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Performance enhancement of trickle bed reactor for the removal of organic compounds from petroleum industrial wastewater.

S A Al-Naimi, F T Al-Sudani, G D A Al-Rawi

Chemical Engineering Department, University of Technology, Baghdad, Iraq

Corresponding author's e-mail address: 80028@uotechnology.edu.iq

Abstract. Catalyst Wet Air Oxidation of phenol Promoted with Hydrogen Peroxide (PP-CWAO) was studied experimentally in this work using a trickle bed reactor operating in both steady state and periodic operation (liquid flow modulation). The effect of cyclic parameters (cycle period and split) are investigated under the same conditions chosen on the basis of the steady state results for PP-CWAO. The results showed that the PP-CWAO of phenol are kinetically controlled for steady state operation. For periodic operation, the time average conversion enhancement is indeed quite considerable in liquid flow modulation as split is lowered from steady state cycle split (σ =1) to a value of (σ =0.5) and reached as much as 6.66 % over the steady state at cycle period (τ_p) = 15 sec.

1. Introduction

Wastewater from a petroleum refinery usually contains hazardous chemicals, as hydrocarbons and phenols. The chemical composition and concentrations of phenolic compounds, even if small, have an undesirable effect on the environment as well as dangerous to human health. Effluents with medium to high phenolic loadings must be subjected to a pre-treatment process that may involves a conventional biological treatment. Catalytic wet air oxidation (CWAO) is an important process for the treatment or pre-treatment of wastewaters with phenolic content because of its high removal [1-5]. Moreover, a set of strategies, such as chemical oxidation, coagulation, biological treatment physical adsorption, and electro-catalytic oxidation technology, have been used in the removal of phenol from liquid effluent [4,6]. All stated processing can be applied individually or combined with other processes to develop the treatment efficiency.

There are considerations that must be taken into account when treating wastewater in any selected method, namely toxicity, concentration and loading of pollutants in the energy requirements of the waste stream and / or the economic aspects and the level of mineralization required [7-12].Of between it, Wet Air Oxidation (WAO) is a beneficial technology because it can be applied to treat wastewaters with organic loads that are as high as (10–100 gm/Liter COD); in addition, at high flow rates toxic contaminants can be treated with this method if high pressures (0.5–20 MPa) and temperatures(125–320 °C) are used , despite that this method does not require high operation costs and does not result in

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any type of pollution in the air, its commercial use is not possible due to the high capital investments required for such process and the requirement of high pressure and temperature for high removal of organic materials [4-7]. The previously mentioned requirements all have driven the attention away from the (WAO) to the more efficient method which is the catalytic wet air oxidation (CWAO) which is a method that was distinguished by operating conditions that are lower than those required in the (WAO) due to the use of a catalyst and this also resulted in reducing the residence time required to achieve an acceptable percentage of organic materials removal from wastewaters which in result reduced the operating cost by half; in addition, if the CWAO method was conducted in a FBR, the separation stage can be excluded[4, 13-14]. From literature review, we can extract some conclusions that are relevant to the work on the CWAO of phenol concern on the obtained durable and efficient catalysts and determine the optimal process conditions at which the process can be done effectively for treating phenolic wastewaters [15]. Also, studied the kinetic of mineralization rate of CWO of phenol [16-17]. Singh et al.,[18], Guo et al.,[19] and Fadel et al.,[20-21] demonstrated the interaction of mass transfer with reactor hydrodynamics and kinetics for CWAO of phenol.

The present H2O2 increased catalytic Wet Oxidation (PP-CWAO) process and biodegradability of phenolic aqueous solution [22-28]. Since 1989, there are numerous studies on the liquid flow interruption(periodic) operation to unveil the transient behavior of cyclic trickle bed reactor (TBR). Tukac et al., [29] found that if the period length of CWAO of phenol was comparable with an effective liquid residence time and thus phenol conversion in wet oxidation was about 10% more than that aquired at steady state operation. Massa et al., [30], observed that the ON-OFF mode liquid flow modulation (slow-mode cycling) had just a small impact on CWAO of phenol conversion but more effect on selectivity to total mineralization, particularly at longer cycle period. The effect of gas feed flow and/or gas composition modulation on activated carbon performance in phenol wet air oxidation also studied [31-32].

