Reaction of Organic Compound Induced by Pulse Discharge Plasma in Subcritical Water

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Abstract: Supercritical fluid with discharge plasmas has high possibilities as one of green reaction fields. In this study, we carried out experiments of organic materials in the presence of discharged plasmas in sub- and supercritical water and evaluated possibility as a novel reaction fields. We developed a plasma generation reactor which can be used at up to 573 K and 30 MPa. The electrode was set up at the center of the reactor. Phenol and aniline were used as a reactant. Reactions were carried out by using discharged plasma in hydrothermal and pressurized water at 373-523 K and 5-25 MPa. After reaction, products in liquid phase and oily phase were obtained. The highest phenol conversion was 17.0 \% at 523 K, 25 MPa and 4000 times discharge. The oily products contained dimeric and trimeric phenol compounds. Aniline conversion of 30 \% was obtained at 373 K, 5 MPa and 10000 times discharge. Azobenzene was identified in the oily phase of the products.

Keywords: Subcritical, hydrothermal, discharge plasma, chemical conversion.

1. Introduction

Recently, the treatment of the toxic components in wastewater emitted from various kinds of industrial units, such as oil refineries and semiconductor manufacturing factories, was focused on the viewpoints for improvement of environments. Wastewater has been conventionally treated by activated sludge method, but the most of aromatic compounds or low degradable compounds is remained. Therefore, degradation technology of phenol has been extensively investigated all over the world. Chen et al. (2004) generated discharge plasma in water, and investigated decomposition of phenol to catechol and benzoquinone [1]. In supercritical water oxidation of phenol, Hayashi et al. (2007) compared phenol decomposition between supercritical water and sub-critical water, and found that suitable of phenol degradation in supercritical water, and investigated the generation of CO\textsubscript{2} from phenol [2]. Tomizawa et al. (2007) studied degradation of phenol by a pulsed discharge plasma treatment in water at ambient condition [3]. In addition, phenol decomposition was discussed in various kinds of methods, such as photocatalytic degradation using TiO\textsubscript{2} nanoparticles. For aniline, Gomes et al. (2005) used catalytic oxidation in sub-critical water [4]. Supercritical water oxidation was applied for aniline decomposition by Qi et al. (2002) [5]. Glow discharge plasma on the surface of electrolytic solution was used by Tezuka et al. (2001) [6].

We have been investigating the pulsed discharge phenomena in sub- and supercritical fluids [7-9]. We have reported DC pre-breakdown phenomena and breakdown voltage characteristics of point-to-plane gap in pressurized CO\textsubscript{2} up to supercritical state. From the experimental results of negative DC discharge; 1) corona discharges proceeding the complete breakdown have observed more clearly in liquid and supercritical phase than in gas phase of CO\textsubscript{2}, 2) the estimated corona discharge onset voltage by streamer theory agrees well with the measured one in the density region of 1.7 to 30 kg m\textsuperscript{-3}, 3) the breakdown mechanism of liquid phase can be classified into two categories depending on pressure: bubble-triggered breakdown at lower pressures and non-bubble-triggered breakdown at higher pressures [7]. Moreover, it was found that negative discharge is desired for the DC plasma reactor since an active corona appeared more stably in supercritical CO\textsubscript{2} under such conditions compared with the positive polarity [8]. We have studied reaction of organic compounds induced by the plasma generated in supercritical CO\textsubscript{2} [9].

Near-critical water has unique properties such as low dielectric constant and high ion product. Subcritical water has been used as a reaction media and separation solvent. We noticed the possibility of making ion-rich atmosphere, degrading and reacting organic compounds by using pulsed discharged plasma in subcritical water. Ion product of water rises to 10\textsuperscript{-11} in subcritical condition from 10\textsuperscript{-14} in atmospheric condition. For that reason, subcritical water is ion-rich atmosphere, and having high ionic reactivity. Forming plasma discharge in sub-critical water generates active species (\textit{H}, \textit{OH}, ion, free electron) which is unstable molecule and has high reactivity. Degradation of phenol in subcritical water using pulsed discharged plasma was conducted in non-catalytic condition with coexisting of ionic reaction and radical reaction. Aniline was also used as a reactant of aromatic compound.

2. Materials and Methods
The experimental setup for plasma production is schematically shown in Fig. 1. The high pressure cell had windows which used for monitoring the performance of plasma production. Figure 2 is photograph of the apparatus. The reactor is made of stainless steel (SUS316) which can be used up to 30 MPa. The total volume of the reaction cell is 900 mL. A power lead was applied through the center of a long bushing made of PEEK resin, and the annular space was sealed with double o-rings placed around its outer surface to prevent water leakage. A thermocouple and a back-pressure regulator were used to control temperature and pressure of the reactor cell, respectively. Discharge plasma in water at 373 K and 1 MPa is also shown in Fig. 2.

