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Kinetics of the Wet Oxidation of Phenol over an Fe/Activated Carbon Catalyst*

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Abstract

Wet oxidation of phenol over an Fe/activated carbon catalyst has been studied in a trickle-bed reactor in the following operational window: inlet C phenol=0.5 and 1 g/L, T=100-127 °C, PT=3-8 atm, W=0-4.8 g, QL=0.125-2 mL/min and QO2=91.6 NmL/min. The experiments were carried out in the absence of mass transfer limitations. Oxidation and mineralization reactions of phenol are proven to take place on the catalyst surface through a heterogeneous mechanism. Due to the complexity of the phenol oxidation route, simple reaction schemes have been assumed by lumping the intermediate species and generalized kinetic models for phenol and TOC abatement have been proposed. Two kinetic expressions, a power law rate and a Langmuir-Hinshelwood type rate expression, have been considered but only a convergence with statistically reliable parameters was found for the former model. A power law model with first order for phenol and 0.74 for oxygen and apparent activation energy of 74 kJ/mol described the experimental results in the oxidation of phenol well. Mineralization of phenol (TOC abatement) was described by a similar rate expression and takes into account the presence of refractory species such as the low molecular weight acids formed upon phenol oxidation.

KEYWORDS: wet oxidation, phenol, Fe/activated carbon catalyst

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1. INTRODUCTION

Catalytic Wet Oxidation (CWO) is an effective technology to treat aqueous hazardous wastes, especially when these are too dilute to incinerate and too concentrated for a biological treatment (COD:10-100 g/L). CWO uses molecular oxygen as oxidant and operates at T<200 ºC and P<100 atm. Homogeneous catalysts such as cupric salts and heterogeneous catalysts such as CuO, MnO_2, CoO, ZnO and noble metals, Pd, Pt and Ru, have been studied. The main limitation of the catalytic heterogeneous systems comes from their unstable long-term performance. The causes of the deactivation are both the metal leaching, in the case of using transition metals, and the fouling by carbonaceous deposits, more frequently with noble metals. As a consequence, deactivation after different times on stream is observed depending on the nature of the deactivation, the loading of catalyst, the operation mode and the operating conditions. In Table 1, this information is summarized for different catalytic systems. Due to the catalyst deactivation, only a few commercial processes employ heterogeneous catalysts (Kolaczkowski, 1999).

Table 1. Life-time for different catalysts in the CWO of phenol

Reference	Catalyst	Mode operation	Inlet C_{Phenol} (mol/L)	T (ºC)	P_{O2} (atm)	Life-time (h)	Cause of deactivation
Fortuny et al., (1998)	$10\%CuO/\tilde{\gamma}Al_2O_3$ AC	continuous	0.05	140	9	24 Continuous fall	Leaching Carbon consumption
Hamoudi et al., (1998)	Mn/Ce (7/3) composite	batch	0.08	130	50	1	Carbonaceous deposits
Alvarez et al., (2002)	10%CuO/AC	batch	0.01	180	7.6	2.7	Carbonaceous deposits and leaching
Maugans and Akgerman (2003)	$4.45\%Pt/TiO_2$	continuous	0.004	175	10	~0.5	uncertain
Chen et al., (2007)	$CeO/\tilde{\gamma}Al_2O_3$ promoted by Cu or Mn	batch	0.01	150	15	4	Carbonaceous deposits and leaching
Massa et al., (2007)	$1\%Ru/CeO_2$-Al_2O_3	continuous	0.05	140	7	35	Carbonaceous deposits and change of Al_2O_3 phase

Activated carbon (AC) has been introduced as a catalyst with satisfactory results in the last decades (Tukac and Hanika, 1998, Fortuny et al. 1999). The most remarkable characteristics of ACs are their high surface area and porosity compared to other supports employed in CWO such as Al_2O_3, TiO_2, and CeO, and the presence of oxygen surface groups (OSGs), responsible of their catalytic activity (Rodríguez-Reinoso, 1998, Quintanilla et al., 2007a). Mild operating conditions are required (T<160 ºC and P<10 atm) to avoid combustion of the carbon itself (Mundale et al., 1991). Even under mild operating conditions, the surface of AC is modified during the oxidation process. As an example, the CWO of phenol with AC catalysts causes a significant loss of microporosity and an increase in the amount of OSGs on the carbon. However, these modifications do not alter the carbon catalyst's activity since wet oxidation takes place mainly in the mesopores and macropores and the new OSG are not active (Quintanilla et al. 2007a).

The incorporation of a metal such as noble metals, Pt and Ru (Gallezot et al. 1997; Oliviero et al. 2000; Gomes et al. 2000; Atwater et al. 1996) and transition metals Cu, Fe, Co and Mo (Hu et al., 1999; Alvarez et al., 2002; Quintanilla et al., 2006a) enhances the activity. With the Fe/Activated carbon catalyst (Fe/AC), phenol conversion increases from 50% with bare AC to 95% with the Fe/AC and TOC conversion from 30% to 65%, both at a space time of 9600 g_{CAT}·min/L at 127 ºC and 8 atm of total pressure. This better performance is due to both higher amounts of initial OSGs, specially the more acidic ones, formed during the calcination process in the Fe catalyst preparation, and the presence of iron oxide itself since for a given amount of OSGs higher conversions were obtained in presence of iron (Quintanilla et al., 2007a). The Fe/AC catalyst was stable for at least 216 h. Fe leaching was negligible (< 2%). The aggregation of α-Fe_2O_3 crystallites from 4 nm to a size of 40 nm without influence on the Fe/AC activity proves that Fe acts mainly as a promoter in the wet oxidation of phenol (Quintanilla et al., 2007b).

In a previous work (Quintanilla et al., 2006b), the route of the oxidation of phenol with Fe/AC catalysts was elucidated, see Figure 1. As can be seen, phenol is oxidized through two different pathways since it can be either hydroxylated or carboxylated, both in para position, yielding hydroquinone or p-hydroxybenzoic acid, respectively. Selectivity towards hydroxylation is higher than to carboxylation. These two primary intermediates (hydroquinone and p-hydroxybenzoic acid) are further oxidized through different routes. Hydroquinone is rapidly oxidized to p-benzoquinone which is mainly mineralized through oxalic acid formation, whereas p-hydroxybenzoic acid decomposes to low molecular weight acids. Small amounts of these short-chain acids were also detected in the CWO of p-benzoquinone. These acids are maleic, malonic, acetic and formic acids. They are quite refractory to the CWO but are oxidizable through a conventional biological oxidation. For this reason, CWO treatment is conceived as part of an integrated processes consisting of a partial chemical oxidation followed by a biological treatment (Mantzavinos and Psillakis, 2004).

