IJCPE
Iraqi Journal of Chemical
and Petroleum Engineering

Iraqi Journal of Chemical and Petroleum Engineering
Vol.10 No.3 (September 2009) 9-17
ISSN: 1997-4884

University of Baghdad
College of Engineering

Recovery of Catalyst from Tar Formed in Phenol Production Unit

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Abstract

This work was conducted to study the recovery of catalyst and desirable components from tar formed in phenol production unit and more particularly relates to such a method whereby better recovery of copper salts, phenol, benzoic acid and benzoate salts from tar by aqueous acid solution was accomplished.

The effect of solvent type, solvent concentration (5, 10, 15, 20, 25 and 30 wt%), agitation speed (100, 200, 300 and 400 rpm), agitation time (5, 10, 15, 20 and 25 min), temperature (90, 100, 110, 120, 130 and 140 oC) , phase ratio (1/1, 2/1, 3/1, 4/1 and 5/1) and number of extraction (1, 2, 3, 4, and 5) were examined in order to increase the catalyst and desirable components extraction.

Four types of solvent were used; hydrochloric acid, acetic acid, propanoic acid and butanoic acid with different concentration.

The results of this work exhibit that the highest removal of copper 80.2 wt%, phenol 89.1 wt%, benzoic acid 90.7 wt% and benzoate salts 87.3 wt% were obtained under the conditions of Acetic acid-water of 15%, Agitation speed = 300 rpm, Agitation time = 20 min, Temperature = 120 ℃, Phase ratio (A/O) = 4 / 1, and Number of extraction cycle = 4.

Introduction

Phenol is one of the most important starting materials for various chemical products, such as phenol resin, bis-phenol, aniline and some agricultural chemicals.

There currently are four process routes (1-5) being used commercially to produce synthetic phenol. Three are based on benzene (1-3) and one on toluene. (4) The major process, which accounts for about 90 % of world capacity, is the cumene hydroperoxide route.(5) The other benzene routes, accounting for less than 4 %, include a chlorination and sulfonation process. The toluene based process, which involves the intermediate production of benzoic acid accounts for 6-8 %.

Beside the desired phenol the reaction yields, as a byproduct, highly viscous product which, during the reaction, remains in solution in the liquid carboxylic acid or derivative. This tarry byproduct must be removed from the reaction mixture and the carboxylic acid or derivative and the catalyst is dissolved by the extraction liquids. The composition of the reaction mixture that is withdrawn from the phenol preparation reactor depends on, among other things, the catalyst system used, the concentration of the catalyst and the starting materials and the process conditions. (6 - 21)

Phenol tar is a heavy, viscous byproduct produced in the industrial synthesis of phenol and acetone. Phenol tar is a complex mixture, which comprises phenol, acetophenon, dimethyl benzeyl alcohol, alpha-methyl styrene dimmers, p-cumyl phenol, small amount of salts and many other chemicals in smaller amounts. It is difficult to dispose of phenol tar in an environmentally acceptable manner. Specifically, burning phenol tar is not good disposal solution because it contains many ingredients, which do not burn readily, such as phenol. Therefore, a need exists to find more environmentally acceptable methods of disposing of phenol tar (22-24).

The present study reduces pollution resulting from the disposal of phenol tar by extracting valuable chemicals from the tar that can be recycled, thus reducing the amount of phenol tar that must be disposed of. Thus this study is intended to recover the copper catalyst and desired components from the tar formed in phenol production unit through the studying different effects of extraction process such as solvent kind, solvent concentration, agitation speed, agitation time, temperature, phase ratio and number of extraction cycle.

Experimental Work

Experimental Apparatus

The experimental apparatus shown in figure 1 was used to extract the copper catalyst and desirable components from tar. The apparatus consisted mainly of the stainless steel autoclave, which had the dimensions 13 cm in diameter and 18 cm high. The autoclave consisted of two parts: lower part, a vessel that contained the materials to be treated. The other part (upper part) is the cover, with a hole, so that the four blades mixer is passed through.

To ensure the prevention of the escape of vapors, the hole was checked to be tightly closed.

There were also two side holes. The first one was used to measure the pressure. Through the other hole, a thermocouple, type J (constantan-iron), was passed. This was connected to a digital thermometer.

The autoclave was surround by a heating source, i.e., the heating tape and it was connected to a thermostat. A variac was used to establish the required temperature.

The autoclave was further surrounded by an insulating material, i.e., glass wool to further ensure the heat conservation.

Other laboratory glassware were also used to carryout the experiments such as: beakers, pipetts, conical flasks, test tubs and graduated cylinders.

