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Phenol Hydroxylation with TS-1 in a Chromatographic Reactor

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ABSTRACT

Phenol hydroxylation with TS-1 was studied in a chromatographic reactor. TS-1 not only acts as the catalyst for the reaction but also the adsorbent for the separation. The reaction/separation was carried out at 60°C with water and 0.2 wt% of aqueous H_2O_2 as the desorbent. Separation of hydroquinone (HQ) can be achieved in all cases. With water as the desorbent, separation of catechol (CT) depends on the phenol feed concentration, which has been confirmed from both reaction/separation in the chromatographic reactor and equilibrium competitive adsorption experiment. Some unknown by-products not commonly reported in batch experiments have been observed here. TS-1 can also be regenerated using just water. With the aqueous mixture of H_2O_2 as the desorbent, separation of HQ and CT

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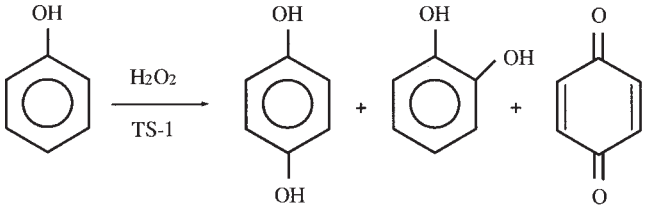
is possible. Reactive separation schemes based on the simulated countercurrent technology have been proposed according to the experimental results.

Key Words: Phenol hydroxylation; TS-1; Chromatographic reactor; Reactive separation; Hydroquinone; Benzoquinone.

INTRODUCTION

Hydroquinone (HQ) and catechol (CT) have their applications predominantly in photographic processing and polymerization inhibitors.[1,2] They can be obtained through hydroxylation of phenol (Eq. 1) with TS-1 as a catalyst and water as a solvent with maximum phenol conversion at 50%.[3] Higher phenol conversion cannot be achieved in part because of tar formation inside the catalyst pore.[3,4] In addition, the reaction may suffer from the thermodynamic equilibrium.



Phenol Hydroquinone Catechol Benzoquinone (1)

The thermodynamic equilibrium may be overcome by removing products out while the reaction is taking place. The method is commonly known as "reactive separation." With a suitable choice of a continuous phase or desorbent, reactant conversion and product yield can be increased. Furthermore, catalyst regeneration may be taking place while the desorbent passes through the reactor. A thorough explanation of reactive separation has been provided elsewhere.[5]

All the work related to phenol hydroxylation has been carried out in a batch reactor[3,4,6–10] and none involves this reactive separation technique. This work reports a preliminary investigation of using reactive separation, more specifically adsorption and reaction, for the phenol hydroxylation with TS-1. In addition, effects of different desorbents and amount of phenol in the feed were studied.

EXPERIMENTAL

Chemicals and Materials

Phenol, hydroquinone (HQ, 99%), benzoquinone (BQ, 98%), catechol (CT, 99%) were obtained from Aldrich (USA) and used without further purification. H_2O_2 (30 wt% in water) was from Aldrich (USA). HPLC grade acetronitrile was also purchased from Aldrich (USA). AR grade phosphoric acid from Mallinckodt Inc. (USA) was used to prepare a mobile phase for HPLC analyses. TS-1 was obtained from NCL Pune, India.

Dynamic Adsorption

Adsorption behaviors of HQ, BQ, CT, H_2O_2, and phenol with TS-1 in a "chromatographic" reactor using water as a desorbent were obtained through three separate adsorption experiments because it is impossible to carry out the adsorption of all species at 60°C and exclude the contribution from the reaction. The three experiments were adsorption of phenol, HQ, and CT; adsorption of BQ; and adsorption of H_2O_2. Each adsorption experiment has been checked and confirmed that there is no reaction taking place during the experiment. In addition, in all three experiments, approximately 2 wt% of KCl was added as a tracer so that the results can be compiled together.

