Hydrothermal Electrolysis of Glycerol Using a Continuous Flow Reactor

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Hydrothermal electrolysis reactions of glycerol were investigated under various operating conditions to determine the effects of applied DC current, electrolysis time, and alkali concentration on the decomposition mechanism of glycerol. In addition, intermediate products were identified, possible reaction schemes for both hydrothermal electrolysis and hydrothermal degradation of glycerol based on experimental data were clarified, and detailed product analysis was conducted using high performance liquid chromatography (HPLC), gas chromatography with a flame ionization detector (GC-FID), and gas chromatography with a thermal conductivity detector (GC-TCD). For the present study, a continuous flow reactor equipped with titanium electrodes (as cathode and anode), an electric furnace, a heater, a pump, a heat exchanger, a back pressure regulator, and DC supply was used. The main gaseous product was hydrogen, whereas glycolaldehyde, lactic acid, and formic acid were the main liquid products. Results indicate that greater than 92% of the glycerol could be decomposed under optimum conditions by hydrothermal electrolysis using the continuous flow reactor.

Introduction

Most of the world's energy needs are supplied through petrochemical sources, such as coal and natural gas. However, these resources are finite, and their extraction and use have high environmental impacts.[1,2] Thus, alternative sources for petroleum-based fuels are needed. Biodiesel, an alternative diesel fuel, is composed of monoalkyl esters and is obtained mainly from base-catalyzed transesterification of oils or fats and is, therefore, biodegradable and nontoxic. Biodiesel also has a high energy yield and low emission profile and is renewable, and so, it has minimal environmental impact.[3,4] However, during the biodiesel production process, a large amount of crude glycerol, the main byproduct, is produced along with free fatty acids, catalyst, and alcohol (biodiesel wastewater). These products can cause serious environmental problems. Although glycerol is an important material in the production of some alternative fuels, such as hydrogen,[5,6] and many chemical intermediates,[7−9] conversion of glycerol present in the biodiesel wastewater into useful components is necessary to minimize both environmental pollution and economical losses.

In foods, glycerol is used as a humectant, solvent, and sweetener. Additionally, it is an important component in medical, pharmaceutical, and personal care preparations, serving as a humectant and a component for improving smoothness and providing lubrication.

Many studies have been conducted on the conversion of glycerol into various compounds. Hydrogenolysis of glycerol into ethylene glycol, propylene glycol (1,2-propanediol), and 1,3-propanediol, as well as further degradation of the glycols has been widely studied. Catalytic hydrogenolysis of glycerol was conducted over different types of catalysts (e.g., nickel, palladium, copper, platinum, zirconia, and ruthenium) as a function of different reaction parameters, such as reaction temperature and pressure, hydrogen pressure, amount of catalyst, and catalyst reduction temperature.[10−16] Additionally, Maris et al. evaluated commercial Ru/C and Pt/C catalysts as well as bimetallic PtRu/C and AuRu/C catalysts in batchwise hydro-

genolysis of glycerol in aqueous solution at 473 K and 40 MPa H_2, both with and without added base.[17,18] Results showed that modification of the Ru surface with Pt did not alter the catalytic activity of PtRu/C for glycerol hydrogenolysis compared to the monometallic Ru/C.

In addition to hydrogenolysis, pyrolysis and gasification of glycerol were also examined. In some previous studies,[19,20] ionic reactions and pyrolysis of glycerol in near-critical and super-critical water were investigated and it was found that glycerol was decomposed into methanol, acetaldehyde, propionaldehyde, acrolein, allyl alcohol, ethanol, formaldehyde, carbon monoxide, carbon dioxide, and hydrogen. In many studies,[21−26] 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 ($CO + H_2$) 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.

Microbial conversion is an alternative for degradation of glycerol to various compounds. Recent studies have focused on the production of 1,3-propanediol using microorganisms such as *Citrobacter freundii*, *Klebsiella pneumoniae*, and *Clostridium butyricum*.[27−29] *Enterobacter aerogenes* has also been used for the biological production of hydrogen and ethanol from biodiesel waste containing glycerol with a high yield and high production rate.[30]

Conversion of glycerol also can be accomplished through a steam reforming process. This technique produces several intermediate byproducts that occur in the product stream and affect the purity of the final hydrogen product.[31−33]

In the present study, conditions under which glycerol could be converted into valuable chemicals such as lactic acid, formic acid, or other intermediates were investigated by hydrothermal electrolysis with a continuous flow reactor. Additionally, the effects of applied current were investigated by comparing the product distribution obtained by hydrothermal electrolysis with the product distribution from dehydrogenation. The gaseous and liquid products and the effects of reaction time and alkali concentration on the decomposition of glycerol also were

