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Study the Catalytic Oxidation of Phenol in both Baskets Stirred Tank and Packed Bed Reactors

Abstract- *The aim of this study, using five types of AL-Fe pillared Iraqi clay to study catalyst wet air oxidation to oxide phenol from synthesis's wastewater and study the limitation criteria in control of operating conditions. Two types of reactor (Batch and packed bed) used to study operation conditions and the best conditions result from Batch reactor was pressure 3.2Mpa, temperature 130 ℃, phenol concentration 500mg/l and pH 3.9, for packed bed reactor with AL-Fe pillared clays of Anbar-Erbil, Mosul, due to high phenol removal, in up-flow mode. The results show that phenol removal is 98-97.8-95% for Erbil-Mosul-Anbar respectively, when the LHSV used in reactor 0.6 h^{-1}, and gas flow 0.28cm/s, also it can be seen that the limitation criteria in control of operating conditions, and Mosul pillared consider more stable and activity than Erbil and Anbar.*

Keywords- *Catalytic, catalyst wet air oxidation, Limitation, phenol.*

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1. Introduction

Phenol is a major pollutant in the wastewater because of its presence in the effluent from major chemical and pharmaceutical industries, such as petrochemical industries, petroleum refineries, and others [1]. Phenol removed from wastewater because it is a complex material which required continuous efforts to develop a treatment, to reduce treatment cost, but the practicality of biological processes dramatically reduces, due to the presence of toxic or inhibitory chemicals [2,3]. Especially, in a high variation of organic charge, causing the emission of the unwanted amount of toxic products in the resulting wastewaters due to generated negative effects during treatment [4]. There are different methods for phenol treatment such as steam distillation [5], Separation by extraction [6], Separation by adsorption [7], Separation by membrane [8], solvent extraction [1], Electrochemical oxidation [9], Biochemical abatement [10], Incineration, and advance treatment. Wet air oxidation (WAO) provides an efficient method for either partial or destruction of organic pollutants such as phenol and substituted phenol, poly phenols and carboxylic acids [11]. In the last decades, the air or pure oxygen is used in catalytic wet air oxidation (CWAO), these process can speed the reaction temperature and pressure, also in these process the organic compounds can be partly converted to less toxic intermediates or completely converted to CO_2 and H_2O [12], also removal chemical oxygen demand (COD) can reach 75-90 % depending on the oxidation of intermediate compounds that are formed during the process [13]. In CWAO that have two types reaction homogenous (same phase) and heterogeneous (different phase) [14], in three-phase catalytic reactions, gas and liquid phase reactants are in contact with a solid phase catalyst (GLS). The gas dissolves in the liquid phase is transported to the catalyst particle in the bulk of the liquid, and both gaseous and liquid phase reactants diffuse into the porous structure of the catalyst where they react at the active sites. Products diffuse out of the particle in the opposite direction. Depending on the catalytic reaction, rate transport through this liquid film and diffusion in pores may be much slower [15].

The aim of this research, used five types of pillared clay that were prepared previously according on clay region (Anbar-Erbil-Mosul-Baghdad-Basrah) Examining the effect of operating parameters (reactor pressure, temperature, catalyst loading, phenol loading, pH, superficial gas velocity, and liquid superficial velocity) on hydrodynamic parameters (dynamic liquid holdup and axial dispersion), from these study can choose the best-pillared clay.

2. Experimental and Method

The first step used AL-Fe pillared. Iraqi clay that prepared previously [16] from five regions (Anbar-Erbil-Mosul-Baghdad-Basrah) after study the surface area as Blumenauer-Emmer-Teller (BET) and pore volume and pore size, the activity

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and stability was studied in Basket stirred Batch reactor, and in packed bed reactor.

I. Description of instrument Basket stirred Batch reactor

The experiment setup was designed to withstand the conditions of high temperature (up to 500 Co) and high pressure (up to 5 MPa). In a Basket stirred tank reactor (BSTR), the reactor consists of the equipment shown in Figure 1.

II. Basket stirred tank reactor (BSTR)

500mg of phenol has been diluted with distilled water to be synthesis's wastewater, as ideal refinery wastewater (500-1500mg/l) add sulfuric acid (1N) to reach pH 3.9-4, putting in 600ml reactor, Catalysts are putting in a fixed basket inside the reactor, while the basket was removed for the reactor to replace the catalysts in each test, the rotation speed was kept at 800 rpm. That to minimize the external-mass transfer resistances, Nitrogen pressured to 1Mpa to inert the reactor, purified air of zero grade or (21% pure oxygen mixed with 79% pure nitrogen was continuously fed into the reactor, five parameters used to study the operation condition with different ranges. Catalyst loadings used in three value (0-5-10 g/L) and the initial phenol concentrations (500- 1000-1500-2000 ppm), whereas the temperatures (90-110-130-150 Co), total pressures (P = 0.8, 2.0, 3.5 MPa) and pH used in (initial pH solution 5.48- 3.9), Once the set temperature was reached (defined as time zero), liquid sample was withdrawn all 30min, each sample were withdrawn, rapidly cooled, filtered and analyzed. The air was introduced and set manually to the required partial pressure for the duration of the experiment. The airflow rate was maintained constant [17]. Every batch was washed to remove all fines, then dried overnight before other use.