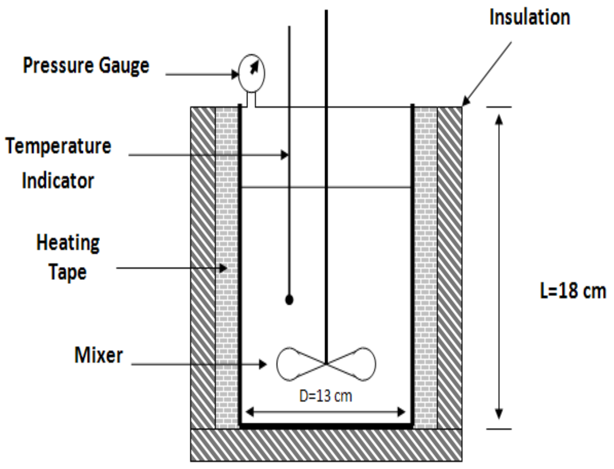

Fig. 1, Schematic diagram of the experimental equipment

Experimental Procedure

At the beginning of the experiment, the tar was melted at 90o C to ensure its homogeneity with the catalyst. Then it was crushed by hand. According to the working conditions a certain volumetric sample of the tar and the solvent was taken and was heated to the required temperature simultaneously with continuous mixing.

At the end of the experiment according to experimental design, the autoclave was left to cool and the sample from the aqueous solution was taken to be tested and to determine the percentage of copper, phenol, benzoic acid and benzoate salts in it.

Atomic absorption spectrophotometer and gas chromatography were used to measure the concentration of copper and desirable components in the aqueous phase throughout the experiments.

Arrangement of Experiments

Solvent Selectivity

In this set of experiments, solvent selectivity was investigated. The aqueous phase (solvent) used is diluted acid of hydrochloric acid, acetic acid, propanoic acid and butanoic acid with concentration of 5, 10, 15 and 20 % (v/v), keeping other variables constant (3/1 phase ratio, 110o C temperature, 300 rpm agitation speed and 15 min mixing time).

A sample of the aqueous phase was taken to evaluate the concentration of copper, phenol, benzoic acid and benzoate salts.

Effect of Solvent Concentration

In this set of experiments, the effect of the solvent concentration was investigated, the ranges of the concentration of the extractant is 5, 10, 15, 20, 25 and 30 % (v/v), keeping other variables constant (3/1 phase ratio, 110o C temperature, 300 rpm agitation speed and 15 min mixing time).

Effect of Agitation Speed

In this set of experiments, the effect of agitation speed was investigated. A sample of the solution was taken at the end of each run of different speed versus 100, 200, 300, and 400 rpm. Keeping other variables constant (3/1 phase ratio, 110o C temperature, and 15 min mixing time).

Effect of Agitation Time

In this set of experiments, the effect of agitation time was investigated. A sample of the solution was taken at the end of each period 5, 10, 15, 20 and 25 min. Keeping other variables constant (3/1 phase ratio, 110o C temperature).

Effect of Temperature

In this set of experiments, the effect of temperature was investigated. A sample of the solution was taken at the end of each run of different temperature versus 90, 100, 110, 120, 130 and 140o C. Keeping phase ratio (3/1).

Effect of Phase Ratio

In this set of experiments, the effect of phase ratio (A/O) was investigated. The phase ratio used in this set varied versus 1/1, 2/1, 3/1, 4/1 and 5/1. So according to the phase ratio above, a known volume of aqueous and organic phase was mixed.

Effect of Number of Extraction Cycle

In this set of experiments, the effect of number of extraction cycles was investigated. A sample of the solution was taken at the end of each run of different cycles i.e. 1, 2, 3, 4 and 5. Keeping other variables constant at the best values from the previous sections.

Results and Discussion

Solvent Selectivity

The results obtained, here, showing that using acetic acid as an extractant gave the highest recovery of copper catalyst and desirable components from tar. Keeping other variables constant (3/1 phase ratio, 110o C temperature, 300 rpm agitation speed and 15 minutes mixing time).

The aliphatic acids which are useful include all acids which are soluble to an extent of at least about 0.5 weight percent and preferably to at least about 9.5 weight percent in water. The preferred aliphatic acids are saturated and contain 1 to 4 carbon atoms. More preferred are the 2-4 carbon atom alkanoic acids. More preferred is acetic acid as shown in the results.

Aqueous formic acid is a good copper extractant, but on recycling to the phenol reactor it would be oxidized in the presence of copper salt. Therefore, if it is employed, the valuable components are preferably separated from the aqueous phase without recycle.

