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Catalytic wet oxidation of phenol in a trickle bed reactor

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Abstract

Catalytic liquid phase oxidation of aqueous phenol was studied in a pilot plant trickle bed reactor using a copper oxide catalyst supported on alumina. Catalysts were prepared by impregnating CuO on alumina extrudates and on computer designed shape (CDS) alumina pellets. Phenol oxidation was carried out in a 2.54 cm diameter reactor with a catalyst bed length of 60 cm and in the pressure range of 1–15 atm and temperature range of 373–403 K Compared to alumina extrudates higher phenol conversion was achieved over CDS pellets under identical conditions. Phenol oxidation reaction was strongly affected by the temperature and pressure, however, pressure had less effect. Hydrodynamics of the reactor had strong influence on phenol oxidation reaction. A one dimensional axial dispersion model was proposed to simulate the experimental results. The model satisfactorily explains the experimental results with a deviation of ±15%.

Keywords: Trickle bed reactor; Oxidation; Phenol; Catalyst; Modelling

1. Introduction

Many industries like petroleum, petrochemical and pharmaceutical generate wastewater that contains organic products hazardous to the environment especially to natural water resources. Phenol is the one of the most serious organic pollutant. The importance of phenol in water pollution stems from their extreme toxicity to the aquatic life and resistance to biodegradation. Phenol imparts a strong disagreeable odor and taste to water even in very small concentration. Direct biological treatment is unfeasible for wastewater stream having phenol concentration more than 200 mg/l. In these cases it may be necessary to employ less conventional techniques, such as chemical oxidation or wet air oxidation to achieve destruction of the recalcitrant organics present. Apart from these methods other techniques, such as photo assisted heterogeneous catalysis [1] and oxidation at supercritical water conditions are used or being used at various stage of development, however, these techniques are cost intensive [2].

Wet air or thermal liquid phase oxidation processes are known to have a great potential in advance wastewater treatment facilities [3]. However, the reaction conditions required to achieve oxidation are severe, typically being in the range of temperature 473–573 K and pressure 70–130 kg/cm^2. Under such extreme conditions, the selection of material for construction becomes critical, as corrosion rates are rather high due to the presence of a wide range of oxygenated compounds; oxidation of dilute aqueous solutions of organic pollutants using oxygen as an oxidizing agent over a solid catalyst offers an alternative to wet air oxidation as means of purifying of wastewater [4–6,8]. In this process organics are oxidized to carbon dioxide and water at much lower temperatures and pressures. Depending on the type and amount of organic compound dissolved in wastewater, the process can be designed either to reduce their concentration or to ultimately destroy them. Moreover, in catalytic wet oxidation, the catalyst can be easily recovered, regenerated and reused. Extensive studies have been carried out for removal of organic compounds from wastewater using small-scale reactors over a series of catalyst [7,9,10]. Relatively few studies have been published concerning catalytic liquid phase oxidation of organic compounds in large-scale trickle bed reactors where hydrodynamic parameters prevail. The present study aims phenol oxidation in a trickle bed reactor using copper oxide impregnated on alumina catalysts. Effect of catalyst

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Nomenclature

a	effective external surface area for mass transfer ($cm^2/(cm^3$of empty tube))
c	concentration (mol/cm^3)
d_p	catalyst pellet diameter (cm)
D	molecular diffusivity in liquid (cm^2/s)
D_L	axial dispersion coefficient (cm^2/s)
G	gas mass flux (kg/m^2 s)
G_{al}	Galaleo number
G_L	liquid mass velocity ($g/(cm^2/s)$)
H	Henry's Law constant, (cm^3 of liquid/$cm^3$of gas)
k_L	mass transfer coefficient from gas to liquid (cm/s)
k_s	mass transfer coefficient from liquid to particle (cm/s)
$k_{sr,app}$	apparent surface reaction constant (mol/(g_{cat} s))
K	adsorption constant (cm^3/mol)
L	liquid mass flux (kg/m^2 s)
P_e	Peclet number
P_{O_2}	oxygen partial pressure (kg/cm^2)
P_{total}	total operating pressure (kg/cm^2 absolute)
$-r_{PhOH}$	phenol disappearance rate (mol/(g_{cat} s))
R_{EL}	Reynolds number
T	reaction temperature (K)
u	superficial velocity (cm/s)
z	axial coordinate in trickle bed reactors (cm)

