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KINETIC STUDY OF PHENOL REMOVAL FROM WASTEWATER OVER A 0.5% Pt/ γ -Al₂O₃ CATALYST IN A TRICKLE BED REACTOR

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Abstract

Catalytic wet oxidation (CWO) of phenol was studied in the present work. The effect of liquid hourly space velocity (LHSV), superficial gas velocity, reactor pressure, temperature and initial phenol concentration on phenols removal was investigated. Results showed that phenol conversion increased with increasing reaction temperature, reactor pressure, and superficial gas velocity of oxygen, yet it decreased with increasing (LHSV). The results exhibited that the highest phenol conversion of (67.47%) was obtained over 0.5% Pt/ γ -Al₂O₃ at the studied reaction conditions (i.e., operating pressure = 0.6 MPa, operating temperature = 140°C, LHSV = 4 h⁻¹, and gas superficial velocity = 0.169 m/s), with phenol concentration = 900 mg/L. According to the kinetic results, the reaction behavior was first order with respect to phenol concentration, (0.69) order with respect to oxygen and the activation energy was equal to (29.299) kJ/mol. Selectivity maps for concentration of intermediate compounds in reactor effluent were introduced which would be helpful for monitoring the reaction pathways of phenol oxidation.

Key words: 0.5%Pt/ γ -Al₂O₃ catalyst, catalytic wet oxidation, phenol removal, trickle-bed reactor, wastewater treatment

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1. Introduction

Wastewater can be divided into four main categories, according to its origin, namely: domestic, industrial, public service and system loss/leakage. Among these, industrial wastewater amounts to 42.4% of the total volume and domestic to 36.4%. In particular, increasing quantities of wastewater with high organic contents originated from numerous industrial and domestic applications (Roy et al., 2010). Since many wastewater streams contain toxic organic pollutants in very high concentrations (more than 200mg/L), direct biological treatment becomes technically impractical, because of their poor biodegradability (Singh et al., 2004).

The physical separation processes may present two drawbacks: first, they are selective in the treatment of waste water; second, they require storage and disposal of the eliminated contaminants. The chemical processes use conventional oxidation agents such as molecular oxygen, chlorine, chlorine

dioxide, potassium permanganate, hydrogen peroxide, ozone, ultraviolet radiations, sulfate ions, or other oxidants (Belhatche, 1995; Benali and Guy, 2007). Phenol and its derivatives has been the subject of many studies in (CWO) as a model reaction (Aihua and Chenglin, 2012; Nikolay et al., 2011). Studies on the mechanisms for oxidation of phenol require some knowledge of the short-lived intermediates as well as the final reaction products that can take place in a homogeneous phase or on the catalyst surface (Eftaxias, 2002).

The oxidation of phenol over noble-metal catalysts has in most cases involved oxidation, decarboxylation, dehydration and rearrangement of the molecules or some combination of these steps while platinum catalysts show the potential to change the reaction pathways of organic compounds to the desired end products, i.e.: CO₂ and H₂O. Numerous papers studied extensively the wet oxidation of phenol and its cyclic aromatic intermediates such as hydroquinone, p-benzoquinone, p-hydroxybenzoic acid

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and traces of catechol as well as short chain organic acids like maleic, acetic and formic acids (Eftaxias et al. 2006; Habtu, 2011; Quintinilla et al., 2007; Santos et al., 2005). Various scientists proposed different pathways (routes) that lead to complete mineralization towards CO_2 and H_2O .

The present work aims to study the performance of a trickle bed reactor for phenol degradation in wastewater by investigating the applicability of a commercial 0.5% platinum/alumina catalyst, which is used currently for desulfurization process in North Refinery Company-Iraq. Also it is investigated the effects of operating conditions (liquid hourly space velocity (LHSV), superficial gas velocity, temperature, reactor pressure, initial phenol concentration) on the kinetic parameters of the operating system relative to phenol and oxygen.

2. Kinetics models for catalytic oxidation of phenol

It is preferred that the kinetic models correspond reasonably with the reaction mechanism and the experimental data. Reaction parameters considered are: reaction temperature, partial pressure of oxygen, reactant concentration, and solid-to-liquid volumetric ratio etc. which influenced the reaction rate. Studies on the kinetics of catalytic wet air oxidation (CWAO) have been extensively conducted by using model compounds over a wide range of temperature and pressure conditions.

For the heterogeneous catalytic oxidation of organic pollutants in aqueous environment, the apparent kinetic models were generally expressed in terms of either the simple power law or more complex mathematical equation based on adsorption-desorption mechanism, i.e. Langmuir-Hinshelwood-Hougen-Watson (LHHW) model. Both kinetic models have provided reasonable simulations of the observed results for the CWAO of reactants (Eftaxias et al., 2001; Eftaxias et al., 2005; Fortuny et al., 1999; Habtu, 2011). Eftaxias et al. (2005) reported that simple power law model accurately predicted the entire experimental data for the CWAO of phenol using AC in a trickle-bed reactor, while more complex LHHW model did not significantly improve the data fitting. Table 1 represents the kinetic parameters of power law model for CWO and CWAO for phenolic compounds.

3. Materials and methods

3.1. Reactor system setup

A schematic illustration of the experimental equipment reactor set up is shown in (Fig. 1). The main unit of the process is the trickle bed reactor. It was made of a stainless steel tube with 0.05m inside diameter, 5mm wall thickness and 0.6m height, packed with 800g of catalyst. Table 2 includes some characteristics of the catalyst, and the phenol used throughout the experiments. The trickle bed reactor was provided with different packing layers of inert particles besides the catalyst layer. The first layer (pre-packing) contains 2x2 mm glass cylinders with a height of 0.45m, which supported the catalyst packing, and the last layer (post-packing) of 2x2 mm glass cylinders was set just on the catalyst bed in order to ensure uniform radial liquid distribution over the reactor cross-section.

