Conversion of Glycerin into Lactic Acid by Alkaline Hydrothermal Reaction

Hisanori Kishida,* Fangming Jin,† Zhouyu Zhou,† Takehiko Moriya,†† and Heiji Enomoto†
Environmental Systems Headquarters, Environmental Research and Development Center Hitachi Zosen Corporation, Kyoto 625-8501
†*Deparment of Environmental Science and Technology, Graduate School of Environmental Studies, Tohoku University, Sendai 980-8579*
††*Research and Development Center, Tohoku Electric Power Co., Inc., Sendai 981-0952*

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Hydrothermal decomposition experiments of glycerin with an alkali showed that glycerin could be converted into lactic acid with a high yield of about 90 mol % based on glycerin used. Discussion on the pathway for the conversion of glycerin to lactic acid suggests that glycerin is first decomposed to pyruvaldehyde with elimination of hydrogen by a H^- shift to the adjacent hydrogen. Pyruvaldehyde formed is then converted into lactic acid ion by the benzilic acid rearrangement.

In recent years, bio-diesel fuel (BDF) derived from the transesterification of oil and fat with alcohols in the presence of an alkaline catalyst has been gathering attention, because BDF has a good potential as an alternative diesel fuel. It is reported that 20 million tons of palm oil is produced per year in Southeast Asia, and it is expected that a portion of this palm oil can be converted into BDF. As the production of BDF increases, an effective and acceptable conversion of glycerin, which is a by-product of the BDF manufacturing process, to useful substances is becoming increasingly important. It has been reported that glycerin can be converted easily into acrolein when treated in a hydrothermal reaction with an acid catalyst.[1,2] However, few studies have been reported about the hydrothermal conversion of glycerin with an alkali. Since the glycerin of the by-product from BDF production process contains a large amount of alkali, a study on the hydrothermal conversion of glycerin with an alkali was performed. In this paper, the hydrothermal conversion of glycerin with an alkali catalyst is discussed.

The reactor used in this study was a Swagelok SUS 316 tube, sealed with two caps. The cap is equipped with a thin nozzle and a pressure valve in order to collect gas samples. The outside diameter of the reactor was 12.7 mm, wall thickness 1 mm, length 111 mm, and capacity 10 mL. The reaction temperature was controlled using a molten salt bath. First, the desired amount of glycerin and sodium hydroxide (NaOH) solution were put into the reactor, and then sealed. Concentrations of glycerin and NaOH solution were 0.33 M (mol/L) and 0.25–1.25 M, respectively. The solution put into the reactor was 5 mL in volume. Then, the reactor was put into a salt bath that had been preheated to the desired temperature, and was kept shaking for a desired reaction time. All experiments were performed with degassed water and by purging the reactor with nitrogen. After the reaction, the reactor was quickly cooled down in cold water. After cooling, liquid and gas samples were collected for analyses. The liquid sample was filtered (to remove solids) through a 0.5 mm filter, and then the pH of the solution was adjusted to 6–7 with sulfuric acid. The gas sample was analyzed with a gas chromatography with a POLA column. The liquid sample was analyzed by high-performance liquid chromatography (HPLC). Two Shodex KC811 columns were used in series. The solvent was 1 mM $HClO_4$ with a flow rate of 1.0 mL/min. The yield of product is defined as a molar fraction of product referring to the initial glycerin.

First, reaction products from glycerin were identified by HPLC analysis. Figure 1 shows a result for liquid samples after reaction of glycerin at a temperature of 300 °C, for a reaction time of 60 min with 0.25 M NaOH. The main product was lactic acid. In addition, small amounts of pyruvaldehyde, acetic acid, and formic acid were detected. Lactic acid has recently been getting attention as a biodegradable lactic acid polymer material with limited environmental impact.

So, further experiments were performed to optimize the reaction conditions by varying the reaction temperature and time, and the concentration of NaOH. Figure 2 gives the yield of lactic acid. As seen in Figure 2, increasing the concentration of NaOH led to a great increase in the yield of lactic acid with a very high lactic acid yield of 90 mol % at 300 °C with a NaOH concentration of 1.25 M. It should be noted that almost no lactic acid was formed without addition of NaOH and the yield of lactic acid at 260 °C was low even with 1.25 M NaOH. These results show that lactic acid can be produced in a large quantity, and both the temperature and the concentration of NaOH have a great effect on the conversion of glycerin into lactic acid. A possible reason that a high concentration of NaOH is required to obtain a high yield of lactic acid is likely that the formed lactic acid can consume NaOH in neutralization.

Next, the reaction pathway of the conversion of glycerin into lactic acid is discussed. As shown in Figure 1, a little amount of pyruvaldehyde was detected. It is generally known in sugar chemistry that pyruvaldehyde readily undergoes the benzilic

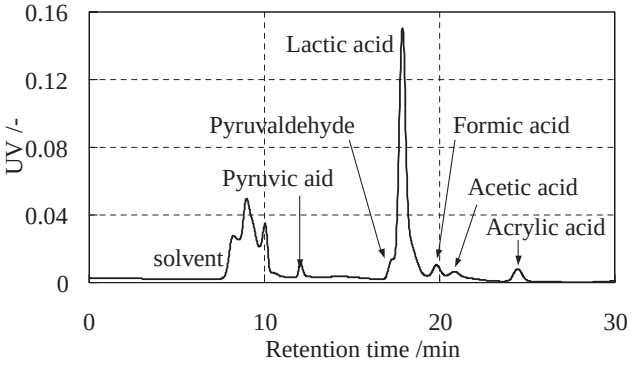

Figure 1. HPLC chromatogram of solution after reaction at 300 °C temperature, 60 min reaction time, with 0.25 M NaOH (Detector UV-210 nm). Retention.