Only a few works have been dedicated in the literature for periodic operation of gas and/or liquid flow rate and composition utilized for the removal of phenol in TBRs by CWAO. Austere experimental effort is necessary and needed, to recognize the phenomena of periodic operation in order to organize a direction for commercial achievement. The present study continued to study further points utilizing the advantages associated with periodic operation of catalytic wet air oxidation promoted with H2O2 (PP-CWAO) to improve the mass transfer characteristics of the limiting reactant and catalyst utilization which are the most attractive features of trickle bed reactors and in PP-CWAO of phenol.

2. Experimental work

The continuous promoted CWAO of phenol with hydrogen peroxide was conducted in a TBR as shown in Figure.1. The reactor is a 0.018 m inside diameter stainless steel tube that is 0.76 m length and thickness of 2 mm enough to operate at a pressure up to 2.5 MPa (25 bar), packed with 70 gm of (0.5% Pt/Al2O3) catalyst particles. The reactor is constructed of two parts with stainless steel flange welded on each end. Characteristics of the bed and catalyst specification, material used through the experiments and operating conditions are given in Tables 1 and 2. The operating conditions used during the experiments cover trickle to pulse flow regimes, as shown in Figure.2. a stainless steel screen with appropriate mesh openings was put at the bottom of the reactor to keep the packing and prevent catalyst loss and bed flooding. Uniform radial liquid distribution was ensured by using a 0.2 m of pre-packing of 2 mm glass beads that was put ahead of the catalyst pack ,

Then a 0.35 m catalyst bed which is comprising of 0.5%Pt/Al2O3 particles and finally a 0.21 m of glass beads as post-packing to support the catalyst bed and this will result in the overall pack which was 0.76 m. An electric heater was used as an external heat source to heat the reactor while the bed temperature was controlled within ±3˚C by (DT109A-230VAC-R) through and on-off type regulator that adjusted the heat supply to the external heater. Three (type T) thermocouples were placed at different positions along the length of the reactor. The pressure inside the reactor was measured by pressure taps at the head of the reactor.Two (Dose pump, DDE6-10B-PVCLVLC-X311001FG, Italy) were used to supply the phenol and hydrogen peroxide solutions into the pre-heater where the two solutions were sufficiently

heated and mixed. The periodic flow modulation was obtained by using two solenoid valves (EVR 15, Danimark) connected through liquid delivery line which were used to switch between steady flow and flow modulation required under change ful condition.