The experimental setup is shown in Fig. 1. The chromatographic reactor was a 20 cm^3 stainless steel 316 reactor having 3/8-in. ID. The reactor was packed with 12 g of 20–40 mesh TS-1 (850–425 μm). Each experiment was started by filling up the reactor with a desorbent, which is water for these experiments, followed by an injection of 5 cm^3 of a feed, which was a mixture of HQ, CT, phenol, and KCl; BQ and KCl; or H_2O_2 and KCl. The desorbent flow rate was 0.35 cm^3/min, corresponding to 1 LHSV. Effluents from the reactor were collected using a fraction collector and quantitatively analyzed by a Hewlett-Packard HPLC series 1100 equipped with a Hypersil BDS-C 18 column (5 μm, 4.0 × 250 mm) and an UV detector. The mobile phase for the analysis consisted of 20% acetronitrile and 80% 0.2 vol% of aqueous phosphoric acid solution. The flow rate of the mobile phase was set at 1 mL/min. The wavelength of the detector was 254 nm. Unreacted H_2O_2 was analyzed using an H_2O_2 test kit (model HYP-1) from Hach (USA). Selectivity of each species with respect to phenol can be calculated using the ratio of the net retention volume of that species to that of phenol.

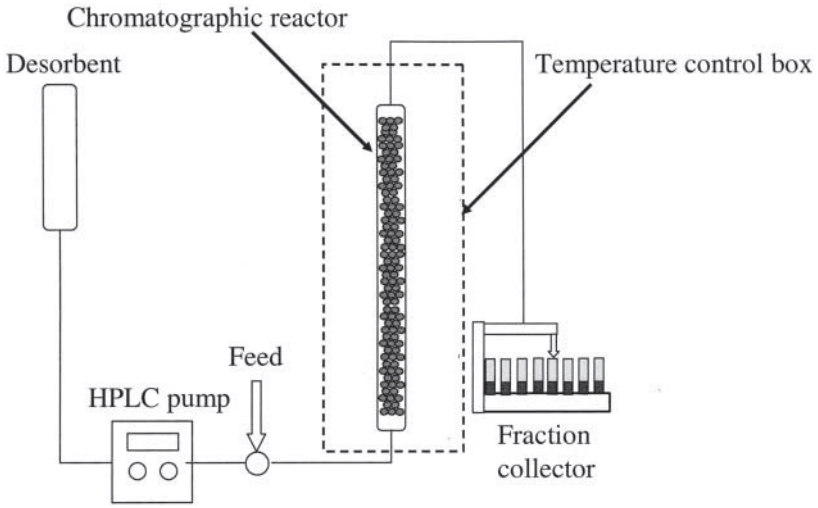


Figure 1. Experimental setup.

Reaction

The same experimental setup and procedure were applied to carry out the hydroxylation of phenol. Temperature of the reaction was maintained at 60°C. Two types of desorbent were used. With water as a desorbent, a 5 cm^3 feed mixture consisting of either 1 : 1, 1.4 : 1, or 2 : 1 phenol to H_2O_2 mole ratio was injected. Only 5 cm^3 of 0.47 M phenol was injected when an aqueous mixture of H_2O_2 (0.2 wt%) was used as a desorbent.

RESULTS AND DISCUSSION

The received TS-1 was characterized using XRD (SCINTAG XDS 2000 theta-theta diffractometer, Cu tube $K_{\alpha 1}$ radiation with Peltier detector) and confirmed that its structure is basically that of silicalite (Fig. 2). Based on the structure of silicalite, activation energy of phenol, HQ, CT, and BQ diffusing into the pore of the zeolite was estimated using Accelrys. The estimation was based on each component, one at a time, diffused into the pore of TS-1. From Table 1, it can be deduced that the order in which the four species adsorb on or desorb from TS-1 is phenol, HQ, BQ, and CT.

