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Removal of Phenols from Refinery Wastewater using Trickle Bed Reactor

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ABSTRACT

The present work aims to study the performance of a trickle bed reactor for phenol degradation in refinery wastewater by investigating the applicability of a commercial 0.5% platinum/alumina catalyst, which is used currently for desulfurization process in the North Refinery Company-Iraq. Synthetic wastewater experimentally was prepared to simulate the specification of samples taken from North Company Refinery. Results showed that initial phenol concentration had adverse effect on phenol removal. The results exhibited that the highest phenol conversion of (98.47%) was obtained over 0.5% Pt/ γ -Al₂O₃ at the studied conditions (i.e., operating pressure 0.8 Mpa, operating temperature 120°C, LHSV 2.5 h⁻¹, and air superficial velocity 0.25 m/s), with initial phenol concentration of 200 mg/L. The present method characterized by low residence time, the end-products are environmentally harmless no sludge production which requires further treatment.

Keywords: Refinery Wastewater, Phenols Removal, Trickle Bed Reactor, 0.5% Pt/ γ -Al₂O₃ Catalyst.

ازالة الفينول من مياه الصرف للمصافي النفطية باستخدام مفاعل الطبقة الوشلة

الخلاصة

تضمن البحث دراسة كفاءة اداء عمود الطبقة الوشلة لازالة الفينول من مياه الصرف للمصافي النفطية باستخدام 0.5 %Pt/Al₂O₃ كعامل مساعد والمستخدم حاليا في وحدة ازالة الكبريت " desulfurization process " في مصافي الشمال. النتائج أظهرت ان اعلى نسبة تحول للفينول (98.47) تم الحصول عليه تحت الظروف التالية LHSV 2.5 سا⁻¹، درجة حرارة=120 م°، الضغط التشغيلي =0.8 ميكاباسكال والتركيز الابتدائي

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للفينول=200 مغم/لتر وسرعة الغاز 0.25 m/s). وان النواتج النهائية في هذه الطريقة المستخدمة في البحث لا تحتاج الى معالجات اضافية اخرى.

NOTATION

A	Frequency factor (case dependent units)	
a	Interfacial area	$^2/m^3$
a_s	Specific packing area	m^2/m^3
C	Concentration of phenol	$kmol / m^3$
D_{AB}	Molecular diffusivity	m^2/s
D_{axl}	Dispersion Coefficient	m^2/s
D_{ei}	Effective diffusivity	m^2/s
$D_{ph,L}^{eff}$	Effective diffusivity for phenol	m^2/s
$D_{O_2}^{eff}$	Effective diffusivity for oxygen	m^2/s
D_p	Particle diameter	m
H	Henry constant	MPa $\left(\frac{mole\% CH_4}{mole\% CH_2} \right)^{-1}$
Ea	Activation energy	Kcal/mol
K_{gl}		m/s
K_{ls}	Gas-liquid mass transfer coefficient	m/s
L	liquid mass flow rate	$kg\ m^{-2}\ s^{-1}$
L_p	Intra-catalyst length	m
N	Order of reaction	(-)
Mwt	Molecular weight	kg/kg_{mol}
R	Universal gas constant	$m^3.atm/mol.K$
r_{obs}	Observed reaction rate	$kmol/kg_{cat}.h$
Pe_L	Peclet number	$\frac{ZU}{D_{ax}}$
Re	Reynolds number	$\frac{\rho u d_e}{\mu}$
Sc	Schmidt number	$\frac{\mu}{D_{AB}\rho}$
T	Temperature	K
U	Superficial velocity	m/s
\tilde{V}_A	Molar volume	$m^3/kmol$
Greek Symbols		
α_{gl}, α_{sl}	Dimensionless coefficient in external mass transfer criteria	(-)
γ	Reactant limitation criteria	(-)
Φ	Weisz-Prat	
ε_p	Particle voidage (porosity)	(-)
μ	Viscosity	kg/m.s

ν	Stoichiometric coefficients of oxygen	(-)
ρ_b	bed density	kg/m ³
ρ	Density	kg/m ³
τ''	Catalyst pellet tortuosity	(-)
Subscripts:		
O_2	Oxygen	
Ph	Phenol	
Obs	Observed	
G	Gas	
L	Liquid	
L	Liquid	
P	Particle	
O	Initial	

