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Phenol oxidation in a periodically operated trickle bed reactor

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Abstract

The present contribution reports an experimental study of the oxidation of phenol aqueous solutions over a CuO/γ-Al_2O_3 catalyst carried out in a trickle bed reactor. Steady-state as well as periodic on–off experiments were performed. In the range of operating conditions studied, it was observed that liquid flow modulation has a mild effect on phenol conversion but it does affect product distribution, favoring the mineralization process. When the liquid flow is halted, the intermediate products remain inside the catalyst and are further oxidized to final products. The residence time of the intermediates and the average oxygen concentrations inside the catalytic pellet during liquid flow modulation are higher than those attained in steady-state operation.

Keywords: Phenol oxidation; Periodic operation; Selectivity

1. Introduction

Phenolic compounds are present in many industrial wastewaters in concentrations high enough as to confer them bactericide properties. Under this condition, biological oxidation cannot be used. One way to overcome this drawback is to pre-treat the effluents in a three phase catalytic reactor. However, the lack of suitable catalysts is a serious disadvantage and has prevented this method from being used more widely in environmental remediation. Supported copper oxide catalytic systems were used to oxidize phenol aqueous solutions in batch and continuous reactors operated at moderate pressures and temperatures [1–4]. In a previous work [5], we reported the results obtained in a semibatch rotating catalytic basket reactor (RCBR) loaded with a CuO/γ-Al_2O_3 catalyst synthesized in our laboratory by the molten salt method. Polymer formation on the catalyst surface and leaching of the active metal were responsible for the loss of catalytic activity observed. To prevent the deposition of solid intermediates on the surface of the catalyst, a reactor with a low liquid to catalyst ratio, such as a trickle bed reactor (TBR), is recommended.

The TBR can be operated under steady-state or with liquid flow modulation. Periodic operation refers to a mode of process in which the system is forced to operate continuously in a transient mode. This process intensification technique seems to be a promising tool to improve the performance of TBRs, especially when the mass transfer of a key reactant is rate controlling or, at least, affects the rate. Particularly, liquid flow modulation is achieved by pulsing directly the liquid loading, i.e. switching the liquid flow rate between a minimum (usually zero) and a maximum value. This is known as on–off cycling. The gas flow rate is kept constant over the entire period.

Previous studies have demonstrated that on–off modulation of the liquid flow in a co-current TBR can lead to a substantial increase in the conversion and/or reaction rate. Some reaction systems under study were:

- SO_2 oxidation over activated carbon [6–8];
- hydrogenation of alphamethylstyrene over Pd/Al_2O_3 catalyst [9,10];
- hydrogenation of crotonaldehyde over Pd/Al_2O_3 catalyst [11];
- hydrogenation of cyclohexene to cyclohexane over Pd/charcoal catalyst [12].

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In most of these works, external mass transfer of the gaseous reactant is the controlling step and liquid flow modulation enhances conversion or reaction rate.

Although significant work on catalytic phenol oxidation in TBRs under steady-state operation has been reported [2,13,14], only one reference related to liquid flow modulation is presented [15]. Recently, the wet oxidation of phenol solutions (5000 ppm) was investigated over an active carbon extruded catalyst at 140 °C and 5 MPa of oxygen pressure [15]. Steady-state and on–off experiments in the fast mode operation were performed. With an optimal period of 60 s and split 0.5, the authors found conversion improvements of about 10% with respect to steady-state conditions. Experimental results on the effect of periodic flow interruption on selectivity were not presented. It remains to be seen if liquid phase or even gas phase composition modulation can affect selectivity or yield when multiple reactions, such as the oxidation of organics in water, occur in TBRs.

The present contribution reports an experimental study of the oxidation of phenol aqueous solutions over a $CuO/\gamma\text{-}Al_2O_3$ catalyst carried out in a TBR. Steady-state as well as periodic on–off experiments were performed. Cycling experiments were done in the so-called slow mode operation in which the periods are in the order of several minutes. Under such conditions the reactor works for some time at the maximum and for some time at the minimum liquid flow rate. By this mode of operation, during the dry cycle, external mass transport coefficients are increased, resulting in higher oxygen concentrations at the catalyst surface.