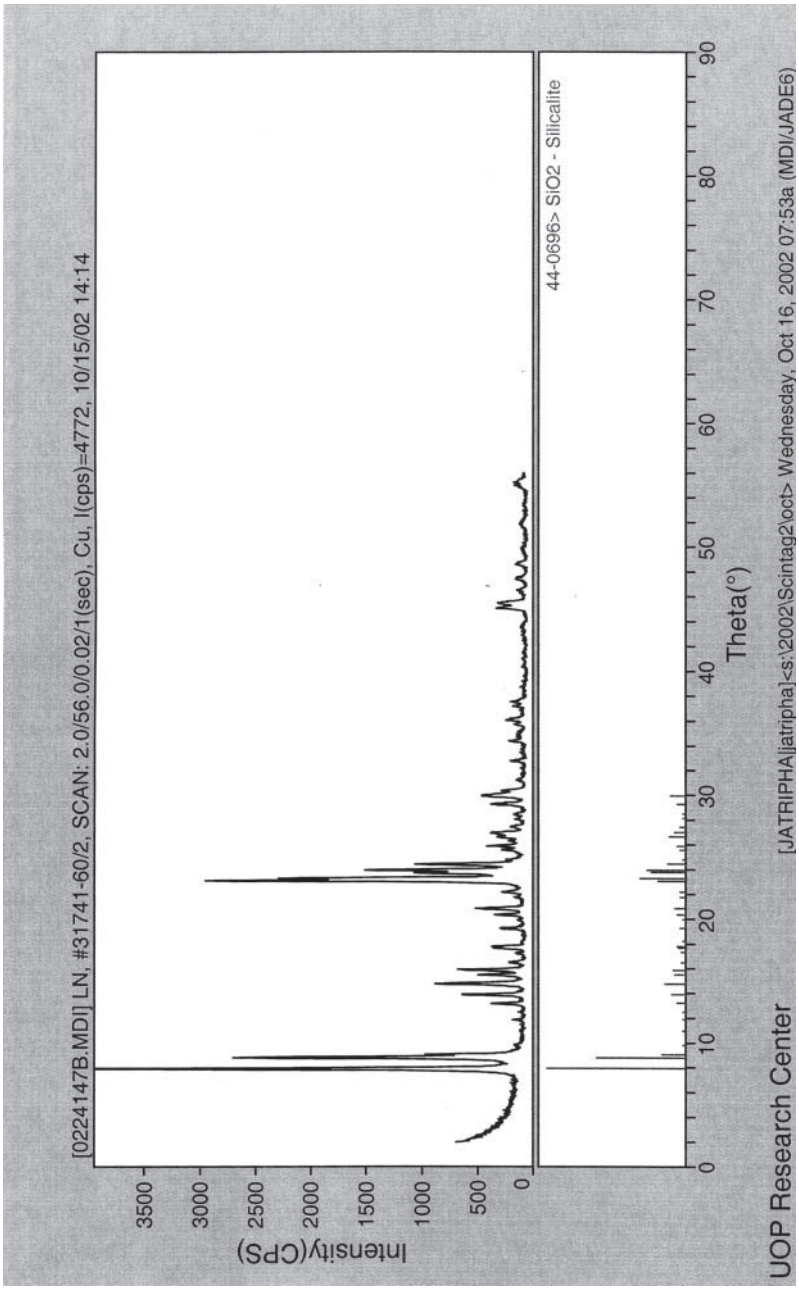


Figure 2. XRD analysis of TS-1.

Table 1. Diffusion activation energy of phenol, HQ, CT, and BQ into silicalite.

	Activation energy* (kcal/mol)
Phenol	8.5
Hydroquinone	10
Catechol	25
Benzoquinone	19

*Provided by M. Gatter, UOP LLC.

Dynamic Adsorption

Adsorption of each species involved in the reaction on TS-1 is shown in Fig. 3. According to the figure, HQ elutes from the column first followed by BQ and CT. In addition, the elution profile of CT seems to drag on long after the experiment duration. Phenol having the lowest-calculated activation energy should have eluted from the column much faster than HQ, BQ, or CT but the experimental result shows otherwise. It implies that there may be strong adsorption of phenol on TS-1. Unlike phenol, the late elution of CT may be due to the diffusion limitation of the molecule.