The reactor dimensions were selected to obtain a ratio of diameter (reactor to particle) equal to 31: 25, which was sufficient to prevent wall effects (Al-Dahhan et al., 1997). The packing was maintained by means of a stainless steel screen placed at the column bottom and had a mesh openings large enough to prevent bed flooding but narrow enough to impede particle crossings.

The reactor was externally heated with electrical tape heater (Heraeus-Wittmann GmbH Heidelberg, type MS6) which was connected to a temperature controller (Yang Ming CX TA 3000) that maintained the bed temperature within $\pm 3^\circ\text{C}$ of the set point temperature by means of an on-off regulator which manipulated the heat supply of the external tap heater. Three thermocouples (Type T) were situated within the bed at different axial positions along the reactor.

The synthetic solution was heated with an immersed electric heater in the storage tank (100 liter capacity) up to 60°C , then it was pumped by means of a metering pump (Dose pump, BALDOR FRUM DUTY, USA) to a high pressure small stainless steel tank (0.04 m id *0.35 m length) to damp the flow pulsation due to pumping. The gas was delivered from a high pressure cylinder equipped with a pressure regulator to adjust the operating pressure. A flow meter coupled with a needle valve enabled the gas flow rate to be set and measured.

Table 1. Kinetic parameters of power law model for CWAO of phenolic compounds

Compound	Catalyst	E_A (kJ/mol)	α	β	Reference
Phenol	Cuo, Zno, Al_2O_3	84	1	0.5	Pinter and Levec, 1992
Phenol	$\text{CuO}/\gamma\text{-Al}_2\text{O}_3$	85	1	0.5	Fourtuny et al., 1995
Phenol	$\text{CuO}/\gamma\text{-Al}_2\text{O}_3$	85	1	0.5	Fourtuny et al., 1999
Phenol	AC	73	1	-	Stuber et al., 2001
Phenol	AC	69.3	1	1.015(± 0.02)	Eftaxias et al., 2005
Phenol	Cu/AC	35.4	-	-	Wu et al., 2005
Phenol	$\text{MnO}_2/\text{CeO}_2$	38.4/53.4	-	-	Luna et al., 2009
Phenol	$\text{Pt}/\gamma\text{-Al}_2\text{O}_3$	33.8657	1	0.87	Safa, 2010

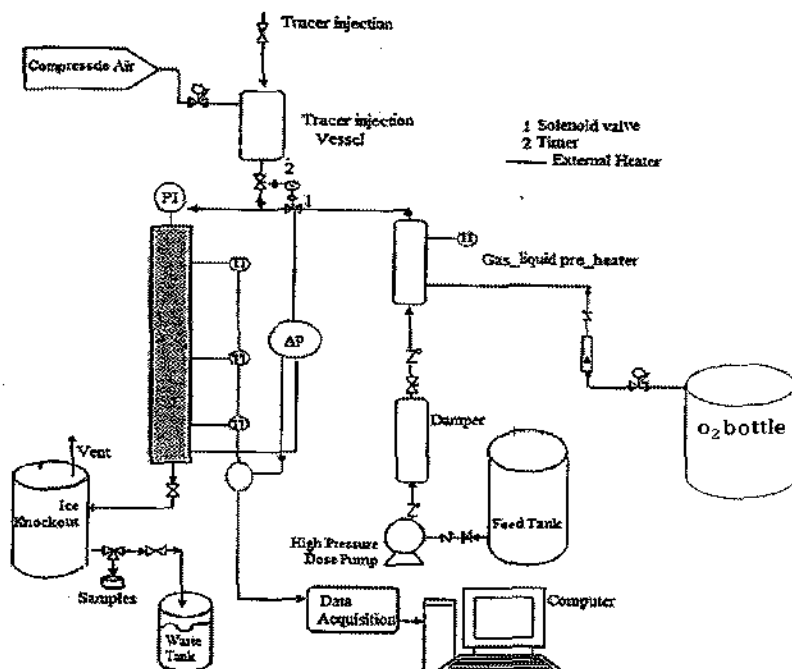


Fig. 1. Schematic diagram for the experimental setup

The liquid and gas streams were mixed and preheated by a pre-heater before entering the reactor at the top through a distributor containing 29 holes ($\phi = 0.5$ mm). Discharged fluids from the reactor flow through an ice knockout gas-liquid separator. At the top flange of the separator, a stainless steel mesh demister was placed to trap the condensed liquid mist from the effluent gas stream. Pressure indicators and safety valves were mounted to prevent pressure build up in the gas and liquid delivery and exit streams. One way valve was located in the gas and liquid line at the top of the reactor to prevent back flow.

3.2. Data acquisition system

An electronic circuit was built to measure the temperature and pressure drop along the catalyst bed. The circuit signals the computer to communicate with the real world through the parallel port which is expanded to three main ports. These ports were used as the control ports (signals were transferred from the computer to the outside world), and were used to transfer data from the outside real world to the computer. Each signal (temperature and pressure drop) owes its meaningful information to appropriate software written and executed in Microsoft Visual Basic, which works under Microsoft excel spreadsheet application.

For temperature measurements, the output transducer signals from the thermocouples (Type T) were incorporated to the terminal block of a multiplexer data acquisition board unit which feeds the electrical signals to an analog-digital (A/D) converter then proceed to a data acquisition board of a personal computer (P₄: Open type). Output signals

from the differential pressure transducer (Rosemount, model E1151 G P5523, 55T) were also connected similarly to a data acquisition multiplexer.