INTROUDUCTION

Rapid development of industry promoted rapid growth of economy , but enviromental pollution has become a constraining factor of economic development , and high concentrations, toxicity , harmfulness , difficults associated with the biological treatment of wastewater and sludge are still major factor of envioromental pollution [1]. Phenolic compounds pose a significant threat to the environment. Due to their stability and bioaccumulation, they remain in the environment for long periods. As they have high toxicity and carcinogenic character, they cause considerable damage and threat to the eco-system in water bodies and human health [2] . The concentration of phenol from different industrial wastewater is shown in Table (1).

Table (1) Concentration of phenol in industrial wastewater [3](Garcia J et al 1989).

Industry	Concentration of phenol (mg/l)
Gas production	4000
Petrochemicals	50-700
Pharmaceuticals	1000

At present, several treatment methods are available: chemical, physical (adsorption, reverse osmosis), biological, wet air oxidation (WAO), and incineration. Selecting a wastewater treatment process among these methods, one should take into account the toxicities and concentration of the pollutants in the waste stream [4]. The wet-air or thermal liquid-phase oxidation (WAO) process, in which the generation of active oxygen species, such as hydroxyl radicals, takes place at high temperatures and pressures, is known to have a great potential for the treatment of effluents containing

a high content of organic matter, or toxic contaminants for which direct biological purification is unfeasible. In this process, molecular oxygen dissolved in the wastewater reacts with the organic and inorganic pollutants. The oxidizing power of the process is based on the high solubility of oxygen at these severe conditions and the high temperature that increases the reaction rates and production of free radicals [5-6]. To reduce the cost, catalyst is added to lower the reaction temperature and pressure, which is referred to as CWAO process. The catalyst is usually made of transitional metal salt/metal oxide. By using CWAO, the oxidation of phenol can be tremendously facilitated at milder conditions as low temperature [7].

Fortuny et al., [8], found that in the catalytic oxidation of phenol in an aqueous solution in a continuous trickle bed reactor the effect of temperature has more pronounced than that of pressure. Miro et al., [9], obtained efficient and durable catalysts and determined that the optimal process conditions are the key to successfully implementing the wastewater treatment from phenolic compound. Their results show that increasing the inlet pH, decrease the rate of deactivation for both catalyst. Wu et al., [7], found that phenol conversion increases with the increase of the temperature of the reaction when using copper nitrate as a homogenous catalytic oxidation. Massa et al., [10], found that the distribution of intermediate products, and consequently the selectivity depends on the mass of catalyst/ volume of liquid ratio. A reactor with low liquid to catalyst ratio such as trickle bed reactor would be more suitable to favor the selectivity towards complete oxidation. Singh et al., [11], Guo and Al-Dahhan [4,12], suggested that CWAO of phenol was strongly affected by the temperature and pressure; however, pressure had less effect. Eftaxias et al., [13], found that the increase of both temperature and pressure increase the phenol conversion and the pressure had a strong positive effect.

The present work aims to study the applicability of commercial 0.5% platinum /alumina catalyst for catalytic oxidation of phenol in TBR. Also, investigating the kinetic parameters of the operating system.

EXPERIMENTAL SETUP

Figure (1) shows a schematic diagram of the experimental setup. The heart of the setup is the trickle bed reactor (TBR) which was made of stainless steel with dimensions of (5cm id x 1.25 m high x 5mm thick.). TBR was packed with different layers. From the top a 0.2 m layer (pre-packing) of 2mmx2mm glass cylinders was set before the catalyst bed to ensure even liquid distribution over the reactor cross-section, then a 0.5%Pt/Al₂O₃ catalyst bed of (800gm) with (0.6m) height. The last layer (post-packing) contains 2mmx2mm glass cylinders with a height of 0.4m to support the catalyst bed. Table (3) shows the catalyst specification and operating conditions.

The two-phase pressure drop across the reactor bed was measured by a differential pressure transducer. The output signal of the transducer was fed to an A/D converter and stored in a data acquisition system with sampling frequency of 250Hz. The reactor was externally heated with electrical tape heater (Heraus-Wittmann GmbH, type MS6) which was connected to a temperature controller (Yang Ming CXTA 3000) that maintained the bed temperature by means of an on-off relay which manipulated the heat supply of the external heater.

