Noncatalytic Oxidation of Phenol in Aqueous Solutions

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The oxidation of phenol in aqueous solution was studied in a semibatch reactor at temperatures between 170 and 220 °C and at pressures of 5.10−10.15 MPa. The reaction showed an induction period followed by a rapid degradation. During the rapid step, the oxidation reaction was first-order in each phenol and oxygen, with an activation energy of 67.4 ± 9.8 kJ mol^{-1}. The kinetic constant depended on the concentration of organics represented by the initial concentration of phenol. A series of consecutive runs without removal of the products showed a progressive acceleration of the reaction and a suppression of the induction period. The length of the induction period was studied following the model of Willms et al. (Willms, R. S.; Balinsky, A. M.; Reible, D. D.; Wetzel, D. M.; Harrison, D. P. *Ind. Eng. Chem. Res.* **1987**, *26*, 148). The activation energy of the induction period was 56 kJ mol^{-1} for reactions below 190 °C and 170 kJ mol^{-1} for higher temperatures, which probably indicates a change in mechanism. The results from reactions performed without removing reaction products suggest that the accumulation of intermediate compounds could explain the observed increase in the rate constant from run to run.

Introduction

Wet air oxidation involves the liquid-phase oxidation of organics and oxidizable inorganic compounds at relatively elevated temperatures and pressures using a gaseous source of oxygen. When the working conditions are above the critical point of water (374.1 °C and 22.1 MPa), the technique is termed supercritical wet oxidation.[2] Wet oxidation is an effective treatment for wastewaters of intermediate concentrations that are difficult to biotreat[3] and for wastewaters containing toxic compounds.[4] There is a wide body of literature concerning phenol wet oxidation.[5] A catalyst is used in many works,[6−9] and even though most authors make use of mechanically stirred tanks,[10−13] some other contactors have also been described. Jaulin and Chornet[14] developed a jet mixer to increase the gas−liquid interfacial area, Thornton and Savage[15] used a plug-flow reactor, and Miró et al.[16] and Pintar et al.[9] oxidized phenol in a trickle-bed reactor. In contrast to the large volume of work available, fundamental information on the oxidation kinetics and reaction mechanisms is still scarce and often contradictory. It has been pointed out that the underlying reasons are the diversity of working conditions, the variety of contactors used in different works, and the difficulty of ensuring that the kinetics is mass-transfer controlled.[1,17]

Different authors have reported values for the activation energy of the uncatalyzed oxidation of phenol. The lowest values correspond to oxidation in supercritical water,[15] but even below the critical point of water, the stated activation energies vary markedly. Pruden and Le[10] determined a value of 45.2 kJ/mol, Jaulin and Chornet[14] found 56.6 kJ/mol, and Willms et al.[1] reported 112 kJ/mol. Most kinetic models found in the literature are first-order in each phenol and dissolved oxygen, but this is more frequently an assumption rather than an experimental result. Some works indicate different values, and for example, Willms et al.[1] found one-half-order in oxygen.

The overall oxidation process consists of a series of two steps. The oxygen from the gas must diffuse to the bulk liquid phase before it reacts with phenol. Mass transfer resistance in the gas and liquid sides of the interface can be evaluated by using the double-layer theory of Lewis and Witman.[18] Earlier authors[10,19] demonstrated that the gas-phase resistance to mass transfer could be overlooked for working conditions similar to those used in wet oxidation. Chemical and diffusional regimes can be elucidated by using the Hatta number, a result of film theory.[20]

The aim of this work was to investigate the oxidation kinetics of phenol in aqueous solutions. Special attention was paid to the controlling regime to determine the conditions for which mass-transfer can be neglected. The experiments were carried out in the kinetic regime, allowing the intrinsic kinetics of the oxidation of phenol to be determined. Special attention was also paid to the role of organic compounds in the initiation of radical reactions.