* To whom correspondence should be addressed. Fax: +81-96-342-3679. Phone: +81-96-342-3664. E-mail: mgoto@kumamoto-u.ac.jp.
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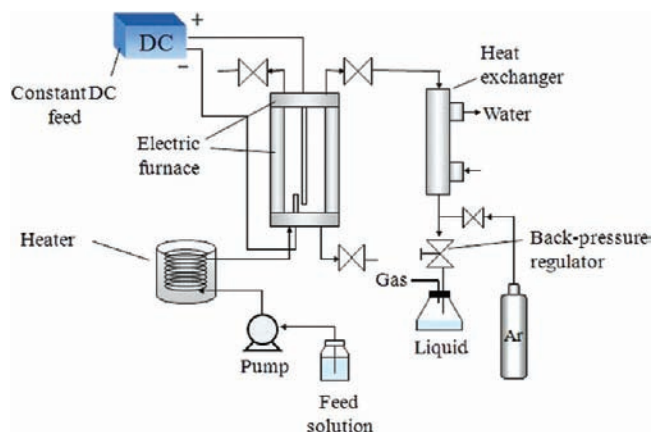**Figure 1.** Flow reactor for hydrothermal electrolysis.

determined. Subcritical water was chosen for this method for reasons explained previously.[34]

Experimental and Analysis

Chemical Reagents. Chemicals used in the present study included glycerol (99%), sodium hydroxide (96%), methanol (99.7%), butyric acid (98%), glycolic acid (98%), acetic acid (99%), acrylic acid (98%), pyruvic acid (97%), formic acid (99%), L-lactic acid, and DL-lactic acid (85−92%) (Wako Pure Chemicals Ind., Ltd., Osaka, Japan).

Experimental Apparatus and Procedures. Aqueous electrolyte solutions were prepared by dissolving a base (NaOH) in deionized water and adding a specified amount of glycerol. Electrolysis was conducted using a sealed 500 mL flow reactor made of SUS 316 stainless steel, as shown in Figures 1 and 2a.

Initially, the reactor was filled with distilled water. Next, the system pressure was set to 10 MPa by adjusting the back-pressure regulator. In our previous study,[34] we tested at which pressure system was stabilized for the hydrothermal electrolysis of glycerol and found that when system pressure was 10 MPa, although current was applied, pressure did not change during the reaction, indicating that the system was in steady-state condition. Therefore, in this present study, we directly set the reaction pressure to 10 MPa. 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 the 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), τ is residence time (s), $\rho_{T,P}$ is the density of water at the reaction temperature (kg/m^3), and $\rho_{To,P}$ is the density of water at room temperature (kg/m^3). For instance, at a residence time of 60 min, the flow rate was 7 mL/min at 220 °C and 6.3 mL/min at 280 °C.

$$F = \frac{V}{\tau} \times \frac{\rho_{T,P}}{\rho_{To,P}} \qquad (1)$$

For hydrothermal electrolysis experiments, constant DC current was passed through the electrodes; no current was applied for hydrothermal degradation runs. A specially designed cylindrical titanium plate electrode (Akico, Japan), illustrated in Figure 2b, was used as an anode. The reactor wall, also made

of titanium, was used as the cathode to protect the reactor from corrosion. The time needed for the solution to reach the bottom of the reactor from the pump was 25 s. Therefore, the residence time at the bottom of the reactor was assumed to be zero, and no conversion of glycerol occurred.

For the present study, 0.1 M glycerol and varying concentrations of NaOH (10, 25, 50, and 100 mM) were used as feed materials. Reaction temperature and pressure were kept constant at 280 °C and 10 MPa, respectively. Various current values (0, 0.25, and 1.0 A) were passed through the electrodes at electrolysis times of 30, 60, 90, and 120 min.

Product Analysis. Gaseous products were added to a 1 L gas pack along with argon gas for analysis by gas chromatography with a thermal conductivity detector (GC-TCD). Liquid products were identified and quantified by high performance liquid chromatography (HPLC). For the conversion of glycerol (X), eq 2 was used, where C_0 is the initial concentration of glycerol and C is the concentration of remaining glycerol in the product solution. After each experiment, C was diagnosed by analyzing the liquid product solution by gas chromatography with a flame ionization detector (GC-FID).

$$X = \frac{C_0 - C}{C_0} \times 100 \qquad (2)$$

Results and Discussion

After hydrothermal electrolysis of glycerol using a continuous flow reactor, glyceraldehyde, glycolaldehyde, glycolic acid, lactic acid, formic acid, and acetic acid were produced as liquid products and hydrogen gas was generated from electrolysis of both glycerol and water separately under alkaline conditions. Typical refractive index (RI) and UV−vis spectra obtained from HPLC analysis of liquid products are shown in Figure 3a,b.

Effect of Electrolysis Current. Further experiments were performed by varying the applied current, 0 to 1 A, for residence times of 30−120 min for 0.1 M glycerol and 50 mM NaOH at a reaction temperature and pressure of 280 °C and 10 MPa, respectively.