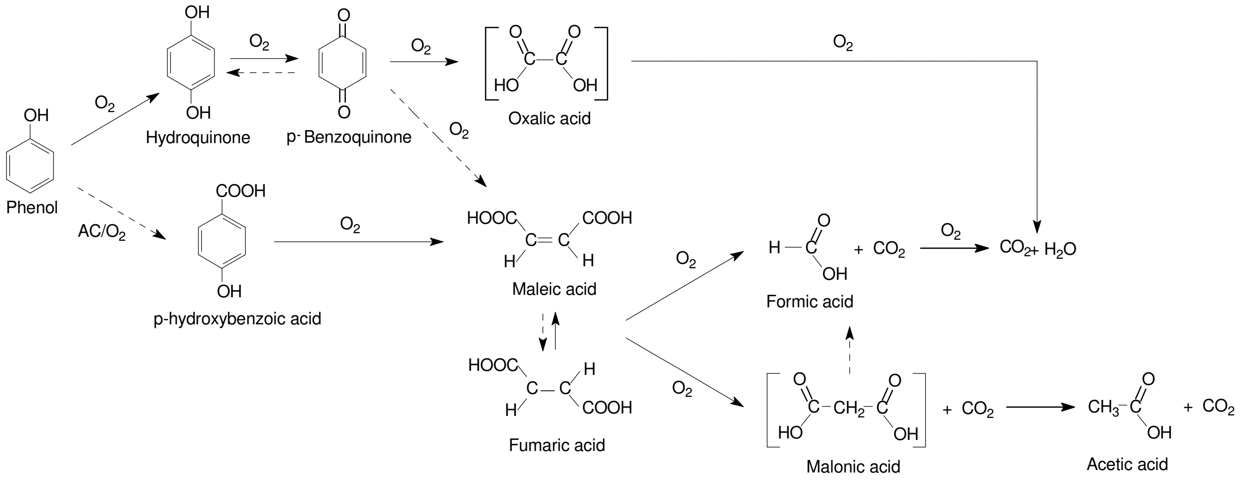

Figure 1. Oxidation pathway of the CWO of phenol with Fe/AC catalysts (Quintanilla et al., 2006b)

Once the uncertainty about catalyst stability has been eliminated and the oxidation pathway elucidated, it is feasible to study the kinetics for the CWO of phenol with the Fe/AC catalysts. The aim of this work is to elucidate the kinetics of this reaction. Considering the complexity of the oxidation route presented in Figure 1, lumping was necessary and, therefore, global rate expressions for phenol and TOC abatement have been proposed. Also, mass transfer considerations have been taking into account. In Table 2, some model equations found in the literature have been summarized and their parameters estimate for different types of catalysts. Power law and mainly Langmuir-Hinshelwood type rate expressions have been proposed. Commonly, reaction orders of 1 and 0.5 for phenol and oxygen, respectively, have been reported and the values of the apparent activation energy ranged from 34 to 110 kJ/mol. The discrepancy in this value is not well known, but likely the lowest activation energy values suffer from diffusion limitations. Some authors (Santos et al., 2001; Guo and Al-Dahhan, 2003) found a reaction rate not linearly dependent on the catalyst concentration due to the influence of the homogeneous reaction caused by metal dissolved from the catalyst.

Table 2. Overview of kinetic models discriminated in literature for CWO of phenol

Reference	Catalyst	Model equation	Parameter estimation*
Sadana and Katzer (1974)	10%CuO/γ–Al_2O_3	Initial rate: $r\left(\frac{mol}{g_{CAT}\cdot s}\right)=k_1\cdot P_{O2}\cdot C_{Phenol}$ Steady state: $r\left(\frac{mol}{g_{CAT}\cdot s}\right)=k_2\cdot P_{O2}^{0.5}\cdot C_{Phenol}$	k_1=1.83 $e^{-1928/RT}$ mL/(g_{CAT} s atm) k_2= 14.51$e^{-8314/RT}$ mL/(g_{CAT} s $atm^{0.5}$)
Pintar and Levec (1994)	CuO/ZnO/CoO	$r\left(\frac{\mathrm{mol}}{\mathrm{g_{CAT}}\cdot h}\right)=\frac{k_{app}\cdot K_{Phenol}\cdot K_{O2}^{0.5}\cdot C_{Phenol}\cdot C_{O_2}^{0.5}}{1+K_{Phenol}\cdot C_{Phenol}}$	K_{Phenol}=610^{-6}$e^{-61500/RT}$ L/mol $K_{app}K_{O2}^{2}$=4.810^{12}$e^{137137/RT}$ $mol^{0.5}L^{0.5}/(g_{CAT}h)$)
Santos et al., (2001)	CuO/2CuO·Cr_2O_3/ 1% graphite	$r\left(\frac{\mathrm{g\ of\ C}}{\mathrm{L}\cdot\mathrm{min}}\right)=\frac{k\cdot C_{Phenol}\cdot P_{O_2}^{0.7}}{\left(1+K_{Phenol}\cdot C_{Phenol}\right)^2}\cdot C_{CAT}^{0.4}$	k=$e^{(98.4-340874/RT)}$ $L^{0.4}/(atm^{0.7}g_{CAT}^{0.4}$ min) K_{Phenol}= $e^{(53.4-172931/RT)}$ (L/mg C)
Guo and Al-Dahhan (2003)	Al-Fe/pillared clay	$r\left(\frac{mol\ of\ C}{m^3\cdot\mathrm{min}}\right)=\frac{k_1\cdot K_{Phenol}\cdot K_{O_2}^{0.5}\cdot C_{Phenol}\cdot C_{O2}^{0.5}}{(1+K_{Phenol}C_{Phenol})}\cdot C_{CAT}^{0.82}$	k_1=0.31·10^{5}$e^{-34290/RT}$ mol of C/(($m^3)^{0.18}kg^{0.82}$min) K_{Phenol} =0.98·10^{4}$e^{-39059/RT}$ m^3/mol of C K_{O2}= 0.97·10^{4}$e^{-46061/RT}$ m^3/mol O_2
Maugans and Akgerman (2003)	4.45%Pt/TiO_2	$r\left(\frac{\mathrm{mol}}{\mathrm{g_{CAT}}\cdot\mathrm{min}}\right)=\frac{k\cdot C_{Phenol}\cdot C_{O_2}^{0.5}}{\left(1+K_{Phenol}\cdot C_{Phenol}+\left(K_{O2}\cdot C_{O2}\right)^{0.5}\right)^2}$	k_1=8.52·10^{12} $e^{-110000/RT}$ $L^{1.5}$ g_{CAT}/min/$mol^{0.5}$ K_{Phenol} =5.76·10^{12}$e^{-100000/RT}$ L/mol K_{O2}= 3.09·10^{8}$e^{-67000/RT}$ L/mol
Singh et al., (2004)	10%CuO/γ–Al_2O_3	$r\left(\frac{mol}{g_{CAT}\cdot s}\right)=\rho_B\cdot\eta\cdot\frac{k_{app}\cdot K_{Phenol}\cdot K_{O_2}^{0.5}\cdot C_{Phenol}\cdot C_{O2}^{0.5}}{(1+K_{Phenol}C_{Phenol})}$	$K_{app}K_{O2}^{2}$=3.510^{-5}$e^{11781/RT}$ $mol^{0.5}$(cm3)$^{0.5}$/(g_{CAT} s)) K_{Phenol} =7115$e^{11742/RT}$ cm^3/mol
Santos et al., (2005)	AC	$r\left(\frac{\mathrm{mg\ of\ C}}{\mathrm{g_{CAT}}\cdot\mathrm{min}}\right)=\frac{k_1\cdot P_{O2}\cdot C_{Phenol}}{\left(1+K_{O2}\cdot P_{O2}\right)\cdot\left(1+K_{Phenol}\cdot C_{Phenol}\right)}$	k_1=0.059 $e^{-46600/RT}$ $L^{1.5}$ g_{CAT}/min/$mol^{0.5}$ K_{O2} =7.30·10^{-7}$e^{41753/RT}$ L/mol K_{Phenol}= 3.01·10^{6}$e^{-76613/RT}$ L/mol
Eftaxias et al. (2005)	AC	$r\left(\frac{mol}{kg_{CAT}\cdot h}\right)=k\cdot x_{O2}\cdot C_{Phenol}$	k=10$^{13.81}$ $e^{-69300/RT}$ L/(kg_{CAT} h)
Wu et al., (2005)	10%CuO/AC	$r\left(\frac{mg}{g_{CAT}\cdot s}\right)=\frac{k\cdot C_{O2}\cdot C_{Phenol}}{\left(1+K_{O2}C_{O2}\right)^2}$	k=8.58 $e^{-35400/RT}$ L^2/(mg O_2 g_{CAT} s) K_{O2} not given