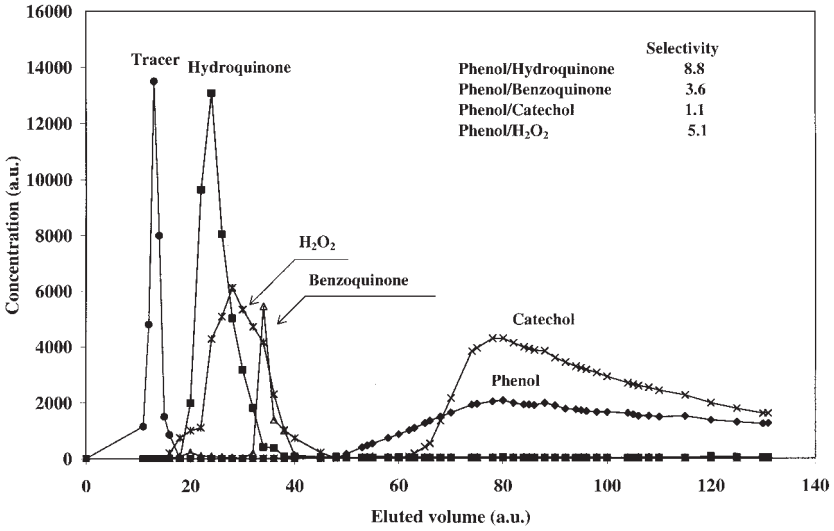


Figure 3. Dynamic adsorption of phenol and the products from phenol hydroxylation at 60°C.

Selectivity of HQ, BQ, and H_2O_2 with respect to phenol is well above one indicating good separation of those three species from the reactant. That is, however, not so for CT, which has its selectivity close to one. From the dynamic adsorption experimental results, TS-1 acts not only as a catalyst for phenol hydroxylation but also as an adsorbent to separate reactants and products from the reaction, provided that water is the desorbent.

Reaction

Phenol hydroxylation was carried out in the chromatographic reactor with two types of desorbent—water and an aqueous mixture of H_2O_2.

Water as the Desorbent

With water as the desorbent, the elution profiles of phenol, HQ, CT, BQ, and H_2O_2 from the chromatographic reactor are shown in Figs. 4–6. Using 1 : 1 phenol to H_2O_2 mole ratio in the feed gives the elution profiles (Fig. 4) that are approximately the same as observed from the adsorption experiment. That is the long tailing of both CT and phenol still present, and the separation of

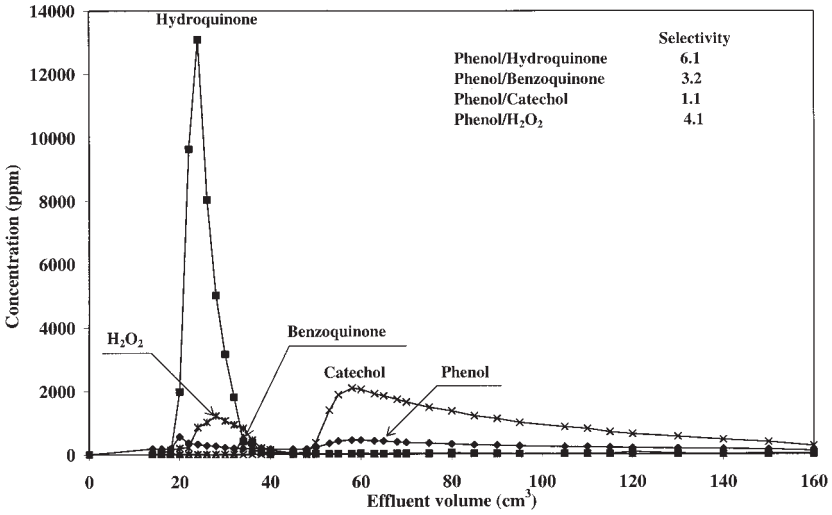


Figure 4. Results from phenol hydroxylation with TS-1 at 60°C. (Phenol : H_2O_2 = 1 : 1 mole, desorbent: 1 LHSV of water).