III. Packed bed reactor (PBR)

The packed bed reactor system consists as in Figure 2, that used the AL-Fe pillared clay for AL- Anbar, Erbil, Mosul as catalyst because that has a higher activity to remove phenol in the Batch Reactor. The operation condition in Table 1 used to operate the packed bed reactor in upflow mode that performs better for high pressures and low feed concentrations when the liquid reactant limitation controls the rate[18], eight experimental done for each type of catalyst used in reactor for treated phenol from the wastewater, the first four constant gas superficial velocity (0.2cm/s) and different in liquid hourly superficial velocity (LHSV) (0.2-0.4-0.6-0.8 hr-1), but the last four experimental have constant in liquid hourly superficial velocity (0.6hr-1) and different in gas superficial velocity (uG), (0.2-0.4-0.6-0.8 cm/s). As previously synthesis's wastewater pumped from fed tank to the reactor in required velocity to wetted the catalyst, with Controlled the high-pressure limit (3.2 Mpa), then the temperature raised to 150ºC, the pressure and temperature should be controlled along the space-time, the air pumped in the limited velocity when the air mixed with liquid after the needle valve, The liquid and gas streams were mixed and preheated in the inert zone before entering the reactor at the bottom through a distributor, when arrived at 3.2Mpa, 150C° and in desired (gas, liquid superficial velocity), the liquid cooled in exchanger, separator will be collected to turn off the sign and the liquid is drained, then the next experimental is beginning with reduce the velocity (gas or liquid) to desired required it, the sampler collected every drained, to study phenol and intermediate. Some Instrument required for measurement samples, such as HPLC YL 9100 HPLC System, YL 9101 Vacuum Degasser. And YL 9110 Quaternary pump, YL 9120 UV/Vis Detector with C18 column (Germany) to detect of low molecular weight (Intermediates) carboxylic acids was performed with the UV absorbance method at a wavelength of 450 nm, while at the end of the sample analysis the wavelength was switched to 550 nm to detect phenol, and the total organic carbon (TOC) has been measured by Shimadzu TOC-LCSH/CSN Standalone Model TOC analyzer, the procedure method as in (ASTM 5310B).

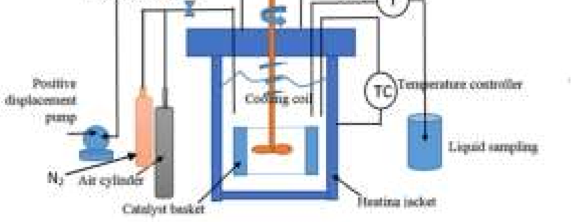

Figure. 1: Diagram of the experimental setup of (BSTR) Experimental procedure

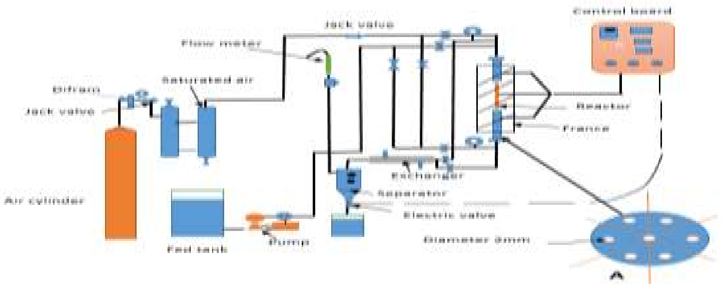

Figure 2: Diagram of the experimental setup of (PBR)

Table 1: Selection of design and operating conditions

Property Range	Anbar	Erbil	Baghdad	Mosul	Basrah
			Reactor Characteristics		
Active metal	0.3(Fe/AL+Fe) % Fe	0.2 (Fe/AL+Fe) % Fe	0.3 (Fe/AL+Fe) % Fe	0.5 (Fe/AL+Fe) % Fe	0.4 (Fe/AL+Fe) % Fe
Equilibrium vapor pressure,	MPa 0.79	MPa 0.79	MPa 0.79	MPa 0.79	MPa 0.79
Total pressure,	MPa 3.2	MPa 3.2	MPa 3.2	MPa 3.2	MPa 3.2
Reactor diameter,	cm 2.1	cm 2.1	cm 2.1	cm 2.1	cm 2.1
Bed height,	cm 60	cm 60	cm 60	cm 60	cm 60
Volume cm^3	200	200	200	200	200
Bed porosity	0.2	0.225	----------	0.223	------------
LHSV,	0.2-5 h-^{1}	0.2-5 h-^{1}	0.2-5 h-^{1}	0.2-5 h-^{1}	0.2-5 h-^{1}
			Catalyst Characteristics		
particle porosity	70.214	81.2734	77.435	77.0176	71.1473
Particle shape	Cylindrical	Cylindrical	Cylindrical	Cylindrical	Cylindrical
density(gm/Cm^3)	0.7744	0.5103	0.5940	0.6376	0.7710
(BET) Surface area (m ^{2}/g)	97.815	100.74	56.973	93.605	61.371
Average Pore volume m ^{3}/g	0.0962	٠.١٢٢١	0.0907	0.1430	0.1109
Pore size width Å	78.4	124.2	150.4	89.7	75.1

2. Result and Discussion

The result of the Batch reactor using AL- Anbar- Erbil- Mosul-Baghdad- Basrah pillared clays by CWAO show the TOC removal degrees with time and degrees of temperature that shown in Figures (٣-٤-٥-٦-٧).

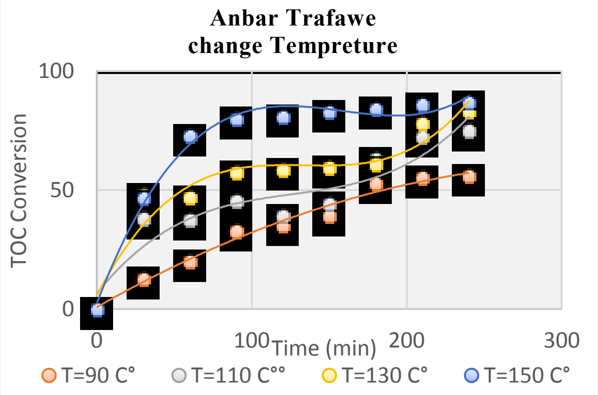

Figure 3: TOC conversion during 4hr in catalyst loading 7mg/l,pressure 2.5Mpa,500mg/l phenol concentration in Anbar

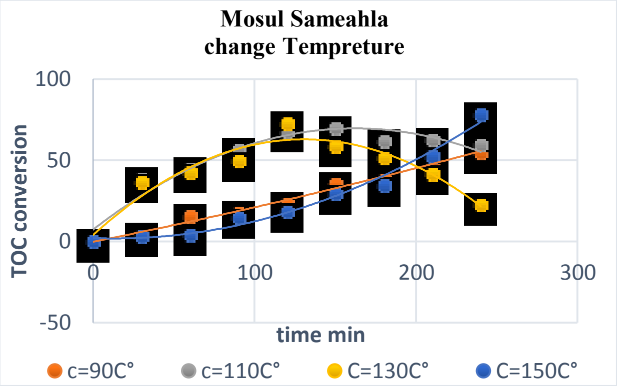

Figure 4: TOC conversion during 4hr in catalyst loading 7mg/l, Pressure 2.5Mpa, 500mg/l phenol concentration in Mosul

