

Gas feed composition modulation in phenol CWAO over active carbon

B. Larruy^a, A. Ayude^b, J. Font^a, A. Fortuny^a, C. Bengoa^a, A. Fabregat^a, F. Stüber^{a,*}

^aDepartament d'Enginyeria Química, ETSEQ, Universitat Rovira i Virgili, Paisos Catalans 26, 43007 Tarragona, Catalunya, Spain

^bInstituto Nacional de Tecnología de los Materiales INTEMA, CONICET, UNMDP, J.B. Justo 4302, 7600 Mar del Plata, Argentina

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Abstract

The long-term stability of active carbon in the CWAO of phenol was investigated in a fixed-bed reactor at steady state operation and different oxygen partial pressures, temperatures, phenol inlet concentrations and gas–liquid flow modes. To further improve the catalyst stability, gas feed composition modulation (air/N₂) was tested in the slow mode (large period lengths) to establish in situ oxidation–adsorption cycles. The unsteady operation significantly reduced the active carbon burn-off and performed a higher long-term conversion of phenol.

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1. Introduction

Nowadays, increasing attention is paid to the remediation and reuse of biotoxic or refractory organic process waters generated in large quantities by diverse industrial sectors. Catalytic wet air oxidation (CWAO) in trickle bed reactors (TBR) proved to be an efficient technique to reduce the initial biotoxicity of such process waters, then allowing for biological end-treatment. A critical issue for the industrial application of CWAO is the availability of cheap and stable catalysts. Active Carbon (AC) is a promising alternative to supported catalysts, but deactivation can occur due to its simultaneous burn-off during the oxidation (Fortuny et al., 1998). Therefore, this work focuses on the study of long-term stability and activity of AC in phenol CWAO. On the other hand, periodic or unsteady operation is an emerging concept to improve the performance of catalytic fixed-bed reactors. At present, only liquid flow modulation was tested in CWAO of phenol (Tukac et al., 2003; Massa et al., 2005). When AC is used as catalyst, gas flow modulation to establish in situ adsorption–oxidation cycles may also become of interest in order to reduce the AC burn-off. The second aim of this work is thus to explore if periodic gas feeding of air and N₂ can replace discontinuous adsorption–regeneration processes, typically employed in physical treatment of organic wastewater.

2. Experimental

Phenol CWAO was conducted in a small TBR ($D_R = 1.1$ cm, $L_R = 20$ cm) filled with 7.5 g of a commercial AC (Merck, $d_p = 0.5$ mm). Catalyst activity and stability were tested in downflow (and upflow) operation during 140–240 h time on stream (TOS) at a fixed liquid space-time of 0.12 h, air flow rate of 9 NL/h (O₂ excess of 250%), 140–160 °C, 1–9 bar of oxygen partial pressure and phenol inlet concentrations of 1–10 g_{Ph}/L. At otherwise same conditions, modulation of gas feed composition was studied in downflow at $P_{O_2} = 2$ bar, 5 g_{Ph}/L, different period lengths (0.3–4 h), air/N₂ splits (1/3–5/6) and TOS of 50–140 h. The split is defined as the time fraction of air flow with respect to the total period length. In all runs, the temperature and liquid flow fluctuations were recorded, exited liquid samples were automatically collected, each during 15 min, and analysed by HPLC for phenol. At the end of each long-term experiment, the used catalyst was recovered, dried and weighted. More experimental details are given in Fortuny et al., 1998.

3. Results

The steady state experiments showed that the AC stability strongly depends on the operating conditions used. At 140 °C, 5 g_{Ph}/L, and 1 or 2 bar of P_{O_2} , after an initial adsorption dominating period of 8 h (100% conversion) followed by a transition of 10–12 h (conversion decreases), stable phenol conversion of

* Corresponding author. Tel.: +49 228 2874114; fax: +49 228 2874125.
E-mail address: frankerich.stuber@urv.cat (F. Stüber).

