ELSEVIER

Catalysis Today 53 (1999) 107–114

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Water pollution abatement by catalytic wet air oxidation in a trickle bed reactor

A. Fortuny [a], C. Bengoa [b], J. Font [b], F. Castells [b], A. Fabregat [b,*]

[a] Departament d'Enginyeria Química, EUPVG, Universitat Politècnica de Catalunya, Av. Víctor Balaguer, s/n, 08800 Vilanova i la Geltrú, Barcelona, Catalunya, Spain

[b] Departament d'Enginyeria Química, ETSEQ, Universitat Rovira i Virgili, Carretera de Salou, s/n, 43006 Tarragona, Catalunya, Spain

Abstract

Catalytic wet air oxidation of an aqueous phenol solution was carried out in a trickle bed reactor at mild conditions of temperature (120–160°C) and oxygen partial pressure (0.6–1.2 MPa). Tests were performed at space times up to 1 h. A commercially available copper oxide supported over γ-alumina was used as catalyst. The results show that the phenol conversion, the chemical oxygen demand (COD) reduction and the distribution of oxidation products are considerably affected by the temperature, whereas the oxygen partial pressure only has minor influence. The process exhibits high selectivity towards the production of carbon dioxide. Oxalic, acetic and formic acids were found to be the main partial oxidation products but also traces of maleic and malonic acids and quinone-like products, such as dihydric phenols and benzoquinones, were detected. First order with respect to the phenol concentration and one half order with respect to the oxygen partial pressure was found for both phenol disappearance and COD reduction. The apparent activation energy was calculated to be 85 kJ/mol for phenol oxidation and 76 kJ/mol for COD abatement. These values favourably compare with those cited in the literature for intrinsic kinetics, which indicates minimal mass transfer limitations in the trickle bed reacting system used in this study. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Phenol; Waste water; Copper catalyst; Trickle bed; Wet air oxidation

1. Introduction

The growing concern about the environment requires feasible solutions for processing toxic waste waters that cannot be biologically treated. Phenol commonly appears in aqueous effluents from sources such as petrochemical, chemical and pharmaceutical industries. Unless the concentration is low enough, phenolic waste waters are poorly biodegradable because of their bactericidal properties [1]. Therefore, phenolic compounds must be specifically destroyed before discarding the effluent for subsequent treatment in conventional sewage plants.

Catalytic wet air oxidation (CWAO) has been shown to be an effective technique for eliminating organic compounds, such as phenol [2,3]. Its main advantages lie in the small investment needed and the low operation costs because of the mild requirement of pressure and temperature. Only the lack of suitable catalysts has prevented it from being used more widely in environmental remediation. Supported copper oxide catalysts have often been investigated for the wet oxidation of phenol [4–11]. These studies, in which phenol was oxidised in batchwise slurry reactors, reported

---

[*] Corresponding author. Tel.: +34-977-559643; fax: +34-977-559667
E-mail address: afabrega@etseq.urv.es (A. Fabregat)

PII: S0920-5861(99)00106-6

that the catalyst underwent an induction period of increasing catalytic activity followed by a steady state regime [4–6]. This induction period was related to the heterogeneous-homogeneous free radical mechanism postulated for phenol oxidation in aqueous phase [6]. However, there are contradictory results for the reaction order with respect to the phenol concentration and the oxygen partial pressure as well as for the activation energy. Thus, first order with respect to phenol is mostly accepted [5–8,10] although it has also been reported to be 0.44 [4]. Likewise, several studies give one half reaction order with respect to oxygen [4–6] but 0.25 has also been reported [7,8]. On the other hand, the reported activation energies for phenol oxidation in aqueous phase go from 85 to 176 kJ/mol. Generally, copper-based catalysts exhibit a very high activity in batchwise tests but polymer formation on the catalyst surface [7,8] and leaching of active metal have been reported [7,8,11], although no substantial loss of catalytic activity was observed in consecutive runs [4–6]. Nonetheless, when phenol was oxidised in a fixed bed reactor operating in trickle flow regime, the loss of activity was significant due to the leaching of the active metal [9–14]. These contradictory results suggest that the kind of reactor can considerably affect the performance of the catalyst.

