Hydrothermal Degradation of Glycerol by Electrolysis in Subcritical Water

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Biodiesel has become an attractive fuel recently, because it is renewable, non-toxic, biodegradable, environmentally friendly, etc. With the increase in the production of biodiesel, the problem of disposing crude glycerol, which is produced as main by-product from biodiesel process such as transesterification, has been raised. Therefore, we have been developing a new green technology-Hydrothermal electrolysis- by which crude glycerol inside the biodiesel wastewater can be converted into more value added products such as lactic acid and formic acid under high-temperature and high-pressure conditions. In this study, hydrothermal electrolysis reactions of model biodiesel wastewater was investigated by varying operating parameters such as electrolysis time, applied current value and alkali concentration, etc. We tried to understand the effects of these parameters on the decomposition of glycerol and clarify possible reaction mechanisms. We carried out experiments by applying current and without any current then compared the product distribution obtained by hydrothermal electrolysis with hydrothermal degradation. The experiments were carried out by using both continuous and batch type reactors equipped with titanium and iridium electrodes, a current supplier, an electric heating device, a temperature control unit and a pressure gauge. At the end of the experiments, liquid products were analyzed by high performance liquid chromatography and gas chromatography with flame ionization detector. For the identification of gas products, gas chromatography with thermal conductivity detector was used. Total organic carbon was monitored by using TOC analyzer.

Key words: Hydrothermal electrolysis, glycerol, biodiesel waste water

INTRODUCTION

Petrochemical sources such as coal, natural gas, etc. supply most of the world’s energy needs. However, they are finite and their usage have huge impact on the environment. Therefore biodiesel as an alternative fuel has gained more attention recently. It is renewable, nontoxic, biodegradable [1]. However, as shown in Figure 1, by commercial techniques such as transesterification process, together with biodiesel some byproducts mainly including glycerol were also generated. In order to avoid environmental pollution and economic loses, this crude glycerol should be treated and converted into more value added chemicals.
Many studies have been conducted on the conversion of glycerol into various compounds. Catalytic dehydration, hydrogenolysis, pyrolysis, gasification and steam reforming are some common methods for the decomposition of glycerol to gas and liquid products. By catalytic dehydration in sub- and supercritical water, glycerol was converted into 3-hydroxypropionaldehyde, 1,3-propanediol, acrolein and other degradation products through subsequent hydrogenation [2-4].

Catalytic hydrogenolysis of glycerol has been widely studied over different types of catalysts (e.g., nickel, palladium, copper, platinum, zirconia, and ruthenium) [5-8]. Series of experiments were carried out by changing reaction temperature and pressure, hydrogen pressure, amount of catalyst, and catalyst reduction temperature and found that as well as further degradation of the glycols, glycerol was decomposed into ethylene glycol, propylene glycol (1,2-propanediol), and 1,3-propanediol.

In many studies [9-13], researchers focused on the gaseous products from pyrolysis and gasification of glycerol. Hydrogen could be generated for use as clean fuel or as feedstock gas such as syn-gas (CO+H₂) from gasification or pyrolysis of glycerol at high temperatures and high pressures. In these systems, char and tar formation were the most significant technological problems. Catalyst use produced high yields of hydrogen and decreased the amounts of char and tar.

Conversion of glycerol also can be accomplished through a steam reforming process. This technique produces several intermediate by-products that occur in the product stream and affect the purity of the final hydrogen product [14, 15].

One method of particular interest is the conversion of glycerol to lactic acid [16]. Kishida et. al. showed that glycerol can be converted into lactic acid by hydrothermal decomposition experiments of glycerol in sub-critical water under alkaline conditions. Studies on the conversion pathway have suggested that glycerol is first decomposed to pyruvaldehyde with elimination of hydrogen by a H- shift to the adjacent hydrogen. The pyruvaldehyde is then converted into lactic acid ion by the benzilic acid rearrangement.

The main purpose of this work is to convert glycerol inside the model biodiesel wastewater into more value-added chemicals, especially lactic acid which plays an important role in several biochemical processes by using both batch and flow reactors. For this purpose, first
we tried to understand the mechanism for pure glycerol conversion. We additionally aimed to clarify the gaseous and liquid products, effects of electrolysis current and alkali concentration on the decomposition of glycerol. In this study, sub-critical water was selected as a reaction medium because it is cheap, non-toxic, non-flammable, non-explosive and offers essential advantages compared to other substances, particularly in the field of “green chemistry” [17].

MATERIALS AND METHODS

The experiments were done first by using batch reactor and then continued with flow type reactor. For the first set of experiments, aqueous electrolyte solutions were prepared by dissolving an alkali (NaOH) in deionized water and then a given amount of glycerol was charged in the solutions. Then series of experiments were done by using flow reactor in order to compare the effects of two systems on the decomposition of glycerol under alkaline conditions. The batch and flow reactors were shown in Figure 2 and Figure 3, respectively.

