

# Effect of gas feed flow and gas composition modulation on activated carbon performance in phenol wet air oxidation

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## Abstract

Modulation of gas feed composition (air/N<sub>2</sub> cycling) and gas feed flow (on–off air cycling) was investigated in the catalytic wet air oxidation of phenol over activated carbon (AC). Fifty hours lasting experiments were conducted in a laboratory trickle bed reactor at 140–160 °C, 2 bar of oxygen partial pressure and different splits and periods to determine the set of cycling parameters that optimise the periodic reactor operation. To follow the dynamic behaviour of the phenol oxidation, temperature and conversion were continuously monitored by means of computerised data acquisition and automatic liquid sampling. Several long term tests over 144 h were also run using both periodic operating strategies to compare the activity and stability of AC with those obtained in a steady state operation at otherwise same conditions. The results show that, depending on the selection of split and period, modulation of the gas phase significantly improves the stability of AC compared to steady state operation, thereby performing a superior long term phenol conversion.

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## 1. Introduction

In the last few years, the interest in catalytic wet air oxidation (CWAO) for economically removing refractory and biotoxic organics from wastewater has been strongly renewed due to the development of stable supported catalysts. As an alternative to more expensive metal based catalysts, activated carbon (AC) has been recently proposed because of its low market price, excellent adsorption capacity and catalytic activity for phenol and certain phenolic compounds (Fortuny et al., 1999; Suarez-Ojeda et al., 2005). A major drawback of AC is its loss due to combustion when it is exposed to oxygen under the conditions typically used in liquid CWAO. A detailed review on carbon materials and its application in CWAO can be found in Stüber et al. (2005). These authors reported that one efficient way to avoid the undesired loss of carbon in liquid phase oxidation of phenol is to control temperature and oxygen concentration at

the carbon surface. Moreover, the AC burn-off has been shown sensitive to the inlet phenol concentration, suggesting that adsorbed phenol molecules and/or reaction products protect the carbon surface from being attacked by dissolved molecular oxygen.

On the other hand, a growing number of contributions concerning periodic operation in trickle bed reactors (TBRs) at laboratory or pilot scale have been presented in literature over the past 15 years. Several works report on hydrodynamics (partial wetting), mass transfer enhancement and modelling of the forced dynamic behaviour of TBRs. Typical reactions studied are liquid phase hydrogenations of aromatics or oxidation of SO<sub>2</sub> (Silveston and Hanika, 2002), while only a few papers are directly related to periodic operation of CWAO (of phenol) in TBRs (Tukac et al., 2003; Massa et al., 2005; Larruy et al., 2007). In fact, many ways can be used to operate a TBR under periodic conditions, e.g. forced liquid and gas flow rate, inlet phase composition, pressure and temperature modulation (Haure et al., 1989). At present, however, most of the works available on periodic operation of TBR are dealing with modulation of liquid flow to improve partial wetting of catalyst and

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external mass transfer conditions. It has been shown that, for certain sets of parameters, reactor performance (conversion and intermediate product distribution) can be improved or influenced by liquid flow modulation even for moderately exothermic/endergonic reactions (Tukac et al., 2003; Massa et al., 2005; Lange et al., 1994; Khadilkar et al., 1999; Muzen et al., 2005). In contrast, studies on the modulation of gas phase composition or gas flow rate are very scarce in literature (Silveston and Hanika, 2002). Turco et al. (2001) investigated the effect of the gas flow modulation on the hydrogenation of  $\alpha$ -methyl styrene on Pd/Al<sub>2</sub>O<sub>3</sub>. Results were not promising since all the time-average conversion measurements fell below the continuous flow performance. Alternatively, Xiao et al. (2001) studied the effect of modulating the gas flow rate on the hydrodynamic behaviour of a TBR. These authors showed that the radial liquid distribution is more uniform under the forced pulsing flow than in the natural pulsing flow regime.

Larruy et al. (2007) found that the modulation of air/N<sub>2</sub> feeding may serve to improve the long term stability of AC, while maintaining an acceptable phenol conversion. Gas phase modulation in CWAO over AC establishes in situ adsorption–oxidation cycles, thereby expecting to reduce the AC burn-off. The unsteady state operation of the reactor can be easily achieved by means of a simple timer controlled on–off three-way valve mounted in the gas feed lines.

In this contribution, an experimental study of phenol CWAO over AC is done to analyse the impact of gas feed composition and flow rate modulation on the short time activity of AC (50 h of operation). Different sets of cycling parameters were explored in a TBR to determine optimal conditions of dynamic operation. With this information, the long term activity and stability of the AC were then assessed to establish whether or not the catalyst burn-off observed in steady state CWAO can be reduced by periodic reactor operation.

## 2. Experimental

### 2.1. Materials

Analytical grade phenol purchased from Aldrich and deionised water was used without further purification for the preparation of phenol feed solution. The gas fed to the reactor was either high purity compressed air or nitrogen (Carburros Metálicos, Spain). The AC supplied by Merck (Ref. #102518) as 2.5 mm pellets is manufactured from wood and has a mineral ash content of about 4 wt%. Prior to use, the pellets were crushed and sieved to obtain the 25–50 mesh fraction (0.3–0.7 mm) to optimise both pressure drop and internal mass transfer limitations during the oxidation experiments. After sieving, all catalyst samples were washed (to remove fines) and dried at 105 °C overnight, cooled and finally stored under dry atmosphere.

