Kinetic study of phenol oxidation in a trickle bed reactor over Al/Zr-pillared clay catalyst

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Abstract. Catalytic wet air oxidation of phenol was studied in a trickle bed reactor operated at 10 bar and temperatures between 120–160 °C over pillared clay wash-coated monolith catalyst. Different variables were studied including reaction temperature and liquid flow rate. The obtained results indicated that phenol conversion increase with an increase in temperature, whereas an increase in liquid flow rate has a negative effect on phenol conversion. Simple power law was used to model the kinetics of the process. When a simple power law model was used experimental results were predicted successfully with $R^2 = 0.9988$ at 160 °C and the activation energy was 42.289 kJ/mol.

1. Introduction
The world is moving away from the treatment of industrial wastewater by conventional processes like biological process due to the toxicity of phenol towards microorganisms. Emerging technologies like wet air oxidation (WAO) can be used to depollute wastewater that contains high concentrations of toxic organic pollutants. However, to completely mineralize phenol and its derivatives to carbon dioxide and water the process requires higher temperature and pressure which makes the process unfavourable due to high operating cost [1–3]. On the other hand, catalytic wet air oxidation (CWAO) is a more suitable process because of mild operating conditions due to catalyst incorporation resulting in lower activation energy. The reaction mechanism of phenol oxidation is influenced by reactor configuration and the type of catalyst used as well as reaction intermediates that can take place on the surface of the catalyst or in the homogeneous phase [4].

The use of a trickle bed reactor (TBR) in CWAO process is common due to the high ratio of catalyst to liquid, wide range of operating conditions (high to low pressure) and the reactor can be operated close to plug flow [5–7]. However, TBR has some drawbacks like high-pressure drop and liquid maldistribution, which can result in the formation of hot spots. On the other hand, monolithic catalyst can be used to reduce pressure drop and liquid channelling. Furthermore, scaling up of monolithic catalyst is not complicated since the conditions within individual channels remain the same [7]. In this work, the aim is to develop a kinetic model of phenol oxidation in a fixed bed monolithic reactor operated in a trickle flow mode over Al/Zr-pillared clay catalyst. Furthermore, the effect of operating conditions (temperature and liquid flow rate) on kinetic parameters will be investigated.
2. Materials and Method

2.1 Chemicals
Bentonite clay purchased from ECCA Holdings (Pty) Ltd., was used as a starting material during the pillaring process. The pillaring solution was prepared by mixing Al(NO₃)₃·9H₂O, ZrOCl₂·8H₂O, NaOH and monolith which was acid-treated using 37% H₂SO₄. Drierite was purchased from W.A Hammond Drierite Company LTD. Cordierite monolith was purchased from Ghophin Chemical. Synthetic wastewater was prepared by mixing phenol supplied by Sigma-Aldrich Chemical Co with high purity water. Anhydrous methanol used in this study was bought from Sigma-Aldrich Chemical Co.

2.2 Experimental Methods

2.2.1 Catalyst testing
The experiment was conducted in a stainless steel fixed bed reactor of 56 mm inside diameter, 9 mm wall thickness and length of 430 mm operated in a trickle flow region and the feed flow rates were kept constant (liquid flow = 10 mL/min, gas flow = 0.012 m/s) while reaction temperature and pressure were also kept constant (160 °C, 10 bar). The experiment continued for 3 h and a sample was withdrawn every 30 min and analyzed using High Performance Liquid Chromatography (HPLC). Two cordierite monoliths wash-coated with Al/Zr pillared clay catalyst (55 mm diameter and 50 mm height each) were packed inside the reactor. A top layer of (230 mm height) silica sand was used as a packing material and after catalyst packing another layer of silica was added (120 mm) at the bottom of the reactor. Drierite was used as a moisture trap to avoid liquid entering the gas chromatograph. Operating conditions of the reactor are listed in Table 1 for each experiment [8]. The performance of the catalyst was evaluated in terms of phenol conversion ($x_{ph}$) as defined by the following equation,

$$x_{ph} = \left( \frac{C_{ph}^0 - C_{ph}}{C_{ph}^0} \right) \times 100$$  \hspace{1cm} (1)

where $C_{ph}$ is phenol concentration measured during the reaction and $C_{ph}^0$ is initial phenol concentration.

