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# Catalytic oxidation of phenol in aqueous solutions

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## Abstract

The objective of this work is to investigate catalyst systems for the oxidation of phenol in water in a batch autoclave. The main experimental variables are the type and the composition of the catalyst, the catalyst loading, temperature, oxygen partial pressure, initial phenol concentration and the stirrer speed. Commercial catalysts were used. Experimental work was conducted in two different laboratories. In one laboratory, the catalysts tested were 35% CuO+65% ZnO; 5–15% CuO+85–95% $Al_2O_3$; 26% CuO+74% Cu Chromite. In the other laboratory, the catalysts tested included 35% CuO+65% ZnO; 5–10% $Ba_2CO_3$+<5% C+30–40% CuO+60–70% ZnO; and 8–15% $Al_2O_3$+1–5% C+35–45% CuO+40–50% ZnO. With some of these catalysts depending on the operating conditions, complete phenol conversion could be obtained within 90 min. Under certain experimental conditions, the reaction underwent an induction period after which there was a transition to a much higher activity regime. The induction period may be due to an autocatalytic reaction system or to a very slow rate of formation of hydroquinone and catechol which then readily oxidize to *o*- and *p*-benzoquinone. An increase in the temperature and the oxygen partial pressure decreased the induction period, which increased as the catalyst to phenol ratio increased. 26% CuO+74% Cu Chromite and 8–15% $Al_2O_3$+1–5% C+35–45% CuO+40–50% ZnO were found to be the most active catalysts. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Catalytic oxidation; Phenol oxidation; Phenol water; Waste water treatment

## 1. Introduction

Increasing stringent water quality regulations and the demand for recycling of waste water create a need for the efficient treatment of waste water streams containing pollutants. Oxidation of dilute aqueous solutions of refractory pollutants by using oxygen over a solid catalyst offers an alternative to other techniques (for example, noncatalytic wet-air oxidation, biological oxidation, oxidation in supercritical water, and physical adsorption) as a means of purifying waste waters. Current wet oxidation processes require high temperatures (423–623 K) and high pressures (6–17 MPa). In the process of oxidation in supercritical water, temperatures in the range 600–700 K and pressures in the range 22–28 MPa are employed [1]. These conditions tend to make the pertinent processes expensive and inefficient with respect to energy use. Similarly physical separation processes, such as carbon adsorption, become expensive as the adsorbent needs to be regenerated and follow up treatment, such as biological oxidation which is particularly effective at low pollutant concentrations, is needed. Hence there is incentive to search for alternative processes which have the poten-

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tial of becoming economically advantageous. Catalytic oxidation which can be carried out under milder conditions is one such process.

The key issue in the process of effective oxidation of organics in water is the catalyst which must have high mechanical strength, chemical stability, and hydrophobicity; actively participate in the oxidation reaction; be stable in water and the secondary impurities in it; and facilitate the complete oxidation of the organics to carbon dioxide. In the aqueous phase oxidation, deactivation of a catalyst due to metal or oxide dissolution is likely to occur. This prevents the use of catalysts which are soluble in hot acidic water or that can be converted to a soluble state during reaction due to the presence of oxygen. Once an active and stable catalyst is at our disposal, it would be possible to determine whether the catalytic liquid-phase oxidation of organics in waste water is economically advantageous over the other processes.

Another important factor in the process of oxidation of organics in the aqueous phase is the means of contacting the phases. The equilibrium oxygen concentration in aqueous solution is expected to be low; increasing the system pressure will increase the equilibrium oxygen concentration. Therefore, the reactor choice for this reaction system will be of utmost economical importance.