Acetic, propionic and butyric acids are not oxidized appreciably on recycle and thus are preferably used, because they can be readily recovered from the aqueous of the phenol reaction system for reuse in the tar extraction process.

Figures 2 to 6 indicate that acetic acid gave the highest recovery of copper and desirable components, also gave the highest extraction coefficient.

Effect of Solvent Concentration

From the results of the previous section, water-acetic acid soultion gave the highest recovery of copper and desirable components.

The proportion of the two solvents in the solvent mixture is not critical, though of course enough of each must be used to produce two phases in the solvent mixture. Also, there must be enough of each to dissolve to suspend substantially all of those components which are intended to be separated. It is, of course, desirable to operate with as small a volume of solvent as will do the job.

The results clearly demonstrate that increasing the acid concentration up to 15 % causes the recovery of copper and desirable components increase, beyond that it remains almost constant.

The concentration of the aliphatic acid in water can range from about 5 to about 50 weight percent. The upper limit of acid concentration is not determined by the ability of the acid to extract copper and the desired constituents from the tar only, but the ability to achieve phase separation of tar from the aqueous acid.

The preferred alkanoic acid concentration ranges from about 10 to 20 percent in water, preferably 15 percent.

Figures 7 to 9, exhibit the effect of solvent concentration on recovery of copper and desirable components.

Effect of Agitation Speed

As noticed from the previous sections that water- 15 % acetic acid was used to carry out the experiments in this section.

Figures 10 to 12 show that the agitation speed of 300 rpm gave the highest values of copper recovery and desirable components also.

The surface area of the dispersed phase will depend on the amount of the agitation speed. However, it should not be thought that the greater the agitation speed the greater the rate of components extraction. Too much agitation speed can result in formation of a solute or semi-stable emulations. Furthermore, decreasing the drop size of dispersed phase can result in making the drop resemble rigid spheres. In this condition, there is no internal movement within the spheres, no new surfaces are produced and the extraction within the sphere cannot get to the surface to reach with solute. Consequently, the extracting rate is slow (25).

Effect of Agitation Time

The results are plotted in figures 13 to 15 indicating that using an agitation time of 20 min gave the highest extracting coefficient and percentage of copper and desirable components removal. The solvent extraction is an equilibrium process, it was found that the equilibrium is completed at 20 min of contact time and the increasing in the agitation time has no influence on the loading of aqueous phase.

The mixing or contact time for the extracting of copper and desirable components from the tar-containing liquid reaction mixture must be sufficient to obtaine equilibrium between the polymeric tar and the aqueous aliphatic acid phase. This depends on the mixing vessel configuration, rate of stirring and efficiency of stirrers.

Settling time for separating the aqueous liquid and tar phases must be sufficient to allow the upper aqueous phase to become substantially free of any significant quantity of suspended tar.

Settling time can range from about 10 to 20 min to achieve a clear phase.

Effect of Temperature

The results plotted in figures 16 to 18 indicate that increasing the temperature lead to an increase in the extracting coefficient and percentage of copper and desirable components recovery.

The temperature at which the extracting is affected can range from 90 to about 140o C. Below 90o C the tar is solid and is difficult to extract except by resort to long extraction period. Above about 140o C, the vapor pressure of the aqueous acid becomes troublesome. The preferred extraction temperature is about 140o C. in this way, substantially all the phenol, benzoic acid and benzoate salts were dissolved in the aqueous phase. This phase was then separated from the tar phase and returned to the reactor as part of the water fed thereto.

Effect of Phase Ratio

The results obtained, showing that increasing the phase ratio (A/O) cause a significant increase in the extracting coefficient and the phase ratio 4/1 gave the highest value for the system as indicated in figure 19. This might be attributed to the increase in the quantity of transferred component which is related to quantity of extracting that will furnish the necessary molecules to reach the equilibrium state. The behavior is valid to an extent beyond it the extracting coefficient will decrease, because the quantity or volume of the aqueous phase increases, the amount of metal transferred will undergo somewhat smaller increase leading to a decrease in the concentration of metal. Hence, causing a decrease in the extracting coefficient.

Figures 20 and 21 further support the above conclusion where these figures represent the percentage recovery of copper and desirable components, this percentage increases up to a limit then it remains nearly constant.

The proportions of the aqueous alkanoic acid to tar can range from about 1/1 to 5/1 volume. As the ratio of aqueous acid to liquid reaction mixture reduced below 1/1, the separation of tar and aqueous acid phase becomes progressively more difficult. At a ratio above 5/1, the increased quantities of recycled dilute aqueous alkanoic cause evaporative overloading of the phenol reactor.