### 2.2. Experimental set-up and procedures

Both steady state and periodic phenol CWAO were conducted in a laboratory TBR of 1.1 cm ID and 20 cm

length typically loaded with 7–7.5 g of AC catalyst. The experimental set-up was described in detail by (Fortuny et al., 1995).

In all runs, liquid space-time (liquid flow rate) and gas flow rate were kept constant at 0.12 h (0.06 L/h) and 8.6 NL/h, respectively. Air was fed at 2 bar of oxygen partial pressure corresponding to total pressures of 14 or 16.5 bar for oven temperatures of 140 or 160 °C. A flow metre coupled with a high precision needle valve was mounted at the gas–liquid separator outlet line to set and measure the gas flow rate. The standard phenol inlet concentration was 5 g/L, although steady state experiments were also conducted with inlet concentration ranging from 1 to 10 g/L. Some of the experiments were repeated and the reproducibility of runs matched within  $\pm 5\%$ .

Modulation of gas feed flow and composition was achieved by simple means of an automatically controlled on–off three way solenoid valve placed in the gas feed lines of air and N<sub>2</sub>. The control was effectuated by a programmable timer that periodically cycled the gas feed either between air and nitrogen for composition modulation at same gas flow rate or between air and no gas flow for on–off flow modulation. Thus, two important parameters can be defined for periodic operation: the split, being the fraction of the cycle, in which air and liquid flow through the TBR and the period length, corresponding to the total time of a whole cycle.

The effect of gas feed flow or composition modulation was studied in downflow mode during 50 h of time on stream for slow mode cycle periods of 0.3, 0.6, 0.9, 2.4 and 4.2 h and different splits of  $\frac{1}{3}$ ,  $\frac{1}{2}$ ,  $\frac{2}{3}$  and  $\frac{5}{6}$ .

Also, different reactor start-up procedures, i.e. beginning directly with air/N<sub>2</sub> cycles or previously saturating the AC bed under N<sub>2</sub> flow have been tested. The aim was to investigate if the initial saturation of the AC bed can affect the catalyst performance in periodic CWAO.

Finally, the AC long term stability and activity were assessed over 144 h in cycling conditions but only at the highest temperature of 160 °C, where significant AC burn-off has been observed during steady state operation (Stüber et al., 2005). To contrast the dynamic results, steady state experiments were also conducted during 50 and 144 h time on stream at 140 or 160 °C and otherwise same operating conditions.

At the end of each run, the used AC was recovered, dried over night at 105 °C under nitrogen flow and weighed to detect any carbon loss that may have occurred during the experiments. Part of the dried AC was also used to determine the phenol adsorption isotherm for comparison with that of a fresh AC. All adsorption isotherms were obtained at 25 °C under oxic conditions in stirred 100 mL-batch flasks following a standard protocol (Cooney and Xi, 1994). For each adsorption isotherm, seven flasks were loaded with 50 mL of phenol solution in the range of 500–7000 ppm and 0.25 g of AC. Liquid samples from each flask were collected at zero time and after 2 h of stirring to allow for equilibrium. The samples were then analysed by HPLC to calculate the amount of phenol adsorbed on the AC as a function of the equilibrium phenol concentration measured in the liquid phase.

### 2.3. Analysis

In all runs, temperature and liquid flow fluctuations were continuously recorded by means of a PC data acquisition system (LabView, National Instrument). Liquid samples in the outlet were automatically collected at a given time interval and later analysed for phenol and total organic carbon (TOC) concentrations.

Quantification of phenol was performed with an HPLC (Beckman System Gold) using a C18 reverse column (Tracer Extrasil ODS-2, 5  $\mu\text{m}$ , 25  $\times$  0.4 cm). To properly separate phenol from the partial oxidation products, the mobile phase was fed at 1 mL/min with a composition of 35/65 (v/v) of methanol and deionised water, acidified to pH = 1.5 with concentrated sulphuric acid. The presence of phenol was detected with UV absorbance at a wavelength of 254 nm. TOC of the samples was measured by an Analytik Jena Multi N/C 2100 equipment (Jena, Germany) following the standard method 5310B (American Water Association, 1999).

The experimental results are compared in terms of phenol and TOC conversion, which are calculated according to the general expression:

$$X = \frac{[C]_{\text{In}} - [C]_{\text{Out}}}{[C]_{\text{In}}}$$

where  $[C]_{\text{In}}$  and  $[C]_{\text{Out}}$  denote inlet and outlet phenol or TOC concentrations (g/L), respectively. For periodic operation, the mean cycle conversion is evaluated from all experimental conversion points of a complete cycle (high conversions during air flow, low conversions during  $\text{N}_2$  flow).

