

Catalytic Wet Air Oxidation of Phenol in a Trickle Bed Reactor

Wadood T. Mohammed, Sama M. Abdullah, and Atheer M. Ghalib

Chemical Engineering Department - College of Engineering - University of Baghdad - Iraq

Abstract

Catalytic wet air oxidation of aqueous phenol solution was studied in a pilot plant trickle bed reactor using copper oxide catalyst supported on alumina and silica. Catalysts were prepared by impregnating method. Effect of feed solution pH (5.9, 7.3, and 9.2), gas flow rate (20%, 50%, 80%, and 100%), WHSV (1, 2, and 3 h⁻¹), temperature (120°C, 140°C, and 160°C), oxygen partial pressure (6, 9, 12 bar), and initial phenol concentration (1, 2, and 4 g/l). Generally, the performance of the catalysts was better when the pH of feed solution was increased. The catalysts deactivation is related to the dissolution of the metal oxides from the catalyst surface due to the acidic conditions. Phenol oxidation reaction was strongly affected by WHSV, temperature, oxygen partial pressure, and initial phenol concentration. While gas flow rate had a marginal effect.

Keywords: oxidation of phenol, trickle bed reactor.

Introduction

Disposal of wastewater is acquiring increasing importance all over the world; due to the progressively more restrictive environmental constrains⁽¹⁾. Phenol commonly appears in aqueous effluents from sources such as petrochemical, chemical, and pharmaceutical industries⁽²⁾. The importance of phenol in water pollution stems from their extreme toxicity to the aquatic life and resistance to biodegradation. Phenol imparts a strong disagreeable odor and taste to water even in very small concentration⁽³⁾. Moreover, phenol and its derivatives are powerful bactericides which prevents them from being treated in classical sewage processing plants even at concentrations as low as 50 g/l⁽⁴⁾. As one of wastewater abatement technologies, wet air oxidation (WAO) emerges recently and non-biodegradable industrial effluents⁽⁵⁾. In WAO, air or pure oxygen is used to oxidize refractory pollutions either dissolved or suspended in water⁽⁶⁾. However, wet oxidation of wastewater without the aid of catalyst, is usually conducted at very high temperature and pressure, thus, leading to high equipment and operation costs⁽⁷⁾. The oxidation of organic aqueous solutions over a solid catalyst has been shown to be a useful and inexpensive non-conventional treatment process⁽⁸⁾. Nevertheless, the development of a satisfactory catalyst for this process has

been reported yet. Such catalyst should be able to oxidize low concentrations in aqueous media and possess resistance to inactivation by leaching⁽⁹⁾. Unfortunately, the lack of catalysts which are active and durable under these process conditions has largely prevented CWO from being implemented for environmental remediation⁽¹⁰⁾. Supported copper oxide catalysts have frequently been tested for the wet oxidation of organic compounds⁽¹¹⁾. Despite the fact that copper-based catalysts are very active in batch processes, tests using continuous reactors reveal that there is a substantial loss of activity due to the dissolution of the catalytic species in the acidic reactive medium⁽¹⁾. These apparently contradictory results can be explained by the different duration of the tests. For instance, in continuous reactors, the tests usually runs for several days, while, in batch experiments, the reaction only occurs for a few hours, which is too short a period for finding significant activity changes⁽¹⁰⁾.

Experimental Work

Material and catalyst preparation

The phenol used as reagent was purchased from Griffin. High purity synthetic air was used as oxidant.

Deionized water was used to prepare catalyst and different aqueous solutions. Glass balls were used in the tests with inert material. γ -alumina or silica were used as supports for the copper. Copper nitrate from Fluka was used as active component. Zinc nitrate, and nickel nitrate from BDH Chemicals Ltd. were used as promoters.

Copper-based catalyst was prepared using γ -alumina as support. The alumina, which was supplied as spheres of 2.5 mm diameter, was dried for 4 h at 110°C. The catalyst was made with a copper oxide loading of 10% and prepared by the pore volume impregnation method using aqueous solutions of copper nitrate (26 g copper nitrate dissolved in 45 ml hot deionized water) for impregnating the support. Later, the catalyst was dried at 110°C overnight, followed by calcining at 400°C for 8 h with air. The same procedure was followed to prepare one catalyst supported over silica, also with a copper oxide loading of 10%, and two catalysts supported over γ -alumina with a copper oxide loading of 10%, and 2% of zinc oxide and nickel oxide. Table 1 lists the main physical characteristics of different catalysts prepared and supports used.