Table 2. Catalyst and phenol characteristics

Parameter	Value
Catalyst Characteristics	
Active metal	0.5%Pt
Catalyst support	γ -Al ₂ O ₃
Particle shape	Sphere
Particle diameter (cm)	0.16
Surface area(m ² /g)	250
Pellet density (g/cm ³)	1.56
Phenol Characteristics	
Color	White
pH	(4.5-6)
Molecular weight (g/gmol)	94.11
Chemical structure	C ₆ H ₆ O
Purity (%)	99.5
Freezing point(°C)	(40-41)

3.3. Analytical procedures

As the operating system reached a steady state condition, liquid phase samples were taken from the outlet of the gas-liquid separator. The samples were analyzed by means of HPLC DIONEX (UV (JYNKOTEK)/VIS160S), which contains a C18 reverse phase column (Philips, 5 μ m 25 x 0.4 cm). A mixture of (65:35)vol % methanol : water (slightly acidified) was used as a mobile phase. For all samples, the flow rate of the mobile phase was 1 mL/min. Detection of the compounds was performed using a UV absorbance at a wavelength of 254 nm. Detection of low molecular weight carboxylic acids

was performed with the UV absorbance method at a wavelength of 210 nm.

To detect the concentration profiles of phenol and intermediates correctly, sample measurement of wavelength was switched to 254 nm. To properly separate phenol from the partial oxidation products, single compounds were quantitatively identified by injecting pure samples of the expected partial oxidation products. However not all of these compounds could be identified in the reaction sample solution. Table 3 shows the approximate retention times of all injected pure compounds.

Table 3. HPLC retention times of phenol and possible partial oxidation products (Analytical Laboratory – Chemical engineering Department- University of Tikrit)

Compound (pure)	Retention time(min.)
Formic acid	1.761
Maleic acid	2.988
Acetic acid	3.051
Phenol	4.425

4. Operating conditions

Table 4 shows the range of studied operating conditions through the experimental course. All CWO runs performed in this study were conducted in the low-interaction (LIR) trickle-flow regime (Fukushima and Kusaka, 1977).

Table 4. Operating conditions in the kinetic study

Kinetics experiments	
System	{phenol - oxygen}
Temperature (°C)	(85-140)
Pressure (MPa)	(0.1-0.6)
Superficial liquid velocity (m/s)	(0.0013-0.0085)
Superficial gas velocity (m/s)	(0.08-0.13)
Initial phenol concentration (mg/L)	(900-5000)

5. Results and discussion

5.1. Reactant limitation

Performance of the TBR depends upon the type of reactant limitation used. Beaudry et al., (1987) developed a criterion shown by (Eq. 1) which was used to diagnose the operation mode (reactant limiting).

$$\gamma = \frac{D_{ph,L}^{eff} C_{ph,L}}{v D_{O_2,L}^{eff} C_{O_2,L}} \quad (1)$$

To determine the limiting reactant of the reaction, if $\gamma \gg 1$, the reaction will be limited by the gas reactant; if $\gamma \ll 1$, it will be limited by the liquid reactant. Based on the employed operating conditions, the resulting ratio of the diffusion fluxes (γ) of the two reactants are listed in Table 5. It can be noticed from Table 5 that, under various phenol concentrations, temperatures and oxygen pressures,

the reaction varied from gas to liquid limiting reactant mode.

5.2. Interface mass transfer (external diffusion)

The influence of external solid - liquid mass transfer resistance must be ascertained before a true kinetic model could be developed. For this purpose, α_{gl} and α_{ls} criteria which defined by (Eqs. 2 and 3) were calculated (Eftaxias, 2002).

$$\alpha_{gl} = \frac{r_{obs} \rho_b}{(K_{gl} a)_{O_2} C_{ph}} < 0.05 \quad (2)$$

$$\alpha_{ls} = \frac{r_{obs} \rho_b}{(K_{ls} a)_{O_2} C_{ph}} < 0.05 \quad (3)$$

The mass transfer coefficients of gas-liquid k_{gl} and liquid-solid k_{ls} were estimated at various operating conditions by using (Wu et al., 2003) correlation. Table 6 includes these values. They demonstrate that mass transfer limitations in the present study can be neglected and the reaction rate may either be the surface reaction controlled or intraparticle diffusion controlled.

5.3. Intraparticle diffusion (internal diffusion)

Wisze-Prater criterion modified for n-order reactions (Fogler, 1997) was used to validate the existence of internal diffusion limitations (Eq. 4).

$$\Phi = \frac{(r \times \rho_b)_{obs} L_p}{C_{ph0} D_{ph}^{eff}} \ll \frac{2}{n+1} \quad (4)$$

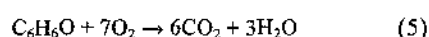
where L_p is the ratio of catalyst volume to catalyst surface area. For n-order reactions, if $\Phi \ll 2/(n+1)$, internal diffusion limitations may be neglected.

As can be seen from Table 7, Φ values are low, thus internal mass transfer resistances should have only a slight influence. In conclusion, the comparison of our experimental reaction rates with mass transfer rates calculated from literature correlations clearly suggests that phenol oxidation was kinetically controlled in the present study.

5.4. Estimation of reaction kinetic parameters

To study the reaction kinetics of phenol in a trickle bed reactor, a set of experiments were carried out at various operating conditions of [(0.1-0.6MPa), (85-140°C), ($u_g=0.086-0.169$ m/s) and initial phenol concentration of (900-5000 mg/L)].

The first step was to consider only the phenol degradation reaction described by (Eq. 5).



In agreement with observations in the literature (Eftaxias, 2002; Eftaxias et al., 2005; 2006; Fortuny et al., 1995; 1999), a simple power law was convenient to describe the phenol oxidation.