## 3. Results

### 3.1. Steady state operation

Fig. 1 gives the evolution of steady state phenol conversion with time on stream for different operating conditions, while Table 1 summarizes the values of phenol conversion and weight of recovered AC samples after 95 h of time on stream. The steady state results indicate that the performance of AC in CWAO strongly depends on the operating conditions used. After an initial adsorption/reaction period of about 20 h, stable catalytic activity ( $X_{\text{Ph}} = 45\%$ ) and AC weight (7.5 g after 95 h) were observed for 140  $^{\circ}\text{C}$  and 2 bar of oxygen partial pressure. Increasing either the oxygen partial pressure to 9 bar or the reaction temperature to 160  $^{\circ}\text{C}$  resulted in a much higher levels of conversion after the initial stage of adsorption, although a continuous decay of activity occurred then in both cases (see Fig. 1 for 160  $^{\circ}\text{C}$ ) leading to values of phenol conversion of only 60% or 55%, respectively, after 95 h (see Table 1). This observation can be mainly attributed to the enhanced AC burn-off, particularly at 160  $^{\circ}\text{C}$ , where a final catalyst weight of 5.7 g was measured only after 95 h of time on stream compared to 5 g at 140  $^{\circ}\text{C}$  and 9 bar of oxygen after 240 h of time on stream.

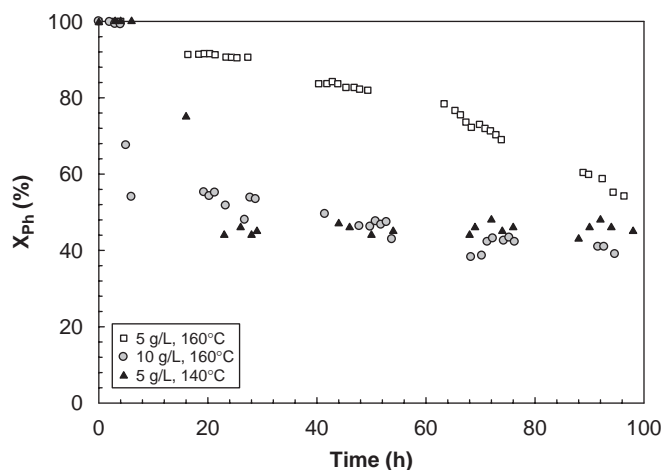


Fig. 1. Steady state phenol conversion–time profiles obtained in downflow mode at different operating conditions;  $F_L = 0.06 \text{ L/h}$ ,  $F_G = 8.6 \text{ NL/h}$ ,  $P_{\text{O}_2} = 2 \text{ bar}$ ,  $W_{\text{AC},0} = 7.5 \text{ g}$ .

Table 1

Phenol conversion and final AC weight measured after 95 h time on stream for different operating conditions

$P_{\text{O}_2}$ (bar)	$T_{\text{Oven}}$ ( $^{\circ}\text{C}$ )	$C_{\text{Ph,In}}$ (g/L)	$X_{\text{Ph}}$ (%)	$W_{\text{AC,fin}}$ (g)
2	140	5.0	45	7.5
9	140	5.0	60	5.0 <sup>a</sup>
2	160	5.0	55	5.7
2	160	5.0	35	1.8 <sup>b</sup>
2	160	10.0	38	9.9

$F_L = 0.06 \text{ L/h}$ ,  $F_G = 8.6 \text{ NL/h}$ ,  $W_{\text{AC},0} = 7.5 \text{ g}$ .

<sup>a</sup>After 240 h of time on stream.

<sup>b</sup>After 144 h of time on stream.

Only by increasing the phenol inlet concentration from 5 to 10 g/L, a roughly constant phenol conversion, although on a lower level, was performed along with a 33% weight gain. The sudden drop of phenol conversion right after bed saturation in case of a 10 g/L inlet phenol concentration may indicate the presence of external oxygen mass transfer limitations rather than to the eventual non-linear nature of the reaction with respect to phenol concentration. Overall, the demonstrated sensibility of carbon burn-off to temperature, oxygen pressure and phenol inlet concentration suggests that adsorbed phenol molecules and/or reaction products protect the carbon surface from being attacked by dissolved molecular oxygen, even at higher reaction temperature.

From a point of view of activity, it is recommended to work at 160  $^{\circ}\text{C}$  provided that additional AC burn-off can be avoided. Thus, modulation of air/ $\text{N}_2$  feeding may serve to improve the stability of AC, while maintaining acceptable phenol conversions. This dynamic reactor operation establishes in situ adsorption–oxidation cycles, which should allow re-saturating (and protecting) the AC surface during adsorption. In this way, the AC fixed bed could be more efficiently regenerated by oxidation within an air/ $\text{N}_2$  cycle.

## 4. Periodic operation

### 4.1. Initial saturation of AC bed

Prior to investigate the modulation of gas composition in phenol CWAO, two 50 h experiments with different initial phenol saturation of the AC bed were conducted at 164 °C, 2 bar of oxygen partial pressure, 5 g/L of phenol solution, a period of 1.5 h and split of  $\frac{2}{3}$ . Figs. 2a and b illustrate the observed temperature– and conversion–time profiles corresponding to situations of CWAO start-up with air/N<sub>2</sub> cycling (2a) or previous saturation of the AC bed with phenol under N<sub>2</sub> flow (2b).