EXPERIMENTAL WORK

Experimental Procedure

The synthetic wastewater was prepared in a feed tank of 100Lit. electrically heated by an immersed heater up to 60°C. Then, the liquid was pumped via a metering pump (Dose pump, Baldor Frum Duty, USA) to a stainless steel damper with dimensions of (4cm idx0.35m length) to damp the pulsation due to pumping. Air was supplied by an oil-free air compressor. Gas and liquid were measured by calibrated flow meters before mixing and injected cocurrently via a preheater into the top of the reactor. The effluents of the reactor were discharged at the bottom through a gas-liquid separator. At the top of the reactor one-way valve was located to prevent backflow.

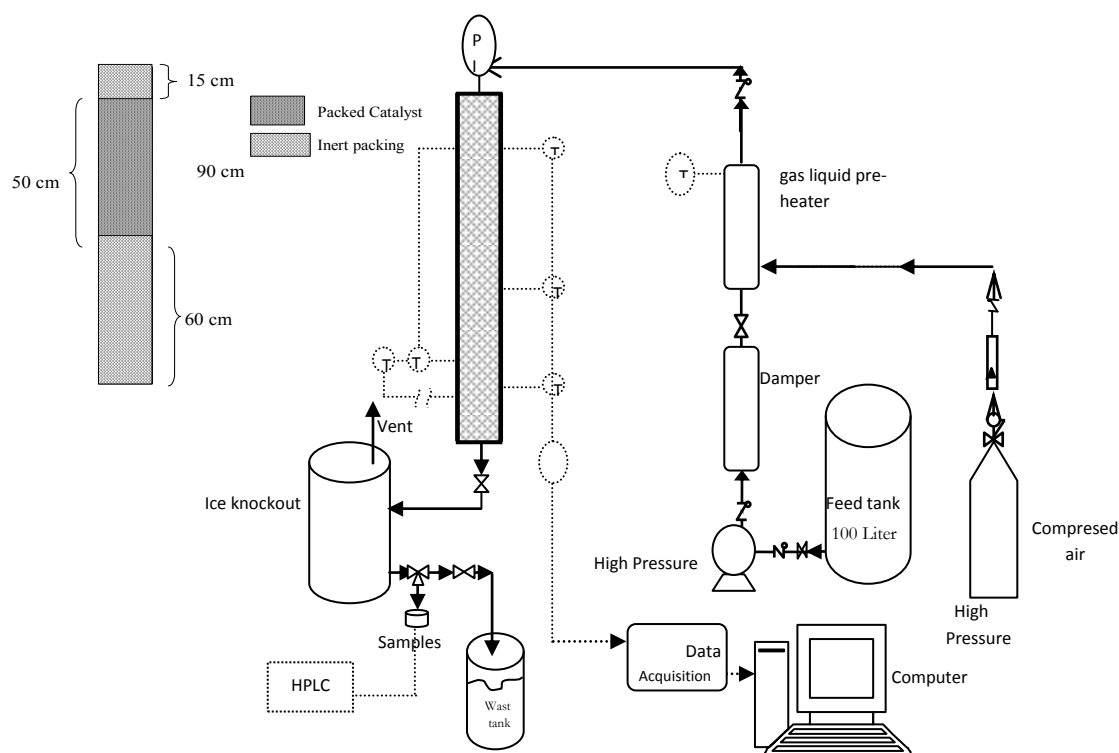


Figure (1) Schematic diagram for the experimental setup.

Table (3) Bed Characteristics, Catalyst Specification and Operating condition.

Reactor properties

Reactor diameter (i.d)	0.05 m
Total length	1.25 m
Pre packing depth	0.2 m
Post packing depth	0.45 m
Bed porosity	0.38-0.4
Pellet porosity	0.52
Catalyst bed depth	0.6 m
Operating condition	
System	(phenol - air)
	Conventional Condition
Temperature (°C)	(85-120)
Pressure(MPa)	(0.1-0.8)
Superficial liquid velocity(m/s)	(0.001-0.1)
Superficial gas velocity(m/s)	(0.09-0.25)
Initial phenol concentration(mg/l)	(200-1000)
Catalyst properties	
Active metal	0.5% pt
Catalyst support	Alumina (Sphere)
Particle diameter	0.0016 m
Surface area	250 m ² / gm
Pellet density	0.56 gm/cm ³

Thermo-Physical and Reactor Properties

The physical properties for the gas and liquid phase used in the present work were measured in the laboratory such as viscosity and density .The mass transfer parameters used to determine for reactor performance were estimated from correlations cited in Table (2).

