

## Catalytic Oxidation of Phenol in Aqueous Solution

Murat HARMANKAYA, Gönül GÜNDÜZ\*

Department of Chemical Engineering, Ege University, Bornova, Izmir-TURKEY

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**Abstract:** The oxidation of phenol in aqueous solution over a supported copper oxide, zinc oxide catalyst was studied at atmospheric pressure. The reaction involved an introduction period and a steady-state-activity regime, both of the regimes exhibiting first-order behavior with respect to the phenol concentration. The rates decreased as the catalyst concentration increased which implies that the reaction involves a heterogeneous-homogeneous free-radical mechanism. The rate constants  $k_1$  and  $k_2$  for the initial rate and steady-state-activity regime are represented by  $k_1=1.3*10^{10} e^{-93/RT}$  and  $k_2=2.0*10^{-4} e^{-47/RT}$ , respectively, where R is in kJ/mol K.

**Key Words:** Catalytic Oxidation, Phenol, Destruction, Heterogeneous Reaction.

### Sulu Çözeltide Fenolün Katalitik Oksidasyonu

**Özet:** Taşıyıcılı bir çinko oksit, bakır oksit katalizörü üzerinde atmosfer basıncında fenolün oksidasyonu incelenmiş ve reaksiyonun, her ikisinde fenol derişimine göre birinci mertebeden davranış gösteren bir başlangıç periyodu ile bir kararlı hal aktivite rejimi içerdiği gözlenmiştir. Katalizör derişimi arttıkça hız azalmıştır. Bu, reaksiyonun heterojen-homojen bir serbest radikal mekanizması içerdiğini destekler. Başlangıç hızı ve kararlı hal aktivite rejimleri için hız sabitleri  $k_1$  ve  $k_2$  hesaplanmış ve R, kJ/mol K cinsinden olmak üzere sırası ile  $k_1=1.3*10^{10} e^{-93/RT}$  ve  $k_2=2.0*10^{-4} e^{-47/RT}$  olarak bulunmuştur.

**Anahtar Sözcükler :** Katalitik Oksidasyon, Fenol, Parçalanma, Heterojen Kataliz.

### Introduction

The petrochemical, chemical and pharmaceutical industries produce waste waters containing organics, such as phenols, which are extremely toxic to aquatic life. It is difficult to oxidize them biologically, since biological processes are very time-consuming and operate well only in the case of relatively dilute wastes. Chemical oxidation of phenolic wastes offers an alternative treatment method when the phenol concentration is too high for direct biological systems. When effluent is also present at higher temperatures, the use of chemical oxidation especially may be favored, Pintar and Levec (1972), Sadana and Katzer (1974), Kulkarni and Dixit (1991). Apart from biological and chemical oxidation processes, several systems, such as wet-air oxidation, photo-assisted catalytic destruction and deep-well oxidation are known to have great potential in advanced waste-treatment facilities, Pruden and Le (1976), Randell and Knopp (1980), Chang and Lin (1993), Wei and Wan (1991), Lovo et al. (1990).

The oxidation of phenol has been carried out with pure oxygen, ozone gas,  $H_2O_2$ , permanganate, chlorine and hypochlorite at atmospheric and above atmospheric pressures over several catalysts, such as manganese dioxide, Hamilton et al. (1969), zinc aluminate promoted with at least one of the following: copper, nickel, manganese, bismuth, platinum, palladium, iridium, rhenium, cerium and lanthanum Box et al. (1974); or over supported copper oxide, Sadana and Katzer (1974 a, 1974 b), Ohta et al. (1980). Devlin and Harris (1984) used the stopped-flow technique in the oxidation of aqueous phenol. Hamilton et al. observed that the reactor wall has to be of essentially non-electroconducting materials to obtain efficient oxidation rates.

