

Loss Prevention and Waste Minimization with Cascade-Engineered Green Synthesis of Bisphenol-A from Cumene Hydroperoxide and Phenol using Heteropoly Acid-Supported Clay Catalysts

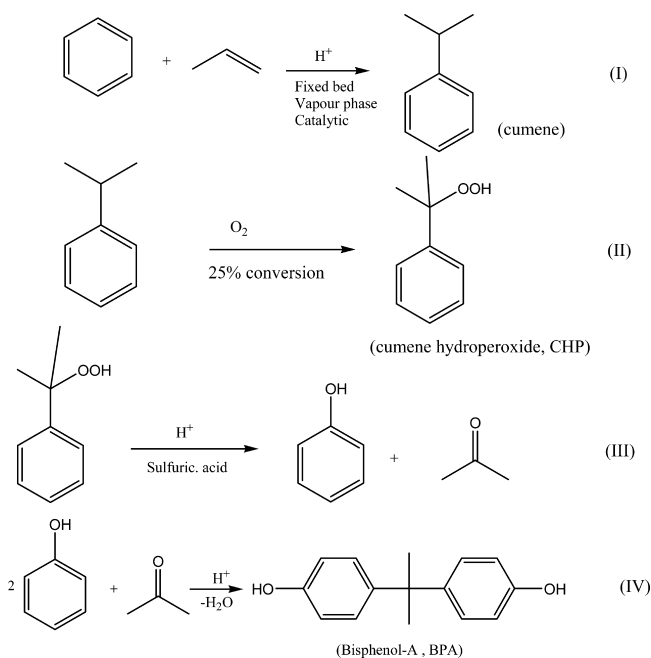
Ganapati D. Yadav* and Sanket S. Salgaonkar

Department of Chemical Engineering, University Institute of Chemical Technology, University of Mumbai, Matunga, Mumbai-400 019, India

Abstract:

Bisphenol-A (BPA), an important raw material for the synthesis of epoxy resins and other polymers, is conventionally synthesised by acid-catalysed condensation of phenol and acetone, which produces 28 known byproducts. This leads to heavy costs for purification of the final product and loss of raw material. Phenol itself is almost exclusively manufactured via the three-step Hock process which includes vapour-phase isopropylation of benzene to cumene, autoxidation of cumene to cumene hydroperoxide (CHP), and finally the highly exothermic liquid acid-catalysed cleavage of CHP to acetone and phenol. The second step in the Hock process produces around 35% w/w CHP, which is then concentrated to 80% w/w. There are inherent process hazards involved in the manufacture and/or concentration of CHP, leading to run-away situations and explosions. Cascading these two series reactions in a single pot using the same catalyst fits elegantly into the concept of waste minimization and results in a greener and cleaner environment with added economic incentives. Traditionally, single-pot synthesis overlooks the concepts of atom economy, reaction mass efficiency and the environmental impact factor which are of prime importance to any methodology desiring to be called “green synthesis”. In this work, a novel technique of BPA synthesis from CHP and phenol was engineered in a single pot by using 20% w/w dodecatungstophosphoric acid (DTP) supported on acidic clay (K-10) at 100 °C, wherein CHP produced in cumene itself and was used along with phenol to make BPA. The process is atom economical, producing water as a coproduct. In comparison with the traditional process of making BPA from phenol and acetone, there is 58% enhancement in yield and 33% enhancement in BPA selectivity. There is also a 28% improvement in reaction mass efficiency and 25% reduction in the environmental impact factor. Along with preserving the atom economy, the hazard involved in the concentration and handling of CHP, which has resulted in numerous accidents in process industries, has been eliminated. In the current process CHP produced from cumene by the Hock process is used as such without separation, and this strategy avoids the hazards of concentration and costs of separation. Finally, a comprehensive parametric sensitivity was also done, and a Langmuir–Hinshelwood–Hougen–Watson (LHHW) model was developed to describe the reaction mechanism. The theoretical predictions were found to match the experimental data.

Scheme 1. Hock process of phenol manufacture (steps I–III) and BPA manufacture from phenol and acetone (step IV)



Introduction

Phenol, acetone, and bisphenol are very important chemicals, having their own market shares. Bisphenol-A (BPA) is an important precursor in polycarbonate and polyester carbonate resins, plastics industries and fire-retardant chemicals. It is produced by phenol condensation with acetone over an acid catalyst (Scheme 1, step IV) and it can produce up to 28 byproducts leading to cumbersome separation processes for achieving resin-grade purity of BPA.¹ Phenol is almost exclusively produced by the three-step Hock process¹ (also called the cumene peroxidation method; Scheme 1, steps I–III). In the first step, benzene and propylene are reacted in a fixed bed of a suitable solid acid catalyst to yield cumene, which is purified and oxidized in the second step with oxygen to generate cumene hydroperoxide (CHP). CHP is then isolated and decomposed in the third step with sulfuric acid to obtain phenol along with equimolar quantities of acetone. Step I necessitates the use of a large quantity of benzene (to avoid dialkylation) much of which must be recovered and reused. As the main

* Corresponding author. Telephone: 91-22-2410 2121, 2414 5616. Fax: 91-22-2410 2121, 2414 5614. E-mail: gdyadav@yahoo.com, gdyadav@udct.org.

(1) *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH: Weinheim, Germany, 2002.

product peroxide produced in step II is an explosive, conversion of the cumene is restricted to ~25% in order to keep the concentration of CHP low. This is the most hazardous step, and several accidents have been reported.² Step II produces around 35% w/w CHP, which is then concentrated to 80% w/w in order to produce phenol and acetone at commercially competitive prices. There are inherent process hazards involved in the manufacture and/or concentration of CHP, leading to runaway situations and explosions.² The unreacted cumene must consequently be recovered and reused. In step III, CHP is decomposed by sulfuric acid to yield phenol and acetone; however, there are other byproducts which need to be controlled.^{3–6} Various Brønsted and Lewis acids are used to decompose CHP in a temperature range of 0–75 °C to yield phenol and acetone with some dicumyl peroxide (DCP), but sulfuric acid is still preferred to get high yields of phenol. DCP in turn gets converted into a mixture of α -methyl styrene (AMS), phenol, and acetone.^{7–10} The strength of the catalyst as well as reaction temperature greatly influences selectivity of the products during the decomposition of CHP.^{11–14}