Experimental Section

Apparatus and Experimental Procedure. Figure 1 presents a scheme of the equipment used. The oxygen flow from a compressed cylinder was controlled by a Brooks electronic mass flow controller. Runs were performed in a 1-L stainless steel Parr T316SS autoclave (diameter = 100 mm diameter) equipped with two six-blade turbines (diameter = 58 mm) that were 45 mm apart, with the lowest 15 mm from the bottom of the autoclave. Before reaching the autoclave, oxygen was bubbled though a 2-L stainless steel water reservoir in order to saturate it. The inner temperature was measured and controlled in both vessels. Another reservoir connected to the autoclave was used to introduce a
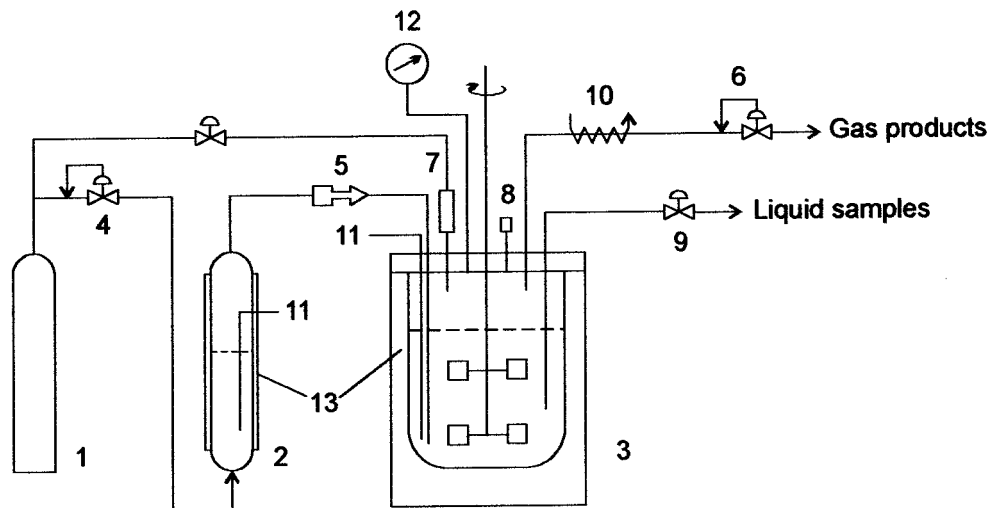
Figure 1. Diagram of the experimental equipment: 1, oxygen; 2, water reservoir; 3, reactor; 4, mass flow meter; 5, nonreturn valve; 6, back-pressure device; 7, reactant reservoir; 8, rupture disk; 9, sampling valve; 10, cooler; 11, thermocouples; 12, pressure gauge; 13, heating jackets.

predetermined amount of a concentrated solution of phenol at the end of the heating period by means of the pressure applied by the bottled compressed oxygen. A valve and a coil fitted on the top of the vessel allowed for the withdrawal of samples during the reaction. The pressure was kept constant by means of a back-pressure controller located at the end of the gas line.

The water reservoir and the reactor vessel were filled with deionized water up to about 70% of the total capacity of each. The equipment was pressurized with oxygen and preheated to the desired working conditions. Once the chosen temperature was reached, the concentrated solution of phenol (90% in deionized water) was injected into the reactor. This time was considered the start of the reaction. No change in reaction rate was detected for variations in the rotation speed, so it was adjusted to 500 min⁻¹ for all runs. Liquid samples were periodically withdrawn and analyzed until the concentration of phenol was less than 1% of its initial value.

Analysis. The concentration of phenol in the aqueous phase was measured using the 4-aminoantipyrine colorimetric method developed by Ettinger et al.[21] This method is based on the formation of a red-colored complex between the 4-aminoantipyrine and the phenolic compound in the presence of an oxidant such as potassium hexacyanoferrate III, $K_3Fe(CN)_6$, whose absorbance was measured at 510 nm with a Perkin-Elmer cpectrophotometer. The chemical oxygen demand (COD) was determined according to the Standard Methods for the Examination of Water and Wastewater.[22]

Experimental Results. Like other free-radical reactions, the oxidation of phenol takes place in two distinct periods. The initial slow induction stage is followed by a steady-state reaction. The length of the induction period is determined by the time required for the free-radical reacting species to reach a critical concentration. A mathematical model for such aqueous-phase oxidation reactions has been developed by Willms et al.,[1] who correlate the length of the induction period by means of a mechanistic analysis. The rapid step begins when the concentration of radicals reaches the critical value required for a stationary reaction. The mechanism of the radical chain reaction taking place during the steady-state period has received more attention, but it remains poorly understood. Tufano[23] proposed a simpli-

