

초임계수에서 페놀의 산화반응

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Kinetic Study on Phenol Oxidation in Supercritical Water

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Introduction

Supercritical Water Oxidation (SCWO) is an excellent waste treatment process which can perfectly and rapidly convert hazardous organics into carbon dioxide and water. Currently some pilot plants and a few commercial scale projects for wastewater treatment using SCWO are under operation in USA and Europe. Pure water is in a supercritical state if its temperature and pressure exceed 374.3°C and 218 atm, respectively. Water has fascinating properties as a reaction medium in its supercritical states where it behaves very differently from that of normal liquid or water vapor to make supercritical water an ideal medium for oxidation of organic wastes. In addition, it exhibits high diffusivity, low viscosity, and low solubility and dissociation of inorganics.

Most of the workers contributed in the kinetics of SCWO have used continuous flow system of which reactor was constructed with 1/4" outside diameter tubing. Since the reactor is long in order to have sufficient reaction volume, precise temperature control becomes difficult. The local temperature deviations in the reactor cause inconsistent reaction rate and sometimes it may cause hot spots. Moreover, determining the individual effects, such as temperature, pressure, pollutant concentration etc., on reaction rate is difficult because the process variables are complexly interrelated in the continuous flow system.

A lot of works in SCWO kinetic study with existing system cannot exactly identify the individual effects, such as system pressure and water concentration, on reaction rate. In many cases, some variable effects on SCWO are neglected with or without assumption. Therefore, the kinetics or models have some weak points for general purpose usage. The shortcomings of existing reaction system make a need to design a new one for SCWO kinetic study. In this work, we designed a reaction system which can reduce the problem mentioned above. With this system, we can determine a individual parameter effect clearly.

Experimental Study

Figure 1 displays a schematic of the reactor system that we used for our oxidation studies in supercritical water. The reactor system was designed so that the phenol and oxygen do not contact with each other until the temperature reaches desired one. Two bombs with different internal volume were used together. The internal volume of large one, referred as preheater, is about 50 mL. The small one, referred as reactor has internal volume of about 25 mL. The preheater and reactor is made of SUS 316 and was designed to overcome the condition of 600°C, 400 atm.

For experiments, small amount of feed solution is injected to the reactor with the 10-mL syringe. The reactor is then purged by the helium gas to remove oxygen. Excess water is injected to the preheater, then excess oxygen is added from the oxygen bomb according to the reaction condition. When the reaction assemble obtains the desired temperature, the pressure in preheater is much higher than that of reactor. This make the water and oxygen move to the reactor in short time when the valve between the reactor and preheater is opened. The concentration of phenol at reaction is confirmed by the mixing experiments which have no oxygen in reactor and preheater.

Reaction product must be cooled immediately to prevent after-reaction. In our system, reaction product is immediately passed to sampler by the pressure difference between the reactor and sampler. Sampler was designed to have internal volume of about 50 mL. One side of sampler is assembled to high pressure fitting to connect reactor. The other side is connected to swagelok 1/4" fitting for gas phase sampling. It is confirmed from experiments that reaction in sampler is negligible because of the drastic depressurization occurring after opening the valve between the high temperature reactor and room temperature sampler.

The temperature of the system is controlled in a molten-salt bath. This bath has an advantage to control temperature homogeneously than fluidized sand bath because it is operated in liquid state while fluidized sand bath is operated in solid state. The salt used is a eutectic mixture of potassium nitrate and calcium nitrate in ratio of 55.2/44.8 on weight base. This liquid system seems to have some majority in homogeneous temperature control than fluidized sand bath. This molten-salt bath can be used upto 500°C within the temperature variation of $\pm 1^\circ\text{C}$ for desired temperature.

Reaction Kinetics

The parameters which can affect the reaction rate are temperature, system pressure, phenol concentration, oxygen concentration and water concentration.

Identification of reaction order of phenol in oxidation was carried out by changing reaction time with all other parameters constant. The global rate equation was then as below.

$$\text{Rate} = -\frac{d[\text{Phenol}]}{dt} = k'[\text{Phenol}]^\alpha \quad (1)$$

$$\int \frac{d[\text{Phenol}]}{[\text{Phenol}]^\alpha} = -k' t \quad (2)$$

We integrated a left term of equation (2) for various α and plotted to the right term. The result of this procedure is given in figure 2 and it reveals that the reaction order of phenol is 1.

The study of pressure effect was carried by changing the pressure with inert helium gas. We had a three condition experiments for pressure effect. First was a 400°C, 220 atm and second was same condition as first one except of injecting helium gas. The helium gas was added to the preheater which was charged with oxygen. Helium addition made reaction pressure 250 atm. The last experiments were carried out with same condition of first except for water content. The water was added to make reaction pressure to be 250 atm. The effect of pressure is shown in figure 3. The oxidation rate of 220 atm is similar to that of 220 atm with helium. This shows that the pressure itself has no clear effect on reaction rate. Reaction rate at 250 atm is faster than 220 atm. The only difference between 220 atm and 250 atm experiments was a water content. Hence we can conclude that the water participates in phenol oxidation.

From the works for pressure effect, we knew that water is participate in reaction as a reactant. To quantify the water effect, reaction rate was expressed first order reaction for phenol as equation 1 and the rate constant k_2 can be written as equation (4)

$$k_2 = k[\text{H}_2\text{O}]^\beta[\text{O}_2]^\gamma = k''[\text{H}_2\text{O}]^\beta \quad (4)$$

The results of this work is presented in figure 4. The regression of water concentration versus k_2 suggests that β to be 1.48.