Table 1: Fixed bed monolithic reactor operating conditions for CWAO.

| Kinetics experiment | Temperature (°C) | Pressure (bar) | Liquid velocity (mL/min) | Gas velocity (m/s) | Phenol Conc. (mg/L) |
|---------------------|------------------|---------------|--------------------------|-------------------|-------------------|
|                     | (120-160)        | (10)          | (10-40)                  | (0.012)           | 1000              |

2.2.2 Analytical techniques
Phenol and intermediates were measured by Shimadzu HPLC with a UV detector at a wavelength of 210 nm. For stationary phase, waters spherisorb S5ODS2 (25 cm x 4.6 mm x 5 µm) column was used. The mobile phase of (65/35) % anhydrous methanol in water was used and the flow rate was adjusted to 1 mL/min with an injection volume of 0.5 µL [9]. An online gas chromatograph (GC) was connected to the reactor and used to quantify the CO₂ release. The liquid sample was taken every 30 min from the reactor to determine phenol conversion.
3. Results and Discussions

3.1 Catalyst activity test

Figure 1 shows phenol conversion with time on stream when Al/Zr pillared clay catalyst was used. The maximum conversion (100%) was reached after 3 h and this increase can be attributed to an increase in the number of active sites available on the catalyst surface. Similar results were reported by Baloyi et al [10,11] when they studied the removal of phenol by CWAO using Al/Zr-PILCs.

![Figure 1](image1.png)

**Figure 1:** Phenol removal with time in a trickle bed reactor over Al/Zr-PILCs catalyst supported on a monolith (Experimental conditions: 160 °C, 10 bar, 0.012 m/s).

Generally, phenol is broken down to aromatics, carboxylic acid and CO$_2$ inside the reactor depending on the reaction pathway followed [10]. In this work, the amount of CO$_2$ released was measured by an online GC connected to the reactor and the results were plotted in Figure 2. As shown in Figure 2 the amount of CO$_2$ released increases with time and a large peak appeared within 3 h and immediately a sharp decrease was observed afterward signalling complete conversion of the pollutant.

![Figure 2](image2.png)

**Figure 2:** Amount of CO$_2$ released with time during phenol oxidation in CWAO process.
3.2 Influence of main operational parameters

Our preliminary investigation found 10 bar to be the optimum pressure and results are not shown in this paper. Figure 3 shows that at 120 °C and liquid flow rate of 10 mL/min the conversion of phenol is 86%. Moreover, an increase in temperature to 140 °C or 160 °C while keeping liquid flow rate and pressure constant (10 mL/min, 10 bar) resulted in the high conversion of phenol 91 and 100%, respectively. This behaviour can be attributed to the fact that the reaction rate constant is a function of temperature and activation energy, according to the Arrhenius equation:

\[ k = A \exp \left( \frac{-E_a}{R T} \right) \]  

where \( k \) is reaction rate constant, \( A \) is a pre-exponential factor, \( E_a \) is activation energy, \( R \) is ideal gas constant and \( T \) is the temperature. Furthermore, an increase in temperature results in a decrease in liquid viscosity which facilitates the transfer of reactants from bulk liquid to the surface of the catalyst [12]. The same observations were reported by Abid et al [13] when activated carbon catalyst was used. They reported that 64, 87 and 97% of phenol was converted at 120, 140 and 160 °C. Similarly, Mohammed [12] reported that 88% of phenol was converted at 120 °C and when the temperature was increased to 140 °C or 160 °C phenol conversion increased to 91 and 93%, respectively.