An additional matter is expected here, due to the semiconductor nature of the catalyst. In catalytic processes the semiconductor does act as an active participant and takes part in the intermediate stages of the reaction as one of the reaction components [16]. The surface of a metal oxide catalyst has a dynamic character that depends on the properties of reactants [17]. Therefore, catalyst activity will be modified as the catalyst is exposed to different oxygen concentrations. These concepts are supported by other authors [17], who studied the catalytic liquid-phase oxidation of aqueous phenol solutions under partial wetting conditions. A mixture of copper, cobalt and zinc oxides supported on cement catalyst was used. When the catalyst surface was directly exposed to the gas phase stream due to partial wetting of the particles, catalyst abruptly changed its composition from an excess of metal to a deficiency of metal, in which the crystal contains mainly cation vacancies and valence-band holes (which are believed to be active sites for phenol activation). The liquid-phase phenol oxidation follows a stepwise mechanism in which oxygen acts as an oxidizing agent but it also determines the concentration of active sites. So, any effort to enhance oxygen concentration would be, in principle, two-fold favorable.

2. Experimental

Phenol oxidation was studied in a packed bed reactor operated in the trickle regime. The experimental set-up is shown in Fig. 1. It consisted of a packed SS-316 bed reactor equipped with an axial thermocouple. The reactor was placed in a temperature-controlled oven. Gas and liquid preheated feed were introduced at the top of the reactor. The equipment was provided with pressure and temperature control units and a separation and sampling system for the outlet products.

The tubular reactor had an internal diameter of 2.1 cm and a length of 40 cm. The trickle bed reactor had three

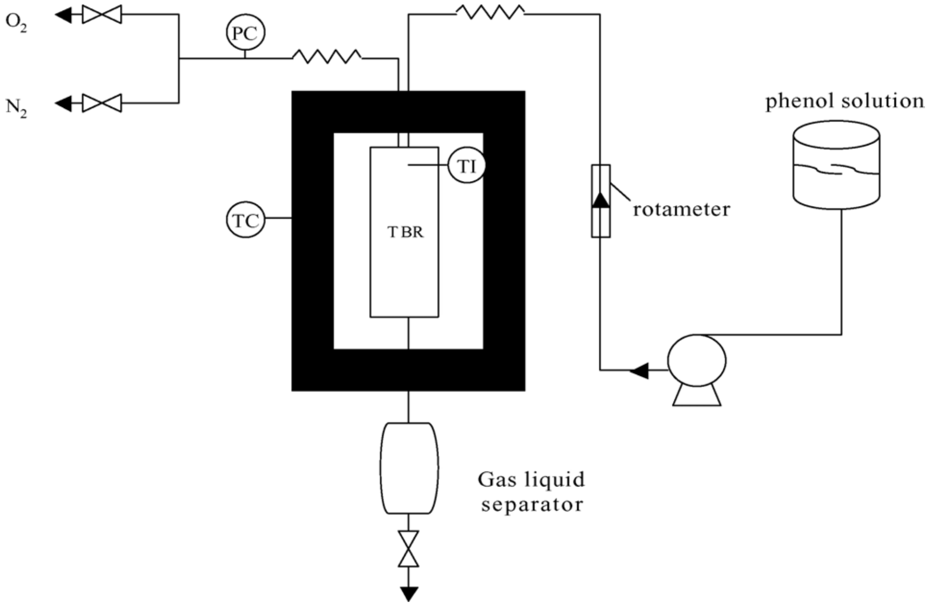

Fig. 1. Experimental set-up.

Table 1
Physical characterization of fresh catalyst

Copper content (wt.%)	30
BET surface area (m^2/g)	154
Average pore diameter (nm)	11.7
Average pore volume (cm^3/g)	0.46
Calcination temperature (°C)	400
XRD detected phases	γAl_2O_3-CuO

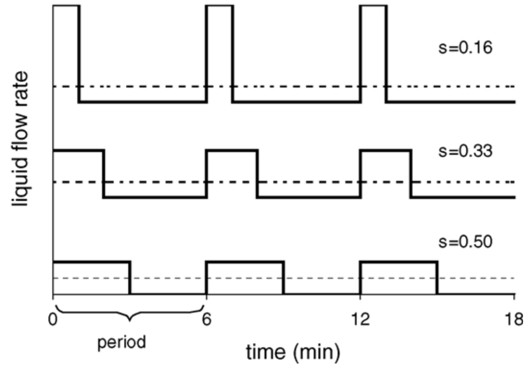

Fig. 2. On–off cycling operation for 6 min period and splits 1/6, 1/3 and 1/2.

distinguished zones: pre-bed of inert glass particles, the catalytic bed and a post-bed section of inert particles.