In studies of the oxidation of aqueous phenol, two distinct periods namely, an induction period and a steady-state-activity regime have been observed. The length of the induction period was found to depend on the process conditions, such as temperature, oxy-

\* Author to whom correspondence should be addressed.

gen partial pressure and catalyst loading. An increase in these parameters drastically decreased the length of the induction period. It was reported that the induction period could be completely eliminated when a sufficiently high partial pressure of oxygen was used, Kul-karni and Dixit (1991). Sadana and Katzer (1974 a, 1974 b) found that the reaction was first order with respect to the phenol concentration in both regimes, but the oxygen dependency decreased from first- to one-half order in shifting from the induction period to the steady-state-activity regime. The rate exhibited behaviour other than first order with respect to catalyst loading. The unusual dependence on catalyst loading was explained by a homogeneous-heterogeneous free-radical mechanism. This mechanism in the oxidation of aqueous phenol was supported by the studies of Pintar and Levec (1992 a, 1992 b) in a slurry system over a catalyst comprising CuO, ZnO and gamma-alumina above atmospheric pressure at up to 13 bars. Their rate measurements showed that the reaction progressed autocatalytically. Pintar and Levec (1994) also studied the liquid-phase oxidation of phenol in a differential liquid-filled operated fixed-bed reactor over a zinc, copper and cobalt-oxide catalyst. The proposed intrinsic-rate expression for the phenol disappearance was based on the Langmuir-Hinshelwood kinetic approach. Although the oxidation rates of aqueous phenol in atmospheric-pressure conditions are too slow to be of practical interest, more kinetic and mechanistic studies are needed to develop an effective catalytic process for purifying industrial waste waters containing phenol.

The purpose of this research was to study the oxidation of aqueous phenol at atmospheric pressure in detail, that is, to investigate the effects of parameters such as temperature, oxygen-feed rate, stirring speed, catalyst and initial phenol concentrations on phenol oxidation over the active catalyst chosen and to develop a rate equation for the reaction.

## Experimental

### Catalyst Preparation

Five different catalysts were prepared, employing  $Al_2O_3$  and silicagel as carriers in order to determine the most effective catalyst for the catalytic oxidation of phenol. The compositions of the catalysts prepared are presented in Table 1.

Catalyst A used here was prepared as follows: copper oxide (Merck) and zinc oxide (Merck) were dispersed in 100 ml. of distilled water at 50 °C and

Table 1. The Composition of the Catalysts Prepared

Catalyst	Comp. of Act. ingre. wt%	Type of Carrier wt%
A	CuO, 47.2; ZnO, 52.8	$Al_2O_3$ , 11
B	CuO, 100.0	$Al_2O_3$ , 58
C	CuO, 100.0	Silicagel, 58
D	$MnO_2$ , 100.0	-
E	$V_2O_5$ , 1100.0	-

then a gamma-alumina carrier was added and the mixture was evaporated over a water bath with continuous stirring so that a thick paste formed. The paste was then dried in a 140 °C oven and activated in a 400 °C furnace overnight. Catalysts B and C were similarly prepared. In catalyst C, silicagel was used as the carrier and it was activated by treatment with a mixture of HCl and  $HNO_3$ , Tufan and Akgerman (1980).

### Experimental Setup

The runs were made in a four-neck, 250 ml. pyrex round-bottom flask. The necks housed a sampling tube, a contact thermometer, a sparger for oxygen introduction and a condenser connected to a gas-washing bottle open to the atmosphere. The gas-washing bottle contained NaOH solution of known concentration for the absorption of carbon dioxide (Figure 1). The flask was heated with a heating mantle and stirred magnetically. Oxygen was sparged at a metered rate into the liquid phase through a coil containing 18 holes, each 0.15 cm in diameter.

For a typical run, 250 ml. of water and a known weight of phenol and catalyst in powder form were loaded into the flask and heated to the desired temperature. The mixture was stirred vigorously, slurring the catalyst uniformly throughout the liquid. Cooling water was started and oxygen was sparged into the flask. Representative samples were withdrawn periodically using a syringe (Birgi) and the catalyst was separated from the aqueous phase by centrifugal forcing.

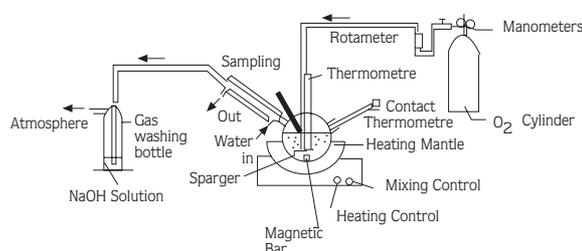


Figure 1. Experimental Set-up

The samples prepared were analysed with gas chromatography (GC), Hewlett-Packard 5980/series 2 on a capillary column (HP-5). A calibration curve was used to determine the unreacted phenol concentration in the reaction products in each run. The amount of  $\text{CO}_2$  generated during the experiment was determined by absorption in a NaOH solution of known concentration.

