8947(02)00003-7

Nomenclature

A_p	surface area of the particle (m^2)
C	concentration ($mol\,m^{-3}$)
C_b	concentration of CHP in the bulk liquid ($mol\,m^{-3}$)
C_D	trag coefficient
C_s	concentration of CHP at the surface of the particle ($mol\,m^{-3}$)
d_p	average diameter of the particle (m)
D_{Am}	mass diffusion coefficient in the liquid phase ($m^2\,m^{-1}$)
f	corrected coefficient
g	acceleration of gravity ($m\,s^{-2}$)
$k_{c,s}$	mass transfer coefficient between the liquid and solid ($m\,s^{-1}$)
k_m	reaction rate constant ($m^3\,(kg\,s)^{-1}$)
r_A	reaction rate ($mol\,s^{-1}$)
Sh	Sherwood number
t	time (s)
Δu	slip velocity of the liquid and solid ($m\,s^{-1}$)
v_{CHP}	space velocity of CHP (h^{-1})
V	volume of liquid in the reactor (m^3)
w	weight of the catalyst (kg)
w_p	weight of the catalyst particle (kg)
x	weight fraction of CHP (%)

Greek letters

ε_s	solid holdup
η	effectiveness factor of internal diffusion in the catalyst
μ_L	viscosity of liquid (Pa s)
ρ_L	density of liquid in the reactor ($kg\,m^{-3}$)
ρ_p	wet particle density ($kg\,m^{-3}$)

Friedel–Crafts catalysts such as $AlCl_3$, inorganic and organic acids, silicates, metallic oxides such as Al_2O_3 and TiO_2, phosphorous compounds such as PCl_3, PCl_5 and $POCl_3$, and sulfonated phenol formaldehyde resins and sulfonated styrene resins. To avoid the disadvantages of the traditional process, it is preferable to utilize a safer and simpler catalyst in the solid state. In the recent two decades, many researches have the aim to develop new acid catalysts, especially solid acids to replace sulfuric acid.

The solid acid catalysts have some important advantages including adequate catalytic activity, less byproducts, no erosion, easy separation of catalysts and products and easy catalyst recovery and recycling. Catalysts of clay, zeolite and acid resin were studied extensively. The clays consists of Si, Al, O and a small amount of Mg and Fe. Montmorillonite has the highest catalytic activity for CHP decomposition of the clays. In 1989, Knifton [4] studied a series of montmorillonites and concluded that a conversion over 99% and a phenol selectivity over 99% can be achieved. However, there had been no report on the process scale up of CHP decomposition using clay catalysts. For zeolites, an effective catalyst is β-zeolite, with an acidity expressed as the α value between 5 and 1000 as the most effective [5]. Mobil Oil Corporation [6] studied CHP decomposition catalyzed by β-zeolite in 1984. The conversion and selectivity is higher than the traditional process catalyzed by sulfuric acid. However, there are few reports concerned with the lifetime, deactivation and regeneration of the zeolite catalyst [7], which are important factors for its industrialization. Acidic resins are the other solid acid catalysts which can be used for CHP decomposition reaction. A relatively simple process can be developed using resin catalysts. There are already some reports about pilot scale experiments [8] and an industrial application with a scale of up to 15 000 t per year [9] using a sparge bed reactor. Up to now, there are no reports about the further scale up of this process, which may be due to difficulties in the reactor scale up, e.g., the phase distribution and the fragmentation of the resins.

CHP decomposition is a strong exothermic reaction and there even exists the danger of explosion. A fast and effective removal of reaction heat is absolutely necessary for the process. The typical method of heat removal is by acetone evaporation. This method is also adopted in this new process. In the traditional process of CHP decomposition catalyzed by sulfuric acid, a strong stirrer is used to ensure the uniform distribution of CHP concentration and temperature in the reactor to avoid any local accumulation of CHP and heat to make the process stable and safe. However, when the process is catalyzed by sulfonic resins, a mechanical stirrer used to increase mixing and heat transfer can breaks the resins into pieces. Even though the broken resins still have catalytic activity, these can escape with the exit stream and can block the pipeline and cause a sudden accumulation of CHP in the reactor. Therefore, continuous stirred reactors are inappropriate for the process catalyzed by sulfonic resin. To industrialize the new process, a new reactor that has good heat transfer and can avoid the fragmentation of resin is absolutely necessary. In this paper, a novel three-phase circulating fluidized bed (TPCFB) reactor is proposed and used for the process [10]. In order to operate the reactor smoothly, the kinetics and mass transfer are studied systematically for a better understanding of the process and to propose a new method to operate the reactor.

In this reactor, the mass transfer includes external diffusion transfer and internal diffusion transfer. Since diffusion limitation has a negative effect on the activity, selectivity and lifetime of the catalyst, it is necessary to get a better understanding about the diffusion processes for improving the process. For the internal diffusion, the resistance can be derived from the efficiency factor of the catalyst pellets measured by experiments. For the external diffusion, the resistance of external diffusion cannot be detected directly, but can be calculated from mass transfer correlations from the literature that are suitable to this process.