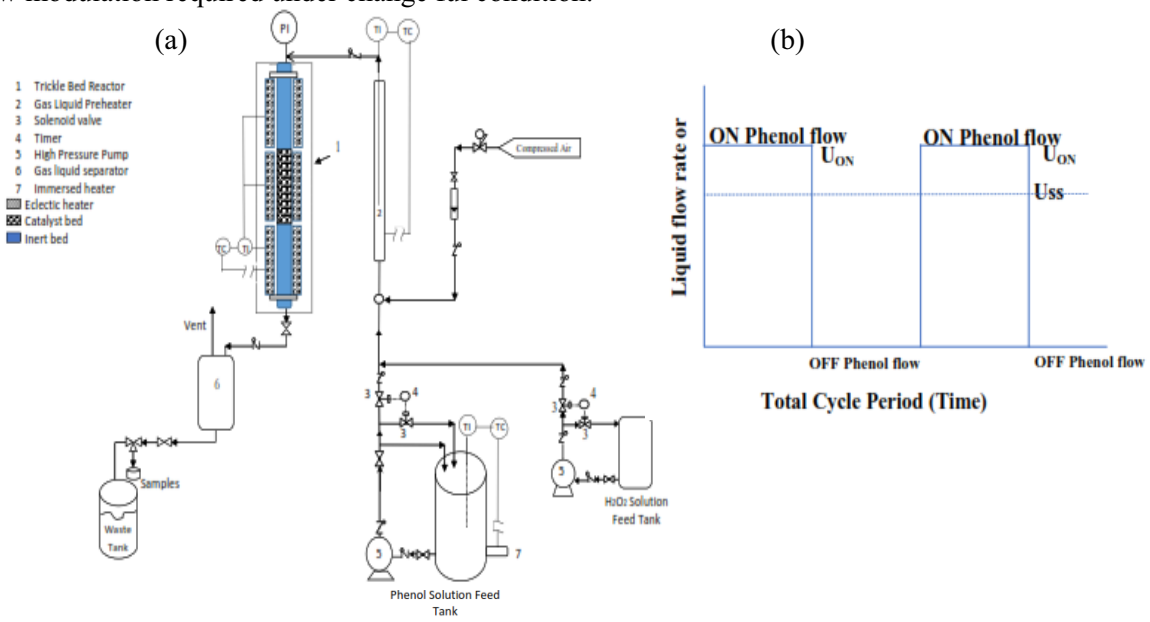


Figure 1. Experimental Setup for steady state and unsteady state experiment
a) experimental setup, b) ON-OFF liquid flow modulation arrangement

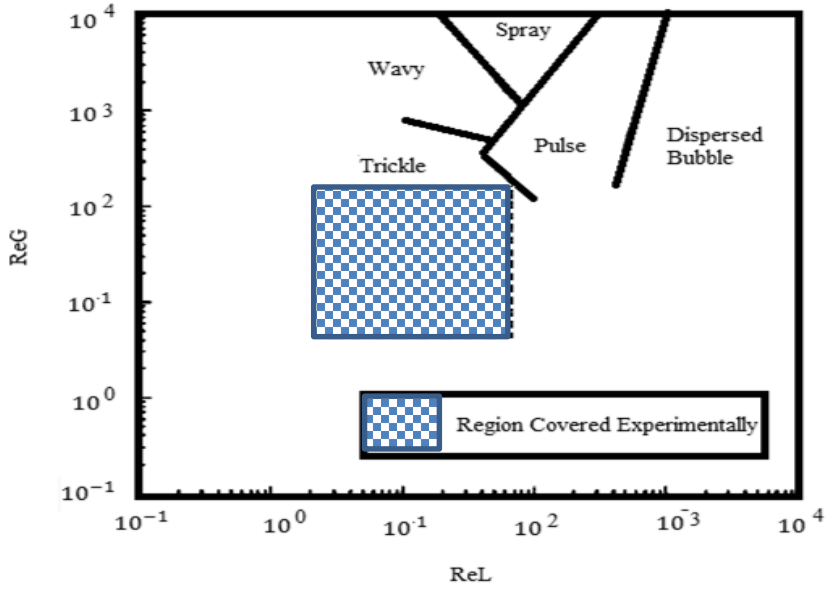


Figure 2. Flow region map [33-34].

The solenoid valves were dominance by an electronic timer (2TIL GARANTILIDIR) which supplied the cycle period and split data were.The exodus solutions from the reactor go through the gas-liquid line separator and then split into a sampling stream and a waste stream. The sampling stream was linked to a needle valve for withdrawal of samples to be tested. To prevent pressure build in the gas and liquid delivery and exit stream pressure indicator and safety valve were installed, also to assure the flow in one direction, one-way valve was located in gas and liquid line.During the pulse time (ON), the liquid

was allowed to reach the reactor through the first solenoid valve. While during the base time (OFF), it was recycled to the feed tank through the second solenoid valve, so that the pump operation remained unaffected. The performance enhancement conversion was evaluated to identify the degree of improvement over the steady state operation [29-30]: -.

$$\text{Enhancement Conversion} = \frac{\text{Average Conversion(Un} - \text{steady state)}}{\text{Conversion(Steady state)}} \quad (1)$$

Table 1. Catalyst, reactor and material characteristics.