Decomposition of CHP to acetone and phenol has been successfully demonstrated by numerous research groups, with a variety of catalysts like metals, clays, and resins. Huang et al.¹⁵ used a novel three-phase circulating fluidized bed reactor with sulfonic resins to get 100% conversion and selectivity. Selvin et al.¹⁶ tested acid-activated montmorillonite K-10 at 30–60 °C. Yadav and Asthana¹⁷ studied the decomposition of CHP at 40 °C on various K-10 clay-supported heteropoly acids (HPA) such as dodecatungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$; DTP), $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (Cs-DTP), and ZnCl_2 . The efficacy of 20% w/w DTP/K-10, 20% w/w $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ /K-10 and 20% w/w ZnCl_2 /K-10 was evaluated. Amongst these catalysts, 20% w/w DTP/K-10 offered 70% conversion of CHP. Use of Amberlyst-15 is also reported for this reaction.¹⁸

The condensation of phenol with acetone (Scheme 1, step IV) requires an acid catalyst similar to those reported for CHP

decomposition. Our laboratory reported for the first time 20% w/w DTP/K-10 as a novel catalyst for the reaction of acetone with phenol, and it proved to be better than ion-exchange catalysts at 125 °C with 23% conversion of acetone and 60% selectivity of BPA.¹⁹ Nowinska and Kaleta²⁰ modified MCM-41 with DTP and dodecatungstosilicic acid and obtained around 30% conversion of phenol with 60% selectivity of BPA at 160 °C in both cases. Selectivity of 90% was reported with sulfonic acid-functionalised MCM-41^{21a} with a 30% conversion of phenol at 70 °C in 24 h. Mesoporous MCM-41 and -48 silicas anchored with sulfonic acid ($-\text{SO}_3\text{H}$) groups via postsynthesis modification are very effective for the synthesis of bisphenol-A by liquid-phase condensation of phenol with acetone.^{21b} Higher amounts of thiol groups can be incorporated in MCM-48 silicas, presumably due to the presence of larger numbers of surface silanol groups. The use of cation-exchange resins along with a free mercaptan promoter²² has also been reported. Decomposition of organic hydroperoxides in the presence of a particulate catalyst containing highly fluorinated polymer having sulfonic acid groups has also been patented.²³

A number of catalysts synthesised in this laboratory have already been investigated independently²⁴ for both CHP decomposition¹⁷ and BPA synthesis.¹⁹ Out of these catalysts, 20% w/w DTP/K-10 was very efficient in numerous industrially important reactions²² and was found to catalyse efficiently both of these reactions.

In the current work, we report a cascade-engineered greener and safer synthesis of BPA from CHP and phenol using 20% w/w DTP as a catalyst.

Experimental Section

Chemicals. All the chemicals were A.R. grade and procured from reputed firms. Dodecatungstophosphoric acid and phenol (M/s s.d. Fine Chem. Ltd., Mumbai, India), CHP (Lancaster), cumene (M/s Schenectady Herdillia Chemicals, Mumbai), Montmorillonite-K-10 (Fluka, Germany).

Experimental Setup. The synthesis of BPA with 20% w/w DTP/K-10 catalyst was conducted in a 100 mL Parr autoclave fully equipped with a four-blade pitched turbine agitator, and temperature and speed controller. The temperature of the reactor could be maintained within ± 1 °C.

Reaction Procedure. Three types of experiments were conducted to decide a cascading strategy.

- (i) CHP decomposition
- (ii) Acetone self-condensation
- (iii) CHP and phenol reaction

The reaction mixture consisted of known amounts of CHP, cumene (as solvent), and phenol, making the liquid phase volume reach 50 mL. The catalyst was fed into the reactor, and stirring started after the reaction mixture reached the desired

- (2) <http://www.eng.miami.edu/~shyu/Paper/2001/safety.pdf>. (b) http://www.eng.miami.edu/~shyu/Paper/2002/DSC_TAM.pdf. (c) Luo, K. M.; Chang, J. G.; Lin, S. H.; Chang, C. T.; Yeh, T. F.; Hu, K. H.; Kao, C. S. *J. Loss Prev. Process Ind.* **2001**, *14*, 229–239. (d) Wang, Y. W.; Shu, C. M.; Duh, Y. S.; Kao, C. S. *Ind. Eng. Chem. Res.* **2001**, *40*, 1125–1132.
- (3) Kirk-Othmer *Encyclopedia of Chemical Technology*, 4th ed.; Wiley-Interscience: New York, 1996; Vol. 18, pp 592–602.
- (4) Hock, H.; Lang, S. *Ber.* **1944**, *77B*, 257.
- (5) Kohn, P.M.; L.; Bolton, J.; Cottrell, R.; S.; McQueen, S.; Ushio, S. *Chem. Eng. (U.S.A.)* **1979**, *86*, 62–64.
- (6) Lyavinets, A. S. *Russ. J. Gen. Chem.* **2000**, *70*, 563–567.
- (7) Barton, D. H. R.; Delanghe, N. C. *Tetrahedron Lett.* **1997**, *38*, 6351.
- (8) Seibold, F. H.; Waughan, W. E. *J. Am. Chem. Soc.* **1953**, *75*, 3790.
- (9) Karasch, M. S.; Fono, A.; Nudenberg, W. J. *Org. Chem.* **1950**, *15*, 748.
- (10) Vodnar, J.; Fejes, P.; Varga, K.; Berger, F. *Appl. Catal., A* **1995**, *122*, 33.
- (11) Weissmermel, K.; Arpe, H. J. *Industrial Organic Chemistry*, 2nd ed.; VCH: Weinheim, 1993; p 351.
- (12) U.S. Patent 5,786,522, 1998.
- (13) Weber, M.; Tanger, U.; Kleinloh, W. PCT Int. Appl. WO 0130732, 2001. *Chem. Abstr.* **2001**, *134*, 341824.
- (14) Selvin, R.; Rajarajeswari, G. R.; Roselin, L. S.; Sadasivam, V.; Sivasankar, B.; Rengaraj, K. *Appl. Catal., A* **2001**, *219*, 125–129.
- (15) Huang, D.; Han, M.; Wang, J.; Jin, Y. *Chem. Eng. J.* **2002**, *88*, 215–223.
- (16) Selvin, R.; Rajarajeswari, G. R.; Roselin, L. S.; Sadasivam, V.; Sivasankar, B.; Rengaraj, K. *Appl. Catal., A* **2001**, *219*, 125–129.
- (17) Yadav, G. D.; Asthana, N. S. *Appl. Catal., A* **2003**, *244*, 341–357.
- (18) Iditoui, C.; Segal, E.; Gates, B. C. *J. Catal.* **1978**, *54*, 442–445.