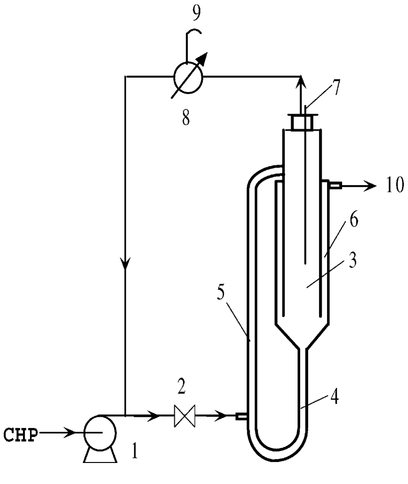

Fig. 1. Experimental apparatus for CHP decomposition: 1—metering pump; 2—valve; 3—main reactor; 4—loop; 5—riser; 6—liquid–solid separator; 7—thermocouple; 8—condenser; 9—gas vent; 10—product exit.

2. Experimental

Continuous stirred tank reactors are inappropriate for CHP decomposition catalyzed by sulfonic resins because of the following reasons: (a) the resin catalyst is easily broken by the agitation, (b) there exist difficulties and problems in the scale up of the stirred tank reactor and (c) the energy consumption is high when mechanical agitation is used. As shown in Fig. 1, a novel TPCFB reactor is proposed for the CHP decomposition in this work. Mechanical stirring can be avoided when using the proposed TPCFB reactor. The experimental reactor is made of glass, and consists of a riser, a main reactor, a liquid–solid separator and a loop. The main reactor is 90 mm in inner diameter and 1200 mm in height. The liquid–solid separator is 110 mm in inner diameter and 800 mm in height. The dimensions of the riser and the loop are $\phi 10\,\mathrm{mm} \times 1500\,\mathrm{mm}$ and $\phi 10\,\mathrm{mm} \times 700\,\mathrm{mm}$, respectively. In the experiments, CHP mixed with acetone is pumped into the reactor at the bottom of the riser and converted into phenol and acetone after contacting sulfonic resin catalysts from the loop. The liquid and the solids in the riser are lifted by the acetone steam gasified by the reaction heat and enter the main reactor where the reaction proceeds further. In the main reactor, the liquid and solids flow downwards while the gas flows upwards. This countercurrent flow improves mass and heat transfer and the distribution of liquid and solids. Acetone evaporation and the exiting condensed acetone stream, which is mixed with CHP, remove the reaction heat. The condensed acetone stream, which is mixed with CHP, is also cycled to the reactor as reaction feed. Part of the liquid leaves the reactor as the products via the liquid–solid separator, and the remaining together with the solids flow into the riser via the loop.

CHP is provided by Yanshan Petrochemical, and is an industrial material containing 84.5 wt.% CHP and about 15.5 wt.% cumene. Other reagents are from the Beijing Chemical Reagent, with purity over 99.0%. The concentration of CHP and the compositions of the products are analyzed by iodometry and GC (FID, 50 m quartz capillary column, Shimadzu GC-14B), respectively. The pulse input method using saturated KCl as the tracer is used to measure the residence time distribution of the liquid.

3. Results and discussion

3.1. Fragmentation of resin

Many kinds of commercially available resins were tested in this work and after the screening we selected one of them as the catalyst for the CHP decomposition. This is a kind of macroporous sulfonic resin and entitled TH-02 for convenience. Some characteristics of the TH-02 resin are listed in Table 1. The main microframes of TH-02 are stereo cross-links of styrene polymer chains and the cross-linking agent. The ion-exchange groups, which are sulfonic acid groups, attach on the main frames via chemical bonds. To obtain higher exchange capacity and large internal pores, which both contribute to high catalytic activity, more chemical groups and precipitant are inducted into the resins. The cross-linking degree is definitely reduced and this weakens the mechanical strength. Therefore, continuous stirred reactors, which will cause the resins to fall to pieces, are inappropriate for the CHP decomposition process catalyzed by macroporous sulfonic resins.

For designing the reactor and determining the optimum operation conditions for the process, the factors that lead to resin fragmentation are investigated systematically. The mechanical strength of TH-02 resins is tested experimentally under different conditions. The influence of temperature, agitation speed and solvent on resin fragmentation has been studied experimentally. In the tests, 5 g of resins are put into a 500 ml three-necked bottle with an acetone/phenol mixed solvent of different proportions. Then after 30 min stirring, the solids, including fragmented and original resins, are separated from the solvent by filtration. After washing and drying, an 80-mesh sieve is used to separate the fragments and spherical particle resins.