The effect of electrolysis current on the decomposition of glycerol under alkaline conditions is shown in Figure 4. Residence time was recorded starting from 30 min because, when samples were analyzed at 15 and 20 min, it was realized that these residence times were too short for the complete mixing of glycerol solution with water inside the reactor. At 0.25 A, the conversion of glycerol increased almost linearly with electrolysis time. When the current was increased to 1 A, glycerol conversion reached a maximum value of 93% by 90 min. However, despite the stability of glycerol, in hydrothermal electrolysis, it started to decompose within the first 30 min, even when no current was applied. The reason for this was probably the large volume of the reactor (500 mL). Complete filling of this reactor with electrolyte solution takes about 30 min. During this feeding step, some of the glycerol converted into organic acids and aldehydes under high pressure (10 MPa) and high temperature (280 °C), and therefore, in Figure 4, the conversion of glycerol was around 48% when no current was passed through the electrodes during 30 min.

Thus, the yields of gaseous and liquid products, shown in Figures 5 and 6, respectively, were used to further understanding of the effect of current on decomposition of glycerol.

The hydrogen concentration increased with electrolysis current, as shown in Figure 5. The volume percentage of hydrogen gas at 1 A was 53-fold greater than that generated at 0 A for the same reaction time of 120 min. This explains the effect of
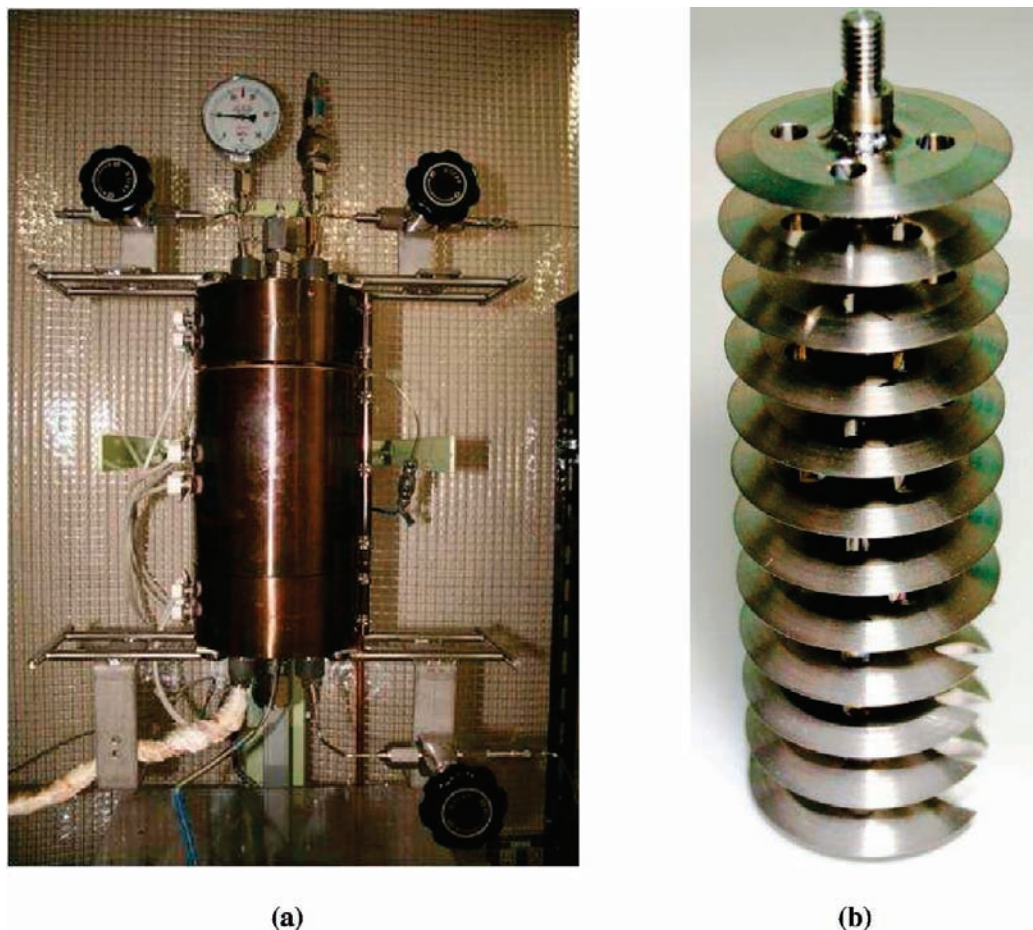
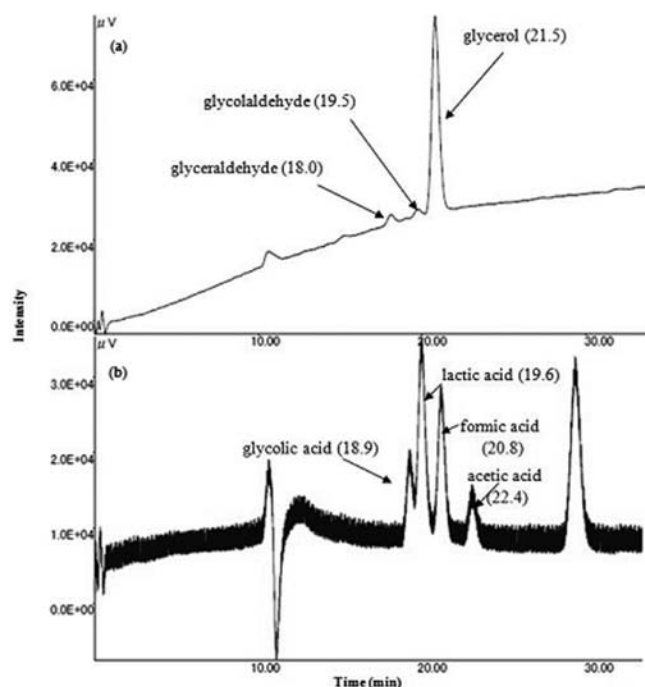**Figure 2.** (a) Flow reactor; (b) titanium plate electrode (anode).

