

CHEMICAL PRODUCTION FROM LIGNIN AND CARBOHYDRATES WITH NEAR-CRITICAL WATER ELECTRICAL TREATMENTS

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In this study, hydrothermal electrochemical reactions of various biomass-related compounds were investigated by using the autoclave and continuous flow-type reactors in order to understand main reaction pathways for 1-butanol to understand conversion behavior of hydroxyl group in organic compounds and to predict reaction feature of saccharides under hydrothermal electric atmosphere. As a result, it was found that 1-butanol could be converted into butylaldehyde and butyric acid via partial oxidation at 250 °C, 3 MPa and 1 – 3 A-DC for more than 30 min while no formation of oxidation products was observed in the case of the experiment with no current loading at identical conditions. Next, glycerol which has two primary hydroxyl groups and one secondary one was treated in dilute alkaline solution at 240-280 °C by using the batch-type autoclave. The experimental results showed that glycerol could be converted into lactic acid although the yield and selectivity was lower than those in concentrated alkali solution at 300 °C.

INTRODUCTION

Nowadays, many industries generate large quantities of aqueous wastes containing organic substances. Treatment of these pollutants has become a major social, technological and economical problem. As an alternative way to the commercial processes for the treatment of these organic substances, we have been trying to develop a new technique called hydrothermal electrolysis, by which the pollutant organics can be converted to innocuous compounds or valuable chemical intermediates under high-temperature and high-pressure aqueous conditions. For this method, sub-critical water was chosen because water near the critical point has very different properties from those of ambient liquid water. The dielectric

constant is much lower, and the number and persistence of hydrogen bonds are both diminished. The ion product or dissociation constant (K_w) for water as it approaches the critical point is about three orders of magnitude higher than it is for ambient liquid water. As a result, water becomes an excellent solvent for organic compounds; it can also boast a higher H^+ and OH^- ion concentration than liquid water under certain conditions. In this work, reactions of various organic compounds regarding biomass resource were carried out by using both a batch-type electric autoclave and a continuous flow-type reactor in order to know fundamental reaction pathways for the compounds.

Next, in recent days, bio-diesel fuel (BDF) has paid attention to as one of new energies. In the conventional production method for BDF, however, glycerol has been generated as a main byproduct and it is a current situation to affect the economy in the BDF manufacturing. Kishida et al. conducted the experiments of glycerol in a 1.25 mol/L NaOH aqueous solution at 300 °C for 90 minutes and found that lactic acid could be obtained from glycerol in the maximum yield of 90%. However, the method has problems about the corrosion of tubes and pipes because of the use of concentrated alkali, and requirement of considerable treatments. Therefore, in this work, the hydrothermal electrolysis treatment of glycerol under dilute alkali conditions was examined to obtain lactic acid in high yield and selectivity.

MATERIALS AND METHODS

In the batch experiments, the batch-type electrolytic autoclave shown in **Figure 1** was used. Aqueous electrolyte solutions were prepared by dissolving commercially available salts in de-ionized water and then a given amount of starting material (1-butanol) was charged in the solutions. Electrolysis was carried out in sub-critical water (240-280 °C and 5-20 MPa) using a sealed 500 mL batch autoclave equipped with a stirring impeller, electrodes, electric heating device, temperature control unit and a pressure gauge. Half of the autoclave's inner volume (250 mL) was charged with aqueous electrolyte solution. A cylindrical iridium plate electrode (23 mm in diameter, 30 mm in length), coaxial to the titanium beaker (74 mm in diameter, 100mm in length), was used as the anode. The titanium beaker was used as the cathode to promote cathodic protection of the autoclave from corrosion. The air in the autoclave, after charging the autoclave with aqueous solution, was purged with inert gas (Ar) in all experiments. The total gas initially charged into the autoclave was kept at 2 or 7 MPa and the existence of the aqueous phase was ensured for all temperatures below the critical point of water. The electrolyte solution inside the autoclave was continuously stirred throughout the experiment by means of a magnetically driven mixer. Temperatures and concentration were assumed to be uniform inside the autoclave. The sealed autoclave was