* Apparent activation energy in J/mol

2. EXPERIMENTAL SECTION

2.1 Catalyst preparation and characterization

A hydrocarbon derived granular activated carbon supplied by Merck (Ref.:102514) was used as catalytic support. After crushing and sieving, the fraction of 0.5-1 mm particle size was selected. Using the incipient-wetness impregnation method, a catalyst containing 2.5 wt% of Fe on the active carbon was prepared. An aqueous solution of $Fe(NO_3)_3{\cdot}9H_2O$ was employed as iron precursor; the solution volume exceeded by 10% the total pore volume of the support. Impregnation was followed by drying at room temperature for 2 h and overnight at 60 ºC. The sample was then heated up to 200 ºC within 2 h in air at two heating rates (1h at 0.67 ºC/min and 1h at 1.67 ºC/min) and then calcined in air at 200 ºC during 4 h.

N_2 adsorption-desorption (77 K) and mercury porosimetry were used to characterize the porous structure of the catalyst. An Omnisorp analyzer (100 CX) and a Carlo Erba Porosimeter 4000 were respectively used. The results were: S_{BET}=890 m^2/g, A_t=72 m^2/g, $V_{micropore}$=0.393 cm^3/g, $V_{mesopore}$=0.168 cm^3/g, $V_{macropore}$=0.212 cm^3/g. The Fe content of the catalyst was 2.4%, determined by total reflection X-ray fluorescence (TXRF). The Fe in the catalyst was found as α-Fe_2O_3 by Mössbauer spectroscopy, using a conventional spectrometer with ^{57}Co(Rh) source.

2.2 Oxidation experiments

The CWO experiments were conducted in a trickle-bed reactor consisting of a stainless steel tube of 0.85 cm of internal diameter with a steel porous plate at 100 mm from the entrance where the catalyst was placed. The temperature was measured by a thermocouple located in the catalytic bed. The liquid and gas phases were passed through the bed in cocurrent down-flow. Pure oxygen was used as oxidising agent. Detailed information about the components and operation procedure of this setup has been reported elsewhere (Quintanilla et al., 2006a).

An aqueous solution of phenol at acidic pH (around 3.5) was continuously fed to the reactor at different concentrations of phenol, 0.5 and 1 g/L, and at different flow rates (from 0.125 to 2 mL/min) to cover the experimental range of space time values (W/Q_L= 1200-19200 $g_{CAT}{\cdot}$min/L). A 91.6 NmL/min pure oxygen flow was continuously passed in all the experiments. The oxidation runs were performed at different temperatures (100-127 ºC) and total pressures (3-8 atm). Also, catalyst loading ranged from 0 to 4.8 g. Results of the experiments at 100 and 127 ºC, 8 atm,1 g/L of phenol and 2.5 g of catalyst were already reported in Quintanilla et al., (2006). Before oxidation, the fresh catalytic bed was first saturated with phenol under the same experimental conditions as for the CWO runs except for the gas fed (N_2 instead of O_2).

2.3 Analytical techniques

The progress of the reaction was followed by taking periodically liquid samples from the reactor outlet. The steady state was reached after 4-8 h, depending on the space time used in the experiment. The liquid samples were analyzed by different procedures. Phenol and ring compounds were determined by HPLC (Varian, mod. ProStar), low molecular weight acids by anionic suppression IC (Metrohm, mod. 761 Compact IC) and total organic carbon (TOC) using a TOC analyzer (O.I. Analytical, model 1010). Iron in the reactor effluent was analyzed by TXRF. More detailed description of these chemical analyses can be found in previous work (Quintanilla et al., 2006b).

3. RESULTS AND DISCUSSION

3.1 Mass transfer considerations

To evaluate external mass transfer resistance under the reaction conditions, the gas to liquid (k_la) and the liquid to solid (k_Sa_p) mass transfer groups have been calculated at the highest temperature used in this work (127 ºC) and for a liquid flow rate of 2 mL/min (Ramachandra and Chaudhari, 1983). The experimental operating conditions of the reactions and the physical properties of the reactants used for calculations are summarized in Table 3 and 4, respectively.

