Polymerization of Phenol by Using Discharged Plasma under Hydrothermal State

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Abstract. Supercritical fluid with plasma is a type of green processing media because this technique does not use catalyst and toxic solvents. In this study, we carried out experiments of organic materials in the presence of discharged plasma in sub- and supercritical water to evaluate the possibility for new reactions. For this purpose, we used SUS316 reactor that generates plasma at temperature and pressure up to 573K and 30MPa, respectively. 100 mmol/L aqueous phenol solution was used as starting material. The reactions were carried out at temperature of 523K and under pressure of 25MPa. After a series of reactions, water-soluble, water-insoluble (oily products), solid residue and gaseous product were obtained. For the analysis of these products, HPLC, GC-MS, TOC, GC-TCD and TOF-MS were used. The highest phenol conversion was 16.96% obtained at 523K, 25MPa and with 4000 times discharged plasma. Polymerized phenol was obtained as a product.

1. Introduction

Recently, the treatment of toxic components in wastewater emitted from various kinds of industrial units (such as oil refineries, semiconductor manufacturing factories, etc.) focused on the improvement of environment. Generally, wastewater is treated with activated sludge method, but the most of aromatic compounds or low degradable compounds are remained in the solution. Therefore, degradation technology of phenol has been investigated by many researchers. For example, Chen et al. (2004) generated plasma discharge in water, and investigated decomposition of phenol to catechol and benzoquinone [1]. In supercritical water oxidation (SCWO) of phenol, Hayashi et al. (2007) compared phenol decomposition in supercritical water and sub-critical water, and found that the highest conversion of phenol was achieved in supercritical water. Then they investigated the generation of CO₂ from phenol [2]. Additionally, phenol decomposition was examined by photocatalytic degradation using TiO₂ nanoparticles, wet air oxidation techniques, etc. However, most of them have various kinds of problems such as addition of catalysts to increase the reaction rate and treatment of small volume per processing time. So these technologies have not reached practical use yet.

We aimed to make ion-rich atmosphere together with many active species such as various radicals while degrading and reacting phenol with using pulse discharged plasma in sub-critical water, because in sub-critical region, ion product of water rises to 10^{11} [3]. For that reason, sub-critical water has high ionic reactivity. Forming plasma discharged in sub-critical water generates active species (·H, ·OH,
ion, free electron) which are unstable and have high reactivity. Degradation of phenol in sub-critical water using pulse discharged plasma was conducted in non-catalytic condition with coexisting of ionic reaction and radical reaction. Another purpose of this work is to establish the treatment of phenol in non-catalytic condition.

2. Experimental

2.1 Experimental materials
HPLC grade of phenol and methanol were supplied by Wako Pure Chemical Industries Inc. (Tokyo, Japan) with a purity of 99.0 %, respectively. Ar (with a purity of > 99.9999 %) was purchased from Uchimura Sanso Co., Ltd. (Kumamoto, Japan)

2.2 Experimental setup
The experimental setup of plasma production is schematically shown in Figure 1. It has two windows which are used for monitoring the performance of plasma production. The reactor is made of stainless steel (SUS316) having a compressive strength of 30 MPa. The total volume of the reaction cell is 900 mL. A power lead is applied through the centre of a long bushing made of peak resin, and the annular space is sealed with double o-rings placed around its outer surface to prevent water leakage. A thermocouple and a backpressure regulator are used to control temperature and pressure of the reactor cell, respectively.

![Figure 1. Experimental setup for the degradation of phenol with using pulse discharged plasma in sub-critical water. 1, reaction cell; 2, gas outlet; 3, solution outlet; 4, pump; 5, supply vessel; 6, Argon container; 7, current transformer; 8, pulses power supply (Blumlein type Pulse Forming Network); 9, high voltage probe; 10, digital oscilloscope; 11, heater; 12, cooling pool; 13, filter; 14, back pressure regulator (B.P.R.); 15, safety valve; 16, pressure transmitter;](image)

The phenol solution was prepared by dissolving phenol in distilled water. The methanol-soluble fractions of oily products were identified by Gas Chromatography – Mass Spectrometry (GC-MS; HP model 6890 series GC system and 5973 mass selective detector) with a HP-5 MS capillary column. The temperature program was 1.0 min at 318 K, 5 K/min to 543 K, and 10 min at 543 K. Helium carrier gas was used at a flow rate of 1.5 mL/min. The treated solution in a receiving vessel and the collected condensate in the flask were mixed and analyzed by High Performance Liquid Chromatography (HPLC) with a Jasco MD-2010 Plus under the following conditions: column Inertsil ODS-3; flow rate 1.0 mL/min; eluent CH₃CN/H₂O = 20/80; detector UV 280 nm; temperature 313 K. The conversion of phenol was calculated based on the results of HPLC analysis. The residual ratio of
organic carbon in the aqueous solution was calculated by Total Organic Carbon (TOC) with TOC-5050A (Shimadzu Co.). The exhaust gas was collected and analyzed by Gas Chromatography – Thermal Conductivity Detector (GC-TCD). Matrix Assisted Laser Desorption/Ionization – Time of Flight – Mass Spectrometry (MALDI-TOF-MS) was conducted using a Bruker Tektronix TDS 504D GmbH Reflex III (Germany) with dual microchannel plate detectors for both linear and reflectron modes. The acceleration voltage was +25 kV and the ions were measured in the reflectron mode. A nitrogen laser at 337 nm and 3 ns pulse width was used. The applied laser energy was focused over a spot size of 200 µm x 50 µm. The laser energy was measured using a Laser Probe Rm-3700 Universal Radiometer (Laser Probe, Inc., Utica, NY, USA) placed after the optics and before the last mirror prior to the source. The laser energy range used for each polymer sample was determined by the ease of obtaining a measurable mass signal for the polymer. Samples used for MALDI analysis were prepared as follows. 2, 5-Dihydroxybenzoic acid (DHB) was used as a matrix. 10 µL of aqueous solution was mixed with 30 µL of DHB solution (10 mg mL⁻¹ in methanol), and 1 µL of this mixture was spotted on the MALDI sample holder and slowly dried to allow co-crystallization. Each recover samples were immediately analyzed.

