COMPARATIVE STUDY OFCWO PROCESS OF PHENOLS IN FALLING – FILM AND BACK MIXING REACTORS

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Abstract

A comparative study of the CWO process of phenol in two different types of flow reactors (e.g. falling film and back mixing reactors) under atmospheric pressure was carried out .It was found that the oxidation rate of phenol was low due to the solubility of oxygen at atmospheric pressure . At low flow rates of liquid reactant the falling film reactor showed a better performance due to lower resistance to mass and heat transfer while the image is completely different at higher liquid flow rates .Non-isothermal operation evidence that water evaporation has a strong impact on phenol conversion and must be taken into account in scale up and adiabatic CWO reactor design.

A kinetic analysis of the oxidation of phenol in aqueous solution over a supported (0.7% Pt)/Al₂O₃ catalyst was also investigated under atmospheric pressure in batch operating system . The kinetic analysis proved that the reaction consist of two mechanisms, that is the initial rate and steady state activity regimes which exhibited first order behavior with respect to phenol concentration. The reaction rates show an unusual dependence on catalyst loading which proposed a heterogeneoushomogeneous free radical mechanism .Power law technique has been utilized to correlate the phenol conversion with operating parameters in falling and back-mixing reactors with standard deviation of 1.18% and 1.1% respectively.

Keywords: Catalytic wet oxidation (CWO),

phenol, platinum catalysts, Falling –film reactors, Back-mix reactor.

1- Introduction

Oxidation of dilute aqueous solution of organic pollutants with or without catalysts offers an attractive alternative process to biological oxidation as a mean to purify liquid water. This is particularly true when the pollutant is toxic, hazardous and in some cases non-biodegradable (refractory). Further, the liquid phase oxidation is definitely more cost effective as compared with incineration (Joshi et al.1985).The petrochemical, chemical and pharmaceutical industries produce waste water containing organics, such as phenols, oxalic acid, etc. which are toxic to aquatic life. These pollutants are difficult to oxidize them biologically, since biological processes are very time - consuming and operate well only in the case of relatively dilute wastes. The use of chemical oxidation especially may be favored when the pollutants concentration are too high for direct biological systems and / or effluent is present at higher temperature (Murat and Gonul (1998); Imamura, (1999); Kumar et al (2006)). The application of a particular method depends on, among others, the nature of the pollutant, the desired removal efficiency, effective ability to form secondary toxic product and cost. Many researchers reported that among the wastewater treatment techniques, catalytic wet oxidation (CWO) of organic wastes in water seems to be effective and promising [Luck, 1999, Matatov-Meytal and Sheintuch, 1998; Mishra et al, 1995].CWO is a reaction involving an organic compound in water and oxygen over a catalyst. Although many studies have shown that metal oxide catalysts of transitional metals like Zn, Cu, and Mn etc. are very effective for the removal of organic wastes, the use of noble metal catalysts for liquid phase oxidation is preferred since no leaching or dissolution of the active metal occurs even in hot acidic condition [Gallezot, 1997; Luck, 1999]. Among the noble catalysts reported for liquid phase oxidation, platinum - supported catalysts seem to be promising. Platinum catalysts are well - known to be effective during aqueous phase oxidation of alcohols [Besson and Gallezot, 2000; Kluytmans et al; 2000; Mallat and Baiker, 1994] and ammonia [Ukropec et al,1999,] . However, there is still meager information on the application of platinum catalysts for CWO of organic pollutants [Gomes et al. 2000; (Chollier et al, 1999; Harmsen et al., 1997; Gallezot et al., (1996). One of the important criteria in CWO is the selection of a suitable reactor. Most laboratory studies have been carried out either in slurry or fixed -bed reactor. [Pintar and Levec, 1994; Stuber et al., 2001] have carried out a comparison between these two reactor types. They reported that the latter is more advantageous in terms of process selectivity and stability. They concluded that agitated reactors, such as slurry or spinning basket, exhibited high liquid - to - catalyst ratio which adversely favors parallel homogeneous polymerization reactions, thereby leading to catalyst activity loss and lower selectivity towards complete mineralization products.