fied model in which phenol reacts with oxygen, hydroxyl, and perhydroxyl radicals. Gopalan and Savage[24] derived a mechanism for phenol oxidation under supercritical conditions. Rivas et al.[25] applied a mechanism that considers the main radical reactions that are believed to take place during the oxidation of phenol. By comparing their predictions with the experimental results from Kolaczkowski et al.,[13] they concluded that the main reactions of phenol are those with hydroxyl (HO•) and phenoxyperoxyl (PhOO•) radicals. Their mechanism reduces to a first-order law for phenol depletion if the concentration of all intermediate compounds is constant throughout the reaction. Pruden and Le[10] and Joglekar et al.[26] also found first-order kinetics with respect to both reactants. Experimental results show that the rate constant rises with increasing initial concentration of phenol in the reaction mixture. This fact suggests that other organics in the mixture might undergo reaction with oxygen or other radicals that subsequently interact with phenol.[14] The total amount of organic compounds able to participate in the chain of reactions is very difficult to determine, but it depends on the initial concentration of phenol, which justifies the rate expression proposed in this work, in which the rate of consumption of phenol depends on the initial concentration of phenol, $C_{Ph,o}$

$$-\frac{dC_{Ph}}{dt} = k_r(C_{Ph,o})C_{Ph}C_{O_2} \qquad (1)$$

Phenol was practically eliminated at the end of the quick degradation period, but the presence of other organics could be determined by measuring the COD.[16] At the beginning of the reaction, the total COD corresponded with the theoretical COD value given by phenol, which was the only substance in the reaction medium. During the reaction time, both the COD and the concentration of phenol decreased following the same pattern, but whereas the phenol practically disappeared (<5 ppm), the COD reached a constant value. This was attributed to the formation of low-molecular-weight and refractory carboxylic acids, which remain in the reaction medium and are not oxidized.[5,11,27] Figure 2 shows these results by plotting simultaneous
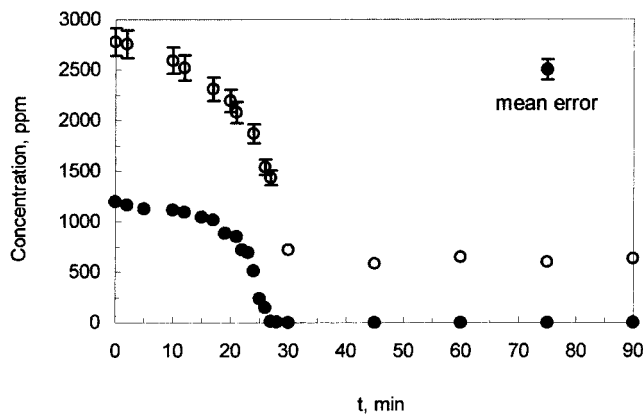
Figure 2. Evolution of COD (○) and concentration of phenol (●) for a run performed at 200 °C, 10.2 MPa, and $C_{Ph,o}$ = 1000 ppm.

plots of the phenol degradation curve at 200 °C, 10.2 MPa, and 1000 ppm and the corresponding COD profile. The error bars represent an estimation of the experimental error. For phenol depletion, the error represents an average value. The theoretical COD for a 1000 ppm solution of phenol in water is 2390 ppm. The relatively low value of COD at the end of the reaction suggests that the oxidation of phenol mainly yielded carbon dioxide and a certain amount of low-molecular-weight molecules. For example, stoichiometric conversion to acetic acid would lead to a COD of 2027 ppm. The evolution of the pH was also followed. The initial value rapidly dropped to an essentially constant value in the interval 2.5–3.0 that was essentially the same for all runs. The reduction could be attributed to the formation of carboxylic acids from phenol.

The rate of oxygen transfer from the gas phase to the liquid phase is a function of the convective mass transfer coefficient in the liquid phase, $k_L a$, and the driving force on the liquid side

$$\frac{dC_{O_2}}{dt} = k_L a(C_{O_2,sat} - C_{O_2}) \qquad (2)$$

The oxidation of 1 mol of phenol to carbon dioxide requires 7 mol of oxygen. The rate of oxygen required by the reaction under chemical control is the product of the stoichiometric coefficient and the rate of disappearance of phenol

$$-\frac{dC_{O_2}}{dt} = bk_r C_{Ph} C_{O_2} \qquad (3)$$

At stationary state, the rates of oxygen transfer and consumption must be equal, and the overall rate can be obtained by combining the preceding equations with the mass balance. If the chemical process controls the overall kinetics