The initial pH of 3.9 and (5.48) and temperature 110°C to 130°C, the later corresponds to the natural pH of the wastewater. Without pH adjustment, phenol conversion curves show a sigmoidal profile, which is typical of radical reactions. Also, Figures show an increase in the decomposition rate when the pH is 3.9, while this rate is less at pH of 5.48 for all regions. Because pH values between 3 and 4 led to the least decomposition of air and higher amounts of available hydroxyl radicals in the solution [19]. The degradation rate in Anbar is higher than that of the rest of the regions, followed by Mosul, Erbil, Baghdad, and Basra, respectively as a result of the nature clay (pore size and surface area) of the pillared clay (catalyst) .

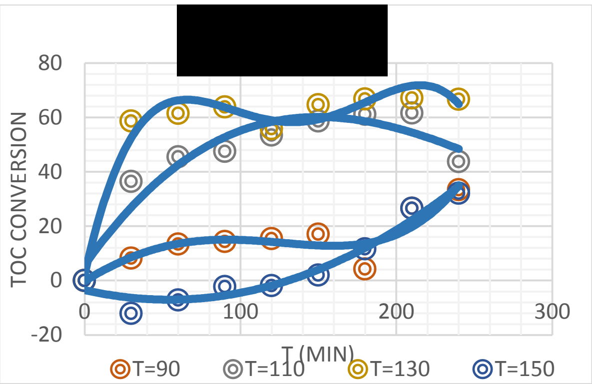
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Figure 5: TOC conversion during 4hr in catalyst loading 7mg/l,pressure 2.5Mpa ,500mg/l phenol concentration in Baghdad

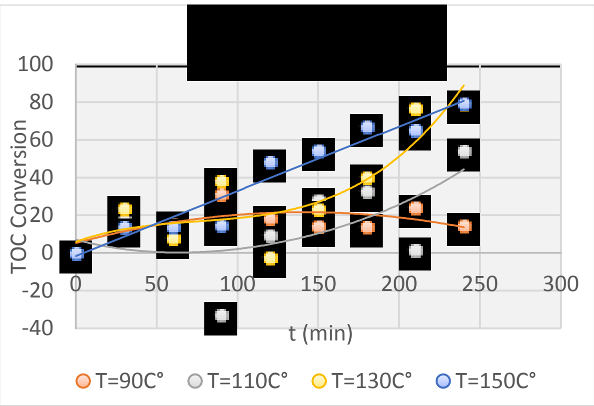
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Figure 6: TOC conversion during 4hr in catalyst loading 7mg/l,pressure 2.5Mpa ,500mg/l phenol concentration in Erbil

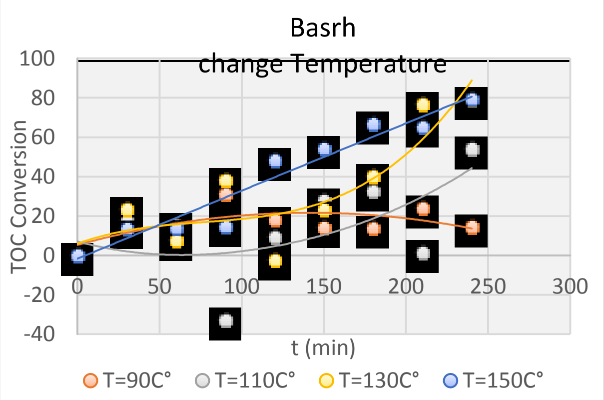

Figure 7: TOC conversion during 4hr in catalyst loading 7mg/l، pressure 2.5Mpa, and 500mg/l phenol concentration in Basrah

I. Effect of pH solution

The initial pH value of phenol solution between (5.48-5.87), pH between 3.9-4 it is referred to optimum types of advanced oxidation processes, and this point led to decomposition in higher amount of hydroxyl radical in the solution by air oxidation [20], during the phenol conversion curve show two different exist, the first part standing for induction period, but second part after inflection point refer to steady state, in present work Figure (8) show that the result of Al-Anbar that presented the same effect with all pillared clays region, the pH 3.9 and temperature 150ºC show the high phenol conversion profiles for reaction tests carried out with an initial air concentration 1.5 Mpa, from the result phenol conversion 91.2, 87.3, 79.1, 70.6, 68.34% for Baghdad, Anbar, Mosul, Basrah, Erbil, respectively.

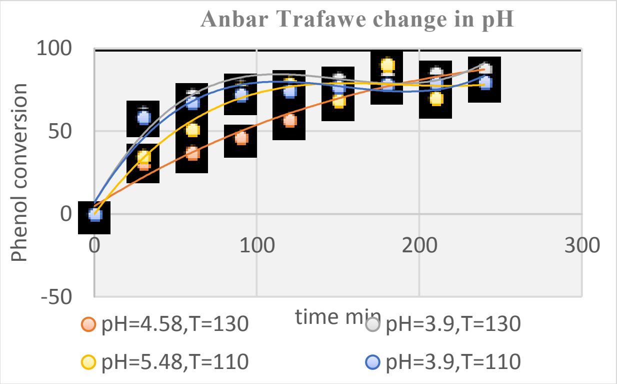

Figure 8: phenol conversion during 4hr in catalyst loading 7mg/l, pressure 1.5Mpa ،and٥٠٠ mg/l phenol concentration in Anbar

II. Effect of Temperature

The effect of the reaction temperature in the activity of the heterogeneous catalytic system was also studied. The result of Figure 9 shows that Erbil phenol conversion by using of air as oxidation and an initial pH of 3.9, which presented the same effect with all pillared clays region, the temperature is seen to be high effects evaluation of phenol removal, the results reveal that a temperature of 150ºC is necessary to obtain an appreciable phenol conversion along the process. The reaction rate is increasing gradually with time and more influence on the reaction rate is at a temperature of 150, Erbil has high value of phenol degradation rate then Mosul, Anbar, Baghdad, and Basrah, the highest rate of reaction phenol, from the result phenol conversion 96.2, 95.44, 93.7, 80, 76.3% for Erbil, Mosul, Anbar, Baghdad, Basrah, respectively.