Table 5. Values of γ

140°C	120°C		100°C		85°C			C_{pho} (kmol/m ³)
0.6MPa	0.6MPa	0.3MPa	0.6MPa	0.3MPa	0.6MPa	0.3MPa	0.1MPa	
0.09	0.09	0.18	0.09	0.18	0.09	0.18	0.54	0.009432
0.49	0.51	1.02	0.51	1.02	0.51	1.01	3.04	0.05311

Table 6. Values of α_{gl} and α_{ls} (at 0.129 m/s gas velocity and 0.0045 m/s liquid velocity based on initial phenol concentration of 900 mg/L)

Temperature (°C)	P (MPa)	$\alpha_{ls} \times 10^5$	α_{gl}	r_{obs} kmol/kg.h	K_{gl}^s (s ⁻¹)	$K_{ls}a_s$ (s ⁻¹)
85	0.1	6.6934	0.002566	0.000106	26.817	0.699556
140	0.6	9.92	0.004912	0.0002267	53.39442	1.077897

Table 7. Values of Φ (at 0.129m/s gas velocity and 0.0085m/s superficial liquid velocity)

C_{pho} (kmol/m ³)	140°C	120°C		100°C		85°C		
	0.6MPa	0.6MPa	0.3MPa	0.6MPa	0.3MPa	0.6MPa	0.3MPa	0.1MPa
0.009432	0.674842	0.714792	0.68622	0.6143	0.580717	0.529621	0.50925	0.448141
0.05311	0.648169	0.69666	0.69592	0.6554	0.537661	0.476761	0.45639	0.395281

Thus, the oxidation rate could be described by Eq. (6).

$$-r_{ph} = K_{ob} C_{ph}^{\alpha} \quad (6)$$

and (Eq. 6) can be rewritten as (Eq. 7):

$$-r_{ph} = k_o \exp [-E_{ob}/RT] \cdot C_{ph}^{\alpha} \cdot P_{O_2}^{\beta} \quad (7)$$

Because the reaction actually takes place in the liquid phase, the solubility of oxygen characterizes its contribution to the kinetic expression rather than the oxygen partial pressure. Therefore, the oxygen mole fraction in the liquid phase was considered to be more representative. This mole fraction was calculated using Henry law (Wu et al., 2003). The observed rate constant (k_{ob}) can be calculated from experimental data (Stuber et al., 2001).

$$k_{ob} = -\left(\frac{1}{\tau}\right) \ln(1 - X_{ph}) \quad (8)$$

where, k_{ob} (g_L g_{cat}⁻¹ h⁻¹) is the apparent kinetic rate constant, τ (g_{cat} h g_L⁻¹) is the liquid space-time and X_{ph} is the measured phenol conversion.

The slope of plotting $\ln(1 - X_{ph})$ versus τ as shown in Fig. 2 represents k_{ob} . As can be seen from Fig. 3, the values of k_{ob} seem to be independent of inlet phenol concentrations, i.e. the same k_{ob} should result for every conversion obtained (at different inlet phenol concentrations).

This means that k_{ob} is not correlated to the inlet phenol concentration (Eftaxias et al., 2005). This result may also suggest that phenol concentration at the catalyst surface is directly proportional to its bulk liquid concentration. To calculate the other unknown kinetic parameters (k_o , E_{ob} and β), (Eq. 7) can be linearized in the following way (Eqs. 9 and 10).

$$\ln K_{ob} = \ln k_o + \beta \ln X_{O_2} - \left(\frac{E_{ob}}{RT}\right) \quad (9)$$

$$P_{O_2} = X_{O_2} H \quad (10)$$

To evaluate these parameters, "Least Square" method was used with different values of K_{ob} made available at different temperatures and pressures. The results are shown in (Table 8). At studied operating conditions, oxygen order of (0.69) was determined, which is close to the value of (0.74) obtained by Quintanilla et al., (2007). The observed activation energy for phenol decomposition was found to be 29.3 kJ/mol, which is much lower than the values reported by other studies, e.g., 35.4 kJ/mol by Wu et al. (2005), and 38.4 kJ/mol by Luna et al. (2009).

These data and results are shown in Table 9. It is a well-known fact that the high (gas/liquid) ratio employed by this type of reactor permits an improved contact between gas and liquid phases, thus improving mass transfer between phases and confirms that mass transfer limitations can indeed be neglected. The frequency factor was found to be $(2.7 \times 10^{10} \text{ (L/kg}_{cat}\text{.h)})$ at the studied operating conditions which was lower than a value of (10^{11}) obtained by (Fortuny et al., 1999); $10^{11.36}$ obtained by (Eftaxias, 2002) and $10^{14.36}$ obtained by (Eftaxias et al., 2006). When these results were compared with that of the present study, it can be seen that the kinetic parameters are slightly different or closed to the values given in the literature. The differences in the results may arise from the reaction conditions and type of catalyst used.

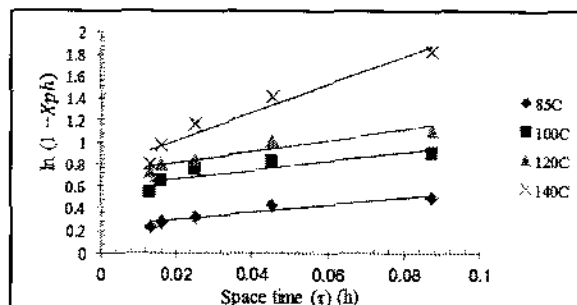
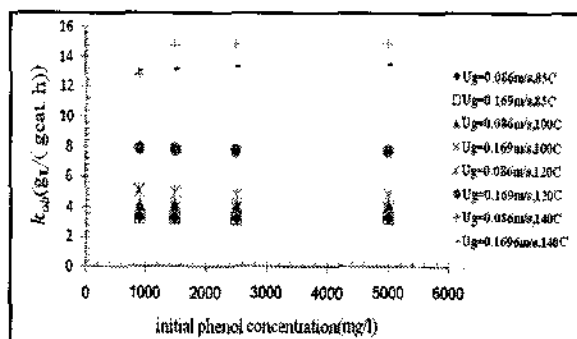
6. Effect of operating variables on CWO of phenol

6.1. Effect of liquid and gas flow rates on CWO of phenol

The effect of LHSV and gas velocity on conversion of phenol at different gas velocities and temperatures is illustrated in (Fig. 4).