$$\frac{1}{k_r C_{Ph}} \gg \frac{b}{k_L a}$$

and then

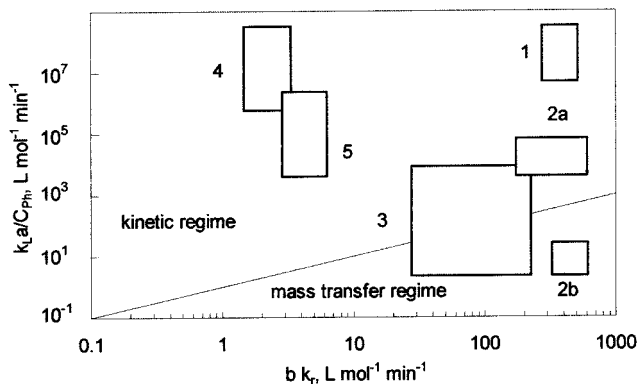$$-\frac{dC_{O_2}}{dt} = bk_r C_{Ph} C_{O_2} \qquad (4)$$

Figure 3. Reaction regimes following several authors and experiments: 1, Gasso et al.[28] (1992); 2a and 2b, Beyrich et al.[29] (1979); 3, Pruden and Le[10] (1976), 4, Jaulin and Chornet[14] (1987); 5, this work.

In contrast, if mass transfer is the rate-limiting process

$$\frac{b}{k_L a} \gg \frac{1}{k_r C_{Ph}}$$

and then

$$-\frac{dC_{O_2}}{dt} = k_L a C_{O_2,sat} \qquad (5)$$

Figure 3 shows a plot of the relative values of mass transfer and chemical resistance for the conditions used in this work compared with the data from other authors. The region close to the parity line represents a mixed regime where both chemical and mass transfer resistances should be taken into account. Beyrich et al.[29] used a bubble column and a stirred tank with different initial concentrations of phenol. Experiments marked as 2a started with 1.06×10^{-3} mol of phenol L^{-1}, whereas for those represented by 2b, the initial concentration of phenol was 0.532 mol L^{-1}. Pruden and Le[10] worked in the mixed regime to enable the simultaneous determination of mass transfer coefficients and rate constants. All of the reactions described in this work were performed under kinetic control conditions. The Hatta number, developed from film theory, has also been used to check the interfacial condition

$$Ha = \sqrt{\frac{bk_r C_{Ph} D_{O_2}}{k_L{}^2}} \qquad (6)$$

The diffusivity of oxygen was evaluated using the empirical expression proposed by Wilke and Chang,[30] and the mass transfer coefficient was evaluated according to Calderbank and Moo-Young.[31] In all runs, the higher values of the Hatta number, corresponding to the beginning of the rapid reaction step, were always less than 10^{-3}. As the reaction proceeded, the concentration of phenol decreased, resulting in a lower Hatta number. Therefore, no mass transfer limitations existed for the experimental conditions tested in this work, as the kinetic regime is ensured for $Ha < 0.02$.

Figure 4 shows a plot of the evolution of the phenol concentration for runs performed at 200 °C, an initial phenol concentration of 1000 ppm, and an oxygen pressure varying in the range 5.1–10.2 MPa. The flow rate of oxygen was 0.023 L s^{-1} (normal conditions),
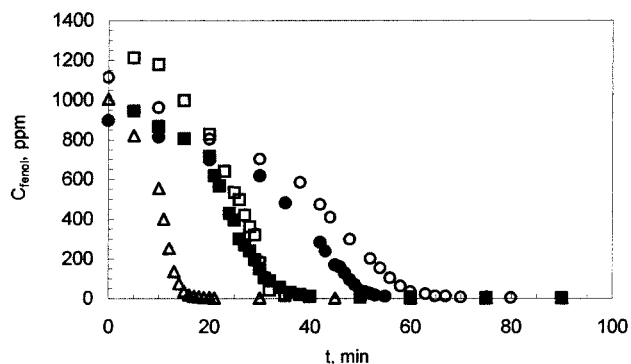
Figure 4. Evolution of phenol during oxidation as a function of oxygen pressure: 5.1 MPa (○), 7.1 MPa (●), 8.1 MPa (□), 9.1 MPa (■), and 10.2 MPa (△).