Table (2) Correlations for Transport Parameters.

Diffusion in Liquid Phase (Willke and Chang ,[14])	$D_{AB,L} = 7.4 * 10^{-8} \left(\frac{M_{wt,B}^{0.5} T}{\mu_B \tilde{V}_A^{0.6}} \right)$
Effective Diffusivity (Levenspiel, [15])	$D_{ei} = \frac{D_{AB} \varepsilon_p}{\tau''}$
Mass Transfer Coefficients (Wu et al., [16])	$\frac{K_{gl} d_p}{D_{O_2,L}} = 25.1 Re_L^{0.45} Sc_{O_2l}^{0.5}$ $\frac{K_{sl} d_p}{D_{Ph,L}} = 3.77 Re_L^{0.8} Sc_{Phl}^{1/3}$

Henry Law constant (Wu et al., [16])	$H(T) = 761.1 - 108.9 \ln(T) - \frac{40785.5}{T}$
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RESULT AND DISSCUATION

Wall Effect on Reactor Performance

In the present work such effects were greatly reduced by the correct choice of particle and reactor geometry (reactor hight $L_R=1.25\text{m}$, reactor diameter $D_R=0.05\text{m}$ and partical diameter $d_p= 0.0016\text{m}$). The relevant criteria of L_R/d_p and D_R/d_p take values of 781.25 and 31.25, respectively, which match the critical value of 20 established for safe operation [17].

Axial dispersion effects estimated using Mears criteria:

$$\frac{L}{d_p} = \frac{20n}{P_{eL}} \ln \frac{C_{feed}}{C_{exit}} \quad \dots (1)$$

The calculated axial dispersion coefficient has a very small value in the order of $(10^{-3} \text{--} 10^{-5}) \text{ m}^2 \text{ s}^{-1}$, which ensures the absence of axial dispersion in present study, which confirm a good assumption of plug flow.

Determination of kinetic regime in TBR

Gas–liquid hydrodynamic and mass transfer parameters were evaluated from appropriate high-pressure literature correlations. Under the operating conditions tested, it was shown with the help of three-phase reactor flow maps that the TBR always operated in the trickle regime. The values calculated from the reactant flux ratio (γ) confirmed the reaction varied from gas to the liquid limiting reactant [18] :-

$$\gamma = \frac{D_{ph,L}^{eff} C_{ph,L}}{v D_{O_2}^{eff} C_{O_2,L}} \quad \dots (2)$$

$\gamma \gg 1$, the reaction is limited by the gas reactant;

$\gamma \ll 1$, the reaction is limited by the liquid.

The extent of external and internal diffusion limitation was estimated at all operating condition through the common diagnostic criteria α_{gl} , α_{ls} and Weisz–Prater Φ . These quantities are defined as [19] .

$$\alpha_{gl} = \frac{r_{obs} \rho_b}{(K_{gl} a)_{O_2} C_{ph1}} < 0.05 \quad \dots (3)$$

$$\alpha_{ls} = \frac{r_{obs} \rho_b}{(K_{ls} a_s)_{O_2} C_{ph1}} < 0.05 \quad \dots (4)$$

$$\Phi = \frac{(r_{obs} \rho_b) L_p^2}{C_{ph0} D_{ph,L}^{eff}} \ll \frac{2}{n+1} \dots (5)$$

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.

Table (4) Reactant Flux Ratio (γ) for Conventional Operation.

C_{ph0}		85°C		100°C		120°C	
Ppm	(kmol/m ³)	0.8MPa	0.4MPa	0.8MPa	0.4MPa	0.8MPa	0.4MPa
200	0.00212	0.01474	0.0294	0.01511	0.0302	0.0150	0.03007
500	0.005319	0.0368	0.07369	0.0377	0.0755	0.0375	0.0751
800	0.00851	0.0589	0.1179	0.0604	0.12088	0.0601	0.1202
1000	0.010638	0.0736	0.1473	0.07555	0.15109	0.0751	0.1503

Table (5) Values of α_{gl} and α_{ls} at 0.09m/s gas velocity and 0.0045m/s liquid velocity based on initial phenol concentration (1000mg/l) for conventional operation.