In case of start-up with air/N<sub>2</sub> cycling, a temperature peak of about 5 °C occurs when the reaction temperature reaches its set point and the AC bed is contacted with air for the first time. The conversion stays at 100% over the first 7–8 h mainly due to continuous phenol adsorption until bed saturation is achieved as observed for steady state experiments under same conditions. Then, the conversion drops and the cycle maximum quickly levels to a pseudostable value of about 88%, whereas the cycle minimum gradually decreases to about 45%. The evolution of temperature is different, since the cycle minimum rapidly attains the corresponding reactor temperature without reaction, contrary to the cycle maximum, which increases during 15 h before stabilising at about 169 °C.

Previous bed saturation under nitrogen flow at reaction temperature takes about 5–6 h and the first contact with air causes a sudden rise in temperature and conversion up to 10–11 °C and 100%, respectively (see Fig. 2b). The AC bed is effectively cleaned up in the first cycle and therefore conversion remains at 100% for almost 3–4 h. Stabilisation of temperature cycles follows then a similar pattern as for direct air/N<sub>2</sub> cycling start-up. Conversion evolution differs in the sense that the cycle minimum rapidly drops down to the same pseudostable value of 45%, but the cycle conversion needs several hours to recover its maximum of 88%. Despite the fact that both cycle temperature and conversion profiles do not follow the same pattern, the residual phenol conversion after 50 h of time on stream is almost the same (65%) in both cases (see Fig. 2). This is in line with weight measurements of the used AC, giving close values of 7.5 and 8 g for air/N<sub>2</sub> cycling start-up and previous bed saturation under nitrogen, respectively.

The above results point out that the influence of the start-up procedure on the overall process is apparently not significant. However, subsequent experiments will be initiated with air/N<sub>2</sub> modulation since a slightly higher time average phenol conversion was obtained.

### 4.2. Gas feed composition modulation

Several experiments were conducted over 50 h of time on stream using different cycling parameters in order to explore the effect of composition gas feed modulation on phenol and TOC conversion. This reactor operation induces a periodic behaviour in phenol conversion and reactor temperature (and also of pH and TOC concentration), which developed to pseudo stable cycles (see Figs. 3a and b).

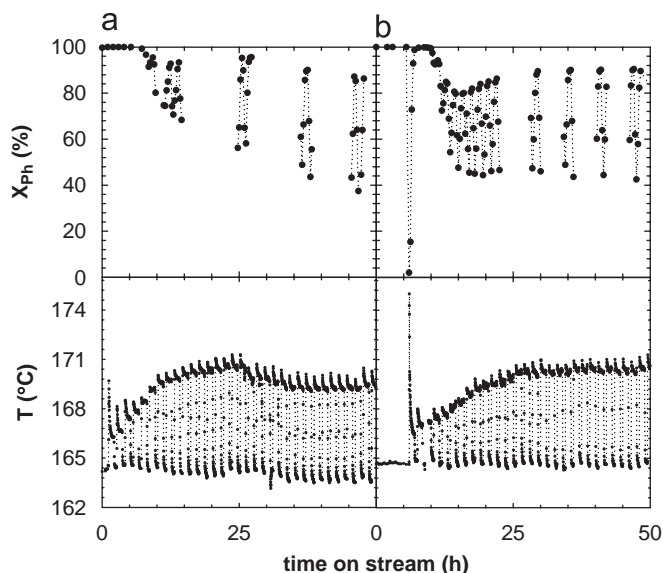


Fig. 2. Periodic phenol conversion and temperature profiles with time on stream for (a) bed saturation with air–nitrogen cycles and (b) bed saturation under N<sub>2</sub> flow.  $T_{\text{Oven}} = 164$  °C,  $P_{\text{O}_2} = 2$  bar,  $C_{\text{Ph},0} = 5$  g/L,  $F_L = 0.06$  L/h,  $F_G = 8.6$  NL/h,  $W_{\text{AC},0} = 7.5$  g,  $s = \frac{2}{3}$ , cycle period = 1.5 h.

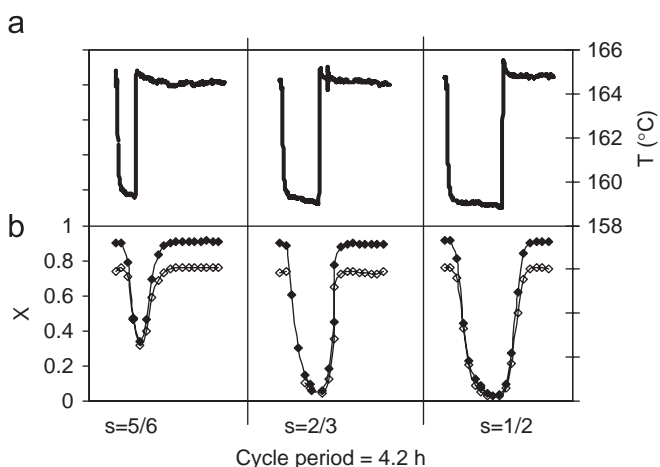


Fig. 3. Temperature, phenol (♦) and TOC (◇) conversion–time profiles for a cycle period of 4.2 h and different splits.  $T_{\text{Oven}} = 160$  °C,  $P_{\text{O}_2} = 2$  bar,  $C_{\text{Ph},0} = 5$  g/L,  $F_L = 0.06$  L/h,  $F_G = 8.6$  NL/h,  $W_{\text{AC},0} = 7.5$  g.