Reactor characteristics		Phenol characteristics	
Reactor diameter m (I.d)	0.018	Color	White
Wall Thickness m	0.002	Molecular weight, (gm/gmol)	94.11
Total length m	0.76	Chemical structure	C_6H_6O
Pre packing depth m	0.2	Purity, (%)	99.5
Post packing depth m	0.21	Freezing point, ºC	40-41
Type of inert bed(Glass bead)	0.2m.		White
Catalyst characteristics		Hydrogen peroxide characteristics	
Active metal	0.5%Pt	Colorless in solution	
Catalyst support	γ-Al_2O_3	Molecular weight, (gm/gmol)	34.01
Particle shape	Sphere	Chemical structure	H_2O_2
Particle diameter (cm)	0.16	Purity, (%)	50
Surface area($\mathbf{m^2}$/gm)	250	Boiling point (ºC)	150.2
Pellet density(gm/$\mathbf{cm^3}$)	0.56		34.01
Boiling point (ºC)	150.2		

Table 2. Range of operating condition for steady and unsteady state experiments.

Operating Conditions	Liquid flow modulation
Pressure, P (bar)	1
Oxygen partial pressure, P (bar)	0.021
Inlet phenol concentration, Cph,o (g/L)	1.35
Bed temperature, T (˚C)	80
Inlet hydrogen peroxide concentration %	35%
Liquid flow rate (phenol solution), FL ,ph(L/h)	0.224
Superficial liquid velocity(phenol solution); uL (m/s)	0.000245
Gas flow rate, FG(NL/h)	150
Superficial gas velocity, uG (m/s)	0.163
hydrogen peroxide flow rate, FL , H2O2 (L/h)	0.099
Superficial liquid velocity (H2O2 solution); uL (m/s)	0.00011
LHSV, (h-1)	1.16
Space time, (h) τ	0.86163

Cycle time (period), (Sec) τ_p	5 - 180
Cycle split (ON flow fraction) **σ**	0.2, 0.5, 0.7

3. Theoretical aspect

3.1. Reactant limitation

The overall reaction for the complete oxidation (mineralization) of phenol to inorganic product proceeds as: -

$$C_6H_6O + 7O_2 \rightarrow 6CO_2 + 3H_2O \quad (2)$$

For the study of CWO of phenol in TBR, it is an important information to determine in which phase-gas or liquid-the limiting reacting is in under the operating conditions in order to choose the appropriate reactor configuration (steady state and/or periodic operation). According to Beaudry et al., [35], the criterion was particularly useful to diagnose the gas and liquid reactant limitation.

$$\gamma = \frac{D_{e_B} C_B}{\nu D_{e_A} C_A^*} \quad (3)$$

If $\gamma > 1$ the reaction is gas limited reactant.
$\gamma < 1$ the reaction is liquid limited reactant.

Where ν stoichiometric coefficients of oxygen, De_A , De_B effective diffusivity of species A and B component in the catalyst m^2/s, C_B concentration of liquid reactant kmol /m^3 , C_A^* equilibrium concentration of gaseous reactant in liquid phase kmol /m^3 ,

3.2 External mass transfer (interface)

The possibility of external mass transfer limitations of oxygen has to be addressed prior to any kinetic analysis of the obtained results. For this purpose, α_{gL} *and* α_{LS} ,and Mears' criterion (C_m) were used to diagnose the external diffusion limitation from the bulk gas phase to the bulk liquid phase, from the bulk liquid phase to the catalyst surface , and from the bulk gas phase to the catalyst surface [17,36] :-

$$\alpha_{gL} = \frac{(-r_A')_{obs} \rho_p}{(k_{gL}a)_{O_2} C_A^*} \leq 0.05 - 0.1 \quad (4)$$

$$\alpha_{LS} = \frac{(-r_A')_{obs} \rho_p}{(k_{Ls}a)_{O_2} C_A^*} \leq 0.05 - 0.15 \quad (5)$$

$$C_m = \frac{(-r_A')_{obs} (d_p/2) \rho_p \ n}{(k_{gs})_{O_2} C_{Ab}} < 0.15 \quad (6)$$