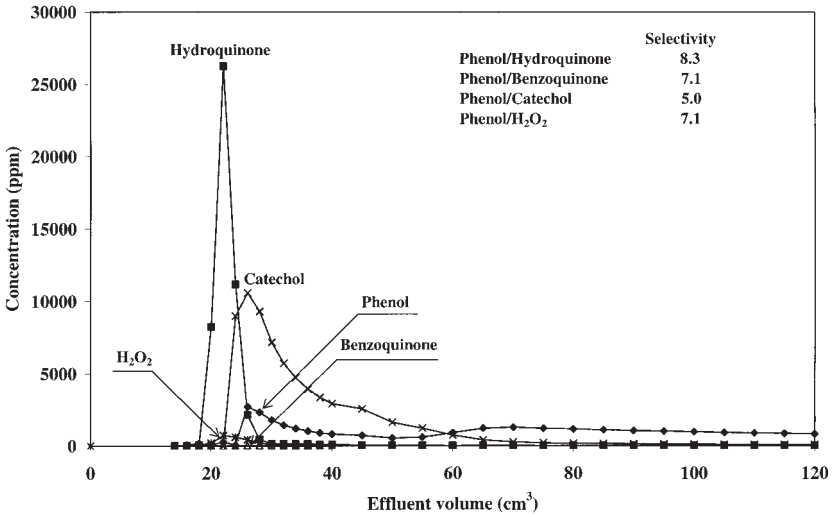


Figure 5. Results from phenol hydroxylation with TS-1 at 60°C. (Pheno1 : H_2O_2 = 1.4 : 1 mole, desorbent: 1 LHSV of water).

HQ from the reactant is possible as indicated by the selectivity. Regarding the reaction results, high HQ selectivity is achieved while an insignificant amount of BQ is produced.

During the experiment, there are some other by-products, as observed by colors of the effluents collected, which are likely to be dimers or products from polymerization of some products. And these by-products have higher selectivity than HQ, BQ, and CT. These by-products are either present at a very low concentration so that they have not been reported with a batch-type reactor or strongly adsorbed by TS-1 and a suitable desorbent is needed to desorb them out from the catalyst. It is not the intention of this work to identify all the by-products produced from the phenol hydroxylation in the chromatographic reactor. Because of the unidentified by-products and the strong adsorption of both phenol and CT, conversion of phenol and product yields are not determined here.

Another observation during this work is that TS-1 can be easily regenerated using pure water.

When the phenol to H_2O_2 ratio is increased from 1 : 1 to 1.4 : 1, the elution profiles are approximately the same as those with 1 : 1 ratio (Fig. 5). Unlike the 1 : 1 mole ratio case, concentration of HQ, the main product, is twice as much as that from the low amount of phenol case. Again, only a small amount of BQ

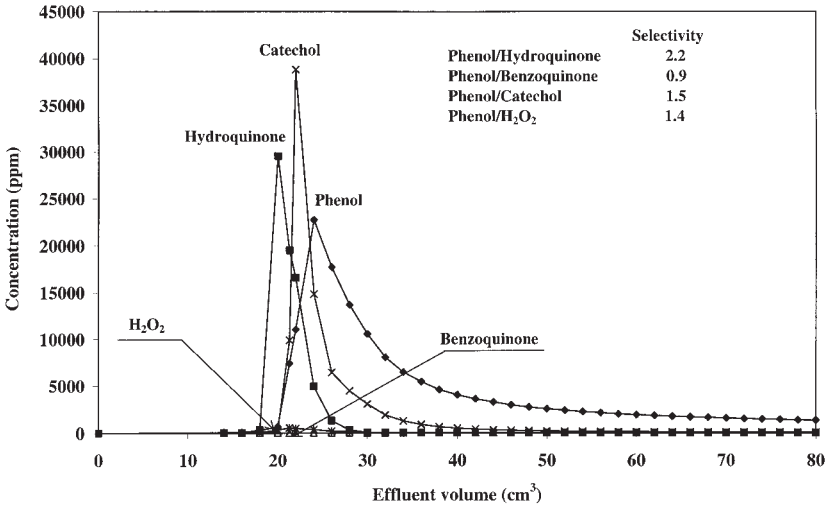


Figure 6. Results from phenol hydroxylation with TS-1 at 60°C. (Pheno1 : $H_2O_2 = 2:1$ mole, desorbent: 1 LHSV of water).

is obtained. Furthermore, CT and phenol elute out from the reactor much sooner than those from the low phenol feed concentration. A window for HQ separation with a certain degree of purity is still present here as indicated by the selectivity of HQ with respect to phenol. Although the long tailing of CT is present here, it is not so long as the one previously observed.

