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Kinetic Study on Catalytic Wet Air Oxidation of Phenol in a Trickle Bed Reactor

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Abstract

Kinetics study on the phenol oxidation by catalytic wet air oxidation (CWAO) using $CuO.NiO/Al_2O_3$ *as heterogeneous catalyst is presented. 4 g/l phenol solution of pH 7.3 was oxidized in a trickle bed reactor with gas flow rate of 80% stochiometric excess (S.E).. In order to verify the proposed kinetics, a series of CWAO experimental tests were done at two temperatures (140 and 160° C), oxygen partial pressures (9 and 12 bar), and weight hourly space velocity (WHSV) (1, 1.5, 2, 2.5, and 3* h^{-1}*). According to Power Law, the reaction orders are found to be approximately 1 and 0.5 with respect to phenol concentration and oxygen solubility, respectively. These values favorably compare with those cited in the literature for intrinsic kinetics, which indicates minimal mass transfer limitations in the trickle bed reacting system used in this study.*

Introduction

The petrochemical, chemical and pharmaceutical industries produce waste waters containing organics, such as phenols, which are extremely toxic to aquatic life [1]. The phenol and derivatives are generally toxic even at very low concentrations [2]. In general, these pollutions exist in concentration range of 500-10000 ppm, mostly too toxic for conventional biotreatment methods, and too low to treat by combustion [3]. Thus, chemical oxidation emerges as a promising route for phenol removal at intermediate concentrations [4]. Wet air oxidation (WAO) is considered an emergent technology that economically can depollute organic wastewaters in order to meet the progressively more stringent environmental regulations [5]. Normally a typical WAO process requires elevated pressure (0.5-20 Mpa) and temperature (125-320 °C) in order to enhance the solubility of oxygen in aqueous solution. In reality such requirements will inevitably lead to higher equipment and operational costs (6). Thus, CWO appears as an economically and ecologically promising technique to convert refractory organic compounds, such as phenol, into carbon dioxide or harmless intermediates at mild pressure and temperature conditions (7).

This work deals with kinetics study of the catalytic phenol oxidation in aqueous phase using fixed bed reactor working in trickle flow regime. Air was used as oxidizing agent. Copper based catalyst supported on γ-alumina was employed. The detailed examination of the product dependence on the space time is provided in the temperatures 140 and 160 °C, and between 9 and 12 bar of oxygen partial pressure.

Theory

The ideal plug flow pseudo-homogeneous model presented in the equation 1 that proposed by Froment and Bkchoff (1990) was modified to describe the reactor in terms of space time, instead of reactor length.

$$\frac{d(U_l.C_{ph})}{dz} + \rho_b.R_{ph} = 0 \tag{1}$$

$$-\frac{dC_{ph}}{d\tau} = R_{ph} \tag{2}$$

The first step is to consider only the phenol degradation reaction described by equation 3

$$C6H6O + 7O2 \rightarrow 6CO2 + 3H2O \tag{3}$$

In agreement with observations in the literature (8, 9, 5, 10, 2, 11, 12), a simple power law was convenient to accurately describe the phenol oxidation. Thus, the following rate equation for phenol destruction was used:

$$-r_{ph} = K_{ob}.C_{ph}^{\alpha} \tag{4}$$

$$K_{ob} = k_o.\mathrm{EXP}\left(-\frac{E_{ob}}{RT}\right).P_{O_2}^{\beta} \tag{5}$$

$$R_{ph} = -r_{ph} \tag{6}$$

$$-\frac{dC_{ph}}{d\tau} = K_{ob}.C_{ph}^{\alpha} \tag{7}$$

Equation 4 can be line raised in the following way:

$$Log(-r_{ph}) = Log(K_{ob}) + \alpha Log C_{ph} \tag{8}$$

In the present study, the above expression for K_{ob} was modified to incorporate the oxygen mole fraction in the liquid phase, X_{O_2} instead of the partial pressure, leading to:

$$K_{ob} = k_o.\mathrm{EXP}\left(-\frac{E_{ob}}{RT}\right).X_{O_2}^{\beta} \tag{9}$$

i.e.

$$-r_{ph} = k_o.\mathrm{EXP}\left(-\frac{E_{ob}}{RT}\right).X_{O_2}^{\beta}.C_{ph}^{\alpha} \tag{10}$$

This was done because the reaction actually takes place in the liquid phase. Thus, the solubility of oxygen characterizes the oxygen contribution to the kinetic expression rather than the oxygen partial pressure. Furthermore, the oxygen solubility is not only a function of pressure but also of temperature. Therefore, the oxygen mole fraction in the liquid phase was considered to be more representative. This mole fraction was calculated using Henry law (13), Henry law is given by equation 11.

$$P_{O_2} = H_{O_2}.X_{O_2} \tag{11}$$

Experimental Work

Material and catalyst preparation

The phenol used as reagent was purchased from Griffin. High purity synthetic air was used as oxidant. Deionized water was used to prepare catalyst and different aqueous solutions. Glass balls were used in the tests with inert material. γ-alumina was used as support for the copper. Copper nitrate from Fluka was used as active component. Nickel nitrate from BDH Chemicals Ltd. was used as promoter.