#### Determination of the Most Active Catalyst in Phenol Oxidation

Experiments were carried out with the same reaction conditions for each of the five catalysts prepared in order to determine the most active catalyst in phenol oxidation. The reaction conditions were as follows: initial phenol concentration: 4 g/l, catalyst concentration: 6 g/l, oxygen flow rate: 5 ml/s, temperature: 100 °C, stirring speed: 1200 rpm, pressure: 1 atm. The samples withdrawn periodically in each run were analysed with GC and the conversion of phenol (proportion of phenol eliminated) was plotted versus time for each catalyst prepared.

#### Effect of the Initial-Phenol-Concentration-to-Catalyst-Concentration Ratio

The catalytic oxidation of phenol over catalyst A was studied by varying the phenol concentration and catalyst loading in order to determine the effect of the phenol-to-catalyst ratio on conversion under the same reaction conditions, namely, at 373 K, with an oxygen flow rate of 5 ml/s and with a stirring speed of 1200 rpm. The experiments were carried out at phenol-to-catalyst ratios of 0.40, 0.50, 0.67, 1.50, and 2.00.

#### Effect of the Catalyst Concentration

At a constant initial phenol concentration (4 g/l) the effect of the catalyst concentration on the rates of the initial period and steady-state activity regime were studied at 373 K by varying the catalyst concentration from 2 g/l to 10 g/l.

#### Effect of the Oxygen Feed Rate

To determine the effect of the oxygen feed rate on phenol conversion, the reaction was carried out with different oxygen flow rates, 2.5, 5.0 and 10 ml/s, keeping the other parameters constant.

#### Effect of Stirring Speed

In slurry reactors, the reaction mixture is stirred vigorously in order to slurry the catalyst uniformly throughout the liquid. The preliminary experiments showed that adequate mixing was obtained at a mix-

ing speed of 1200 rpm. Hence, the stirring speed was kept constant at this value in all the experiments. However, in order to observe the effect of stirring speed on the phenol oxidation rate, experiments carried out with two different stirring speeds, 1200 rpm and 600 rpm, were compared.

#### Kinetic Analysis of the Catalytic Oxidation of Phenol

In the kinetic analysis of the reaction, the rate equations proposed by Sadana and Katzner (1974a) were tested. Equations 1 and 2 represent these equations for the initial rate and the rate in the steady-state-activity regime, respectively.

$$-\frac{V_l}{M_c} \frac{dC_{phx}}{dt} = k_1 \frac{C_{phx}}{(M_c/V_l)^{0.5}} \quad (1)$$

$$-\frac{V_l}{M_c} \frac{dC_{phx}}{dt} = k_2 \frac{C_{phx}}{(M_c/V_l)^3} \quad (2)$$

where  $M_c$ =weight of the catalyst (g),  $V_l$ =volume of the liquid ( $\text{cm}^3$ ) and  $C_{phe}$ =concentration of phenol ( $\text{mol}/\text{cm}^3$ ). If these equations are written in terms of conversion and  $-\ln(1-x)$  values are plotted versus time, the slope of the curve at  $x=0$ ,  $t=0$  gives  $k_1$  and the slope in the steady-state-activity regime gives  $k_2$ . For the effect of temperature on phenol oxidation, reactions were carried out at different temperatures, 100 °C, 90 °C and 70 °C, keeping the other variables constant.

## Results and Discussion

#### Determination of the Most Active Catalyst in Phenol Oxidation

Figure 2 presents a comparison of the activities of the catalysts prepared. It can be seen that the catalyst composed of only  $\text{V}_2\text{O}_5$  (Catalyst E) is the most active

