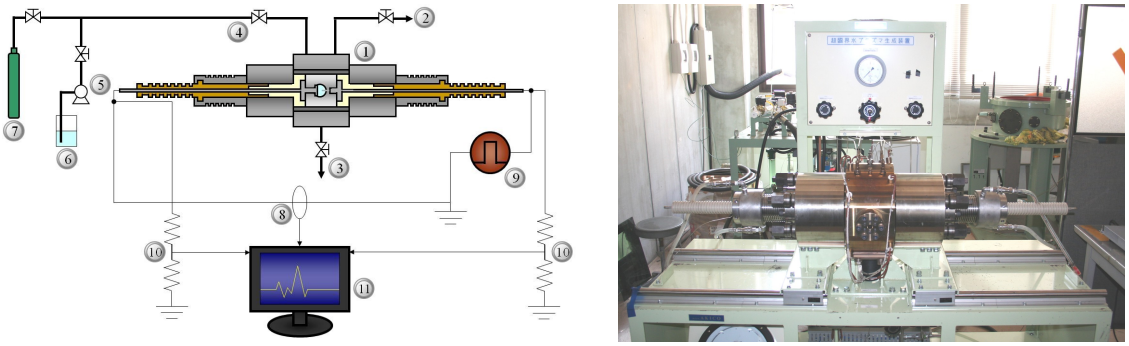
Research Activity on Supercritical Fluids Technology at Kumamoto University

Reaction of Aromatic Compounds using Pulsed Discharge Plasma in Supercritical Fluids

Investigation of pulsed discharge phenomena in sub- and supercritical fluids has been conducted in our laboratory [40-42]. The DC pre-breakdown phenomena and breakdown voltage characteristics of point-to-plane gap in pressurized CO_2 up to supercritical state has been reported. By using negative DC discharge, corona discharges proceeding complete breakdown has been observed more clearly in liquid and supercritical state than in gas state of CO_2. We also reported that the estimated corona discharge onset voltage by streamer theory had good agreement with the measured one in the density region of 1.7 to 30 kg/m^3. In addition, the breakdown mechanism in liquid state can also be classified into two categories depending on pressure: bubble-triggered and non-bubble-triggered breakdown at lower and higher pressures, respectively [40]. Moreover, it was also found that negative discharge was desired for DC plasma reactor since an active corona appeared more stable in supercritical CO_2 under such conditions compared to the positive polarity [42].

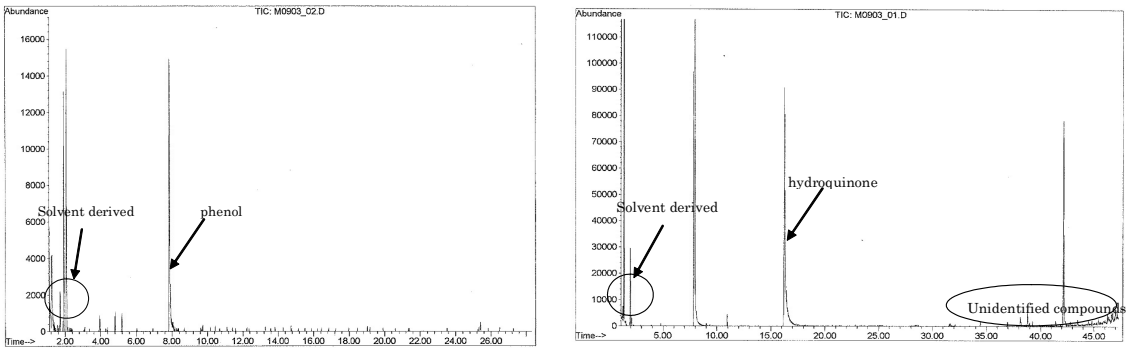
Furthermore, it is possible for making ion-rich atmosphere, degrading and reacting aromatic compounds by using pulsed discharge plasma in sub-critical water. Ion product of water rises to 10^{-11} at sub-critical condition, while it is 10^{-14} at atmospheric condition. Forming plasma discharge in sub-critical water generates active species (H radical, OH radical, ion, free electron) which is unstable molecule and has high reactivity. In this work, non-catalytic reaction synthesis of aromatic and phenolic compounds using pulsed discharge plasma in sub-critical water and supercritical CO_2 or argon were developed to establish novel environmentally treatment technology.