Copper-based catalyst was prepared using γ-alumina as support. The alumina, which was supplied as spheres of 2.5 mm diameter, was dried for 4 h at 110°C. The catalyst was made with a copper oxide loading of 10% and 2% nickel oxide prepared by the pore volume impregnation method using aqueous solutions of copper nitrate (26 g copper nitrate and 6.3 g nickel nitrate dissolved in 45 ml hot deionized water) for impregnating the support. Later, the catalyst was dried at 110°C overnight, followed by calcining at 400°C for 8 h with air. Table 1 lists the main physical characteristics of the catalyst prepared and support used which were done in the State Company of Geological Survey and Mining.

Fig. 1: Experimental setup

Table 1 The main physical characteristics of different catalysts prepared and supports used.

Catalyst	γ-Al_2O_3	Cat.
Active phase (CuO), %	-	10
Promoter (NiO), %	-	2
Support	-	γ-Al_2O_3
Calcinations temperature, ^{o} C	-	400
Pore volume, cm^3/g	0.44	0.352
Bulk density, g/cm^3	0.68	0.748
Surface area, m^2/g	289	237

Experimental set-up and procedure

The continuous oxidation of phenol was carried out in a packed bed reactor. The fixed bed reactor consists of a SS-316 tubular reactor, 80 cm long and 1.9 cm inner diameter and controlled automatically by for sections of 15 cm height steel-jacket heaters. Independent inlet systems for gas and liquid feed allow working at various liquid to gas flow rate ratios.

The liquid feed is stored in a feed tank, which is connected to a high-pressure metering pump (dosing pump) that can dispense flow rates between 0 and 15 ml/min at constant pressure. The air oxidant comes from a high pressure cylinder equipped with a pressure controller to maintain the operating pressure constant. A flow-meter coupled with a high precision valve is used to measure and control the gas flow rate. The liquid and gas streams are mixed and then entered to the reactor at the required temperature. The mixture flows along the bed packed with 85 cm3 (30 cm height) of the catalyst enclosed between two layers of inert material (also a flexible grid put at the top and bottom of the reactor to prevent movement of particles).The exited solution goes to a liquid-gas separation and sampling system, regularly, liquid samples were withdrawn for analysis. Figure 1 illustrated the experimental setup.

To verify that only the catalyst causes the oxidation of the phenol, test was made using an inert material (γ-alumina). The phenol removal was negligible, less than 0.1 %, which falls within the experimental error.

PH-adjustments

The pH of 4 g/l phenol solution is slightly acid, about 5.9. However, for phenol solution of pH 7.3, the feed solution was adjusted by adding sodium hydroxide solution. To measure pH of the solution OAKION PH2100 Series was used. The procedure was summarized as following:

pH meter was calibrated previous to use by using Buffer solutions.

Measuring the pH of 4 g/l phenol solution.

Adding particular quantities of NaOH solution to the 4 g/l phenol solution according to the titration method to obtain solution of pH 7.3.

Products analysis

To analysis phenol concentration in the outlet samples, Shimadzu model UV-160A ultraviolet/visible spectrophotometer was used.

Estimation of reaction orders

According to the differential method, the derivatives

$\frac{dC_{ph}}{d\tau}$ are evaluated from the experimental data to obtain the reaction rate (r_{ph}) as shown in the figure 2. Then, $Log(-r_{ph})$ is plotted against $Log(C_{ph})$ in equation 8 as shown in the figure 3, to determine values of α and K_{ob}. It should be noted that all above calculations were done using computer. To calculate the other unknown kinetic parameters k_o, E_{ob} and β, equation 9 can be line raised in the following way:

$$\ln K_{ob} = \ln k_o + \beta \ln X_{O_2} - \frac{E_{ob}}{RT} \qquad (12)$$

Alternative steps were done using different values of K_{ob} available at different temperatures and pressures to evaluate these parameters.

Results and Discussion

A first reaction order for phenol concentration given by equation 10 was found, in agreement with findings of the other studies conducted in slurry reactor (14, 15) or trickle bed reactor (TBR) (10, 16, 11, 12).

A 0.5 oxygen order was found on reaction rate as found by (14, 15, 10, 11, 12). This results explained that as disscociative oxygen adsorption is an elementary step during CWAO of phenol over copper oxide catalyst and reported 0.5 oxygen order (15), while reported 0.5 (±0.1)(9).

