Production of Hydrogen and Monomer Aromatics by In-liquid Plasma Treatment of Lignin

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A lignin solution in methanol was treated with in-liquid plasma at 27.12 MHz radio frequency to produce H₂ and aromatic monomers. Gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) analyses were performed to characterize the produced gases and degradation products contained in the solution. GC analysis identified H₂, CO, CH₄, C₂H₂, CO₂, and C₂H₄ in the sample. GC-MS analysis identified several products, including benzene, toluene, and phenol. The quantity of each of these products was determined. These results indicated that the bonds around the benzene ring were broken in the plasma and reacted with OH radicals and CH₃ radicals from methanol.

Key Words
Radio-frequency, In-liquid plasma, Lignin, Hydrogen, Aromatic monomer

1. Introduction

The present chemical industry relies on fossil fuels. Phenolic compounds and aromatic hydrocarbons (BTX) such as benzene and toluene play an important role as raw materials for the production of basic chemical products. Lignin is one of the main constituents of wood (18-40 wt%) 1). Lignin has a large number of benzene rings and has drawn great interest as a new raw material for the production of aromatic monomers 2). There are many proposed methods to decompose lignin, such as thermal decomposition and supercritical fluid extraction 3) − 5). Hydrogen energy is the most promising energy source to enable sustainable development. Many scientists are working on improving the current H₂ generation methods 6) − 8). Previous studies have described the decomposition of solutions, such as water, waste oil, and cellulose suspensions for H₂ production, using in-liquid plasma 9) − 11). Plasma is generated in the solutions by applying a radio frequency (RF) as well as microwave radiation 12) − 13). Hydrogen production efficiency obtained using in-liquid plasma was 0.045 µmol/J to 0.259 µmol/J for the decomposition of a cellulose solution and 1.333 µmol/J for the decomposition of n-dodecane 9) − 11). However, for practical applications, it is necessary to increase the hydrogen production efficiency or to generate other valuable byproducts.

2. Experimental

Methanol (100 mL) was used as the solvent for 0.1-5.0 g of lignin (catalogue number L0045 Tokyo Chemical Industry Co., Ltd.); a solution containing 99 mL methanol and 1 mL benzene was alternatively used as the solvent for comparison. Only the soluble part of the lignin, which represents about 60-70% of the total lignin, was used by filtering the lignin solution through a filter paper (Advantec...
Part of the filtrate was volatilized in a water bath and weight of the remaining lignin was determined to dilute the solution with methanol to reach the target concentration. A schematic of the apparatus for the decomposition of lignin dissolved in methanol is shown in Fig. 1. A copper electrode with a diameter of 3.0 mm was inserted vertically from the bottom of the reactor and was enveloped by a ceramic tube, which is composed of a dielectric substance to minimize energy loss. An aluminum circular plate (diameter: 39 mm) with a tiny hole in the center was placed over the counter electrode. The gas production rate was measured and the produced gases were analyzed using gas chromatography. The solution was analyzed before and after the experiment by gas chromatography-mass spectrometry.

The experimental procedures are as follows: the pressure of the reactor was first reduced to the range of 5-7.5 kPa using an aspirator. Under this condition, the power input from a 27.12 MHz radio frequency generator and the impedance were simultaneously adjusted using a matching box. Plasma was discharged at the tip of the electrode instantly after the electric breakdown. The discharge power was 200 W, which was calculated by subtracting the reflected power from the input power. The reactor valve was opened once the inner pressure of the reactor reached the atmospheric pressure. The produced gas was then sampled by an air-tight glass syringe.

The spectra of the plasma generated were obtained using an optical emission spectroscope (Hamamatsu PMA11) in the range of 200-950 nm. The light emitted from the plasma was guided to a spectrometer through a quartz window. The quartz window was 5 mm thick and it was mounted on the side of the reactor and fixed using an acrylic cap. The optical fiber was mounted in front of the quartz window.

A Shimadzu GC-8A instrument was used to analyze the produced gases. The column used was a SHIMADZU GC Stainless Column SHINCARBON ST (length, 4 m; diameter, 3 mm). The temperature was controlled from 60°C for 6.0 min to 160°C at a rate of 10.0°C/min and the it was held at 160°C for 14 min. An argon carrier gas was applied at a flow rate of 50 mL/min. The produced gases were identified based on their retention times compared with those of authentic gases.

Shimadzu GCMS-QP2010 Ultra and GC-2010 Plus instruments were used to analyze the solution. The capillary column was a Rxi-1 ms column (length, 30 m; diameter, 0.25 mm; thickness, 0.25 µm). The temperature was controlled from 40°C for 1.0 min to 300°C at a rate of 10.0°C/min and it was held at 300°C for 10 min. A helium carrier gas was applied at a flow rate of 1.5 mL/min. The injector temperature was 230°C. One microliter of the solution was directly injected. The lignin-derived monomeric products were identified from their mass spectra by comparing their retention times with those of authentic compounds.