- (19) Yadav, G. D.; Kirthivasan, N. *Appl. Catal., A* **1997**, *154*, 29.
- (20) Nowinska, K.; Kaleta, W. *Appl. Catal. A* **2000**, *203*, 91.
- (21) (a) Das, D.; Lee, J.; Cheng, S. *Chem. Commun.* **2001**, 2178–2179. (b) Das, D.; Lee, J.; Cheng, S. *J. Catal.* **2004**, *223*, 152–160.
- (22) (a) U.S. Patent 2003/212299, 2003. (b) U.S. Patent 5,786,522, 1998.
- (23) (a) U.S. Patent 6,586,640, 2003. (b) WO 03/002499 A1, 2003.
- (24) (a) Yadav, G. D.; Kirthivasan, N. *J. Chem. Soc., Chem. Commun.* **1995**, 203–204. (b) Yadav, G. D.; Doshi, N. S. *J. Mol. Catal. A: Chem.* **2003**, *194*, 195–209. (c) Yadav, G. D.; Doshi, N. S. *Green Chem.* **2002**, *4*, 528–540. (d) Yadav, G. D.; Doshi, N. S. *Org. Process. Res. Dev.* **2002**, *6*, 263–272.

temperature. Temperature was maintained within ± 1 °C of the set value, and stirring was started at a known speed of agitation. The initial sample was withdrawn at the start of the experiment.

A typical experiment consisted of 50 mL of reaction mixture in cumene containing 0.02 mol CHP, 0.1 mol phenol, and 1.25 g of 20% w/w DTP/K-10 catalyst.

Method of Analysis. Clear samples, free from solid particles, were analysed on a Chemito model 8510 GC equipped with a 10% SE-30 column (3.175 mm dia $\times$ 4 m length).

Results and Discussion

Catalysts Characterisation. DTP/K-10 (20% w/w) is completely characterised by XRD, BET surface area, FTIR, and SEM, and the details were published earlier by us.¹⁷ Only a few salient features are reported here.

A comparison of the XRD diffractogram of DTP/K-10 and K-10 indicated that in the impregnation process, the clay had lost some of its crystallinity compared to K-10. The surface areas of the K-10 and DTP/K-10 were measured by the BET method using the nitrogen adsorption technique as 230 m²/g and 107 m²/g, respectively. The surface area of DTP/K-10 is nearly 50% lower than that of K-10 probably due to blockage of the smaller pores by the HPA crystals. The active species are held in a few junctions of such dimensions from where the access to smaller pores is denied, thereby leading to reduction in accessible surface area. The pore volume and pore diameter of DTP/K-10 was 0.36 cm³/g and 64 Å, respectively while the particle size was found to be 80–100 μ m.

The cation exchange capacities (CEC) of the catalysts, determined photometrically by methylene blue adsorption, were found to be 35 and 39 mequiv/100 g for K-10 and DTP/K-10, respectively. The CEC of DTP/K-10 exhibits a slightly higher value than K-10 due to some additional surface protons which come by way of heteropoly acid impregnation which may play a role on account of easy availability for the exchange reaction.

Results and Discussion

In order to arrive at a cascading strategy that would eliminate process hazard and make the BPA process greener three different types of experiments were conducted.

CHP Decomposition in Cumene and Formation of BPA. Yadav and Asthana²¹ had studied CHP decomposition over 20% w/w DTP/K-10 catalyst at 40 °C to get phenol and acetone as coproducts with 100% selectivity. There was no formation of BPA in the process. It was also observed that there was no byproduct formation from 30 to 50 °C. The reaction of phenol and acetone formed in situ can lead to formation of BPA as well as self-condensation of acetone, depending on temperature, catalyst loading, and acetone concentration. The formation of byproduct in the BPA synthesis originates from the acetone self-condensation reaction to mesityl oxide,¹⁹ resulting in a conversion of 23% and selectivity of 60% (acetone: 0.091 mol, phenol: 0.451 mol, catalyst: 1.25 g, temperature: 135 °C, mole ratio acetone/phenol = 1:5).

Scheme 2 was thus formulated to make BPA from CHP at higher temperatures. Step a leads to phenol and acetone. Phenol and acetone can react to produce BPA (step b). Further CHP also reacts with phenol to give BPA (step c). Thus, the overall

reaction in Scheme 2 shows that 3 mol CHP reacts with 1 mol phenol to produce 2 mol BPA, 1 mol acetone, and 2 mol water. All three steps are strong functions of temperature and concentrations. Therefore, Scheme 3 was envisaged, according to which, if an excess of phenol is taken, there is no formation of acetone, and thus, all byproducts arising out of acetone condensation could be eliminated. Further, it was also necessary to determine the maximum concentration of acetone, if produced in situ, which could be tolerated in the process. Thus, self-condensation of acetone was studied.