Greek letters

η	effectiveness factor, dimensionless
μ	fluid viscosity (gm/cm s)
ρ_B	bulk density of particles in bed (gm/cm^3)

Subscripts

eq	equilibrium
f	feed
g	gas phase
L	liquid phase
O_2	oxygen
PhOH	phenol
s	external surface of catalyst

shape, temperature, pressure and effect of hydrodynamics of trickle bed has been investigated on phenol oxidation.

2. Experimental details

2.1. Catalyst preparation

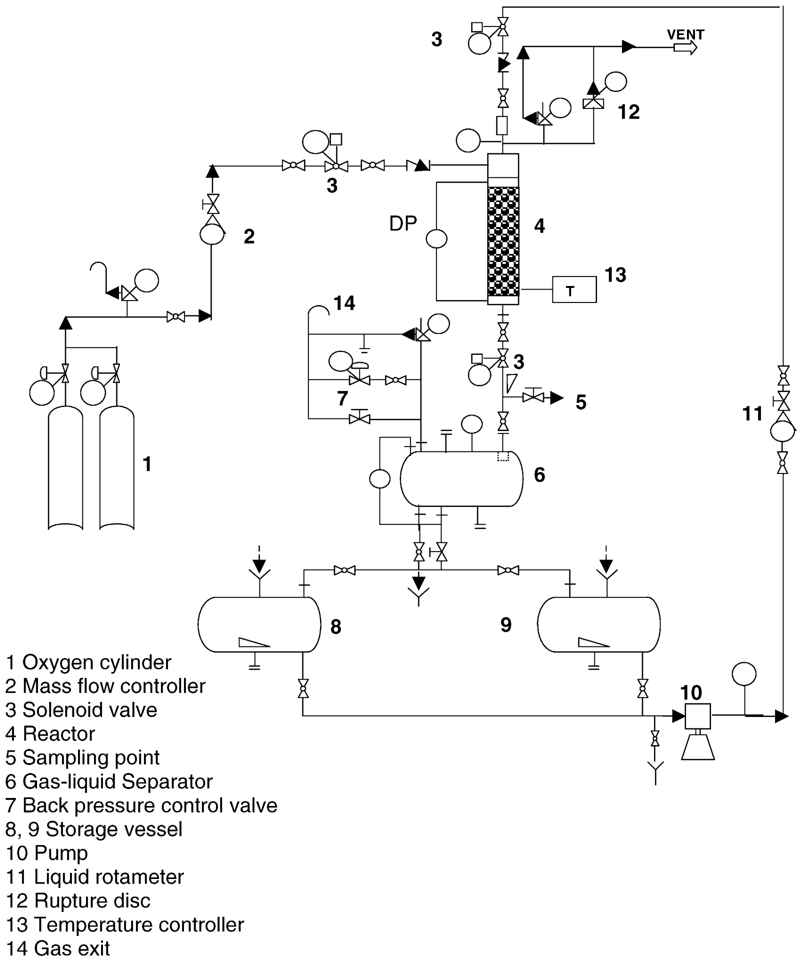
Catalysts (10% CuO/Al_2O_3) were prepared by impregnation technique. In this technique alumina extrudates (0.159 cm) or computer designed shape (CDS) trilobe (0.127 cm) (Sud–Chemie India Pvt. Ltd.) were dipped in the copper nitrate solution for 6 h in order to complete soaking of the liquid. The CDS pellets are trilobe in shape having higher surface area with minimal pressure drop compared to extrudates. The physical properties of the pellets are given in Table 1. These pellets were dried over night at 383 K to remove the excess water and then calcined for 5 h at 823 K for calcinations. The pellets were crushed and dipped in conc. HNO_3 solution for 1 h under stirring to dissolve the copper in to acid. The solution was diluted with distilled water and Cu concentration was measured by atomic absorption spectroscopy. There was some weight loss of CuO during preparation and heat treatment and the final wt.% of CuO on the catalyst was 8.5 ± 0.5%. The total surface areas of the catalyst pellets were determined by BET surface area analyzer (Micromeritics USA) using N_2 as adsorbent. The surface areas of alumina extrudates and CDS shaped pellets were 210 and 235 m^2/g respectively. After impregnating with CuO the surface area is significantly reduced to 190 and 210 m^2/g respectively for these two different catalysts. The pore volume of catalyst was also approximately reduced by 40%. Coating of Copper oxide on to the pore surface also reduced the pore size. A reduction in pore volume suggests that copper oxide coated on to the surface should be multilayer rather than monolayer.