As an example, Fig. 3 illustrates the typical evolution of temperature, phenol and TOC conversion observed during a whole cycle at the pseudostable state for a given oven temperature of 160 °C, period of 4.2 h and three splits. A cycle is usually started with nitrogen flow to stop the oxidation reactions. The AC bed, now exposed to higher phenol axial concentrations, can be partially re-saturated with phenol (thereby protecting the AC surface). Depending on the split (and period) employed, phenol and TOC conversion decrease gradually towards zero. Higher splits are beneficial as it avoids that the conversion completely drops to zero (Fig. 3). At the onset of nitrogen flow, the temperature instantaneously reaches a minimum, which equals the oven temperature, if the exposure time to nitrogen is long enough, as for  $s = \frac{1}{2}$  and  $\frac{2}{3}$ . When the bed is contacted again with air, the exothermic oxidation proceeds

and causes a fast increase in temperature and conversion. Thus, during air flow phenol and TOC conversions rapidly tend to the reference steady state values of 0.91 and 0.74, respectively. Accordingly, the temperature increases to a maximum of 165 °C, which corresponds to the reactor temperature of steady state operation. The pH profiles (not shown here) exhibit a corresponding periodic behaviour. As soon as nitrogen is introduced and the reaction stops, the pH starts to rise and for splits of  $\frac{1}{2}$  and  $\frac{2}{3}$  approaches values close to that of the inlet phenol solution. Then, the pH decays again to values between 2.5 and 3 during the exposure to air due to the formation of carboxylic acids, in particular acetic and formic acid.

Regarding the dynamic response of temperature and conversion to the gas feed composition modulation, Fig. 3 shows that heat transfer dynamics develops faster than that of reaction. Steeper decrease and increase in temperature are observed for all splits on both onsets of adsorption and oxidation. Moreover, there is a visible delay of about 20–25 min in the response of phenol and TOC conversion (best seen at the start of the cycle). This dead time is certainly due to experimental circumstances, since liquid samples are collected just before the gas liquid separator, whereas temperature is directly measured in the AC bed.

To determine the best operating conditions (split and cycle period) for maximum phenol conversion and minimum AC burn-off, cycling results should be compared with those performed at same steady state conditions. Fig. 4 plots the mean phenol conversion (4a) and AC weight (4b), resulting after 50 h of operation, against the cycle period with the split as a parameter.

It is seen that the mean cycle conversion always falls below the steady state value, which is an expected result. For a given cycle period, as the split increases, the total time of exposure to air is higher and therefore the conversion goes up. For a constant split, when relatively small cycle periods are employed, the mean cycle conversion approaches the steady state conversion. On the other hand, for long cycle periods, the mean phenol conversion profile is asymptotic to the split times the steady state phenol conversion. As Fig. 4b shows, no AC burn-off has been observed after 50 h for cycle periods greater than 1 h. Indeed, values even higher than the initial 7.5 g were found. This is related to the strong adsorption of carbonaceous species on the catalyst surface formed by oxidative coupling reactions during CWAO of phenol (Stüber et al., 2005). On the other hand, if very small cycle periods are used, AC consumption becomes evident and the AC weight moves towards the steady state value.

Concluding, the best set of parameters will arise from a balance between the catalyst activity and its stability. The above results indicate that both acceptable phenol conversion and no AC burn-off after 50 h of periodic operation are feasible, as long as a the cycle period and split are superior to 1.5 h and  $\frac{5}{6}$ , respectively.

#### 4.3. On-off gas feed flow rate modulation

Several 50 h experiments with on-off gas flow rate modulation were also performed and Fig. 5 presents the typical