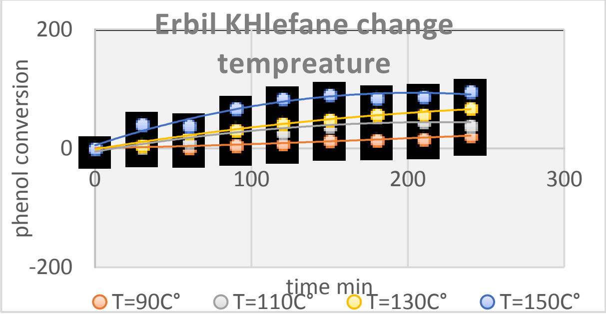

Figure 9: phenol conversion during 4hr in catalyst loading 7mg/l, pressure 2.5 Mpa, 500mg/l phenol concentration in Erbil

III. Effect of Phenol Concentration

The reaction rate change along the duration time, that effect on kinetic rate law, therefore, in this study investigates the initial phenol concentration in range 500-2000mg/l at 130C°, the result of Baghdad phenol conversion show in Figure 10 which presented the same effect with all pillared clays region, for five region, the Baghdad have high value of degradation phenol, the lower phenol conversion result show with high initial phenol concentration, the concentration solution as 2000mg/l, the pillared clay remained active in some region and completed mineralization after 4hr, and in another region uncompleted it as Al Anbar, deactivation appear on the surface of pillared clay during the CWO of phenol ,polymeric compounds can be formed and carbonaceous that deposited on surface of pillared prevent the adsorbs on catalyst active sites, these deactivation formed duo to acid sites on this catalyst. From the result phenol conversion 94.3, 93.4, 80, 70.68, 62%for Mosul, Anbar, Erbil, Basrah, Baghdad, respectively.

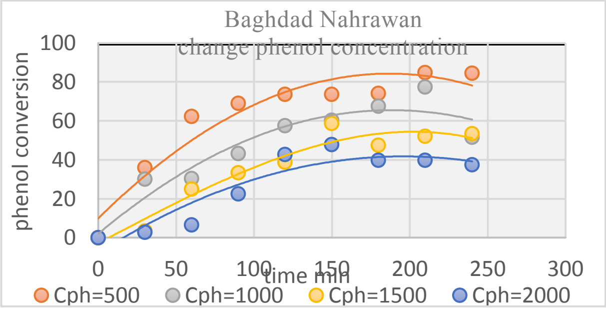

Figure 10: phenol conversion during 4hr in catalyst loading 7mg/l ،pressure 2.5Mpa, deferent phenol concentration in Baghdad

IV. The Air Pressure Effect

The air used for oxidation, and according to Henry's law the oxygen cannot be dissolved in the liquid phase, so that air should be maintained high pressure in the reactor to dissolved in this phase, the oxygen concentration in this reactor was considered equal to solubility in the pure water, the behaver of vapor phase as an ideal solution, the fugacity of the pure gas that means as the deviation from ideal gas, is evaluated the total pressure and temperature in the vapor phase, therefore the pressure air should exceed the vapor pressure of the liquid phase at temperature given, so that in this work to keep the wet oxidation in liquid phase at temperature between 90-150C° the vapor pressure range between 0.1-0.45Mpa, the oxygen capable to oxidation the phenol and substitute oxygen atom an aromatic ring to be quinine or dihydric phenol, and also capable to attract the phenol double bond of Carbone to form carboxylic acid, that represents the very low concentration in aqueous phase . The result of Basrah phenol conversion shown in Figure 11 which presented the same effect with all pillared clays region, for five regions, the Basrah have a high value of degradation phenol،

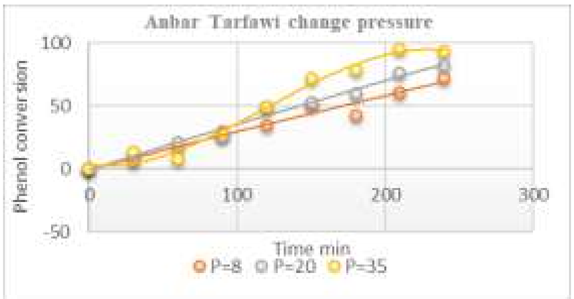

Figure11: phenol conversion during 4hr in catalyst loading mg/l, temperature 130C°, 500mg/l phenol concentration in Basra

V. Effect of Catalyst Loading

The different catalyst loading (0-5-8-10mg/l) investigate in this work to oxidation phenol at 110C° and 1.5 Mpa, that show result of Erbil in Figures 12 which presented the same effect with all pillared clays region, as conversion of phenol degradation during 4hr of reaction , from these result notes that unanalyzed loading lead gradually increased in phenol concentration during 4hr but considerable less than other value of catalyst loading ,as result the air or oxygen not significant on homogenous reaction but very effect on heterogeneous reaction to oxidation of phenol, during the heterogeneous reaction the phenol oxidation on active site that acidity but for all type of catalyst the deactivation not significant in this study, the catalyst load in Anbar and Basrah (8mg/ l) beater than in Mosul (10mg/l). From the previously show Mosul, Erbil, and Anbar was very active than Baghdad and Basrah. Therefore, the continuous study included this area only .

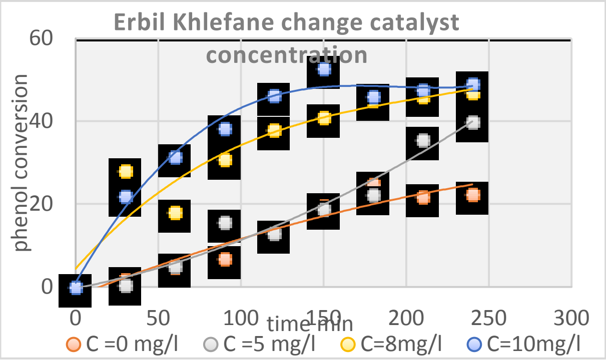

Figure 12: phenol conversion during 4hr in different catalyst loading, temperature 130C°, 500mg/l phenol concentration in Erbil

From these result show Mosul, Erbil and Al-Anbar have the higher ratio in the conversion of phenol than Baghdad and Basrah, so that these pillared of Mosul, Erbil, and Al-Anbar used in the study of hydrodynamic in packed bed reactor.in operation condition temperature 150ºC, pressure 3.2Mpa, Phenol load 500mg/l.