2.2. Experimental setup

Fig. 1 shows a schematic diagram of the experimental setup. The system consists of a reactor, one liquid feed pump, flow measurement for the liquid and gas, gas–liquid separator and back pressure regulator for accurate pressure control. The reactor was made of stainless steel (SS-316, 2.54 cm i.d., 135 cm length) and heated by using an electrical heating tape wound externally to the central portion of the reactor where the catalyst was placed. Catalyst (220 g) was placed in the reactor for each run. Temperature of the reactor was controlled by temperature-controller. Isothermal conditions were maintained in the reactor during experiments. Aqueous phenol was pumped by a high pressure-reciprocating pump. Pure oxygen gas provided by a rack of gas cylinders was passed co-currently from the top of the reactor at desired pressure. The ranges of operating conditions are given in Table 2. The pressure in reactor system was maintained through back-pressure regulator connected with gas-liquid separator. The

Table 1
Physical properties of the alumina pellets

Catalyst	Cylindrical extrudates	Trilobe/CDS
Particle diameter (mm)	1.58	1.27
Average length (mm)	10.96	15.96
Void fraction	0.47	0.53
Particle porosity (cm^3/g)	0.40	0.50
Bulk density (kg/m^3)	550	500
Surface area (m^2/g)	210	235



1 Oxygen cylinder
2 Mass flow controller
3 Solenoid valve
4 Reactor
5 Sampling point
6 Gas-liquid Separator
7 Back pressure control valve
8, 9 Storage vessel
10 Pump
11 Liquid rotameter
12 Rupture disc
13 Temperature controller
14 Gas exit

Fig. 1. Schematic diagram of experimental set-up.

Table 2
Operating conditions

Reactor diameter (cm)	2.54
Catalyst bed length (cm)	60
Mass of catalyst (g)	220
Catalyst	10% CuO/Al_2O_3
Operating temperature (K)	373–403
Operating pressure (kg/cm^2) absolute	1–16
Liquid flow rate (l/h)	0.6–1.2
Gas flow rate (l/h)	40–80
Inlet phenol concentration (mg/l)	500–2000

steady state conditions were maintained during the experiments. Phenol concentration was measured by UV spectrophotometer (Shimadzu, model UV 1201) at wavelength 510 nm. Differential pressure gauge was used to measure the pressure drop across the catalyst bed.

3. Results and discussion

3.1. Hydrodynamic studies

The performance of the trickle bed reactor is very much affected by the hydrodynamic parameters. Runs were carried out for liquid hold up and pressure drop with two different shape catalysts under various experimental conditions. It can be seen from the Fig. 2 that CDS pellets have higher dynamic liquid hold up in comparison to extrudates.