Prior to use, part of the CuO/Al_2O_3 catalyst was crushed and sieved. The mean equivalent diameter for the powdered particles was 570 μm. This sample was used in stability experiments. However, most runs were performed with cylindrical pellets of 2.6 mm size, to minimize deactivation by leaching [4]. The reactor contained 8 or 15 g of CuO/Al_2O_3 catalyst (powdered or in pellets, respectively) whose physical characteristics are given in Table 1.

The catalysts were characterized by temperature programmed reduction (TPR). This analysis was performed with 5% H_2/Ar with 0.04 g of catalysts in a conventional TPR set-up. The temperature was increased linearly at 5 °C/min. The temperature range was 20–500 °C and a thermal conductivity detector (TCD) monitored the H_2 uptake.

Specific surface area (method BET), as well as pore size distribution were measured with a Micromeritics ASAP 2000 instrument using N_2 adsorption at the temperate of the liquid nitrogen. All samples were degassed at 130 °C for 10 h before analysis.

X-ray diffraction (XRD) patterns were obtained with a PW 1830/00 Philips XRD diffractometer employing Cu Kα radiation. The X-ray was operated at 40 kV and 30 mA. Diffraction patterns were obtained using a scanning rate of 1.0°/min (in 2θ) with divergence slit and scatter slit widths of 1°.

The copper content was determined by atomic absorption (AA) spectrophotometry ANALYST 300, Perkin-Elmer. The samples were attacked with nitric acid to remove the Cu^{2+} species.

The liquid feed consisted of a solution of 5 g/L of phenol (reagent grade) placed in a 0.5 L glass vessel. The tank was connected to a high pressure-metering pump (ELDEX Model AA-94-2, San Carlos, CA, USA) that supplied the phenol solution at flow rates between 0.3 and 3 mL/min. The gas phase was pure oxygen at 7 atm pressure. Gas flow rate was monitored and controlled at 460 mL/min by means of a mass controller (SIDE TRACK III). Gas and liquid feed were pre-heated before entering the reactor.

To evaluate a periodically operated TBR, the volumetric liquid flow rate was cycled by means of an on–off three-way solenoid valve (Jefferson Model 365) activated by timers. There was no liquid flow during the dry period (on–off cycling strategy). Since only a few seconds are needed to drain the bed, on–off operation was considered as square-waves cycling. Gas mass flow rate was kept constant for all the experiments.

The liquid flow rate was set as to obtain the same productivity as in steady-state operation. The liquid velocity for steady state (u_{ss}) and during the wet cycle of periodic operation (u_{cyc}) are related as:

$$u_{ss} = s u_{cyc}$$

The cycle split s is the fraction of the cycle during which the liquid phase flushes the bed. Cycle periods of 3, 6 and 10 min were investigated with different splits (1/6, 1/3 and 1/2). Fig. 2 shows liquid flow modulation for a period of 6 min and different splits.

Reaction experiments were carried out at 140 °C and 7 atm of oxygen pressure. The bed was pre-wetted and operated for several hours before samples were taken. This preliminary practice guarantees complete internal wetting of the catalyst and also pre-heats the bed. Since catalytic activity varied slightly between runs, steady-state tests were performed before and after each set of unsteady-state experiments to ensure reproducibility. Liquid samples were withdrawn from the gas–liquid separator after steady state was reached at each liquid flow rate and analyzed for phenol content by a direct photometric method (Spectrophotometer Shimadzu, UV 1601PC) [18]. Chemical oxygen demand (COD) was determined by a closed reflux, colorimetric method, which is a rapid system for measuring the amount of oxygen consumption in the solution by $K_2Cr_2O_7$ (HACH DR/890) [18]. Phenol conversion was calculated according to:

$$X = \frac{[\mathrm{Ph}]_0 - [\mathrm{Ph}]_{\mathrm{out}}}{[\mathrm{Ph}]_0}$$

where $[\mathrm{Ph}]_0$ and $[\mathrm{Ph}]_{\mathrm{out}}$ are inlet and outlet phenol concentrations, respectively.

According to previous works [1–4], a simplified reaction scheme can be stated:

$$\text{phenol} \rightarrow \text{intermediate products} \rightarrow CO_2 + H_2O$$

Identification of intermediates was done in a GC/MS equipped with a capillary column. The samples consisted in a mixture of phenol, benzoquinones, hydroquinones, resorcinol, benzenediol and oxalic, acetic, malic and maleic acids that were recognized by this technique. Quantification was not precise so results are not reported here.