The experimental work was conducted in the apparatus with schematic diagram and picture as shown in Figure 4 (a) and (b), respectively. The apparatus was supplied by AKICO co., Japan. Two saphire windows were installed in the reactor to monitor the performance of plasma production. The reactor is made of stainless steel (SUS316) with volume of 900 ml. The maximum temperature and pressure are 300^{o}C and 30 MPa, respectively. For sub-critical water experiment, initially Ar gas was introduced to the reactor to replace air, and then 550 ml of aniline solution was loaded into the reactor using a pump. While for supercritical CO_2 or argon, phenol solution was loaded into the reactor, and then CO_2 or argon was introduced to the reactor to reach reaction pressure. After the experimental temperature and pressure were achieved, the pulse power was applied to produce electric discharges at a constant temperature. The electrode configuration consisted of a point (positive electrode) and a planar surface (negative electrode). They were made of tungsten and stainless steel, respectively. After a certain reaction time, the products obtained by these experiments were introduced to methanol in a flask. The remaining fraction inside the reactor was then washed out with methanol at 90^{o}C for about 2 h. Each fraction collected with methanol was analyzed by using GC-MS, HPLC, and MALDI TOF-MS. The surface of the electrode before and after every treatment was observed by SEM.



(a) (b)

Figure 4. Experimental apparatus for reaction synthesis of aromatic compounds in supercritical CO_2 or argon with discharged plasma. (a) Schematic diagram, 1. reaction cell, 2. gas outlet, 3. solution outlet, 4. gas inlet; 5. pump, 6. supply vessel, 7. CO_2/argon container, 8. current transformer, 9. Magnetic Pulse Compressure (M.P.C.), 10. high voltage probe, 11. digital oscilloscope; (b) Apparatus photograph.



(a) (b)

Figure 5. GC-MS chromatogram of reaction synthesis product of phenol in supercritical argon with discharge plasma at 40°C and 5 MPa. (a) product, (b) remaining material.

Figure 5 shows a GC-MS chromatogram of product obtained during phenol reaction in supercritical argon with discharge plasma (a) and remaining material (b) at 40 °C and 5 MPa. The GC-MS chromatograms exhibit the presence of compounds with lower and higher molecular weight. It can be shown that phenol and solvent derived compounds were detected clearly in the product. However, some phenolic compounds with higher boiling point than phenol were detected in the remaining material. It could be explained that phenol radicals allowed alkyl rearrangement and re-polymerization to form heavier cross-linked phenolic char.

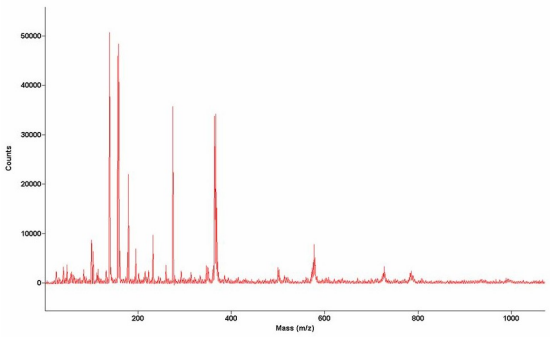


Figure 6. MALDI TOF-MS chromatogram of methanol soluble fraction obtained after pulsed arc discharge treatment in supercritical argon.

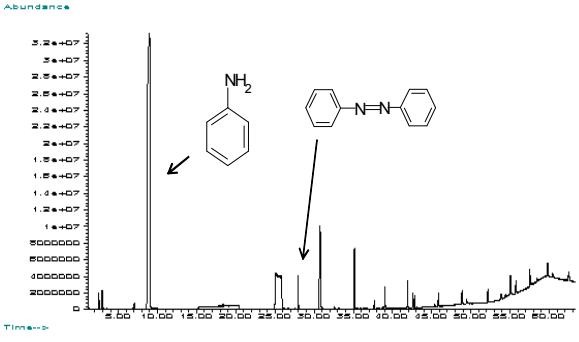


Figure 7. GC-MS chromatogram of aniline treated with discharge plasma at 100°C and 5 MPa

Figure 6 shows the MALDI spectra of the remaining material after washed out by using methanol. The results show that the formation of species in low molecular weight (less than 100 amu) occurred due to the scission of an O-H bond of phenol. At the same time, the higher molecular weight compounds (phenol oligomers; more than 200 amu) were formed via the association reaction of phenol and its derived compounds. These results provide evidence that functional groups react with other phenolic structures to form higher molecular weight compounds.

GC-MS chromatogram of aniline treated with discharge plasma at 100°C and 5 MPa is shown in Figure 7. Diphenylazene which consisted of aniline dimers was obtained in the lipophilic substance. The result provided evidence that functional groups react with other nitrogen structures to form higher molecular weight compounds (oligomers). It is considered that synthesis reaction of aniline in subcritical water with discharged plasma probably proceeded through the scission and association, which leads to the formation of lower or higher molecular weight compounds.

References

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