Table 8. Kinetic parameters of empirical correlation of present work

Coefficients	K_{ob} (Liter/kgcat.h)	β	E_{ob} (kJ/mol)
	2.7×10^{10}	0.69	29.299
Correlation Coefficient=98.5%; variance=97.5%			

**Fig. 2.** $\ln(1 - X_{ph})$ vs. space time at 0.6MPa**Fig. 3.** Variation of k_{ob} against initial phenol concentration at 85-140°C, and 0.6MPa of O_2

As can be seen, increasing LHSV has an adverse impact on phenol conversion. Phenol conversion of 63.27% was achieved at $LHSV=4h^{-1}$, while at LHSV equal to 20 and $24h^{-1}$ phenol conversions were 55% and 51.66%, respectively. This may be attributed to the residence time of reactants which was reduced as the liquid flow rate increased. Moreover, higher liquid flow rate resulted in greater liquid holdup which evidently decreases the contact of liquid and gas reactants at the catalyst active site, but by increasing the film thickness, a higher resistance to mass transfer (Akram et al., 2011; Vallet et al., 2012) resulted. Fig. 4 also demonstrates the variation of conversion with superficial gas velocity; the phenol conversion was accelerated by increasing the gas velocity.

It can be seen from Fig. 4 that phenol conversion of 67.47% was achieved at 0.169 m/s gas

velocity, while at the same LHSV and gas flow rate of 0.086 m/s, a conversion of 63.27% was obtained.

This can be rationalized in terms of the liquid film thickness which thinned when higher gas flow rate was utilized due to higher shear forces, leading to a better spreading of the liquid film over the external packing area and across the reactor diameter. Accordingly, the catalyst wetting efficiency and gas-liquid interfacial area improved considerably.

6.2. Effect of operating parameters on intermediate compounds occurrence

Concentrations of intermediate compounds in reactor effluents were investigated at steady state conditions during experiments using HPLC DIONEX (UV (JYNKOTEK)/VIS160S). Fig. 5 illustrates the effect of LHSV and gas velocity on the formation rate of intermediate compounds, where acetic acid, formic acid and maleic acid concentrations were increased as LHSV decreases. This may be due to the increasing time required to achieve phenol oxidation. These results were in agreement with other research (Eftaxias et al., 2005, 2006; Singh et al., 2004).

Increasing the gas flow rate provides sufficient quantity of oxygen for competitive reactions of intermediates over catalyst active sites and also thinning the liquid film spreading on the catalyst particles, consequently decreasing resistance to mass transfer across the gas-liquid film. Our results were also in agreement with the findings of other scientists (Eftaxias et al., 2001; Miro et al., 1999). It was observed that no traces of hydroquinone, p-benzoquinone, p-hydroxybenzoic acid and catechol were detected in the reactor effluent. This may be attributed to the low operating LHSV which was sufficient to oxidize these intermediates.

This result was confirmed by Quintinilla et al. (2006) who studied the oxidation of phenol on Fe/AC catalyst. They revealed that p-benzoquinone was detected as intermediate product at lower space-times but as the liquid space-time is increased, its concentration decreased due to the rapid oxidation to lower molecular acids (maleic, acetic and formic acids). P-hydroxybenzoic acid on the other hand, oxidizes directly to short chain acids (maleic, acetic and formic acids).

Moreover, it was observed that all samples withdrawn from the liquid effluent were colourless, which indicates that they were quinones-free (since liquid with quinones are characterised by a brownish colour solutions).

Table 9. Kinetic parameters estimation in comparison with data in related literature

Kinetic parameter	Quintanilla et al. (2007)	Eftaxias et al. (2006)	Wu et al. (2005)	Fortuny et al. (1995); (1999)	Présent Work
k_{ob} (L/kgcat.h)	-	$10^{14.36}$	-	10^{11}	2.7×10^{10}
β	1	1	-	-	1
α	0.74	-	-	0.5	0.69
E_{ob} (kJ/mol)	-	-	35.4	-	29.299

It is also worthy to mention the hypothesis of Cybulski and Trawczynski (2004) who reported that Pt catalysts favours direct oxidation of phenol, although this hypothesis requires more detailed work to test it. During phenol oxidation experiments, catechol was not detected since it was easily converted into oxidation products, mainly CO₂ (selectivity of 90%). The obtained concentration-LHSV profiles for the three main intermediates shown in Figs. 5 to 8 revealing that phenol oxidation follows a complex pathway of parallel and consecutive reactions. It seems that phenol undergoes two parallel reactions to form benzoquinone and P-hydroxybenzoic acid. For the Pt catalyst, benzoquinone forms and disappears rapidly suggesting that there is a direct pathway from phenol or benzoquinone to formic acid. On the other hand, the formed p-hydroxybenzoic acid was immediately converted to malic acid, which normally oxidizes at a slower rate. Finally, acetic acid should be formed following malic acid according to the Devlin and Harris pathway. Acetic acid is claimed to be the most resistant to oxidation among all lower carboxylic acids (Matatov-Meythal and Sheintuch, 1998).

Fig. 6 illustrates the effect of operating temperature on composition of the liquid effluent. As can be seen, there is a positive influence of the temperature on phenol oxidation and mineralization rate of the intermediates. The higher the temperature the higher the LHSV value at which the maximum concentration of intermediates occurs. This was attributed to the reaction rate constant which is positively affected by the operating temperature. These results are in agreement with (Fortuny et al., 1999; Garg and Mishra, 2013; Sanchez et al., 2007). Fig. 7 illustrates the intermediate compounds formed (i.e. acetic acid, formic acid and maleic acid) as a function of reactor pressure and LHSV. As it can be seen from Fig. 7, intermediate compounds achieved their highest concentration at reactor pressure of 0.6 MPa. This is due to the same reasons mentioned previously. These results are in agreement with those in other works (Eftaxias et al., 2005, 2006; Fortuny et al., 1995; Singh et al., 2004; Suwanprasop, 2005; Zhan, 2013).