Table 3. Experimental conditions in the TBR

Reactor volume, V_R (cm^3)	4.25
Reactor diameter, d_T (m)	$8.5\cdot10^{-3}$
Particle diameter, d_p (m)	$7.5\cdot10^{-4}$
Equivalent diameter, d_{pe} (m)	$2\cdot10^{-3}$
Characteristic length, L (m)	1.310^{-4}
Liquid hold up*, ε_L	0.2
Mass of catalyst, W (g)	2.5
Catalyst density, ρ_{CAT} (kg/m^3)	2500
Bed porosity, ε_B	0.8
Particle porosity, ε_p	0.6
Catalyst concentration in the reactor, C_{CAT} (g/L)	2727
Initial concentration of phenol, $C_{inlet\ phenol}$ (mol/L)	$1.06\cdot10^{-2}$ and $5.3\cdot10^{-3}$
Initial concentration of TOC, $C_{inlet\ TOC}$ (mol/L)	$63.3\cdot10^{-3}$ and $31.6\cdot10^{-3}$
Liquid flow rate, Q_L (mL/min)	2-0.125
Superficial liquid velocity, u_L (m/s)	$5.9\cdot10^{-4}$-3.710^{-5}
Gas flow rate, Q_G (NmL/min)	91.6
Superficial gas velocity at reaction conditions, u_{GR} (cm/s)	4.910^{-3}
Residence time, t_R (min)	0.4-6.8
Space time, W/Q_L (g_{CAT}·min/L)	1200-19200

*Calculated according Larachi correlation valid in the gas and liquid velocity range employed in this study (Al-Dahhan et al., 1997)

Table 4. Physical properties of the fluids at 127 ºC and 8 atm

	Phenol	Oxygen
ρ (kg/m^3)	934	5.36
μ (kg/(m·s))	$1.7\cdot10^{-4}$	$2.2\cdot10^{-5}$
D (m^2/s)	$5.3\cdot10^{-9}$	$1.7\cdot10^{-8}$
D_{eff} (m^2/s)	$1.1\cdot10^{-9*}$	$4.2\cdot10^{-9}$

Data from Eftaxias (2002)
* Estimated by Bhatia et al., (1990)

The corresponding values of the calculated mass transfer groups k_la and k_Sa_p, are collected in Table 5 and 6, respectively. The wetting efficiency, $F_w=a_w/a_p$, was calculated from two correlations (Tucka and Hanika, 1998; El-Hisnawi et al., 1981) in the interval of superficial liquid velocity employed in this study ($u_L = 5.87\cdot10^{-4}$-$3.67\cdot10^{-5}$ m/s). Both correlations predict $F_w= 0.75$.

The Wheeler-Weisz criterion has been used to test whether slow internal diffusion was limiting the reaction:

$$\Phi = \eta \cdot \phi^2 = \left(\frac{k_{obs} \cdot L^2}{D_{eff}} \right) < 0.15 \tag{1}$$

The value of effective diffusivity (D_{eff}) of phenol in ACs at 127 ºC is around $1.1\cdot10^{-9}$ m^2/s (Table 4) (Bhatia et al., 1990). To calculate the observed kinetic rate constant, a pseudo-first order plug flow model has been used. The integrated equation results:

$$Ln\left(\frac{1}{1-X} \right) = k_{obs} \cdot \left(\frac{W}{Q_L} \right) \tag{2}$$

For the highest temperature and oxygen pressure, the value of the observed kinetic rate constant is $2.2\cdot10^{-4}$ L/(g_{CAT}·min) or 0.014 s^{-1}. By substituting the corresponding values in Equation 1, Wheeler-Weisz modulus results 0.17 and considering the wetting efficiency, a value of 0.22 is obtained. Therefore, the internal effectiveness factor (η) for the highest rate, which represent 'worst case scenarios' is 0.95, so internal diffusion limitation can be excluded.

In addition, the Carberry number for the gas to liquid (Ca_{G-L}) and liquid to solid (Ca_{L-S}) mass transport can be calculated considering the average value of the external mass transfer groups from Table 5 and 6, respectively, (k_La=0.140 s^{-1} and k_Sa_w=0.083 s^{-1}). The values obtain are $6.7\cdot10^{-4}$ and 0.17 for Ca_{G-L} and Ca_{L-S}, respectively. Therefore, the liquid to solid mass transfer is slightly limiting in the most extreme case. Oxidation of phenol with Fe/AC catalysts can be considered to occur under kinetic control at the operating conditions used in our experiments.

Table 5. Estimation of gas-liquid mass transfer coefficients

Reference	Correlation	k_la (s^{-1})
Goto and Smith (1975)	$\frac{k_la}{D}=1.9\cdot\left(\frac{\rho_L\cdot u_L}{\mu_L}\right)^{0.41}\left(\frac{\mu_L}{\rho_L\cdot D}\right)^{0.5}$	$1.07\cdot10^{-2}$
Fukushima and Kusaka (1977)	$k_la=2\cdot\left(\frac{S_P}{d_p^2}\right)^{0.2}\cdot\mathrm{Re}_L^{0.73}\cdot\mathrm{Re}_G^{0.2}\cdot\left(\frac{\mu}{\rho_L\cdot D}\right)^{0.5}\cdot\left(\frac{d_p}{d_T}\right)^{0.2}\cdot D\cdot\frac{(1-\varepsilon_L/\varepsilon_B)}{d_p^2}$ $\varepsilon_L/\varepsilon_B = 0.25$ Re_L= 2.42 Re_G=1.31 S_p/d_p^2= 6.28	$2.67\cdot10^{-1}$

Table 6. Estimation of liquid-solid mass transfer coefficients for the Fe/AC

Reference	Correlation	k_sa_p (s^{-1})	k_sa_w (s^{-1})
van Krevelen and Krekels (1948)	$\frac{k_sa_p}{Da_t^2}=1.8\cdot(\mathrm{Re}_L\acute{})^{1/2}\cdot\left(\frac{\mu_L}{\rho_L\cdot D}\right)^{1/3}$ dp^* (m)= $7.50\cdot10^{-4}$ a_t (m)= $1.60\cdot10^3$ Re_L`=2.02	$1.12\cdot10^{-1}$	8.4210^{-2}
Hirose et al., (1976)	$\frac{k_s\cdot d_p}{D}=0.8\frac{\mathrm{Re}_L^{0.5}}{\varepsilon_L}\cdot\left(\frac{\mu_L}{\rho_LD}\right)^{0.333}$ a_p (m^2/m^3)= $7.32\cdot10^3$	$2.61\cdot10^{-1}$	$1.95\cdot10^{-1}$
Dharwadkar and Sylvester (1977)	$k_s=1.637\cdot u_L\cdot\mathrm{Re}_L^{-0.331}\cdot\left(\frac{\mu_L}{\rho_L\cdot D}\right)^{-0.666}$ a_p (m^2/m^3)= $7.32\cdot10^3$	$4.97\cdot10^{-1}$	$3.73\cdot10^{-1}$

3.2 Influence of reaction conditions

3.2.1 Inlet phenol concentration: the conversion of phenol is independent of the inlet concentration within the range investigated (Figure 2) and therefore the order of reaction with respect to phenol is 1.