In general, the ion-exchange resins have high heat resistance but will thermally decompose if the temperature exceeds a certain value, e.g., 150 °C. Fig. 2 shows the influence of temperature on resin fragmentation. The fragmentary ratio of resins increases nonlinearly with the increase of temperature. However, within the temperature

Table 1
Performance characteristics of TH-02 resins

Type	Frame	Full exchange capacity ($\mathrm{mol\,kg^{-1}}$)	Surface area per mass unit ($\mathrm{m^2\,g^{-1}}$)	Mean pore diameter (nm)
TH-02	Macropore	5.0	30	65

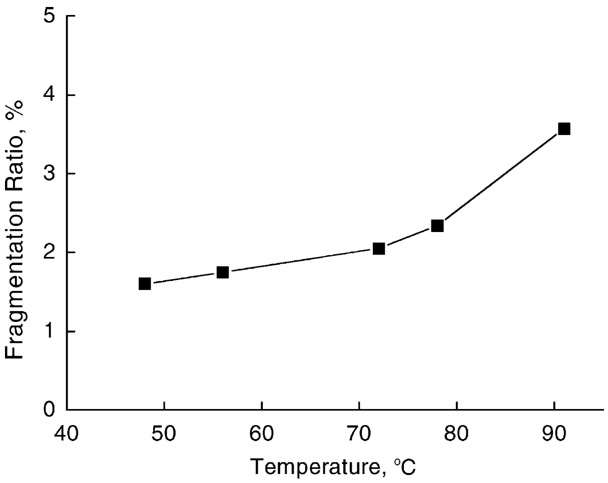

Fig. 2. Effect of temperature on the fragmentation of resins. Stirring speed = 150 rpm, solvent = 10% acetone and 90% phenol in volume ratio.

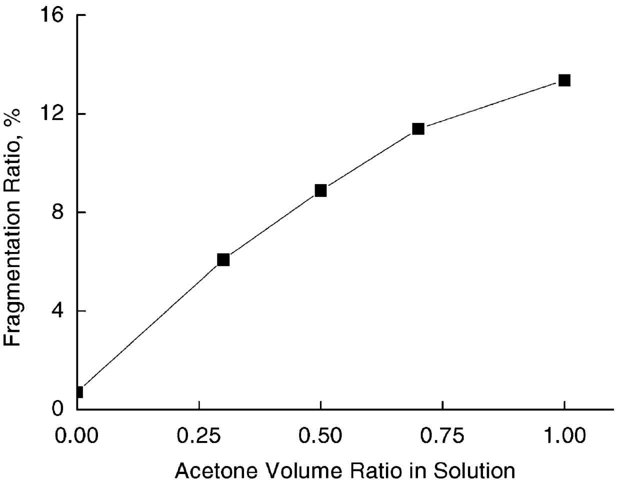

Fig. 4. Effect of solution composition on the fragmentation of resins. Temperature = 56 °C, stirring speed = 150 rpm.

range 50–90 °C, the fragmentation ratio does not increase much whereas the speed of accretion increases. Therefore, the reaction experiments are carried out in this temperature range, where the temperature does not have a large influence on resin fragmentation. Fig. 3 shows the influence of the stirring speed on resin fragmentation. The fragmentation ratio increases linearly with the increase of agitation speed. Agitation has a more pronounced influence on the fragmentation ratio compared to temperature. Therefore, mechanical agitation should be avoided in the CHP decomposition process using sulfonic resins, while the temperature can be selected between 50 and 90 °C. In order to verify the influence of agitation on the fragmentation, the TH-02 resin has been boiled in acetone without stirring for more than 150 h, and no broken resins are found.

The solvent also has an impact on the mechanical strength of the resins in the reaction system. The main components of the mixed organic solvent are phenol and acetone, which account for over 90 wt.%. Solutions, made up of acetone and phenol in different proportions, in a 500 ml three-necked bottle were used to study the influence of solvent on the mechanical strength of the resins. The curve in Fig. 4 shows that the acetone concentration in the solution is a large factor in resin fragmentation. The dipole moment of acetone is 2.9 Debye while that of phenol is 1.6 Debye. Acetone has a larger polarity than phenol, which gives a larger solvation effect with polymer chains and exchange groups. Therefore, the resins will swell and fall to pieces easier in solutions with a higher acetone concentration.

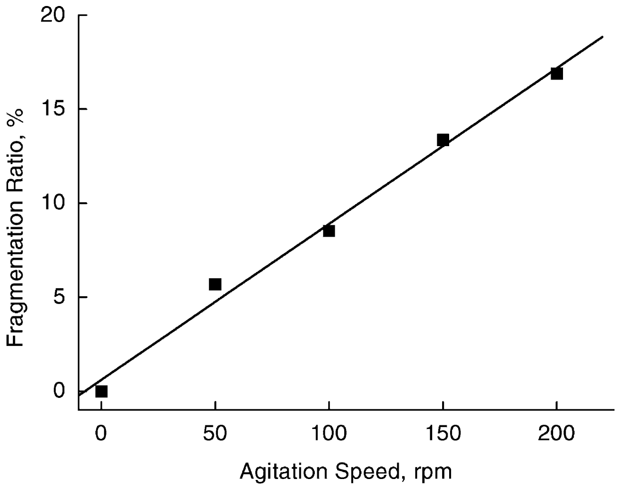

Fig. 3. Effect of stirring speed on the fragmentation of resins. Temperature = 56 °C.