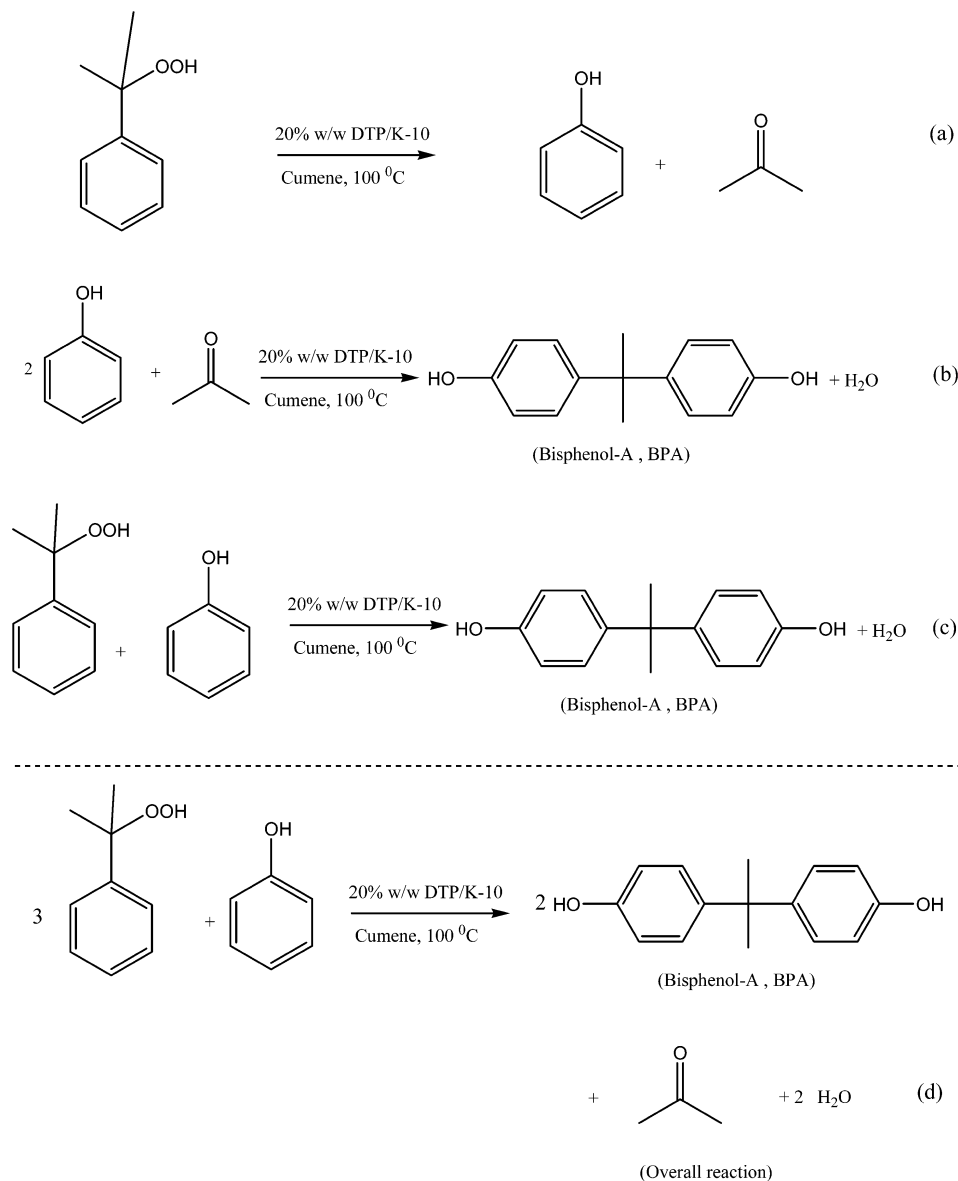
Acetone Condensation Reaction. Synthesis of BPA from phenol and acetone (Scheme 1, step IV) in industrial processes results in as many as 28 byproducts, and all initiated are by the self-condensation of acetone to diacetone alcohol and mesityl oxide. To suppress these side reactions, it is necessary to employ a low concentration of acetone and also a low temperature. In the industrial processes, this is achieved by maintaining a phenol to acetone molar ratio of 10:1. However, Yadav and Kirthivasan¹⁹ observed that the conversions at a mole ratio of 10:1 were only marginally better than those at a ratio of 5:1. Ortho and para isomers of BPA, another common impurity, actually function as colour stabilisers in the polycarbonate resins prepared from BPA and could be thus preferred in appropriate concentrations.¹⁹

Thus, acetone was taken in cumene as solvent, and its self-condensation was studied at 100 °C with 20% w/w DTP/K-10. Independent experiments were done with CHP and phenol to find that 3% of acetone was also formed; when 100% CHP reacted, there was 100% selectivity towards acetone. Therefore, self-condensation of acetone was studied at 3% acetone in cumene, and it was observed that there was no conversion of acetone. Even under solventless reaction conditions (i.e. containing only acetone) merely 9% conversion was achieved. This observation confirms that acetone self-condensation and subsequent byproduct formation could be effectively suppressed by maintaining low temperatures ($\sim$ 100 °C) and low concentrations of CHP.

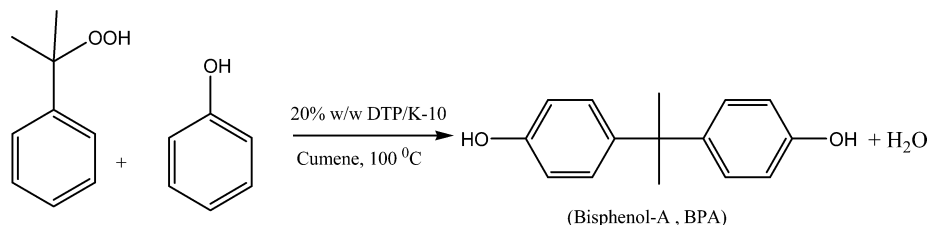
CHP Reaction with Phenol. CHP decomposition is strongly exothermic ($\Delta H_R = -252$ kJ/mol), and its thermal decomposition is facilitated by the presence by acids, bases, metal ions, and other impurities. The onset temperature of thermal decomposition with FeCl₃ present as an impurity is as low as 40 °C, leading to phenol, methane, acetophenone, 2-phenyl-2-propanol, and α -methyl styrene as the decomposition products.^{1,2} Complete selectivity to acetone and phenol is witnessed at lower temperatures, whereas byproducts such as dimethyl carbinol, cumyl phenyl, and tar are predominant at high temperatures.² In order to dissipate the heat of reaction and prevent runaway conditions, CHP must be maintained at low concentrations.

Thus, a cascade engineering scheme of CHP to BPA was devised with CHP and phenol using 20% w/w DTP/K-10 (Scheme 3). The comparison of the proposed strategy was to be evaluated with reference to the safety issues, atom economy, conversion, yield, selectivity, number of byproducts formed, reaction mass efficiency, environmental impact factor, and waste generated. Scheme 2 shows that in the cascade-engineered approach, three reactions are likely to take place, and the sequence in which they occur is very important to decide the

Scheme 2. Analysis of reaction mechanism and product profile for BPA production starting from CHP alone



Scheme 3. Cascade-engineered synthesis of BPA from CHP and phenol



overall product distribution. If the rate of reaction c is much faster, addition of phenol will help. Such a possibility needed experimental proof. Further, the temperature of the reaction was another important parameter.

Since the current investigation covered a temperature range of 50–100 °C, the CHP decomposition was expected to result in the formation of byproduct and thus reduce the selectivity towards acetone and phenol as reported in the literature. Therefore, CHP decomposition was carried out at 100 °C at a low concentration of 0.4 mmol/cm³ CHP in cumene. CHP conversion of 100% with a selectivity of 90% towards acetone

was realised (Figure 1). Increasing the temperature to 120 °C reduced the acetone selectivity further to 30%. In both cases, no BPA was formed even after 4 h of reaction time. This is due to high mole ratio of phenol in the reactor to acetone generated in situ. Since the acetone concentration is lower, all series and parallel reactions of acetone such as aldol condensation are suppressed. The isolation of BPA was done as discussed in our earlier work.¹⁹

Table 1 lists the results of the CHP decomposition and condensation of acetone with phenol conducted independently versus the cascade engineering route. As is apparent from this