3.2.2 Catalyst loading: increasing the amount of catalyst leads to a significant increase of phenol and TOC conversion, as shows Figure 3. Moreover, the residence time of the liquid phase does not affect the conversions. The homogeneous reaction is negligible and phenol oxidation and mineralization take place on the catalyst surface through a heterogeneous mechanism.

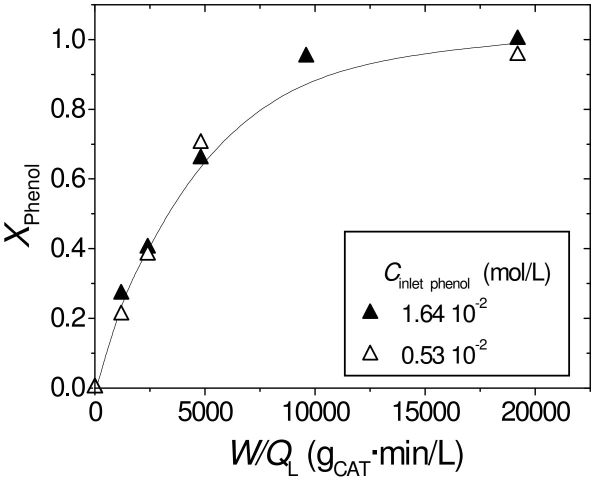

Figure 2. Phenol conversion as a function of space time at two inlet concentrations. T=127 ºC, P_T=8atm and W=2.5 g

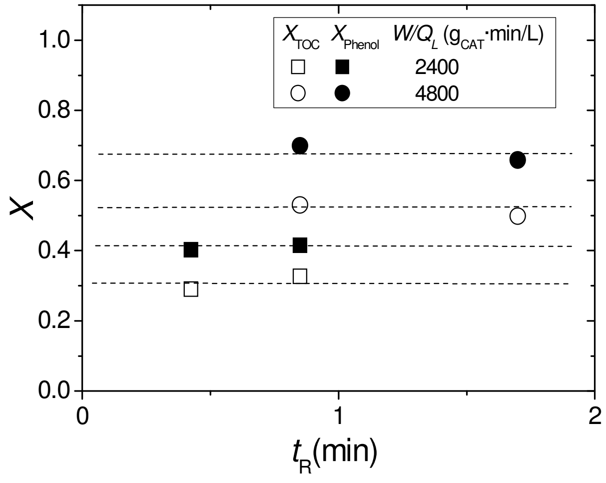

Figure 3. Conversion of phenol and TOC as a function of residence time at two different space times. T=127 ºC, inlet C_{Phenol}= 1g/L and P_T=8atm.

3.2.3 Oxygen partial pressure: to check the influence of the oxygen pressure, total pressure has been tested at 3, 5 and 8 atm at 127 ºC which corresponds to oxygen partial pressures of 0.53, 2.53 and 5.53 atm, respectively, due to the vapour pressure of water. The phenol and TOC conversions *vs.* space time, shown in Figures 4a and b, respectively, indicate an important oxygen partial pressure dependency. The initial reaction rate does not increase linearly with an increase in the oxygen pressure (Figure 5). An apparent order of 0.6 with respect to oxygen is obtained for both phenol and TOC conversion rates.

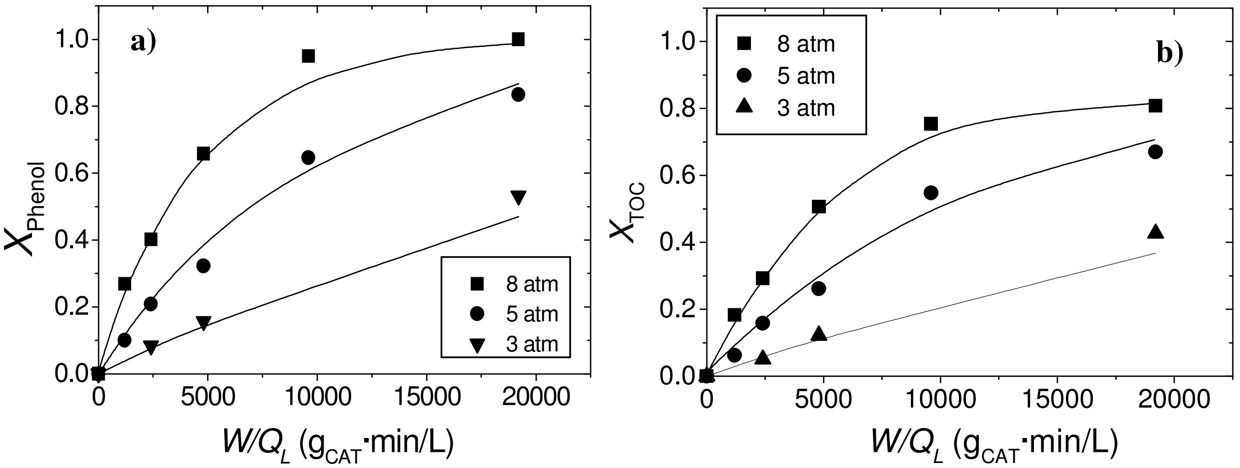

Figure 4. Conversion of phenol (a) and TOC (b) as a function of space time at different oxygen pressure. T=127 ºC, inlet C_{Phenol}= 1g/L and W=2.5 g. Experimental data (dots) and predicted values (lines).