Effect of Number of Extraction

The results obtained, showing that increasing the number of extraction cause a significant increase in the extracting coefficient up to a limit then it becomes nearly constant as show in figure 22.

Multiple extractions results increased removal of copper from the tar, but as the number of extractions increase the total amount of copper removed per extraction tends to decrease. At equilibrium the second and all succeeding extraction tend to have progressively lower copper concentrations in the liquid phase.

Figures 23 and 24 further support the above conclusion where these figures represent the percentage recovery of copper, phenol, benzoic acid and benzoate salts.

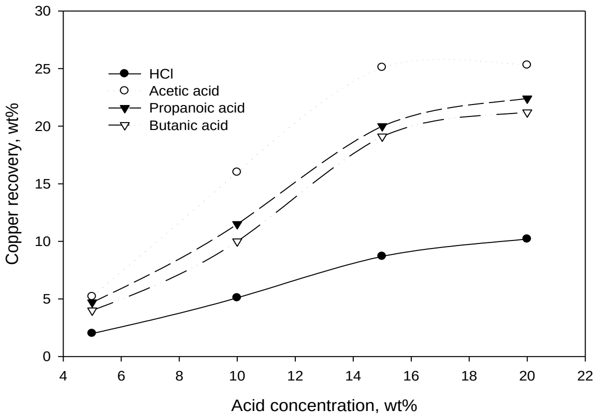

Fig. 2, Copper recovery versus acid concentration at 3/1 phase ratio, 110^{o} C temperature, 300 rpm agitation speed and 15 minutes mixing time

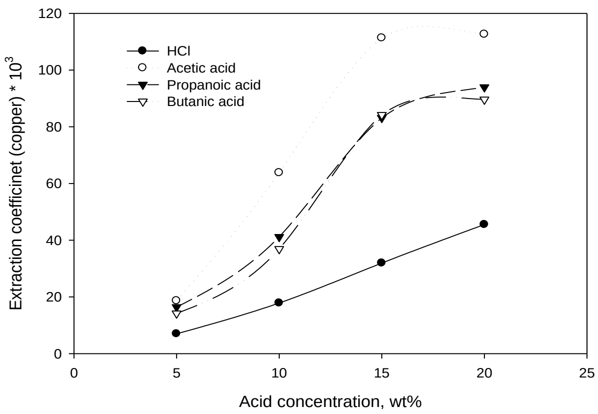

Fig. 3, Extracting coefficient versus acid concentration at 3/1 phase ratio, 110o C temperature, 300 rpm agitation speed and 15 minutes mixing time

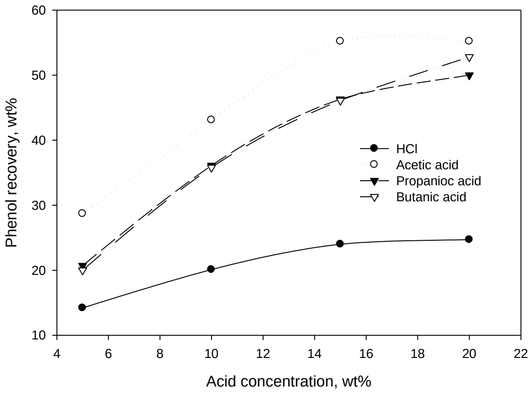

Fig. 4, Phenol recovery versus acid concentration at 3/1 phase ratio, 110o C temperature, 300 rpm agitation speed and 15 minutes mixing time

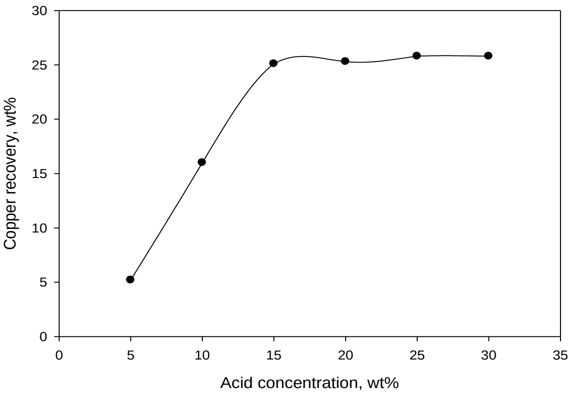

Fig. 7, Copper recovery versus acid concentration at 3/1 phase ratio, 110o C temperature, 300 rpm agitation speed and 15 minutes mixing time