The effect of liquid flow rate on phenol conversion was also studied in the range (10, 20, 30 and 40 mL/min) while keeping other parameters constant (gas flow rate = 0.012 m/s and pressure = 10 bar). As shown in Figure 3 an increase in liquid flow rate has a negative impact on phenol conversion due to the fact that an increase in liquid flow rate reduces residence time resulting in less contact time between the phases. Furthermore, the high liquid flow rate increases film thickness and liquid holdup which decreases contact time between gas and liquid on the catalyst active sites resulting in high resistance to mass transfer. When the reaction temperature was kept constant at 120 °C while varying liquid flow rate between (10, 20, 30 and 40 mL/min), phenol conversion decreased as follow 86, 79, 69 and 64%, respectively. Similarly, phenol conversion decreased from 91 to 70% when the liquid flow rate was increased from 10 to 40 mL/min while keeping the temperature constant at 140 °C. Moreover, when the temperature was increased to 160 °C while varying liquid flow rate between 10 and 40 mL/min phenol conversion also decreased from 100 to 85%. Abid et al [13] reported similar behaviour, phenol conversion was 79% at 1.662 mL/min, while the conversion increased to 87% and 96% at 0.996 and 0.6 mL/min.

**Figure 3:** Phenol conversion with liquid flow rate and change in reaction temperature.

3.3 Kinetic model

The reaction kinetics is required to provide a complete interpretation of data obtained in a fixed bed monolithic reactor operated in a trickle flow mode during phenol oxidation. When a simple power law model was used to estimate kinetic parameters as in [4,13,14] equations 3 to 8 were employed.
\[-r_{ph} = k_{ob} \cdot C_{ph}^α \]

(3)

And $k_{ob}$ can be expressed as follow,

$$K_{ob} = k_o \cdot e^{\frac{-E_{ob}}{RT}} \cdot P_{O_2}^β$$

(4)

Since the reaction takes place in a liquid phase the above equation becomes,

$$K_{ob} = k_o \cdot e^{\frac{-E_{ob}}{RT}} \cdot X_{O_2}^β$$

(5)

Assuming that the vapour phase behaves ideally [15], then the oxygen mole fraction ($X_{O_2}$) was calculated using Henry’s law [5]

$$P_{O_2} = X_{O_2} \cdot H$$

(6)

Equation 5 can be linearized by taking logarithm on both sides of the equation,

$$InK_{ob} = Ink_o + βInX_{O_2} - \left(\frac{-E_{ob}}{RT}\right)$$

(7)

Where $α$ and $β$ are reaction order with respect to phenol and oxygen, $E_{ob}$ is activation energy, $H$ is Henry’s constant while $k_o$ is the pre-exponential factor. By assuming ideal plug flow and first order with respect to phenol, equation 5 was integrated and rearranged to obtain $K_{ob}$ as follow,

$$k_{ob} = (-\frac{1}{β})ln(1 - x_{ph})$$

(8)

$K_{ob}$ was applied to the experimental data by plotting the graph of $In(1 - X_{ph})$ vs $τ$ as in Figure 4 and a perfect fit was found at 160 °C with $R^2$ value equal to 0.9988 [4,13]. The activation energy was calculated from the slope of the line in Figure 5.

Figure 4: Graph of $In(1-X_{ph})$ vs $τ$ at 10 bar and temperatures ranging between 120, 140 and 160 °C.

$$Ink_{ob} = -\frac{5086.5}{T} + 12.425$$

(9)

$E_{ob} = 42.289$ kJ/mol

A wide range of activation energies were reported in open literature as 21.306 kJ/mol [11], 85 kJ/mol [16], 29.299 kJ/mol [4], 35.4 kJ/mol [17] and 74.9 kJ/mol [3] using different catalysts and the results obtained in this study are within the range. These results provide a basis to develop a computational
fluid dynamics model of this system which would be instrumental to identifying liquid maldistribution and preventing formation of hotspots [18].

\[ y = -5086.5/T + 12.425 \]

**Figure 5:** Plot of \( \ln(k) \) versus \( 1/T \) at a pressure of 10 bar and temperatures of 120, 140, and 160 °C.

4. **Conclusions**
Phenol oxidation was studied in a fixed bed monolithic reactor operated in a trickle flow mode over Al/Zr pillared clay catalyst. The rate of phenol degradation was improved by an increase in temperature whereas an increase in liquid flow rate showed an opposite trend. The complete conversion was reached after 3 h. A simple power law model was used to determine activation energy from a linear plot and found to be 42.289 kJ/mol.

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