This work deals with the catalytic phenol oxidation in aqueous phase using a fixed bed reactor working in trickle flow regime. Air was used as oxidising agent since a previous study showed no significant difference between the use of pure oxygen or air at the same oxygen partial pressure [12]. A commercially available copper oxide catalyst supported on γ-alumina was employed. The detailed examination of the product dependence on the space time is provided in the temperature range 120–160°C and between 0.6 and 1.2 MPa of oxygen partial pressure. A kinetic analysis of the phenol disappearance and chemical oxygen demand (COD) reduction is also given.

2. Experimental

The equipment in which catalytic wet oxidation was carried out consists of a packed bed reactor placed in a temperature controlled oven, independent inlet systems for gas and liquid feed with pressure and temperature control equipment, and a separation and sampling system for the outlet products. A detailed scheme of the experimental set-up is available in the literature [12].

A 5 l stirred glass tank contains the liquid feed, which is a 5 g/l aqueous solution of phenol (reagent grade). This tank is connected to a high-pressure metering pump (Eldex AA-100-S2, Napa, CA, USA) that can dispense flow rates between 10 and 150 ml/h. The tubular reactor is constructed of SS-316 with an internal diameter of 1.1 cm and a length of 20 cm. This reactor is placed in an isothermal air convection oven that allows the temperature to be with a precision of ±1°C. A cylinder of high purity synthetic air supplies the gaseous feed at the desired pressure. The gas and liquid streams are mixed before entering a coil in the oven, which allows the mixture to reach the reaction temperature. Then, this mixture downwards flows through the reactor filled with catalyst. A sintered metal disc is placed at the top of the reactor in order to assure good flow distribution thus preventing channelling and other flow problems. The catalytic bed is supported by another sintered metal disc that prevents the catalyst from dragging. The effluent leaves the reactor and then passes to a small separator (2 ml) also used for sampling, and is finally collected in a second separator (2 l) used for liquid product storage. The gas then goes to a high precision flowmeter provided with a needle valve, which measures and controls the air flow rate.

The reactor contains 14.5 g of a commercially available catalyst (Harshaw Cu-0803 T1/8 manufactured by Engelhard, Houston, USA). The catalyst, hereafter referred to as Cu-0803, is a copper oxide supported over γ-alumina with a loading of 10.1% as CuO. It should be pointed out that this catalyst is mostly used for catalytic processes in gaseous phase. The main physical characteristics provided by the manufacturer were 1.03 g/cm^3 of apparent density, 137 m^2/g of surface area, 0.42 cm^3/g of pore volume and 95 Å of average pore diameter. Prior to use, the catalyst, which was received as 1/8 in pellets, was crushed and sieved and then the particles between 25 and 50 mesh (0.7–0.3 mm) were taken. It was experimentally proved that this particle size assures that there are no intraparticle mass transfer limitations in the performance of the catalyst. The above fraction was thoroughly washed to remove all fines, dried in an oven at 110°C for one day, allowed to cool and finally stored under inert atmosphere.

Reaction experiments were carried out for three temperatures (120, 140 and 160°C), three oxygen partial pressures (0.6, 0.9 and 1.2 MPa), hereafter simply referred to as oxygen pressure, and a range of liquid flow rates from 10 to 150 ml/h), i.e. space times up to 1 h. For each temperature, the operating pressure was selected taking the water partial pressure into account. Thus, the total pressures were respectively 3.1, 4.6 and 6.3 MPa. It should be noted that the water vaporised to give the vapour pressure is less than 2% of the liquid feed at the highest temperature and the lowest liquid flow rate, so it will be neglected in the balances throughout the work. The air flow rate was 2.4 ml/s (STP conditions), which guarantees oxygen in excess. It should be pointed out that, in all the above conditions, the fixed bed operates in trickle flow regime [15]. Lifetime tests made in a preliminary work [12] revealed that the catalyst Cu-0803 undergoes a serious deactivation, approximately 50% of the initial activity, during the first 72 h of operation. After this deactivation period, the catalyst shows steady activity for several days. In order to prevent the catalytic activity from affecting the results, the data shown in this study were taken during the constant activity period, i.e. 72–168 h of operation, in which the reproducibility is acceptable since differences between phenol conversions from duplicate experiences were found to be always lower than 5%.