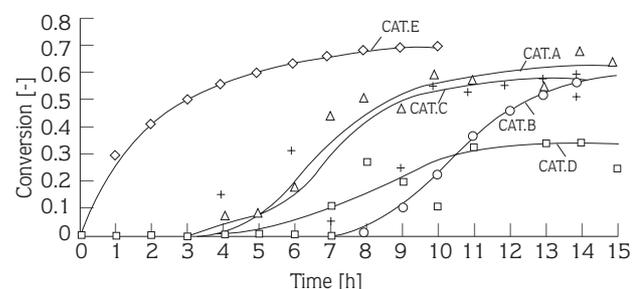


Figure 2. Comparison of the Activities of the Catalysts

one. The catalysts can be ranked as follows in terms of activity in phenol oxidation:

$$\text{Cat.E} > \text{Cat.A} > \text{Cat.C} > \text{Cat.B} > \text{Cat.D}$$

Since with Cat.E the reaction mixture became very difficult to stir due to the increasing gelation of  $V_2O_5$  with time, Cat.A (47.2% CuO, 52.8% ZnO in weight) was chosen as the most active catalyst in this study. Figure 2 shows that the reaction exhibits an induction period in which the rate of reaction increases with time until an apparent steady-state activity is reached. If the induction periods of the catalysts are compared, the following order is observed.

$$\text{Cat.B} > \text{Cat.D} > \text{Cat.A} > \text{Cat.C} > \text{Cat.E}$$

### The Effect of the Initial-Phenol-Concentration-to-Catalyst-Concentration Ratio

Figure 3 shows some of the  $-\ln(1-x)$  vs. time curves with different phenol-to-catalyst ratios. From Figure 3, it is clear that the induction period, defined experimentally as the time required to reach the steady-state-activity regime, decreases as the initial-phenol-concentration-to-catalyst-concentration ratio increases and it almost disappears after a phenol-to-catalyst-ratio of 1.5 is reached. For example, a comparison of curves 1 and 3 shows that the induction period is 4.5 h in the experiment with a phenol-to-catalyst ratio of 0.40 and in the experiment with a phenol-to-catalyst ratio of 1.00 the induction period is 2 h. The decrease in the length of the induction period with the phenol-to-catalyst ratio was also observed by Sadana and Katzer (1974a) in the oxidation of phenol in aqueous solution over copper oxide at atmospheric pressure.

### The Effect of the Catalyst Concentration

With a constant initial phenol concentration, the initial rate of phenol oxidation per gram of catalyst de-

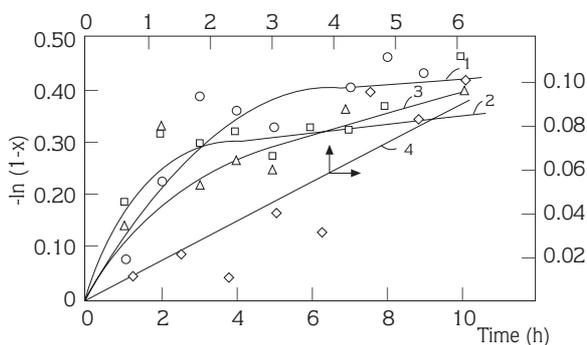


Figure 3.  $-\ln(1-x)$  vs. Time Curves at Phenol/Catalyst Ratio: for Curve 1  $(4/10) = 0.40$ ; for Curve 2  $(2/4) = 0.50$ ; for Curve 3  $(4/4) = 1.00$ ; for Curve 4  $(6/4) = 1.50$

creased sharply with increases in the catalyst concentration at low catalyst concentrations and became almost independent of catalyst concentration in higher concentrations. Similar behavior was observed in the steady-state-activity regime. Figure 4 shows these results. This unusual dependence on catalyst loading can be explained by the phenomena of a heterogeneous-homogeneous-reaction mechanism which was first proposed by Sadana and Katzer (1974 a, 1974 b). According to this mechanism, the reaction begins on the catalyst surface, and after the homogeneous propagation step, the chain carriers are destroyed by a homogeneous or heterogeneous termination process depending on the catalyst concentration.