VI. Effect of operating parameter

a. *Effect of Liquid hourly space Velocity (LHSV)*

The liquid flow rate is commonly considered as an important factor due to its influence on the mass transfer and hydrodynamic parameters (liquid holdup, wetting efficiency), The packed beds in laboratory scale, used to match the LHSV of the commercial unit due to low liquid velocity is frequently, most of the upflow cases can be classified in the babble flow regime. The effect of LHSV on phenol concentration and removal rate for Anbar –Mosul, and Erbil is presented in Figure 13 and Figure 14.

Higher liquid flow rates give greater liquid hold up which decreases the contact of liquid and gas reactants at the active catalyst site, by increasing the film thickness, which leads to decrease the phenol conversion to CO_2 and water, at a pressure of 3.2 MPa and a temperature of 150C°. The effect of liquid superficial velocity on the axial phenol conversion profile is observed. Where gas flows through the liquid in bubble flow, a lower feed flow rate is preferred because the longer residence time will allow for complete phenol removal .

From result show the phenol conversion in Mosul have highest value reach to (97.8 %) at LHSV equal to 0.2hr-1 and gradually degrees to (10%) with LHSV increases to (0.8 hr-1), for the same reasons as the previous, the phenol conversion in Erbil reach to (98%) at (0.2hr-1), but in Anbar (95%) in the same LHSV.

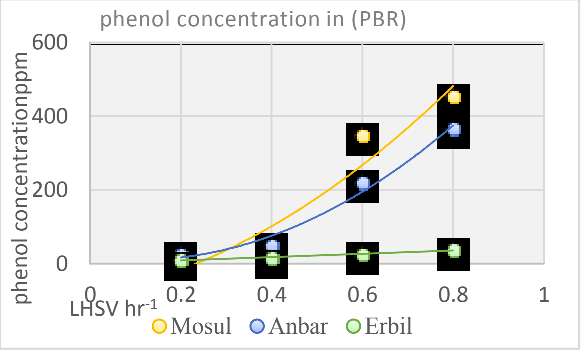

Figure 13: phenol concentration at different LHSV Pressure= 3.2 MPa, phenol=500 ppm and Gas flow=0.28 cm/s).

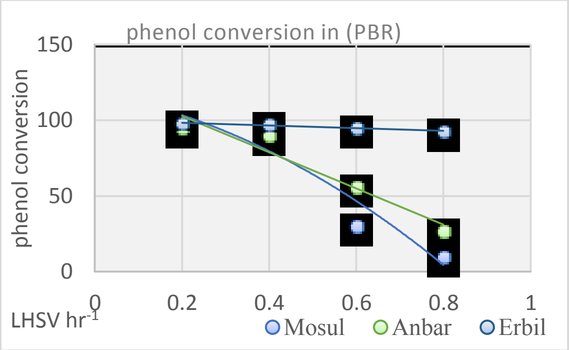

Figure 14: phenol conversion at different LHSV Pressure= 3.2 MPa, phenol=500 ppm, and Gas flow=0.28 cm/s).

b. *Effect of Gas Superficial Velocity*

The flow rate of air was increased the percent of phenol removal was increased when other variables are kept constant. In spite of that, increasing gas flow rate provides an enough quantity of air (oxygen) for /reactions of intermediate over active sites of catalyst forming other undesirable compounds like p-benzoquinone and maleic acids which were both detected in the brownish colored liquid effluent at a high concentration, Whatever the case may be, the conversion of phenol favor increase in air flow rate but, at low gas velocities. The flow regime was bubble flow but, when the flow rates of liquid and gas increased and has no or little effect on removal of phenol could be explained by the flow approached pulsing flow in both directions, since the hydrodynamics were mainly governed by inertial force, and the flow direction dose not play a role any more [21], However, operation in pulsing flow is not always practical in industrial reactor due to higher pressure drop and shorter residence time of the liquid which leads to lower conversion per unit reactor length [18].

Figure 15 shows the phenol concentration, but Figure 16 show increasing the gas velocity Couse to increases the phenol conversion at a constant LHSV at high reactor pressure. The gas velocity very dependence on gas- liquid and liquid-solid mass transfer coefficients that in linearly increase [٢٢]. From result show the Mosul has highest conversion of phenol reach to (98.7%) at LHSV equal to 0.6hr-1 and gradually degrease to (97.43%) with constant LHSV, For the previously reasons, the Anbar Figures show the higher conversion of phenol reach to (98%) at gas superficial velocity equal to 0.8hr-1 and gradually degrease to (35%) with gas superficial velocity decreases. In Erbil show the higher conversion of phenol reach to (96.7%) at a superficial gas velocity equal to 0.8hr-1 and gradually decreases to (96.5%), for the same reasons as the previous.

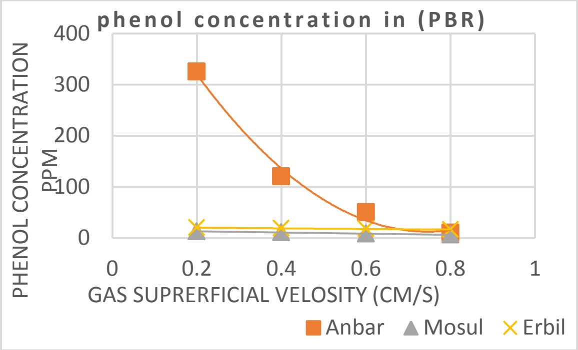

Figure 15: Effect of gas velocity on phenol concentration at LHSV=0.6hr-1.