heated with an electrical furnace from room temperature at a rate of approximately 250 °C per hour until the temperature, measured using a thermocouple inserted in the autoclave, reached the prescribed value. The inner pressure of the autoclave increased as a function of temperature, and the typical reaction pressure was 7 MPa when the autoclave temperature was 250 °C. Once the autoclave had reached the intended temperature, the prescribed constant electrical current was passed between the electrodes for wet electrolytic oxidation experiments. No current was passed for wet oxidation runs. Gas products were analyzed by GC-TCD and liquid products from 1-butanol were analyzed by GS-MS and GC-FID. The total organic carbon in the aqueous product solution was monitored by TOC analyzer.

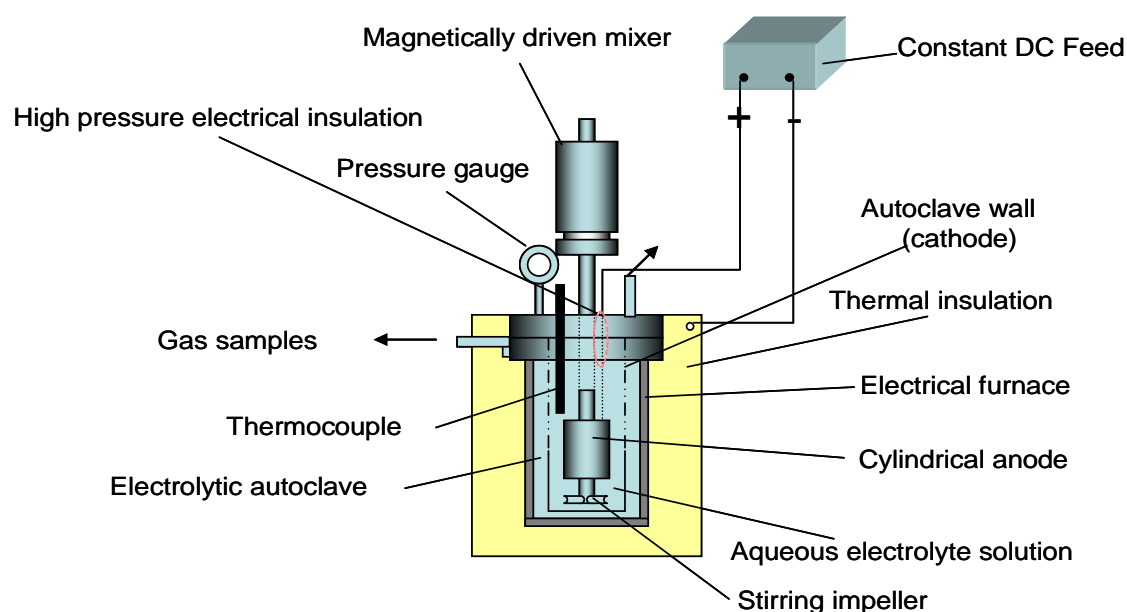


Figure 1. Schematic illustration of a batch-type electrolytic autoclave used in this work.

Also, 0.1 mol/L of glycerol aqueous solution and 0.01 mol/L of NaOH aqueous solution were used as starting materials for hydrothermal electrolysis experiments at 250 °C, 7 MPa and 1 - 3 A-DC current. The water soluble portion and gaseous portion were collected after the reaction, respectively. The water soluble portion was filtrated and analyzed by using HPLC after the pH of the solution had been adjusted to 4 - 6 with sulfuric acid. The MCI GEL CRS10W (Mitsubishi chemical Co., Ltd., Japan) was used for the HPLC analysis and the 2.0 mmol/L-CuSO₄ was used as a HPLC solvent. The gaseous portion was analyzed by GC-TCD.