Figure 5. Evolution of phenol during oxidation at several temperatures: 170 °C (○), 180 °C (●), 190 °C (□), 200 °C (■), 210 °C (△), and 220 °C (▲).

providing an excess of oxygen large enough to guarantee oxygen saturation during the reaction. The concentration of oxygen was constant for a given run but varied from run to run as the temperature changed. The equilibrium concentration of oxygen was calculated according to Himmelblau.[32] The data were fitted to a kinetic expression that is nth-order in oxygen, yielding a value of $n = 1.14 \pm 0.12$ (95% confidence intervals). This value was considered as not significantly different from first-order kinetics. The oxygen concentration could be changed by manipulating the total pressure in the autoclave, which might explain the difference.[33] This value also agrees with those provided by other authors such as Pruden and Le[10] and Shibaeva et al.[34] A significant disparity exists, however, in the values for the oxygen reaction order reported in the literature, which is probably due to the huge variety of experimental equipment and working conditions used in different works. Willms et al.[1] reported a one-half-order dependence on dissolved oxygen. Orders different from 1 have also been found in most catalytic processes.[6,35]

The dependence of the kinetic constant expressed in eq 1 on the phenol concentration was determined by changing the initial concentration of phenol from 200 to 3000 ppm. For the lowest initial concentration of phenol (200 ppm), the reaction did not show the usual pattern consisting of an induction step followed by rapid first-order degradation. The reason might be that the initial concentration of the organic compound was too low to provide the amount of free radicals required to start the rapid step. The kinetic constant increases with the initial concentration of phenol according to

$$k_{\mathrm{r}}(C_{\mathrm{Ph,o}}) = kC_{\mathrm{Ph,o}}{}^{m} \tag{7}$$

The fitting of the experimental values for the initial concentration of phenol from 500 to 3000 ppm yielded $m = 1.04 \pm 0.16$ and $k = 6.5 \pm 0.6$ L^{n+1} mol$^{-(n+1)}$ s^{-1}. The intervals correspond to 95% confidence limits. The dependence expressed in eq 7 reflects the fact that the higher the initial concentration of organics, the greater the amount of free radicals generated, and the faster the reaction rate during the rapid degradation step.

The influence of temperature on phenol degradation was studied in the range 170−220 °C. Figure 5 shows the result of a set of runs performed with an oxygen pressure of 10.15 MPa, an oxygen flow rate of 0.023 L s^{-1}, and an initial phenol concentration of 1000 ppm. The kinetic regime was verified to ensure kinetic control conditions. Kinetic constants for the steady sstate that follows the induction period were considered to depend
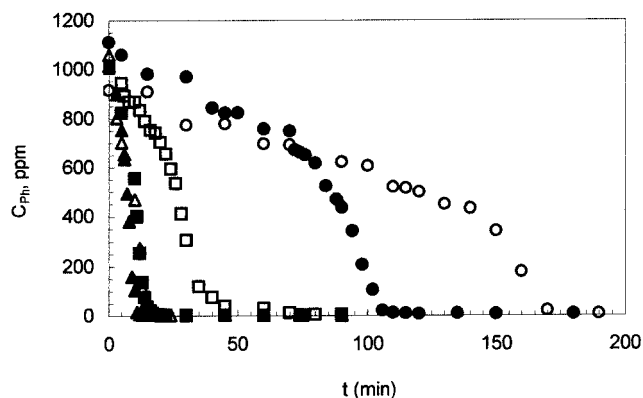
on temperature following an Arrhenius-type expression

$$k_{\mathrm{r}}(C_{\mathrm{Ph,o}}) = A\mathrm{e}^{-E_{\mathrm{a}}/RT} \tag{8}$$

The activation energy was $E_{\mathrm{a}} = 67.4 \pm 9.8$ kJ mol^{-1}, and the preexponential factor was $A = (2.05 \pm 0.42) \times 10^{6}$ L mol^{-1} s^{-1}, where the confidence intervals are given at 95% level. Shibaeva et al.[34] reported an activation energy of 107 kJ mol^{-1} for runs at 180−210 °C. Willms et al.[1] oxidized phenol at 130−200 °C and found a value of 112 kJ mol^{-1} for the activation energy. Pruden and Le,[10] Jaulin and Chornet,[14] and Joglekar et al.[26] indicated values of 45.1, 56.6, and 50 kJ mol^{-1}, respectively, for runs in the 150−250 °C range. The activation energy obtained in this work is in good accord with those obtained under conditions that avoid the formation of tar. Rivas et al.[25] calculated an activation energy of 46.9 $\pm$ 3.2 kJ mol^{-1} for degradation due to phenol hydroperoxide. Those authors also found an activation energy of 125.6 $\pm$ 4.2 kJ mol^{-1} for phenol hydroperoxide decomposition, whereas they assumed that the reactions involving hydroxyl radicals had a negligible activation energy.

