Treatment of BDF Wastewater with Hydrothermal Electrolysis

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Recently, interest for biodiesel fuels (BDF) have gained more attention because they have many advantages compared to petroleum-based fuels. For instance, they are renewable, non-toxic and environmental friendly techniques. However, during this process, some by-products such as crude glycerol are also produced. Although this crude glycerol is very important for the production of more valuable chemicals, in many biodiesel plants with low capacity, it is discharged in the wastewater together with some alkali, methanol and salts without any utilization. As a result, both economical losses and environmental pollution are generated. Therefore, we have been developing a new hydrothermal electrolysis system, by which BDF wastewater can be converted to more value added chemicals under high-temperature and high-pressure aqueous conditions. In this study, hydrothermal electrolysis reactions of model BDF wastewater was investigated under various operating conditions in order to know current efficiencies, intermediate products and possible reaction schemes. We next tried to understand the effects of electricity loading on the molecular transformation of starting materials through the comparison of the product distribution obtained by hydrothermal electrolysis with that by hydrothermal degradation. The experiments were carried out by using both flow reactor and batch autoclave equipped with a stirring impeller, electrodes, electric heating device, temperature control unit and a pressure gauge. At the end of experiments, liquid products were analyzed by HPLC and GC-FID. Total organic carbon was monitored by using TOC Analyzer and for the identification of gas products GC-TCD was used.

INTRODUCTION

Biodiesel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats. It is biodegradable and non-toxic has low emission profiles and so is environmentally beneficial.

The production of biodiesel fuel (BDF) is one of the key technologies for the treatment of waste oil and the recycling of food processing and domestic residues [1]. Several methods of BDF production, such as transesterification using alkali catalysis, acid catalysis and supercritical methanol, ultrasonic irradiation and thermal decomposition of oil using alkali catalysis, have been developed [2-4]. The transesterification using alkali catalysis is a useful method that enables a high conversion of triglycerides (oil) to fatty acid methyl esters (BDF) and glycerol as by-product by a simple chemical reaction in a short time. In many biodiesel plants with low capacity, this crude glycerol is discharged in the wastewater together with some alkali, salts and methanol. By this manner, environmental pollution is created. Therefore this glycerol should be treated before releasing to the environment.

There are several methods for the conversion of glycerol. In one study, glycerol conversion in aqueous solution under hydrogen over an ion exchange resin was done. It was found that the OH group on the resin could catalyze the dehydration of glycerol to 3-hydroxypropionaldehyde, which can be converted to 1,3-propanediol and other degradation products through subsequent hydrogenation [5]. In another study, ionic reactions and pyrolysis of glycerol in near- and supercritical water were investigated. It was shown that the products of the glycerol degradation were methanol, acetaldehyde, propionaldehyde, acrolein, allyl alcohol, ethanol, formaldehyde, carbon monoxide, carbon dioxide, and hydrogen. One of the reaction pathways consist of ionic reaction steps, which were preferred at higher pressures and/or lower temperatures. The second reaction pathway was free radical degradation and dominates at lower pressures and/or higher temperatures [6].

Conversion of glycerol to lactic acid was one method of particular interest. In one study, it was showed that glycerol could be converted into lactic acid with a high yield by hydrothermal decomposition experiments of glycerol in sub-critical water under alkaline conditions. Studies on the conversion pathway suggested that glycerol was first decomposed to pyruvaldehyde with elimination of hydrogen and the pyruvaldehyde was then converted into lactic acid ion by the benzilic acid rearrangement. In this study, except lactic acid, small amounts of pyruvaldehyde, acetic acid and formic acid were also detected. The results showed that lactic acid could be produced in large quantities, and both the temperature and the concentration of NaOH had a great effect on the conversion of glycerol into lactic acid in sub-critical water [7].

The main purpose of this work is to decompose model biodiesel wastewater by hydrothermal electrolysis under various operating conditions by using an electrolytic autoclave and flow type reactor. We also tried to understand the effects of electricity loading on the molecular transformation of glycerol inside the model BDF wastewater through the comparison of the product distribution obtained by hydrothermal electrolysis with hydrothermal degradation. For this method, sub-critical water was chosen because the dielectric constant is much lower, and the number of hydrogen bonds is diminished. Additionally, the ion product or dissociation constant (Kw) 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 [8].