P (MPa)	Temperature (°C)	$K_{ls}a_s$ (s ⁻¹)	$K_{gl}a$ (s ⁻¹)	r_{obs} Kmole/kg .h	α_{gl}	α_{ls}
0.4	85	0.633	23.687	0.0001	0.00236	5.96×10^{-5}
0.4	100	0.741	30.335	0.000132	0.003437	8.92×10^{-5}
0.8	85	0.704	26.98	0.000103	0.00362	6.31×10^{-5}
0.8	100	0.872	34.344	0.000139	0.00369	9.98×10^{-5}

Table (6) Values of Φ at 0.09m/s gas velocity and 0.0045m/s superficial liquid velocity.

C_{ph0} (kmol/m ³)	85°C		100°C		120°C	
	0.4MPa	0.8MPa	0.4MPa	0.8MPa	0.4MPa	0.8MPa
0.010638	0.5092	0.5296	0.5807	0.805	0.6862	0.7147
0.00212	0.489	0.5021	0.538	0.768	0.628	0.7001

EFFECT OF OPERATING PARAMETERS

Effect of LHSV and Superficial Gas Velocity

The effect of LHSV on phenol removal rate is presented in Figure 2. As can be seen, increasing LHSV has an adverse impact on phenol conversion, Figure 2 depicts the effect of liquid flow rate on phenol conversion. Phenol conversion of 78.3% was achieved at LHSV 2.5h⁻¹, while at LHSV equal to 20 and 24 h⁻¹ phenol conversions were 68% and 61.1% respectively. Actually increasing liquid flow rate reduces the

residence time of the reactant thus reducing the time of reaction of phenol with oxygen. Moreover, higher liquid flow rates give greater liquid-holdup which evidently decreases the contact of liquid and gas reactants at the catalyst active site, by increasing film thickness. The findings of Singh et al., [11] and Guo and AL-Dahhan, [4, 12] confirm our results.

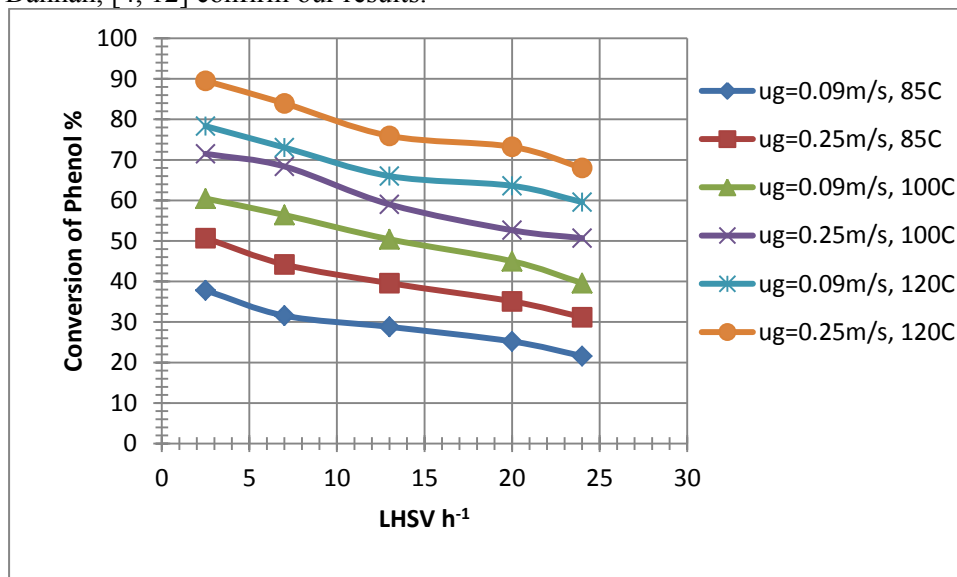


Figure (2) Effect of LHSV and gas velocity on conversion of phenol at [initial phenol concentration 200ppm and 0.4 MPa].