For each test, outlet reactor samples were withdrawn in duplicate, quickly cooled and immediately analysed by HPLC (Beckman System Gold, San Ramon, CA, USA) using a C_{18} reverse phase column (Spherisob ODS-2). To separate the phenol and the partial oxidation products, a mobile phase of variable composition was programmed at 1 ml/min starting from 100% water and ending at a 40/60% mixture of methanol and water. In this case, the detection was performed by UV absorbance at wavelength 210 nm. Single compounds were qualitatively identified by injecting pure samples of the expected partial oxidation products [16]. Then, calibration curves were made for each intermediate detected using aqueous samples of known composition. A standard mixture of oxidation products was periodically tested to correct deviations in retention time due to variations in flow rates or temperature programming.

The main parameter to compare the results in the discussion section will be phenol conversion, X_{Ph} defined as

$$X_{\mathrm{Ph}}(\%) = \frac{[\mathrm{Ph}]_{\mathrm{in}} - [\mathrm{Ph}]_{\mathrm{out}}}{[\mathrm{Ph}]_{\mathrm{in}}} \times 100 \qquad (1)$$

Similarly, the chemical oxygen demand (COD) of the effluent was also determined and then compared with the original feed COD. The results are presented as COD reduction, X_{COD}, defined as

$$X_{\mathrm{COD}}(\%) = \frac{[\mathrm{COD}]_{\mathrm{in}} - [\mathrm{COD}]_{\mathrm{out}}}{[\mathrm{COD}]_{\mathrm{in}}} \times 100 \qquad (2)$$

COD was determined by the standard open-type reflux method using potassium dichromate as oxidant [17]. This method was experimentally validated by using a standard solution of potassium hydrogen phthalate with a known COD of 500 mg/l. The error was found to be lower than 2%.

Nevertheless, phenol destruction by itself is not enough to show the efficiency of the oxidation process because some byproducts may be as harmful as the phenol itself. Thus, since all the compounds in the liquid phase were quantified by HPLC, the carbon dioxide production was calculated by difference from an atomic balance of carbon. In order to prove the goodness of the carbon mass balance, TOC analyses were also conducted in some selected cases. Then, carbon dioxide production was again calculated from TOC measurements and compared with that from HPLC. In all the cases, the differences were found to be below 5%. The results will also be discussed in terms of carbon dioxide yield, Y_{CO2}, which is defined, in a molar basis, as the part of phenol converted into carbon dioxide. Note that carbon dioxide yield is a measure of the selectivity rather than just a production parameter.

3. Results and discussion

The evolution of phenol conversion against space time is shown in Fig. 1 at the three different temperatures and oxygen pressures tested. Taking into account the uncertainty in the phenol conversion, which was experimentally evaluated to be ±5%, the strong influence of the temperature is clear. On the other hand, oxygen pressure seems only to have a slight effect.

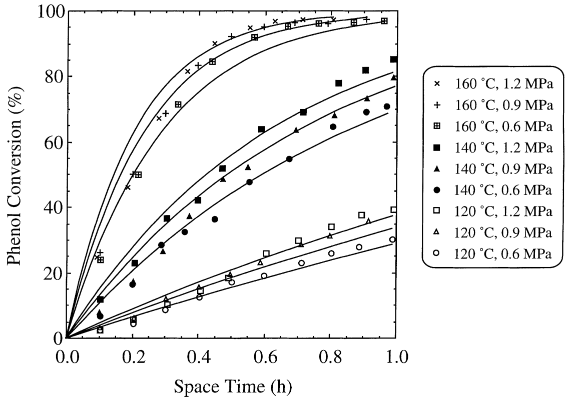

Fig. 1. Experimental and predicted phenol conversion.

As expected, phenol conversion was greatest (97%) at the highest temperature (160°C), oxygen pressure (1.2 MPa) and space time (1 h).