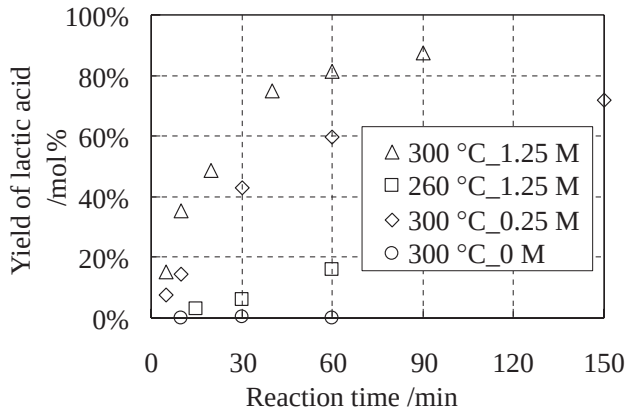

Figure 2. Yield of lactic acid by an alkaline hydrothermal treatment of glycerin. (NaOH; 0–1.25 M) based on the glycerin used.

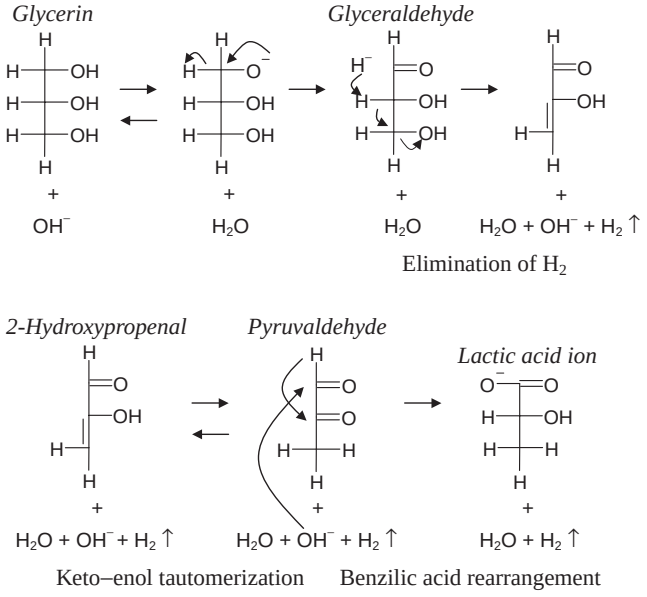

Figure 3. Proposed reaction pathway for conversion of glycerin into lactic acid.

acid rearrangement to give lactic acid in an alkaline solution, and our previous study found that pyruvaldehyde can also be converted into lactic acid in a hydrothermal reaction at 300 °C without using an alkaline catalyst by a mechanism similar to that of the benzilic acid rearrangement.[3] Therefore, pyruvaldehyde is likely an intermediate product involved in the formation of lactic acid from glycerin.

Then, the formation mechanism of pyruvaldehyde from glycerin is discussed. A reaction scheme that may appear best to explain the formation mechanism of pyruvaldehyde from glycerin is shown in Figure 3.

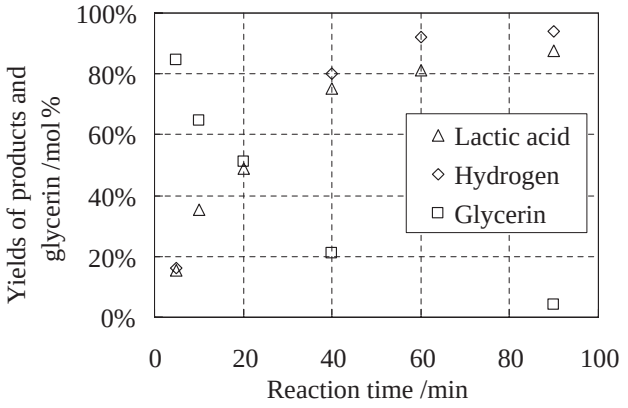

Figure 4. Yields of hydrogen and lactic acid and glycerin by an alkaline hydrothermal treatment of glycerin. (Temperature; 300 °C, NaOH; 1.25 M).

First of all, glycerin may produce glycerin alkoxide because the acidity constant of glycerin (pK_a of glycerin is 14.4)[4] is similar to that of water. Then, glycerin alkoxide formally lose a H^- to yield glyceraldehyde, which is then dehydrated in E2 mechanism via α-hydrogen abstraction by the H^- followed by OH^- elimination. The α-hydrogen abstraction by the H^- may be rapid due to the high acidity of α-hydrogen. As the result, glycerin eliminates H_2 and water to give 2-hydroxypropenal which has a conjugated double bond and is thermodynamically stable, which could be the reason why this reaction shifts toward the formation of 2-hydroxypropenal. Pyruvaldehyde is formed by keto–enol tautomerization of 2-hydroxypropenal.

According to the mechanism proposed in Figure 3, H_2 would be formed in a hydrothermal reaction of glycerin with an alkali and one mole of glycerin would generate one mole of hydrogen and one mole of lactic acid as follows:

$$C_3H_8O_3 + NaOH \rightarrow C_3H_5O_3 \cdot Na + H_2\uparrow + H_2O \qquad (1)$$

To test this, gas composition was analyzed for reactions at 300 °C with 1.25 M NaOH, by varying the reaction time from 5 to 90 min. As shown in Figure 4, a large amount of hydrogen was formed, and the yield was almost the same as that of lactic acid formed. The slightly lower yields for lactic acid than those for hydrogen after 40 min may be caused by decomposition of lactic acid. These results strongly support the formation mechanism of lactic acid from glycerin shown in Figure 3.

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