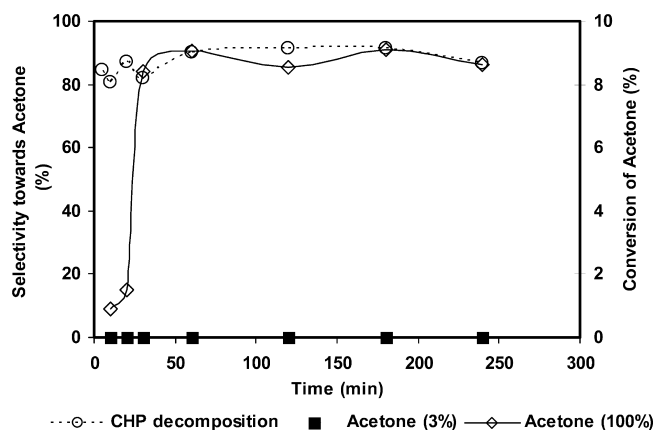


Figure 1. Independent reactions of CHP and acetone over DTP/K-10. Reaction conditions: (i) CHP: 0.4 mmol/cm³ CHP; solvent cumene; total volume: 50 mL; temperature: 100 °C; speed of agitation: 1000 rpm; catalyst loading: 0.025 g/cm³. (ii) Acetone (3%): 0.4 mmol/cm³ acetone in cumene as solvent; total volume: 50 mL; temperature: 100 °C; speed of agitation: 1000 rpm; catalyst loading: 0.025 g/cm³. (iii) Acetone (100%): 50 mL acetone; temperature: 100 °C; speed of agitation: 1000 rpm; catalyst loading: 0.025 g/cm³.

comparison, the sole drawback with CHP decomposition to produce phenol and acetone in the conventional process is the hazard involved in the concentration and/or separation of CHP from cumene. This is totally eliminated in the cascade-engineered route at the expense of a 5% reduction in selectivity towards acetone, which is acceptable as compared to the hazards involved in the runaway reaction. As regards the synthesis of BPA, the cascade-engineered route reduces the byproduct formation, thus enhancing the yield by 25% and reducing the waste generated by a quarter.

The waste reduction and enhanced safety of the cascade-engineered synthesis was supplemented by the parametric sensitivity analysis of this system. Thus, further experiments were systematically planned to calculate the effect of various operating parameters on the conversion of CHP and the yield of BPA.

Reaction Kinetics and Mathematical Modeling. A mathematical model facilitates reactor selection and design strategies, parametric sensitivity, and scale-up studies. Thus, a detailed

model was first developed so that further experiments could be planned accordingly.

Development of a Mechanistic Model. CHP decomposition to acetone and phenol can be written as:



High temperature leads to the formation of byproducts such as methanol (E) and acetophenone (F), 2-phenyl-2-propanol (G) and α -methyl styrene (H) as given below:



Assuming the rate of decomposition of CHP is rate controlling, the following rate equation is obtained:

$$-\frac{dC_C}{dt} = (k_{SR1} + k_{SR2} + k_{SR3} + k_{SR4})C_{CS} \quad (6)$$

Gates²⁶ has modeled the reaction of phenol and acetone by a third-order kinetic model with adsorption of acetone and phenol on two different sites. Yadav and Kirthivasan¹⁹ developed an extensive mechanism in which they proposed that a bimolecular reaction of acetone with phenol resulted in an *p*-isopropenylphenol, which subsequently reacts with a mole of phenol to form BPA. A number of possible rate-determining steps such as formation of *p*-isopropenylphenol, its reaction with phenol, adsorption of acetone were investigated. They concluded that the rate-determining step is the formation of *p*-isopropenylphenol from chemisorbed acetone and phenol from the liquid

Table 1. Advantages of cascade engineering

	decomposition of CHP ⁵	synthesis of BPA ⁷	cascade-engineered synthesis ^a
safety issues	inherent safety hazards in concentration and/or separation of CHP	safe process	safe process
temp (°C)	40–60	120–150	50–100
no. of byproducts	0	28	3 (thermal decomposition of CHP) + 1 (<i>o,p</i> -BPA)
conversion	75% CHP	30% acetone	100% CHP; 60% acetone
selectivity	100% acetone	60% BPA	80% BPA
atom economy ^b (%)	100	92.68	92.68
yield ^c (%)	100	18	46.48
reaction mass efficiency ^d	100	13.28	17
environmental impact factor ^e	0	6.5	4.86

^a Reaction conditions: 0.4 mmol cm⁻³ CHP, 2.0 mmol cm⁻³ phenol; solvent cumene; total vol: 50 mL; temperature: 100 °C; speed of agitation: 1000 rpm; catalyst loading: 0.025 g cm⁻³. ^b Atom economy = mol wt of desired product/total mol wt of products formed. ^c Yield = moles of desired product formed per mole of reactant. ^d Reaction mass efficiency = mass of desired product formed/total mass of reactants used. ^e Environmental impact factor = total mol wt of waste products/mol wt of desired product.

phase within pores according to Eley–Rideal mechanism. Thus, it is assumed here that acetone reacts with phenol to form an *p*-isopropenylphenol (I), which further reacts with a mole of phenol to form BPA and water.



Accounting for the formation of *o,p*-BPA (D),



Thus, the rate of reaction of acetone can be expressed as:

$$-\frac{dC_A}{dt} = -k_{\text{SR}_1}C_{\text{CS}} + k_{\text{SR}_5}C_{\text{AS}}C_{\text{P}} \quad (10)$$

Assuming that the rate of reaction of *p*-isopropenylphenol is fast, at steady state,

$$-\frac{dC_{\text{IS}}}{dt} = k_{\text{SR}_5}C_{\text{AS}}C_{\text{P}} - (k_{\text{SR}_6} + k_{\text{SR}_7})C_{\text{IS}}C_{\text{P}} = 0 \quad (11)$$

$$C_{\text{IS}} = \frac{k_{\text{SR}_5}}{(k_{\text{SR}_6} + k_{\text{SR}_7})}C_{\text{AS}} \quad (12)$$

Finally the rate of formation of BPA is given by:

$$\frac{dC_{\text{BS}}}{dt} = k_{\text{SR}_6}C_{\text{IS}}C_{\text{P}} \quad (13)$$

$$\frac{dC_{\text{BS}}}{dt} = \frac{k_{\text{SR}_6}k_{\text{SR}_5}}{k_{\text{SR}_6} + k_{\text{SR}_7}}C_{\text{AS}}C_{\text{P}} \quad (14)$$

The total site concentration is given by:

$$C_{\text{T}} = C_{\text{S}} + C_{\text{CS}} + C_{\text{AS}} + C_{\text{FS}} + C_{\text{GS}} + C_{\text{HS}} + C_{\text{IS}} + C_{\text{BS}} + C_{\text{DS}}$$