In comparison with numerous studies for pure organic liquids, relatively few investigations have been published for catalytic oxidation of organic compounds in aqueous solutions. Sadana and Katzer [2] studied the catalytic oxidation of phenol in an aqueous solution over supported copper oxide (10% CuO on $\gamma$-alumina) and manganese oxide (19% $MnO_2$ on $\gamma$-alumina) in a batch reactor at atmospheric and above-atmospheric (1–17 atm) pressure and between 369 and 419 K. Baldi et al. [3] investigated the catalytic oxidation of formic acid in water using a commercial CuO (16.5%)–ZnO (82.5%) catalyst at 473–513 K and 40 atm. Levec and Smith [4] measured the rates of oxidation of dilute aqueous solutions of acetic acid at 525–559 K and 67 atm in trickle-bed reactors with ferric oxide catalyst particles. They also used untreated copper chromite, which was the most active; palladium on alumina and CuO–ZnO, which were inactive; and copper and iron oxides, which both demonstrated intermediate activities. Levec et al. [5] used a catalyst consisting of 4% Cu, 2% Mn, and 1% La on a support of 51.5% $Al_2O_3$ and 48.5% ZnO for the oxidation of aqueous acetic acid solutions. Ohta et al. [6] studied the catalytic oxidation of phenol in aqueous solution over supported copper oxide by oxygen in a slurry reactor and a rotating catalytic basket reactor. They determined the reaction intermediates by liquid chromatography to be hydroquinone, pyrocatechol, maleic acid, and oxalic acid. Kochetkova et al. [7] investigated the oxidation of phenol in aqueous solutions using industrial catalysts like Ag on pumice, Co on pumice, Bi/Fe, Bi/Sn, Mn/$Al_2O_3$, and Cu/$Al_2O_3$. Their most active catalyst was CuO/$Al_2O_3$; they added $TiO_2$ to alumina to reduce the acid function and cobalt oxide as a promoter. For this catalyst, a high activity was only found for mixtures of copper and titanium cobaltite spinels with a specific concentration of cobalt oxide, the catalyst activity being dependent on an optimum cobalt oxide content. Pintar [8] and Pintar and Levec [9,10] studied the aqueous oxidation of phenol, *p*-chlorophenol, and *p*-nitrophenol by $O_2$ to carbon dioxide over a catalyst comprising of CuO, ZnO, and alumina in a slurry system. The same authors also investigated the kinetics of phenol oxidation in aqueous solutions on a proprietary catalyst comprising of supported copper, zinc and cobalt oxides in a differential, liquid-full operated fixed-bed reactor [11]. The available work in literature on the catalytic oxidation of organic pollutants in aqueous solutions is summarized in Table 1.

Given the fact that various technologies have been developed for the removal of phenol from waste water, the decision to select among the existing technologies would ultimately depend on which technology is available at the lowest cost. The literature survey on the catalytic oxidation of phenol given here indicates considerable variability in activity and stability among the different catalysts used. Since the economics of the catalytic oxidation technology is significantly influenced by the activity and the selectivity of the catalyst, it is important that sufficiently comprehensive data on these areas are available. The work presented here addresses this need. Such an investigation will also facilitate an explanation of the source of activity and selectivity of such catalysts and this will result in better catalyst design, contributing to making the process viable.