Figure 3. (a) RI and (b) UV−vis spectral data of glycerol after 60 min of hydrothermal electrolysis at 280 °C and 1 A with 50 mM NaOH.

Figure 4. Effect of applied current on the decomposition of 0.1 M glycerol with 50 mM NaOH at 280 °C and 10 MPa.

current on the production of hydrogen gas from glycerol by hydrothermal electrolysis. Figure 5 verifies the generation of hydrogen at 30 min into the reaction, despite the lack of hydrogen generati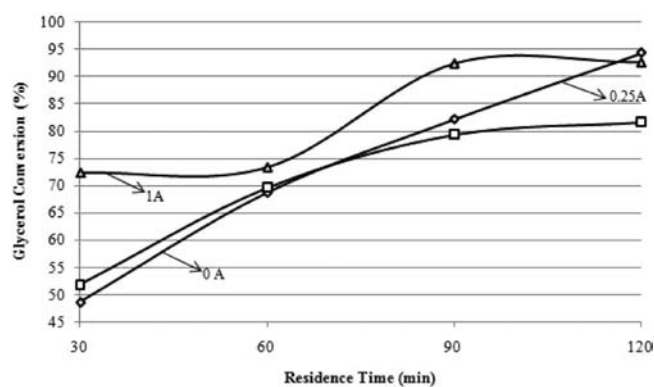on at 60 to 120 min during hydrothermal degradation (0 A). This might be the result of the short residence time, as explained earlier.

The volume percentage of hydrogen shown in Figure 5 is the total amount of hydrogen generated from glycerol decomposition and water electrolysis. To clarify the percentage of hydrogen arising from water alone, experiments using alkali and water were conducted under similar conditions. Electrolysis results showed that the hydrogen volume percentage from water electrolysis was 2.63 vol % at 1 A and 280 °C for 60 min. Therefore, as seen in Figure 5, during the 60 min electrolysis at 1 A, 5.7 vol %, which was the total hydrogen amount, is the sum of 2.63 vol % H_2 from water electrolysis and 2.97 vol % H_2 from the electrolysis of glycerol solution. This means that
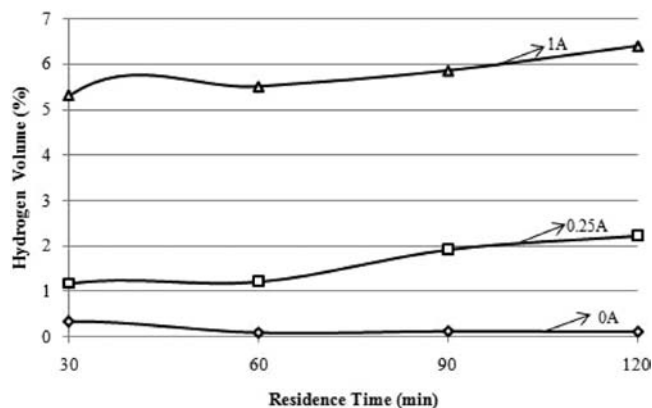
Figure 5. Effect of applied current on the volume percentage of hydrogen gas at 280 °C and reaction pressure of 10 MPa.
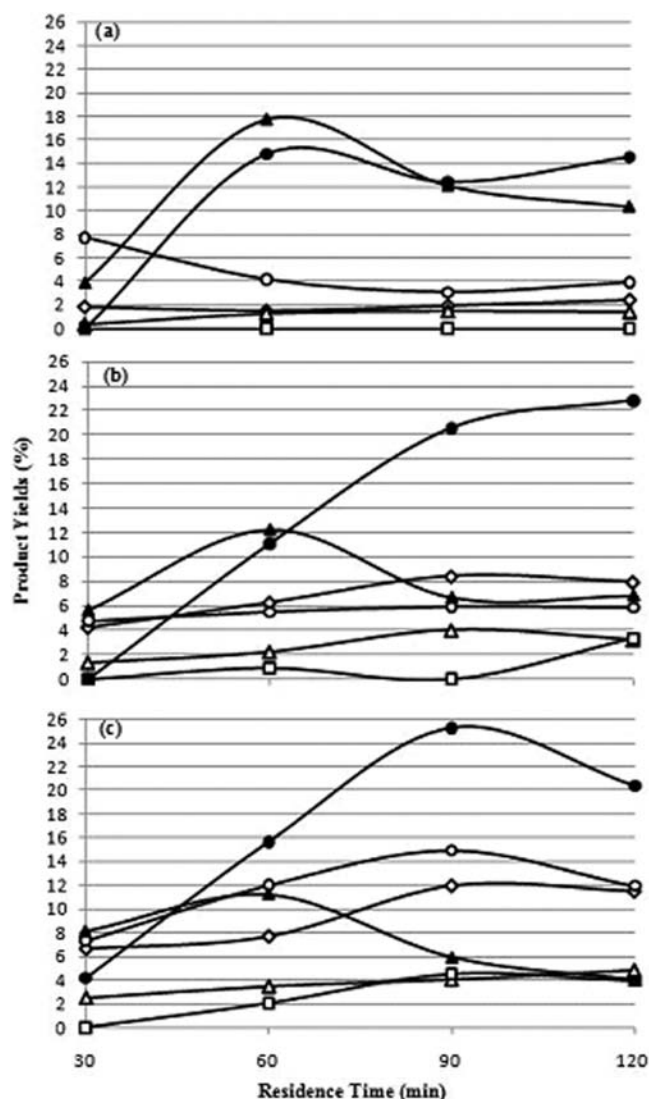