According to these criteria the external mass transfer can be neglected when α_{gL} *and* $\alpha_{LS} \leq 0.05 - 0.1$, *and* $C_m < 0.15$. Where a interfacial area m^2/m^3, $r_{A_{obs}}'$ observed reaction rate kmol/kg_{cat}.h, C_{Ab} bulk reactant concentration kmol/m^3, k_{gL} gas-Liquid mass transfer coefficient m/s , k_{Ls} liquid-solid mass transfer coefficient m/s , k_{gs} gas-solid mass transfer coefficient m/s, n reaction order, ρ_p particle density kg/m^3.

3.3. Intra particle diffusion (internal diffusion)

The internal diffusion limitation was estimated by using modified Weisz-Prater criterion for nth order reaction [17,36,38]:

$$\varphi = \frac{(-r_A')_{obs} \, dp^2 \, \rho_p}{36 \, D_{e_A}} \ll \frac{2}{n+1} \quad (7)$$

If $\varphi \ll \frac{2}{\beta+1}$ it can be considered that the internal diffusion limitations can be neglected. The present work will be considered as nth order reaction [37-38]. Where dp particle diameter m.

3.4. Axial dispersion

Liquid misdistribution (channeling, wall flow) and Axial dispersion can reduce the obtained conversion. According to the Young and Finlayson Criterion [42], the axial dispersion /diffusion can be neglected when: -

$$\left|\frac{(-r_A^{'})_{obs}\, dp_p\, \rho_p}{U_0\, C_{A_b}}\right| \ll \left|\frac{U_0\, dp_p}{D_{a_x}}\right| \quad (8)$$

Where D_{ax} Dispersion Coefficient m^2/s , Uo initial Liquid velocity m/s

4. Results and discussions

4.1. Kinetic regime and reactor performance

The performance of the TBRs depend upon the type of reactant limitation used, the results of the diffusion fluxes (γ) of both reactants from Eq.(2) are shown in Table 3. It can be noticed that the results of the diffusion fluxes (γ), confirms that the oxygen is the limiting reactant (near - liquid-limited reactant) in our operating conditions. Furthermore, the liquid phase oxygen concentration which has a value of about (1.71) $*10^{-4}$ kmol/m^3 was 29 times lower than the initial phenol concentration (8.92-16)$*10^{-3}$ kmol/m^3.

Table 3. Values of diffusion fluxes (γ)

C_{phenol}^0		γ
ppm	(kmol/ m^3)	
1350	0.0144	3.742

Table 4 shows the results of α_{gL} *and* α_{LS} and Mears' criterion for the external mass transfer limitations of oxygen , it can be noticed that the gas liquid mass transfer limitation slightly influences in the performance of TBR. However, as the reactor operates under partial wetting conditions, the direct gas - solid mass transfer will further diminish the weak influence of gas – liquid mass transfer limitations.

Table 4. External mass transfer limitations

LHSV h^{-1}	$-r_{Phénol}^{'}$ $*10^5$ kmol/kg .h	$\mathbf{k_{gL}}$ a (s^{-1})	$\mathbf{k_{Ls}\,a}$ (s^{-1})	$\mathbf{k_{gs}}$ (m/s)
1.16	1.233	0.041	1.613	0.00275
		α_{gL}	α_{LS}	$\boldsymbol{C_m}$
		0.117	0.0029	0.00072

As shown in table 5, the overall rate of reaction was found to be free from the effects of internal diffusion as the results falls within the limits of the most appropriate criteria [REF].

