

ELECTROCHEMICAL REACTION OF ALCOHOLS IN SUBCRITICAL WATER

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Abstract

We have been developing electrolysis of organic compounds in subcritical water as a waste treatment technology and molecular conversion technology. Organic molecules can be converted to innocuous compounds, such as carbon dioxide, water, and hydrogen by electrolysis under hydrothermal condition.

In this study, we have applied the hydrothermal electrolysis to reactions of alcohols, such as butanol and glycerol. Batch type and continuous flow-type reactors were used in order to reveal the main reaction pathways of organic compounds containing hydroxyl group in the electrolysis in subcritical water to predict reaction feature of biomass-related compounds such as saccharides.

As a result, it was found that 1-butanol was converted into butylaldehyde and butyric acid via partial oxidation at 250 °C and 1 - 3 A of DC current while no oxidation products was observed without electrical current loading at identical conditions. As a gas phase product, hydrogen was generated according to electrochemical reaction. Glycerol which has two primary hydroxyl groups and one secondary one was treated in dilute alkaline solution at 240-280 °C. The experimental results showed that glycerol was converted into lactic acid, glycolaldehyde, and formic acid. As a gas product, only hydrogen was obtained. The yield and selectivity of lactic acid was lower than the reaction 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 developing 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 [1-5]. 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 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.

In recent days, bio-diesel fuel (BDF) that has been 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 [6] 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. As a simple primary alcohol, we also used 1-butanol as a starting material.

Experimental Setup and Procedure

In the batch experiments, the batch-type electrolytic autoclave shown in Fig. 1 was used. Aqueous electrolyte solutions were prepared by dissolving 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, 100 mm 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.

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 Fig. 2.