3.2. Residence time distribution

The residence time distribution (RTD) is a characteristic of the flow pattern in the chemical reactor, and is one of the most informative characterizations of the reactor [11–14]. It provides a quantitative measurement of the degree of back-mixing within the system, and the knowledge of the liquid RTD is important for a number of reasons [13,14] including allowing an accurate kinetic modeling of the system, and in reactor design to achieve or preserve a desired flow pattern. To get knowledge of the distribution of the liquid and solids in the reactor, we measure the RTD of the liquid phase. A reactor made of Plexiglas, which has the same dimensions as the glass one, is used in the RTD experiments. Water and air are used to simulate the liquid and gas fluids, respectively. The solid phase is the same TH-02 resins as used in the hot model. Since the density of the liquid is approximately that of the particles, the RTD of the particles can be considered the same as that of the liquid. The curve in Fig. 5 represents the RTD of the pulse tracer, with the ordinate scale expressed as $C/C_{\max}$. From the curve, we can see that a dead time of approximately 1 min exists, which is much less than the average residence time. The back-mixing

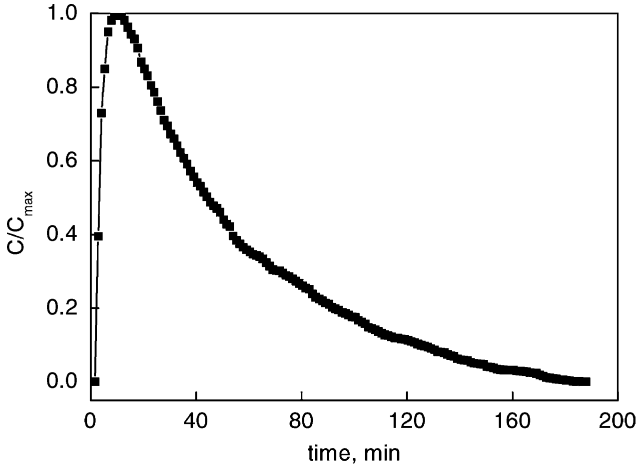

Fig. 5. RTD of liquid in the TPCFB reactor. Liquid feed rate is $7\,\mathrm{l\,h^{-1}}$, superficial gas velocity is $0.074\,\mathrm{m\,s^{-1}}$ in riser and $0.054\,\mathrm{m\,s^{-1}}$ in main reactor, no liquid circulation.

behavior of the liquid phase fitted with the remainder of the curve, i.e., excluding the dead time, by a tank-in-series model is equal to 1.6 CSTRs in series. The experimental results are consistent with the assumed liquid behavior that the reactor can be treated as a combination of a PFR and a CSTR.

In common situations, the liquid circulating rate has a significant impact on its back-mixing behavior. In order to estimate this impact, we set a valve on the loop tube to modify the liquid circulating rate and measured the different liquid phase RTDs. The superficial gas velocities both in the riser and the main reactor, as well as the water feed rate, are fixed when the experiments are carried out with different liquid circulating ratios, defined as the liquid circulating rate to the feed rate and ranging from 0 to 50. The results of the experiments are listed in Table 2.

The fact that similar back-mixing behaviors are obtained with different liquid circulating ratios indicates that in this case the liquid circulating ratio has a very slight effect on the liquid back-mixing behavior. Therefore, the agitation from the injected gases into the main reactor is the major factor that affects the back-mixing behavior of the liquid when it is intensive enough (in this case the superficial gas velocity is $0.06\,\mathrm{m\,s^{-1}}$). Other researchers have also mentioned the same conclusion [15]. In the hot model experiments, 2.7 kg acetone vapor will be generated by the decomposition of 1 kg CHP. Thus the average superficial gas velocity can be high to 0.06–$0.07\,\mathrm{m\,s^{-1}}$ if the hot reactor has the same size as the cold reactor. Accordingly, it is unnecessary to set a valve on the circulating tube.

3.3. Operation conditions

The effect of temperature on the CHP decomposition reaction, including conversion and selectivity, is illustrated in Fig. 6. The results show that with increased reaction temperature, the conversion increases while the selectivity decreases. In industry, the conversion and the selectivity of CHP can reach 99.9 and 98%, respectively, using the process catalyzed by sulfuric acid. It can be concluded from Fig. 6 that the suitable temperature range for our reactor is 75–85 °C in order to obtain similar conversion and selectivity.