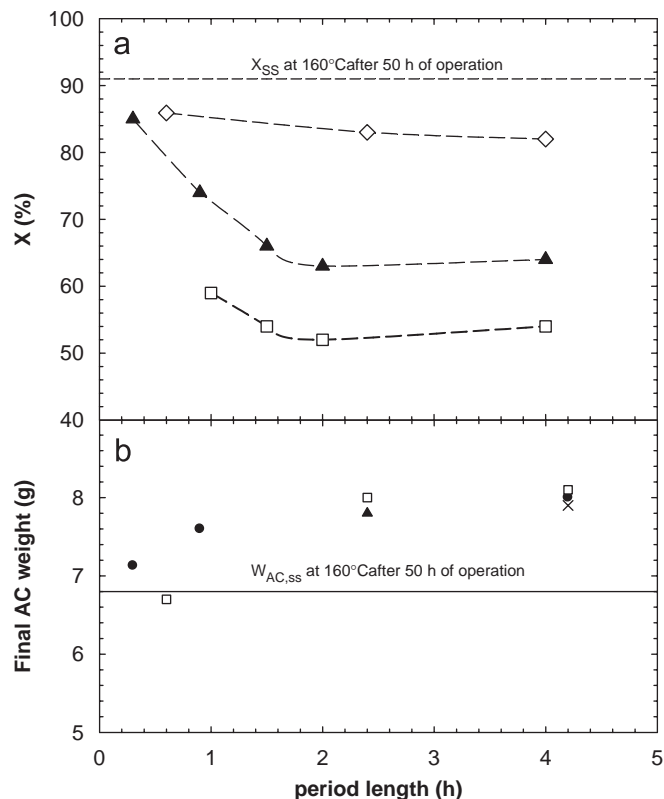


Fig. 4. Phenol conversion (a) and AC weight (b) after 50 h against period length.  $T_{\text{Oven}} = 160\text{ }^{\circ}\text{C}$ ,  $P_{\text{O}_2} = 2\text{ bar}$ ,  $C_{\text{Ph},0} = 5\text{ g/L}$ ,  $F_L = 0.06\text{ L/h}$ ,  $F_G = 8.6\text{ NL/h}$ ,  $W_{\text{AC},0} = 7.5\text{ g}$ ; (a) □  $s = \frac{1}{2}$ ; ▲  $s = \frac{2}{3}$ ; ◇  $s = \frac{5}{6}$ ; (b) ×  $s = \frac{1}{2}$ ; ●  $s = \frac{2}{3}$ ; □  $s = \frac{5}{6}$ ; ▲  $s = \frac{5}{6}$  on-off air cycling.

temperature, phenol and TOC conversion profiles for a whole cycle at the pseudostable state (5a). For comparison, cycle profiles obtained by composition gas feed modulation at same conditions are also given (5b).

The most important conclusion of Fig. 5 is that despite the differences in the temperature profiles, almost the same phenol and TOC conversions result from both periodic operations. This makes the on-off mode particularly attractive for industrial application since the operating costs due to no nitrogen consumption are significantly reduced. The abnormal decrease in temperature below the oven temperature in case of the on-off mode is caused by a slow decrease in the system pressure during the off interval. When the inlet gas flow is cut off, the gas outlet line after the gas-liquid separator is not automatically closed and the gas (and pressure) stored in the separator is continuously released at the same gas flow rate. As soon as the airflow is established again, system pressure and temperature rapidly recover the fixed set-point values.

#### 4.4. Long term stability of AC in periodic CWAO

The previous 50 h experiments allowed optimising cycle conditions that apparently led to high and stable mean conversion as well as negligible AC burn-off. However, it is known that possible deactivation mechanism of AC (burn-off, pore

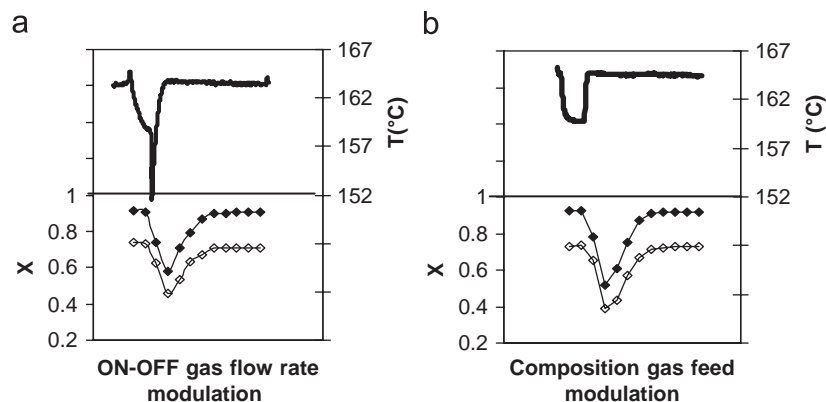


Fig. 5. Temperature, phenol ◆ and TOC ◇ conversion–time profiles for different gas phase modulations.  $T_{\text{Oven}} = 160^\circ\text{C}$ ,  $P_{\text{O}_2} = 2$  bar,  $C_{\text{Ph},0} = 5$  g/L,  $F_L = 0.06$  L/h,  $F_G = 8.6$  NL/h,  $W_{\text{AC},0} = 7.5$  g,  $s = \frac{5}{6}$ , cycle period = 4.2 h.