Writing equations for the desorption of all species:

$$C_{\text{AS}} = K_{\text{A}}C_{\text{A}} \quad (15)$$

$$C_{\text{BS}} = K_{\text{B}}C_{\text{B}} \quad (16)$$

$$C_{\text{CS}} = K_{\text{C}}C_{\text{C}} \quad (17)$$

$$C_{\text{DS}} = K_{\text{D}}C_{\text{D}} \quad (18)$$

$$C_{\text{FS}} = K_{\text{F}}C_{\text{F}} \quad (19)$$

$$C_{\text{GS}} = K_{\text{G}}C_{\text{G}} \quad (20)$$

$$C_{\text{HS}} = K_{\text{H}}C_{\text{H}} \quad (21)$$

$$C_{\text{IS}} = K_{\text{I}}C_{\text{I}} \quad (22)$$

Substituting eqs 16–23 in eq 15, the following is obtained:

$$C_{\text{S}} = \frac{C_{\text{T}}}{1 + K_{\text{C}}C_{\text{C}} + K_{\text{A}}C_{\text{A}} + K_{\text{F}}C_{\text{F}} + K_{\text{G}}C_{\text{G}} + K_{\text{H}}C_{\text{H}} + K_{\text{I}}C_{\text{I}} + K_{\text{B}}C_{\text{B}} + K_{\text{D}}C_{\text{D}}} \quad (23)$$

Also $C_{\text{T}} \propto w$, the catalyst loading, so $C_{\text{T}} = K_{\text{T}}w$. Thus, the rate of decomposition of CHP can now be written as:

$$-\frac{dC_{\text{C}}}{dt} = \frac{(k_{\text{SR}_1} + k_{\text{SR}_2} + k_{\text{SR}_3} + k_{\text{SR}_4})K_{\text{T}}wC_{\text{C}}}{1 + K_{\text{C}}C_{\text{C}} + K_{\text{A}}C_{\text{A}} + K_{\text{F}}C_{\text{F}} + K_{\text{G}}C_{\text{G}} + K_{\text{H}}C_{\text{H}} + K_{\text{I}}C_{\text{I}} + K_{\text{B}}C_{\text{B}} + K_{\text{D}}C_{\text{D}}} \quad (24)$$

Similarly the rate expressions for acetone and BPA are as given below:

$$-\frac{dC_{\text{A}}}{dt} = \frac{K_{\text{T}}w(-k_{\text{SR}_1}K_{\text{C}}C_{\text{C}} + k_{\text{SR}_5}K_{\text{A}}C_{\text{A}}C_{\text{P}})}{1 + K_{\text{C}}C_{\text{C}} + K_{\text{A}}C_{\text{A}} + K_{\text{F}}C_{\text{F}} + K_{\text{G}}C_{\text{G}} + K_{\text{H}}C_{\text{H}} + K_{\text{I}}C_{\text{I}} + K_{\text{B}}C_{\text{B}} + K_{\text{D}}C_{\text{D}}} \quad (25)$$

$$-\frac{dC_{\text{B}}}{dt} = \frac{K_{\text{T}}wk_{\text{SR}_6}k_{\text{SR}_5}K_{\text{A}}C_{\text{A}}C_{\text{P}}}{(k_{\text{SR}_6} + k_{\text{SR}_7})\left(1 + \sum_i K_i C_i\right)} \quad (26)$$

If adsorption of all species is weak, i.e. $1 \gg \sum K_i C_i$, integration of eq 25 gives the concentration profile of CHP.

$$C_{\text{C}} = k_1 K_{\text{T}}wC_{\text{C}_0} e^{-k_1 K_{\text{T}}wt} \quad (27)$$

where

$$k_1 = (k_{\text{SR}_1} + k_{\text{SR}_2} + k_{\text{SR}_3} + k_{\text{SR}_4})$$

This is similar to the first order model validated by Selvin et al.¹⁴ and the Langmuir–Hinshelwood–Hougen–Watson (LHHW) model developed by Yadav and Asthana,¹⁷ assuming weak adsorption of all species on the catalyst sites.

Since phenol was employed in 5 molar excess over CHP (mole ratio, $M = 5$), it can be assumed that it remains constant at $C_{\text{P}} = MC_{\text{C}_0}$.

Substituting equation 28 and incorporating these simplifications, eqs 26 and 27 reduce to

$$-\frac{dC_A}{dt} = -k_2 e^{-k_1 K_T w t} + k_3 C_A \quad (28)$$

where

$$k_2 = K_T^2 k_{SR_1} K_C k_1 w^2 C_{C_0}$$

and

$$k_3 = K_T k_{SR_5} K_A w M C_{C_0}$$

$$-\frac{dC_B}{dt} = k_4 C_A \quad (29)$$

where

$$k_4 = \frac{K_T k_{SR_6} k_{SR_5} K_A w M C_{C_0}}{(k_{SR_6} + k_{SR_7})} \quad (30)$$

If acetone concentration is measured as a function of time, the constants can be evaluated. Furthermore, all other constants can also be elucidated from this equation, and thus the yield of BPA can be simulated. However, to estimate rate constants and validate the mathematical model, all mass transfer resistances need to be eliminated. Thus, further experiments were planned to eliminate these resistances.

Effect of Speed of Agitation. In order to ascertain the influence of external resistance to mass transfer of the reactants to the catalyst surface, the speed of agitation was varied over range of 800–1200 rpm. The conversion of acetone (defined with reference to the maximum concentration of acetone at 100% conversion of CHP with 100% selectivity towards acetone) at different intervals of time is shown in Figure 2. It was observed that the speed of agitation had no effect of conversion beyond 1000 rpm, and thus there was no limitation of external mass transfer of reactants from bulk liquid phase to the outer surface of the catalyst at and beyond this speed. Further experiments were conducted at 1000 rpm.

Effect of Catalyst Loading. In the absence of external mass transfer resistance, the rate of reaction is directly proportional to catalyst loading based on the entire liquid-phase volume. The catalyst loading was varied over a range of 0.01–0.03 g/cm³. Figure 3 shows the effect of catalyst loading on the conversion of phenol. The conversion increased with an increase in catalyst loading, which is due to the proportional increase in the number of active sites. However, beyond a catalyst loading of 0.025 g/cm³, there was no significant increase in the conversion since the number of sites was much more than the number of molecules, and hence all further experiments were carried out at this catalyst loading.