The WHSV, which is defined as the mass flow rate of pure CHP per unit weight resin catalysts, is also an important parameter for reactor design and operation. A high value of WHSV can enhance the process capacity, but it will lead to a low conversion of CHP. Fig. 7 presents the effect of WHSV on the conversion of CHP at the outlet of the reactor. It can be seen in Fig. 8 that the WHSV has a significant influence on the conversion of CHP. In industry, the concentration of CHP in the product must be less than 0.1% and so the WHSV should be in a range 30–$40\,\mathrm{h^{-1}}$.

Local solid holdup is important in a heterogeneous catalytic system. It will influence the local reaction rate directly and the quality of products finally. Fig. 8 illustrates how the conversion of CHP varies with different solid holdup when the feed rate of CHP remains constant. It can be seen that the concentration of CHP decreases with an increase of the solid holdup. To ensure that the conversion of CHP in the product is greater than 99.9%, the solid holdup must be more than 1%. On the other hand, with an increase of the solid holdup, the WHSV decreases when the feed rate of CHP remains constant. Therefore, the suitable solid holdup should be in the range 1.0–1.5 wt.%.

The reaction heat of CHP decomposition is removed by the evaporation of acetone in the reactor. The temperature depends on the liquid composition in the reactor, specifically, the bubble point of the liquid phase. Through regulating the acetone concentration in the reactor by feeding extra

Table 2
RTD data of liquid under different circulating ratios

Liquid circulating ratio	Superficial gas velocity in riser ($\mathrm{m\,s^{-1}}$)	Superficial gas velocity in main reactor ($\mathrm{m\,s^{-1}}$)	Water feed rate ($\mathrm{l\,h^{-1}}$)	Average residence time (min)	Equivalent number of tanks[a]
0	0.074	0.054	7.0	45.5	1.63
19.2	0.073	0.053	6.9	45.3	1.61
43.5	0.073	0.054	6.9	45.3	1.58
50.1	0.072	0.054	7.0	45.4	1.56

[a] Fitted to experimental results by the tank-in-series model.

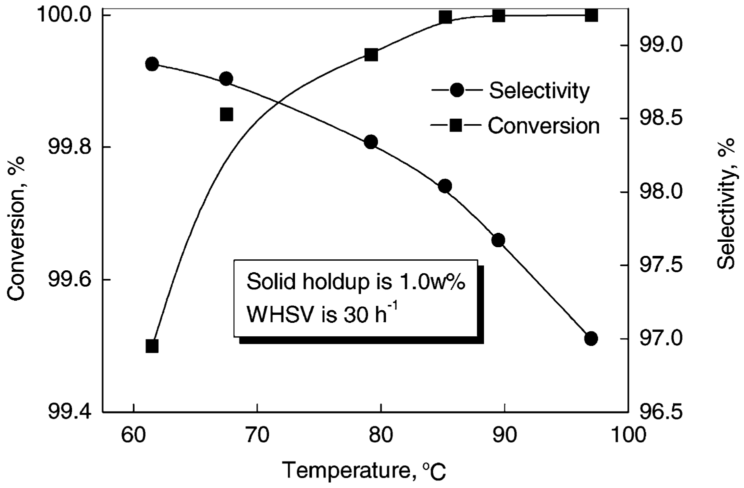

Fig. 6. Effect of temperature on conversion and selectivity.

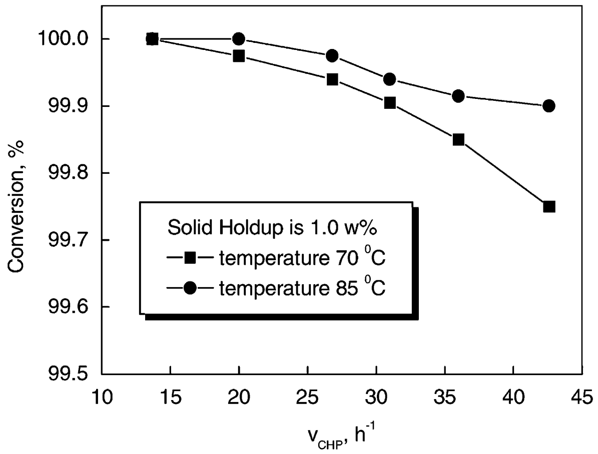

Fig. 7. Effect of WHSV of CHP on the reaction.