Table 5. Intra particle diffusion limitations (φ)

C_{phenol}^0 ppm	LHSV h^{-1}	$-r_{Phénol}^{'}$ $*10^5$ kmol/kg .h	$\phi<2/\boldsymbol{\beta}+1$ ($\phi<1.538$)
1350	**1.16**	**1.177**	0.000704

Such effects of the axial dispersion and liquid misdistribution were minimized due to the appropriate

geometry of both the reactor and the particle (L_R= 35 cm, Dr=1.8 cm and d_p= 1.6 mm). The value of the criteria L_R/dp was found to be 218.75 while Dr /dp took a value of 11.25, which are similar to the critical values of 50 and 10, respectively established for safe operation [39-41]. In addition, from Young and Finlayson Criterion Eq. (6), the results ensure that our process was free from the axial dispersion effects as can be seen in Table 6.

Table 6. Axial dispersion /diffusion (young and finlayson criterion) for liquid and gas phase.

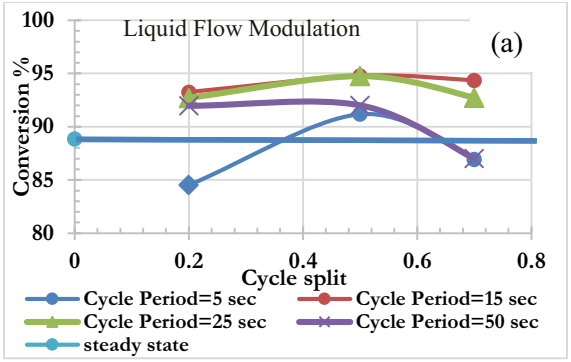
LHSV h^{-1}	$-r_{Phenol}$ kmol/kg .h *10^5	Axial Dispersion of Liquid Phase	
		$\left\|\frac{(-r_A')_{obs}\, dp_p\, \rho_p}{U_0\, C_{A_b}}\right\|$	$\left\|\frac{U_0\, dp_p}{D_{a_x}}\right\|$
1.16	1.4349	0.013387	0.092789
		Axial Dispersion of Gas Phase	
		$\frac{(-r_A')_{obs}\, dp_p\, \rho_p}{U_0\, C_{A_b}}$	$\left\|\frac{U_0\, dp_p}{D_{a_x}}\right\|$
		2.012E-05	59.4465

Several conclusions can be withdrawn from the TBR results, which are as follows : -

- The wet catalytic oxidation of phenol was controlled by chemical reaction in this case of study.
- The effects of the hydrodynamics were at least with respect to the wetting efficiency, external mass transfer, intra particle diffusion and axial dispersion/diffusion, which are the key parameters for the TBRs performances

4.2 Effect of cyclic parameters for PP-CWAO of phenol.

A set of cyclic experiments (cycle split and cycle period) were performed at a varied cycle period and split for ON-OFF mode of operation for promoted CWAO of phenol with hydrogen peroxide at reaction temperature =80°C, LHSV = 1.16 h-1, initial phenol concentration =1350 ppm, gas flow rate =2.5 liter/min, 35%hydrogen peroxide and U_L,H_2O_2=1.08933*10-4 m/sec were shown in Figure 3 and 4. Increasing gaseous reactant supply to the catalyst; varying the ratio of the gas to liquid access times at a constant average liquid flow rate (i.e., varied cycle split (σ) at a given cycle period).They were experimented to investigate the possibility of an additional enhancement in the time average conversion as compared to the conventional conversion obtained from operating the reactor at the steady state mode.Figure 3 and 4 show the results of time average conversion and enhancement conversion.It can be seen that at a given cycle period, the time average conversion enhancement is in fact considerable as split is less than steady state operation (cycle split σ =1) to a value of cycle split σ =0.5 and reached as much as 6.66 % over the steady state for CWAO at τp = 15 sec. These results are similar to those of Lange et al [43]; Banchero et al., [44]; Liu et al., [45] and [46] and Al-Sudani, [47].