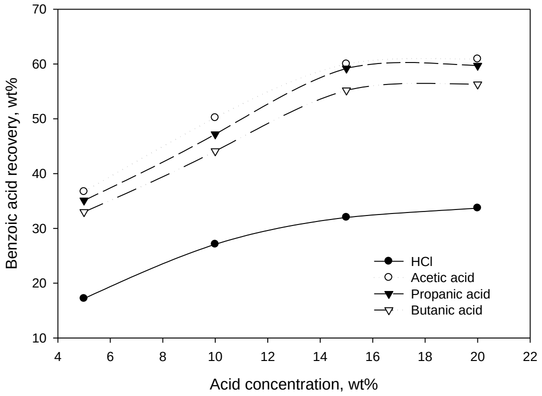

Fig. 5, Benzoic acid recovery versus acid concentration at 3/1 phase ratio, 110o C temperature, 300 rpm agitation speed and 15 minutes mixing time

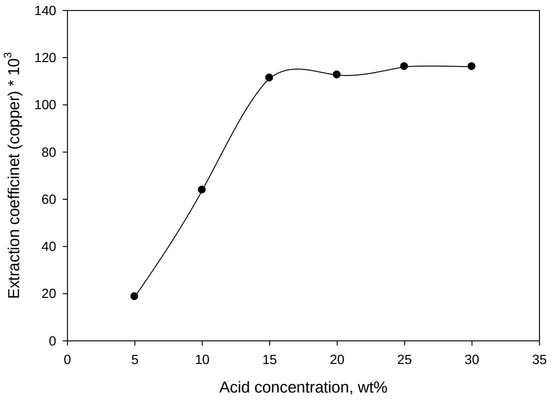

Fig. 8, Extraction coefficient versus acid concentration at 3/1 phase ratio, 110o C temperature, 300 rpm agitation speed and 15 minutes mixing time

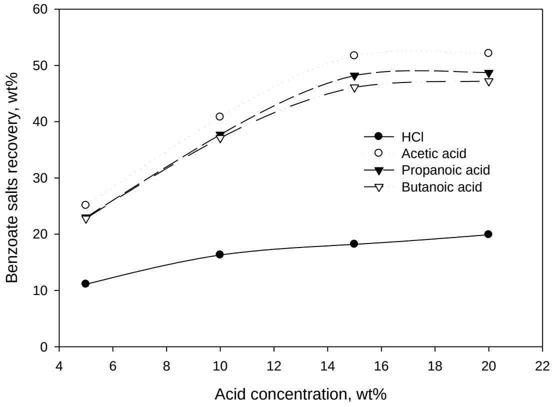

Fig. 6, Benzoate salts recovery versus acid concentration at 3/1 phase ratio, 110o C temperature, 300 rpm agitation speed and 15 minutes mixing time

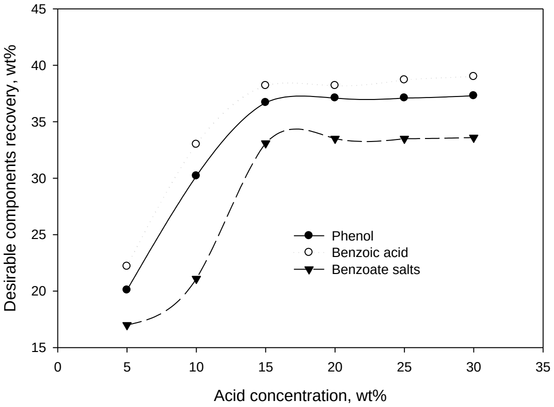

Fig. 9, Desirable components recovery versus acid concentration at 3/1 phase ratio, 110o C temperature, 300 rpm agitation speed and 15 minutes mixing time

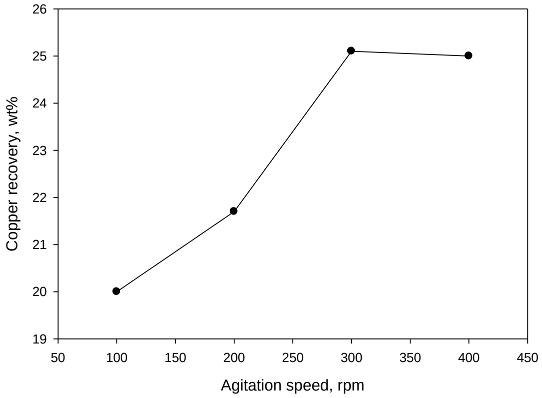

Fig. 10, Copper recovery versus agitation speed at water-15% acetic acid solution, 3/1 phase ratio, 110o C temperature and 15 minutes mixing time