acetone, the reaction temperature can be easily controlled. Fig. 9 shows the correlation of the reaction temperature and the concentration of acetone in the feed stream. It is obvious that the actual acetone concentration in the reactor is not equal to the feed concentration. However, the temperature can be controlled by adjusting the proportion of acetone in the feed without knowing its concentration in the reactor. In addition, it can be seen from Fig. 9 that the WHSV has almost no effect on the reaction temperature, i.e., the reaction temperature depends only on the concentration of acetone. To obtain selectivity that is as high as possible, the reaction temperature should be controlled to be as low as possible, which needs more extra acetone to be added into the reactor. However, this will increase the solvation effect and results in the resins falling to pieces easily as discussed above. Furthermore, the extra acetone also will exacerbate the load of the condensation system. Therefore, based on the consideration of resin fragmentation and selectivity, 80 °C is an optimum reaction temperature for the CHP decomposition

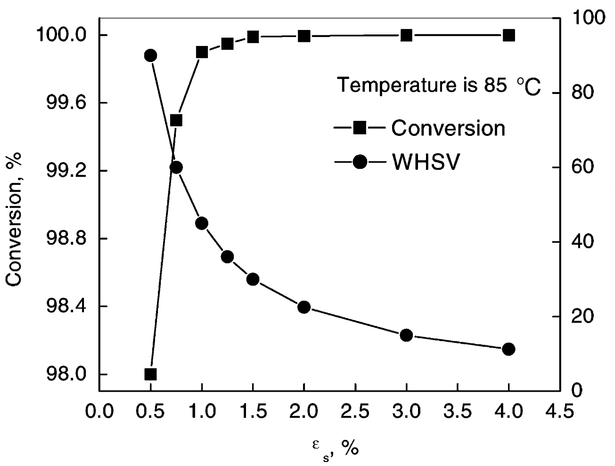

Fig. 8. Effect of solid holdup on the reaction.

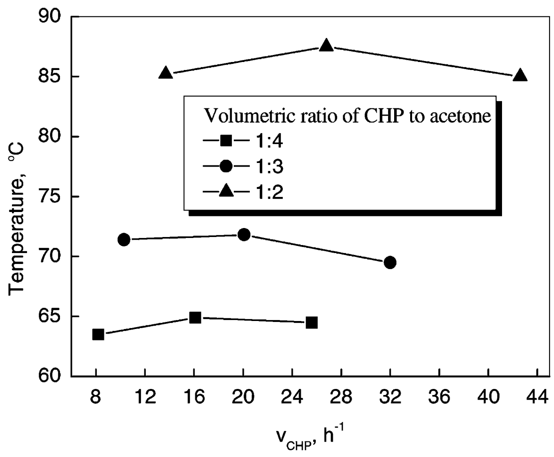

Fig. 9. Effect of the concentration of feeding on the reaction temperature.

Table 3
Experimental data for the intrinsic kinetics

Reaction time (s)	Concentration of CHP (%) at				
	61.5 °C	67.5 °C	78.5 °C	88.8 °C	97.0 °C
0	17.46	18.36	17.485	16.61	17.29
60	15.80	13.33	12.815	12.30	13.46
120	14.15	11.25	9.875	8.50	10.18
180	11.59	8.85	7.245	5.64	5.21
240	10.59	6.96	5.465	3.97	3.32
300	8.76	5.75	4.055	2.36	1.75
360	7.24	4.81	3.085	1.36	1.16
600	3.78	2.16	1.16	0.16	0.08

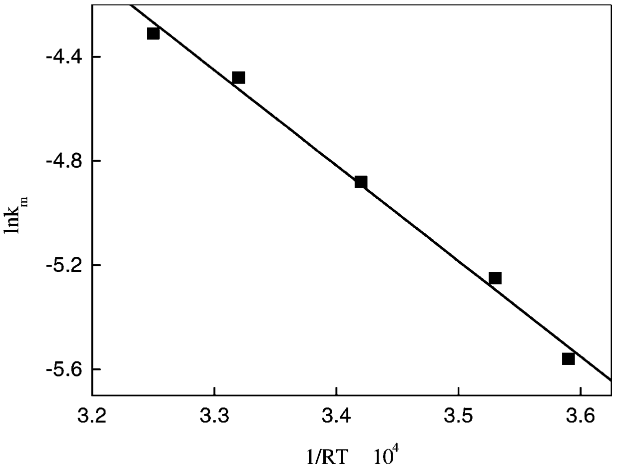

Fig. 10. Variation if $\ln k_\mathrm{m}$ with $1/RT$.

reaction. To realize this temperature, the volumetric ratio of CHP to acetone should be about 1:2.5 according to Fig. 9.

3.4. Rate controlling step of the process

In order to have a better understanding on this reaction in the TPCFB reactor, the rate controlling step of it is studied in this paper. The information of mass transfer and reaction is also important to the scale up of the reactor.

The errors of the kinetic rates from different experimental measurements are within 3–5%. By various experiments with different sizes of resin pellets and adjustable stirring speed, it is verified that the resistance of internal and external diffusion can be eliminated when the diameter of the resin pellets is less than 0.02 mm and the stirring speed is over 160 rpm.