Additionally, reactions of 1-butanol, glycerol and other related chemicals were conducted by using a continuous flow-type reactor which was shown in **Figure 2**.

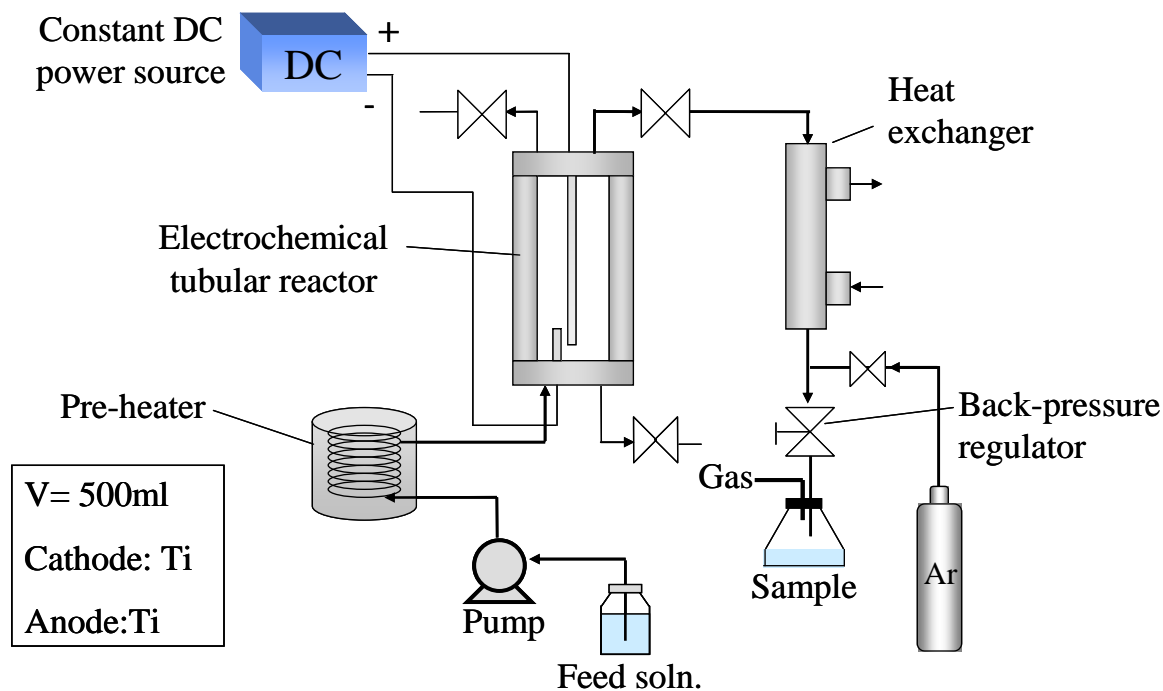


Figure 2. A continuous flow-type reaction system used in this work.

RESULTS AND DISCUSSION

Gas detected after the hydrothermal electrolysis of 1-butanol was hydrogen (H_2). **Figure 3** shows the amount of H_2 generated at a temperature of $250\text{ }^\circ\text{C}$ and an initial pressure of 3 MPa. The amount of hydrogen generated by this reaction increased with an increase in DC current value, whereas no gas was generated for the hydrothermal degradation of 1-butanol, i.e., no

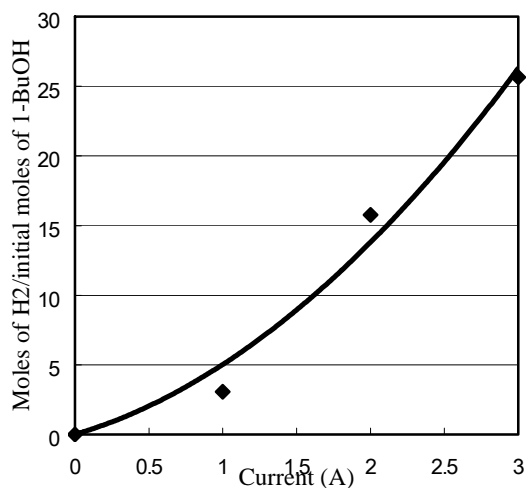


Figure 3. Amount of hydrogen obtained by hydrothermal electrolysis of 1-butanol at $250\text{ }^\circ\text{C}$, 3 MPa for 60 min.