Table 1
Summary of the literature cited

| Reference | Catalysts used | $T$ (K) | $P$ (MPa) | Hydrocarbon | Remarks |
|---|---|---|---|---|---|
| [2] | 10% Cu on $\gamma$-Alumina Harshaw Cu-0803T1/8 surface area=140 $m^2$/g; | 369–419 | 0.1–1.7 | Phenol | Oxidation very slow under atmospheric pressure conditions. Rate inversely proportional to oxygen partial pressure. Rate is highly dependent on temperature |
| | Unsupported copper oxide, 19% $MnO_2$ on $\gamma$-Alumina Harshaw MN-0201T1/8 | | | | Inactive for phenol oxidation. Similar to supported copper oxide catalyst |
| [3] | CuO–ZnO catalyst, Chemetron G-66B | 473–513 | 4.0 | Formic acid | Catalyst found to be effective for liquid-phase oxidation. Rate linear to oxygen concentration |
| | 16.5% CuO, 82.5% ZnO surface area=35.9 $m^2$/g | | | | Activation energy=37 kcal/mol |
| [4] | *Chemetron catalysts* Copper chromite: G-13, G-T531 | 525–559 | 6.7 | Acetic acid | Most active, yellow colored liquid effluents, deactivated within several hours |
| | 0.1% Palladium on Alumina (G-63D) | | | | Inactive |
| | CuO–ZnO: G-66B; Copper: G-T317; Iron Oxide:G-3A | | | | Intermediate activity, no early deactivation. Rate 1/2 order in oxygen; first to zeroth order in Hac as its conc. increased; $E$=21 kcal/mol |
| [5] | Support: 51.5% $Al_2O_3$–48.5% ZnO; 4% Cu, 2% Mn, 1% La on support; surface area=89 $m^2$/g | 523–553 | 6.8 | Acetic acid | Sharply higher oxidation rates than iron oxide catalysts. $E$=17 kcal/mol |
| [6] | 10% CuO on $\gamma$-Alumina Harshaw Cu-0803T1/8 surface area=140 $m^2$/g | 386–418 | 0.6–1.4 | Phenol | 0.55 Order dependence on oxygen partial pressure; apparent activation energy: 20.4 kcal/mol; intermediates: hydroquinone, pyrocathecol, maleic acid; products: $CO_2$, oxalic acid, some maleic acid |
| [7] | Ag on pumice, AP-64, Co on pumice, GIPKh-105B' GIPKh-108, Bi/Fe, Bi/Sn, MnO/$\gamma$-$Al_2O_3$ | 392–444 | $O_2$ partial Pressure= 0.4–1.2 | Phenol | Best catalyst was CuO/$\gamma$-$Al_2O_3$. Nearly complete oxidation of phenol occurs on catalyst modified with titanium oxide and 3% cobalt oxide with this catalyst. Initial rate has first order dependence on $O_2$ and phenol. $E$=53.6 kJ/mol |
| [8] | 42% CuO+47% ZnO+ 10% $Al_2O_3$ | 403 | 0.6 | Phenol | Total conversion to $CO_2$; 1st order wrt phenol, 1/2 order wrt $O_2$ |
| | | | | Chlorophenol; butyl alcohol | Oxidation rates similar to phenols |
| | | | | Nitrophenol | Lower rate; no induction period for butyl alcohol and nitrophenol. |
| [9,10] | CAT-1: 42% CuO+ 47% ZnO+10% $Al_2O_3$ | 378–403 | 0.56 | Phenol | Highest activity on CAT-3, lowest activity on CAT-1. Order w.r.t. $O_2$=0.25; apparent $E$=84 kJ/mol |
| | CAT-2: 10% CuO on $Al_2O_3$ | | | *p*-Chlorophenol | Rate higher than that for phenol. Order w.r.t. $O_2$=0.5; $E$=123 kJ/mol |
| | CAT-3: 4% Cu+2% Mn+1% La on zinc aluminate | | | *p*-Nitrophenol | Slowest oxidation rate; all exhibited an induction period |
| [11] | Proprietary catalyst containing supported Cu, Zn, Co oxides | 423–483 | 3 | Phenol | Langmuir–Hinshelwood type kinetics with dissociative $O_2$ adsorption, leading to 1/2 power dependence on oxygen concentration. Apparent $E$=139 kJ/mol |

## 2. Experimental

In one laboratory, catalyst screening studies were performed in a one liter batch stainless steel autoclave reactor (Autoclave Engineers, Erie, PA), equipped with an impeller, temperature and pressure control units and sampling facilities. The reaction conditions were 363–423 K and 1–20 atm. The extent of the reaction was determined based on the results of the analysis of the liquid phase in the reactor by gas chromatography using a Varian Vista 6000 equipment; a Hewlett-Packard fused silica capillary column (HP-5 cross-linked 5% phenyl methyl silicone) (0.5 mm i.d., 30 m long, 2.65 $\mu$m film thickness, and a phase ratio of 50) was used for the analysis of the liquid phase. In the other laboratory, a similar, one liter, Hastelloy C, batch autoclave reactor was used (Parr Instrument). Analysis was based on the determination of the phenol concentration in the aqueous solution by using a gas chromatograph (HP-5890) equipped with an electron capture detector and a fused silica capillary column having a stationary phase of 5% diphenyl and 95% dimethyl polysiloxane. Data were collected in the temperature and pressure ranges 383–418 K and 1–6.5 atm, respectively.

In a typical experiment, fresh catalyst was charged into reactor; measured amounts of distilled water and phenol were subsequently added. For the experiments performed with the AE reactor, after the reactor was closed, nitrogen was passed through in order to purge the air left in the reactor, which is then heated under 1 atm of nitrogen. When the reaction temperature was reached, oxygen was introduced into the system at the required pressure, the stirrer was turned on and the reaction was, thus, initiated. In the experiments where the Parr reactor was used, oxygen was not purged from the reactor. Instead, the reactor containing the aqueous phenol solution and the catalyst was pressurized with oxygen and heated to the reaction temperature and the reaction was initiated by turning on the stirrer. (Although no phenol conversion was detected during the preheating period at 393 K, it was found that about 10% phenol conversion took place at 403 K prior to stirring.) Liquid samples were withdrawn periodically through a liquid sampling line, which was fitted with a fine filter. These samples were analyzed for the phenol content by the gas chromatograph.