MATERIALS AND METHODS

Model BDF wastewater was prepared by dissolving in de-ionized water. Electrolysis was carried out using a sealed 500ml batch autoclave made of SUS 316 stainless steel and flow type reactor as illustrated in Figure 1 and 2, respectively.

Both of the reactors were pressurized with argon gas before starting each experiment. This internal pressure of the system was defined as the initial pressure of the experiment. After loading the aqueous solution into the reactor, the temperature in the system increased and subsequently the internal pressure gradually increased. Typical temperature and pressure profile for autoclave during heating to $280^{\circ}C$ is shown in Figure 3. The internal pressure at the time when the temperature reached the desired reaction temperature and the DC current was applied to the solution was defined as the reaction pressure.
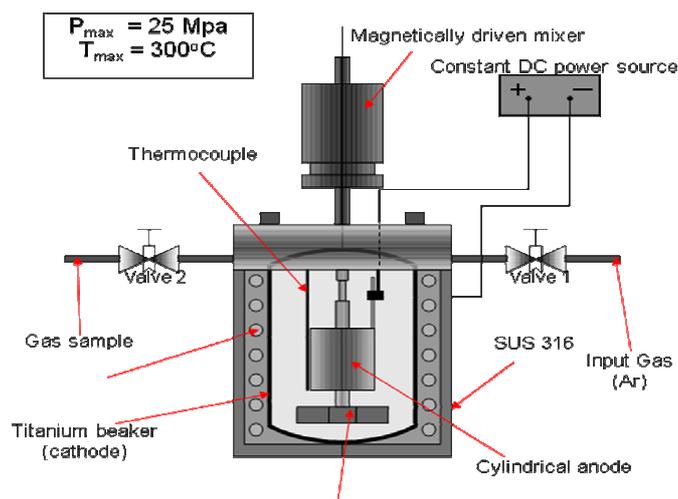
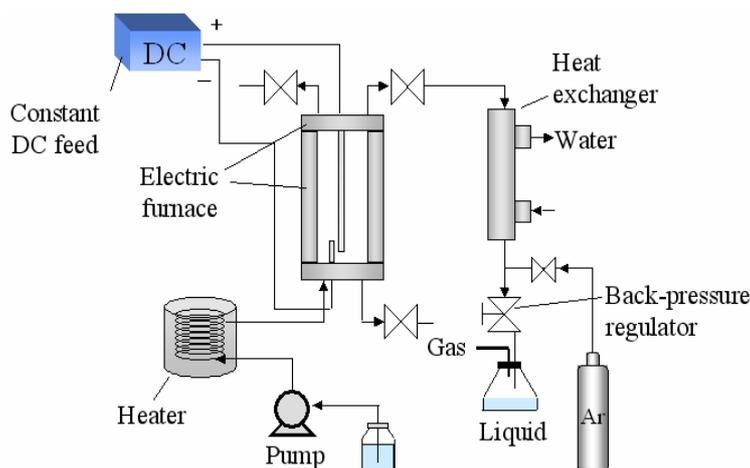**Figure 1:** Autoclave for hydrothermal electrolysis

Figure 2: Flow type reactor for hydrothermal electrolysis

For the experiments done by using batch reactor, after heating the system up to desired temperature, half of the autoclave's inner volume (250ml) was charged with the aqueous electrolyte solution at a rate of 25ml/min. In the case of flow reactor, 500ml of model BDF wastewater was loaded into the reactor at different flow rates.