Table 1. The main physical characteristics of different catalysts prepared and supports used.

Catalyst	γ -Al ₂ O ₃	Silica	Cat.1	Cat.2	Cat.3	Cat.4
Active phase (CuO), %	-	-	10	10	10	10
Promoter (ZnO), %	-	-	-	-	2	-
Promoter (NiO), %	-	-	-	-	-	2
Support	-	-	γ -Al ₂ O ₃	SiO ₂	γ -Al ₂ O ₃	γ -Al ₂ O ₃
Calcinations temperature, °C	-	-	400	400	400	400
Pore volume, cm ³ /g	0.44	0.486	0.356	0.374	0.35	0.352
Bulk density, g/cm ³	0.68	0.62	0.746	0.704	0.752	0.748
Surface area, m ² /g	289	750	251	593	235	237

Experimental set-up and procedure

The continuous oxidation of phenol was carried out in a packed bed reactor. The fixed bed reactor consists of a SS-316 tubular reactor, 80 cm long and 1.9 cm inner diameter and controlled automatically by four sections of 15 cm height steel-jacket heaters. Independent inlet systems for gas and liquid feed allow working at various liquid to gas flow rate ratios.

The liquid feed is stored in a feed tank, which is connected to a high-pressure metering pump (dosing pump) that can dispense flow rates between 0 and 15 ml/min at constant pressure. The air oxidant comes from a high pressure cylinder equipped with a pressure controller to maintain the operating pressure constant. A flow-meter coupled with a high precision valve is used to measure and control the gas flow rate. The liquid and gas streams are mixed and then entered to the reactor at the required temperature. The mixture flows along the bed packed with 85 cm³ (30 cm height) of the catalyst

enclosed between two layers of inert material (also a flexible grid put at the top and bottom of the reactor to prevent movement of particles). The exited solution goes to a liquid-gas separation and sampling system, regularly, liquid samples were withdrawn for analysis. Figure 1 illustrated the experimental setup.

To verify that only the catalyst causes the oxidation of the phenol, two tests were made using an inert material (silica and γ -alumina). In both cases, the phenol removal was negligible, less than 0.1 %, which falls within the experimental error.



Fig. 1, Experimental setup

pH-adjustment

The pH of 4 g/l phenol solution is slightly acid, about 5.9. However, for both tests of pH 7.3 and 9.2, the feed solution was adjusted by adding sodium hydroxide solution. To measure pH of the solution OAKION PH2100 Series was used. The procedure was summarized as following:

1. pH meter was calibrated previous to use by using Buffer solutions.
2. Measuring the pH of 4 g/l phenol solution.
3. Adding particular quantities of NaOH solution to the 4 g/l phenol solution according to the titration method to obtain solutions of pH 7.3 and 9.2.

Products analysis

To analysis phenol concentration in the outlet samples, Shimadzu model UV-160A ultraviolet/visible spectrophotometer was used. The intermediate

compounds are determined by gas Liquid chromatography analysis (PYE UNICAM). The apparatus consists of a stainless steel capillary column with 5 m long and 0.25 mm inside diameter (SE-30) name type, packing with silica; and column temperature programming from 343 to 423 K for C₂ to C₆ analysis. The carrier gas is nitrogen flowing at 12 cm³/min.

Phenol conversion, X_{ph}, will be used as the main parameter for comparing the results, X_{ph} is defined as:

$$X_{ph} = \frac{[Ph]_{in} - [Ph]_{out}}{[Ph]_{in}} \quad (1)$$

Results and Discussion

Determination of the most Active Catalyst

Figure 2 presents a comparison of the activities of the prepared catalysts. All four catalysts show similar behavior. The necessary time to reach this steady state conversion (induction period) is smaller for all catalysts. This is due to the high temperature and oxygen partial pressure used in this study, in addition to the using of packed bed continuous reactor. Also, it can be seen that phenol conversion for these catalysts started from low values after that reaches to high values. That observed difference in phenol conversion can be explained by the effect of sequence of initial exposure of the catalyst to the reactant. The catalyst can be ranked as follows in terms of activity in phenol oxidation.