The main experimental variables were the type of the catalyst, the catalyst loading, temperature, oxygen partial pressure, initial phenol concentration and the stirrer speed. Preliminary experiments were performed at various stirrer speeds to select the stirrer speed where there were no mass transfer limitations. Consequently, all the main runs were performed either at 1000 rpm in the AE reactor or 300 rpm in the Parr reactor. (The Parr reactor has two impellers resulting in more effective agitation for the same rpm.) Commercial catalysts were used. The following catalysts were tested in the AE reactor:

1. 35% CuO+65% ZnO (C61-3, United Catalysts, Louisville, KY);
2. 5–15% CuO+85–95% $Al_2O_3$ (T-317, United Catalysts, Louisville, KY);
3. 26% CuO+74% Cu Chromite (CU-1850P, Engelhard Corporation, Elyria, OH).

The catalysts used in the Parr reactor were as follows:

4. 35% CuO+65% ZnO (C61-3, United Catalysts, Louisville, KY);
5. 5–10% $Ba_2CO_3$+<5%C+30–40% CuO+60–70% ZnO (C61-2-01, United Catalysts, Louisville, KY);
6. 8–15% $Al_2O_3$+1–5% C+35–45% CuO+40–50% ZnO (C18-7 United Catalysts, Louisville, KY).

Since catalyst 6 was available in tablet form, it was crushed and sieved to sizes smaller than 53 microns before use.

## 3. Results and discussion

For the first three catalysts, complete phenol conversions were observed in a 2 h period at 403 K with a catalyst loading of 5 g/l (Figs. 1 and 2) with the third catalyst being the most active (Fig. 3). It was also observed from these results that the reaction undergoes an induction period after which there is a transition to a much higher steady-state activity regime. This is an indication that there are no gas–liquid mass transfer limitations. The induction period may be due to an autocatalytic reaction system or to a very slow rate of formation of

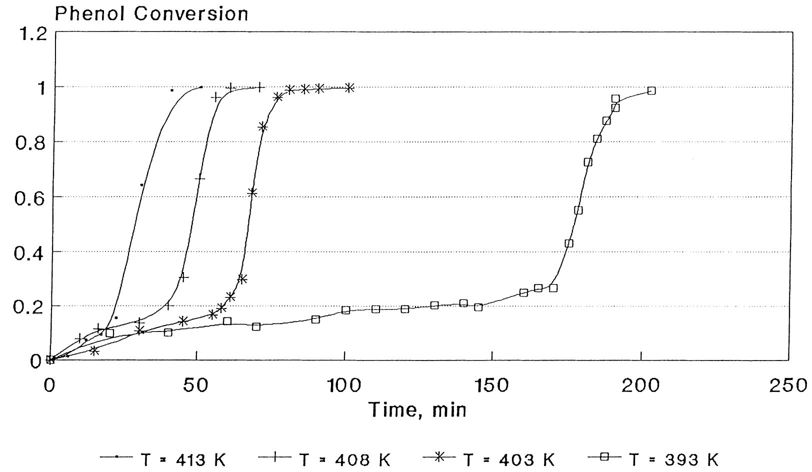


Fig. 1. Effect of temperature: catalyst: CuO–ZnO; feed: 3000 ppm of phenol; oxygen partial pressure: 300 psig; 5 g/l catalyst; 1000 rpm. (●) $T$=413 K; (+) $T$=408 K; (*) $T$=403 K; (□) $T$=393 K.