Selectivity towards mineralization (*S*) is defined as the ratio between CO_2 production over phenol conversion. The COD measurement indicates the intensity of the oxidation process. Therefore, production of CO_2 was evaluated from COD decrease as:

$$CO_2\ \text{production} : \frac{COD_i - COD_f}{COD_i}$$

where COD_i and COD_f are initial and final COD values, respectively.

For cycling operation, the liquid flow rate was set to the one corresponding to the wet period and liquid flow modulation was started. Once the cycle invariant state was reached, a liquid ‘‘mixing cup’’ sample was collected over an entire wet cycle. Phenol conversion and COD were measured and compared with values obtained under steady-state conditions at the same average liquid flow rate.

3. Results and discussion

Fresh CuO/γ-Al_2O_3 catalyst was characterized by AA, XRD, TPR and BET surface area determination. Results are resumed in Table 1.

Fresh samples presented high copper content (30%), as determined by means of AA analysis as indicated in Table 1. This high metal loading would induce the segregation of CuO *bulk*-like phase on the catalyst [19]. This is confirmed by XRD results that showed the presence of characteristic CuO phase peaks [5].

Fig. 3 shows the TPR profiles obtained for fresh and used CuO/Al_2O_3 catalysts. Additionally, the CuO standard curve is included as a reference. These profiles exhibit a maximum in the H_2 uptake in the range of 310–320 °C. According to the CuO reference curve and the XRD analysis, this peak is assigned to CuO-like species [5]. After 80 h of operation, the TPR profiles show a markedly decrease in the area under the thermoreduction curve (curves B and C, Fig. 3). This decrease is more pronounced for the powdered catalyst than for the pelletized sample. The copper content of used samples was determined by AA and also verified by TPR; the results are reported in Table 3.

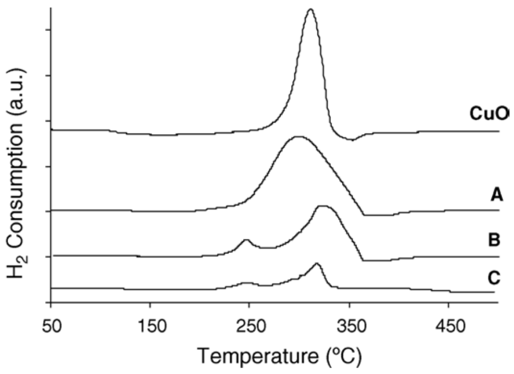

Fig. 3. TPR profiles of fresh and used CuO/Al_2O_3 catalysts. (A) Fresh catalysts (powdered and pelletized), (B) used sample of pelletized catalyst and (C) used sample of powdered catalyst.

Table 2
Steady-state results with powdered catalyst

Modified residence time (g h L^{-1})	Phenol conversion	CO_2 production
66	0.27	0.22
133	0.42	0.38

In preliminary blank experiments, phenol conversion was irrelevant when powdered alumina was used instead of the catalyst. In order to test the activity of the powdered CuO/Al_2O_3 catalyst, the reactor was charged with 8 g of sample. Preliminary experiments were made at liquid flow rate of 2 mL/min but no significant phenol conversion was achieved. To enhance bed porosity the catalyst was diluted with fine glass spheres and two runs were made investigating the effect of the liquid flow rate. Results are expressed in Table 2. As the modified residence time was increased from 66 to 133 g h L^{-1} phenol conversion increased from 27 to 42%. The CO_2 production (determined from COD experiments) varied from 22 to 38%, and hence, selectivity towards mineralization S_0 varies from 81 to 90%. The results clearly indicate that total phenol conversion is favored while operating at low liquid flow rates, where partial wetting is small and oxygen transport resistance is reduced. In addition, a richer oxygen environment will favored the formation of more active sites and promotes the oxidation of reaction intermediates.

In order to investigate the stability of crushed catalyst several runs were made at 66 g h L^{-1} and phenol conversion as well as COD values were monitored from liquid samples withdrawn periodically. Fig. 4 shows phenol conversion and CO_2 production against time during steady-state experiments made with 8 g of powdered catalyst diluted with fine glass spheres to improve liquid distribution. Initially, phenol conversion was 27% while the CO_2 production was 22%. Thus, the initial selectivity towards mineralization S_0 was

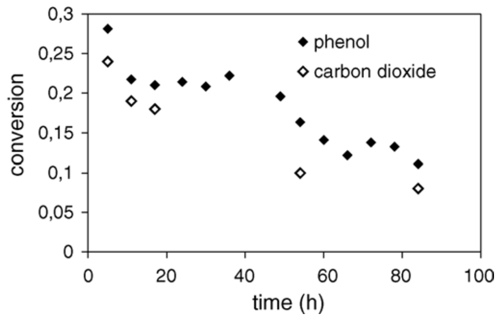

Fig. 4. Phenol conversion and CO_2 production vs. time with powdered catalyst diluted with fine glass spheres.