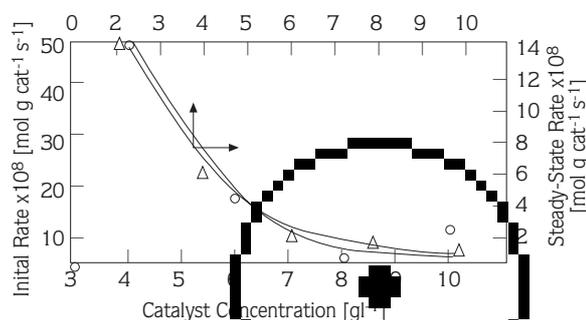


Figure 4. Effect of Catalyst Concentration on Rate at 1 atm., 4 g. phenol/l for Initial Rate,  $\Delta$  for Steady State Activity Regime

### The Effect of the Oxygen Feed Rate

Figure 5 shows the conversion-of-phenol-versus-time curves for different oxygen feed rates. The highest phenol conversions were obtained with an oxygen feed rate of 5 ml/s. It is evident that phenol removal increases with increasing amounts of bubbled oxygen gas. The decrease in phenol conversion observed with an oxygen feed rate of 10 ml/s can be explained by

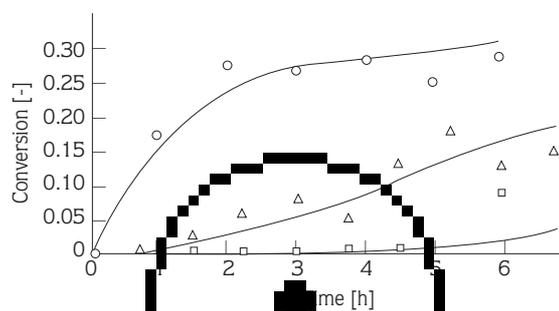


Figure 5. Effect of Oxygen Feed Rate on Conversion at 373 K, 1200 rpm, 2 g. phenol/l, 4 g. cat./l for 5 ml s<sup>-1</sup>,  $\Delta$  10 ml s<sup>-1</sup>,  $\square$  2.5 ml s<sup>-1</sup>

the decreased gas/liquid interface and shortened residence time of large oxygen bubbles formed by the collapsing of fine bubbles at oxygen rates greater than a critical value, Wei and Wan (1991). Figure 5 also shows that the induction period, IP, tends to increase with the oxygen flow rate as follows:

$$IP_{2.5} < IP_{10} < IP_5$$

#### Effect of Stirring Speed

Figure 6 presents the variation of phenol with time at different stirring speeds in experiments of 6 hrs. As the stirring speed increases from 600 rpm to 1200 rpm, the conversion of phenol increases appreciably and the induction time decreases significantly.

The stirring speed was 1200 rpm in all the runs in this study, ensuring vigorous mixing and uniformity throughout. Thus, increasing the liquid-to-particle mass-transfer coefficient ( $k_c$ ) causes the absence of liquid-to-particle mass-transfer resistance. 600 rpm, some parts of the catalyst particles remained at the bottom due to gravity, causing a significant decrease in phenol consumption.

#### Kinetics of the Catalytic Oxidation of Phenol

The rate constants  $k_1$  and  $k_2$  were calculated from the  $-\ln(1-x)$  vs. time curves. Figure 7 shows the curves of two runs. The rate constant  $k_1$  was determined from the initial-rate equation at the point  $x=0$ ,  $t=0$  by means of the differential method and  $k_2$  for the steady-state-activity regime was established from the slope of the  $-\ln(1-x)$  vs. time line drawn using the least squares techniques of the steady-state-activity-region data. The linearity of the experimental data in the steady-state-activity regime displays first-order kinetics with respect to phenol concentration. The rate constants  $k_1$  and  $k_2$  for two runs given in Figure 7 were found to be:

with Phenol/Catalyst ratio =  $2/4 = 0.5$

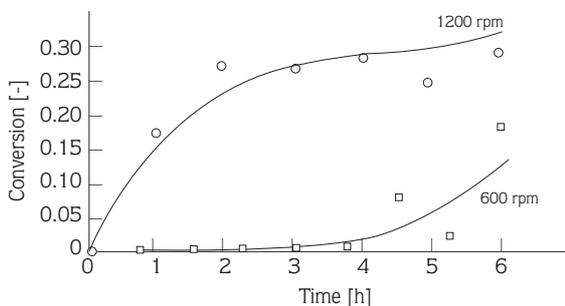


Figure 6. Effect of Stirring Speed on Conversion at 373 K, 2 g. phenol/l, 4 g. cat./l, and oxygen feed rate of  $5 \text{ ml s}^{-1}$ .