$$Cat.4 > Cat.3 > Cat.1 > Cat.2$$

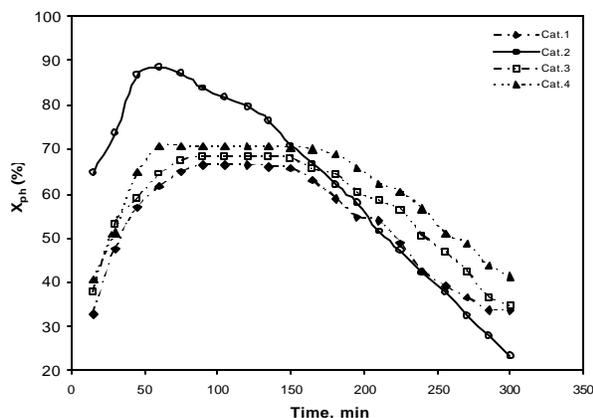


Fig. 2, Comparison of the activities of the catalyst. Reaction conditions: feed solution pH=5.9, S.E. = 50 %, WHSV= 2h⁻¹, T=140°C, P_{O₂}= 6 bar and C_{ph}= 4 g/l

The evolution of the catalytic activity for Cat.1, Cat.3 and Cat.4 that appear in the figure 2 has been related to the presence of two different species of copper attached to the alumina surfaces. The first would be more active

but also less stable in the reaction conditions. On the other hand, the second species would be more stable and responsible for the residual activity of the catalyst. X-Ray characterization of the catalysts proved that these species are respectively "free" copper oxide and nonstoichiometric copper aluminates. It is well-known that most metal oxides, as copper oxide, dissolve in hot acidic media such as the one existing in the reactor. On the other hand, the treatment at high temperature, e.g. a calcinations temperature of 400°C, of a mixture of copper and aluminum oxides forms copper aluminates that is more resistant to the acidic medium but is less catalytically active than the "free" copper oxide.

Catalyst deactivation has been related to attack on the catalyst by the extremely hot acidic medium where the oxidation takes place. The acidic medium is provided by the phenol itself because it is capable of dissociating to form phenolate; however the partial oxidation products are the main cause of the total acidity of the aqueous reaction system. The intermediates in the phenol oxidation have been found to be mainly mono and dicarboxylic acids such as oxalic, acetic or formic acid.

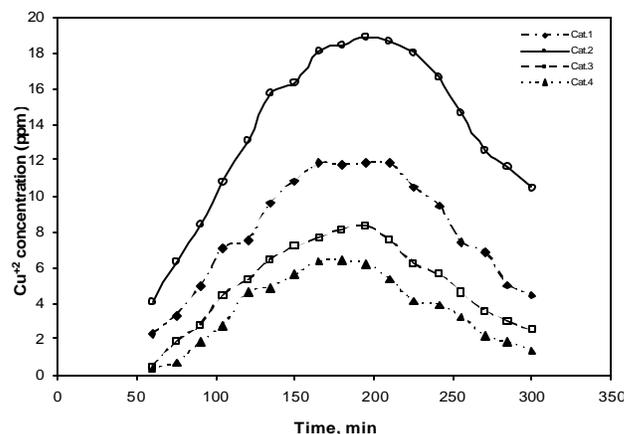


Fig. 3, Copper concentration profile in the reactor effluent. Reaction conditions: feed solution pH=5.9, S.E. = 50 %, WHSV= 2h⁻¹, T=140°C, P_{O₂}= 6 bar and C_{ph}= 4 g/l.

One possible reason for the catalyst deactivation could be the dissolution of the metal oxides in the acidic medium. This speculation is proved by figure 3 for the Cat.1, Cat.2, Cat.3, and Cat.4 respectively, which shows the Cu⁺² concentration in the outlet stream through the activity test. At first, the rate of dissolution of copper oxide rapidly increases until giving a maximum Cu⁺² concentration (11.8, 18.9, 8.29, and 6.4 ppm) for the catalysts Cat.1, Cat.2, Cat.3, and Cat.4 respectively. This behavior agrees with the presence of the two different species, the "free" copper oxide being easily dissolved during the first hours. The possibility that deposition of phenol condensation products on the catalyst surface causes the catalyst deactivation was rejected. This may be

directly related to use of packed bed as reacting system, which its conditions (high catalyst to liquid ratio) favor the heterogeneous reactions rather than homogenous reactions, which enable the formation of polymers, due to the high contact surface.

Therefore, the catalyst (Cat.2) was prepared using silica as support in order to find whether or not a different support for the copper oxide could improve the resistance against leaching. Cat.2 shows very characteristic trends, it has a short induction period in which the phenol conversion increases until it reaches a maximum conversion. Then, it loses its activity very fast and progressively approaching 23.4 %. This behavior could be explained by the existence of only "free" copper oxide linked to the silica, which is easily and continuously dissolved during the activity test. In this case, copper cannot form aluminates and all the copper loading is present as copper oxide. Thus, due to the higher activity of this species, Cat.2 renders a higher peak of conversion but the leaching is substantially more important.