At the end of the induction period, the reaction rate rapidly increased and reached a maximum. This allowed for an accurate determination of the length of the induction period for runs performed with an initial concentration of phenol above 500 ppm. Willms et al.[1] found that the length of the induction period could be correlated with an Arrhenius-type equation developed by means of mechanistic arguments. They assumed that the initiation reaction is zeroth-order in the organic phenol and that a critical concentration of radicals exists at which the rapid degradation period starts. As a result, a plot of $\ln(t_i C_{\mathrm{O_2,o}})$ vs $1/T$ should yield a straight line with a slope E_i/R, where E_i is the activation energy of the initiation reaction. Figure 6 shows the Arrhenius plot for the induction period for oxygen pressures in the range 5.1−10.15 MPa and initial concentration of phenol of 1000−3000 ppm. The error bar represents the 95% confidence interval determined with five degrees of freedom. There seems to be a change in mechanism from an apparent activation energy of 56 kJ mol^{-1} at less than 190 °C to approximately 170 kJ mol^{-1} for higher temperatures. Above 200 °C, however, the induction periods are relatively short and therefore difficult to measure. Willms et al.[1] reported an activation energy of 94 $\pm$ 31 for runs in the interval 130−170 °C. Even though the difference is significant, the lack of data makes it difficult to compare results. In fact, the lowest
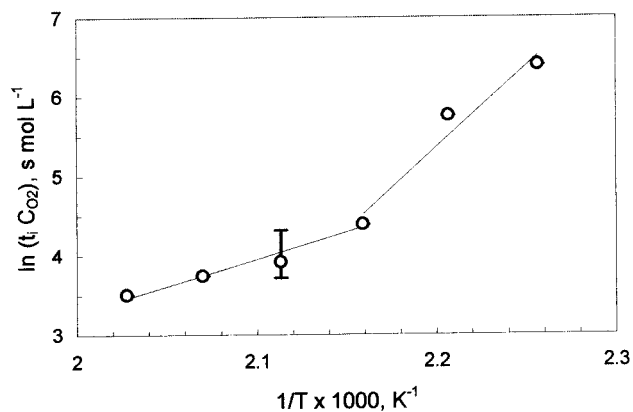
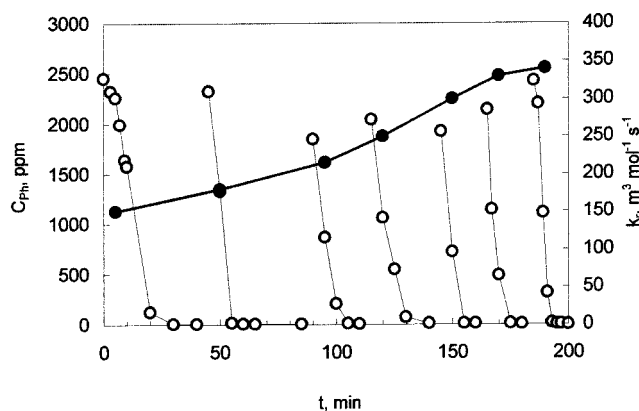**Figure 6.** Arrhenius plot for the induction period.

Figure 7. Result of a series of consecutive runs without removal of reaction products.

temperature used in this work is 170 °C, corresponding to the highest temperature reported by Willms et al.[1] The effects of the oxygen pressure and the initial concentration of phenol on induction time were not significant.

To gain further insight into the role of the radicals in the reaction, a series of consecutive runs was performed without removal of the phenol degradation products. The experiment consisted of making repeated phenol injections once the conversion from the preceding run reached at least 99% without stopping the oxygen flow. The results are shown in Figure 7 and represent a set of runs performed at 200 °C and 10.15 MPa with an initial phenol concentration of 2500 ppm after each new injection. Because of the accumulation of free radicals from preceding runs, the reaction rate in subsequent cycles increased. Moreover, the induction period could only be detected at the beginning of the first cycle, with subsequent runs starting directly at the rapid degradation step. The reaction time needed to accomplish each cycle decreased for successive runs, and whereas the first cycle required about 30 min to yield a 99% conversion, the second run took only 20 min. After the fifth run, the reaction time decreased to about 5 min. The figure also shows that the kinetic constant steadily increased from run to run. The reaction rate during the fast oxidation step probably increased from run to run as a result of the accumulation of intermediate compounds whose role in radical chain degradations has been previously stated.[14] The presence of these compounds was related to the brownish-yellow coloration of the samples.[6] The COD value measured at the end of the last cycle was practically the same as the value for single oxidation runs, i.e., 540 ppm. This has been

attributed to the formation of a certain amount of carboxylic acids (acetic, oxalic, glyoxalic, succininc, and propanoic, among others) that are difficult to oxidize under these working conditions.[11]