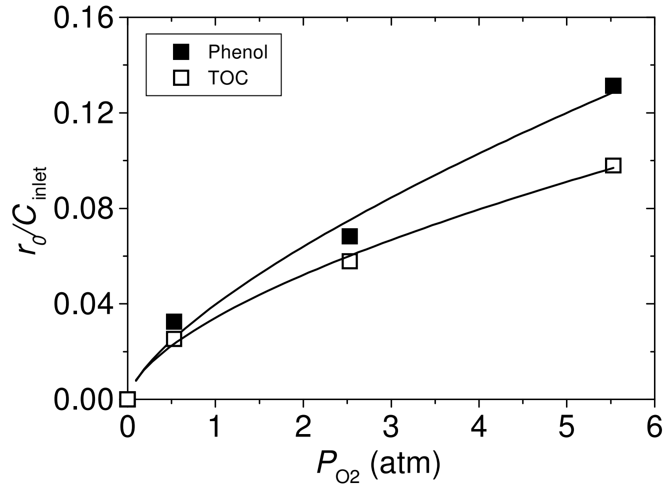

Figure 5. Initial oxidation rates of phenol and TOC normalized to their inlet concentration as a function of the oxygen partial pressure at T=127 ºC, inlet C_{Phenol}= 1g/L and W=2.5 g.

3.2.4 Reaction temperature: a moderate increase of temperature from 100 to 127 ºC produces a significant effect on the activity of the catalyst (Figure 6). A complete removal of phenol and a high TOC reduction (up to 80%) has been achieved at moderate operating conditions (127 ºC and 8 atm). The logarithm of the initial rate plotted against the reciprocal temperature (Figure 7) yield apparent activation energy values of 73 and 69 kJ/mol for phenol and TOC disappearance, respectively.

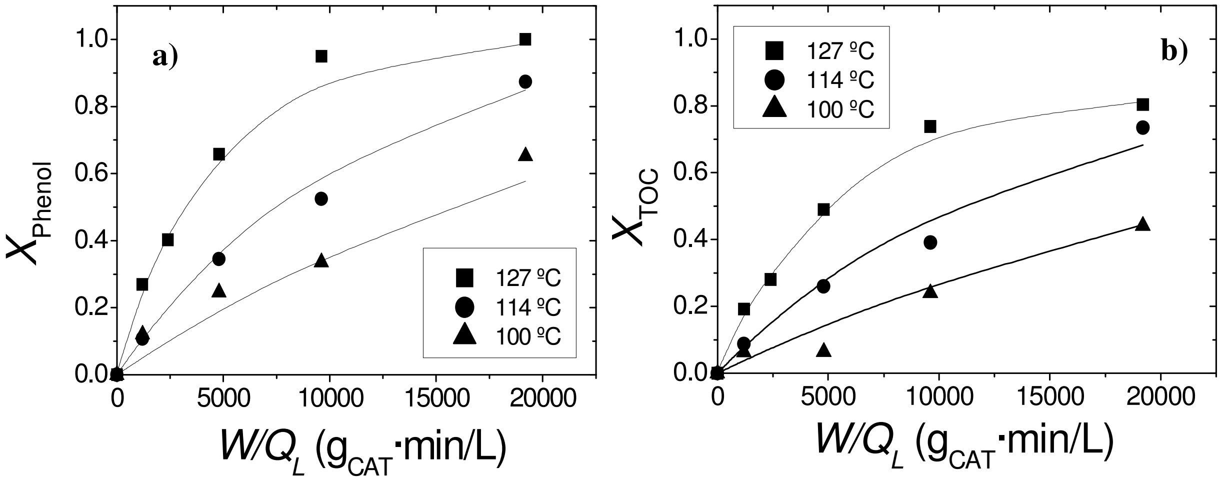

Figure 6. Influence of temperature on the conversion of phenol (a) and TOC (b) at P_T= 8 atm, inlet C_{Phenol}= 1g/L and W=2.5 g. Experimental data (dots) and predicted values (lines).

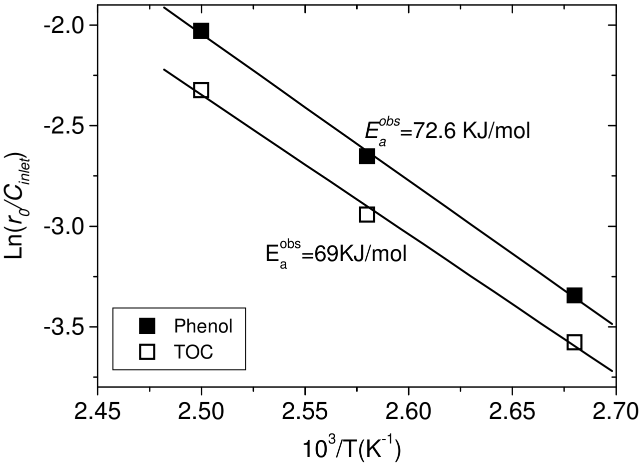

Figure 7. Arrhenius plot for the initial oxidation rate of phenol and TOC normalized to their inlet concentration at P_T= 8 atm, inlet C_{Phenol}= 1g/L and W=2.5 g.

3.3 Kinetic analysis

CWO of phenol with Fe/AC catalyst proceeds through a complex scheme of reactions involving many intermediate species as shown in Figure 1. A simplified approach has been used to describe phenol and TOC abatement. Disappearance of phenol is formulated by a single reaction where all the intermediate species are lumped.

$$Phenol \xrightarrow{r_1} \mathrm{Pr}oducts$$
$$\frac{dC_{Phenol}}{d\left(W/Q_L\right)} = -r_1 \qquad (3)$$

For TOC, a lumped reaction approach has also been used, as follow:

$$A \xrightarrow{r_2} xB + (1-x)CO_2$$
$$TOC = A + B$$
$$\frac{dC_A}{d(W/Q_L)} = -r_2 \qquad (4)$$
$$\frac{dC_B}{d(W/Q_L)} = xr_2$$
$$\frac{dC_{TOC}}{d(W/Q_L)} = -r_2 + xr_2 = (x-1)\cdot r_2$$

Here, A represents all species that undergo oxidation (phenol and aromatic intermediates) and B corresponds to the refractory organic acids, all of them expressed in mol of carbon/L. The coefficient x is the molar fraction of oxidizable carbon that gives rise to refractory species.

For both, phenol and TOC abatement, two different types of kinetic expressions have been used to fit the experimental results of Figures 2, 4 and 6, see Table 7. A power law expression with first order with respect to phenol and n-order with respect to oxygen, and a Langmuir-Hinshelwood expression, in which reaction between molecularly adsorbed oxygen and phenol in the liquid phase has been considered.