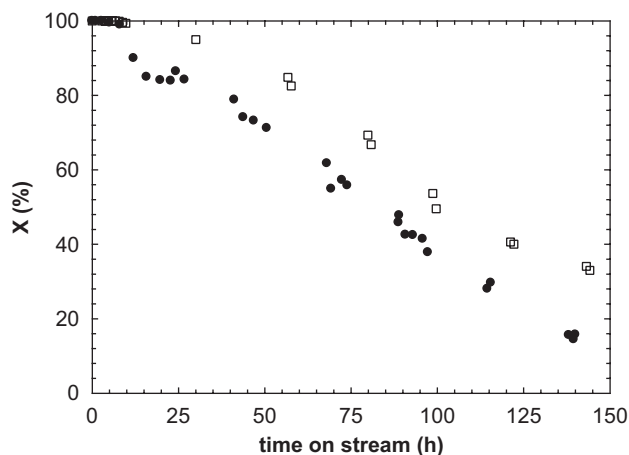


Fig. 1. Evolution of steady state conversion of phenol obtained in downflow (□) and upflow (●) operation; $T = 160\text{ }^{\circ}\text{C}$, $P_{\text{O}_2} = 2\text{ bar}$, $C_{\text{Ph},0} = 5\text{ g/L}$, $\tau = 0.12\text{ h}$, $F_{\text{Air}} = 9\text{ NL/h}$, $w_{\text{AC},0} = 7.5\text{ g}$; $w_{140\text{h}} = 1.8\text{ g}$ (downflow), $w_{140\text{h}} = 7.6\text{ g}$ (upflow).

20% or 40% was performed over 240 h in downflow mode. Runs at higher P_{O_2} (9 bar) resulted in a progressive loss of conversion, surface area (66%) and catalyst weight (33%) after 240 h due to enhanced AC burn-off. A temperature rise from 140 to 160 °C at 2 bar of P_{O_2} even caused a more severe AC burn-off of 75% after only 140 h of TOS in downflow operation. However, by increasing $C_{\text{Ph},0}$ from 5 to 10 g/L, it was possible to roughly maintain constant the catalyst stability and AC weight at 160 °C. The change of flow direction from downflow to upflow at same operating conditions had two opposite effects. No AC weight loss was detected in upflow mode after 140 h of TOS (final 7.6 g compared to 1.8 g in downflow). Although, phenol conversion also continuously decreased with TOS being always below that observed in downflow as illustrated in Fig. 1. Partial wetting in downflow at the present conditions enhances phenol destruction (and AC burn-off) due to direct gas–solid oxygen mass transfer, whereas fully wetted AC in upflow seems less prone to combustion. The constant AC weight during upflow may also indicate a significant enhancement of liquid phase formation of oxidative coupling products (compared to downflow), which irreversibly adsorb onto and/or block the access to the active sites. This is in line with the shorter adsorption dominating period of only 4 h observed in upflow mode. Overall, it appears that not too high oxygen surface concentration and adsorbed phenol (and water) can protect the active carbon surface from being oxidised, even at higher reaction temperature. However, to reduce eventual catalyst deactivation by carbonaceous deposits, the use of trickle flow regime should be recommended.

Thus, modulation of air/ N_2 feeding in downflow mode may serve to improve the long-term stability of AC, while maintaining an acceptable phenol conversion. During the N_2 flow, the bed is periodically resaturated with phenol (protecting the AC surface), and high reaction rates should be possible when the surface is contacted again with oxygen. To assess adequate periodic operating conditions (split and cycle period) for max-