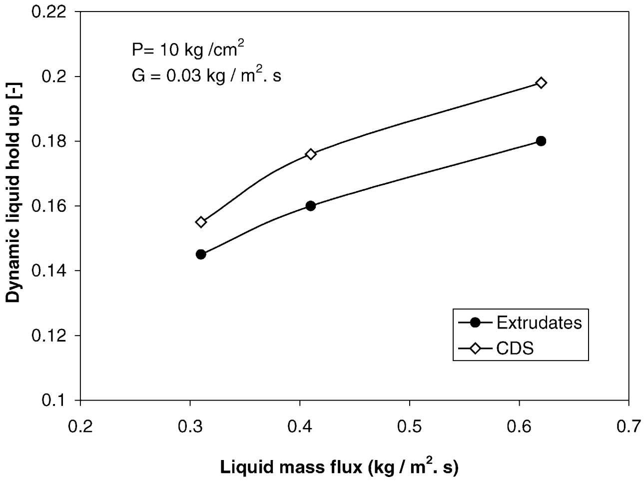


Fig. 2. Effect of catalyst shape on dynamic liquid hold-up at various liquid mass flux.

This could be due to the higher bed porosity of CDS than extrudates. The effect of catalyst shape on pressure gradient at various liquid mass flux is shown in Fig. 3. CDS pellets have lower pressure gradient in comparison to extrudates due to their shape. The reactor pressure also has pronounced effect on pressure drop and liquid hold up in the reactor.

3.2. *Effect of temperature and pressure on phenol conversion*

The effectiveness of the CuO catalyst for phenol conversion was investigated. Impregnation of CuO on to alumina pellets significantly accelerates the oxidation rate of phenol. Negligible conversion was obtained with alumina pellets without copper oxide loading. The products were mainly carbon dioxide and water. This means that CuO/Al_2O_3 catalyst has a better capacity of further oxidizing the intermediate organic products in to CO_2 and water. Effect of temperature on phenol conversion is shown in Fig. 4. Higher conversion was achieved at higher temperature due to the fact that at higher temperature the mass transfer coefficient and kinetic constant are favorably affected resulting an increase in phenol conversion.

Effect of reactor pressure on conversion at various temperatures is shown in Fig. 5. Compared to temperature, pressure has less influence on the conversion of phenol. It can be seen from Fig. 5 that increasing pressure from 5 to 15 kg/cm^2, resulted an increase in phenol conversion from 40 to 56%. Increasing pressure increases the density of gas and its solubility in the liquid. An increase in gas pressure provides a lateral push force for the reactants to cover as much surface area as possible.

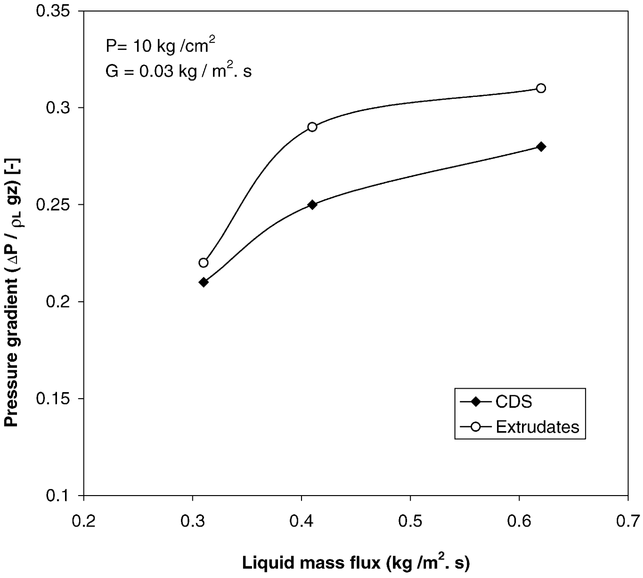


Fig. 3. Effect of catalyst shape on pressure gradient at various liquid mass flux.