electric current. Butanal and butyric acid were detected as main liquid products from the electrical treatment of 1-butanol in sub-critical water. **Figure 4** shows the degradation profile of 1-butanol for 0 - 3 A-DC current charged electrolysis at 250 °C. The yield of 1-butanol decreased with an increasing current value. At hydrothermal degradation run, the conversion of 1-butanol was confirmed, but the generation of gas such as hydrogen was not observed. The experiments showed that although 1-butanol is very stable compound under high-temperature and high-pressure, hydrothermal electrolysis has an enhancing effect on the decomposition of 1-butanol in sub-critical water. We could understand the fundamental reaction behavior of 1-butanol as a starting material under a wide range of operating conditions through various kinds of experiments and product analysis. Recently, additional series of experiments using ethylene glycol, glycerol and other compounds are carrying out to know reaction pathways and mechanism under hydrothermal electrical atmosphere.

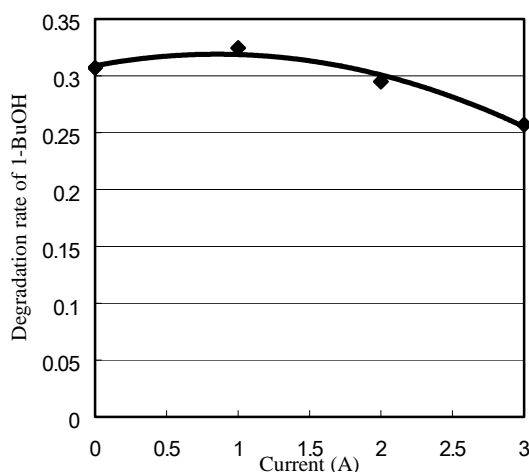


Figure 4. Conversion of 1-butanol by hydrothermal electrolysis experiments at 250 °C, 3 MPa for 60 min.

Next, in the case that the glycerol was electrolyzed with 1 A-DC charge under hydrothermal state, main products in the water soluble portion were L-lactic acid, D-lactic acid, glycolaldehyde, and formic acid, as shown in **Figure 5**, and other unidentified components were detected on the HPLC chromatogram. On the contrary, only the hydrogen was generated as a gas product. Now hydrothermal electrolysis reactions of glycerol with various operating conditions such as temperature, current value and treatment time, etc. have been carrying out in order to elucidate possible reaction pathway and to explore suitable condition where L-lactic acid can be obtained in high yield and selectivity.

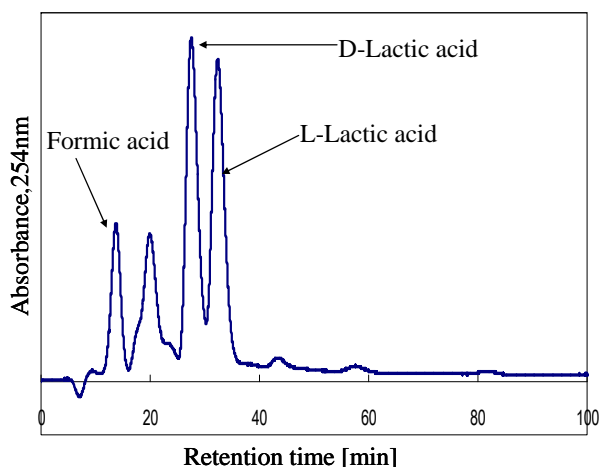


Figure 5. A typical HPLC chromatogram of the liquid product solution obtained from the glycerol reaction at 250 °C, 7 MPa and 1 A-DC for 60 minutes.

Acknowledgement

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