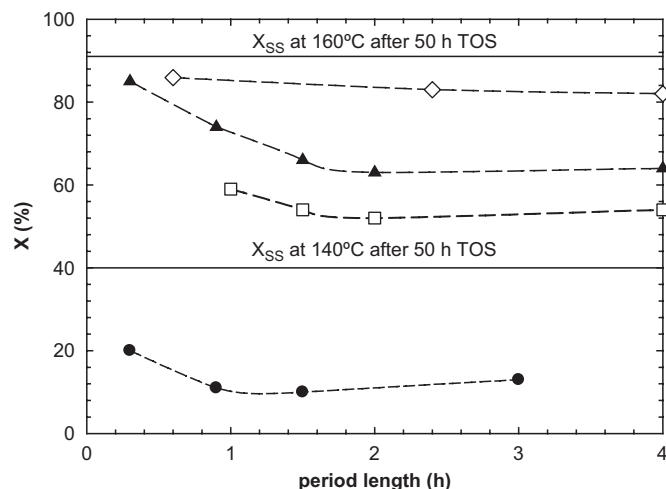


Fig. 2. Phenol conversion after 50 h TOS as a function of period length; $P_{\text{O}_2} = 2\text{ bar}$, $C_{\text{Ph},0} = 5\text{ g/L}$, $\tau = 0.12\text{ h}$, $F_{\text{Air}} = 9\text{ NL/h}$; (□) $s = 1/2$, 160 °C; (▲) $s = 2/3$, 160 °C; (◇) $s = 5/6$, 160 °C; (●) $s = 1/3$, 140 °C; - - - tendency lines.

imum phenol conversion, the dynamic results should be compared with the corresponding steady state conversion values. Fig. 2 gives the steady state conversions as well as the mean phenol conversions resulting after 50 h of TOS as a function of both the period length and cycle split. In each case, the mean cycle conversion has been evaluated from experimental conversion points of the last cycle of air flow (high concentration) and N_2 flow (apparent low conversion due to phenol readsorption). As seen in Fig. 2, the mean cycle conversion of phenol always falls below the steady state value for both temperatures (0.4 at 140 °C and 0.91 at 160 °C). However, for a given cycle period, as the split increases, the total time of exposure to air is higher and therefore the level of conversion increases and can become close to the steady state conversion. Also, for a constant split, when relatively small cycle periods are employed, the mean cycle conversion approaches the reference steady state. On the other hand, for long cycle periods, the mean phenol conversion should tend to a value, which equals the split times the steady state phenol conversion as is confirmed by Fig. 2.

The conversions, shown in Fig. 2, are a result of both the catalytic activity and adsorption capacity of AC after 50 h of TOS. Due to the combustion of AC and the deposit of oxidative coupling products during phenol CWAO, the former ones are time dependent. Thus, it is of interest to establish also phenol conversion and temperature profiles over a sufficiently long operating period. Fig. 3 shows the evolution of conversion (3a) and temperature (3b) with TOS obtained in periodic CWAO ($s = 2/3$, $p = 1.5\text{ h}$) at 160 °C. Figs. 3a and b give a rough idea on how the system behaves during periodic gas feed composition modulation. After saturation of the fixed-bed with phenol under N_2 atmosphere (not shown in Fig. 3a), the first air injection causes a spontaneous temperature and conversion increase of up to 172 °C and quasi 100%, respectively. In the next cycle, the maximum temperature rapidly falls down to 164 °C, although the conversion stays at quasi 100% for a