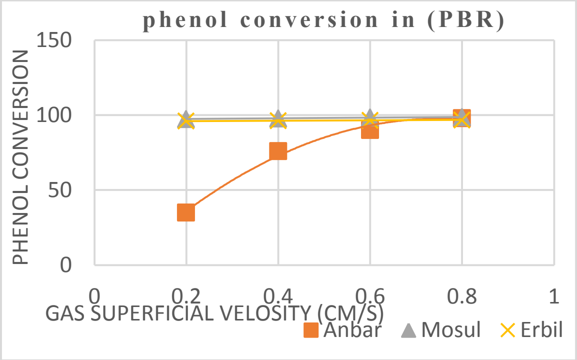

Figure 16: Effect of gas velocity on phenol conversion at LHSV=0.6hr-1

V 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 correlation cited in Table 2.

V-1 Reactant limitation

A criterion was developed by [26]. Equation (1) was used to diagnose the operation mode (reactant limiting):-

$$\gamma = \frac{D^{eff}_{ph,L}\, C_{ph,L}}{b\, D^{eff}_{O2}\, C_{O2,L}} \qquad (1)$$

The criterion depend upon the type of reactant limitation that was developed by [26] in equation (1). That used to performance the PBRs, and the result of these reactant limitation shown Table 3 (4) (5) for (Anbar, Erbil, Mosul) respectively, the limiting reactant of reaction If $\gamma >>1$, the reaction will be limited by the gas reactant; if $\gamma <<1$, it will be limited by the liquid. Based on the employed operating conditions, from the result for all region (Anbar, Erbil, and Mosul) show the reactant of reaction $\gamma <<1$, so that the reaction in liquid phase.

V-2 Interface mass transfer (external diffusion)

The possibility of external mass transfer limitations of oxygen.To this purpose, the α_{gl} , αls and C_m (Mears, criteria) were well-defined in Equations (2), (3) and (4) for (Anbar, Erbil, Mosul) respectively, that calculated in the following way [27] were used to determine external diffusion limitation from bulk gas to bulk liquid and from bulk liquid to bulk solid (Catalyst)

$$\alpha_{gl} = \frac{r_{obs}\,\rho_b}{(K_{gl}\,a)_{O2}C_{ph}} < 0.05 \qquad (2)$$

$$\alpha_{ls} = \frac{r_{obs}\,\rho_b}{(K_{ls}a_s)_{O2}C_{ph}} < 0.05 \qquad (3)$$

$$C_m = \frac{-r_{Aobs} * \rho_p\,(\frac{d_p}{6})^2}{D_{eff.A} * C_A} < 0.15 \qquad (4)$$

The result of solid – liquid K_{ls}, gas–liquid K_{gl} and C_m (Mears, criteria) mass transfer coefficient values were obtained by using [28] for various operating condition correlation see the result in the Table (6 , 7, Table 8) show the result of gas–liquid K_{gl} , Table (9, 10, and 11) shows that the result of solid- liquid K_{LS}. Table (12, 13, and 14) illustrate that Mears, criteria (C_m) for all region (Anbar, Erbil, and Mosul) respectively. The result of PBR show that the mass transfer limitation for all region, so that can be neglected it, also the rate may be intra particle diffusion controlled either the surface reaction controlled.

Table 2: Correlation for transport parameters

Henry's constant: [23].	In (He_{O2}/ MPa) =-35.4408 +5.5897*10^4/T -2.6721 *10^7/ T^2 + 5.8095 *10^9/ T^3 -4.9167 *10^{11} /T^4
Effective diffusivity [24]	$D_e = \frac{\varepsilon}{\tau}\, D_m$
Diffusivity in liquid phase [24] (bulk diffusivity)	$D_{AB} = 7.4 * 10^{-8} (\frac{\Phi B\, M^{0.5}_{wt.B} * T}{\mu_B\, V_A^{0.6}})$
Mass Transfer Coefficients [25]	$\frac{K_{gl}\, d_P}{D_{O2L}} = 25.1\, Re_L^{\ 0.45} Sc_{O_2L}^{\ 0.5}$

	$\frac{K_{sl}\, d_P}{D_{PhL}} = 3.77\, Re_L{}^{0.8} Sc_{Phl}{}^{1/3}$

Table 3: The limited reactant of the reaction for Anbar

	liquid superficial velocity			**gas superficial velocity**	
Concentration mg/l	**(C_{Ph}) Phenol concentration kmol/m^3**	**γ for Anbar**	**Concentration mg/l**	**Phenol concentration kmol/m^3**	**γ for Anbar**
		Temperature 150 ºC			**Temperature 150 ºC**
		32bar			32bar
500	0.005319149	0.104526361	500.00000	0.005319149	0.104526362
325	0.003457447	0.067942134	359.999978	0.003829787	0.075258975
120	0.001276596	0.025086327	289.999964	0.003085106	0.060625282
50	0.000531915	0.010452636	100.0000	0.00106383	0.020905276
10	0.000106383	0.002090527	70.000014	0.000744681	0.014633693

Table 4: Tlimited reactant of the reaction for Erbil

	liquid superficial velocity			**gas superficial velocity**	
Concentration mg/l	**(C_{Ph}) Phenol concentration kmol/m^3**	**γ for Erbil**	**Concentration mg/l**	**(C_{Ph}) Phenol concentration kmol/m^3**	**γ for Erbil**
		Temperature 150 ºC			**Temperature 150 ºC**
		32bar			**32bar**
500	0.005319149	0.237114112	500	0.005319149	0.23711411
20.14	0.000214255	0.009550956	36.37	0.000386915	0.01724768
18.58	0.0001976	0.00881116	25.2	0.000268085	0.01195055
17.5	0.00018617	0.008298994	14.64	0.000155745	0.00694270
16.3	0.000173404	0.00772992	10.05	0.000106915	0.00476599

Table 5: The limited reactant of the reaction for Mosul

	liquid superficial velocity			**gas superficial velocity**	
Concentration mg/l	**(C_{Ph}) Phenol concentration kmol/m^3**	**γ for Erbil**	**Concentration mg/l**	**(C_{Ph}) Phenol concentration kmol/m^3**	**γ for Erbil**
		Temperature 150 ºC			**Temperature 150 ºC**
		32bar			**32bar**
500	0.005319149	0.237114112	500	0.005319149	0.23711411
20.14	0.000214255	0.009550956	36.37	0.000386915	0.01724768
18.58	0.0001976	0.00881116	25.2	0.000268085	0.01195055
17.5	0.00018617	0.008298994	14.64	0.000155745	0.00694270
16.3	0.000173404	0.00772992	10.05	0.000106915	0.00476599

All the result for all-region <<1 the reaction will be in the liquid.