The observed activation energy for phenol destruction over CuO.NiO.Al2O3 was found to be 78.5 kJ/mol. Falls in the range of the 85(±2) kJ/mol (9) and 77.1(±4) kJ/mol (10) in the same TBR using the Cu0803 Catalyst, while for stirred slurry reactors intrinsic kinetic values of 85 kJ/mol (17) and 84 kJ/mol (15) for different copper oxide catalysts with similar characteristics. Considerably, the oxidation reactions of phenol to 4-HBA (equation 13) and p-benzoquinone (equation 14) have activation energies of 82.4 and 72 kJ/mol were obtained in the TBR over active carbon as catalyst (12)

$$C_6H_6O + CO_2 \rightarrow C_7H_6O_3 \qquad 13$$

$$C_6H_6O + O_2 \rightarrow C_6H_4O_2 + H_2O \qquad 14$$

It is well known that the big gas/liquid ratio employed by this type of reactor permits better contact between the gas and liquid phases thus improving the mass transfer between phases and suggesting that the mass transfer limitation can indeed be neglected.

The frequency factor was found 3.2×1011.36 L / kg Cat. h close to the values 1011 L/kg Cat. h (9), 1011.36 L/kg Cat. h (10) and 1014.35 and 1013.66 respectively (12).

When those results are compared with the once in this study, it can be seen that the kinetic parameters are slightly different or closed to the values given in the literature. The difference in the results may arise from the reaction conditions and the type of catalyst used. Finally the reaction rate equation is:

$$-r_{ph} = 3.2\times10^{11}.\mathrm{EXP}\left(-\frac{785385}{RT}\right).C_{ph}X_{O_2}^{0.5} \qquad 15$$

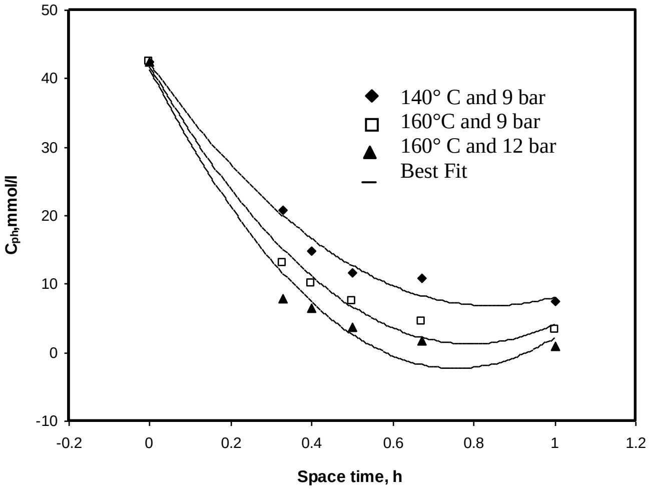

Fig.2: Concentration of phenol versus space time at various conditions.

Reaction conditions: type of catalyst= Cat.4, feed solution pH=7.3, S.E. = 80%, and initial phenol concentration= 4 g/l.

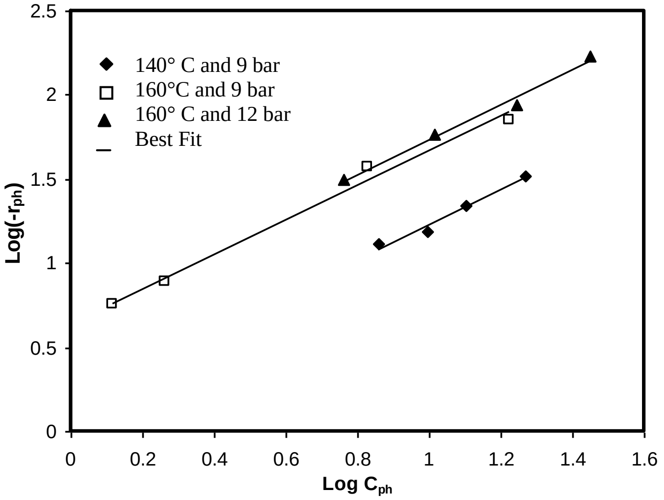

Fig. 3: Log (-r_{ph}) versus Log C_{ph} at various conditions

CONCLUSIONS

The experimental results of CWAO of phenol showed that the oxidation reaction of phenol is first order with respect to phenol concentration and o.5 order with respect to oxygen solubility, observed activation energy equal to 78.5 kJ/mol and pre-exponential factor equal to 3.2 ×1011 L/kg Cat. h.

Nomenclature

Cph : Concentration of phenol mmol /l
Ea : Activation energy J / mol
H : Henry constant
ko : Frequency factor (case dependent units)
Kob : Observed rate constant (case dependent units)
P_{O_2} : Oxygen partial pressure bar
R : Universal gas constant, 8.314 J / mol. K
rph : Phenol reaction rate mol / kg. s
T : Temperature K
x_{O_2} : Mole-fraction of oxygen
z : Reactor length (case dependent units)

α Oxygen order
β Organic order
P_b Bed density kg / m^3
τ Space time h

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