3 Result and discussion

The conversion and the residual ratio of phenol were calculated by the following equations (1) and (2).

\[
Conversion(\%) = \left\{1 - \frac{\text{Recovered (AREA)}}{\text{Initial Sample (AREA)}}\right\} \times 100 \tag{1}
\]

\[
Residual\; ratio(\%) = \left\{\frac{\text{Recovered (ppm)}}{\text{Initial Sample (ppm)}}\right\} \times 100 \tag{2}
\]

Figure 2 shows the conversion of phenol at 523 K and 25 MPa. In this figure, phenol was decomposed in 4,000 times discharged plasma and its conversion reached to 16.96 %. As seen in this figure, the reactivity of phenol increased in the presence of plasma discharge. As a result, it is possible to say that rise in the input energy is an important factor on the decomposition of phenol.

Residual ratio of organic carbon in the aqueous phase was showed in Figure 3. The residual ratio was calculated based on TOC analysis. The amount of organic carbon in water was not affected by the discharge times. This graph also shows that the transformation of phenol increased with the increase in the application of plasma discharge.

![Figure 2](image2.png)  
**Figure 2.** Conversion of phenol vs. plasma discharge times at 523 K, 25 MPa.

![Figure 3](image3.png)  
**Figure 3.** Yield of phenol (TOC) vs. plasma discharge times at 523 K, 25 MPa.
Figure 4 illustrates the chromatograph of oily products at 4,000 times discharged plasma. It showed that phenol was decomposed into its oligomer, such as dimer and trimer. In trimer, hydroxyl radical of phenoxy radical was bonded at meta-position in phenol. The results were different from the principle of chemistry. Therefore it was suggested that the reaction pathways in the atmospheric condition and in the sub-critical water - plasma condition without catalyst may be different from each other.

The molecular weight of phenol derived compounds in oily product was measured by MALDI-TOF-MS, which is considered to give highly reliable information on polymer molecular weights. Figure 5 shows the MALDI spectra of oily product obtained by sub-critical water treatment of phenol with 5,000 times discharged plasma. For MALDI-TOF-MS analysis, the oily product to be analyzed was mixed with a matrix, which absorbs laser energy. Unique advantage of the MALDI-TOF-MS method lies in the ability of this matrix to dissipate the heat energy created by rapid laser heating. Hence, the product vaporizes with almost no decomposition, and can be easily detected [4]. The peaks in each spectrum were separated by the mass of the monomer unit, allowing clear observation of molecular weight distribution. At 523 K, 25 MPa and 5,000 times discharged plasma, phenolic compounds produced are with molecular weight around 92 amu or its association. However the structures of them were not presented.

4 Conclusion
The phenol removal phenomena were studied experimentally by applying pulsed high-voltage to a point-to-plate electrode geometry in sub-critical water (523 K, 25 MPa). Phenol degradation in sub-critical water - plasma discharge condition could be enhanced considerably by increasing pulsed high-voltage discharge times. The highest phenol conversion was 16.96 % obtained at 523 K, 25 MPa and 4,000 times discharged plasma. Oily products obtained at 523 K, 25 MPa and 4,000 times discharge produced phenoxy trimer whereas at the same temperature and pressure but with 5,000 times discharged plasma, phenolic compounds with a molecular weight around 92 amu or its association were produced. However the structures of them were not presented here. The result suggested that the principle of the routes reaction chemistry is changed with the existence of the plasma discharge in sub-critical water.

5 References
[1] Chen Y -S, Zhang X -S, Dai Y -C and Yuan W -K 2004 Sep. Purif. Technol. 34 5-12
[2] Hayashi R, Ohkuma K and Tonokura K 2007 J. Chem. Eng. Jpn. 40 7 556-64
[3] Oka H, Yamago S, Yoshida J and Kajimoto O 2002 Angew. Chem. Int. Ed. 114 4 645-7
[4] Wetzel S J, Gutman C M and Girard J E 2004 Int. J. Mass Spectrom. 238 215-25