![Fig. 1. Experimental setup for reaction by using pulsed discharge plasma in subcritical water.](image)

![Fig. 2. Photograph of the experimental apparatus for sub-critical water reactor with plasma discharge (left) and discharge plasma in subcritical water at 373 K and 1 MPa (right).](image)

The feed solution was prepared by dissolving of phenol or aniline using the distilled water. The experiments were performed under the conditions as listed in Table 1. The methanol-soluble fractions of oily products were identified by GC-MS (HP model 6890 series GC system and 5973 mass selective detector) with a HP-5 MS capillary column. The solution treated in a receiving vessel and the condensate collected in the flask are 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 CH$_3$CN/H$_2$O = 20/80; detector UV 280 nm; temperature 313 K. The conversion of phenol was calculated based on HPLC analysis. The residual ratio of organic carbon in aqueous solution was calculated by total organic carbon (TOC) with TOC – 5050A (Shimadzu Co.). The exhaust gas was sampled and analyzed by GC/TCD. Each recovered samples are analyzed immediately.

### Table 1. Experimental conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak voltage (kV)</td>
<td>60 – 150</td>
</tr>
<tr>
<td>Distance of between electrodes (mm)</td>
<td>0.1</td>
</tr>
<tr>
<td>Times of discharge (times)</td>
<td>0 – 4,000</td>
</tr>
</tbody>
</table>

3. Results and discussion

After the reaction, water-soluble and water-insoluble (oily) fractions was recovered in short time. All the products obtained after the treatment less than 3500 discharge shot were clear liquid with slightly brownish color. As the phenol aqueous solution was discharged more than 3500 shot, however, some black solid particles and water-insoluble (oily) portion was recovered.

![Fig. 3. Conversion of phenol vs. plasma discharge times at 523 K, 25 MPa.](image)

The effect of the number of discharge shot on the conversion of phenol in the aqueous solution was investigated. Figure 3 shows the measured phenol conversion in subcritical water as a function of the number of shot. The conversion of phenol during the heating process from room temperature to the reaction temperature (523 K) was about 4 % and became 12 % after 1000 shot. The conversion of phenol was gradually increased with increasing
the shot and reached about 17% at 4000 shot at 523 K.

The amount of organic carbon in water was not affected by discharge times. This figure also shows that the conversion of phenol increased with increasing the application of plasma discharge. It was also found from the TOC analysis that most organic carbons were still existed in aqueous phase and no gaseous product except hydrogen was confirmed under the operating condition.

From the HPLC analysis of water-soluble portions, only the peak for phenol was detected through the present experiments. The water-insoluble (oily) fractions were analyzed by GC-MS. Figure 4 shows chromatogram of oily products at 4000 times discharge shot. It is found that phenol was polymerized into phenoxy dimer and trimer. In trimer, hydroxyl radical of phenoxy radical was bonded at meta position in phenol. At low temperatures and pressures (301 - 373 K and 0.1 - 5 MPa), small amount of H$_2$O$_2$ and catechol were generated, but no formation of these species could be confirmed at 523 K and 20 MPa. The phenoxy trimer was found to be the meta connected material, which cannot be formed from the general principle of organic chemistry. This result suggests that the reaction pathway for phenol at the subcritical water discharged plasma atmosphere is quite different from that at ambient condition.

The reaction pathway and mechanism for phenol conversion with pulsed discharges in sub-critical water was proposed on the bases of previous works on the degradation of phenol in aqueous system [2, 3]. One of key points on the phenol conversion is found to be the generation of OH radicals. Increase in the concentration of OH radicals during the reaction would affect the degradation of phenol and also the dimerization of phenol. At the present, effect of these chemical species and other discharge events such as shock wave and local high temperature and pressure at the instant of complete breakdown on the conversion of phenol could not be clarified, but it should be argued by the present research that possible reaction pathway for phenol might be considered on the basis of the previous researches on the phenol degradation with the supercritical water oxidation [2] and with the pulsed discharge plasma treatment in water at ambient condition [3].
Aniline was also treated in subcritical water with discharge plasma. Figure 7 shows the conversion of aniline at 373 K and 5 MPa as a function of discharge times for aniline concentration of 0.001 and 0.1 mol/L. The conversion gradually increased with increase in the discharge times. The conversion was higher for higher initial concentration of aniline.

![Fig. 7 Conversion of aniline vs. plasma discharge times at 374 K and 5 MPa.](image)

Similar to the results for phenol, oily phase was produced and colored brown. Figure 8 shows the GC-MS chromatogram of the oily phase at 10000 times discharge. Among the various products, azobenzene was indentified in the products.

![Fig. 8 Chromatogram of oily products at 10000 times discharged for aniline reaction](image)

4. Conclusion

The conversion phenomena phenol and aniline were studied experimentally by applying plasma generated by high-voltage pulsed discharge with a point-to-plate electrode geometry in sub-critical water. Phenol conversion was enhanced in sub-critical water discharge plasma considerably by increasing pulsed discharge shot times. The highest phenol conversion was 17.0 % at 523 K, 25MPa and 4,000 times discharge. Oily products contained phenoxy trimer. For aniline reaction, the conversion of 30 % was obtained for the treatment at 374 K and 5 MPa. Oily products contained azobenzene.

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References