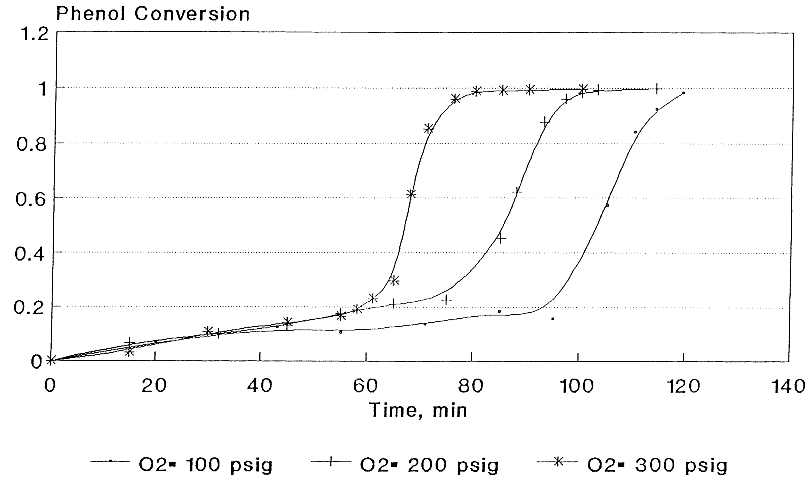


Fig. 2. Effect of oxygen partial pressure: catalyst: CuO–ZnO; feed: 3000 ppm of phenol; temperature: 403 K; 5 g/l catalyst; 1000 rpm. (●) $P_{O_2}$=100 psig; (+) $P_{O_2}$=200 psig; (*) $P_{O_2}$=300 psig.

hydroquinone and catechol which then readily oxidize to *o*- and *p*-benzoquinone. The latter hypothesis is supported by the change in the color of the reaction mixture from clear to a brownish color as the reaction progressed, the brownish color being due to the formation of *o*- and *p*-benzoquinone [2]. It was observed that once the brown color was established, the transfer to the higher activity region occurred and the mixture became clear by further conversion. These observations support the hypothesis forwarded by Sadana and Katzer [12], who postulated that the heterogeneously catalyzed aqueous-phase phenol oxidation occurs by a free-radical mechanism, involving initiation on the catalytic surface, followed by homogeneous propagation. Thus, the main rate-determining step may be the formation of an

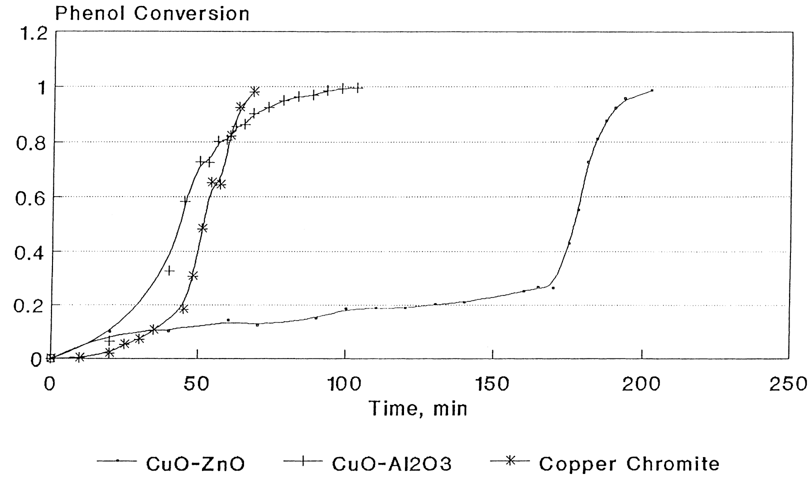
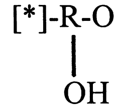


Fig. 3. Comparison of catalysts: feed: 3000 ppm of phenol; temperature: 393 K; oxygen partial pressure: 300 psig; 5 g/l catalyst; 1000 rpm. (●) CuO–ZnO; (+) CuO–$Al_2O_3$; (*) copper chromite.

intermediate like:



$$[*]\text{-R-}\underset{\substack{| \\ \text{OH}}}{\text{O}}$$

which may facilitate the formation of the phenoxy radicals in the liquid.

An experiment has been performed without the catalyst, forming the brown intermediate, but the reaction mixture did not become clear at very long times and the phenol conversion stayed at about 50%; when a catalyst was added to this reaction mixture, the reaction went to completion. This observation is regarded as an evidence to the hypothesis mentioned above that the intermediates formed during the induction period by a free-radical mechanism [2] need a catalyst to be further oxidized. This indicates that an optimum catalyst is indispensable for the aqueous oxidation of phenol.

An increase in temperature and the oxygen partial pressure decreases the induction period (Figs. 1 and 2). The dependence of induction time on temperature is exponential as shown in Fig. 4. The slope in that figure is an estimate of the activation energy for the initiation reaction and it was calculated to be 139 kJ/mol. Fig. 5 presents the inverse of induction period as a function of oxygen partial pressure; the slope of the dependence is 0.46. This indicates an order of 0.5 with respect to oxygen for the initiation reaction.