Figure 2: Batch reactor for hydrothermal electrolysis experiments

The batch reactor was pressurized with argon gas before starting each experiment. This internal pressure of the autoclave was defined as the initial pressure of the experiment [18]. At the beginning, the aqueous solution loaded in the autoclave expanded thermally as the temperature in the autoclave was increased and subsequently the internal pressure also gradually increased. 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. The profile of internal pressure in the autoclave is plotted in Figure 4.

Half of the autoclave's inner volume (250 mL) was charged with the 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 an anode. The titanium beaker was employed as a cathode to promote cathodic protection of the autoclave
from corrosion. The autoclave, after being charged with aqueous solution, was purged with inert gas (argon) in all experiments. The total gas initially charged into the autoclave was kept at 3 MPa and the existence of the aqueous phase was ensured for all temperatures below the critical point of water. The sealed autoclave was heated with an electrical furnace from room temperature to the desired temperature (280 °C). The typical reaction pressure was 10 MPa as the temperature of the autoclave reached 280 °C. Once the autoclave had been heated to the desired temperature, a constant electric current was passed between the electrodes for hydrothermal electrolysis experiments. No current was passed for hydrothermal degradation runs.

**Figure 3:** Continuous flow reactor for hydrothermal electrolysis experiments

**Figure 4:** Temperature and pressure profiles for batch hydrothermal electrolysis at 280 °C
In flow experiments, initially the reactor was filled with distilled water. Next, the system pressure was set to 10 MPa same as batch reactor by adjusting the back-pressure regulator. After adjusting pressure, four heaters, connected to the bottom and top of the reactor, were set to the desired reaction temperature. After the system reached the set temperature, the aqueous electrolyte solution was fed into the system at a flow rate of 25 mL/min. Once the reactor was filled with the feed solution (ca. 30 min), the reaction was initiated and allowed to proceed for 30-120 min. During reaction, the flow rate of the feed solution was changed depending on the temperature and residence time. To calculate the flow rate, Eq. 1 was used, where \( F \) is flow rate (mL/min), \( V \) is volume of the reactor (mL), \( \tau \) is residence time (s), \( \rho_{T,P} \) is the density of water at the reaction temperature (kg/m³), and \( \rho_{T_{o,P}} \) is the density of water at room temperature (kg/m³).

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F = \frac{V}{\tau} \times \frac{\rho_{T,P}}{\rho_{T_{o,P}}}
\]

Eq. (1)

Table 1 summarizes the experimental conditions applied to batch and flow experiments.

| Table 1: Experimental conditions both for batch and flow hydrothermal electrolysis |
|-----------------------------------------|----------|----------------------|
| Concentration of aqueous glycerol solution (M) | Batch | 0.1 |
| Concentration of NaOH (mM) | 10 and 50 | 10, 25, 50 and 100 |
| Reaction temperature (°C) | 280 |
| Reaction pressure (MPa) | 8.0-11.0 | 10.0 |
| Initial argon gas pressure (MPa) | 3.0 | ---- |
| Electrolysis time (min) | 15-90 | 30-120 |
| Applied dc (A) | 0, 1 and 2 | 0, 0.25 and 1 |

At the end of reaction, both gas and liquid samples were collected for analysis. Solid samples were not specifically analyzed, because no measurable solid products were observed. Gas formed during the reaction was collected in sampling plastic bags and analyzed by gas chromatography with a thermal conductivity detector (GC-TCD). Liquid products were identified by high performance liquid chromatography (HPLC) and quantified by gas chromatography with a flame ionization detector (GC-FID). Total organic carbon in the liquid product solution was monitored by using TOC analyzer.

RESULTS

After the hydrothermal electrolysis of glycerol with alkali, lactic acid (L- and D-) was formed as the main organic acid by batch reactor. Additionally, small amounts of formic acid and...
glycolic acid were produced. In addition to these organic acids glyceraldehyde which is an important intermediate for lactic acid was also generated as a liquid product. After hydrothermal electrolysis of glycerol by continuous flow system, it was seen that the yields of formic acid and glycolaldehyde were higher than lactic acid.

Figure 5 shows the glycerol conversion under various operating conditions by both reactors. Actually by batch reactor, maximum 3 A current could be applied however we passed at most 2 A current through the electrodes because when 2 A current was applied, product distribution showed a wide variation. This was probably caused by the formation of small amount of char, stuck to the electrode and as a result obstructed the electrolysis.

By batch reactor, maximum conversion of glycerol was 84% by applying 2 A current during 90 min. However, in Figure 5, only the results of hydrothermal degradation (0 A) and 1 A were shown in order to compare the results of batch and flow reactors after hydrothermal electrolysis and hydrothermal degradation experiments. As for NaOH effect, by increasing the concentration of alkali from 10 to 50 mM only 6% difference in the conversion value was observed at the end of 90 min. At same conditions, max 92% of glycerol was converted into gas and liquid products by flow reactor under the influence of 1 A during 90 min.