Proof of Absence of Intraparticle Resistance. Since the average particle size of 20% w/w DTP/K-10 was found to be in the range of 2–10 μm and the catalyst is amorphous in nature, it was not possible to study the effect of catalyst particle size on the rate of reaction. The average particle diameter of DTP/K-10 was 0.001 cm, and thus a theoretical calculation was done by using the Wiesz–Prater criterion to assess the influence of intraparticle diffusion resistance. According to the Wiesz–Prater criterion, the dimensionless parameter C_{WP} , which represents the ratio of the intrinsic reaction rate to intraparticle diffusion rate, can be evaluated from the observed rate of reaction, the particle radius (R_p), effective diffusivity of the

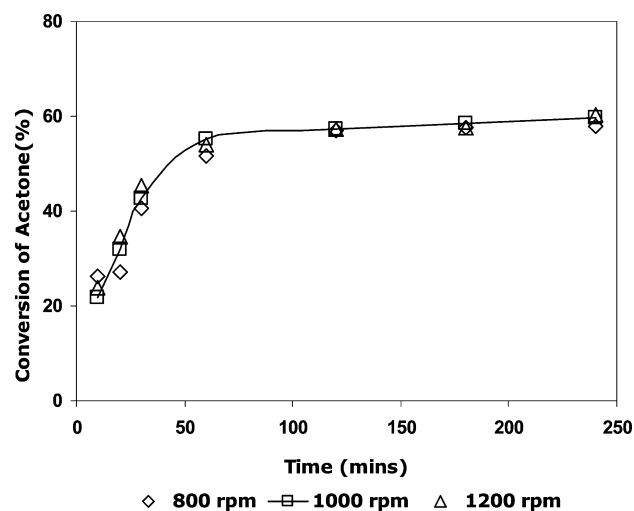
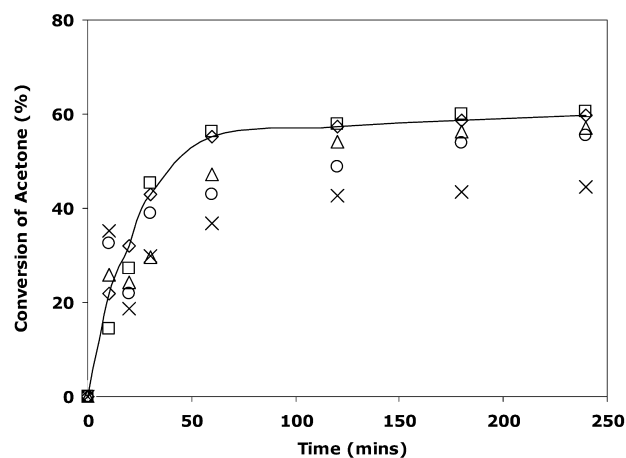


Figure 2. Effect of speed of agitation. Reaction conditions: mole ratio of CHP/phenol = 1:5; temperature: 100 °C; catalyst loading: 0.025 g/cm³.



× 0.01 g/cm³ ○ 0.0164 g/cm³ + 0.02 g/cm³ ◇ 0.025 g/cm³ □ 0.03 g/cm³

Figure 3. Effect of catalyst loading. Reaction conditions: mole ratio of CHP/phenol = 1:5; temperature: 100 °C; speed of agitation: 1000 rpm.

limiting reactant (D_e), and concentration of the reactant at the external surface of the particle. If $C_{WP} = -r_{obs} \rho_p R_p^2 / D_e [A_S] \gg 1$, then the reaction is limited by severe internal diffusional resistance. For the current reaction system, C_{WP} was calculated to 7.538×10^{-5} . Since this value is far less than 1, the reaction is intrinsically kinetically controlled.

Effect of Temperature. The effect of temperature was studied for the cascade-engineered reaction. The conversion increased substantially with increasing temperature. Figure 4 shows the effect of temperature on conversion of acetone. The conversion profile reached equilibrium within an hour. The maximum conversion was obtained at 100 °C; BPA yield of 80% was obtained at 60% acetone conversion. These results are much better than those reported in literature with ion-exchange resins⁸ and comparable with modified MCM-41.⁹ The high yield is a result of in situ formation and reaction of acetone which is similar to the semibatch mode of addition of acetone, which is known to enhance BPA yields.¹⁰ The initial fluctuations in the conversion profiles is due to the series reactions. The yield of BPA is nearly linear at all temperatures and was highest at 100 °C (Figure 5). The conversions and yield are much more than reported previously by us⁷ at 135 °C. The improvement

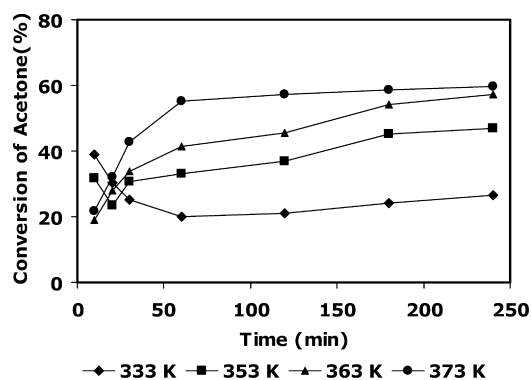


Figure 4. Effect of temperature on conversion of acetone. Reaction conditions: mole ratio of CHP/phenol = 1:5; speed of agitation: 1000 rpm; catalyst loading: 0.025 g/cm³.

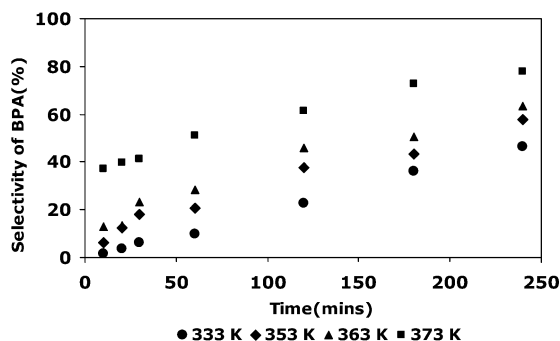


Figure 5. Effect of temperature on selectivity of BPA. Reaction conditions: mole ratio of CHP/phenol = 1:5; speed of agitation: 1000 rpm; catalyst loading: 0.025 g/cm³.

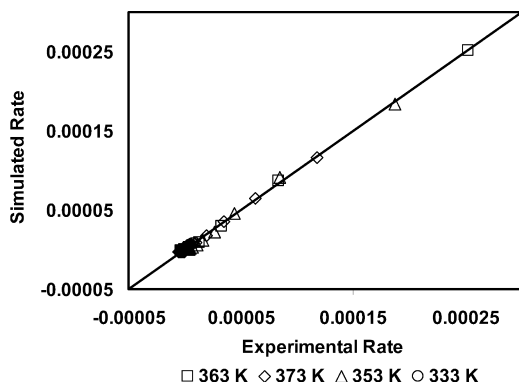


Figure 6. Parity plot of simulated rate vs experimental rate of acetone.

in BPA yield is attributed to the low temperature and low concentrations used wherein side reactions of acetone are suppressed.