In autoclave, a cylindrical iridium plate electrode was used as anode whereas, the titanium beaker was employed as a cathode to promote cathodic protection of the system from corrosion. On the other hand, in flow reactor, titanium beaker acted as both anode and cathode. The air in the reactor was purged with inert gas (argon) in all experiments. The total gas initially charged into the reactors was kept at 3MPa and the existence of aqueous phase was ensured for all temperatures below the critical point of water. The electrolyte solution inside the both reactors was continuously stirred throughout the experiment. Temperatures and concentrations of solution were assumed to be uniform inside the reactors. The reactors were heated with an electrical furnace from room temperature to a desired temperature which was measured using a thermocouple inserted in the system during the experiments. The inner

pressure of the reactors increased as a function of temperature, and the typical reaction pressure was between 10MPa and 14MPa. Once the system had been heated up to the desired temperature, the constant electrical current was passed between the electrodes for hydrothermal electrolysis experiments. No current was passed for hydrothermal degradation run.
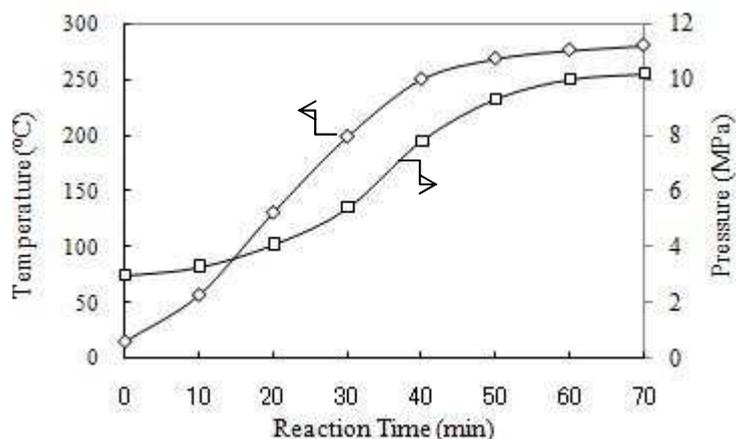

Figure 3: Typical temperature and pressure profile for hydrothermal electrolysis at 280°C

After cooling the reactors up to about 35°C, both gas and liquid products were collected. Gas products were analyzed by GC-TCD and liquid products were analyzed by HPLC and GC-FID. The total organic carbon in the aqueous product solution was monitored by TOC analyzer.

RESULTS

Gas detected after the hydrothermal electrolysis of model BDF wastewater including 0.1M glycerol were hydrogen (H_2) and small amount of carbon dioxide (CO_2). Figure 4 shows the volume percentage of H_2 and CO_2 generated at a temperature of 280°C and an initial pressure of 3Mpa by using flow reactor. The amount of hydrogen generated by this reaction increased with an increase in DC current value and the production of carbondioxide was only confirmed in the hydrothermal electrolysis run. For the comparison, no current was passed in the hydrothermal degradation run. As it can be seen below, negligibly small amount of hydrogen gas was generated at 0A.
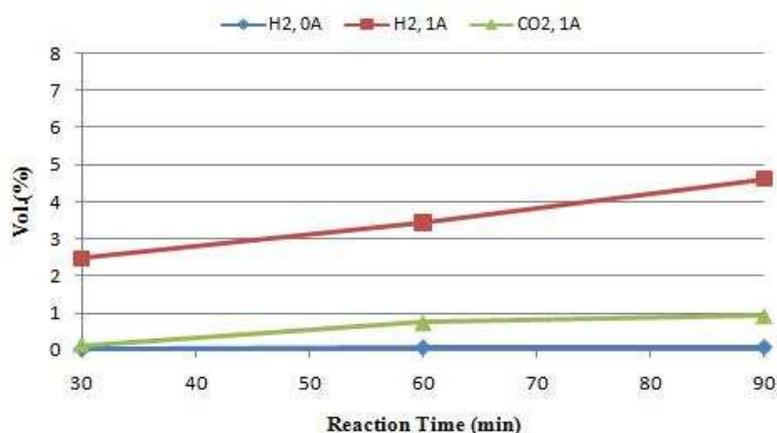

Figure 4: Volume percentage of gas products produced after hydrothermal electrolysis of BDF wastewater including 0.1M glycerol by flow type reactor at 280°C

As liquid products, formic acid, glycolic acid, acetic acid and lactic acid were formed after hydrothermal electrolysis of model BDF wastewater including 0.1M glycerol by flow type reactor. The yield of these organic acids was shown in Figure 5.