Since the decomposition of CHP catalyzed by resins is a first-order reaction [16], the reaction rate can be expressed as

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -\frac{W}{V} k_\mathrm{m} x \tag{2}$$

The parameter k_m can be estimated by fitting the experimental data in Table 3 with the reaction rate equation (2) and the fitting formula for k_m shown as Eq. (3). It can be seen from Fig. 10 that the variation of $\ln k_\mathrm{m}$ with $1/RT$ is linear, and so the kinetic rate model is suitable:

$$k_\mathrm{m} = 1939.1 \exp\left(\frac{-36.43 \times 10^3\,\mathrm{J\,mol}}{RT}\right) \tag{3}$$

The effective factor η is 0.036 when the average diameter of the resin is 0.48 mm and the reaction temperature is 80 °C, and shows that the internal diffusion resistance is large and the intrinsic kinetic rate is $27.7(1/\eta)$ times as large as the internal diffusion rate of reactants in the catalyst pellets.

The mass transfer resistance of the solid–liquid film can be expressed as $1/k_{\mathrm{c,s}}a_\mathrm{p}$, in which $k_{\mathrm{c,s}}$ can be calculated by a suitable mass transfer correlation. From a comparison of some transfer correlations for solid–liquid films, it is found that Levich's correlation [17] is suitable to a liquid–solid reactor accompanied with reactions. The correlation equation is

$$Sh = \frac{k_{\mathrm{c,s}} d_\mathrm{p}}{D_\mathrm{Am}} = 1.01 \left(\frac{d_\mathrm{p}\,\Delta u}{D_\mathrm{Am}}\right)^{1/3} \tag{4}$$

where $D_\mathrm{AM} = 4.5 \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$ [16].

If the reactor is operated at steady state, the fluid dynamics can be described as

$$\tfrac{1}{6}\pi d_\mathrm{p}^3 \rho_\mathrm{P} g = \tfrac{1}{6}\pi d_\mathrm{p}^3 \rho_\mathrm{L} g + \tfrac{1}{4} \times \tfrac{1}{2} \times C_\mathrm{D} \pi d_\mathrm{p}^2 \rho_\mathrm{L}\,\Delta u^2 \tag{5}$$

$$\Delta u = \sqrt{\frac{4(\rho_\mathrm{p} - \rho_\mathrm{L}) g d_\mathrm{p}}{3\rho_\mathrm{L} C_\mathrm{D}}} \tag{6}$$

where

$$C_\mathrm{D} = \frac{18.5}{Re_\mathrm{p}^{0.6}}, \quad Re_\mathrm{p} = \frac{d_\mathrm{p}\,\Delta u\,\rho_\mathrm{L}}{\mu_\mathrm{L}}, \ 2 < Re_\mathrm{p} < 1000$$

When the reaction temperature is 80 °C, $\mu_\mathrm{L} = 0.623 \times 10^{-3}\,\mathrm{Pa\,s}$, $\rho_\mathrm{L} = 0.88 \times 10^3\,\mathrm{kg\,m^{-3}}$, $d_\mathrm{p} = 0.48 \times 10^{-3}\,\mathrm{mm}$, $\rho_\mathrm{p} = 1.18 \times 10^3\,\mathrm{kg\,m^{-3}}$, and Δu calculated from Eq. (6) is

$$\Delta u = 0.025\,\mathrm{m\,s^{-1}}$$

The Δu is obtained from above on the assumption that there are only liquid phase and solid phases but no gas phase in the reactor. In the decomposition of CHP, there is a large amount of acetone steam in the reactor and the slip velocity Δu between the solid and liquid phases should be larger than the value calculated by Eq. (6). To modify Δu, we introduce a coefficient of correction f and calculate $k_{\mathrm{c,s}}$ from Eq. (4) using $f\Delta u$ instead of Δu:

$$\frac{k_{\mathrm{c,s}} \times 4.8 \times 10^{-4}}{4.5 \times 10^{-10}} = 1.01 \times \left(\frac{4.8 \times 10^{-4} \times f \times 0.025}{4.5 \times 10^{-10}}\right)^{1/3},$$

$$k_{\mathrm{c,s}} = 2.83 \times 10^{-5} f^{1/3}\,\mathrm{m\,s^{-1}} \tag{7}$$

For a single pellet, the external mass transfer rate is

$$r_\mathrm{A} = k_{\mathrm{c,s}} A_\mathrm{p} (C_\mathrm{b} - C_\mathrm{s}) \tag{8}$$

Table 4
The effect of the auxiliary gas on the reaction system[a]

Auxiliary gas flow rate ($m^3 h^{-1}$)	Volume fraction ratio of the auxiliary gas (%)	Temperature (°C)	Concentration of CHP in the product (%)	Efficiency of the auxiliary gas (%)
0	0	69.5	0.95	0
0.012	0.7	65.9	0.57	40
0.054	3.2	64.1	0.10	98.5
0.114	6.7	61.5	0.10	98.5
0.168	9.9	60.1	0.18	81.1
0.228	13.4	57.8	0.27	71.6