Levec and Smith (1967) have reported the kinetics of catalytic oxidation of formic acid (CuO- ZnO catalyst) and acetic acid (Fe₂O₅ catalyst), respectively, using trickle bed reactors. The values of activation energy and effectiveness factors for catalysts have been reported. The rate data have been explained on the basis of the oxidation – reduction mechanism.

Pal et al. (1982) have shown that when the size of catalyst particles is less than the liquid film, a substantial increase (by a factor of 10) in the rate of oxidation of sodium sulfide can be obtained even when, in the absence of the catalyst, the reaction occurs in the diffusion film. They presented a theoretical analysis for a comparison of the performance of bubble columns, sectionalized bubble columns, horizontal sparged contactor, packed columns and pipeline reactors. The optimum values of height – to diameter ratio and the total pressure in the case of bubble column are also given.

Pintar and Levec (1992 a, 1992 b) studied the oxidation of aqueous phenol in a slurry reactor over a catalyst comprising CuO, ZnO and gamma alumina above atmospheric pressure at up to 13bars. Their rate measurements showed that the reaction progressed autocatalytcally. Pintar and Levec (1994) also studied the liquid - phase oxidation of phenol in a differential liquid - filled operated fixed - bed reactor over a zinc, copper and cobalt - oxide catalyst. Roy et al. (2010) presented a review paper for the application of platinum catalysts in bubble column reactor for CWAO of oxalic acid. It has been shown that temperature, pressure, inter gas flow rate and pH during oxidation evolution are important parameters to be taken into account when predicting the performance of wet air oxidation unit.

The purpose of the present work was to study the kinetic analysis of phenol oxidation in aqueous solution over a supported Pt catalyst at atmospheric pressure and to carry out a comparative study of a CWO process of aqueous phenol in two different types of continuous flow reactors (e.g. Falling – film and back – mixing reactors) by investigating the effect of operating parameters such as temperature, liquid and oxygen-feed rates and initial phenol concentration on process performance.

1-1 Mechanisms and reaction pathways

According to Gallezot (1997) catalytic oxidation of organic molecules can proceed via different mechanisms, namely:

- 1- Enzymatic oxidation;
- 2- Free radical auto oxidations initiated by transition metal cations;
- 3- Metal ion oxidation of coordinated substrates;
- 4- Oxygen transfer to the substrate mediated by metaloxo or peroxo complexes.
- 5- Oxidative dehydrogenation on metal surface. In alcohol oxidations, oxidative dehydrogenation on metal surfaces is commonly reported (Gallezot, 1997 Mallat and Baiker, 1994). The mechanism of alcohol oxidation on a noble metal catalyst involves the dehydrogenation of the organic substrate on the metal surface, while oxygen is needed to scavenge the adsorbed hydrogen from the surface.

Sadana and katzer (1979) found that, during phenol oxidation, the oxidation involves an induction period, in which the generation of radicals is poor, followed by a higher steady – state activity period with a fate free – radical reaction regime. These mechanisms are likely to occur even for noble metal catalysts.

Matatov – Meytal and Sheintuch (1998) reported that in wet oxidation, water with dissolved oxygen is used to oxidize the target compound. The main reactions are described in equations (1 - 8). Hydroxyl radicals are produced from the dissociation and oxidations of water according to equation (1) and (2). Hydroperoxyl radicals are formed from the oxidation of water (eqn. 3) and the target compound RH (eqn. 6). Hydroxyl radicals are also produced from hydrogen peroxide (eqn 4) and from the reaction of atomic oxygen with the target compound (eqn 8). Although the Hydroperoxyl radical is less reactive than the hydroxyl radical, it plays an important role because of its relative abundance.