Induction period increases as the catalyst to phenol ratio increases (Fig. 6). This may be due to the fact that the catalyst may be active in some of the termination reactions in the free-radical mechanism, thus, causing some of the active intermediates to disappear faster. Therefore, the induction period will be longer with higher catalyst loading.

Catalyst stability will be an important factor in the industrial applications. Therefore, to test the stability of the first catalyst used in this study, a catalyst batch has been retained and used for several cycles. The induction period disappears with catalyst usage; in cycles 4 and 5, there is even some phenol conversion at zero time when oxygen is first introduced into the reactor (Fig. 7). This may be due to the fact that there are already some active intermediates on the catalyst, which supply oxygen for oxidation. The catalyst activity subsequent to the induction period seems to decrease very slowly with usage.

Experiments with the catalysts 4–6 were performed in the Parr reactor. Comparison of these catalysts at 403 K is shown in Fig. 8. No induction period is apparent in these results. Since catalysts 1 and 4 are the same, the absence of the induction period in the experiments with the Parr reactor is most likely due to the difference in the experimental procedure where the

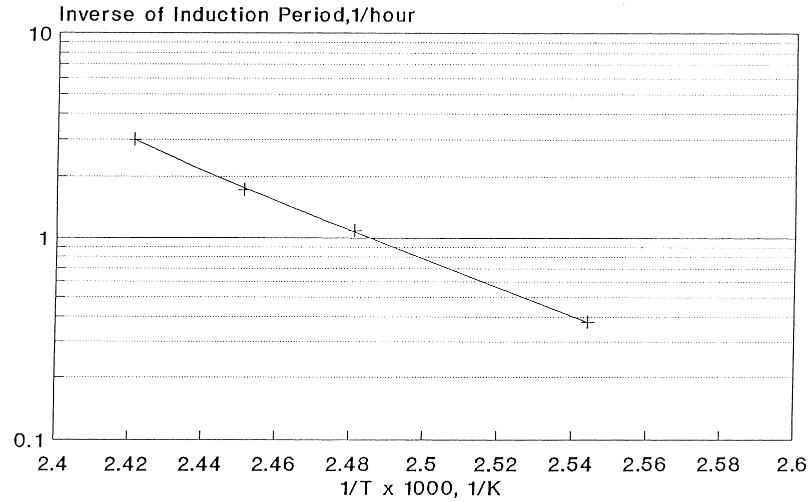


Fig. 4. Effect of temperature on the induction period: catalyst: CuO–ZnO; feed: 3000 ppm of phenol; oxygen partial pressure: 300 psig; 5 g/l catalyst; 1000 rpm.

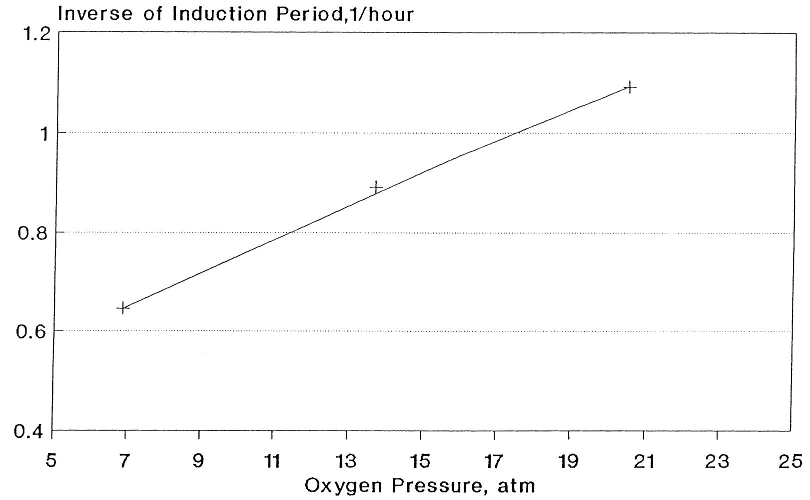


Fig. 5. Effect of oxygen partial pressure on the induction period: catalyst: CuO–ZnO; feed: 3000 ppm of phenol; temperature: 403 K; 5 g/l catalyst; 1000 rpm.

contents of the Parr reactor were brought to the reaction temperature with the aqueous solution already saturated with oxygen as opposed to the experiments with the first three catalysts where the oxygen was first purged with nitrogen and oxygen introduced after preheating. In the experiments with the Parr reactor, although stirring did not take place during the preheating process (the reactor was pressurized to 72 psig with oxygen at room temperature), the presence of oxygen resulted in 10% phenol conversion at 403 K for catalyst 6 which is the most active catalyst.