The influence of promoter's metal oxides on the phenol oxidation reaction was studied too. These promoters (ZnO and NiO) have the advantages of, changing the vulnerability of the copper oxide poisoning; protect the active metal against over-oxidation. Although the very different sources and compositions of these catalysts make it very difficult to compare their respective performances.

Effect of Feed Solution pH

The previous results demonstrate the intrinsic relationship between the catalyst activity and feed solution pH. In order to examine the influence of the pH on the ability of catalysts to oxidize phenol, various tests at different pHs were conducted for Cat.2 and Cat.4

Figure 4 illustrates the dependence of the phenol conversion upon the feed solution pH using Cat.4. Where was used feed solution with pHs 7.3 and 9.2 in addition to unmodified phenol solution (pH=5.9). As can be seen, the behavior of this catalyst maintains the general trends given by Cat.4 regardless of the pH, so two different activity zones are observed. In the first zone (steady state zone), the catalyst shows high activity for a short period in which the phenol conversions nearly reach higher value. Then after a progressive fall, the phenol forms a second zone (falling rate zone). The loss in catalytic activity can be delayed by increasing the pH but, in turn, the residual conversion lower at high basic solution. Thus at pH=5.9, the residual phenol conversion is slightly higher than 41.38 % and decrease to 40 % and 37 % at pHs 7.3 and 9.2 respectively.

As discussed above, the two zones can be explained because of the two different copper species over the alumina surface, both with different catalytic activity. The decrease in activity occurs when the most active

copper oxide dissolves. Because of their characteristics, these oxides dissolve more slowly as pH increases, so the first zone is longer in the basic medium. However, the remaining conversion is also lower, which is opposite to what could be expected. A probable explanation for this lower conversion is that basic medium interferes with the catalyst during the induction period, giving less active catalysts.

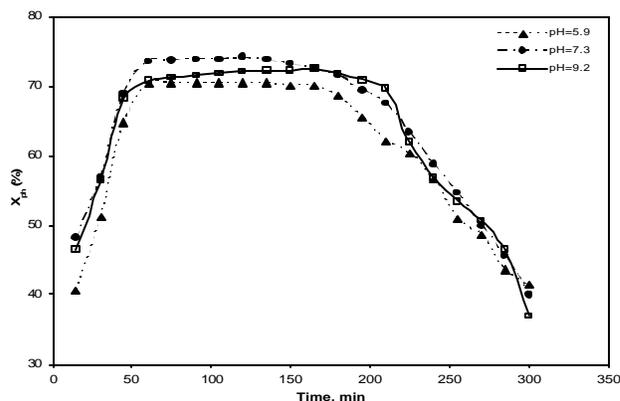


Fig. 4, Effect of feed solution pH on phenol oxidation. Reaction conditions: type of catalyst= Cat.4, S.E. = 50%, WHSV=2 h⁻¹, T=140°C, P_{O2}= 9 bar, and C_{ph}= 4 g/l.

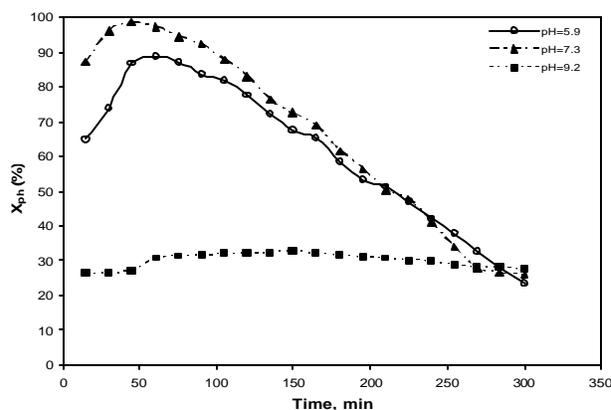


Fig 5, Effect of feed solution pH on phenol oxidation. Reaction cond.: type of catalyst= Cat.2, S.E. = 50%, WHSV=2 h⁻¹, T=140°C, P_{O2}= 9 bar, and C_{ph}= 4 g/l.

The influence of the feed solution pH on the catalytic activity was also tested for Cat.2 at higher pHs (7.3 and 9.2) in order to improve the activity or decrease the leaching of copper for this catalyst. Figure 5 displays the phenol conversion profiles over Cat.2 feeding these solutions at 5.9, 7.3, and 9.2.