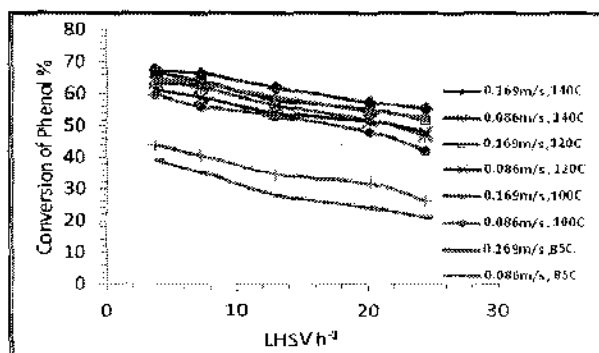


Fig. 4. Effect of LHSV and gas velocity on conversion of phenol at different gas velocities and temperatures (initial phenol concentration = 900 mg/L and $P = 0.6$ MPa)

6.3. Effect of phenol conversion on intermediates occurrence

Figs. 9 to 12 plot the variation of intermediates concentration against phenol conversion at different operating conditions. Fig. 9 illustrates the effect of gas velocity and phenol conversion on the concentration of intermediates. As can be seen, phenol conversion and gas velocity have a positive impact on the rate of formation of intermediates. The results confirmed the oxidation pathway of phenol. It was observed that at any specific phenol conversion and gas velocity, the refractory intermediate (i.e. acetic acid) has the main proportion of effluent since it needs higher temperature for destruction than other intermediates. It seems that at higher phenol conversion, the gas velocity becomes less effective.

Fig. 10 shows the effect of operating pressure on intermediates concentration. As can be seen, an increase of oxygen pressure increases the concentration of intermediates. This may be attributed to the solubility effect of oxygen which has a direct relationship with the operating pressure. The effect of operating temperature on the concentration of intermediates is shown in Fig. 11 (a, b, c and d). As indicated, the phenol conversion and consequently the formation rate of the intermediates was positively influenced by operating temperature.

Fig. 12 (a, b and c) illustrates the effect of inlet phenol concentration on concentration of intermediates at the reactor effluent. Fig. 12 depicts the negative impact of phenol initial feed on the rate of intermediates and consequently on phenol conversion.

6.4. Effect of initial feed concentration on phenol conversion

Phenol feed concentration is another reaction parameter. Phenol conversion is plotted in Fig. 13 as a function of LHSV at different inlet phenol concentration; it is shown that phenol conversion decreases with increasing LHSV.

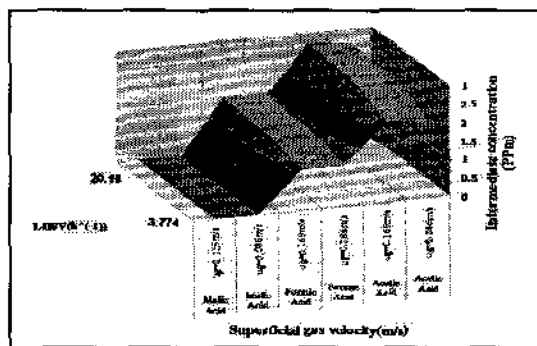


Fig. 5. Variation of intermediates concentration against LHSV and gas velocity at $T = 100^\circ\text{C}$, $P = 0.3$ MPa, and $C_{pho} = 900$ mg/L.

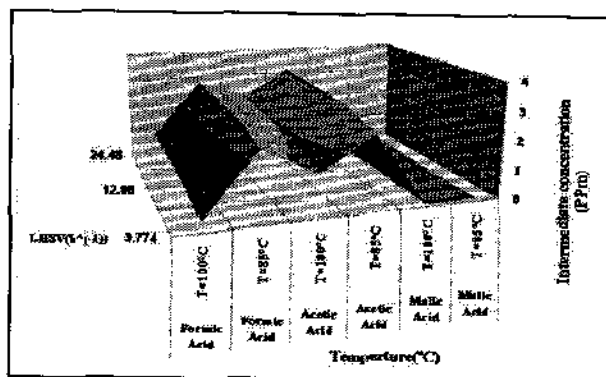


Fig. 6. Intermediate concentration against temperature at 0.6MPa, $U_g=0.086\text{m/s}$, and $C_{pho}=900\text{mg/L}$

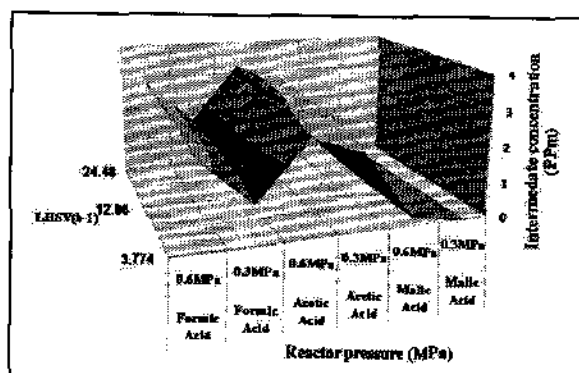


Fig. 7. Effect of operating pressure on intermediates concentration

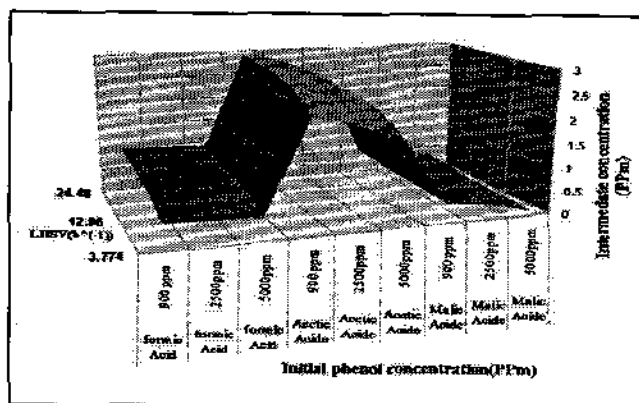


Fig. 8. Intermediate concentration at different initial phenol concentration at $T=120^\circ\text{C}$, $P=0.3\text{MPa}$ and $U_g=0.169\text{m/s}$

