OXIDATION OF NAPHTHOL IN SUPERCRITICAL WATER

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ABSTRACT

The apparatus for the oxidative decomposition of organic compounds in supercritical water (SCW) was established and in which the decomposition of 2-naphthol in SCW was carried out at different conditions. The results show that naphthol is easily oxidized in SCW and its main aromatic residues are o-phthalic acid and benzoic acid. The concentration of naphthol, mass flow or residence time, and excess oxygen are the main factors affecting the decomposition of naphthol. The corrosion of stainless steel reactor becomes more severe under basic condition.

Keywords: supercritical water, 2-naphthol, oxidation

Keywords: wastewater, supercritical water, organic compounds, oxidation, naphthol,
waste treatment

1. INTRODUCTION

As the amount of toxic wastewaters and sludges generated by industrial and domestic sources approaches 470 million metric tons per year, the development of effective and acceptable waste treatment processes is becoming increasingly important. Furthermore, in conjunction with future waste minimization and rigorous effluent quality control, high destruction of some compounds and use of totally enclosed treatment facilities are suggested. To accomplish these objectives, novels waste treatment and process concepts are needed. Also, it must be noted that increase environmental constraints and unfavorable public opinion have challenged the continuing application of conventional waste management techniques that include incineration.

Recent studies show that when the oxidation of organic compounds and wastewater is conducted above the critical point of water (Tc=374 °C, Pc=218 atm), the organic compounds conversion is relatively rapid and potential complete. At these conditions, the properties of water such as dielectric constant, viscosity, and conductance differ greatly from those at lower temperatures and pressure[1]. Supercritical water (SCW) displays gas-like properties: high solubility of organic compounds [2], complete miscibility in all proportions with oxygen [3, 4], high diffusibility, low viscosity, and low solubility of inorganic salts. The complete miscibility of oxygen and organic compounds in supercritical water creates a single-phase fluid, which greatly reduces interfacial diffusion. In supercritical water, high organic conversion levels (>99.99%) of many priority pollutants can be achieved with a short residence time (<5 min) in a totally enclosed facility, and the chemical oxygen demand (COD) removal may typically be about 75 % to 90 %. Therefore, supercritical water oxidation (SCWO) provides a viable and environmentally attractive option to managing the growing the sludge and toxic wastewater treatment problems.

However, kinetic information describing SCWO is limited. Clearly defined and validated mechanisms for SCWO are not available. Furthermore, these sources of kinetic data are scattered and the values of the reported kinetic parameters differ considerably. Therefore, for the design and development of SCWO processes, general, yet reliable and kinetic models are needed. The objectives of this study are to analyze SCWO reaction mechanisms and to examine the reactivity of naphthol.

2. EXPERIMENTAL

We oxidized naphthol in a isothermal, plug flow reactor. The test apparatus used in this study was a laboratory-scale, continuous-flow SCWO reactor system. As shown in **Figure 1**, the major components of the system comprised a feed tank 4, feed pump 8, preheater 11 (influent heat exchanger), silicon carbide heater 13, coiled-tube reactor 14, water bath 15 (effluent heat exchanger), and gas-liquid separator 16. Oxygen was used as oxidant and was supplied from oxygen cylinder 1.
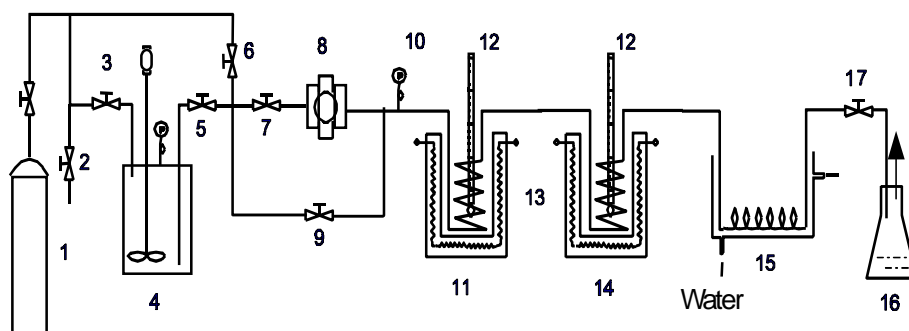

Figure 1 schematic diagram of SCWO reactor system

A previously prepared aqueous solution of naphthol was loaded into the feed tank 4. The reactor feed streams were prepared by dissolving oxygen into the prepared aqueous solution of naphthol in the feed tank and the concentration of oxygen in feed streams is determined by controlling the pressure of feed tank 4. High-pressure metering pumps 8 were used to pressurize the feed streams, which were then preheated by flowing through a preheater 11. The isothermal, plug flow reactor was constructed from a length of 6 m, 8-mm.-o.d.$\times$ 2 stainless steel (1Cr18Ni9Ti) tubing and immersed in a temperature-controlled, isothermal silicon carbide heater. The feed streams were preheated to a given temperature and passed through the reactor. After passing through the reactor, the mixture was cooled and depressurized. This product stream was then separated into liquid and vapor phases prior to analysis.