Fig. 9 illustrates the effect of catalyst concentration on conversion where it is seen that at any given time,

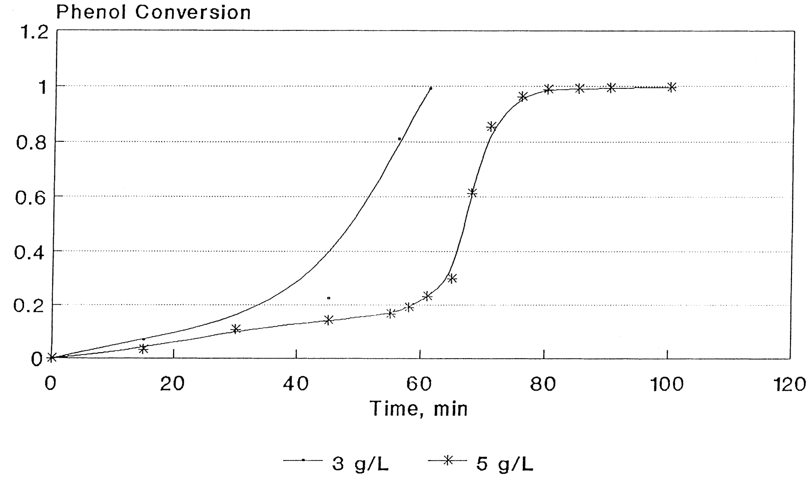


Fig. 6. Effect of catalyst loading: catalyst: CuO–ZnO; feed: 3000 ppm of phenol; temperature: 403 K; oxygen partial pressure: 300 psig; 5 g/l catalyst; 1000 rpm. (●) 3 g/l; (*) 5 g/l.

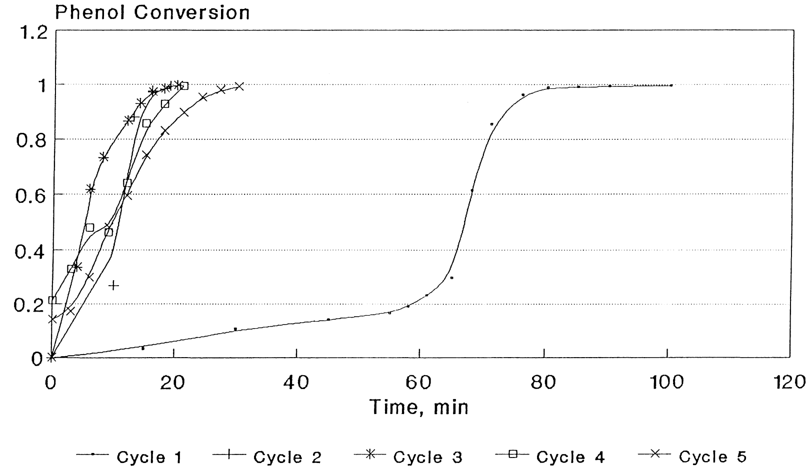


Fig. 7. Catalyst stability: catalyst: CuO–ZnO; feed: 3000 ppm of phenol; temperature: 403 K; oxygen partial pressure: 300 psig; 5 g/l catalyst; 1000 rpm. (●) Cycle 1; (+) cycle 2; (*) cycle 3; (□) cycle 4; (×) cycle 5.

conversion is higher for higher catalyst concentrations. This is expected since no induction period was observed for catalyst 6.

Fig. 10 illustrates typical error in experiments conducted with the Parr reactor. The filled circles represent the average of three repeat experiments. The error bars associated with each set of data are based on 95% confidence.