COD can be measured before a new injection, but the analyses did not allow for the value to be attributed to single compounds. If it is considered that a single carboxilic acid accounted for all of the measured COD, it would became possible to relate the observed reaction rate to the initial amount of organics. In such a case, the rate constant exhibits a linear dependence on the concentration of organics at the beginning of each run. The rate coefficient k, defined in eq 7, would yield a value of 5.9 L mol^{-1} s^{-1} if oxalic acid accounted for all of the residual COD, 5.5 L mol^{-1} s^{-1} if oxidation led to propanoic acid, and 4.8 L mol^{-1} s^{-1} if acetic acid were the only organic compound in the reaction mixture before any new injection. These results are in good agreement with the above-mentioned value for the rate constant, $k = 6.5 \pm 0. 6$ L mol^{-1} s^{-1}, obtained from experiments with different initial concentrations of phenol. It was stated above that the phenol concentration in eq 7 should represent the overall load of organics leading to free radicals during the reaction. In single runs, the initiation of radical chains is expected to originate mainly with phenol molecules, but in runs with repeated injections, the phenol practically disappears before a new injection is made. The effect of organic compounds other than phenol is clear and has been previously reported.[17] The results obtained in this work suggest that the increase in the rate constant can be attributed only to reactive compounds produced from phenol. Other compounds such as hydrogen hydroperoxide have been reported to play a role in the enhancement of the phenol reaction rate.[13,34] Other authors have indicated that the main radical initiation step for the wet air oxidation of phenol is the bimolecular reaction between phenol or other organics and oxygen.[24,25]

Conclusions

Experimental results showed that the oxidation of phenol at 170−220 °C and 5.10−10.15 MPa takes place under chemically controlled conditions. The reaction proceeds in two stages, an induction period and a rapid degradation step, following the usual pattern of radical chain reactions. The reaction rate increased with the amount of organics in the reaction mixture, a relationship revealed by a practically linear dependence of the rate constant on the initial concentration of phenol. A series of runs performed by successive injections of phenol without removal of reaction products showed that the reaction rate doubles after seven runs. The rate constant increased with the overall amount of organic compounds in the reaction mixture. Considering that the residual content of organic compounds consists essentially of low-molecular-weight organic acids, the dependence of the rate constant on the amount of organics was similar to the dependence obtained for the initial concentration of phenol in single runs. Because of the effect of residual organic compounds, the induction period disappeared after the first run. A mechanistic analysis of the induction period showed a change in the activation energy at approximately 190 °C from 56 to 170 kJ, probably indicating a change in the initiation mechanism. The rapid degradation step was first-order in each phenol and dissolved oxygen. The

activation energy was 67.4 $\pm$ 9.8 kJ mol^{-1}, in good agreement with other reported values.

Acknowledgment

Nomenclature

a = gas$-$liquid interfacial area per unit liquid volume of reactor, m^2 m^{-3}

A = preexponential factor, L mol^{-1} s^{-1}

b = stoichiometric coefficient

Ha = Hatta number = $\sqrt{b k_r C_{Ph} D_{O_2} k_L^{-2}}$

C_i = concentration in the reaction mixture, mol L^{-1} or ppm

$C_{i,o}$ = initial concentration in the reaction mixture, mol L^{-1} or ppm

D_{O_2} = diffusivity of oxygen in the liquid phase, m^2 s^{-1}

E_a = activation energy, kJ mol^{-1}

k_i = kinetic constant, units depending on reaction order

k_r = second-order rate coefficient, L mol^{-1} s^{-1}

k = Rate coefficient defined by eq 7

k_L and $k_L a$ = mass transfer coefficient for oxygen in the liquid phase, m s^{-1} and s^{-1}

n, m = order of reaction

t_i = induction period, s

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