1-2 Kinetic Analysis of the Catalytical oxidation of Phenol

Figure (1) shows the experimental apparatus of the kinetic study for the oxidation of phenol. The runs were made in a four –neck, 500ml .pyrex round – bottom flask. The necks housed a sampling tube, a contact thermometer to measure gas-liquid mixture temperature, a sparger for oxygen introduction and a condenser connected to a gas washing bottle

open to the atmosphere. The gas washing bottle contained NaOH solution of known concentration for absorption of carbon dioxide. The flask was heated with a heating mantel and stirred magnetically. Oxygen was sparged at a metered rate into the liquid phase through a coil containing 20 holes, each 0.2 cm in diameter. For a typical run 250 ml, of water and a known weight of phenol and catalyst in powder form were loaded into the flask and heated to the desired temperature. The mixture was stirred vigorously, slurrying the catalyst uniformly throughout the liquid. Cooling water was started and oxygen was sparged into the flask , representative samples were withdrawn periodically using a syringe and the catalyst was separated from the aqueous phase by centrifugal forcing .The samples prepared were analyzed with gas chromatography (GC) (ZB-FFAP, capillary column, 30m long, 0.32 mm inside diameter, nitroterephalic acid modified ploy ethylene) .A calibration curve was used to determine the unreacted phenol concentration in the reaction products in each run. The amount of CO₂ generated during the experiment was determined by absorption in a NaOH solution of known concentration. In the kinetic analysis of the reaction, the rate equations proposed by Sadan and Katzer (1974) were tested.

Equation (1) and (2) represent these equations for the initial rate and the rate in the steady state activity regime, respectively.

$$\frac{Vliq.}{Wcat.} \cdot \frac{dx}{dt} = k1 \cdot \frac{1-x}{\sqrt{Wcat.\frac{1}{Vliq}}} \dots \dots \dots (1)$$

$$\frac{Vliq.}{Wcat.} \cdot \frac{dx}{dt} = k2 \cdot \frac{1-x}{(Wcat.\frac{1}{Vliq})^3} \dots \dots (2)$$

Where :-

If $-\ln(1-x)$ is plotted verses time, the slope of the curve at x=0 and t=0 gives (k_1) , while the slope in the steady state activity regime gives (k_2) .

2- Experimental

2-1 Setup

The primary components of the experimental apparatus were catalytic falling _ film reactor (CFFR), back - mix reactor (CSTR) with suspended catalyst, solution tank, return solution

tank, heating system, pumping system and solution sampling system. Figure (2) shows the compact experimental setup. The (CFFR) was a concentric tube which defines the space in which reaction took place. The stainless steel inner tube (5) has a 2.9 cm OD, a total length of 1.6 m and an effective test section length of approximately 95 cm which was covered by a 3 mm thickness layer consisting of catalyst pellets (0.7% Pt on Al₂O₃) which were stacked on the outer surface of the tube using a special type of adhesive .The outer tube (6) has a 8 cm OD and was made of pyrex glass pipe permitting flow observation. The contaminated liquid solution was introduced to the distributor (4) at the top of the reactor and flows downward by gravity through the wetted catalyst and into the collector which attached to the bottom of the reactor and interacts with the upward flowing gaseous oxygen where reaction occurs. The contaminated solution was prepared at the desired concentration in a stainless steel tank(12) of 60 liter volume equipped with an agitator and an electric heater. The back – mix reactor (CSTR) was a stainless steel made of 10 lit - volume equipped with an agitator and a gas sparger, these mixing tools helped to keep the catalyst particles suspended in the flowing solution through the reactor. To prevent the catalyst particles from escaping out of the reactor, a perforated stainless steel plate of 0.2mm holes was installed at the outlet line of the reactor. The heated contaminated solution was discharged from tank (12) to (CFFR) and (CSTR) via pump (2) and through the calibrated rotameter (F2) and (F3) respectively. A compressed gas bottle (11) was used as a feeding source of pure oxygen which was entered (CFFR) at the bottom and flowing to the top. Drops of solution which carried by the gaseous oxygen out of the reactor were separated in a stainless steel separator (14). The oxygen continued to flow from (14) to (CSTR) (15) while separated liquid droplets were collected into (13). Flow rates of pure Oxygen fed to (CFFR) and (CSTR) were adjusted using calibrated flow meters (F1) and (F4). Samples were collected at equal time intervals using sample ports (S1 and S2) and analyzed using HPLC. Temperature managements were performed by K- type thermocouples (T1 to T5) calibrated to an accuracy $\pm 0.1^{\circ}$ C. To compare the performance of the two different types of reactors, a similarity was established by considering the same operating parameters (i,e) weight of catalyst, inlet temperature and residence time of all reactants in each reactor. Characteristics of phenols catalyst and dimensions of reactors are presented in table(1).