As seen in Figure 5, the yield of organic acids increased when the applied current was raised to 1A. In the case of hydrothermal degradation run, no acetic acid was produced and the generated amount of glycolic acid and formic acid were also very small. The yield of lactic acid, which is a combination of D- and L- lactic acid, was 3.2 at the end of 90min electrolysis time when 1A current was passed between the electrodes. However, in the hydrothermal degradation run, it was 0.6 even after 90min.
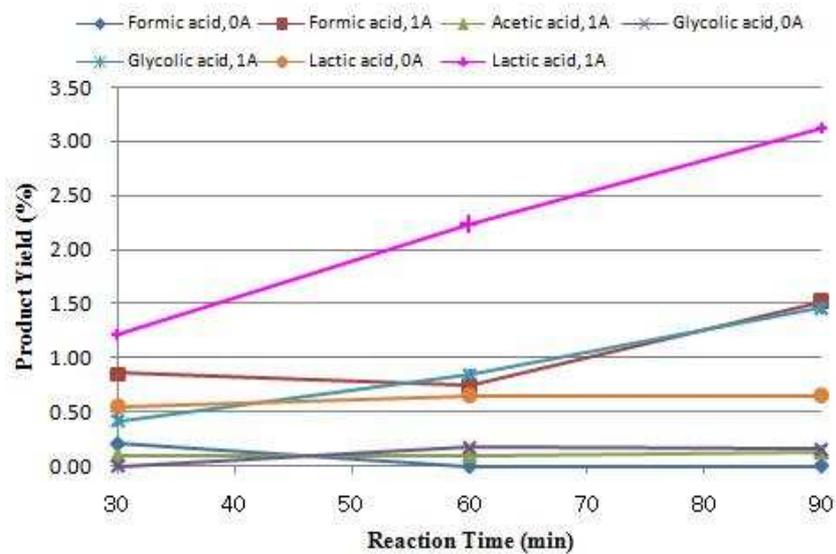

Figure 5: Yields of organic acids produced after hydrothermal electrolysis of BDF wastewater including 0.1M glycerol by flow type reactor at $280^{o}C$

When no current was applied, the conversion of glycerol inside the model BDF wastewater was almost kept constant at 72% between 30min and 60min as shown in Figure 6. Then started to decrease gradually and at the end of 90 min it was around 65%. However, in hydrothermal electrolysis run, the conversion value increased with increasing reaction time and reached its maximum value as 85% at 90min.
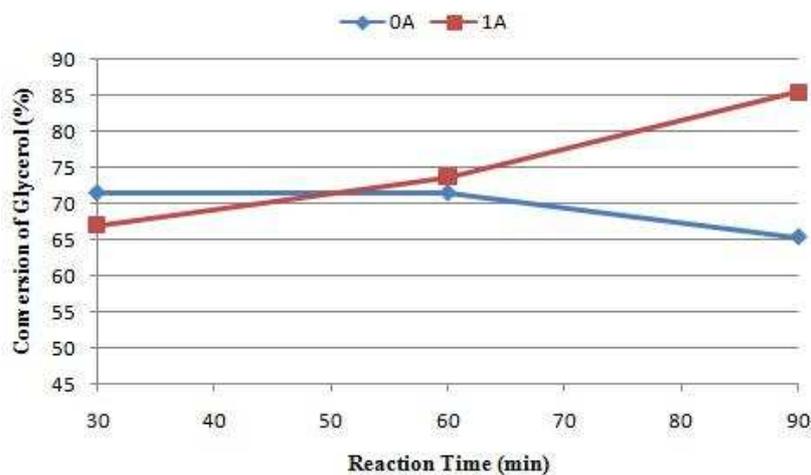

Figure 6: Conversion of glycerol inside the model BDF wastewater by flow type reactor at $280^{o}C$

The hydrothermal electrolysis of model BDF wastewater including 0.5M glycerol have being done by using batch reactor at reaction temperatures between 230-270°C. In these series of experiments, the effects of applied current, amount of alkali, concentration of glycerol inside the model BDF wastewater, the amount of hydrogen generated from the electrolysis of water are also examined. We are still carrying on these experiments by using autoclave.

CONCLUSION

Electrical treatment experiments of model BDF wastewater were carried out in sub-critical water. The experiments showed that although glycerol is very stable compound under high-temperature and high-pressure, hydrothermal electrolysis has an enhancing effect on the decomposition of glycerol inside the model BDF wastewater under alkaline conditions.

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