The reactor effluent samples are analyzed by using high-performance liquid chromatography (HPLC) (Waters-810). We used a column of C18, a mobile phase of methanol: water (1:1 v/v), eluant flow rate of 1.4 ml/min, and UV detection at 254 nm. The column temperature is 30°C. Conversion of naphthol was estimated from the difference of its concentration between the inlet and outlet. The product stream still includes a number of intermediates, which were identified as aromatic-ring substances and were lumped as a component.

The SCWO experiments were carried out at temperatures of 360, 380, 400 and 420 °C and pressures of 22 and 28 MPa under different influent flow rates, different concentration of naphthol and different excess oxygen in the plug flow reactor. Influent flow rate, the concentration of naphthol and excess oxygen were varied from 11.1 to 20 g/min (residence time varying from 45 to 25 s), 100 to 400 mg/L and 2 to 8, respectively.

Experimental data for naphthol oxidation in supercritical water are provide in **Table** 1.

Table1 Experimental data for naphthol oxidation in supercritical water

| Reactor temperature T,	Reactor pressure P, MPa	Concentration of naphthol C_A, mg/L	Mass flux rate G, g/min	Excess oxygen E_{O_2}	Aromatic substance C_s, mg/L	Conversion of naphthol X, %
400	22	200	20	4	78	61
	24				72	64
	26				68.5	65.8
	28				65	67.5
360	24	200	20	4	82	59
380					75	62.5
400					72	64
420					63.5	68.3
400	24	100	20	2	62	38
		200			72	64
		300			88	71
		400			86	78.5
400	24	200	20	2	75.5	62.5
				4	72	64
				6	68.5	65.8
				8	64	68
400	24	200	20	4	72	64
			16.7		67	66.5
			14.3		63.5	68.3
			11.1		55	72.5
380	24	200	20	4	75	62.5
			16.7		69	64.5
			14.3		63	68.5
			11.1		59	70.5

3. RESULTS AND DISCUSSION

3.1 Mechanistic aspect

The analyses by HPLC did not found any naphthol in the effluent samples. This indicates that there is no naphthol in the effluent and that naphthol was converted into small molecular products. However, a number of transition products resulting from the oxidation of

naphthol in supercritical water were found in the liquid effluent by using HPLC. The major transition products are identified using IC are benzene-o-dicarboxylic acid and benzoic acid. A trace amount of benzaldehyde and phenylcarbinol was found in effluent samples. This shows that the naphthol in supercritical water was firstly converted into benzene-o-dicarboxylic acid and benzoic acid, and then into benzaldehyde and phenylcarbinol. It is reported that acetic acid or formic acid is small molecular intermediates in SCWO of organic compounds. The reduction of pH of reactor effluent indicates the presence of acetic acid or formic acid in this study.

It was assumed that the first step of naphthol oxidation is ring-opening step, which related to the formation of benzene-*o*-dicarboxylic acid, which then decarboxylation. On the basis of these identified reaction transition products, a network of simplified reaction pathways for the oxidation of naphthol in supercritical water can be supposed as:

$$\text{Naphthol} \longrightarrow \text{Benzene-}o\text{-dicarboxylic acid} \longrightarrow \text{Benzoic acid} \longrightarrow CO_2, H_2O$$
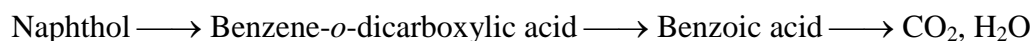
3.2 Influence of pressure on the decomposition of naphthol

Figure 2 shows the influence of pressure on the decomposition of naphthol in supercritical water. The decomposition of naphthol increases with increasing pressure. This attributes to the increase of reactant concentration because the density of supercritical water increases with increasing pressure. On the other hand, increasing pressure increases the density of supercritical water, which implies the increase of residence time. Therefore, the increase of pressure is advantageous to the decomposition of naphthol in supercritical water.
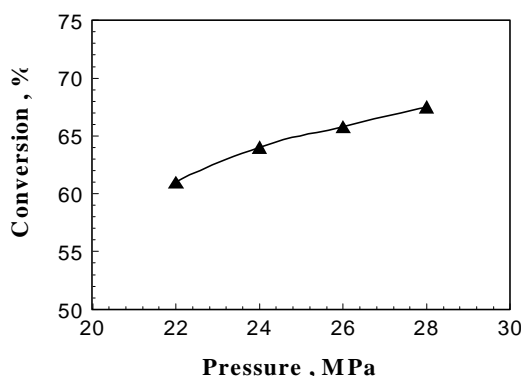