As for gaseous product, in both systems hydrogen gas was generated and the vol% was illustrated in Figure 6. The hydrogen concentration increased with electrolysis current. With flow reactor, the volume percentage of hydrogen gas at 1 A was 53-fold greater than that generated at 0 A. This explains the effect of current on the production of hydrogen gas from glycerol by hydrothermal electrolysis. In the case of batch reactor, the volume percentage of hydrogen gas at 1 A was 6.6 times that generated at 0 A for the same reaction time of 90 min.
When hydrothermal degradation of glycerol was carried out by batch reactor under influence of 0 A current (Figure 7 (a)), although the conversion of glycerol was almost kept constant at about 60% during 90 min, lactic acid yield increased with increasing reaction time. This was because of the generated amount of glyceraldehyde, which is an important intermediate for the production of lactic acid, was consumed during heating step. As it can be seen in Figure 7 (a), the yield of glyceraldehyde decreased with increasing reaction time while the yield of lactic acid increased about 9% at the end of 90 min. Additionally, almost no glycolic acid was generated during 90 min treatment.

In the case of flow reactor, the effect of reaction time on the yield of liquid products at 0 A current is shown in Figure 7 (b). After hydrothermal electrolysis of glycerol under alkaline conditions, glyceraldehyde, glycolaldehyde, glycolic acid, lactic acid, formic acid, and acetic acid were generated by flow reactor. In the hydrothermal degradation experiment, glyceraldehyde and glycolaldehyde were the main products. Among organic acids, acetic acid was generated only under the influence of current. At 0 A, the yields of other organic acids (glycolic, lactic, and formic acids) also were very low.

By batch reactor, when the applied current was raised from 0 A to 1 A (Figures 7 (a) and 8 (a)), the conversion of glycerol was almost same with hydrothermal degradation run (0 A). Although current was applied during 90 min, there was still unreacted glycerol. There may be several reasons: one of them is dead volume. The autoclave includes two valves and pressure gauge which may include some dead volumes. Another possibility might be the concentration of alkali. In our system, we tried to keep NaOH concentration as low as possible (at most 50 mM) because of the corrosion risk which is higher in the electrolytic systems.
When current was applied to the flow reactor, (Figs. 8 (b)) the yield of glyceraldehyde began to decrease as electrolysis time increased, due to an increase in lactic acid concentration under the influence of current 1 A. The last 60 min of electrolysis, shown in Figure 8 (b), indicates that glyceraldehyde yield was decreasing while lactic acid production rate was increasing. As we explained previously [17], glyceraldehyde is an important intermediate product in the generation of lactic acid by hydrothermal electrolysis under alkaline conditions. Therefore, in some cases, despite a small change in the conversion of glycerol, lactic acid yield continued to increase, which may be explained by the consumption of glyceraldehyde. Lactic acid also may be formed from glycolaldehyde with alkali. However, the yield of glycolaldehyde did not decrease as much as that of glyceraldehyde, while lactic acid amount was increasing. Therefore, lactic acid must have been generated by two different routes. The selectivity of glycolic and acetic acid was generally low during hydrothermal electrolysis experiments. At 90 min under a current of 1 A, the yield of formic acid reached its maximum value of 15%.

Figure 7: Yields of liquid products without current with 50 mM NaOH at 280 °C with (a) batch and (b) flow reactors
CONCLUSION

The development of a specially designed autoclave and flow type reactor for the hydrothermal electrolysis of glycerol with an alkali and analysis techniques to investigate the conversion of glycerol to organic acids, especially lactic acid, in sub-critical water has led to several conclusions. The advantage of a batch reactor is that a current up to 3 A could be applied because the autoclave was purged with argon gas before starting each experiment. Therefore, although hydrogen gas was formed, a high electrolysis current could be applied. With a batch reactor, maximum glycerol conversion of 84% was achieved at a current of 2 A and an electrolysis time of 90 min. Under the same conditions, with a current no greater than 1 A, results showed that more than 92% of glycerol can be decomposed by hydrothermal electrolysis with the continuous flow reactor. After the hydrothermal electrolysis of glycerol with NaOH, hydrogen gas was generated as a gaseous product in both systems. Lactic acid was the main product by autoclave electrolysis. Increasing the concentration of NaOH led to a
great increase in the amount of lactic acid with a yield of 34.7% at 280 °C with a NaOH concentration of 50 mM at the end of 90 min reaction time. With flow reactor, formic acid and glycolaldehyde yields were greater than lactic acid yield at 1 A. Therefore, if obtaining lactic acid from glycerol by hydrothermal electrolysis is desirable, an autoclave should be preferred.

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REFERENCES