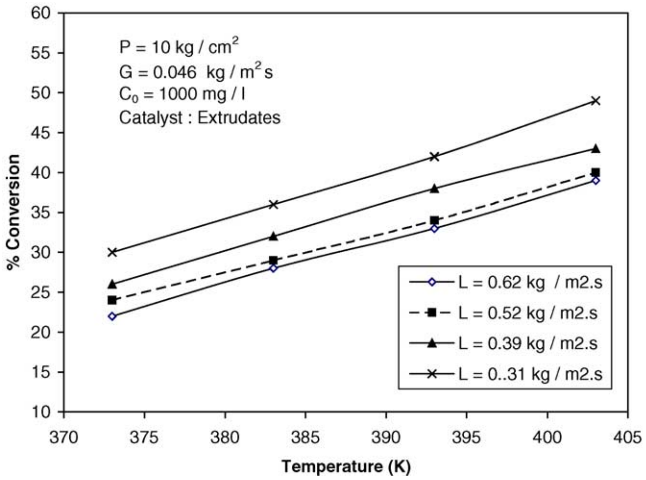


Fig. 4. Effect of temperature on conversion at various liquid mass flux.

3.3. *Effect of liquid and gas flow rate on phenol conversion*

The effect of liquid mass flux on conversion is also shown in Fig. 4. Conversion gradually decreased with increasing liquid mass flux. Hydrodynamic studies over trickle bed reactor revealed four major factors affected by changing the liquid flow rate; the mass transfer coefficient which increases with increase in flow rate, liquid hold-up, which increases with liquid flow rate, the utilization of the reactor bed which increases with flow rate and decrease in solid hold up to accomplish itself which decreases with increasing flow rate. Increasing liquid flow rate reduces the residence time of the reactant thus reducing the time of reaction of phenol with the catalyst and oxygen (gas reactant). Moreover, higher liquid flow rates give greater liquid hold up which evidently decreases the contact of liquid and gas reactants at the catalyst active site, by increasing the film thickness [12,13]. It has also been observed that a constant gas flow rate the wall

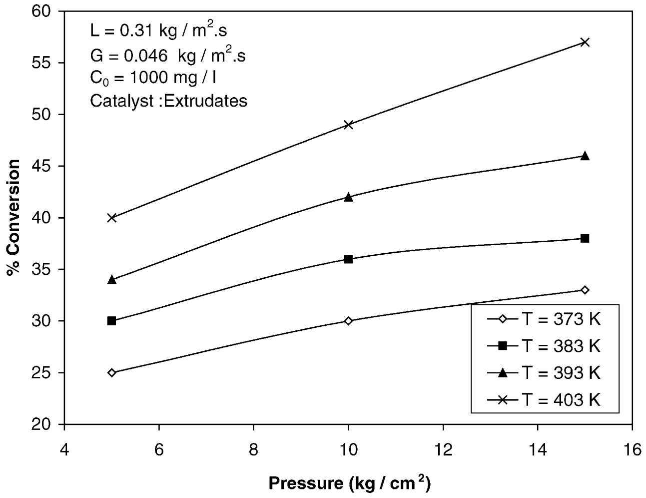


Fig. 5. Effect of pressure on conversion at various temperatures.

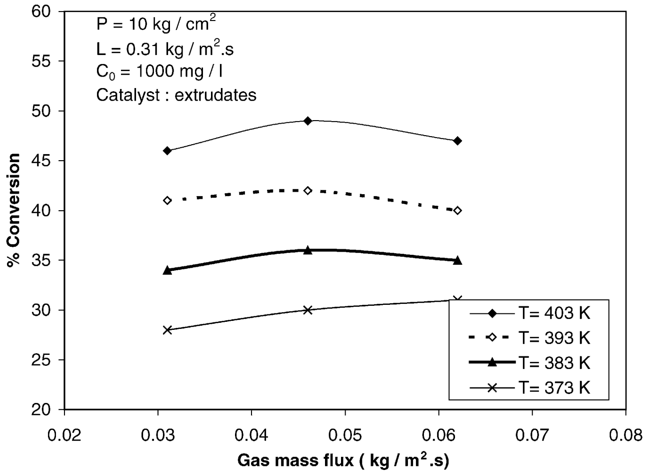


Fig. 6. Effect of gas mass flux on conversion at various temperatures.