At feed pH of 7.3, the induction period almost short giving an initial conversion 98.43 %. Then, the conversion goes steadily down, which indicate that this pH doesn't completely prevent the copper oxide from being dissolved. The reason for this behavior is that,

although the inlet pH is basic, the outlet pH is still acid. The induction period nearly disappears for run in which the feed solution was fixed at pH 9.2. It should be pointed out this case has almost constant phenol conversion throughout the test; the phenol conversion is nearly 27.67 %. Thus, the higher pH, the higher the remaining phenol conversion, so the inlet pH clearly affects catalyst activity. This can be explained by the different rates of dissolution of copper oxide in the aqueous solution. The solubility of any metal oxide is usually higher at low pH than at higher pH. Hence, in run of pH 5.9, the rate of copper oxide dissolution should be the highest. A visual inspection at the end of the test certainly should an intense de-coloration was less important as the pH increased, which proves that a high pH prevents the leaching of copper.

Nonetheless, it is difficult to discern whether or not the different remaining conversion is only due to the different rate of catalyst deactivation or there is also some change in the mechanism reaction. It has been shown that phenolate ion is much more reactive than phenol in basic media so the reaction occurs faster and gives a better phenol conversion. However, both show similar reaction rates in acidic media because the phenolate concentration is very low. At high pH (i.e. pH=9.2), the phenolate form predominates in comparison with the un-dissociated phenol. Therefore, the higher remaining conversion observed for experiment of pH=9.2 could also be due to the higher reactivity of the phenolic species present.

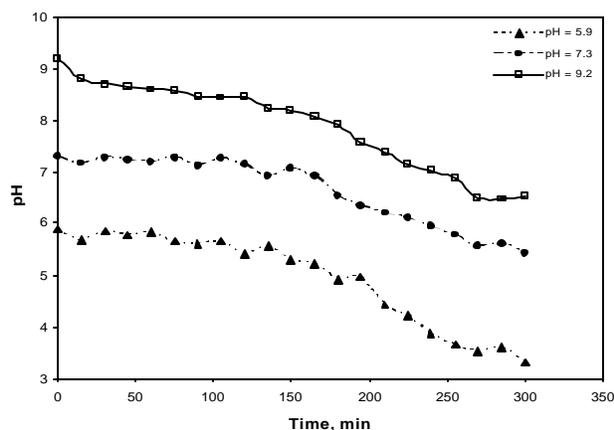


Fig. 6, Evolution of the effluent pH for Cat.4 at different feed solution pH. Reaction conditions: S.E. = 50%, WHSV=2 h⁻¹, T=140°C, P_{O2}= 9 bar, and C_{ph}= 4 g/l.

Figures 6, 7 show the pH evolution of the outlet effluents produced for both Cat.2 and Cat.4. Note that the inlet pH is 5.9, which correspond to a phenol solution of 4g/l. In general terms, the trends of pH evolution for Cat.2 at different pHs are the same as for Cat.4 except at pH=9.2. As can be seen, the pH of the reaction effluent

considerably varies throughout the test. It must be noted that, in the first zones, the pHs are nearly steady around 5.66, 7.23, and 8.64, when the phenol conversion's are about 70.5 %, 74 % and 72 % respectively. Likewise, in the second zones, when the phenol conversions reach to 43.67 %, 48.6 % and 52.5 %, the pHs are close to 3.67, 5.56 and 6.51 respectively. In addition, the rapid fall in phenol conversion coincides with the decrease in the pH, but also with the highest leaching of copper, which proves that a good correlation can be established between them.

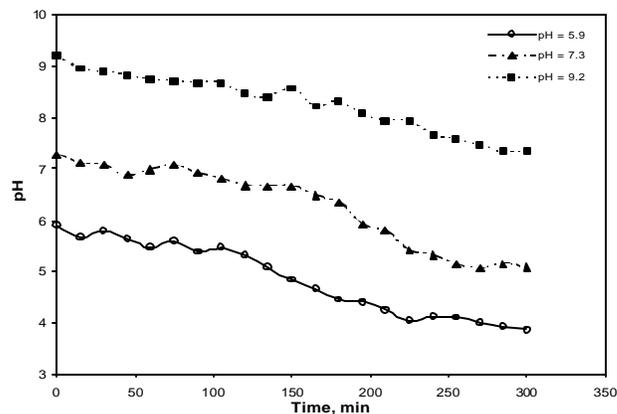


Fig. 7, Evolution of the effluent pH for Cat.2 at different feed solution pH. Reaction conditions: S.E. = 50%, WHSV=2 h⁻¹, T=140°C, P_{O2}= 9 bar, and C_{ph}= 4 g/l.