Phenol , p	urity 99%
from Baye	r GmbH
CFFR (OD/H) , m/	0.035 / 0.95
m	
CSTR (OD/H), $m/$	0.487 / 0.536
m	
Composition of the	0.7% pt / Al ₂ O ₃
catalyst	
Density of catalyst	1030
particle, kg/m ³	
Catalyst Particle	0.43
Porosity	
Catalyst Particle	2
diameter, mm	
Catalyst Bed Porosity	0.36
-	
Packing specific surface	$1.43 * 10^3$
area m^2 / m^3	

Table (1)Characteristics of Phenol , catalystand dimensions of reactors.

2-2 Design

In the present work, factorial design method was used for planning the experiments because of its reliability in finding out the effects and interaction between the controlled variables of the operating system. The real value of controlled variables (F) and their corresponding levels (L) are shown in table (2).

 Table (2): Selected levels and factors

F	Real variable			
	Phenol	Liquid	Gas	Temp.
	concentra	flow rate	flow	۳C
	tion mg /	(ℓ min ⁻¹)	rate (l	
	ł		min ^{-r})	
1	500	0.1	4	80
2	1000	0.4	8	90
3	1500	0.7	12	100
4	2000	1.0	16	110

The operating pressure and the weight of catalyst inside the two reactors were kept constant at 0.5 bar and 222 gm respectively for all experimental runs. Also, the two reactors were operated with the same parameters represented in table (2).

3- Results and discussion

3-1 The Rate Constants

Figure (3) shows that the linearity of the experimental data in the steady – state activity regime displays first – order kinetics with respect

to phenol concentration .The rate constants k_1 and k_2 for two runs gives in figure (3) were found to be :

With Phenol / catalyst ratio=1 / 4 =0.25 $k_1 = 6.97 * 10^{-4}$ ((lit liq. / kg cat)^{0.5} s⁻¹) $k_2 = 3.84 * 10^{-9}$ ((kg cat. / lit liq)² s⁻¹) With Phenol / catalyst ratio=2 /4=0.5 $k_1 = 6.21 * 10^{-4}$ ((lit liq. / kg cat)^{0.5} s⁻¹) $k_2 = 7.63 * 10^{-9}$ ((kg cat. / lit liq)² s⁻¹) These experiments, exhibit first – order dependence on phenol in the initial activity and steady – state activity regime .The effect of arying catalyst loading on the rate constants proved that the reaction involves a heterogeneous – homogeneous free radical mechanics.



Figure (3) $-\ln(1-x)$ vs time for different Phenol/catalyst ratio for kinetic study at

T= 373 K and Vg = 2 l/min 3-2 Effect of Temperature on phenol

conversion.

Figure (4) shows a positive impact between temperature and rate of conversion of Phenol.



Figure (4) Effect of Temperature on Conversion for a kinetic study analysis at Vg = 8 l/min and Ra = 0.25

3-3 Estimation of the activation energies.

Figure (5) was plotted to estimate the activation energies from the slopes of the straight lines calculated by means of the least squares techniques between 353 K and 383 K; k_1 and k_2 were 96 kJ / mol and 50 kJ /mol with R^2 of 0.95 and 0.99, respectively.

The Arrhenius equation of k_1 and k_2 may be represented by:-

 $k_1 = 1.8 * 10^{10} \exp(-96 / R.T)$ and

$$k_2 = 2.4 * 10^{-4} \exp(-50 / R.T)$$



Figure (5) Arrhenius plots ; k_1 for induction period; k_2 for steady activity regime

3-4 Effect of oxygen feed rate on conversion of phenol.

Figure (6) shows the effect of oxygen feed rate on conversion of phenol at different increments of time .The highest phenol conversion were obtained with an oxygen feed rate of 8 L min⁻¹. It is evident that phenol removal increases with increasing amounts of bubbled oxygen gas .The decrease in phenol conversion observed with an oxygen feed rate of 16 L min⁻¹, this can be explained by the decrease in gas / liquid interface and shortened residence time of large oxygen bubbles formed by the collapsing of the fine bubbles at oxygen rate greater than a critical value.