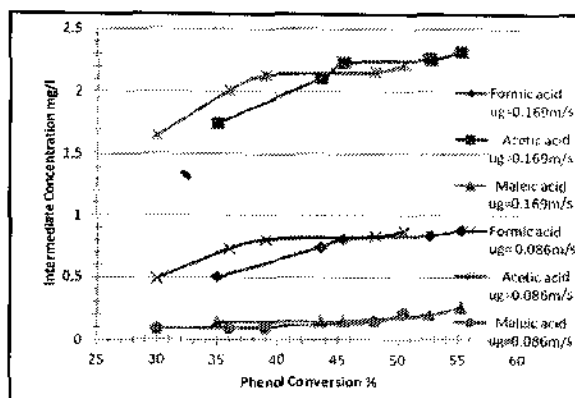


Fig. 9. Variation of intermediates concentration against Phenol Conversion at various gas velocities ($T=100^\circ\text{C}$, $P=0.3\text{MPa}$, and $C_{pho}=900\text{mg/L}$)

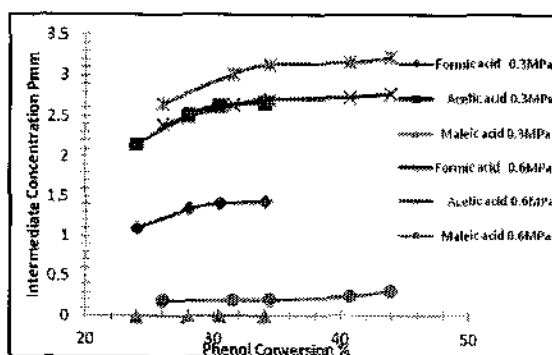
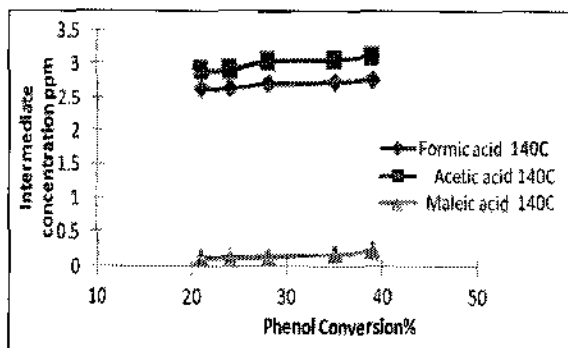
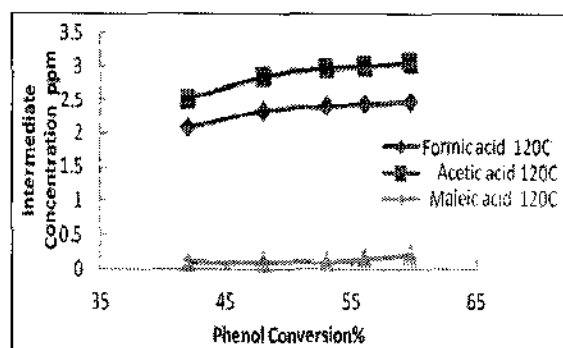


Fig. 10. Effect of operating pressure on intermediates concentration (at $T=85^\circ\text{C}$, 900mg/L , $U_g=0.169\text{m/s}$)



a)



b)

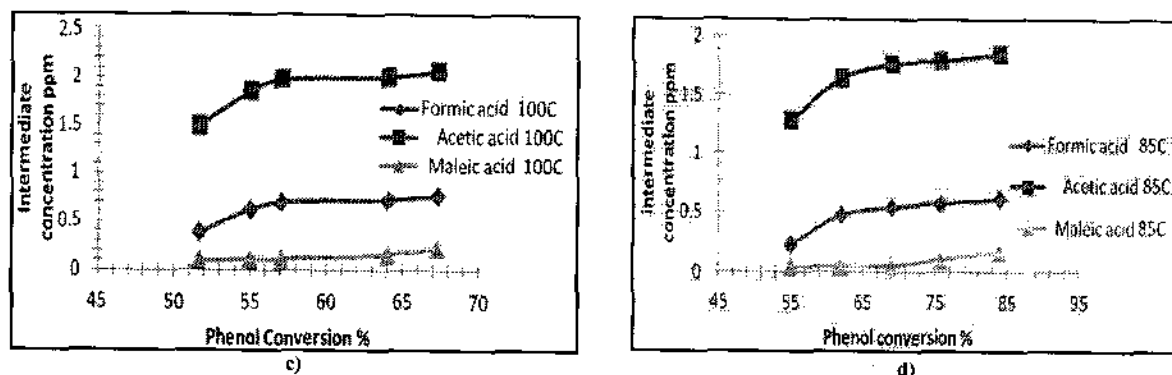


Fig. 11. Variation of intermediate concentration against phenol conversion at different temperatures