Figure 6. Effect of electrolysis current on the yield of liquid products at 280 °C with 50 mM NaOH: (a) 0 A, (b) 0.25 A, and (c) 1 A (symbols: ◇, lactic acid; △, glycolic acid; ○, formic acid; □, acetic acid; ▲, glyceraldehyde; ●, glycolaldehyde).

approximately 46% of hydrogen was produced by water electrolysis under these alkaline conditions.

The effect of electrolysis current on the yield of liquid products is shown in Figure 6. After hydrothermal electrolysis of glycerol under alkaline conditions, glyceraldehyde, glycol-

aldehyde, glycolic acid, lactic acid, formic acid, and acetic acid were generated. In the hydrothermal degradation experiment (Figure 6a), 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. When current was applied (Figure 6b,c), the yield of glyceraldehyde began to decrease as electrolysis time increased, due to an increase in lactic acid concentration under the influence of currents 0.25 and 1 A. The last 60 min of electrolysis, shown in Figure 6b,c, indicates that glyceraldehyde yield was decreasing while lactic acid production rate was increasing. As we explained previously,[34] 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.[35] 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%.

Effect of NaOH Concentration. To clarify the effects of alkali concentration, experiments were conducted under different NaOH concentrations (10, 25, 50, and 100 mM) at 280 °C and 10 MPa by applying 0 and 1 A over 60 min. The effects of alkali concentration on the conversion of glycerol by hydrothermal electrolysis and the yields of liquid products for hydrothermal degradation (0 A) and electrolysis (1 A) are shown in Figure 7a,b, respectively.

The effect of NaOH concentration on hydrothermal electrolysis is shown in Figure 7, especially for the production of lactic acid and formic acid. For hydrothermal degradation (Figure 7a), organic acid yield changed slightly with increasing alkali concentration. Acetic acid production was nearly zero in both cases. When NaOH amount was increased from 50 to 100 mM, glycerol conversion was 76% at 0 A. Upon applying a 1 A electrolysis current and adding 100 mM NaOH, conversion reached 90%. As shown in Figure 7b, glycolic acid and lactic acid production increased with alkali concentration as well as current. Although NaOH concentration has a great influence on the decomposition of glycerol, it is necessary to keep the alkali amount as low as possible to avoid corrosion. In hydrothermal electrolysis systems, in addition to high pressure and high temperature, applied current also can cause corrosion problems. Therefore, addition of alkali was limited to 100 mM NaOH. The experimental results indicate that the concentration of NaOH exerts an important effect on the conversion of glycerol into organic acids, especially glycolic and lactic acids, which increased almost linearly with alkali concentration during hydrothermal electrolysis.

As shown in Figure 8, the percentage of hydrogen gas was almost zero during hydrothermal degradation, because no current was applied. However, it increased slightly upon increasing NaOH concentration from 50 mM. When a 1 A electrolysis current was applied, the yield (5.5%) of H_2 with 100 mM NaOH was less than that with 50 mM (4.3%).

