

# Comparative Study of CWO of Phenols in Falling-Film and Back-Mix Reactors

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The present study was classified into two sections. In the first, a kinetic analysis of the oxidation of phenol in aqueous solution over a supported (0.7% Pt)/Al<sub>2</sub>O<sub>3</sub> catalyst was investigated at atmospheric pressure in a batch operating system. The kinetic analysis proved that the reaction consists of two mechanisms, and that the initial rate and steady state activity regimes which exhibited first order behavior with respect phenol concentration. The reaction rates show an unusual dependence on catalyst loading which suggested a heterogeneous-homogenous free radical mechanism. Phenol removal can be increased by increasing the amount of oxygen gas but at higher flow rates of oxygen a retarding effect of oxygen on phenol oxidation was observed. In the second section, a comparative study of the catalytic wet oxidation (CWO) of phenol in two different types of flow reactors (i.e., falling film and back mixing reactors) was carried out and design parameters such as inlet temperatures, residence time of reactants and catalyst loading in the reactors were used to establish similarity reaction conditions in the two reactors. The study supports the following conclusions: The oxidation rate of phenol was low because of the solubility of oxygen under atmospheric conditions. At low flow rates of liquid reactant the falling film reactor showed a better performance as a result of its lower resistance to mass and heat transfer while the result is completely different at higher liquid flow rates. Non-isothermal operation showed 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. The power law technique has been utilized to correlate the phenol conversion with the operating parameters in the two reactors.

## 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 or in some cases non-biodegradable (refractory). Furthermore, 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 organic pollutants; such as phenols; and oxalic acid, which are toxic to aquatic life. These pollutants are difficult to oxidize biologically, since biological processes are very time consuming and operate well only for relatively dilute organic wastes. The use of chemical oxidation may be especially favored when the pollutants concentration are too high for direct biological systems and/or the effluent has higher temperatures (Murat and Gonul, 1998). The choice of a particular method depends on, among other factors, the nature of the pollutant, the desired removal efficiency, and cost. Many researchers have reported that among the wastewater treatment techniques, catalytic

wet oxidation (CWO) of organic wastes in water seems to be effective and promising (Mishra *et al.*, 1995; Matatov-Meytal *et al.*, 1998; Luck, 1999). 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 transition metals like Zn, Cu, and Mn are very effective in 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 under hot acidic conditions (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 for aqueous phase oxidation of alcohols (Mallat and Baiker, 1994; Besson and Gallezot, 2000; Kluytmans *et al.*, 2000) and ammonia (Ukropec *et al.*, 1999). However, there is still little information on the application of platinum catalysts for CWO of organic pollutants (Gallezot *et al.*, 1996; Harmsen *et al.*, 1997; Chollier *et al.*, 1999; Gomes *et al.*, 2000). One of the important factors 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); and 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 reactors, exhibited high liquid-to-catalyst ratio which adversely favors parallel homogeneous polymerization reactions, thereby

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