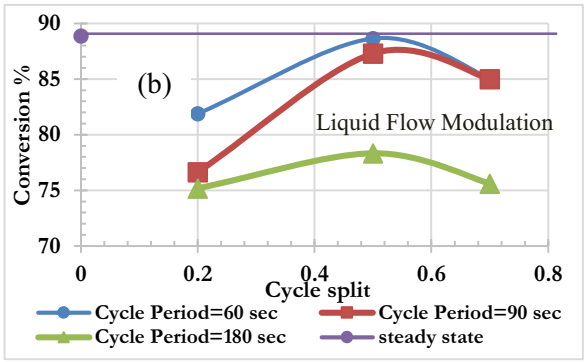


Figure 3. Conversion vs. cycle split at H_2O_2 %=35, LHSV=1.16 h-1, $Cphenol_0$=1350 ppm, superficial gas velocity 0.163 m/s and reaction temperature = 80 ºC, (a) at Cycle Period =5-50 sec, (b) at cycle period =60-90 sec.

When the liquid flow stops, reaction proceeds between the flowing gas reactant and the liquid reactant retained in the reactor. Performance is ascribed to the direct on coming of access of oxygen to the catalyst that tremendously reduction of liquid films during OFF period as compared with steady-state operation, and that high accumulated oxygen concentration on the catalyst surface and increased the rate of reaction during ON period.At higher cycle period ≥ 25 sec, it can be noticed from Figure 3 and 4 that the time average conversion and performance enhancement conversion drops even below the steady-state value. Similar behavior was showed by Haure et al., [49]; Lange et al., [43]; Khadilkar et al., [50]; Massa et al., [30]; Liu et al., [46] and Al-Sudani, [47]. However, the results are not as expected, where all the scientists in this field agree with that. There are different results on the impact of split and there is an optimal period whatever its length.

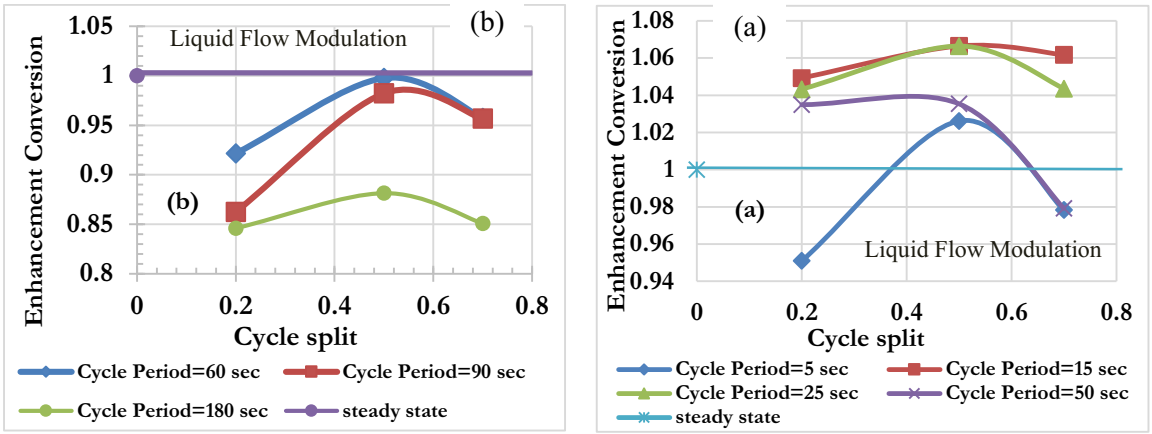


Figure 4. Enhancement conversion vs. cycle split at H_2O_2 %=35, LHSV=1.16 h-1, $Cphenol_0$=1350 ppm, superficial gas velocity 0.163 m/s and reaction temperature = 80 ºC, (a) at Cycle Period =5-50 sec, (b) at Cycle Period =60-90 sec.