From those results, a reaction pathway for the decomposition of glycerol by continuous flow reactor hydrothermal electrolysis under alkaline conditions can be suggested as shown in Figure
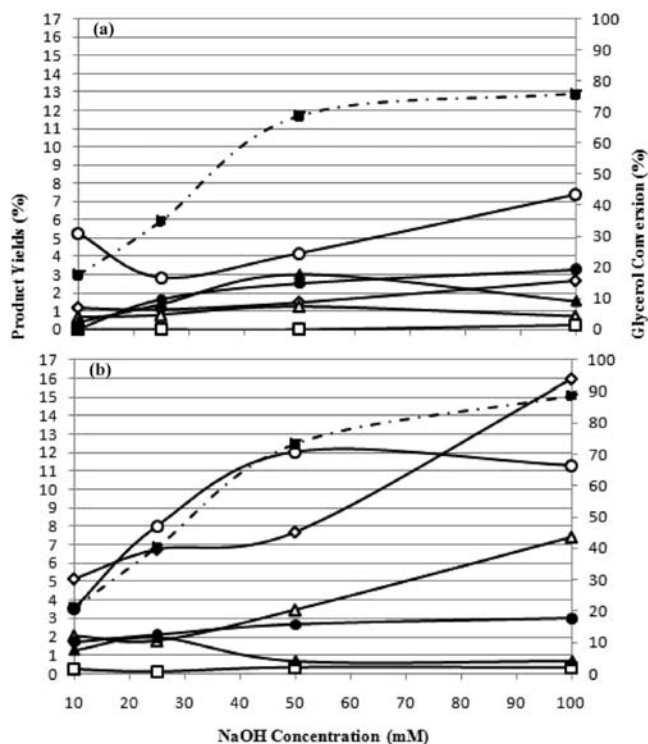
Figure 7. Effect of alkali concentration on the conversion of 0.1 M glycerol and the yield of liquid products at 280 °C, 10 MPa, and 60 min residence time: (a) 0 A and (b) 1 A (symbols: ◇, lactic acid; △, glycolic acid; ○, formic acid; □, acetic acid; ▲, glyceraldehyde; ●, glycolaldehyde; ■, conversion of glycerol).
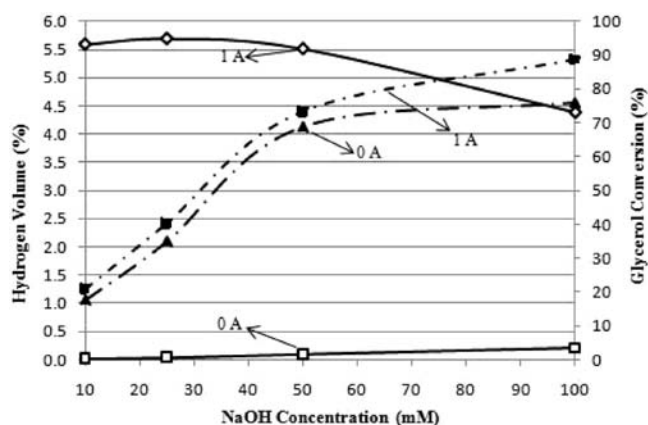

Figure 8. Effect of alkali concentration on the volume percentage of hydrogen gas at 280 °C and 10 MPa, by applying 0 or 1 A over 60 min (symbols: □, H$_2$ at 0 A; ◇, H$_2$ at 1 A; ▲, glycerol conversion at 0 A; ■, glycerol conversion at 1 A).
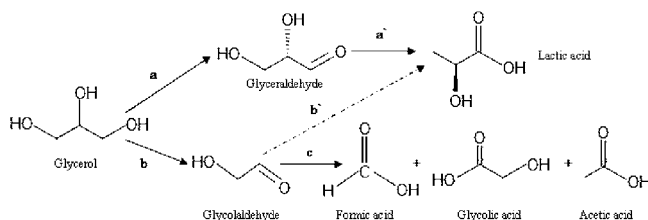

Figure 9. Reaction pathway of glycerol decomposition by continuous flow reactor hydrothermal electrolysis under alkaline conditions.

9. However, this pathway does not correspond with the actual selectivity of electrolysis toward the oxidation of primary alcohols. Under basic conditions, the oxidation of aldehydes (routes a and b) is faster than the oxidation of OH groups.[36] As

mentioned earlier, glyceraldehyde is an important intermediate in the generation of lactic acid by hydrothermal electrolysis.[34] This also can be demonstrated by the decrease in glyceraldehyde amount upon an increase in lactic acid yield. By applying high current values during a long electrolysis time (longer than 90 min), route b becomes more favorable than route c. At low alkali concentrations and under no current, formic acid selectivity among organic acids increased via route c. In excess NaOH, the generation of lactic acid as an oxidation product from glycerol was enhanced.

Our previous study of glycerol electrolysis in subcritical water using a batch reactor reported that glycerol can be decomposed into glyceraldehyde, L-lactic acid, D-lactic acid, formic acid, and glycolic acid at 280 °C with 50 mM NaOH by applying a current of 0−2 A.[34] 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. However, at 2 A, the product distribution showed wide variation because of char that formed and stuck to the electrode, obstructing the electrolysis. 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. Lactic acid was the main product by autoclave electrolysis, whereas formic acid and glycolaldehyde yields were greater than lactic acid yield at 1 A with a continuous flow reactor. Therefore, if obtaining lactic acid from glycerol by hydrothermal electrolysis is desirable, an autoclave should be preferred.