Figure (6) Effect of gas flow rate on conversion for kinetic study at Ra=0.25

3-5 Effect of the initial concentration of the phenol.

Figure (7) plots the effect of the initial concentration of the phenol to be reduced during CWO runs over the 0.7 wt% Pt / Al_2O_4 catalyst at 383K and at a partial pressure of oxygen of 0.5 bar for the CFFR and CCSTR reactors respectively. The removal of Phenol was shown to decrease markedly as LHSV of the influent stream increased, because the retention time during the CWO process was reduced. As can be seen at lower values of LHSV, the conversion for CFFR system was higher than that of the CCSTR . This was attributed to the effect of surface area to volume ratio of liquid which is higher for the CFFR system, this ratio is proportional to the rate of oxygen diffused and reacted in the liquid phase. As LHSV continue to increase, the phenol reduction performed by the CCSTR became increasingly higher than that of the CFFR. This may be attributed to the effect of back mixing which becomes larger in the CCSTR system and predominant on that of the CFFRs.



Figure(7) Effect of initial concentration on Phenol removal at T=383K

3-6 Effects of reaction temperature and space velocity.

Figure (8) illustrates the effects of reaction temperature and space velocity of the influent stream on the reduction of Phenol . An increase in the reaction temperature was observed to result in increased removal of phenol. The effect of temperature was to increase the specific rate constant which pronounced the conversion. CFFR and CCSTR exhibit different levels of performance with increasing both reaction temperature and space velocity. The latter has an adverse impact on conversion for the same reason mentioned for fig (7).



Figure(8) Effect of reaction temperature and LHSV on phenol removal.

3-7 Effect of temperature on the COD.

Figure(9) plots the effect of temperature on the COD for the samples taken from the effluents of the CFFR and CCSTR at the same intervals of time. The operating conditions of the two reactors were the same The figure shows reduction in the COD residual of the effluents from the two reactors as the reaction temperature increased. The experimentally measured reaction rates have shown that the laboratory scale reactors operate in the kinetic control regime when compared with mass transfer rates calculated from available correlations (LLiuta et al. 1999 a,b,c).



Figure(9) Effects of space time and temperature on residual COD.

3-8 Effect of water evaporation on Phenol conversion.

Figure (10) shows the effect of water evaporation on Phenol conversion at different values of GHSV. As can be seen, the water evaporation can have a substantial influence on CFFR and CCSTR performance. The plots are parameterized for two liquid space velocities, corresponding to high and low Phenol conversions. For lower values of LHSV conversion profile higher was obtained at evaporation conditions. For higher LHSV lowest observed conversion profile was without evaporation. The figure shows a positive impact between GHSV and Phenol conversion, with steep increasing rate of conversion at low values of GHSV, while the rate of change of conversion is significantly lower at higher values of GHSV. Also the plot shows the trend of performance for both CFFR and CCSTR respectively. As can be seen the phenol conversion of CFFR is higher than that of CCSTR at lower values of LHSV (≤ 0.6) for both conditions of with and without evaporation, while the image is completely different at higher values of LHSV (≤ 1.2). This may be suggested that operating the reactors at saturation temperature and equivalent pressure would be useful to obtain higher performance.



Figure (10) Phenol conversion as a function of GHSV (h-1).

Lee etal.,2010 studied the Catalytical wet oxidation of phenol using regeneration of Pt/Al_2O_3 . Figure (11) shows the phenol conversion with time for the present work and Lee etal. work in batch kinetic study .Standard operating conditions for both studies are shown in table(3).

	Batch Study		Continuous flow	
			Study	
	Lee etal.	Present work	Lee etal.	Present study
Phenol Concncentration (mg/l)	1000	1000	1000	1000
Phenol/catalyst ratio	0.33	0.25	0.33	0.25
Temperature(K)	423	373	423	373
Pressure (MPa)	1.4	0.1	1.4	0.1
Catalyst type	1 Pt/Al ₂ O ₃	0.7 Pt/Al ₂ O ₃	1 Pt/Al ₂ O ₃	0.7 Pt/Al ₂ O ₃
Reactor type	Batch CSTI	ર	Fluidized Bed	FFR & CSTR

Table (3) Operating conditions of Lee,etal., (2010) and the present work.