Table 3
Copper content (wt.%) of fresh and used catalyst samples

Catalyst	Powder (%)	Pellet (%)
Fresh	30	30
Used—80 h	6	21

calculated as previously. After 11 h of operation, phenol conversion was 22%, CO_2 production was 18% and, from these values, *S* was 81%. These values are constant for about 36 h, and then catalytic activity decays. After 80 h of operation, phenol conversion was 11% and CO_2 production was 9%. Final selectivity was 82%. Phenol conversion decays with usage, while selectivity towards mineralization remains almost constant. The amount of active phase also decreases significantly with usage, as detected by AA and TPR experiments reported in Table 3. This clearly indicates that deactivation was mainly due to lixiviation of the active phase.

Therefore, to improve catalytic stability, the subsequent runs were performed with cylindrical pellets [4]. Intraparticle gradients were evaluated by means of the Weisz modulus ϕ_{we} using the observed rates obtained at different liquid flow rates. In all the experiments, $\phi_{we} \gg 1$. This indicates that internal mass transport limitations are significant. Then, the internal diffusion fluxes of the two reactants should be compared as $\gamma = D_{effB}C_B/bD_{effA}C_A$. The parameter γ is indicative of the relative availability of the species at the reaction site [20]. For the reaction $A + bB \rightarrow P$, where A is oxygen and B is phenol, a mean value of γ was calculated ($\gamma = 15$). A value of $\gamma \gg 1$ would imply an internal gaseous reactant limitation [20]. Additionally, the Mears' criterion for external mass transport control indicates that this resistance is also significant [21]. So, for the pelletized catalyst, internal and/or external oxygen mass transport steps could be restrictive.

Phenol conversion and CO_2 production against the liquid flow rate for 15 g of pelletized catalyst at 140 °C and 7 atm oxygen pressure are shown in Fig. 5. Each point is the average of four equivalent runs. Reproducibility was good, as indicated by confidence intervals in the figure. As the liquid flow rate decreases, wetting efficiency reduces and phenol conversion, CO_2 production and selectivity increase. As pointed out previously, partial wetting not only enhances mass transport of the gaseous reactant but also allows for the formation of a larger number of active sites on the catalyst surface, resulting in increased conversions. In addition, as the liquid flow rate is diminished, the residence time increases and this will also increase phenol conversion, CO_2 production and selectivity. At high residence times, or very small liquid flow rates and, hence, small values of wetting efficiency, most of the phenol destroyed become carbon dioxide, thus *S* approaches unity. The shape of the curve in Fig. 5 is typical of processes that will benefit with liquid on–off flow modulation.

Liquid flow rate modulation experiments at different fixed periods (3, 6 and 10 min) were performed with the pelletized catalyst at 140 °C and 7 atm of oxygen, using a gas flow rate of 460 mL/min. For a given period, different splits were investigated (1/6, 1/3 and 1/2). Liquid flow rate was varied in order to keep a constant fluid velocity through the bed. Comparison between steady state and cycling results are expressed as normalized conversion, which is the phenol conversion obtained during cycling over the steady-state phenol conversion achieved at the same mean liquid flow rate or X_{cyc}/X_{SS} versus cycle split. Results are plotted in Fig. 6. For the experimental conditions studied, cycling does not improve significantly phenol conversion. The small enhancement obtained during cycling can be explained due to the exposure to a richer oxygen environment. However, results are not as remarkable as expected initially. During cycling, many operating variables are periodically changed, such as gas reactant concentration at the catalytic surface, liquid reactant concentration inside/outside the catalyst, wetting condition, liquid holdup, etc. In a recent contribution [22], we model the behavior of a single catalytic particle exposed to on–off liquid flow modulation when a single first order isothermal reaction is considered. While the considerations may not entirely apply to the present reaction system, the model predicts useful trends. In fact, major improvements are expected if wetting is complete at the mean liquid flow rate, external mass transport is the limiting step and a fast instantaneous reaction takes place on the surface of the catalyst (or at very high Thiele modulus). This

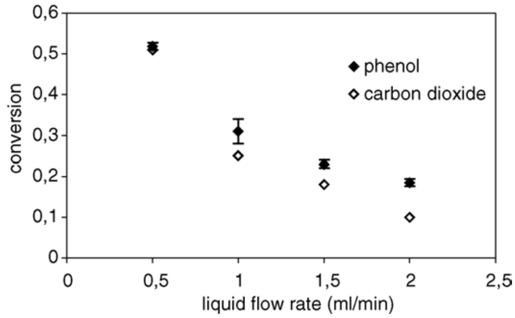

Fig. 5. Phenol conversion and CO_2 production for pelletized catalyst under steady-state operation.