Fig. 2 Influence of pressure on the conversion of naphthol

3.3 Influence of temperature on the conversion of naphthol

The influence of temperature on the decomposition of naphthol in supercritical
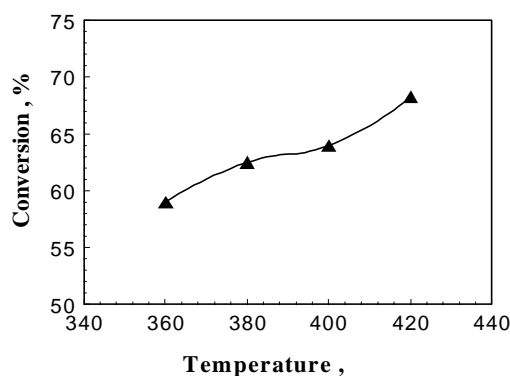

Fig. 3 Influence of temperature on the conversion of naphthol

water is displayed in **Figure 3**. The decomposition of naphthol increases with increasing the temperature, especially when the tempreature is over 380 °C. It can be supposed that naphthol will be decomposited completely at higher temperature in the supercritical water. Unfortunately, experiments at higher temperature were not conducted because of the limitation of experimental test.

3.4 Influence of reactant concentration on the decomposition of naphthol

It was reported that the oxidation rate of organic compounds in supercritical water oxidation is found to be first-order in organic compounds and 0.3-order in oxygen[5]. **Figure 4** and **5** exhibit the effect of naphthol concentration and excess oxygen on the decomposition of naphthol in supercritical water, respectively. The decomposition of naphthol increases with increasing naphthol concentration and excess oxygen, but has weak dependence on oxygen concentration. This confirms the above reported results that the concentration of naphthol has larger reaction order than oxygen.
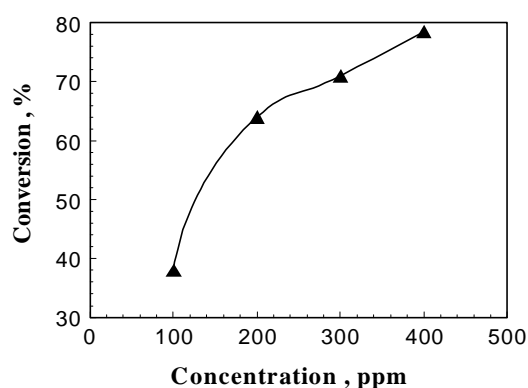

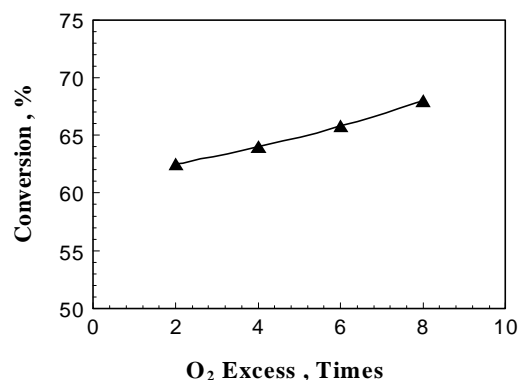**Fig. 4 Effect of concentration on the conversion of naphthol**

Fig. 5 Effect of excess oxygen on the conversion of naphthol

3.5 Influence of influent flow rate on the conversion of naphthol

Figure 6 illustrates the influence of influent flow rate on the conversion of naphthol in supercritical water. It can be found that the higher influent flow rate, the lower the conversion of naphthol because increasing influent flow rate reduces the residence time of reactants in the reactor.
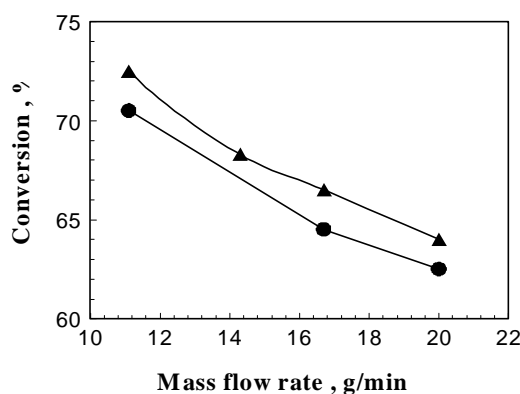

Fig. 6 Effect of the influent flow rate on the conversion of naphthol

Therefore, high decomposition of naphthol in supercritical water oxidation can be obtained by extending residence time of reactants in the reactor.

4. CONCLUSION

Naphthol oxidation in supercritical water proceeds through several major pathways. On the basis of identified transition products, a network of simplified reaction pathways has been proposed. The decomposition of naphthol in supercritical water has strong dependence on naphthol concentration and weak dependence on oxygen concentration. The conversion of naphthol in supercritical water increases with increasing the pressure, temperature and residence time. Residence time, naphthol concentration and temperature are main factors affecting the conversion of naphthol.

NOMENCLATURE

C = concentration, (mol/ L) or (mg/L)

Eo_2 = excess oxygen (-)

G = influent flow rate (mg/min)

P = pressure, (Mpa)

T = temperature, (K) or (°C)

X = conversion, (-)

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