IX. Interface mass transfer (external diffusion)

The possibility of external mass transfer limitations of oxygen.To this purpose, the α_{gl} , αls and C_m (Mears, criteria) were well-defined in Equations (2), (3) and (4) for (Anbar, Erbil, Mosul) respectively, that calculated in the following way [27] were used to determine external diffusion limitation from bulk gas to bulk liquid and from bulk liquid to bulk solid (Catalyst)

$$\alpha_{gl} = \frac{r_{obs}\, \rho_b}{\left(K_{gl}\, a\right)_{O2} C_{ph}} < 0.05 \qquad (2)$$

$$\alpha_{ls} = \frac{r_{obs}\, \rho_b}{(K_{ls} a_s)_{O2} C_{ph}} < 0.05 \qquad (3)$$

$$C_m = \frac{-r_{Aobs} * \rho_p \left(\frac{d_p}{6}\right)^2}{D_{eff.A} * C_A} < 0.15 \qquad (4)$$

The result of solid – liquid K_{ls}, gas–liquid K_{gl} and C_m (Mears, criteria) mass transfer coefficient values were obtained by using [28] for various operating condition correlation see the result in the Table (6, 7, Table 8) show the result of gas-liquid K_{gl} , Table (9, 10, and 11) show that the result of solid-liquid K_{LS}. Table (12, 13, and 14) illustrate that Mears, criteria ($C_{m)}$ for all region (Anbar, Erbil, and Mosul) respectively.

The result of PBR shows that the mass transfer limitation for all region, so that can be neglected, also the rate may be intra particle diffusion controlled either the surface reaction controlled.

Table 6: Interface mass transfer (external diffusion) for Anbar

C_{ph}	r_{obs}	α_{gl}
0.005319	3.51125E-06	0.000179434
0.003457	2.32198E-06	0.000182552
0.001277	8.92204E-07	0.000189975
0.000532	3.85001E-07	0.000196745
0.000106	8.21203E-08	0.000209828

Table 7: Interface mass transfer (external diffusion)for Erbil

C_{ph}	r_{obs}	α_{gl}
0.005319149	3.51125E-06	0.002426464
0.004830851	3.20122E-06	0.002435828
0.003709574	2.4843E-06	0.002461697
0.000204894	1.54071E-07	0.002764053
0.00011383	8.76312E-08	0.00282981

Table 8: Interface mass transfer (external diffusion) for Mosul

C_{ph}	r_{obs}	α_{gl}
6.8617E-05	5.39048E-08	0.000473841
8.5234E-05	6.63807E-08	0.000469748
0.000115426	8.88102E-08	0.000464085
0.000115426	1.04471E-07	0.000460955
0.005319149	3.51125E-06	0.000398159

Table 9: Mass Transfer Coefficients for Anbar

C_{ph}	r_{obs}	α_{ls}
0.005319	3.51125E-06	8.71592E-7
0.003894	2.60251E-06	8.82537E-7
0.00234	1.59653E-06	9.0069E-7
0.000532	3.85001E-07	9.55682E-7
0.000266	1.97912E-07	9.8255E-7

Table 10: Mass Transfer Coefficients for Erbil

[	r_{obs}	α_{ls}
0.005319149	3.51125E-06	1.17865E-05
0.000386915	2.83638E-07	1.30892E-05
0.000271277	2.01711E-07	1.32764E-05
0.000155745	1.18405E-07	1.35744E-05
0.000106915	8.25144E-08	1.37802E-05

Table 11: Mass Transfer Coefficients for Mosul

C_{ph}	r_{obs}	α_{ls}
0.005319149	3.51125E-06	1.93404E-06
0.004830851	3.20122E-06	1.9415E-06
0.003709574	2.4843E-06	1.96212E-06
0.000204894	1.54071E-07	2.20312E-06
0.00011383	8.76312E-08	2.25553E-06

All the result for all-region <<0.05 the reaction will be in the liquid.

Table 12: Mass Transfer Coefficients for Anbar

C_{ph}	r_{obs}	Cm
0.005319	3.51125E-06	0.008410454
0.003894	2.60251E-06	0.008516065
0.00234	1.59653E-06	0.008691232
0.000532	3.85001E-07	0.009221879
0.000266	1.97912E-07	0.009481142

Table 14: Mass Transfer Coefficients for Mosul

C_{ph}	r_{obs}	Cm
0.005319149	3.51125E-06	1.76029E-07
0.004830851	3.20122E-06	1.45754E-07
0.003709574	2.4843E-06	8.68578E-08
0.000204894	1.54071E-07	2.97529E-10
0.00011383	8.76312E-08	9.40146E-11

Table 13: Mass Transfer Coefficients for Erbil

C_{ph}	r_{obs}	Cm
0.005319149	3.51125E-06	2.54888E-06
0.000386915	2.83638E-07	2.8306E-06
0.000271277	2.01711E-07	2.87109E-06
0.000155745	1.18405E-07	2.93553E-06
0.000106915	8.25144E-08	2.98004E-06

All the result for all-region <<0.15 the reaction will be in the liquid.

X. Intra particle diffusion (internal diffusion)

The internal diffusion limitations calculation by wisze-prater criterion modified and used n-order reactions as used by [29]:

$$\Phi = \frac{(r * \rho_b)_{obs} {L_p}^2}{C_{ph_0} {D_{ph}}^{eff}} \ll \frac{2}{n+1} \tag{5}$$

If Φ << 2/ (n+1) it can be considered that internal diffusion limitations can be neglected. The results can be shown in Table (15, 16, and 17) for three regions (Anbar, Erbil, and Mosul) respectively, from these tables it can be seen that the Φ values are law. Thus internal mass transfer resistances should have only a slight influence. Again, due to the higher reaction rates at saturation condition the criteria exhibit higher values. In conclusion, the result for all regions are limited and established for the absence of the internal diffusion contribution to the overall reaction rate.