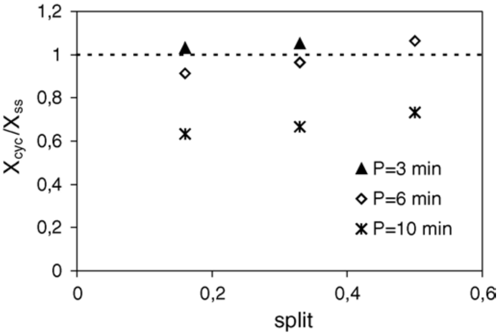

Fig. 6. Normalized phenol conversion vs. split for different periods. Mean fluid velocity: 133 g h L^{-1}.

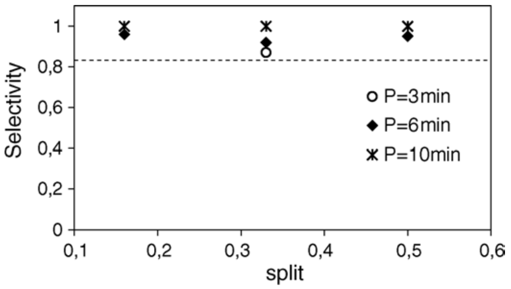

Fig. 7. Selectivity values during cycling vs. split for different periods. Mean fluid velocity: 133 g h L^{-1}. (- - -) Steady-state selectivity.

may not be the situation encountered here, where incomplete wetting promotes partial phenol depletion inside the catalyst. This phenomenon is enhanced during the dry cycle and is favored by the higher catalytic activity promoted by the richer oxygen environment. The results observed at long periods and small splits can be explained taking into account these considerations.

The selectivity to complete mineralization (*S*) is evaluated as the ratio of CO_2 production over phenol conversion obtained during periodic operation. Values obtained during cycling at different splits as well as steady-state results are presented in Fig. 7. Liquid flow modulation shows a positive effect on selectivity, especially at longer periods. In a previous work [23], we model the behavior of a single catalytic particle exposed to on–off liquid flow modulation when two consecutive first order isothermal reactions are taking place. Again, model results are useful as they predict tendencies. Results indicate that selectivity towards final product can be enhanced by liquid flow modulation. When the liquid flow is halted, the non-volatile intermediate products remain inside the catalyst and are further oxidized to final products. The residence time of the intermediates and the average oxygen concentration inside the catalytic pellet during liquid flow modulation, are higher than those attained in steady-state operation. The effect is more pronounced at prolonged periods, where more phenol is totally oxidized.

The activity of the cylindrical pellets remained about constant after 80 h of usage alternating steady-state and periodic experiments. The lixiviation process is present (there is a 30% decrease in the amount of active phase, as seen in Table 3), but the activity remained approximately stable due to the high initial metal content. The main deactivation mechanism of CuO catalysts is the deposition of solids [5], but this process is not favored in TBRs.

4. Conclusions

Phenol is oxidized in a fixed bed reactor operating in trickle flow regime, using the CuO/Al_2O_3 catalyst developed in our laboratory. Phenol conversion and CO_2 production were monitored at 140 °C and 7 atm of oxygen partial pressure for powdered and pelletized catalysts. With the crushed catalyst, the oxidation shows high selectivity towards the production of carbon dioxide. However, the catalyst deactivates due to leaching of the active phase. To minimize this effect, a pelletized catalyst was used. The calculated Weisz modulus and Mears criteria for the cylindrical pellets indicate that internal and external mass transport of oxygen could be restrictive.

Cycling experiments were performed to improve performance. In the range of operating conditions studied, it was observed that liquid flow modulation has a mild effect on phenol conversion but it does affect product distribution, favoring the total oxidation process, hence reducing COD.

More experimental work is under way to cover a wider range of periodic variables (period and split). In addition, we are developing a dynamic model to address the relative importance of mass transport and kinetic steps in the performance of an integral cycled TBR in which a set of consecutive first order isothermal reactions is taking place.

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