Figure (2) demonstrates the variation of conversion with superficial gas velocity. The phenol conversion was enhanced with the increasing of superficial gas velocity. It can be seen from the Figure that the high phenol conversion of 89.4% was achieved at 0.25m/s gas velocity while at 2.5h⁻¹ LHSV achieved 78.3% at 0.09m/s gas flow rate. At low gas velocities, gravity (or buoyancy) force plays an important role. The catalyst particles are not fully wetted at the liquid flow rates used, which facilitates the access of the gas reactant to the pores of the catalyst from the externally dry parts. In addition, the pressure gradient ($\Delta P/Z$) increases significantly and so does the shear stress on the gas-liquid interface (Al-Dahhan and Dudukovic, [20]. Therefore, liquid film thickness at a constant liquid flow rate decreases, which leads 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, which is supported by the finding of Larachi et al., [21]. Since the trickle-bed pellets get progressively entirely wetted by increasing the gas superficial velocity.

Effect Reaction Temperature

Figure (3) shows that high conversion at high temperature is achieved. As shown in this Figure phenol conversion of 98.4% was achieved at 120°C while at temperature 100 and 85°C, phenol conversion were 88%, 74% respectively. The general behavior is, higher conversion is achieved at higher temperature due to the

fact that at higher temperature kinetic constant (i.e., rate constant) is favorably affected resulting in increasing in phenol conversion, according to Arrhenius equation [15] :-

$$K = A \exp\left(-\frac{E_a}{RT}\right) \quad \dots (6)$$

In addition at high temperatures in aqueous solutions; the form in which air participates in chemical reactions is complex. The necessary elevated temperatures can accelerate the formation of oxygen radicals, $O\cdot$, which in turn can react with water and oxygen to form peroxide, H_2O_2 , and ozone, O_3 , so that these four species $O\cdot$, O_2 , O_3 , and H_2O_2 are all capable of participating in the phenol oxidation. In addition, at higher temperature the mass transfer coefficient and kinetic constants are favorably affected resulting an increase in phenol conversion. The result is in agreement with Lee et al., [22].

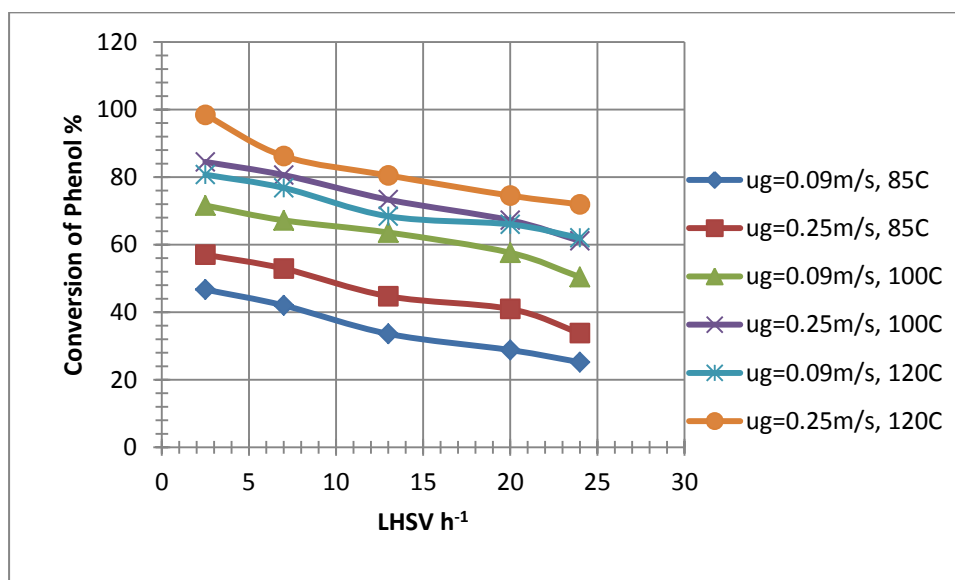


Figure (3) Effect of temperature on conversion of phenol at different gas and liquid velocities [0.8MPa, initial phenol concentration=200ppm].