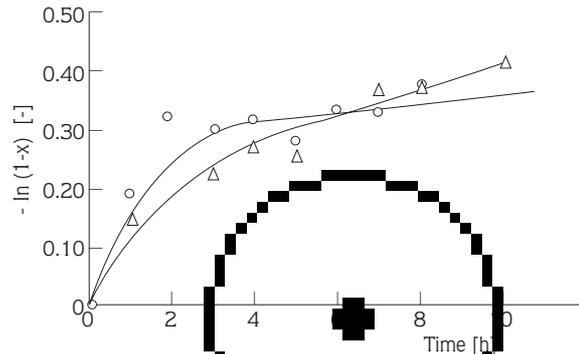


Figure 7.  $-\ln(1-x)$  vs. Time Curves for Phenol/Catalyst Ratio:  $(2/4)=0.50$ ;  $\Delta (4/4)=1.00$

$$k_1 = 6.35 \cdot 10^{-4} \text{ ((cm}^3\text{liq./gcat.)}^{0.5}\text{s}^{-1}) \text{ and}$$

$$k_2 = 0.44 \cdot 10^{-10} \text{ ((gcat/cm}^3\text{liq.)}^2\text{s}^{-1})$$

with Phenol/Catalyst ratio =  $4/4 = 1.0$

$$k_1 = 5.85 \cdot 10^{-4} \text{ ((cm}^3\text{liq./gcat.)}^{0.5}\text{s}^{-1}) \text{ and}$$

$$k_2 = 0.88 \cdot 10^{-10} \text{ ((gcat/cm}^3\text{liq.)}^2\text{s}^{-1})$$

These experiments, in which the initial phenol concentration was changed by a factor of 2 without significantly affecting  $k_1$  and  $k_2$ , exhibit first-order dependence on phenol in the initial activity and steady-state-activity regimes. Information on phenol oxidation in aqueous solution at atmospheric pressure is rather lacking. The rate constants  $k_1$  and  $k_2$  were found to be  $1.29 \cdot 10^{-5} \text{ ((cm}^3\text{liq./gcat.)}^{0.5}\text{s}^{-1})$  and  $2.95 \cdot 10^{-10} \text{ ((gcat/cm}^3\text{liq.)}^2\text{s}^{-1})$ , respectively, by Sadana and Katzer (1974 a) over a 10% CuO on  $\gamma$ -Alumina at 378 K with a phenol-to-catalyst ratio of  $4.4/4 = 1.1$  with a stirring speed of 650 rpm at atmospheric pressure. When those results are compared with the ones in this study, it can be seen that the rate constant for the induction period,  $k_1$ , is different to the value given in the literature, although in the steady-state-activity regime,  $k_2$  is similar to the value obtained by Sadana and Katzer. The differences in the results may arise from the reaction conditions and the type of catalyst used.

Figure 8 shows the effect of temperature on the oxidation of phenol. As expected, as temperature increases, the rate of conversion increases. The Arrhenius plots for  $k_1$  and  $k_2$  are presented in Figure 9.

The activation energies estimated from the slopes of the straight lines calculated by means of the least squares techniques between 70 °C and 100 °C,  $k_1$  and  $k_2$  were 93 kJ/mol and 47 kJ/mol with regression coefficients of 0.944 and 0.993, respectively. The rate constants  $k_1$  and  $k_2$  may be represented by

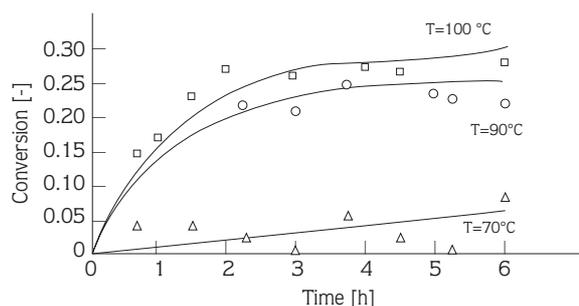


Figure 8. Effect of Temperature on Conversion at 2 g.phenol/l, 4 g.cat./l., Oxygen Feed Rate of 5 ml s<sup>-1</sup>.