The optimal period can only be explained by the following qualitative reasons: time periods are shorter than necessary for their consumption produce to exacerbation of oxygen (i.e. gas reactant starvation). Adverse behavior is shown at longer cycle periods (for the same cycle split). Several factors can negatively affect the attained conversion for long cycle period, since the accumulation of oxygen (longer gas access time) is over the limit of the liquid required for the ON period which leads to the starvation of the liquid reactant (the liquid limitation). Also, for low cycle splits, there is lower chance to reload the liquid through the ON period [43], [48-49].

5. Conclusions

The essential points concluded from the present study are:

1. The PP-CWAO of phenol are kinetically controlled. Where external mass transfer and the internal diffusion limitations can be neglected.
2. The performance of TBR is enhanced under periodic operation to a maximum value at 0.5 cycle split and τp = 15 sec for liquid flow, while it drops to lower steady state value at higher cycle period and split under identical operating conditions with steady-state operation.

Acknowledgment

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technology,Baghdad, Iraq for financially supporting this research.

Appendix A : Transport Parameters

Axial Liquid and Gas Dispersion Coefficients[50] :-

$$D_{a,G} = \frac{u_G d_p}{0.042 R_{eL}^{0.5}} \quad D_{a,L} = \frac{u_L d_p}{1.8 R_{eG}'^{-0.7} * 10^{-0.005 R_{eL}'}}$$

Wetting efficiency f_w [51]:- $f_w = 1 - \exp[-1.35 Re_L^{0.333}\ Fr_L^{0.235}\ We_L^{-0.17}\ (\frac{a_s\, d_p}{(1-a_s)^2})^{-0.0425}]$

Diffusion in Liquid Phase ,(Wilke and Chang correlation [52]):- $D_{AB,L} = 7.4 * 10^{-8}\left(\frac{M_{wt,B}^{0.5} T}{\mu_B \widetilde{V}_A^{0.6}}\right)$

Were A =Ph , B=O_2

Diffusion in gas Phase [53]:- $D_{AB,G} = \frac{1.013 * 10^{-2} T^{1.75}\left(1/M_{wt,A} + 1/M_{wt,B}\right)^{1/2}}{P\left(\sum \vartheta_A^{1/3} + \sum \vartheta_B^{1/3}\right)^2}$

Effective Diffusivity :- $D_{ei} = \frac{D_{AB}\varepsilon_p}{\tau''}$

Mass Transfer Coefficients:- $\frac{K_{gl} d_P}{D_{O2L}} = 25.1\ Re_L^{0.45} Sc_{O_2L}^{0.5}$ [54]

$\frac{K_{ls} d_P}{D_{PhL}} = 3.77\ Re_L^{0.8} Sc_{Phl}^{1/3}$ [54] , $K_{O2GS} = 0.0138\ R_{eG}^{0.79}\ Sc_{Co2G}^{0.5}\ \frac{D_{O2G}}{d_p}$ [36]

Henry Law constant [55]: - $\mathrm{H(T)} = 761.1 - 108.9 \ln(\mathrm{T}) - 40785.5/\mathrm{T}$

Where D_{AB} molecular diffusivity m^2/s, D_r reactor diameter m, u_G and u_G superficial gas and liquid velocity m/s, $\widetilde{V}_A$ molar volume m^3/kmol, ε_L dynamic liquid holdup, ρ_L *and* ρ_g density of liquid and gas kg/m^3, τ'' catalyst pellet tortuosity, F_r froude number $\frac{U_L^2}{g d_e}$, R_e reynolds number $\frac{\rho_L u_L d_e}{\mu_L}$, Sc schmidt number $\frac{\mu}{D_{AB}\rho}$, Sh'' sherwood number $\frac{k_{Ls} d_e}{D_{AB}}$, W_{e_L} weber number $\frac{\rho_L d_p u_L^2}{\sigma_L}$.

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