The kinetic analysis of the data was made assuming that the reactor follows a plug flow model. This assumption is expected to be mostly reasonable because of the high reactor diameter to particle diameter ratio, averaged 22, which exceeds the recommended value to prevent flow distribution problems [18]. It was also presumed that there were no external mass transfer limitations so the kinetics is only governed by the chemical reaction. This speculation will be later discussed. Thus, a differential mass balance was performed for phenol on the reactor. Then, several assumptions for the reaction order with respect to phenol concentration were made and the analytical solution was obtained in each case. Finally, a least squares routine was applied to obtain the apparent kinetic rate constant, k_{ap}, that best fits the experimental data to the analytical solution. The value of the objective function served to discriminate those models that give highly deviated predictions. Note that k_{ap} includes the effect of both the temperature and the oxygen pressure. The best phenol conversion fitting was found when the reaction order with respect to phenol concentration is one, which is in agreement with other studies conducted in slurry [5–8] or rotating basket reactor [4].

Assuming that the reaction rate constant can be expressed according to the Arrhenius law, k_{ap} can be symbolised as

$$\ln k_{ap} = \ln A_o + \alpha \ln P_{O_2} - \frac{E_a}{RT} \qquad (3)$$

where A_o is the frequency factor, P_{O2} the oxygen pressure, E_a the activation energy, R the gas constant, and α is the reaction order with respect to the oxygen pressure. This expression is applicable whenever the oxygen pressure is constant throughout the reactor. Since the highest oxygen consumption during operation has been calculated to be no more than 5% of the oxygen fed, the above condition can be assumed in practice. Thus, the unknown parameters α, A_o, and E_a were estimated by general linear least squares fitting. The best values obtained are 0.5 (±0.1) order with respect to the oxygen pressure, 2.6×10^{10} $(\pm 1 \times 10^{9})\ \mathrm{h}^{-1}\ \mathrm{bar}^{-1/2}$ for the frequency factor, and an activation energy of 85 (±2) kJ/mol. The calculated error is given for 95% confidence interval.

This apparent activation energy favourably agrees with others reported in the literature [4,7,8,19] and only is quite different from that given by Sadana et al. [5]. It is noteworthy that our value is almost identical to those provided by Ohta et al. [4], 85 kJ/mol, and more recently by Pintar and Levec [7,8], 84 kJ/mol. Both studies were conducted in slurry reactors and their kinetics is broadly accepted to be intrinsic. However, it should also be noted that Ohta et al. [4] employed the present commercial catalyst but reported the dependence with respect to phenol concentration to be one half reaction order, whereas Pintar and Levec [7,8] tested a different copper oxide catalyst with similar characteristics. On the other hand, Crynes et al. [19], using a monolith froth reactor, reported a slightly lower activation energy, 67 kJ/mol, which was attributed to mass transfer limitations. Thus, as previously noted, the apparent activation energy calculated in this study is similar to the intrinsic values reported [4,7,8]. This result suggests that the kinetics evaluated in the trickle bed reactor is very close to the intrinsic kinetics, which suggests that the mass-transfer limitations can indeed be neglected. It is well known that the high gas/liquid ratio employed by this type of reactor permits better contact between the gas and liquid phases thus improving the mass transfer between phases.

The predicted phenol conversions are in good agreement with the experimental data as can be seen in Fig. 1 (solid lines). It should be noticed that the average deviation between experimental and predicted phenol conversions was found to be 3%. At 160°C, the experimental phenol conversion increases more slowly than

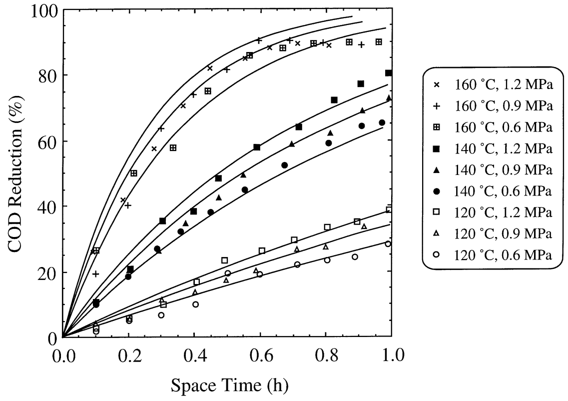

Fig. 2. Experimental and predicted COD reduction.

the mathematical model predicts. Since large phenol conversions are reached in these conditions and the rate of oxygen consumption must be the highest, one could believe that the oxygen mass-transfer governs the reaction thus producing this deviation. However, this effect was also observed by Willms et al. [20] in batchwise studies with negligible oxygen mass transfer limitations. The phenomenon was then attributed to a change in the apparent reaction order which decreases from one to one half. The decrease in reaction order would be due to autoinhibition caused by the buildup of partially oxidised intermediates that compete with phenol for free radicals. In addition, the apparent decrease in reaction order at low concentrations of target compound has also been noticed in other oxidation studies [21,22].