Numerical integration of the differential equations and the parameter estimation have been carried out with the software package Athena Visual Studio (nonlinear optimization), in order to minimize the sum of squares of the residuals (SSR), the difference between the experimental phenol and TOC concentrations and the model predictions. The reparameterization of Arrhenius expression was applied to reduce the interdependency between the activation energy and the pre-exponencial factor, which diminishes the fitting procedure (Berger et al., 2001):

$$k_i = k_{i,ref}\cdot\exp\left\{\left(\frac{E_a}{R}\right)\left(\frac{1}{T_{ref}}-\frac{1}{T}\right)\right\} \tag{5}$$

The temperature of 100 ºC was used as the reference temperature (T_{ref}=373 K).

The results of the fittings are summarized also in Table 7. For phenol removal, only the power law equation M1 yields statistically reliable parameters. The Langmuir-Hinshelwood rate expression (M2 and M3) does not describe adequately the time dependence of both phenol concentration and oxygen partial pressure. With equation M2, the pre-exponential factor of adsorption constant, K_{o3} is not significant since its confidence interval includes the zero. Also, the program fixed the adsorption enthalpy, ΔH_3, in order to get a convergence. When the order in oxygen is also estimated in equation M3, then a kinetic order of 0.74 was obtained and the oxygen adsorption term became zero, leading to the power law model M1. For TOC removal, a similar result was found. Attempts to estimate a site balance, based on Langmuir adsorption was unsuccessful because, to converge, the adsorption enthalpy, ΔH_8, was fixed in M5 and the oxygen adsorption term was zero in M6. Only the power law model M4 resulted in convergence and yielded statistically relevant parameter values.

Table 7. Kinetic models proposed and results of the fittings for the CWO of phenol with Fe/AC catalysts

	Models for the oxidation of phenol: $r_1 = \left(\frac{dC_{phenol}}{d(W/Q_L)}\right)\left(\frac{mol\ Phenol}{g_{CAT}\cdot\min}\right)$	
M1	$k_1 P_{O2}^n C_{Phenol}$	n=0.74±0.17 $k_{o1}=(2.46\pm1.27)\cdot10^{-8}$ L/g$_{CAT}$·min·atm$^{0.74}$ $E_{a1}=(7.40\pm1.56)\cdot10^{4}$ J/mol $SSR=1.09\cdot10^{-5}$
M2*	$\frac{k_2' P_{O2} C_{Phenol}}{1+K_3 P_{O2}}$	$k_{o2}=(9.94\pm4.87)\cdot10^{-6}$ L/g$_{CAT}$·min·atm $E_{a2}=(7.54\pm1.81)\cdot10^{4}$ J/mol $K_{o3}=(8.31\pm9.85)\cdot10^{-2}$ atm^{-1} $\Delta H_3=4.90\cdot10^{3}$ J/mol $SSR=1.30\cdot10^{-5}$
M3*	$\frac{k_4' P_{o2}^n C_{Phenol}}{1+K_5 P_{O2}}$	n=0.74±0.16 $k_{o4}=(1.06\pm0.44)\cdot10^{-6}$ L/g$_{CAT}$·min·atm$^{0.74}$ $E_{a4}=(7.42\pm1.46)\cdot10^{4}$ J/mol $K_{o5}=0$ atm^{-1} $\Delta H_5=-1.4\cdot10^{2}$ J/mol $SSR=1.09\cdot10^{-5}$

* $k_2' = k_2\cdot K_3\cdot K_{Phenol}$, $k_4' = k_4\cdot K_5\cdot K_{Phenol}$

Table 7. (Continued) Kinetic models proposed and results of the fittings for the CWO of phenol with Fe/AC catalysts

Models for the mineralization of phenol: $r_2 = \left(\frac{dC_A}{d(W/Q_L)}\right)\left(\frac{mol\ oxidizable\ Carbon}{g_{CAT}\cdot \text{min}}\right)$		
M4	$k_6 P_{O2}^n C_A$	n=0.73±0.10 k_{o6}=(9.44±2.49)·10^{-6} L/g_{CAT}·min·$atm^{0.74}$ E_{a6}=(7.41±0.95)·10^4 J/mol x=0.155±0.034 SSR=9.58·10^{-4}
M5*	$\frac{k_7' P_{O2} C_A}{1+K_8 P_{O2}}$	k_{o7}=(9.32±3.48)·10^{-6} L/g_{CAT}·min·atm E_{a7}=(7.71±1.00)·10^4 J/mol K_{o8}=(9.61±7.52)·10^{-2} atm^{-1} ΔH_8 =1.03·10^4 J/mol x=0.156±0.035 SSR=1.07·10^{-3}
M6*	$\frac{k_9' P_{O2}^n C_A}{1+K_{10} P_{O2}}$	n=0.73±0.10 k_{o9}=(9.45±2.51)·10^{-6} L/g_{CAT}·min·$atm^{0.74}$ E_{a9}=(7.42±0.95)·10^4 J/mol K_{o10}=0 atm^{-1} ΔH_{10}=4.86·10^3 J/mol x=0.155±0.0336 SSR=1.09·10^{-5}

* $k_7' = k_7 \cdot K_8 \cdot K_A$ and $k_9' = k_9 \cdot K_{10} \cdot K_A$

To demonstrate the quality of the fit by the power law models M1 and M4, the calculated values of phenol and TOC conversions have been included in Figures 2, 4 and 6 (in lines) at all the operating conditions investigated. The validation of the model can also be proven by the parity plots of phenol and TOC concentrations in Figure 8a an b, respectively.

The values of the activation energies for phenol and TOC removal, about 74 kJ/mol, are in the range reported in the literature. These were slighter higher than those initially estimated from the initial reaction rates (Figure 7). On the other hand, an order of around 0.7 in oxygen pressure has been obtained. Usually, a kinetic order of 0.5 is found in CWO with conventional catalysts such as CuO/γ–Al_2O_3 and CuO/ZnO/CoO but a higher order, around 1, has been reported for CWO of phenol with AC catalysts (Table 2). Therefore, the value estimated with Fe/AC catalysts is within the range.