The amount of phenol was further increased to 2 : 1 phenol to H_2O_2 mole ratio, and the results are shown in Fig. 6. As expected, the amounts of HQ and CT increase with the increase of phenol concentration. In addition, the surged increase in the CT amount is observed. Only an insignificant amount of BQ is produced with this feed composition. Another important observation from these results is that CT elutes out from the reactor much faster than the previous cases and the tailing is better here.

The tailing of CT in both low and high phenol concentration cases and the dynamic adsorption is probably due to the diffusion limitation as indicated by the high diffusion activation energy. On the other hand, the tailing of phenol is caused by the strong interaction with the TS-1 surface. Moreover, the selectivity of phenol and CT seems to be concentration dependence.

A separate experiment was carried out to study the equilibrium competitive adsorption of phenol and CT on TS-1 at 60°C. The results are shown in Fig. 7. The figure further substantiates that the adsorbed amounts of phenol and CT on TS-1 depend on both component concentrations as observed

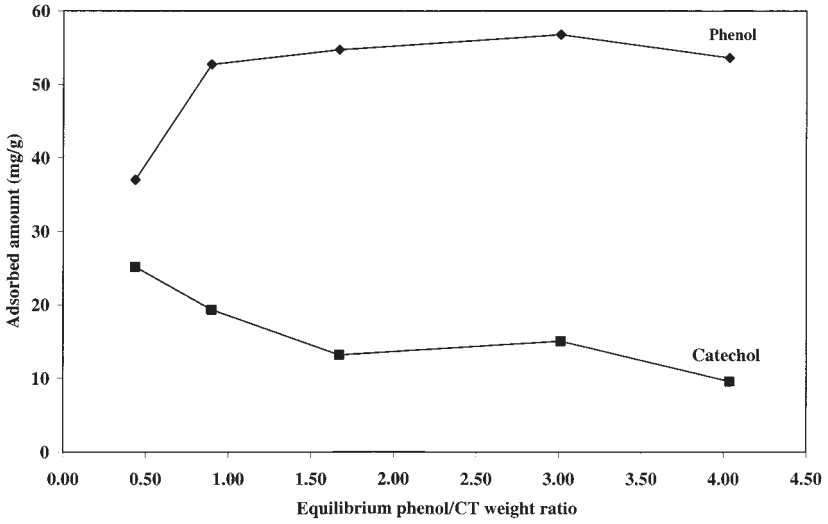


Figure 7. Equilibrium competitive adsorption of phenol and catechol on TS-1 at 60°C.

from the phenol hydroxylation experiments. At low phenol to CT weight ratios, TS-1 is selective to CT. And when phenol reaches a certain concentration, with its strong adsorption on the TS-1 surface, CT tends to be desorbed out. In other words, the higher phenol, the more phenol and the less CT are adsorbed.

From the hydroxylation reaction results, it can be inferred that purity of HQ and CT can be adjusted with the amount of phenol in the feed. However, that is compromised with the concentration of both products.

Aqueous Mixture of H_2O_2 as the Desorbent

Instead of using water as the desorbent, an aqueous mixture of H_2O_2 is used with the rational that H_2O_2 may continuously react with phenol to form the desired products, which are then selectively separated. For this study, a pulse of phenol was injected into the chromatographic reactor. The results (Fig. 8) show a totally different species elution pattern from that with water as the desorbent.

Here, HQ still elutes out first with a small peak and takes about twice as long than that from the experiments with water as the desorbent. BQ was not detected in this experiment. A major elution of HQ comes out later followed by CT and phenol. Good separation of HQ and CT is obtained using the