Because phenol is assumed not to be completely oxidised to carbon dioxide, COD reduction is expected to be always lower than the respective phenol conversion. This can be seen in Fig. 2 in which COD reduction is plotted against the space time for the set of temperatures and oxygen pressures tested. As expected, the COD reductions observed are not as large as phenol conversions. For instance, in the most extreme operation conditions, COD reduction is 90% whereas phenol conversion is 97%. Note that the higher is the difference between COD reduction and phenol conversion the higher is the amount of partially oxidised products present in the liquid effluent. Therefore, the above COD reduction is large enough to expect that Cu-0803 shows a high selectivity towards the production of carbon dioxide. This will be discussed below.

Similarly to phenol conversion, a kinetic analysis was performed for COD reduction following the same procedure. Again, first order with respect to COD and 0.5 (±0.1) order with respect to oxygen pressure best fit the experimental COD reduction. In this case, the frequency factor and activation energy calculated were 1.3×10^9 $(\pm 1 \times 10^8)$ $\mathrm{h}^{-1}\,\mathrm{bar}^{-1/2}$ and 75 (±3) kJ/mol respectively. Since oxidation of all the organic compounds, i.e. phenol and partially oxidised compounds, accounts for COD reduction, the calculated activation energy is different from that of phenol oxidation. This lower value suggests that the oxidation of the most intermediates is more easily completed than the formation of dihydric phenols, i.e. the first step in the phenol oxidation mechanism [16].

As expected, highly oxidised products such as acids and diacids were the main intermediates detected in the product effluent. Thus, oxalic, formic and acetic acids account for almost 90% of the intermediates detected in the liquid phase, although dihydric phenols, benzoquinones, and maleic, fumaric and malonic acids were also identified in measurable quantities. Fig. 3(a, b, c) shows the oxalic acid concentration against the space time at the different temperatures and oxygen pressures studied. The dependence of these profiles with the temperature is characteristic of a consecutive reaction pathway, where oxalic acid is formed from more complex intermediates and progressively degraded to simpler organic compounds, as demonstrated by the existence of a maximum at the three temperatures tested. Similar trends arise from Fig. 4(a, b, c) where the formic acid concentration is plotted against the space time. In this case, the oxidation of the formic acid produces carbon dioxide as unique possible product. Fig. 5(a, b, c) presents the concentration-space time profile for acetic acid. Unlike oxalic and formic acids, the acetic acid concentration does not show any maximum thus indicating that acetic acid can actually be taken as end product in the current operation conditions. Acetic acid has been noticed to be the most refractory compound in the complex phenol oxidation network [16,23]. Although measured in low amount, quinone-like products such as dihydric phenols and benzoquinones were identified as first stages in the phenol oxidation mechanism. These byproducts are of interest because they are as toxic as phenol. As can be seen in Fig. 6(a, b, c) their overall concentration shows a maximum at the three

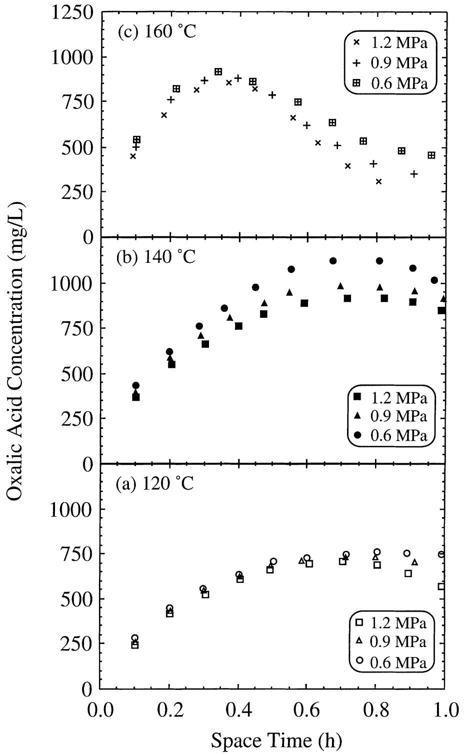

Fig. 3. a,b,c. Oxalic acid concentration evolution at different temperatures.