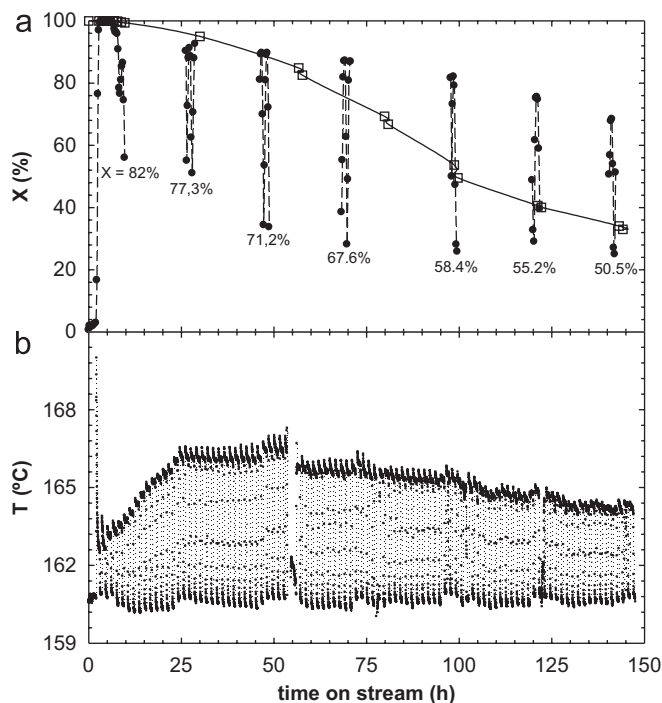


Fig. 3. Evolution of phenol conversion (a) and temperature (b) with TOS; $T = 160^\circ\text{C}$, $P_{\text{O}_2} = 2\text{ bar}$, $C_{\text{Ph},0} = 5\text{ g/L}$, $\tau = 0.12\text{ h}$, $F_{\text{Air}} = 9\text{ NL/h}$; (\square) steady state conversion, $w_{140\text{h}} = 1.8\text{ g}$; (\bullet) periodic conversion, $s = 2/3$, period = 1.5 h, $w_{140\text{h}} = 4.1\text{ g}$; X values represent mean cycle conversion.

couple of hours. Certainly, a big part of the adsorbed phenol was removed from the AC surface during the first cycle and the residual quasi 100% conversion is actually a combination of re-adsorption and oxidation of phenol. During the following 25 h of TOS, a continuous rise in the maximum cycle temperature occurs, most probably indicating that the bed gets slowly saturated again (more phenol can be removed by oxidation) and the minimum apparent cycle conversion goes down to 52–56%. Then, the cycle temperature stabilises (until 60 h of TOS) with a constant maximum cycle conversion of 90%. The minimum cycle conversion, however, drops down to 30% and stabilises only at 65 h TOS suggesting that a new adsorption–oxidation pseudo-equilibrium is reached. Also, a decrease in the adsorption capacity of AC could explain the observed trend. Finally, from a TOS of 70 h on, the cycle ΔT becomes smaller along with the maximum cycle conversion (68% at 140 h), whereas the minimum cycle conversion remains constant. This trend can be related to the slow AC burn-off (and loss of surface area) occurring during CWAO and the subsequent loss of activity for phenol oxidation. The evolution of conversion during steady

state and periodic operation at 160°C is also given in Fig. 3a. For a better clarity, the figure only shows seven cycles and each mean cycle conversion. Initially, steady state oxidation leads to higher conversion, although the difference between steady state and mean periodic conversion decreases with TOS. After about 85 h, both conversions become very similar (60%), but periodic roughly maintains the conversion (50% after 140 h, final $W_{\text{AC}} = 4.1\text{ g}$) and outperforms the steady state operation (35% after 140 h, final $W_{\text{AC}} = 1.8\text{ g}$). Moreover, the performance of the catalyst could be even improved with $s = 5/6$ and $P = 2.4\text{ h}$ leading to a mean cycle conversion of 60% (final $W_{\text{AC}} = 4.5\text{ g}$) after 140 h of TOS.

4. Conclusion

It was shown that the steady state stability of active carbon strongly depends on the range of operating variables employed. Increasing oxygen pressure and temperature enhances AC burn-off, while adsorbed phenol (and water) can protect the catalyst surface to a certain extent. To avoid carbonaceous deposits and eventual catalyst deactivation, downflow is preferred over upflow. The application of periodic gas feed composition modulation to phenol CWAO over AC is beneficial because the AC burn-off is significantly reduced compared to steady state operation, while performing a superior long-term activity in terms of conversion at high splits. The conversion and temperature profiles observed at periodic conditions clearly reveal the complex nature of unsteady reactor operation and modelling efforts are required to better understand the periodic gas feed composition modulation in phenol CWAO over active carbon.

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References

- Fortuny, A., Font, J., Fabregat, A., 1998. Wet air oxidation of phenol using active carbon as catalyst. *Applied Catalysis B: Environment* 19, 165–173.
- Massa, P., Ayude, M.A., Ivorra, F., Fenoglio, R., Haure, P., 2005. Phenol oxidation in a periodically operated trickle bed reactor. *Catalysis Today* 107–108, 630–636.
- Tukac, V., Hanika, J., Chyba, V., 2003. Periodic state of wet oxidation in trickle-bed reactor. *Catalysis Today* 79–80, 427–433.