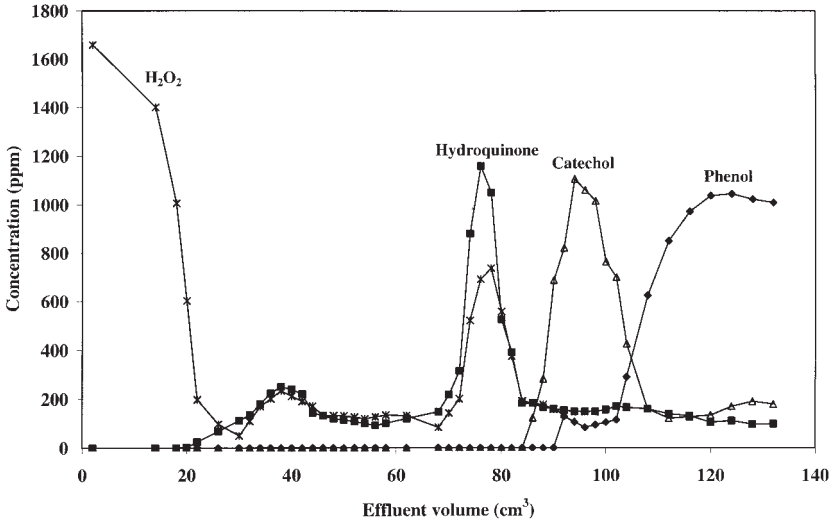


Figure 8. Results from phenol hydroxylation with TS-1 at 60°C. (Phenol = 0.47 M, desorbent: 1 LHSV of aqueous H_2O_2, 0.2 wt%.)

aqueous mixture of H_2O_2 as the desorbent. Phenol, however, seems to exist after the CT peak despite the use of the continuous stream of aqueous H_2O_2 mixture. A further comprehensive study is needed to understand this behavior.

Proposed Reactive Separation Schemes

Three reactive separation schemes, which depend upon a type of desorbent and amount of phenol, can be proposed according to the experimental results. The schemes are based on the simulated moving bed technology.

When water is used as the desorbent, two schemes (Fig. 9) depending on the phenol to H_2O_2 feed mole ratio are possible. With 1 : 1 and 1.4 : 1 phenol to H_2O_2 ratio, the scheme is shown in Fig. 9(a). Although TS-1 is not moving physically, a rotary valve can direct flows of each stream so that the whole catalyst bed behaves as if TS-1 were moving. Through the use of a rotary valve, water is fed as a continuous stream downward while a pulse of a phenol and H_2O_2 mixture injected periodically is carried over upward. The reaction zone is between the feed positions of the water and mixture of phenol and H_2O_2. Because of the long tailing of both phenol and CT indicating that both components are selective to TS-1, they will be carried upward and withdrawn at the top of the column. On the other hand, as HQ is less