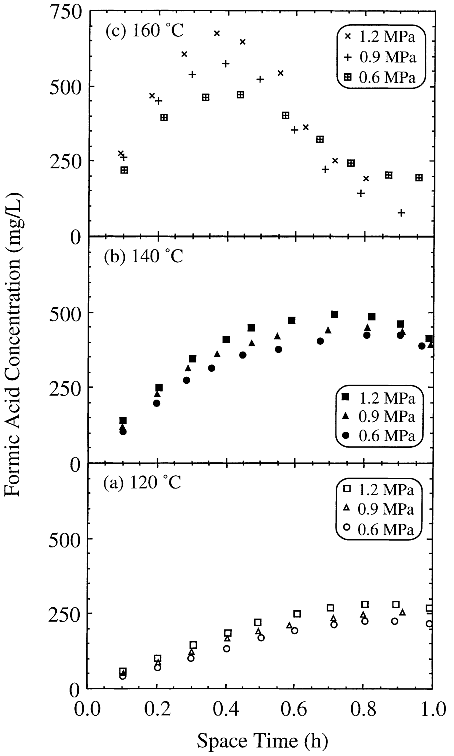

Fig. 4. a,b,c. Formic acid concentration evolution at different temperatures.

temperatures. However, as temperature increases, the locus of the maximum is found at lower space time although its concentration is higher. This behaviour is typical of a model based in consecutive reactions for which the appearance reaction rate is more temperature dependent than the disappearance rate, which agrees with the COD behaviour. Malonic acid was detected in appreciable amounts, up to 150 ppm, in the most severe operation conditions. On the other hand, maleic and fumaric acids were detected only as traces, below 10 ppm. No other compounds were detected in significant amounts. The byproducts detected are in agreement with the classical phenol oxidation mechanism proposed by Devlin and Harris [16]. Nevertheless, it should be noticed that neither succinic acid nor propionic acid was identified in the current study. These compounds were detected by Devlin and Harris [16] only under conditions of limited oxygen availability. Therefore, the non presence of both acids in the present reaction conditions could also evidence minimal oxygen mass-transfer resistance in the reactor.

The HPLC analyses performed on the exited solution showed that no polymers were formed in any reaction conditions. Neither polymers deposited on the catalyst were found by temperature programmed desorption (TPD) analyses conducted at the end of each test. This lack of polymers contrasts with observations made in studies carried out in slurry reactors [4,7,8] but was also noticed by Pintar and Levec [9]. The reason for trickle bed preventing condensation products from being formed is attributed to that this type of reactor operates at higher catalyst to liquid ratio than slurry reactors [9]. After each test, the catalyst was collected, dried at 110°C overnight and then weighed. In comparison with the initial catalyst loading, weight loss was minor (<0.1%), which is another proof of the no presence of adsorbed polymers. This small decrease of weight is attributed to the metal leaching caused by the dissolution of the copper oxide by acid attack [24,25]. Note that, because phenol has acidic properties, the pH of the feed solution is already acid, around 5.9, and the most partial oxidation products

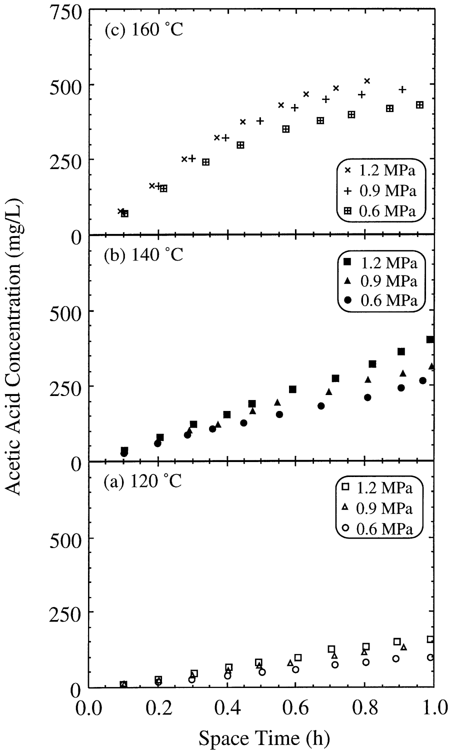

Fig. 5. a,b,c. Acetic acid concentration evolution at different temperatures.