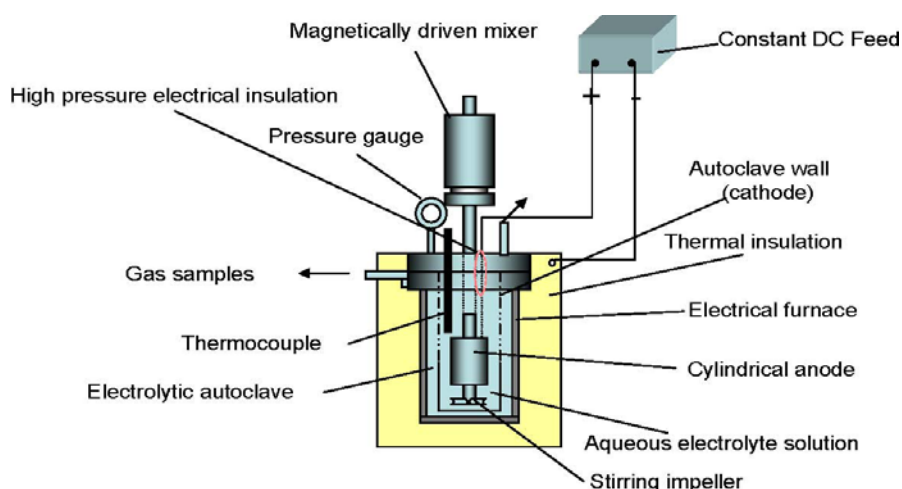


Fig. 1 Schematic illustration of a batch-type electrolytic autoclave

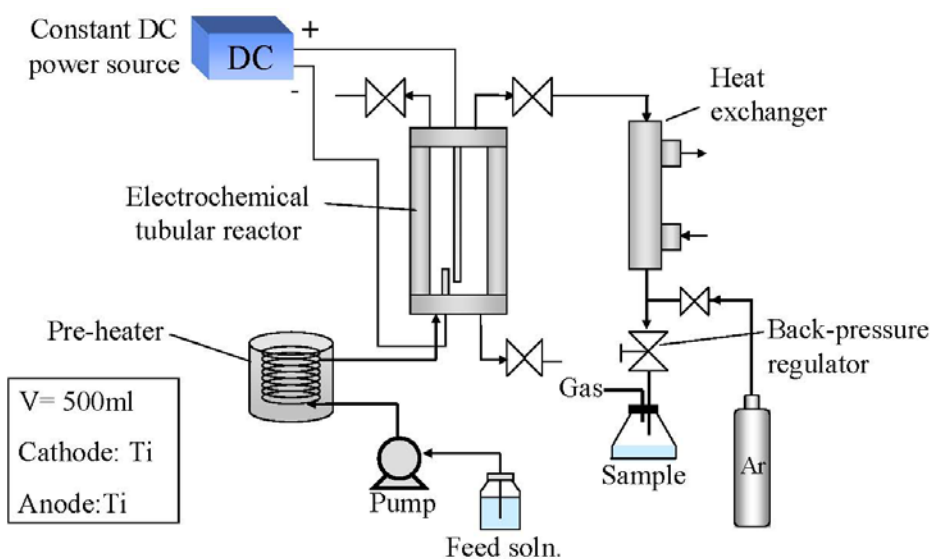


Fig. 2 Schematic illustration of a continuous flow-type electrolytic reactor

Results and Discussions

1-Butanol

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 $250^\circ C$ and an initial pressure of 3MPa. 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 electric current. The amount of hydrogen generated at 3A was 8.4 times that generated at 1A for the same electrolysis time of 60min. Liquid phase products of electrical treatment of 1-butanol in sub-critical water were also analyzed and butanal and butyric acid were detected as main products. Figures 4 and 5 show the yields of butanal and butyric acid, respectively. For hydrothermal degradation run (0A) and 1A, the production of both butanal and butyric acid was not observed. However, as the current increased from 2A to 3A for the same reaction time of 60min, it was seen that the yields of the liquid products also increased. As for butanal the amount of it at 3A was 1.33 times larger than that obtained from the reactions at 2A and the yield of butyric acid at 3A was 1.95 times larger than that at 2A.

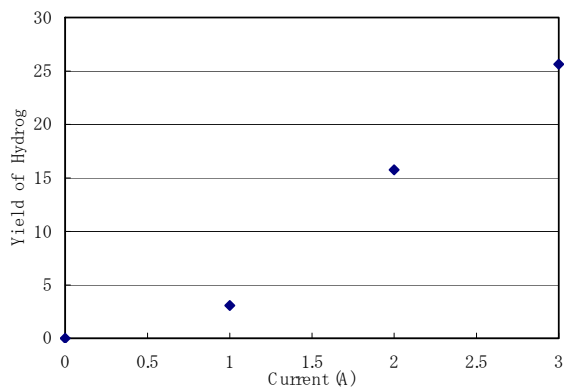


Figure 3: Amount of hydrogen obtained by hydrothermal electrolysis of 1-butanol.

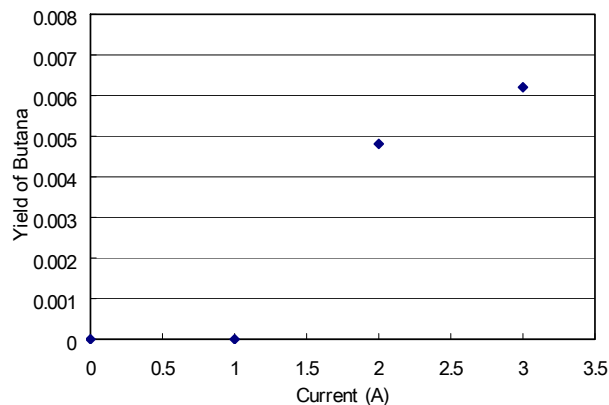


Figure 4: Yield of butanal vs current.