When hydrothermal electrolysis is compared with commercial techniques, some important advantages of this new system draw attention: First of all, it uses subcritical water as a reaction medium, so there is no need to use catalyst because water itself acts as a catalyst in the subcritical region.[34] Second, in the hydrothermal electrolysis system, the generation of oxygen can be controlled that means you do not need to add an oxidizer. Moreover, in hydrothermal electrolysis experiments, current is applied after necessary conditions are reached. As a result, stable components such as glycerol can be decomposed more easily in comparison with commercial techniques. Finally and most importantly, hydrothermal electrolysis is an environmentally friendly green process.

Conclusions

From hydrothermal electrolysis of glycerol using a continuous flow reactor under alkaline conditions, hydrogen gas, glyceraldehyde, glycolaldehyde, lactic acid, formic acid, glycolic acid, and acetic acid were produced. Among them, glycolaldehyde, lactic acid, and formic acid were the main products. When the current was increased to 1 A, glycerol conversion reached a maximum value of 92% at the end of 90 min electrolysis time. Increasing alkali amount and DC current increased the selectivity of lactic acid and formic acid at 280 °C. During hydrothermal degradation (0 A), a negligible amount of hydrogen gas was produced. However, under the influence of electrolysis, hydrogen gas generation increased with electrolysis time. Therefore, as these results show, although glycerol is very stable under high-temperature and high-pressure aqueous conditions, hydrothermal electrolysis, a "green" technology, can decompose more than 90% of surplus glycerol into more valuable products such as lactic acid and formic acid.

Literature Cited

(1) Meher, L. C.; Sagar, D. V.; Naik, S. N. Technical Aspects of Biodiesel Production by Transesterification: A Review. *Renewable Sustainable Energy Rev.* **2006**, *10*, 248.

(2) Srivastava, A.; Prasad, R. Triglycerides-based Diesel Fuels. *Renewable Sustainable Energy Rev.* **2000**, *4*, 111.

(3) Klass, D. L. *Biomass for Renewable Energy, Fuels and Chemicals*; Academic Press: San Diego, 1998, 29.

(4) Ma, F.; Hanna, M. A. Biodiesel Production: A Review. *Bioresour. Technol.* **1999**, *70*, 1.

(5) Douette, A. M.; Turn, S. Q.; Wang, W.; Keffer, V. I. Experimental Investigation of Hydrogen Production from Glycerin Reforming. *Energy Fuels* **2007**, *21*, 3499.

(6) Huber, G. W.; Shabaker, J. W.; Dumesic, J. A. Raney Ni-Sn Catalyst for H_2 Production from Biomass-Derived Hydrocarbons. *Science* **2003**, *300*, 2075.

(7) Monteiro, M. R.; Ambrozin, A. R. L.; Liao, M.; Ferreira, A. G. Critical Review on Analytical Methods for Biodiesel Characterization. *Talanta* **2008**, *77*, 593.

(8) Corma, A.; Huber, G. W.; Sauvanaud, L.; O'Connor, P. Biomass to Chemicals: Catalytic Conversion of Glycerol/Water Mixtures into Acrolein, Reaction Network. *J. Catal.* **2008**, *257*, 163.

(9) Demirbas, A. Conversion of Biomass Using Glycerin to Liquid Fuel for Blending Gasoline as Alternative Engine Fuel. *Energy Convers. Manage.* **2000**, *41*, 1741.

(10) Lahr, D. G.; Shanks, B. H. Kinetic Analysis of the Hydrogenolysis of Lower Polyhydric Alcohols: Glycerol to Glycols. *Ind. Eng. Chem. Res.* **2003**, *42*, 5467.

(11) Chaminand, J.; Djakovitch, L.; Gallezot, P.; Marion, P.; Pinel, C.; Rosier, C. Glycerol Hydrogenolysis on Heterogeneous Catalysts. *Green Chem.* **2004**, *6*, 359.

(12) Dasari, M. A.; Kiatsimkul, P.; Sutterlin, W. R.; Suppes, G. J. Low-Pressure Hydrogenolysis of Glycerol to Propylene Glycol. *Appl. Catal., A* **2005**, *281*, 225.

(13) Perosa, A.; Tundo, P. Selective Hydrogenolysis of Glycerol with Raney Nickel. *Ind. Eng. Chem. Res.* **2005**, *44*, 8535.

(14) Wang, S.; Liu, H. Selective Hydrogenolysis of Glycerol to Propylene Glycol on Cu-ZnO Catalysts. *Catal. Lett.* **2007**, *117*, 62.

(15) Kurosaka, T.; Maruyama, H.; Naribayashi, I.; Sasaki, Y. Production of 1,3-Propanediol by Hydrogenolysis of Glycerol Catalyzed by Pt/ WO_3/ ZrO_2. *Catal. Commun.* **2008**, *9*, 1360.

(16) Alhanash, A.; Kozhevnikova, E. F.; Kozhevnikov, I. V. Hydrogenolysis of Glycerol to Propanediol over Ru: Polyoxometalate Bifunctional Catalyst. *Catal. Lett.* **2008**, *120*, 307.