flow decreases with increase in liquid flux for each type of catalyst. A plot for conversion against gas mass flux (Fig. 6) shows that the conversion reaches a maximum value. Initially conversion increases with increasing gas flow rate and after that decreases with further increasing gas flow rate. At higher superficial liquid velocity in the presence of gas flow, the external wetting efficiency for a hydrophilic catalyst should be close to unity. External wetting efficiency of catalyst plays a very important role in the performance of trickle bed reactors. It has been reported that wetting efficiency increases with increase of gas superficial velocity due to increase in shear stress on gas liquid interface [14]. The results of present study show that an increase in superficial gas velocity resulted a decrease in liquid hold up and liquid film thickness. Consequently there is an improvement of spreading of liquid film over catalyst and hence wetting increases.

3.4. *Effect of catalyst shape on phenol conversion*

The shape of the catalyst plays a vital role in the hydrodynamic behavior, which strongly affects the conversion. Effect of catalyst shape and size on conversion has been shown in Fig. 7 at different liquid flow rates over two types of catalyst pellets. As can be seen from these figures higher conversion was achieved with CDS trilobe compared to extrudates. It has been reported that the wall flow (excess flow rate of liquid adjacent to the reactor wall) affects the performance of the reactor by slowing down the reaction, as the wall is not catalytically active [15]. This wall flow varies with D/d_p ratio, higher value of D/d_p reduces the wall flow. The results of our experiments have shown higher conversion of phenol with CDS catalyst compared to extrudates may be attributed to uniform flow in large part of the bed and reduced wall flow. The catalyst geometry has significant effect on the wall flow as higher wall flow was observed with the extrudates types of packing due to different surface roughness, void fraction and orientation of packing.

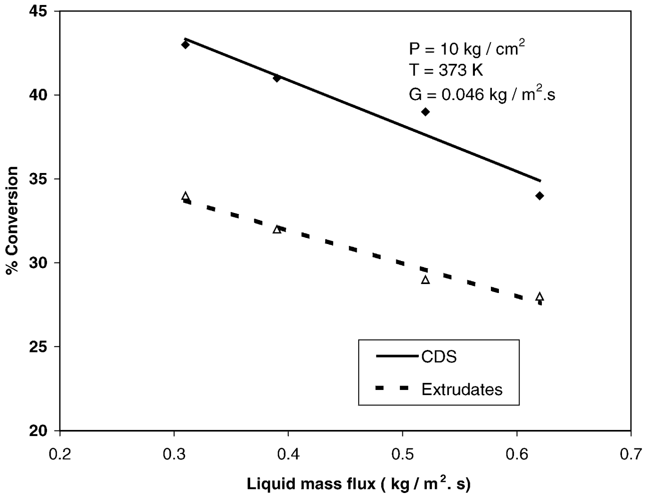


Fig. 7. Effect of catalyst shape on phenol conversion at various liquid mass flux.

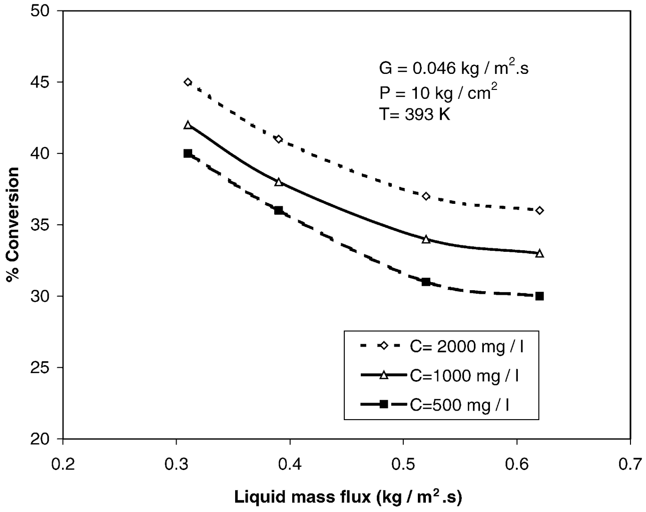


Fig. 8. Effect of inlet phenol concentration on phenol conversion at various liquid mass flux.