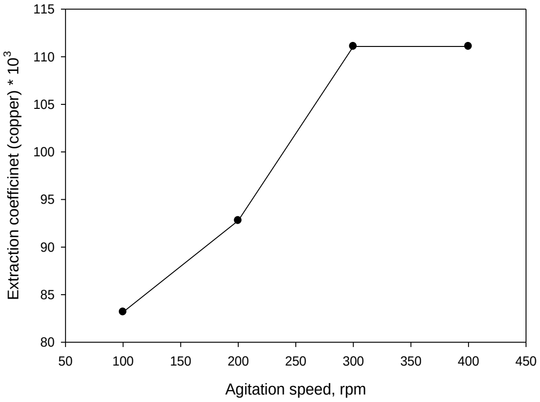

Fig. 11, Extraction coefficient versus agitation speed at water-15% acetic acid solution, 3/1 phase ratio, 110o C temperature and 15 minutes mixing time

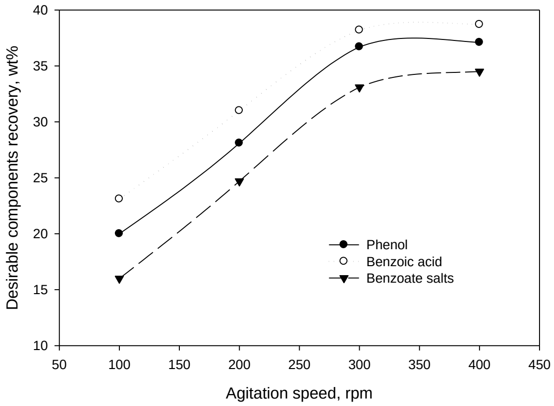

Fig. 12, Desirable components recovery versus agitation speed at water-15% acetic acid solution, 3/1 phase ratio, 110o C temperature and 15 minutes mixing time

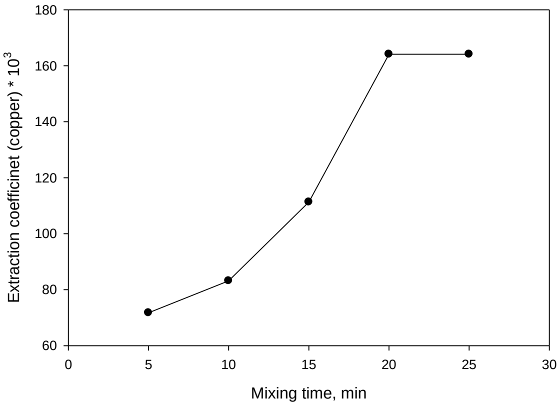

Fig. 13, Extraction coefficient versus mixing time at water-15% acetic acid solution, 3/1 phase ratio, 110o C temperature and 300 rpm agitation speed

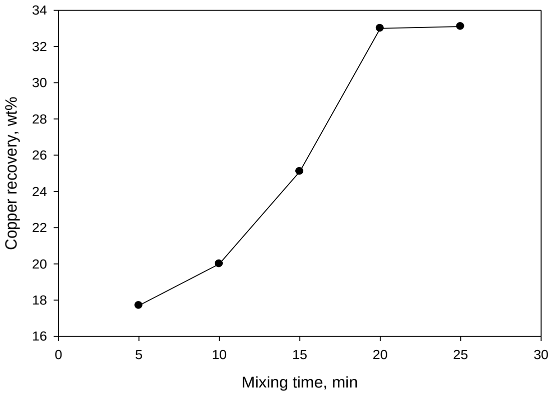

Fig. 14, Copper recovery versus mixing time at water-15% acetic acid solution, 3/1 phase ratio, 110o C temperature and 300 rpm agitation speed

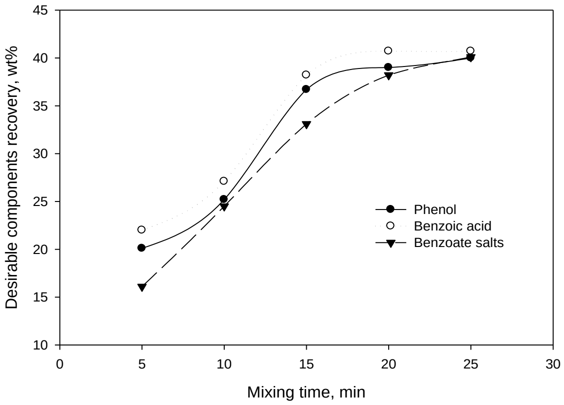

Fig. 15, Desirable components recovery versus mixing time at water-15% acetic acid solution, 3/1 phase ratio, 110o C temperature and 300 rpm agitation speed