Effect of gas flow rate

Figure 8 presents the influence of gas flow rate, which can be expressed as stoichiometric excess (S.E.), on phenol conversion. Although phenol conversion appeared to be slightly sensitive to gas inlet velocity, but phenol conversions were improved when the inlet velocity increased and after that decrease with further increasing in the gas inlet velocity.

The results above show that an increasing gas flow rate to 80 % S.E. causing decreasing in the liquid hold up and liquid film thickness covered catalyst surface, and enhancing oxygen transfer to the liquid phase, and from the liquid phase to the catalyst surface, therefore lead to high conversion. But increasing S.E. to 100 % causes decreasing phenol conversion because of decreasing the spreading of the liquid film over catalyst hence wetting decrease. In addition, increasing S.E. over 80 % provides a sufficient quantity of oxygen for competitive reactions of intermediate over catalyst active sites forming undesirable compounds causing deactivation of catalyst. At high S.E. (i.e. 100 %) both p-benzoquinone and maleic acids were detected in high concentration in the brownish colored liquid effluent.

Also, it can be seen that when insufficient oxygen was fed, the reaction was dominated by the formation of low molecular weight carboxylic acids, which corresponds to the observed low pH.

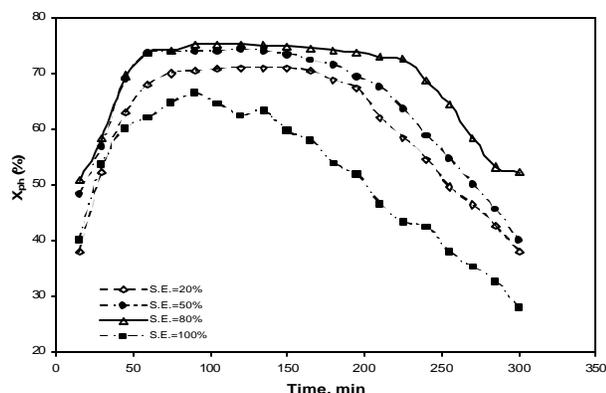


Fig. 8, Effect of gas flow rate on phenol oxidation. Reaction cond.: type of catalyst= Cat.4, feed solution pH = 7.3, WHSV = 2 h⁻¹, T = 140°C, P_{O2} = 9 bar and C_{Ph} = 4 g/l

Effect of WHSV

Figure 9 presents that the liquid flow rate has a large effect on phenol conversion. So as liquid flow rate increases, phenol conversion decreases, this due to reduce the space time of reactant in the reactor (i.e. reducing the time required for phenol reaction with oxygen over the catalyst). Moreover, higher liquid flow rates give greater liquid hold up which evidently decreases the contact of liquid and gas reactants at the catalyst active site, by increasing the film thickness. While at low liquid flow rate, the liquid resides in the column for a longer time, and therefore undergoes more conversion.

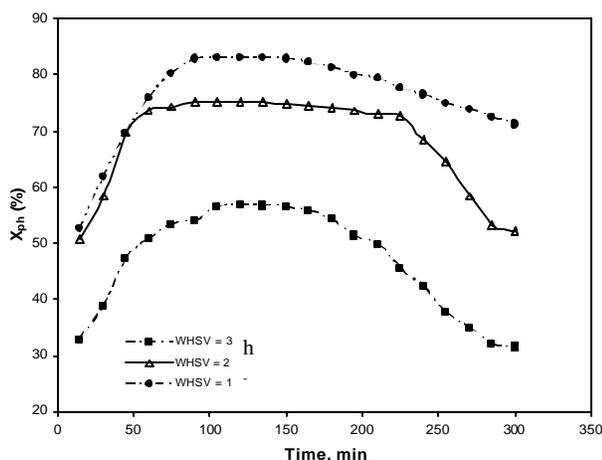


Fig. 9, Effect of WHSV on phenol oxidation. Reaction cond.: type of catalyst= Cat.4, feed solution pH = 7.3, S.E. = 80%, T = 140°C, P_{O2} = 9 bar and C_{Ph} = 4 g/l

Effect of temperature

The general behavior is, higher conversion is achieved at higher temperature due to the fact that at higher temperature kinetic constant (rate constant) is favorably affected resulting an increasing in phenol conversion, according to Arrhenius equation:

$$K = A \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

Also, at high temperatures in aqueous solutions, the form in which oxygen participates in chemical reactions is complex. The elevated temperatures necessary can lead to the formation of oxygen radicals, O[•], which in turn can react with water and oxygen to form peroxide, H₂O₂, and ozone, O₃, so that these four species O[•], O₂, O₃, and H₂O₂ are all capable of participating in the phenol oxidation.