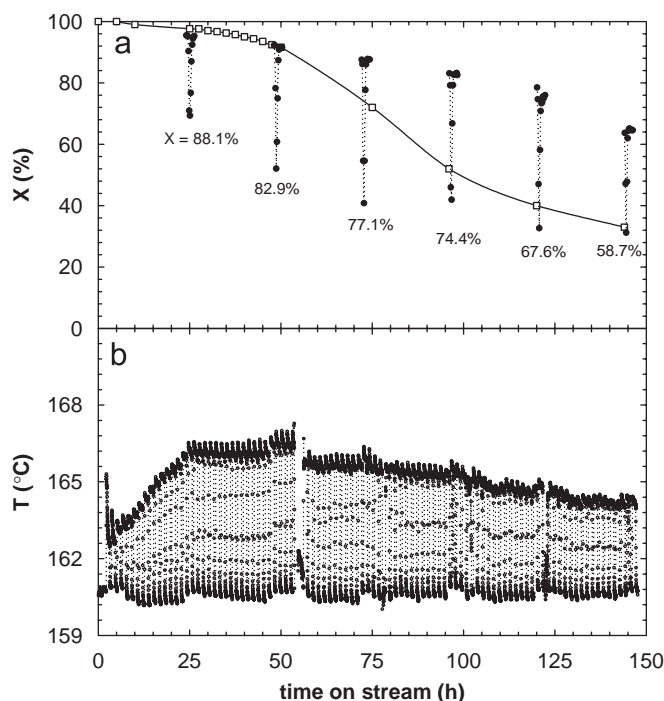


Fig. 6. Phenol conversion (a) and temperature (b) with time on stream;  $T_{\text{Oven}} = 160^\circ\text{C}$ ,  $P_{\text{O}_2} = 2$  bar,  $C_{\text{Ph},0} = 5$  g/L,  $F_L = 0.06$  L/h,  $F_G = 8.6$  NL/h,  $W_{\text{AC},0} = 7.5$  g; □ steady state conversion,  $W_{\text{AC},\text{fin}} = 1.8$  g; ● periodic conversion, split =  $\frac{5}{6}$ , period = 2.4 h,  $W_{\text{AC},\text{fin}} = 4.5$  g,  $X$  values represent mean cycle conversion.

blocking, modification of surface groups) proceeds on a different time scale than does the phenol oxidation (Stüber et al., 2005). Several steady state and periodic oxidation experiments were thus conducted over 144 h to follow the evolution of temperature and phenol conversion. In addition, the weight and phenol adsorption capacity of AC were determined after each long term run.

Fig. 6 reflects conversion and temperature profiles observed for periodic gas composition modulation through air/N<sub>2</sub> cycles

(160 °C, 2 bar of oxygen,  $s = \frac{5}{6}$ , period = 4.2 h). Three zones can be distinguished in the profiles. During the first 8–10 h, phenol conversion remains at 100%, even under N<sub>2</sub> flow, because part of the phenol starts to react and at the same time the AC bed becomes slowly saturated with phenol and reaction products. Moreover, the phenol oxidation rate must be enhanced with time while the AC is being saturated, since a linear increase is observed in the cycle temperature maximum (more phenol of the liquid bulk is consumed). After 10 h, the bed is completely saturated and the phenol conversion starts to decrease during N<sub>2</sub> flow, although the maximum cycle temperature continues to rise until 25 h of time on stream. It can be seen in Fig. 6 that from 10 h of time on stream on the phenol conversion progressively diminishes at the end of each N<sub>2</sub> cycle, suggesting that the phenol adsorption capacity of AC is also decreasing. As a consequence, the phenol concentration in the liquid solution would augment over the bed length during each N<sub>2</sub> cycle, thereby increasing the rate of phenol oxidation beyond the saturation period as well as the maximum cycle temperature. To verify this assumption, phenol adsorption isotherms were determined for fresh AC and AC aged under different operating conditions. Fig. 7 shows the corresponding phenol adsorption isotherms obtained at 25 °C. As expected, the amount of phenol adsorbed increases sharply with the liquid phenol equilibrium concentration for the fresh AC, but not so for the aged ACs. Also, the phenol adsorption is strongly reduced for all spent AC samples, whatever periodic or steady state operation and operation time (50 or 150 h) were employed. It appears from Fig. 7 that the ACs must lose most of its adsorption capacity at an early stage of the oxidation, being 5–10 times less after only 50 h of time on stream compared to a fresh AC. Then, the loss of adsorption is slowed down and adsorption capacities after 50 and 150 h only differ by 20–30%.

At about 25 h of time on stream, temperature cycles stabilize, while both cycle conversion maximum and minimum continue to decrease, although only slightly. Overall, the amount of phenol destroyed in each air cycle must be more or less the same and a pseudosteady state is accomplished and sustained

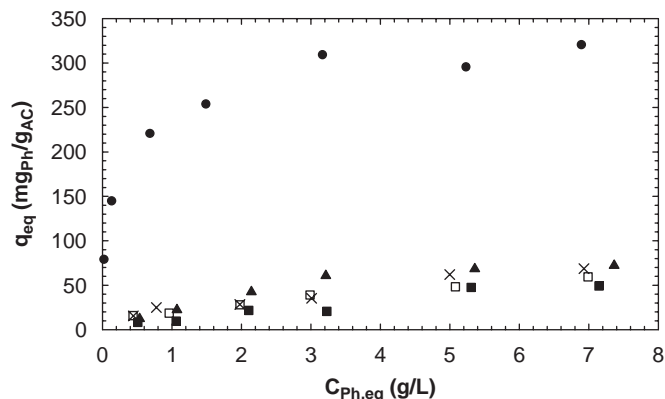


Fig. 7. Phenol adsorption isotherms of fresh and spent AC samples obtained at 25 °C. ● Fresh AC; ▲ after 50 h steady state operation at 160 °C; × after 50 h of periodic operation at 160 °C with  $s = \frac{2}{3}$  and cycle period = 0.3 h; □ after 50 h of periodic operation at 160 °C with  $s = \frac{2}{3}$  and cycle period = 0.9 h; ■ after 150 h of periodic operation at 160 °C with on–off air cycling at  $s = \frac{2}{3}$  and cycle period = 0.3 h.