Compared to reaction temperature, reactor pressure has less influence on phenol conversion. It can be seen from Figure (4), that increasing reactor pressure from 0.4MPa to 0.8MPa at 2.5 LHSV h⁻¹ and 85°C resulted in an increase in phenol conversion from 50.5% to 56.6% . In general increasing pressure improves the solubility of oxygen. This in turn increases the mass transfer driving force for gas to the inactively wetted catalyst surface, and facilitates the rate of mass transport to the wetted catalyst surface. The elevated pressure causes a decrease in liquid holdup. These results are in agreement with the work of Fortuny et al., [8] ; Singh et al., [11]; Suwanprasop, [23] and Eftaxias et al., [13,19].

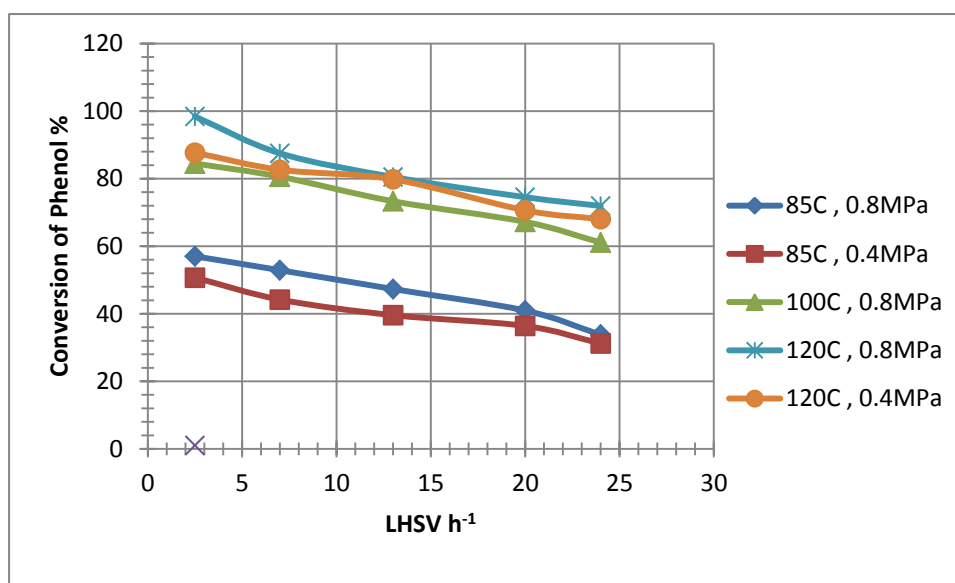


Figure (4) Effect of reaction temperature and pressure on conversion of phenol [$U_g=0.25\text{m/s}$, initial phenol concentration=200ppm].

Effect of Initial Phenol Concentration

Figure (5) shows the effect of initial concentration of phenol to be reduction during catalytic wet oxidation run over $0.5\text{Pt}/\text{Al}_2\text{O}_3$ catalyst at $u_g=0.25\text{m/s}$ and pressure 0.4MPa. The conversion variation from high to the lowest value when initial phenol concentration increased is marginal as illustrated in Figure (5). It is clear that phenol conversion decreases from 98.47% to 98% only, when initial phenol concentration increases from 200 to 1000 mg/l. At high phenol concentration provides a high reaction rate, yet strong oxidation limitation is present. At higher phenol feed concentration can be explained by limited amount of the catalyst needed to fully convert phenol. This suggests that when the reaction is carried out with proper oxygen and phenol loads, platinum catalyst deactivation can be avoided. This was in agreement with findings of Masende, [24].