(17) Maris, E. P.; Ketchie, W. C.; Murayama, M.; Davis, R. J. Glycerol Hydrogenolysis on Carbon-Supported PtRu and AuRu Bimetallic Catalyst. *J. Catal.* **2007**, *251*, 281.

(18) Maris, E. P.; Davis, R. J. Hydrogenolysis of Glycerol over Carbon-Supported Ru and Pt Catalysts. *J. Catal.* **2007**, *249*, 328.

(19) Buhler, W.; Dinjus, E.; Ederer, H. J.; Kruse, A.; Mas, C. Ionic Reactions and Pyrolysis of Glycerol as Competing Reaction Pathways in Near- and Supercritical Water. *J. Supercrit. Fluids* **2002**, *22*, 37.

(20) Watanabe, M.; Lida, T.; Aizawa, Y.; Aida, T. M.; Inomata, H. Acrolein Synthesis from Glycerol in Hot-Compressed Water. *Bioresour. Technol.* **2007**, *98*, 1285.

(21) Calzavara, Y.; Dubien, C. J.; Boissonnet, G.; Sarrade, S. Evaluation of Gasification in Supercritical Water Process for Hydrogen Production. *Energy Convers. Manage.* **2005**, *46*, 615.

(22) Maher, K. D.; Bressler, D. C. Pyrolysis of Triglyceride Materials for the Production of Renewable Fuels and Chemicals. *Bioresour. Technol.* **2007**, *98*, 2351.

(23) Xu, D.; Wang, S.; Hu, X.; Chen, C.; Zhang, Q.; Gong, Y. Catalytic Gasification of Glycine and Glycerol in Supercritical Water. *Hydrogen Energy* **2009**, *34*, 5357.

(24) Valliyappan, T.; Bakhsi, N. N.; Dalai, A. K. Pyrolysis of Glycerol for the Production of Hydrogen or Syn Gas. *Bioresour. Technol.* **2008**, *99*, 4476.

(25) Luo, N.; Fu, X.; Cao, F.; Xiao, T.; Edwards, P. P. Glycerol Aqueous Phase Reforming for Hydrogen Generation over Pt Catalyst: Effect of Catalyst Composition and Reaction Conditions. *Fuel* **2008**, *87*, 3483.

(26) Fernandez, Y.; Arenillas, A.; Diez, M. A.; Pis, J. J.; Menendez, J. A. Pyrolysis of Glycerol over Activated Carbons for Syngas Production. *J. Anal. Appl. Pyrolysis* **2009**, *84*, 145.

(27) Daniel, R.; Stuertz, K.; Gottschalk, G. Biochemical and Molecular Characterization of the Oxidative Branch of Glycerol Utilization by *Citrobacter freundii*. *J. Bacteriol.* **1995**, *177*, 4392.

(28) Menzel, K.; Zeng, A. P.; Deckwer, W. D. High Concentration and Productivity of 1,3-Propanediol from Continuous Fermentation of Glycerol by *Klebsiella pneumoniae*. *Enzyme Microb. Technol.* **1997**, *20*, 82.

(29) Biebl, H.; Marten, S.; Hippe, H.; Deckwer, W. D. Glycerol Conversion to 1,3-Propanediol by Newly Isolated *Clostridia*. *Appl. Microbiol. Biotechnol.* **1992**, *36*, 592.

(30) Ito, T.; Nakashimada, Y.; Senba, K.; Matsui, T.; Nishio, N. Hydrogen and Ethanol Production from Glycerol Containing Waste Discharged after Biodiesel Manufacturing Process. *J. Biosci. Bioeng.* **2005**, *100*, 260.

(31) Adhikari, S.; Fernando, S.; Gwaltney, S. R.; Filip, S. D.; Bricka, R. M.; Steele, P. H.; Haryanto, A. A Thermodynamic Analysis of Hydrogen Production by Steam Reforming of Glycerol. *Hydrogen Energy* **2007**, *32*, 2875.

(32) Slinn, M.; Kendall, K.; Mallon, C.; Andrews, J. Steam Reforming of Biodiesel by Product to make Renewable Hydrogen. *Bioresour. Technol.* **2008**, *99*, 5851.

(33) Adhikari, S.; Fernando, S. D.; Haryanto, A. Hydrogen Production from Glycerin by Steam Reforming over Nickel Catalysts. *Renewable Energy* **2008**, *33*, 1097.

(34) Yuksel, A.; Koga, H.; Sasaki, M.; Goto, M. Electrolysis of Glycerol in Subcritical Water. *J. Renewable Sustainable Energy* **2009**, *1*, 033112, online; DOI: 10.1063/1.3156006.

(35) Kishida, H.; Jin, F.; Yan, X.; Moriya, T.; Enomoto, H. Formation of Lactic Acid from Glycolaldehyde by Alkaline Hydrothermal Reaction. *Carbohydr. Res.* **2006**, *341*, 2619.

(36) Porta, F.; Prati, L. Selective Oxidation of Glycerol to Sodium Glycerate with Gold-on-Carbon Catalyst: An Insight into Reaction Selectivity. *J. Catal.* **2004**, *224*, 397.