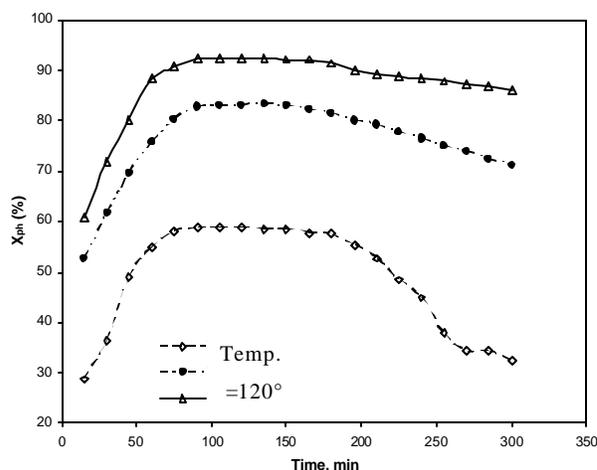


Fig. 10, Effect of temperature on phenol oxidation. Reaction cond.: type of catalyst= Cat.4, feed solution pH = 7.3, S.E. = 80%, WHSV = 1 h⁻¹, P_{O2} = 9 bar and C_{Ph} = 4 g/l

Effect of oxygen partial pressure

Effect of oxygen partial pressures was illustrated in figure 11. Compared to temperature, oxygen partial pressure has less influence on the phenol conversion. It can be seen from figure 11, increasing oxygen partial pressure from 6 bar to 12 bar resulted an increasing in phenol conversion from 87.3 % to 97.84 %, while increasing temperature from 120 to 160°C causes increasing in phenol conversion from 58.6 % to 92.4 %.

In general, an increasing oxygen partial pressure causes an increasing in phenol conversion. In addition, elevated pressure is required in such process, increasing pressure increases the density of gas and it's solubility in the aqueous solution. Also, an increasing in gas pressure may be provide a lateral push force for the reactants to cover as much surface area over catalyst as possible.

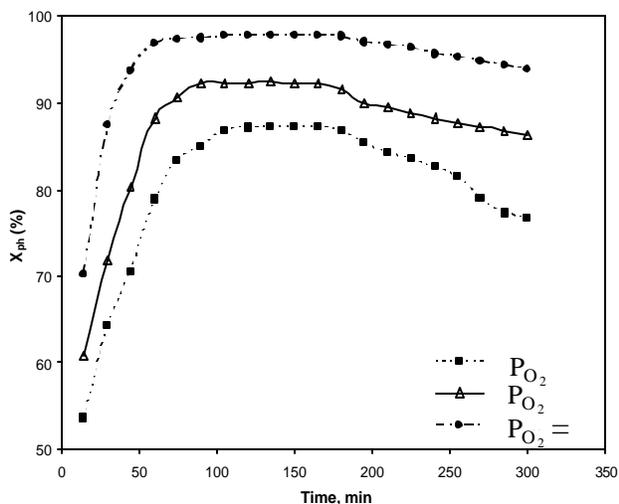


Fig. 11, Effect of oxygen partial pressure on phenol oxidation. Reaction conditions: type of catalyst= Cat.4, feed solution pH = 7.3, S.E. = 80 %, WHSV = 1 h^{-1} , $T = 160^\circ\text{C}$ and $C_{ph} = 4 \text{ g/l}$

Effect of initial phenol concentration

In the range of these experiments phenol conversion decreases by decreasing inlet phenol concentration illustrated in figure 12. This can be attributed to decrease phenol molecules coverage the active site over the catalyst surface. This allows adsorbing the intermediates over vacancy active sites and under the elevated conditions during oxidation process; these intermediates are converted to undesirable deposits. These deposits which cause catalyst deactivation can be indicated by observed changing catalyst color at the end of the oxidation process.