The effect of inlet phenol concentration on conversion is shown in the Fig. 8. In the range of experiments the phenol conversion increased by increasing inlet concentration. The activation energy for phenol oxidation as calculated for these experiments was 40.7 kJ/mol. It should be noted that a higher value of activation energy 67 kJ/mol, has been reported in literature for the kinetic study [11]. The lower value of activation energy in present investigation was attributed to mass transfer limitations in the trickle bed reactor.

4. Development of model

During the course of catalytic liquid phase phenol oxidation in a trickle bed reactor, there was a negligible radial variation of temperature with in the catalyst bed, which could be attributed to the low phenol concentration in the aqueous feed stream. Correspondingly, isothermal model seems to be adequate for simulation of the experimental data. Since the ratio of reactor diameter to catalyst diameter (D/d_p) was in the range 16–20, it was assumed that the conditions in the radial direction are uniform. The experimental results were simulated using one dimensional axial dispersion model for the liquid phase. The following assumptions were made in the model:

- Axial dispersion in the gas phase was negligible.
- Conditions were uniform in the radial direction.
- Gas and liquid flow rates were constant throughout the reactors.
- Mass transfer resistance in the gas phase was negligible, so that the equilibrium existed at the gas liquid interface.
- Liquid hold-up was independent of bed length.

Applying the axial dispersion model the mass conservation equations for phenol and oxygen in the liquid and gas phase following equations were written [7].

(i) Oxygen in gas phase

$$u_g \frac{d(c_{O_2})_g}{dz} + (k_L a_g)_{O_2} \left[\frac{(c_{O_2})_g}{H_{O_2}} - (c_{O_2})_L \right] = 0 \qquad (1)$$

(ii) Oxygen in liquid phase

$$(D_L)_{O_2} \frac{d^2(c_{O_2})_L}{dz^2} - u \frac{d(c_{O_2})_L}{dz} (k_L a_g)_{O_2} \times \left[(c_{O_2})_g / H_{O_2} - (c_{O_2})_L \right] - (k_s a_s)_{O_2} [(c_{O_2})_L - (c_{O_2})] = 0 \qquad (2)$$

(iii) Phenol in liquid phase

$$(D_L)_{PhOH} \frac{d^2(c_{PhOH})_L}{dz^2} - u_L \frac{d(c_{PhOH})_L}{dz} - (k_s a_s)_{PhOH} [(c_{PhOH})_L - (c_{PhOH})_s] = 0 \qquad (3)$$

The equality of mass transfer and reaction rates were expressed by the following equations:

$$(k_s a_s)_{O_2} [(c_{O_2})_L - (c_{O_2})_s] = 7(-r_{PhOH}) \qquad (4)$$

The kinetic model for the reaction was based on Langmuir–Hinshelwood adsorption hypothesis with adsorption of oxygen and phenol and taken from the published literature [4].

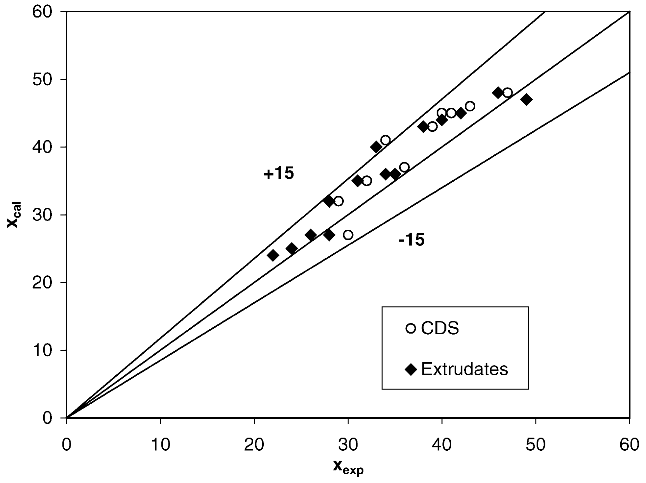


Fig. 9. Experimental vs. simulated phenol conversion.