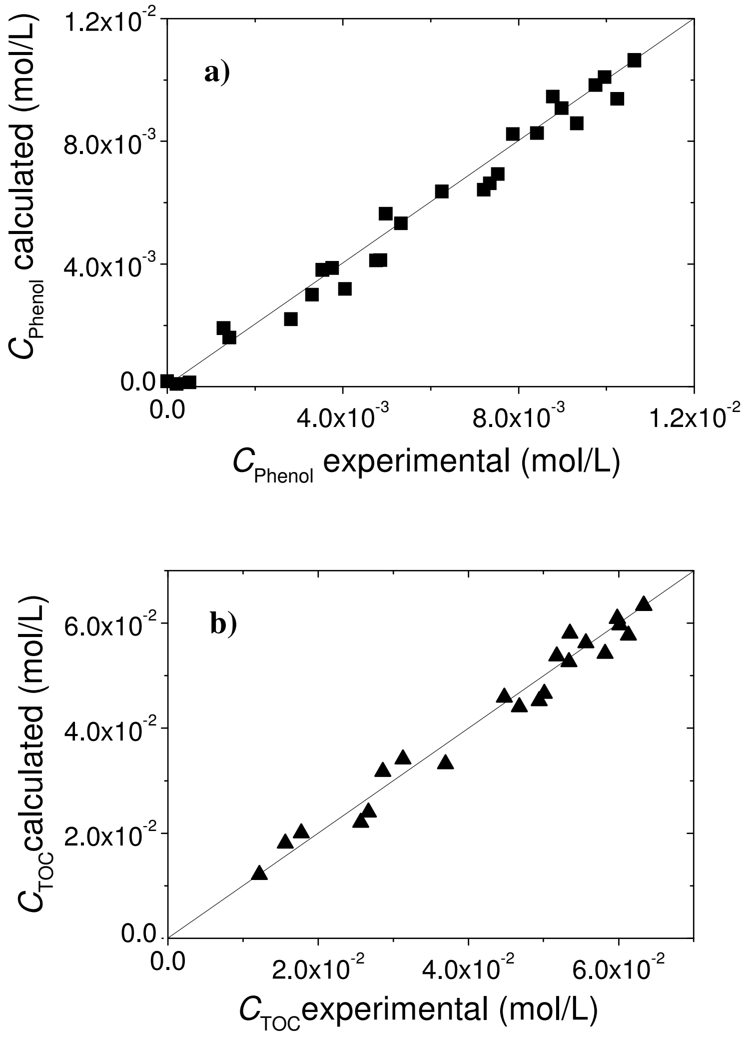

Figure 8. Parity plot for phenol (a) and TOC (b) concentration for the power rate law for all experimental data.

CONCLUSIONS

CWO of phenol with Fe/AC catalysts is a heterogeneous reaction in which the rates of phenol and TOC conversion can be adequately described by a generalized kinetic model according to the following power law equation,

$$r_1\left(\frac{mol\ phenol}{g_{CAT}\cdot\min}\right)=2.46\cdot10^{-8}\cdot e^{-74000/RT}\cdot P_{O2}^{0.74}\cdot C_{Phenol}$$

$$r_2\left(\frac{mol\ carbon}{g_{CAT}\cdot\min}\right)=9.44\cdot10^{-6}\cdot e^{-74100/RT}\cdot P_{O2}^{0.73}\cdot C_{oxidizable\ species}$$

The generalized kinetic model for TOC abatement allows describing the formation of refractory species (low molecular weight acids). The molar fraction of species which can be oxidized to refractory ones is 0.155.

NOTATION

a_p	external area of particles per unit volume of reactor, m^2/m^3
a_t	surface area of particles (a_p) based on the modified diameter, d_p^* (m)
A_t	external area (m^2/g)
a_w	wetted external area of particles per unit volume of reactor (m^2/m^3)
C^*	equilibrium solubility of the gas in the liquid, mol/L
C_A	concentration of oxidizable species (mol/L)
$Ca_{G\text{-}L}$	Carberry number for gas-liquid mass transport define as $r^{obs}{}_{O2}/(k_l a C^*)$
$Ca_{L\text{-}S}$	Carberry number for liquid-solid transport define as $r^{obs}{}_{Phenol}/(k_s a_w C_b)$
C_b	molar concentration in the bulk, mol/L
C_B	concentration of refractory organic acids (mol/L)
C_{CAT}	catalyst concentration (g/L)
COD	chemical oxygen demand (g/L)
C_{Phenol}	concentration of phenol (mol/L)
C_{TOC}	concentration of total organic carbon (mol/L)
D	diffusion coefficient (m^2/s)
D_{eff}	effective diffusivity in activated carbon (cm^2/s)
d_p^*	modified diameter of the particles defined as $d_p/(1+[4d_p/6d_T(1-\varepsilon_B)]$ (m)
E_{ai}	activation energy (J/mol)
k'_i	lumped reaction rate constants (see Table 6)
k_i	reaction rate constant ($L/g\cdot min\cdot atm^n$)
K_i	adsorption rate constant (atm^{-1})
k_l	gas to liquid mass transfer coefficient (m/s)
k_{obs}	observed reaction rate constant, $L/(g_{CAT}\cdot min)$
k_{oi}	pre-exponencial factor, ($L/g_{CAT}\cdot min\cdot atm^n$)
k_S	liquid to solid mass transfer group (m/s)
L	characteristic length ($d_p/6$) (m)
n	reaction order with respect to oxygen
P_{O2}	oxygen partial pressure (atm)
P_T	total pressure (atm)
R	universal gas constant (8.314 J/mol K)
r	reaction rate ($mol/g\cdot min$)
Re_G	Reynolds number of the gas
Re_L	Reynolds number of the liquid, $d_p\cdot u_L\cdot \rho_L / \mu_L$
Re_L'	Reynolds number of the liquid, $\rho_L\cdot u_L/(\mu_L\cdot a_t)$
$r^{obs}{}_{O2}$	observed volumetric reaction rate for oxygen calculated as $7\cdot(C_{inlet\ phenol}-C_{phenol})\cdot C_{CAT}/(W/Q_L)$ (mol $O_2/(L\cdot s)$)
$r^{obs}{}_{Phenol}$	observed volumetric reaction rate for phenol, (mol phenol $/(L\cdot s)$)
R_{Phenol}	production rate of phenol (mol/g min)
S_{BET}	BET area (m^2/g)
S_p	particle geometric area (m)
SSR	sum of the squares of the residuals, $\Sigma(C_{exp}-C_{cal})^2$ (mol^2/L^2)
T	temperature (ºC)
TOC	total organic carbon
W	mass of catalyst (g)
W/Q_L	space time ($g_{CAT}\cdot min/L$)
x	molar fraction of the species that can be oxidized to these refractory ones
X	conversion
ΔH_i	enthalpy of adsorption (kJ/mol)
Φ	Wheeler-Weisz modulus
ε_L	liquid hold-up
ε_p	particle porosity
ε_B	bed porosity

ϕ	Thiele modulus
η	catalyst effectiveness factor
μ	viscosity (kg/(m·s))
ρ	density, (kg/m^3)
ρ_B	bulk density of particles in bed (kg/m^3)

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