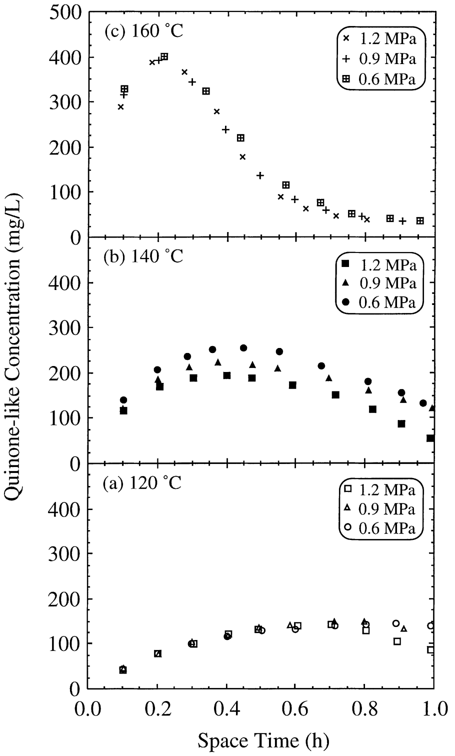

Fig. 6. a,b,c. Quinone-like concentration evolution at different temperatures.

are fatty organic acids which enhance even more the acidity of the reacting medium.

The carbon dioxide production was calculated by difference from atomic carbon mass balances, assuming that all the carbon not accounted for was converted into carbon dioxide. Note that no carbon is accumulated in the system by the formation of polymers and all the compounds participating in the reaction were carefully quantified by HPLC. In addition, the experimental outlet COD measures satisfactorily match the COD estimations inferred from the byproduct experimental data, which permits the carbon mass balances to be confidently closed using the amounts of phenol and intermediates measured in the effluent. Only in four cases of the 96 studied (at the lower space times), the carbon dioxide yield was calculated to be slightly negative (<4%). These estimations, even being obviously erroneous, mean that the phenol oxidation produces mostly partial oxidation products in those soft operating conditions. Anyway, these points are of low interest since they are in the low phenol conversion region. The carbon dioxide yield as defined in the experimental section is shown in Fig. 7. The carbon dioxide yield increases as the operation conditions become more severe. As expected, extreme reaction conditions favour the oxidation of the intermediates, which

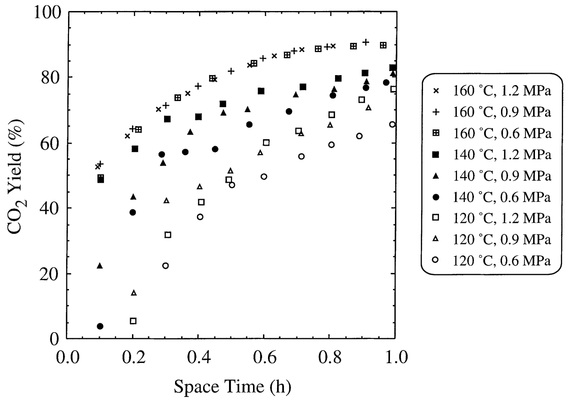

Fig. 7. Carbon dioxide yield at different temperatures and oxygen partial pressures.

otherwise accumulate in the exited solution as byproducts. Carbon dioxide yield reaches a maximum value of about 90%, i.e. 90% of the phenol removed renders carbon dioxide, which means that 90% of the phenol fed is completely destroyed.