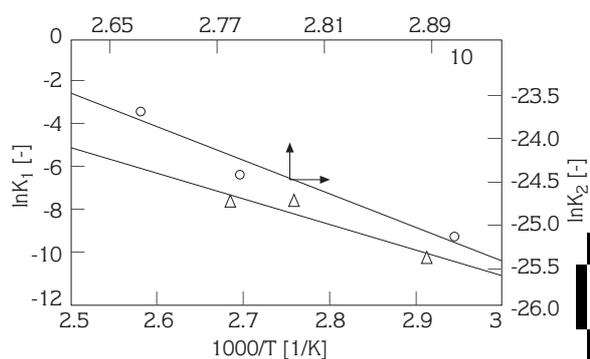


Figure 9. Arrhenius Plots;  $\Delta \ln k_1$  for the Induction Period;  $\ln k_2$  for the Steady-State-Activity Regime.

$k_1 = 1.3 \cdot 10^{10} \exp(-93/RT)$  ((cm<sup>3</sup> of liq./gcat.)<sup>0.5</sup>s<sup>-1</sup>) and

$$k_2 = 2.0 \cdot 10^{-4} \exp(-47/RT) \text{ ((cm}^3 \text{ of liq./gcat.)}^2\text{s}^{-1}\text{)}$$

where R is in kJ/mol K

The catalysts used in all the runs were in powder form and there were no intraparticle diffusional limitations. In conditions at atmospheric pressure (373 K), the phenol oxidation rate was rather low and this slow reaction step influenced the overall rate. Thus, the results for  $k_1$  and  $k_2$  in this study represent intrinsic kinetics. However, it should be noted that the validity eqs. 3 and 4 should be limited in the ranges of operating conditions.

There is information in the literature on activation energies in phenol oxidation in aqueous solutions above atmospheric pressure, but not actually at atmospheric pressure. Taking the differences in operating conditions and catalyst used into consideration, we can say that the activation energies found in this study were lower than those obtained by Sadana and Katzer at pressures above atmospheric pressure up to 10 atm. (1974a), (in the initial-activity regime, 276 kJ

mol and steady-state activity regime, 176 kJ/mol) but there is quite a good correspondence with the activation energies found by Ohta et al. (1980), 85.4 kJ/mol, and Pintar and Lecev (1992a), 84 kJ/mol, in terms of liquid-phase catalytic oxidation of phenol above atmospheric pressure, up to 13 atm.

## Conclusion

In this study, the oxidation of phenol in aqueous solution over a supported copper oxide, zinc oxide catalyst was investigated at atmospheric pressure. The oxidation rate of phenol was low due to the low solubility of oxygen in these conditions. The reaction comprised an induction period and a steady-state-activity regime. The initial-rate and steady-state-activity regime exhibited first-order behavior with respect to phenol concentration. The rates show an unusual dependence on catalyst loading. The initial rate and the rate in the steady-state-activity regime, per unit mass of catalyst, decreased as the catalyst concentration increased. These observations support the conclusion that the reaction involves a heterogeneous-homogeneous free-radical mechanism, that is, as the catalyst concentration increases, the chain termination on the catalyst surface becomes significant.

The experiments showed that the length of the induction period decreased as the ratio of initial phenol concentration to catalyst concentration increased. The rate constants  $k_1$  and  $k_2$  for the initial rate and steady-state-activity regime are represented by

$$k_1 = 1.3 \cdot 10^{10} e^{-93/RT}$$

$$k_2 = 2.0 \cdot 10^{-4} e^{-47/RT}$$

respectively, where R is in kJ/mol K.

Phenol removal may be increased by increasing the amount of bubbled oxygen gas. At high flow rates of oxygen, due to the formation of large bubbles which have a lower gas-liquid interface and a shorter residence time than fine bubbles, the retarding effect of oxygen on phenol oxidation was observed.

An increase in stirring speed, as expected, increased conversion of phenol appreciably and decreased the induction time significantly.

Intermediates of phenol oxidation, such as catechol, hydroquinone and organic acids have been observed in appreciable quantities in aqueous solutions in studies carried out above atmospheric pressure, Pintar and Lecev (1992 a, 1992 b); Kulkarni and Dixit (1991), Ohta et al. (1980), Devlin and Harris (1984), but not

at atmospheric pressure, Sadana and Katzer (1974 a, 1974 b). In the study presented here, carried out at atmospheric pressure, it was also not possible to detect the intermediates mentioned above.