Table 15: Intra particle diffusion (internal diffusion) for Anbar

C_{ph}	r_{obs}	Φ_{ls}	< limitation
0.005319	3.51125E-06	3.15142E-08	1.25
0.003894	2.60251E-06	3.19099E-08	1.25
0.00234	1.59653E-06	3.25663E-08	1.25
0.000532	3.85001E-07	3.45546E-08	1.25
0.000266	1.97912E-07	3.55261E-08	1.25

Table 16: Intra particle diffusion (internal diffusion) for Erbil

C_{ph}	r_{obs}	Φ_{ls}	< limitation
0.005319149	3.51125E-06	4.78609E-08	1.21212
0.000386915	2.83638E-07	5.31508E-08	1.21212
0.000271277	2.01711E-07	5.3911E-08	1.21212
0.000155745	1.18405E-07	5.51211E-08	1.21212
0.000106915	8.25144E-08	5.59568E-08	1.21212

All the result for all-region << 1.25, 1.21212, 1.27388 the reaction will be in the liquid.

XI. Axial Dispersion

Axial dispersion and mildiscerption is another criterial have a negative effect on reactor conversion, in this study work, the correct choice of particle and reactor geometry such effects greatly reduced by (Z = 0.6 m, D_R= 0.2 m and d_p= 0.002 m). The relevant criteria of $Z/d_p$and D_R/d_pTake values of 300 and 10, respectively, which match the critical value of , 50 and 10 respectively, established for safe operation [30]. Some criteria should be calculated to performance of the PBRs, the result shown in Table (18, 19, and 20) for (Anbar, Erbil, Mosul) respectively.

$$\left|\frac{(-r_{A\,obs}*dp_p*\rho_p}{U_0*C_{ABb}}\right| \ll \left|\frac{U_0*dp_p}{D_{ax}}\right| \qquad 6$$

The calculated axial dispersion coefficient for all-region have high than limitation, which ensures the present of axial dispersion in this research.

Table 17: Intra particle diffusion (internal diffusion) for Mosul

C_{ph}	r_{obs}	Φ_{ls}	< limitation
0.005319149	3.51125E-06	7.60406E-08	1.27388
0.004830851	3.20122E-06	7.63341E-08	1.27388
0.003709574	2.4843E-06	7.71448E-08	1.27388
0.000204894	1.54071E-07	8.662E-08	1.27388
0.00011383	8.76312E-08	8.86807E-08	1.27388

Table 18: Axial Dispersion for Anbar

Phenol Axial Dispersion for liquid limit	< limitation	Phenol Axial Dispersion for gas limit	< limitation
0.001873	0.000309346	0.004012	0.109331
0.001896	0.000309346	0.004062	0.109331
0.001936	0.000309346	0.004146	0.109331
0.002053	0.000309346	0.004398	0.109331
0.002111	0.000309346	0.004522	0.109331

Table 19: Axial Dispersion for Erbil

Phenol Axial Dispersion for liquid limit	< limitation	Phenol Axial Dispersion for gas limit	< limitation
0.001873	0.000309346	0.004012	0.109331
0.00208	0.000309346	0.004455	0.109331
0.002109	0.000309346	0.004519	0.109331
0.002157	0.000309346	0.00462	0.109331
0.002189	0.000309346	0.00469	0.109331

All the result for all-region >> 0.000309346 the reaction will be not limited with liquid velocity. All the result for all region << 0.109331the reaction will be limited with gas velocity.

Table 20: Axial Dispersion for Mosul

Phenol Axial Dispersion for liquid limit	< limitation	Phenol Axial Dispersion for gas limit	< limitation
0.001873	0.000309346	0.004012	0.109331
0.00188	0.000309346	0.004027	0.109331
0.0019	0.000309346	0.00407	0.109331
0.002133	0.000309346	0.00457	0.109331
0.002184	0.000309346	0.004678	0.109331

4. Conclusions

Five types of AL-Fe pillared clay based on clays regions (Anbar- Mosul- Basrah- Baghdad- and Erbil) have been tested for phenol oxidation with air. Different conditions temperature, pressure, phenol loading), and catalyst loading, using phenol as target compound, in batch reactor found that phenol degradation would be enhanced by increasing temperature, pressure, pillared load and degrease in phenol load. High degradation rate of phenol of about 97 % was obtained at optimum conditions(pH= 3.9,temperature=130°C, oxygen partial pressure = 3.2 MPa, and phenol concentration = 500 mg/l). Also showed that the best catalysts used in the decomposition of phenol in CWAO are Mosul and Erbil and Anbar, Baghdad and Basrah on Respectively. These results are shown with these best operating conditions that used in experimental packet bed reactor the Anbar pillared unstable and Mosul pillared consider more stable and activity than Erbil. The highest phenol conversion reach to (98%) in Erbil, 97.8 % in Mosul, and in Anbar (95%) in the (0.6hr^{-1}) LHSV, temperature 150°C, superficial gas velocity (0.28cm/s), and initial phenol concentration 500mg/l. The operation mode of (mass transfer, intra particle diffusion, internal diffusion, and axial dispersion) was a limitation for all regions, so that can be neglected it; also the rate may be intra particle diffusion controlled either the surface reaction controlled.

Notation

D_e	effective diffusivity	D_m	molecular diffusivity
T	Temperature	μB	Viscosity of solvent B, (Cp or gm /cm.s)
d_p	Particle diameter	D_{phL}	diffusivity of phenol to liquid
Sc_{o2L}	Schmidt number for oxygen to the liquid	K_{gl}	diffusivity of gas to liquid
M_{wtB}	the molecular weight of solvent B (O2)	ΦB	Association factor for the solvent =2.6 for water as a solvent
Re_l	Reynold number	Sc_{phl}	Schmidt number For phenol to liquid
ε , τ	ε and τ is porosity is the pore-path tortuosity	νA	solute molar volume at its normal boiling (cm3/mol)
K_{Sl}	mass transfer coefficient	D_{AB}	Diffusivity of solute A in very dilute solution in solvent B, (cm2/s)
D_{o2l}	diffusivity of oxygen to the liquid		

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