$$(k_s a_s)_{PhOH} [(c_{PhOH})_L - (c_{PhOH})_s] = (-r_{PhOH}) = \rho_B \eta \frac{k_{sr,app} K_{O_2}^{1/2} K_{PhOH} c_{PhOH} c_{O_2}^{1/2}}{1 + K_{PhOH} c_{PhOH,s}} \qquad (5)$$

The above equations were solved numerically by using a forth order Runge–Kutta method to obtain axial concentration profiles for phenol and oxygen. The surface concentrations were calculated iteratively by solving the Eqs. (4) and (5) by means of Newton Raphson method. The gas to liquid ($k_L a_g$) and liquid to particle ($k_s a_s$) mass transfer coefficients were calculated by means of the correlations given by Goto and smith [16,17].

$$\frac{k_L a_g}{D} = 7.8 \left(\frac{G_L}{\mu} \right)^{0.39} \left(\frac{\mu}{\rho D} \right)^{1/2} \qquad (6)$$

$$\frac{k_L a_s}{D} = 153 \left(\frac{G_L}{\mu} \right)^{0.67} \left(\frac{\mu}{\rho D} \right)^{1/3} \qquad (7)$$

The required values of densities and viscosities for water and diffusivities of phenol and oxygen at the operating conditions were estimated from the correlations available in the literature (Reid et al. [18]. The intrinsic rate constants were obtained from a differential liquid fixed bed reactor from available literature [4]. The axial dispersion coefficient was estimated by the correlation given by Furzer and Michel [19].

Table 3
Estimated values of model parameters

T (K)	D_{O_2} (cm^2/s)	D_{PhOH} (cm^2/s)	K_{PhOH} (cm^3/mol)	$K_{sr,app}\ K_{O_2}^{1/2}$ (mol$^{1/2}$ cm$^{3/2}$/gm$_{cat}$ s)
373	1.7×10^{-4}	3.2×10^{-6}	3.2×10^{5}	6.8×10^{-7}
383	1.8×10^{-4}	5.2×10^{-6}	2.8×10^{5}	7.5×10^{-7}
393	2.0×10^{-4}	7.4×10^{-6}	2.6×10^{5}	8.3×10^{-7}
403	2.2×10^{-4}	8.3×10^{-6}	2.4×10^{5}	9.0×10^{-7}

The correlation may be expressed as

$$P_e = \frac{u_L d_P}{D_L} = 13 R_{EL}^{0.4} G_{aL}^{-0.333} \tag{8}$$

where the Galileo number G_{aL} is defined as

$$G_{aL} = \frac{d_P^3 g \rho_L^2}{\mu_L^2} \tag{9}$$

The calculated values of these parameters have been shown in Table 3. A comparison between experimental and predicted results has been shown in Fig. 9. The simulated values of conversion are with in ±15% of the experimental values. These results show that the developed model can satisfactorily explain the prevalence of gas liquid mass transfer resistance under trickle bed operating conditions.

5. Conclusion

The CuO/Al_2O_3 catalyst was found effective for the phenol oxidation in trickle bed reactor. The performance of the reactor strongly depends on hydrodynamic parameters. Higher conversions were obtained with computer designed shape pellets compared to extrudates due to reduced wall effects. Phenol conversion was affected by the liquid and gas flow rate and decreased with increasing liquid flow rate, however, gas flow rate has marginal effect on conversion. Conversion increased with increasing temperature and pressure of the reactor, however, the temperature has more significant effect on conversion. The overall activation energy for phenol oxidation was 40.7 kJ/mol, which confirms that reaction is mass transfer limited. The axial dispersion model developed for phenol oxidation can satisfactorily explain the phenol oxidation in trickle bed reactor.

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