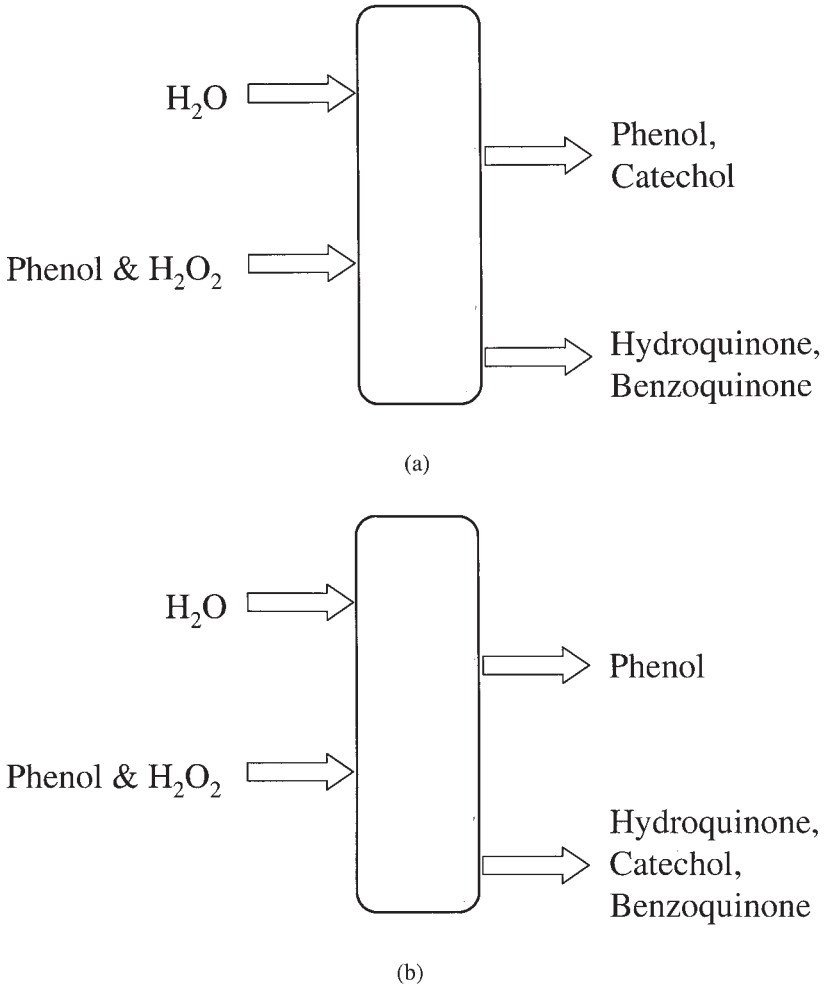


Figure 9. Proposed reactive separation schemes based on the simulated moving bed technology. (Water as the desorbent, phenol to H_2O_2 mole ratio: (a) 1:1 and 1.4:1, (b) 2:1.)

selective to TS-1, it will go downward with the water stream and can be extracted at the bottom of the column. And any trace amount of BQ will be present along with HQ.

Fig. 9(b) shows the proposed reactive separation scheme for phenol hydroxylation when the phenol to hydrogen peroxide ratio is 2:1. As the concentration of phenol increases, CT is rapidly desorbed from TS-1 resulting in

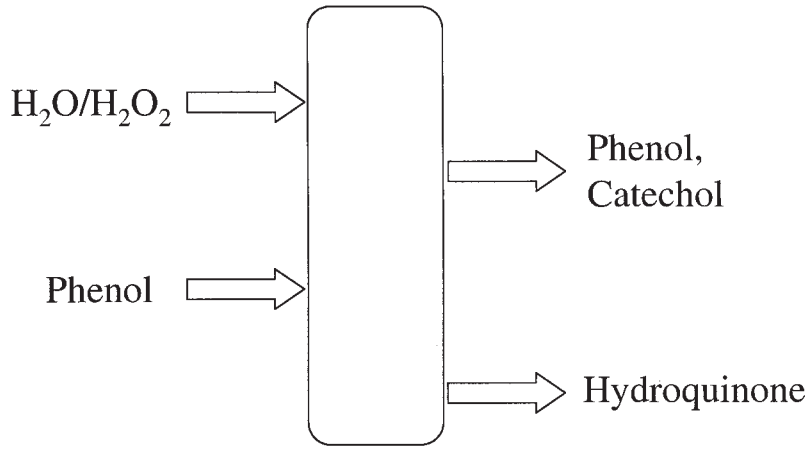


Figure 10. Proposed reactive separation schemes based on the simulated moving bed technology. (Aqueous H_2O_2 as the desorbent.)

good separation of CT from phenol. Consequently, it is proposed here that HQ, CT, and any trace amount of BQ be extracted at the bottom of the column while phenol can be withdrawn from the top of the column.

A similar scheme to Fig. 9(a) is used for the phenol hydroxylation with aqueous H_2O_2 as the desorbent (Fig. 10). A few combinations of each product separation are possible. For example, CT can be withdrawn along with either HQ or phenol. Here, CT will be removed with phenol at the top of the column as both of them are more selective than HQ and because of the wider boiling point difference in CT and phenol than that of CT and HQ. With the difference in the boiling points, CT can then be separated out from phenol later if needed.

CONCLUSIONS

Phenol hydroxylation with TS-1 was studied in the chromatographic reactor. TS-1 not only acts as the catalyst for the reaction but also the adsorbent for the separation. With the chromatographic reactor, some unidentified by-products have been observed albeit not reported with a batch reactor. With water as the desorbent, separation of each product can be achieved depending upon the amount of phenol in the feed. Selectivity of CT on TS-1 was found to be concentration dependence. A further study on the phenol hydroxylation with the aqueous mixture of H_2O_2 is needed. Based on the simulated

moving bed technology, reactive separation schemes have been proposed according to concentration of phenol in the feed and types of desorbent.

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