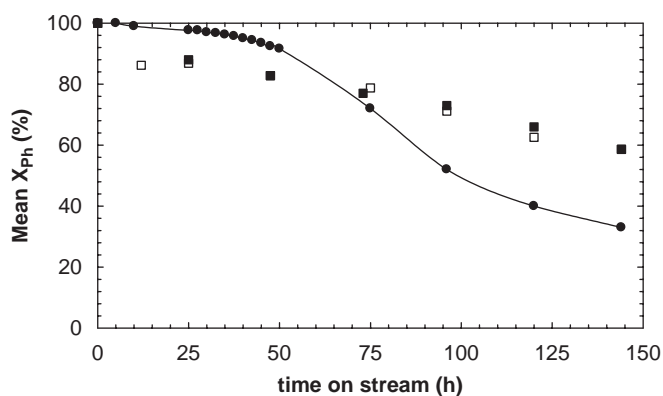


Fig. 8. Mean phenol cycle conversion with time on stream. ■ Air–nitrogen cycles; □ on–off cycles; ● continuous operation;  $T_{\text{Oven}} = 160$  °C,  $P_{\text{O}_2} = 2$  bar,  $C_{\text{Ph},0} = 5$  g/L,  $F_L = 0.06$  L/h,  $F_G = 8.6$  NL/h,  $s = \frac{5}{6}$ , cycle period = 2.4 h.

for about 50 h. This is in line with the fact that phenol adsorption capacity does not undergo great changes after the initial period. Then, the conversion and, in particular, the temperature amplitudes become smaller with time, which is mainly due to the slow but constant AC loss through burn-off. This is confirmed by the evolution of the mean cycle conversion that reveals a more pronounced decline at prolonged times on stream (see Fig. 6).

Finally, Fig. 8 compares the mean phenol conversion profiles for cycling and steady state experiments conducted over 144 h. As for 50 h runs, it is confirmed that periodic air/N<sub>2</sub> and on–off air cycling also lead to very similar mean phenol conversions over 144 h of time on stream. With respect to steady state and periodic operation, the former initially gives fairly higher phenol conversion, although the differences vanish with time on stream. After about 60 h, both conversions take a value of 80%, but then periodic operation clearly outperforms steady state operation giving a final 60% and 35% conversion,

respectively, after 144 h. The much better long term performance can be mainly attributed to a substantial delay in AC burn-off under periodic conditions, the final AC weight being 4.6–4.8 g for periodic cycling and 1.8 g for steady state operation. However, it must be pointed out that the dynamic reactor operation cannot completely avoid AC burn-off at the given operation conditions.

## 5. Conclusions

Oxidation experiments in steady state confirmed that the stability of activated carbon largely depends on the operating conditions employed. At 160 °C and 2 bar of oxygen partial pressure, the conversion performed is high (over 90%), but the AC burn-off is also enhanced leading to a detrimental loss of activity with operating time. The application of periodic gas phase modulation (air/N<sub>2</sub> cycling or on–off air flow) to phenol CWAO is an effective and emergent operating strategy to delay AC burn-off (final AC weight of 4.8 g for periodic operation compared to 1.8 g for steady state after 144 h), while maintaining an acceptable phenol conversion over large run times. The magnitude of improvement over steady state oxidation is given by the selection of the cycling parameters, i.e. split and period. High splits ( $> \frac{5}{6}$ ) and cycle periods larger than 1.5 h were found to benefit best the activity of AC in phenol CWAO (mean conversion of 60% for modulated CWAO over 35% for steady state CWAO after 144 h of operation). Particularly attractive for industrial application appears the air on–off mode since it reduces substantially the operating costs due to the elimination of the N<sub>2</sub> flow without losing in phenol conversion. Nevertheless, it must be stated that the dynamic reactor operation cannot completely avoid AC burn-off at the given operation conditions. Thus, to further improve the AC stability, additional experimental research work is required to test a wider range of pressure, temperature and liquid flow rate as well as the effect of liquid flow modulation in phenol CWAO. Moreover, the conversion and temperature profiles that result from periodic conditions clearly revealed the complex nature of unsteady reactor operation and more efforts should address to detailed process modelling in order to better understand and explore the potential of periodic CWAO of phenol over AC.

## Notation

$C$	concentration, g L <sup>-1</sup>
$F$	flow rate, L h <sup>-1</sup>
$P$	pressure, bar
$s$	air–nitrogen split
$T$	temperature, °C
$X$	conversion, %

## Subscripts

0	initial
AC	active carbon
Fin	final
$G$	gas

In	inlet
L	liquid
O <sub>2</sub>	oxygen
Out	outlet
Ph	phenol
TOC	total organic content

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