### Acknowledgements

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### Nomenclature

$C_{ph}$  : concentration of phenol [mol/cm<sup>3</sup>]  
 $k_1$  : rate constant for initial rate [cm<sup>3</sup> of liq./g of cat.]<sup>0.5</sup>[s]<sup>-1</sup>

### References

- Box, E.O., Farha, F., Okla, B., "Polluted Water Purification", US Patent (CL. 210-63) 3, 823, 088, 9 July 1974.
- Chang, C. J., Lin, J.C., "Effects of Temperature and Cu<sup>++</sup> Catalyst on Liquid-Phase Oxidation of Industrial Waste Waters", J. Chem. Tech. Biotechnol. 57, 355-61, 1993.
- Devlin, H., Harris, I., "Mechanism of the Oxidation of Aqueous Phenol With Dissolved Oxygen", Ind. Eng. Chem. Fundam, 23, 387-92, 1984.
- Hamilton, C.E., Teal, J.I., Kelly, J. A., Midland, M., "Oxidation of Aqueous Organic Dispersions", US Patent (CL. 210-63) 3, 442, 802, 6 May 1969.
- Harmankaya, M. "Investigation of Catalytic Oxidation of Phenol in Aqueous Solution", MS Thesis, Ege University, Chem. Eng. Dep., Izmir-Turkey, 1995.
- Kulkarni, S.U., Dixit, S.G., "Destruction of Phenol from Waste Water by Oxidation with SO<sub>3</sub><sup>-2</sup>-O<sub>2</sub>", Ind. Eng. Chem. Res. 30, 1916-20, 1991.
- Lovo, M., Deans, H.A., Balakotaiah, V.J., "Modelling and Simulation of Aqueous Hazardous Waste Oxidation in Deep Well Reactors", Chem. Eng. Sci. 45 (8), 2703-710, 1990.
- Ohta, H., Goto, S., Teshima, H., "Liquid-Phase Oxidation of Phenol in a Rotating Catalytic Basket Reactor", Ind. Eng. Chem. Fundam. 19, 180-85, 1980.

$k_2$  : rate constant for steady-state activity  
 [g of cat./cm<sup>3</sup> of liq.]<sup>2</sup> [s]<sup>-1</sup>

$M_c$  : weight of catalyst [g]  
 R : universal gas constant [kJ/mol K]  
 T : temperature [K]  
 t : time [s]  
 $V_1$  : liquid-phase volume [cm<sup>3</sup>]  
 x : conversion of phenol [-]

### Indices

c : catalyst  
 f : final  
 i : initial  
 l : liquid

- Pintar, A., Levec, J., "Catalytic Oxidation of Organics in Aqueous Solutions", J. Catal. 135, 345-57, 1992 a.
- Pintar, A. and Levec, J., "Catalytic Liquid-Phase Oxidation of Refractory Organics in Waste Water", Chem. Eng. sci. 47 (9-11), 2395-400, 1992 b.
- Pintar, A., Levec, J., "Catalytic Liquid-Phase Oxidation of Phenol Aqueous Solutions, a Kinetic Investigation" Ind. Eng. Chem. Res. 33, 3070-1994.
- Pruden, B. B., Le., H., "Wet Air Oxidation of Soluble Components in Waste Water", The Canadian J. Chem. Eng. 54, 319-25, 1976.
- Randall, T.L., Knopp, P.V., "Deoxygenation of Specific Organic Substances by Wet Oxidation", J. WPCF 52 (8), 2117-121, 1980.
- Sadana, A. and Katzer, J.R., "Catalytic Oxidation of Phenol in Aqueous Solution over Copper Oxide", Ind. Eng. Chem. Fundam. 13 (2), 127-33, 1974 a.
- Sadana, A., Katzer, J.R., "Involment of Free Radicals in Aqueous-Phase Catalytic Oxidation of Phenol Solution over Copper Oxide", J. Catal. 35, 140-52, 1974 b.
- Tufan (Gündüz), G., Akgerman, A., "Final Research Report MAG-500"-Turkish Scientific Research Council, 1980.
- Wei, T-Y, Wan, C-C, "Heterogeneous Photo Catalytic Oxidation of Phenol with Titanium Dioxide Powders", Ind. Eng. Res. 30, 1293-1300, 1991.