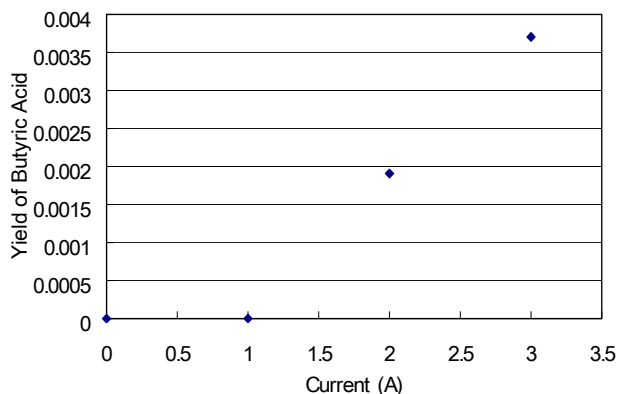


Figure 5: Yield of butyric acid vs current at the conditions of 0.5M 1-butanol

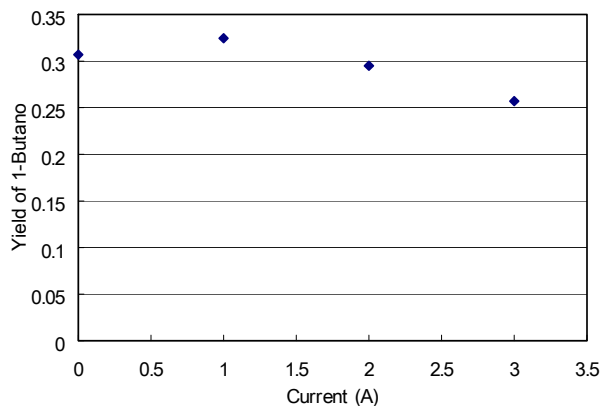


Figure 6: Yield of 1-butanol vs current at the conditions of 0.5M 1-butanol

Figure 6 shows the decomposition profile of 1-butanol for 0-3A 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.

Electrolysis experiments of butanal were also carried out under hydrothermal conditions in order to clarify the decomposition mechanism of 1-butanol. Same as the conversion reaction of 1-butanol, the products were gases and liquid ingredients and from the gas phase hydrogen was detected. As for the generation of this gas, a tendency to increase with electrolysis time was confirmed. In addition, butyric acid was detected from a liquid ingredient.

Glycerin in alkaline condition

Hydrothermal electrolysis of glycerin with an alkali was also studied and showed that glycerin could be converted into lactic acid by this method. As an alkali, NaOH was added to the raw material solution for each experiment.

After the hydrothermal electrolysis of glycerin in alkaline conditions, formic acid, glycolic acid, L-Lactic acid and D-Lactic acid were formed as main organic acids.

Figure 7 shows the conversion profile of glycerin with alkali inside the electrolytic autoclave for 0-2A DC current charged electrolysis at 280°C. From this figure it is possible to say that the conversion of glycerin increased with an electric current value. At 0A, the conversion of glycerin was somehow high but the generation of gas such as hydrogen was too low. We understood that yield of organic acids such as formic acid, glycolic acid, L- and D-Lactic acid increased with electrolysis time. Therefore it is thought that some of glycerin was converted to these organic acids by thermal energy.

Figure 8 shows the variation of concentrations of the main organic acids (formic acid, glycolic acid, L-Lactic acid and D-Lactic acid) when the treatment was carried out at no current loading, 1A loading and 2A loading.

In hydrothermal degradation without current, the formation of formic acid and glycolic acid were very low. The yields of L- and D-Lactic acids became higher as the yield of two acids was nearly constant at 35min. When 1A current was applied, the yields of glycolic acid, L- and D-Lactic acids increased gradually up to 60min and then started to decrease, whereas the amount of formic acid was almost kept constant. For the hydrothermal electrolysis at 2A, it was observed that the amounts of organic acids produced with time had a wide variation. This was probably because of the corrosion problem and solid residue, such as char, formed and stuck to the electrode and as a result obstructed the electrolysis.

Gaseous product detected after hydrothermal electrolysis of glycerin with alkali was hydrogen (H₂). Figure 9 shows the amount of hydrogen generated at a temperature of 280°C and an initial pressure of 3MPa. The amount of hydrogen gas generated by this reaction increased with the increasing reaction time at 280°C and 1A, whereas negligibly small amount of gas was generated even for a reaction time of 90min in hydrothermal degradation run (0A). The amount of hydrogen produced at 1A was 6.4 times that generated at 0A for the same electrolysis time of 90min.

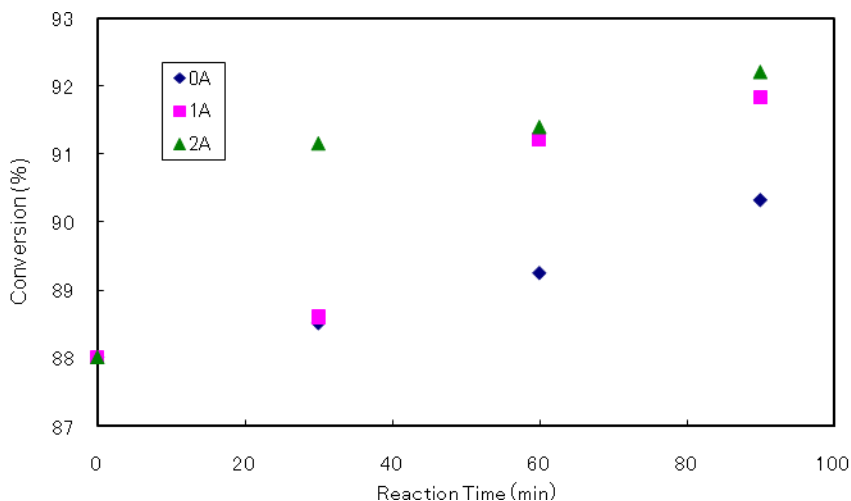


Figure 7: Variation of product concentrations on the hydrothermal electrolysis of glycerin with an alkali at currents of 1A.