The effect of oxygen on reaction rate constant is shown in figure 5. Figure 5 shows that reaction constant increases asymptotically as a ratio of oxygen to phenol concentration increases. We apply Langmuir expression because the power law can not describes this tendency. The reaction rate constant k_3 is expressed as equation 5.

$$k_2 = k[\text{H}_2\text{O}]^{1.48} \left[\frac{\chi}{a + \chi} \right] = k * \frac{\chi}{a + \chi} \quad (5)$$

$$\chi = [\text{O}_2]_o / (7 \times [\text{Phenol}]_o) \quad (6)$$

The regression shows that a is about 1.22.

From the previous analysis we can write the rate equation as shown below.

$$\frac{d[\text{Phenol}]}{dt} = k[\text{Phenol}][\text{H}_2\text{O}]^{1.48} \frac{[\text{O}]_o / [\text{Phenol}]_o}{8.51 + [\text{O}]_o / [\text{Phenol}]_o} \quad (7)$$

Equation 7 is integrated to express reaction rate constant as a function of reaction time, water concentration, phenol concentration and initial oxygen concentration.

$$k = \ln \frac{[\text{Phenol}]}{[\text{Phenol}]_o} / ([\text{H}_2\text{O}]^{1.48} \frac{[\text{O}_2]_o / [\text{Phenol}]_o}{8.51 + [\text{O}_2]_o / [\text{Phenol}]_o} \tau) \quad (8)$$

We determined the reaction rate constants at various conditions by using equation 8. The results of these calculation is shown in figure 6 by Arrhenius relation. Linear regression of $\ln k$ versus inverse temperature leads activation energy to be 27.2 kcal/mol.

Conclusion

New reactor system for supercritical water oxidation was designed and phenol oxidation was carried out. We can determine individual parameter effect on reaction rate separately. Oxidation rate is dependent on temperature, water, phenol and oxygen concentration and independent on system pressure. Reaction rate equation can be expressed as:

$$\frac{d[\text{Phenol}]}{dt} = k[\text{Phenol}][\text{H}_2\text{O}]^{1.48} \frac{[\text{O}]_o / [\text{Phenol}]_o}{8.51 + [\text{O}]_o / [\text{Phenol}]_o}$$

The rate constant is expressed as Arrhenius relation with parameters of $A = 4.0 \times 10^5 \text{ M}^{1.48} \text{ s}^{-1}$ and $E_a = 27.2 \text{ kcal/mol}$. This expression suggests a complex and multi-step reaction mechanism for phenol oxidation in supercritical water.

Reference

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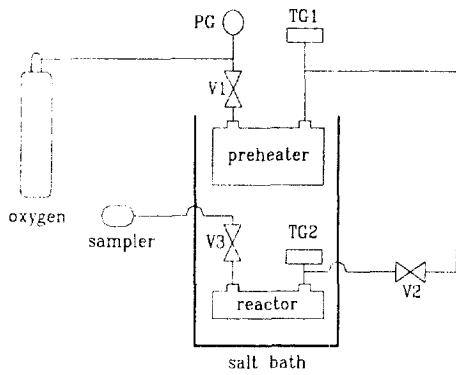


Figure 1. Schematic diagram of experimental apparatus

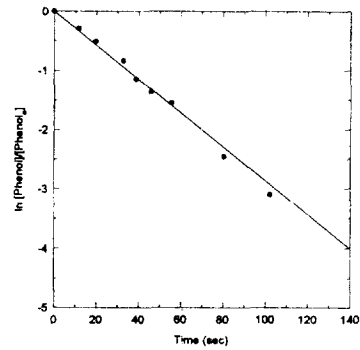


Figure 2. Integral method analysis for determining the phenol reaction order

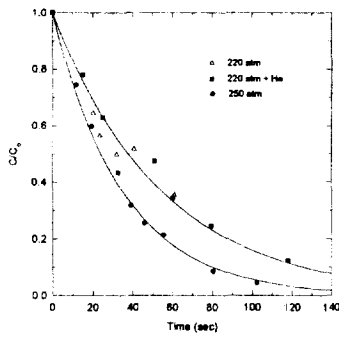


Figure 3. Effect of pressure on phenol oxidation

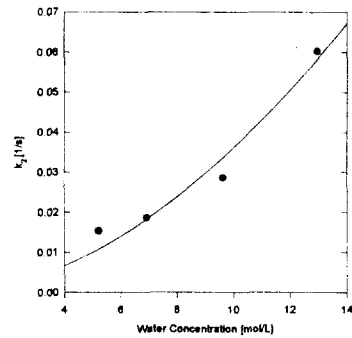


Figure 4. Dependence of phenol oxidation rate constant on water concentration

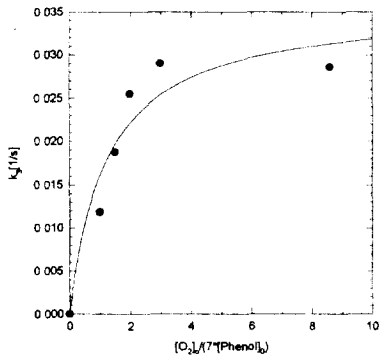


Figure 5. Effect of initial ratio of oxygen to phenol on reaction rate constant

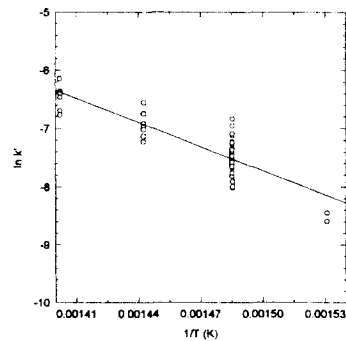


Figure 6. Arrhenius plot for phenol oxidation in supercritical water