4. Conclusions

Phenol can be effectively oxidised in a fixed bed reactor operating in trickle flow regime, using a commercial copper oxide catalyst. Phenol conversion over 95% and COD reduction up to 90% were reached at 160°C and 12 bar of oxygen partial pressure. In these conditions, the oxidation shows high selectivity towards the production of carbon dioxide, and almost 90% of the phenol destroyed becomes carbon dioxide. The partially oxidised products were found to be mostly low molecular weight organic acids such as oxalic, formic and acetic acids, although measurable amounts of hydroquinone, catechol and benzoquinones and trace amounts of malonic, maleic and fumaric acids were also identified. No condensation products were found in the exited solution or deposited on the catalysts. The kinetic analysis of the experimental data shows that, for both phenol disappearance and COD reduction, the reaction order with respect to the phenol concentration or COD is one and one half with respect to the oxygen partial pressure. The estimated activity energies are 85 kJ/mol for phenol disappearance and 75 kJ/mol for COD reduction.

Acknowledgements

Financial support for this research was provided in part by the CICYT (Project AMB92-1092). We particularly thank Josep Maria Borràs for his help in conditioning the analytical methods.

References

[1] R.L. Autenrieth, J.S. Bonner, A. Akgerman, M. Okaygun, E.M. McCreary, J. Hazard. Mater. 28 (1991) 29.
[2] J. Levec, A. Pintar, Catal. Today 24 (1995) 51.
[3] J. Levec, Chem. Biochem. Eng. Quart. 11 (1997) 47.
[4] H. Ohta, S. Goto, H. Teshima, Ind. Eng. Chem. Fundam. 19 (1980) 180.
[5] A. Sadana, J.R. Katzer, Ind. Eng. Chem. Fundam. 13 (1974) 127.
[6] A. Sadana, J.R. Katzer, J. Catal. 35 (1974) 140.
[7] A. Pintar, J. Levec, Chem. Eng. Sci. 47 (1992) 2395.
[8] A. Pintar, J. Levec, J. Catal. 135 (1992) 345.
[9] A. Pintar, J. Levec, Ind. Eng. Chem. Res. 33 (1994) 3070.
[10] V. Tukac, J. Hanika, Collect. Czech. Chem. Commun. 60 (1995) 482.
[11] R.P. Kochetkova, A.F. Babikov, L.I. Shpilevskaya, I.P. Shiverskaya, S.A. Eppel, F.K. Shmidt, Chem. Technol. Fuels Oils 28 (1992) 225.
[12] A. Fortuny, C. Ferrer, C. Bengoa, J. Font, A. Fabregat, Catal. Today 24 (1995) 79.
[13] C. Miró, A. Alejandre, A. Fortuny, C. Bengoa, J. Font, A. Fabregat, Water Res. 33 (1999) 1005.
[14] A. Fortuny, C. Bengoa, J. Font, A. Fabregat, J. Hazard. Mater. 64 (1999) 181.
[15] A. Gianetto, V. Specchia, Chem. Eng. Sci. 47 (1992) 3197.
[16] H.R. Devlin, I.J. Harris, Ind. Eng. Chem. Fundam. 23 (1984) 387.
[17] Norme Française NFT90-101 Octobre 1988. Essais de Eaux. Détermination de la Demande Chimique en Oxygène.
[18] G.B. Froment, K.B. Bischoff, Chemical Reactor Analysis and Design, Wiley, New York, 1990.
[19] L.L. Crynes, R.L. Cerro, M.A. Abraham, AIChE J. 41 (1995) 337.
[20] R.S. Willms, A.M. Balinsky, D.D. Reible, D.M. Wetzel, D.P. Harrison, Ind. Eng. Chem. Res. 26 (1987) 148.
[21] A.K. Chowdhury, L.W. Ross, AIChE Symp. Ser. 71 (1975) 46.
[22] C.R. Baillod, B.M. Faith, Report EPA-600/S2-83-060, US Government Pinting Office, Washington, DC, 1983.
[23] J. Levec, J.M. Smith, AIChE J. 22 (1976) 159.
[24] A. Alejandre, F. Medina, A. Fortuny, P. Salagre, J.E. Sueiras, Appl. Catal. B: Environ. 16 (1998) 53.
[25] A. Alejandre, F. Medina, P. Salagre, A. Fabregat, J.E. Sueiras, Appl. Catal. B: Environ. 18 (1998) 307.