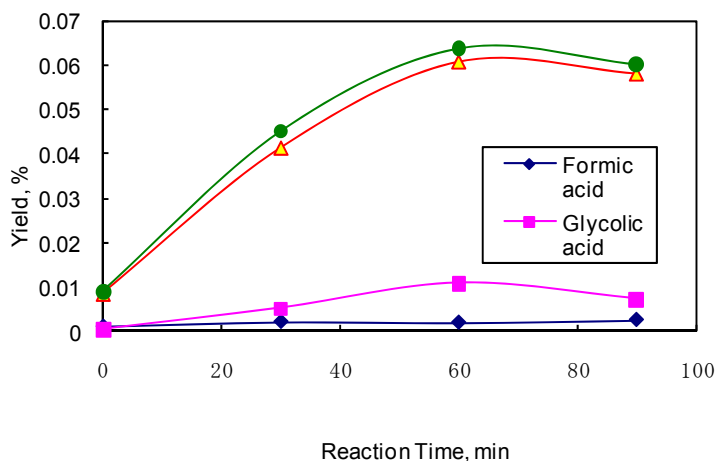


Figure 8: Conversion of glycerin in alkali by hydrothermal electrolysis

Conclusion

Hydrothermal electrolysis experiments using aqueous 1-butanol and glycerin solutions as a starting material were carried out under a wide range of operating conditions using a specially designed autoclave. Despite the uncertainties remaining concerning the oxidation mechanism, differences in the governing reactions of hydrothermal electrolysis were clearly revealed. Electrolysis of aqueous KCl solution under high-temperature/high-pressure conditions greatly suppressed oxygen gas evolution.

We could understand the fundamental reaction behavior and the main products of 1-butanol and glycerin under these conditions through various kinds of experiments and product analyses. By using NaOH as an alkali, another series of experiments of glycerin were carried in order to know the reaction mechanism of glycerin in alkaline conditions. The main liquid products from the hydrothermal electrolysis of 1-butanol with KCl under sub-critical water were butanol and butyric acid, whereas in the case of glycerin with an alkali (NaOH), formic acid, glycolic acid, L-Lactic acid and D-Lactic acid were formed as main organic acids. It was found that the conversion of 1-butanol and glycerin increased with the increasing reaction time. At hydrothermal degradation run (0A), 1-butanol was hardly decomposed. When 2A was applied, the amount of liquid products generated with time had a wide variation. This was probably because of corrosion problem and solid residue, such as char, formed and stuck to the electrode and as a result obstructed the electrolysis.

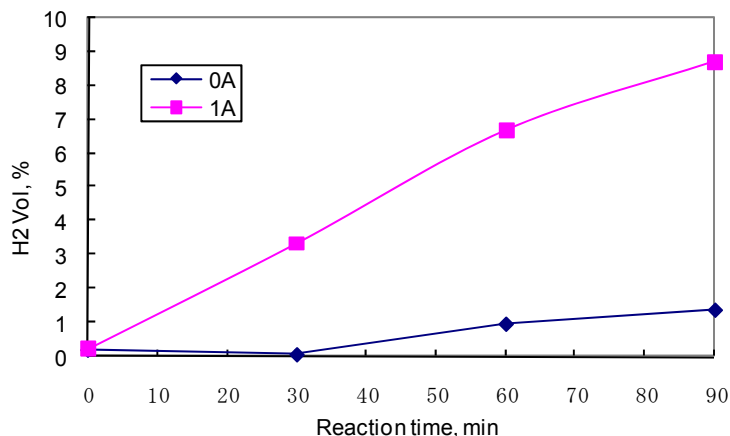


Figure 9: Amount of hydrogen generated by the hydrothermal electrolysis of glycerin in alkaline conditions

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Acknowledgements

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