[a] Solid content = 1.5%, WHSV of CHP = $40\,h^{-1}$.

and the reaction rate is

$$r_A = \eta W_p k_m C_s \tag{9}$$

For the steady state, Eqs. (8) and (9) are equal, i.e.

$$k_{c,s} A_p (C_b - C_s) = \eta W_p k_m C_s \tag{10}$$

$$r_A = \frac{1}{1/k_{c,s}A_p + 1/\eta W_p k_m} C_b \tag{11}$$

As the intrinsic rate is much greater than the internal diffusion rate, then

$$\frac{\text{Internal diffusion resistance}}{\text{External diffusion resistance}} \approx \frac{k_{c,s}A_p}{\eta W_p k_m} = 1.05 f^{1/3} \tag{12}$$

When $f = 1$, i.e. there is no gas in the reactor, the internal diffusion resistance is close to that of the external diffusion resistance. But for the three-phase reactor in this paper, there is a large amount of acetone steam, therefore, $f \gg 1$ and the rate controlling step of the reaction rate is internal diffusion.

In the hot model experiments, there is a noticeable phenomenon that acetone steam is formed intermittently in the main reactor. When there are a few bubbles formed at the bottom of the main reactor, the liquid bumps violently, which is due to overheating of the solution. In order to operate the process safely, we add a stream of auxiliary gas into the main reactor at the bottom of the main reactor. The auxiliary gas improves acetone evaporation and gets rid of the phenomenon that the liquid phase bumps due to overheat. The effects of the auxiliary gas on the mass transfer are listed in Table 4.

It can be seen from Table 4 that the concentration of CHP at the outlet of the reactor first decreases and then increases with the increase of the flow rate of the auxiliary gas. The reason is that the auxiliary gas can enhance the acetone evaporation rate as well as the mass transfer. While a little auxiliary gas is added into the main reactor, a large amount of acetone steam is formed. The slip velocity between solid and liquid increases and mass transfer coefficient increases, external diffusion resistance decreases, and the apparent rate of reaction increases. On the other hand, the evaporation of acetone also removes excessive heat which has accumulated when no acetone steam is formed, which decreases the temperature gradually and contributes mainly to a decrease of the reaction rate. Therefore, the auxiliary gas has two different effects on the concentration of CHP at the outlet of the reactor. To increase the reaction rate, the optimal amount of auxiliary gas is about 3.2 vol.% of the gross amount of the gases in the main reactor.

Furthermore, the reaction is carried out safely after the auxiliary gas is added in the reactor, $f > 1$, the external diffusion resistance decreases, the reaction rate increases, and the internal diffusion is rate controlling step of the process.

Compared to the traditional process catalyzed by sulfuric acid, the new process has following advantages. The substitution of sulfuric acid by sulfonic resins avoids erosion of the facilities. The production period between overhauls can be prolonged from 1 month to about 1 year. The products leaving the reactor contain no acid catalysts and the processes of neutralization and separation is not needed. It can effectively avoid the obstruction of plate openings by salts in the latter distillation system. Moreover, no phenol wastewater is generated because there is no neutralization. The optimum operation conditions are temperature 75–85 °C, preferable 80 °C, WHSV 30–40 h^{-1} and solid holdup 1.0–1.5 wt.%. Under the optimum operation conditions, the conversion and selectivity can reach to above 99 and 98%, respectively. Under the optimum operation conditions, the hot model experiment has been run continuously for 150 h and only less than 0.5 wt.% resin is lost by the operation.

4. Conclusions

A new CHP decomposition process using sulfonic resin as the catalyst and a novel TPCFB reactor is developed and studied. The conversion is as high and the selectivity is higher than the traditional process catalyzed by sulfuric acid.

A novel TPCFB reactor is proposed and used for the decomposition of CHP. This reactor can be viewed as a combination of a PFR and a CSTR. The liquid circulating rate had no effect on the RTD of the liquid phase in this reactor because of the existence of a large amount of gas in the main reactor. The RTD shows that the distribution of liquid in the main reactor is uniform, and so almost are the solid particles. The particular geometry and flow regime of the TPCFB reactor avoid resin fragmentation with high efficiency.

The decomposition of CHP catalyzed by TH-02 sulfonic resin is a first-order reaction. The effectiveness factor of the resin particles is 0.036 when the particle average diameter is 0.48 mm and the reaction temperature is 80 mm. Some auxiliary gas added to the main reactor can reduce the external diffusion resistance and increase the reaction rate, and also make the decomposition of CHP more uniform. However, its effect does not change much with further increasing of the auxiliary inert gas, especially when internal diffusion resistance is the rate-determining step. The optimal quantity of the auxiliary gas is about 3% of the quantity of acetone steam generated by the reaction heat.

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