Model Validation and Simulation Studies. The intrinsic kinetic data obtained at various temperatures were used for elucidation of rate constants. From the concentration profiles of acetone, the rate of reaction was obtained. These data were used to fit eq 29. Polymath 5.1 was used for this purpose with Levenberg–Marquardt algorithm for nonlinear regression. The parity plot of experimental rate and simulated rate is plotted in Figure 6. The scatter of points shows that the experimental and simulated values are in close agreement. With these constants eq 30 was curve-fitted using a similar procedure. The experimental and simulated concentration profiles of BPA are plotted in Figure 7. From the experimental data obtained at various temperatures, the variation of constants with temperature was obtained and tabulated (Table 2).

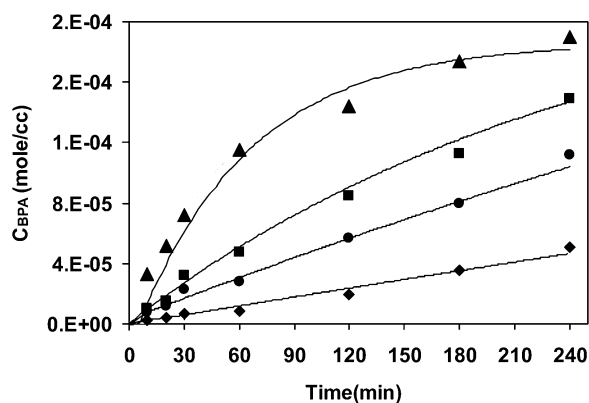


Figure 7. Comparative plot of experimental and simulated concentration profiles of BPA.

Table 2. Constants elucidated from experimental data

rate constants	333 K	353 K	363 K	373 K
k_2 (s ⁻¹)	3.32×10^{-5}	3.05×10^{-4}	4.25×10^{-4}	2.3×10^{-4}
$k_1 K_T$ (s ⁻¹ g ⁻¹ cm ³)	0.041	7.25	39.225	2.75
k_3 (s ⁻¹)	3.95×10^{-4}	1.013×10^{-3}	6.65×10^{-3}	0.0128
k_4 (s ⁻¹)	1.5	1.62	0.7	1.2

Thus, knowing the temperature dependency of various rate constants, it was possible to predict yields and concentrations of various species in the cascade-engineered synthesis of bisphenol-A.

Catalyst Reusability. Since DTP was chemically adsorbed on the catalyst surface, no leaching is observed even under severe operating conditions and in the presence of polar solvents.⁷ Reusability of 20% w/w DTP/K-10 in the cascade-engineered synthesis was examined twice (Figure 8). After completion of the experiment, the catalyst was filtered, washed with 100 mL of acetone, and dried at 110 °C for 1 h. It was then refluxed with 200 mL of acetone for 4 h and dried again at 110 °C for 1 h. The catalyst was successfully regenerated twice. There was a marginal drop in conversion to 57% and 50% during successive usages.

Conclusion

A novel cascade-engineered synthesis of bisphenol A from cumene hydroperoxide in cumene and phenol is reported in this work. It leads to enhancements of 58% in yield and 33% in selectivity of bisphenol A over the conventional process of acetone–phenol reaction. There is also a 28% improvement in reaction mass efficiency and 25% reduction in environmental impact factor. The atom economy is improved since water is the only coproduct. Since CHP produced from cumene is used as such without any separation, at low temperature, the hazards involved in the concentration and/or handling of CHP are eliminated. Finally, a comprehensive parametric sensitivity was also done and a Langmuir–Hinshelwood–Hougen–Watson model was developed to describe the reaction mechanism, and its predictions were found to match the experimental data.

In the cascade-engineered synthesis of BPA from CHP, 20% w/w DTP/K-10 was used for the series reactions (i.e., CHP decomposition and BPA synthesis) to obtain a selectivity of 80% of BPA at 100 °C at a catalyst loading of 0.025 g/cm³. The experimental data were validated against a mathematical model. The simulated profile of BPA fairly matches with the experimental one. The current work proves that with optimization of operating conditions, it is possible not only to eliminate hazards but also to improve the reaction mass efficiency. It is

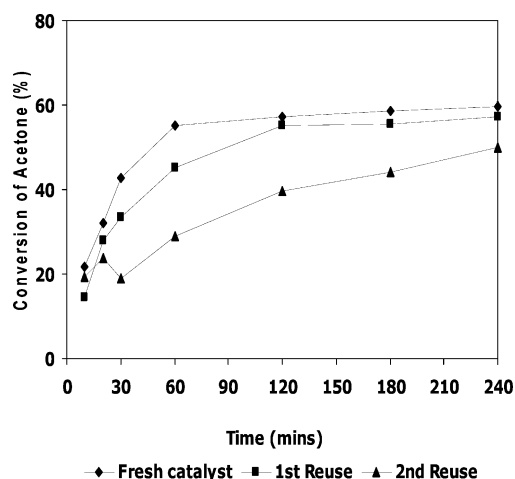


Figure 8. Catalyst reusability. Reaction conditions: mole ratio of CHP/phenol = 1:5; speed of agitation: 1000 rpm; temperature: 100 °C; catalyst loading: 0.025 g/cm³.

also possible to reduce the environmental impact factor while preserving the atom economy. By employing milder conditions of temperature and concentrations, byproduct formation was suppressed which led to an increase in the desired product yield by 25% and a reduction in the waste generated by a quarter. Apart from being in accord with the principles of Green Chemistry, this novel process offers tremendous economic incentive for scale-up.

Acknowledgment

G.D.Y. acknowledges support from the Darbari Seth Professor Endowment for personal chair. Thanks are also due to Reliance Industries Ltd. and the UDCT Golden Jubilee Endowment for supporting S.S.S.

NOMENCLATURE

A Acetone

[A _s]	Concentration of Acetone on the catalyst surface (mol cm ⁻³)
a _p	Surface area of catalyst (cm)
B	BPA
C	CHP
C _i	Concentration of species 'i' (mol cm ⁻³)
D _e	Effective diffusivity (cm ² s ⁻¹)
D _{ij}	Diffusivity of 'i' in 'j' (cm ² s ⁻¹)
d _p	Diameter of catalyst particle (cm)
E	Diisopropyl ether
K _i	adsorption constant of species 'i'
k _i	reaction rate constants
M	Mole ratio of Phenol/CHP
P	Phenol
r _{obs}	Observed rate of reaction (mol cm ⁻³ s ⁻¹)
r _{F-i}	Rate of formation of species 'i' (mol cm ⁻³ s ⁻¹)
r _{R-i}	Rate of reaction of species 'i' (mol cm ⁻³ s ⁻¹)
R _p	Radius of catalyst particle (cm)
t	Time (min)
w	Catalyst loading (g cm ⁻³)

GREEK SYMBOLS

η _p	Density of catalyst particles (g cm ⁻³)
----------------	---

Received for review October 13, 2008.

OP800262U