## 4. Conclusion

Catalytic oxidation may be regarded as an alternative process for treatment of waste water contaminated by phenol. This process may fit in the whole picture as a means of partially oxidizing such compounds to products which may be more readily degraded by biological treatment than their precur-

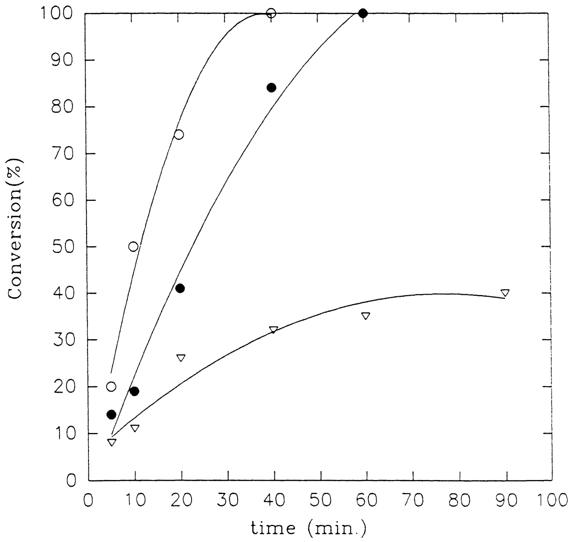


Fig. 8. Comparison of catalysts: feed: 5000 ppm of phenol; temperature: 403 K; oxygen partial pressure: 72 psig (at 293 K); 10 g/l catalyst; 300 rpm. (○) C18-7; (●) C61-3; (▽) C61-2.

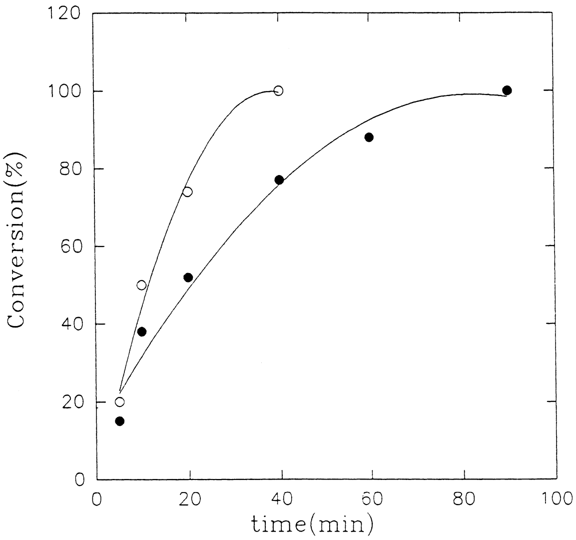


Fig. 9. Effect of catalyst concentration: catalyst: C18-7; feed: 5000 ppm of phenol; temperature: 403 K; oxygen partial pressure: 72 psig (at 293 K); 300 rpm. (●) 5 g/l; (○) 10 g/l.

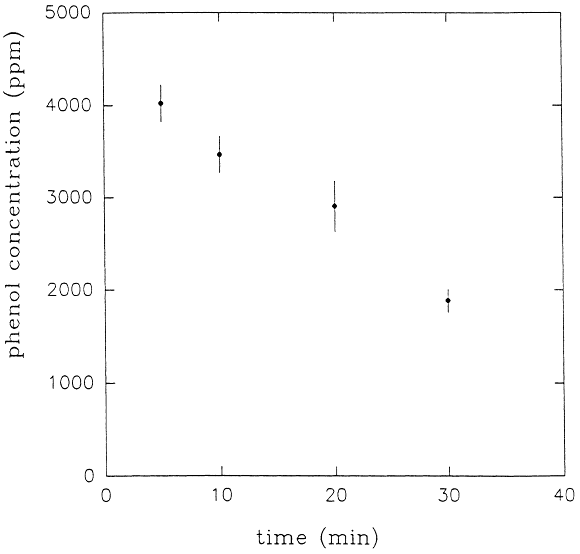


Fig. 10. Error analysis: catalyst: C18-7; feed: 5000 ppm of phenol; oxygen partial pressure: 72 psig (at 293 K); temperature: 403 K; 5 g/l catalyst; 300 rpm.

sors. In this project, several commercial catalysts were investigated for their performance in the catalytic oxidation of phenol in water in two different laboratories using similar batch autoclave reactors. Complete phenol conversions were obtained with some of these catalysts in a 0.5–2 h period depending on the catalyst and the conditions under which the experiments were performed. The reaction typically undergoes an induction period after which there is a transition to a much higher activity regime. However, when the reaction was started after preheating the aqueous solution saturated with oxygen, no induction period was observed. The latter results will be useful for the scale-up of the industrial application of this method. 26% CuO+74% Cu Chromite and 8–15% $Al_2O_3$+ 1–5% C+35–45% CuO+40–50% ZnO were found to be the most active catalysts.

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