Figure (11) Variation of phenol conversion with time of present work and other work of researches in Batch kinetic study.

Figure (12) shows the phenol conversion with LHSV in the present study and Lee .etal study in continuous flow system. It was observed that the phenol conversions in Lee,etal study are higher than that of the present work ,this mey be attributed to the higher operating conditions used in the first work rather than the latest one .



Figure (12) phenol conversion with LHSV of present work and other work of researches in continuous flow study.

3-9 Mathematical Correlations :-

From experimental results the following power law based correlations were proposed. Coefficients were estimated using regression analysis technique.

For CCSTR: -

$$x = 0.502 (\Delta T / T)^{-0.026} (\Delta C / C)^{0.267} (LHSV / GHSV)^{-0.018}$$

(absolute average relative error=1.23%, and standard of deviation=1.1%)

$$\frac{\text{For CFFR}}{\kappa} := 0.426 (\Delta T / T)^{-0.152} (\Delta C / C)^{-0.668} (LHSV / GHSV)^{-0.020}$$

(absolute average relative error=1.16%, and standard of deviation=1.18%)

For	$0.4 < LHSV < 1.3 (hr^{-1})$	and
5 <	GHSV < 20 (hr ⁻¹)	
	300< C < 1200 (mg/lit)	and
	70 < T < 150 (°C)	

4- Conclusions

The present study was classified into two categories .In the first, a kinetic analysis of the oxidation of phenol in aqueous solution over a supported (0.7% Pt) / Al_2O_3 catalyst was investigated at atmospheric pressure in a batch operating system.

The kinetic analysis proved that the reaction consists of two mechanisms, that the initial rate and steady state activity regimes which exhibited first order behavior with respect to phenol concentration. The reaction rates show an unusual dependence on catalyst loading which proposed a heterogeneous – homogenous free radical mechanism. The initial rate constants k_1 and k_2 for the initial rate and steady state activity regime are presented by:-

Phenol removal may be increased by increasing oxygen gas but at higher flow rates of oxygen a retarding effect of oxygen on phenol oxidation was observed.

In the second category, a comparative study of the CWO process of phenol in two different types of flow reactors (e.g. falling film a d back mixing reactors) was carried out when design parameters such as inlet temperatures, residence time of reactants and catalyst loading in the reactors were used to establish the similarity concept between the two reactors. The study support the following conclusions;-

The oxidation rate of phenol was low due to the solubility of oxygen at atmospheric conditions. At low flow rates of liquid reactant the falling film reactor showed a better performance due to lower resistance to mass and heat transfer while the image is completely different at higher liquid flow rates. Nonisothermal operation evidence that water evaporation has a strong impact on phenol conversion and must be taken into account in scale up and adiabatic CWO reactor design. Neglecting evaporation can lead to erroneous calculation of the exit stream phenol conversion and temperature. Power law technique has been utilized to correlate the conversion with the phenol operating parameters in the two reactors respectively. The correlation factor was 0.97 for the CFFR and 0.96 for CSTR.

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Nomenclature

\mathbf{k}_1	rate constant for initial rate (lit of
	liq. /kg of cat.) ^{0.5} (s ⁻¹)
\mathbf{k}_2	rate constant for steady state activity
	$((\text{kg cat. / lit liq })^2 \text{ s}^{-1})$
R	universal gas constant (kJ /mol K)
Т	Temperature (K)
t	time (s)
V	liquid – phase volume (cm^3)
х	conversion of phenol (-)
CCSTR	Catalytic – continuous –
	stirred -tank reactor.
CFFR	Catalytic -falling -film reactor.
CWO	Catalytic- wet- oxidation.
GHSV	Gas hour space velocity (hr ⁻¹).
HPLC	High performance liquid
	chromatography.
LHSV	Liquid hour space velocity (hr^{-1}).

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Figure (1) Experimental apparatus of the kinetic study.



Figure (2) Experimental set-up of the comparative study.