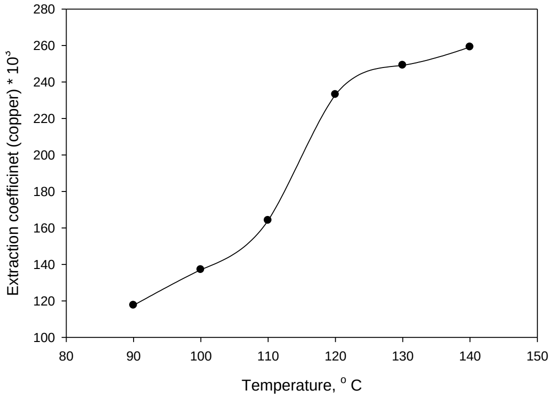

Fig. 16, Extraction coefficient versus temperature at water-15% acetic acid solution, 3/1 phase ratio and 300 rpm agitation speed

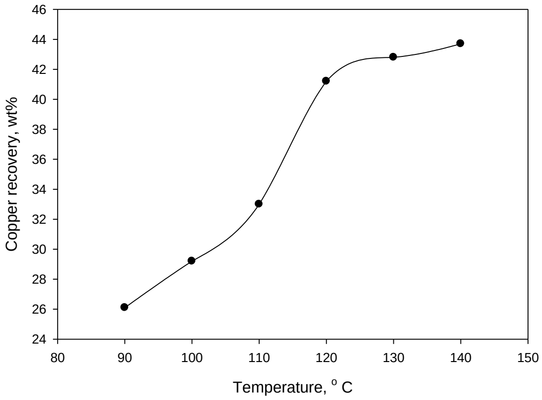

Fig. 17, Copper recovery versus temperature at water-15% acetic acid solution, 3/1 phase ratio and 300 rpm agitation speed

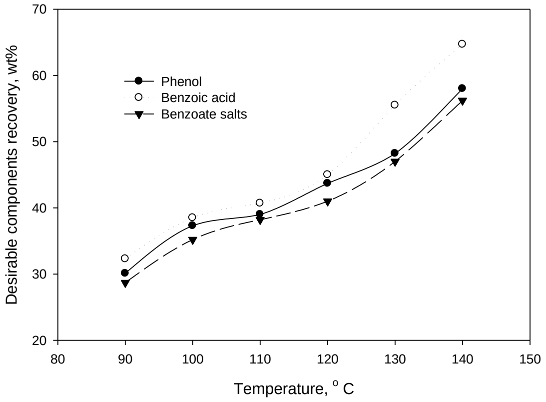

Fig. 18, Desirable components recovery versus temperature at water-15% acetic acid solution, 3/1 phase ratio and 300 rpm agitation speed

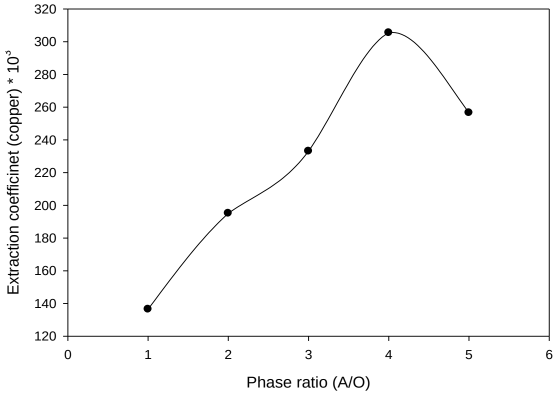

Fig. 19, Extraction coefficient versus phase ratio at water-15 % acetic acid solution, 140o C temperature, 300 rpm agitation speed and 20 min mixing time

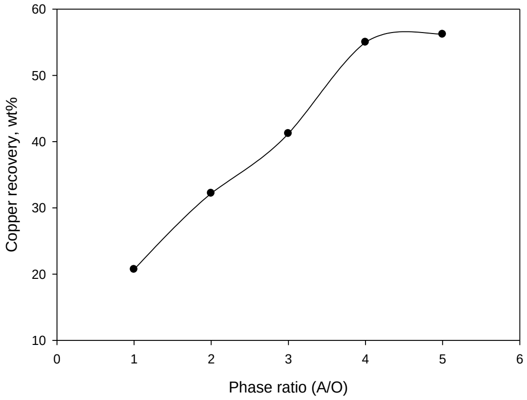

Fig. 20, Copper recovery versus phase ratio at water-15 % acetic acid solution, 140o C temperature, 300 rpm agitation speed and 20 min mixing time