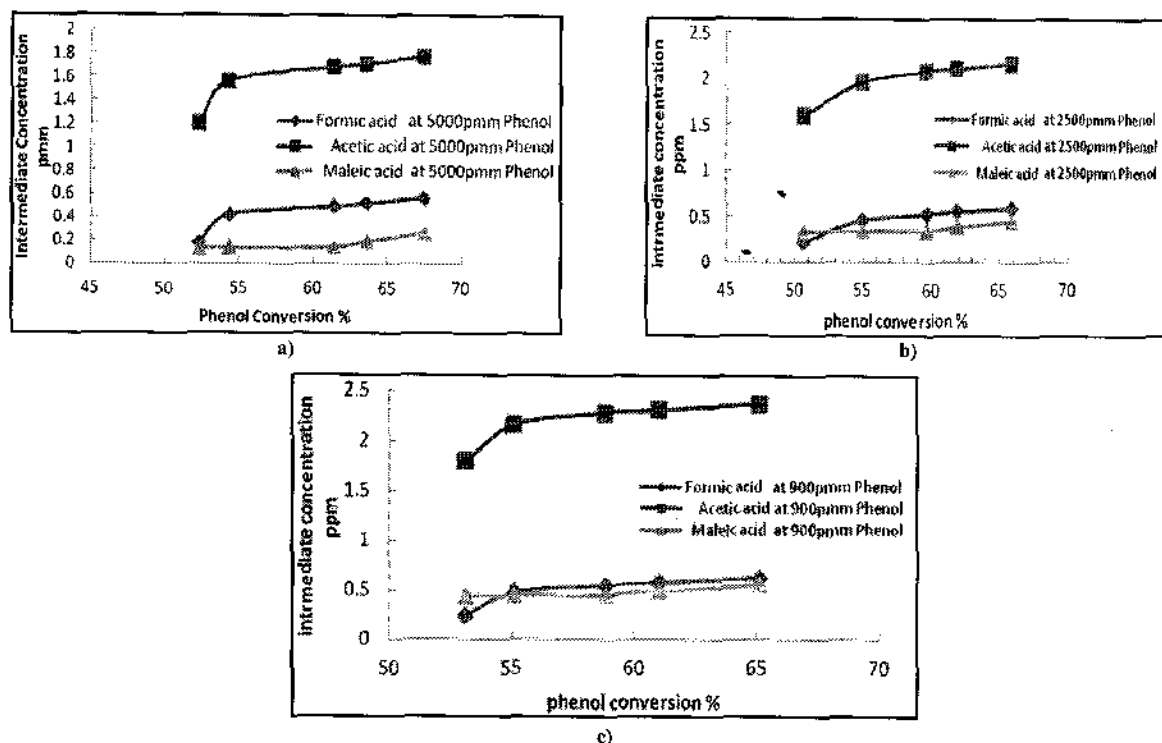


Fig. 12. Intermediate concentration against phenol conversion at various inlet phenol concentration

Fig. 13 also shows that the variation in initial feed concentration has a negative impact on phenol conversion.

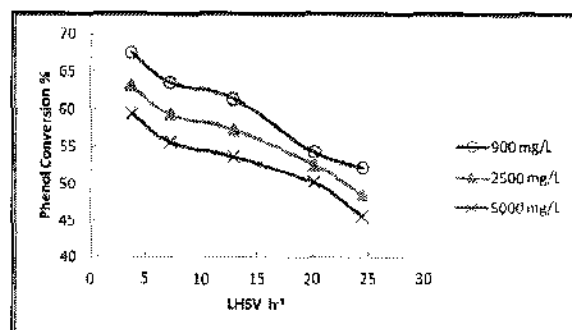


Fig. 13. Conversion of phenol against different initial phenol concentrations at $T = 140^\circ C$, $P = 0.6 MPa$ and $u_g = 0.169 m/s$

As can be observed, at $LHSV = 4 h^{-1}$ and inlet concentration = 900 mg/L, the conversion of phenol is 67.47% which drops to 59.44% when the inlet concentration was increased to 5000 mg/L at the same LHSV. This indicated a reduction in phenol conversion equal to only 8% between the two extremes of the studied inlet phenol concentration.

7. Conclusions

The following conclusions could be drawn out from the present investigation:

1. It was found that phenol conversion increased with increasing reaction temperature, reactor pressure, and superficial gas velocity of oxygen, while decreased with increasing (LHSV).
2. The initial phenol concentration has a negative impact on phenol conversion and intermediates concentrations.

3. The comparison of experimental reaction rates with mass transfer rates calculated from literature correlations clearly suggests that phenol oxidation on Pt/Al_2O_3 catalyst was kinetically controlled in the present study.

4. It was found that the oxidation reaction of phenol is first order with respect to phenol concentration and 0.69 order with respect to oxygen solubility at studied operating conditions, observed activation energy equal to 29.299 kJ/mol, and the pre-exponential factor equal to 2.7×10^{10} L/kg_{cat}.h.

5. Selectivity maps for concentrations of intermediate compounds in reactor effluent revealed that operating parameters could be selected to enhance a certain reaction pathway.

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Notations

a_s	Specific packing area	1/m
C_{O_2}	Concentration of oxygen,	kmol / l
C_{Ph}	Concentration of phenol,	kmol / l
D_{AB}	Molecular diffusivity,	m ² /s
D_{ph}^{eff}	Effective diffusivity for phenol,	m ² /s
$D_{O_2}^{eff}$	Effective diffusivity for oxygen,	m ² /s
D_{axl}	Dispersion Coefficient,	m ² /s
E	Activation energy	kJ/mol
K_{ls}	Liquid -solid mass transfer coefficient,	m/s
K_{gl}	Gas-liquid mass transfer coefficient	m/s
L_p	Ratio of catalyst (volume to surface area)	m
N	Order of reaction	---
P	Reactor pressure	kPa
ΔP	Reactor pressure drop	kPa
R	Universal gas constant	m ³ atm/mol.K
r_{obs}	Observed reaction rate	kmol/kg cat.h
T	Temperature	K
U_g	Superficial gas velocity	m/s
U_l	Superficial liquid velocity	m/s
X	Conversion	---
X_{O_2}	Mole fraction of oxygen in liquid-phase	---
Z	Reactor length	m
<i>Greek Symbols:</i>		
α	Reaction order of phenol	---
α_{gl}^{\dagger}	coefficients in external mass transfer criteria	---
α_{sl}^{\dagger}		
B	Reaction order of oxygen	---
Γ	Reaction limitation criteria	---
N	Stoichiometric coefficient of oxygen	---
ϕ	hole diameter of gas-liquid distributor	mm

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