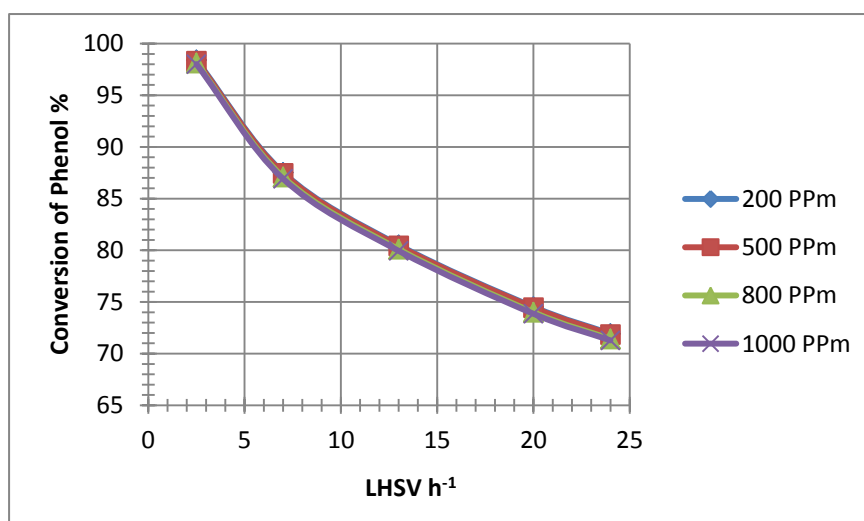
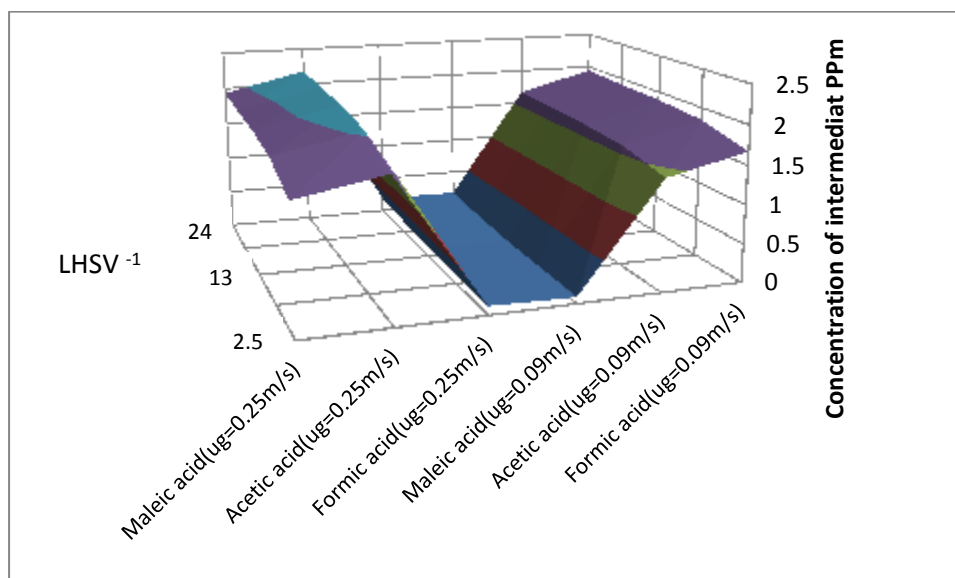


Figure (5) Effect of initial phenol concentration on conversion of phenol at [120°C, $U_g=0.25m/s$, 0.8MPa]

Effect of liquid and gas flow rates on intermediate compounds

Figure (6) illustrates the effect of LHSV and gas velocity on intermediate compounds, where acetic acid, formic acid and maleic acid concentrations increase with increasing LHSV. This is due to reduction in the time required to achieve complete oxidation. These results are in agreement with (Singh et al., [11]; Eftaxias et al., [13,19]. While, increasing gas flow rate provides sufficient quantity of oxygen for competitive reactions of intermediate over catalyst active sites forming increasing intermediate compounds. These results are in agreement with (Miro et al., [9] and Eftaxias et al., [25]).



**Figure (6) Intermediate concentration at different LHSV
and gas velocities [85°C,0.4MPa,200ppm].**

CONCLUSIONS

1. The highest phenol conversion (98.4 %) was achieved under operating conditions (LHSV=2.5h⁻¹, temperature=120°C, superficial gas velocity =0.25m/s, and initial phenol concentration=200mg/l).
2. It was found that phenol conversion increases with increasing gas flow rate.
3. Increasing reactor temperature from (85) to (120)°C enhanced phenol conversion from (74%) to (88%).
4. It was found that conversion of phenol is independent of inlet phenol concentration. When phenol concentration in solution was decreased from 1000 ppm to 200 ppm, the obtained conversion for phenol was varied from 98% to 98.47.
5. Production of an intermediate could be manipulated by selecting specific operating conditions.
6. The effluent of the process was merely CO₂ and slight acidic water without any sludge which favours this process over other conventional treatments.

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