3. Results and Discussion

Fig. 2 shows the gas production rate. The product gas was composed of H₂, CO, CH₄, C₂H₂, CO₂, and C₂H₄. The gas production rates with lignin solutions of concentrations between 1 and 10 kg/m³ were slightly lower than those with a plain methanol solution. It is considered that gasification of lignin occurs near the center of the plasma. However, since it is difficult for nonvolatile polymeric lignin to exist in a plasma state, it is only slightly gasified. The energy of the plasma is used to generate the aromatic compounds, and the gas production rate decreases along with the concentration of lignin. In the 50 kg/m³ condition, the plasma was unstable and disappeared after 2.5 min of plasma irradiation. It was concluded that lignin accumulated on the electrode or between the electrode and the ceramic tube at this point could not be decomposed, impeding plasma generation.

The results of the GC-MS analysis revealed some products, including benzene, toluene, and phenol. The quantity of each of these products was also determined. Fig. 3 shows the amounts of benzene, toluene, and phenol produced as a function of the plasma processing time with a lignin concentration of 1 kg/m³ of solution. These results...
show that benzene was produced at a much quicker rate compared with toluene or phenol.

A mixed solution containing 99 mL methanol and 1 mL benzene was used for comparison. Table 1 shows a comparison of the amounts of the various components produced for the lignin solution and the benzene solution. Toluene and phenol were identified in both solutions after plasma treatment.

Optical emission spectroscopy was used to characterize the plasma. Fig. 4 shows the spectra of methanol solution at 100 kPa. At 100 kPa, the aspirator was stopped and the container was opened to the atmosphere. Emission lines from atomic hydrogen, including H α (656 nm) and H β (486 nm), OH (306 nm), CH (431 nm), and C 2 (460-480 nm and 500-515 nm), were observed and CO emission peaks were observed in the range of 250-650 nm. The methyl radical (CH 3) could not be observed because of the limited wavelength range of the optical measurement. However, the emission lines of OH and CH observed with methanol suggests that production of CH 2 as follows:

OH radicals and CH 3 radicals are produced in the plasma by the decomposition of methanol molecules:

\[ \text{CH}_3\text{OH} \rightarrow \text{CH}_3\cdot + \text{OH}\cdot \]  
(1)

Then, CH 2 and CH radicals were produced as a result of successive activation processes of CH 3:

\[ \text{CH}_3\cdot \rightarrow \text{CH}_2\cdot \rightarrow \text{CH}\cdot \]  
(2)

Benzene, toluene, and phenol were produced by the following processes. First, the bonds around the benzene

![Table 1](image)

| solute          | pretreatment volume (mL) | plasma processing time (min) | obtained benzene (µg) | obtained toluene (µg) | obtained phenol (µg) |
|-----------------|--------------------------|-----------------------------|----------------------|-----------------------|----------------------|
| lignin 0.1 g    | 100                      | 15                          | 105                  | 40                    | 12                   |
| benzen 0.88g    | 100                      | 15                          | -                    | 517                   | 59                   |
ring of lignin were broken in the plasma. Then, the OH radicals and CH$_3$ radicals reacted with benzene:

\[
\text{OH}^- + \text{C}_6\text{H}_6 \rightarrow \text{OH} + \text{C}_6\text{H}_5^- + \text{H}^- \quad (3)
\]

\[
\text{CH}_3^- + \text{C}_6\text{H}_6 \rightarrow \text{CH}_3\text{C}_6\text{H}_4^- + \text{H}^- \quad (4)
\]

A significant amount of research regarding the production of phenol by a reaction of the generated OH radicals with benzene has been reported\textsuperscript{18,19}. Some amount of the produced benzene gets converted into radicals owing to their collision with electrons:

\[
\text{C}_6\text{H}_6 + e^- \rightarrow \text{C}_6\text{H}_5^- + \text{H}^- + e^- \quad (5)
\]

Toluene and phenol are produced easily via a recombination reaction of these radicals:

\[
\text{OH}^- + \text{C}_6\text{H}_5^- \rightarrow \text{C}_6\text{H}_5\text{OH}^- \quad (6)
\]

\[
\text{CH}_3^- + \text{C}_6\text{H}_5^- \rightarrow \text{C}_6\text{H}_4\text{CH}_3^- \quad (7)
\]

In Fig. 3, the reason why benzene was produced at much quicker rate compared to toluene or phenol is considered as follows:

Benzene is produced by decomposition of the lignin solution. Subsequently, the methyl radical and the OH radical generated by the cleavage of methanol react with benzene to produce toluene and phenol. However, not all benzene reacts with radicals. It is considered that since the production rate of benzene is greater than the amount of its reacting with radicals, the amount of benzene production is larger than that of toluene and phenol production.

The amounts of benzene, toluene, and phenol produced for various lignin concentrations are shown in Fig. 5. The amounts of these products increased with the concentration of lignin. In particular, the amount of phenol produced increased significantly as the lignin concentration increased. The ratio of toluene to phenol produced by the decomposition of the benzene solution was approximately 8.8, while those produced by the decomposition of solutions containing 1, 10, and 50 kg/m$^3$ of lignin were 2.0, 0.36, and 0.08, respectively.

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