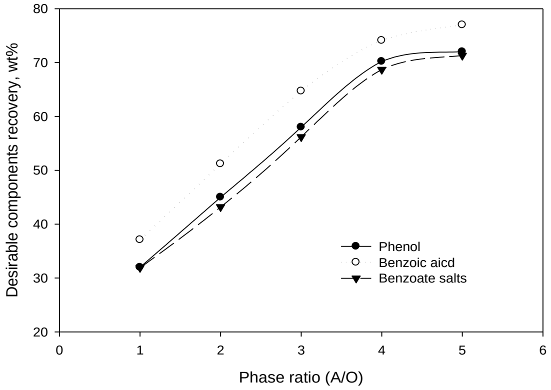

Fig. 21, Desirable components recovery versus phase ratio at water-15 % acetic acid solution, 140o C temperature, 300 rpm agitation speed and 20 min mixing time

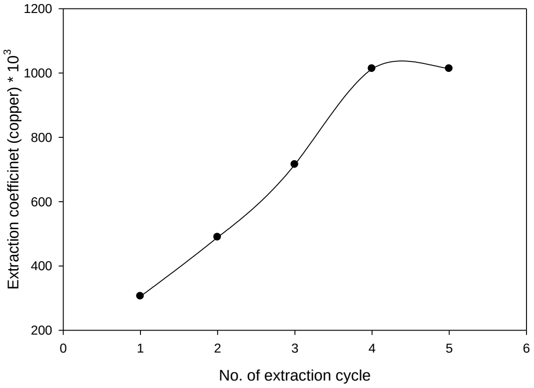

Fig. 22, Extraction coefficient versus No. of extraction cycle at water-15 % acetic acid solution, 140o C temperature, 300 rpm agitation speed and 20 min mixing time

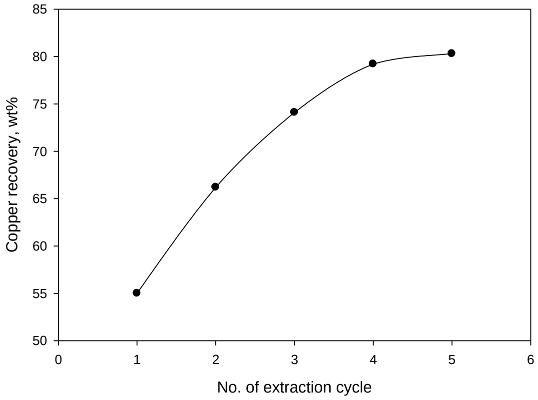

Fig. 23, Copper recovery versus No. of extraction cycle at water-15 % acetic acid solution, 140o C temperature, 300 rpm agitation speed and 20 min mixing time

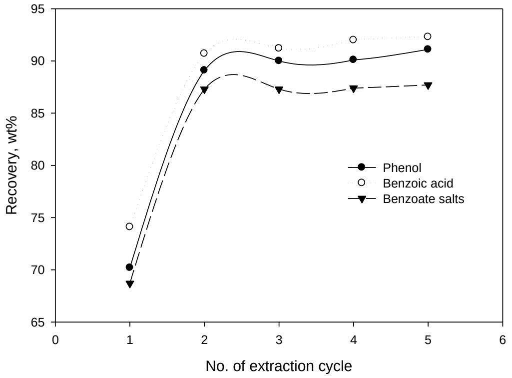

Fig. 24, Desirable components recovery versus No. of extraction cycle at water-15 % acetic acid solution, 140o C temperature, 300 rpm agitation speed and 20 min mixing time

Conclusions

It may be concluded that:

1. It was found that water-15 % acetic acid is an active solvent for the catalyst (copper) and desirable component (phenol, benzoic acid, benzoate salts) recovery and to achieve clear phase separation of tar from the aqueous acid.
2. The highest recovery of catalyst (80.2 wt%) was achieved under the conditions of 300 rpm agitation speed, 20 minute agitation time, 140^o C temperature, 4/1 phase ratio (A/O) and 4 extraction cycle.
3. The highest recovery of phenol (89.1 wt%), benzoic acid (90.7 wt%) and benzoate salts (87.3 wt%) was achieved under the condition of 300 rpm agitation speed, 20 minute agitation time, 140^o C temperature, 4/1 phase ratio (A/O) and 2 extraction cycle.

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