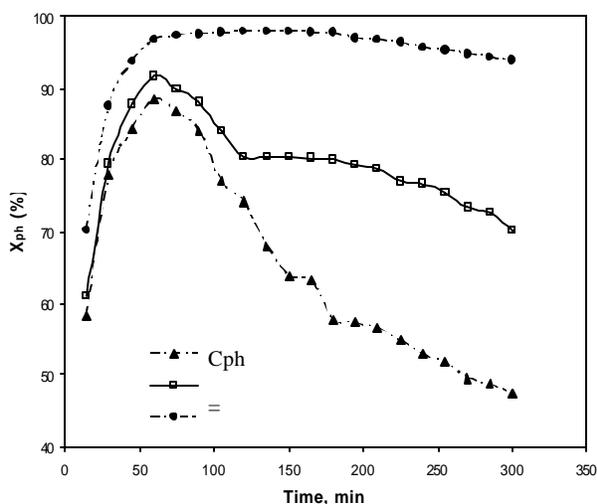


Fig. 12, Effect of initial phenol concentration on phenol oxidation. Reaction conditions: type of catalyst= Cat.4, feed solution pH = 7.3, S.E. = 80 %, WHSV = 1 h^{-1} , $T = 160^\circ\text{C}$ and $P_{O_2} = 12 \text{ bar}$

Conclusions

1. The highest phenol conversion (97.84%) was achieved over the catalyst ($\text{CuO.NiO/Al}_2\text{O}_3$) under the conditions of [feed solution pH=7.3, S.E. =80%, WHSV= 1 h^{-1} , temperature= 160°C , oxygen partial pressure=12 bar, and initial phenol concentration=4 g/l].
2. It was found that the catalyst composition of ($\text{CuO.NiO/Al}_2\text{O}_3$) is the active one among the other prepared catalysts. The following order is observed. $\text{CuO.NiO/Al}_2\text{O}_3 > \text{CuO.ZnO/Al}_2\text{O}_3 > \text{CuO/Al}_2\text{O}_3 > \text{CuO/SiO}_2$
3. The catalysts show fall in activity when feed solution pH is low regardless the support. After variable period, the alumina-support activity remains stable due to present two active species i.e. copper oxide and copper aluminates. In Contrast, the silica-support activity decreases sharply until the phenol conversion is negligible due to present only copper oxide.
4. It was found that phenol conversion increases with increasing gas flow rate until (S.E. =80%), after that decreases with increasing gas flow rate.
5. It was found that phenol conversion increases (56.8% - 83.25%) as weight hour space velocity (WHSV) decreases ($3-1 \text{ h}^{-1}$).
6. Increasing reaction temperature causes enhancement in phenol conversion, and activity of catalyst.
7. Increasing oxygen partial pressure (6-12 bar) causes increasing in phenol conversion (87.3% -97.84%).
8. As phenol concentration decrease, phenol conversion decrease at constant catalyst bed height.

Nomenclature

A	pre-exponential factor (case dependent units)
E_a	Activation energy J / mol
K	rate constant(case dependent units)
R	Universal gas constant, 8.314 J / mol. K
t	Time h
T	Temperature K
X_{Ph}	Conversion of phenol

References

1. Miro, C., Alejandre, A., Fortuny, A., Bengoa, C. Font, J. and Fabregat, A., *Water Research*, 33, 1005-1013 (1999).
2. Fortuny, A., Miro, C., Font, J. and Fabregat, A., *Catalysis today*, 48, 323-328 (1999).
3. Singh, A., Pant, K. K. and Nigam, K. D. P., *Chemical Engineering Journal*, 103, 51-57 (2004).

4. Fortuny, A., Bengoa, C., Font, J. and Fabregat, A., *A Journal of Hazardous Materials*, 64, 181-193 (1999).
5. Wu, Q., Hu, X., Yue, P.L., *Chemical Engineering Science*, 58, 923-928 (2003).
6. Eftaxias, A., Font, J., Fortuny, A., Giralt, J., Fabregat, A. and Stuber, F., *Applied Catalysis- B: Environmental*, 33, 175-190 (2001).
7. Wu, Q., Hu, X., Yue, P.L., Zhao, X.S., Lu, G.Q., *Applied Catalysis B: Environmental*, 32, 151-156 (2001).
8. Fenoglio, R., Rolandi, P., Massa, P. Ganzalez, J. and Haure, P., *Reactor, Kinetic and Catalysis Letters*, 31, 83-90 (2004).
9. Massa, P.A., Ayude, M.A., Fenoglio, R.J., Gonzalez, J.F. and Haure, P.M., *Latin American Applied Research*, 34, 133-140 (2004).
10. Fortuny, A., Font, J. and Fabregat, A., *Applied Catalysis- B: Environmental*, 19, 165-173 (1998).
11. Fortuny, A., Ferrer, C., Bengoa, C., Font, J. and Fabregat, A., *Catalysis today*, 24, 79-83 (1995).