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Racemization of Lactic Acid under Hydrothermal Conditions

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The racemization mechanism of lactic acid was investigated under hydrothermal conditions at the temperature range of 250–350°C and for a period of 30 min. Experiments were performed using a continuous flow tubular reactor made of SUS 316. Under the tested conditions, it was observed that pyruvic acid was formed as an intermediate, which subsequently transformed to both L- and D-lactic acids. The results suggested the hydrothermal racemization of L-lactic acid consists of consecutive-reversible reactions (*i.e.*, L-lactic acid ↔ pyruvic acid ↔ D-lactic acid). The optical purity of L-lactic acid decreased with increasing reaction time and temperature. Further, the addition of NaOH slightly increased the purity of L-lactic acid.

Key Words: Racemization, Lactic acid, Hydrothermal conditions.

INTRODUCTION

Previous studies on the production of lactic acid from poly (L-lactic acid) (PLLA) under hydrothermal conditions showed that a considerably high yield of lactic acids (*ca.* 90%) could be recovered at 250°C and 20 min of reaction time[1]. However, a significant racemization of the formed lactic acids occurred due to the high temperature. When this low purity of lactic acid is polymerized to PLLA, the strength and melting point of PLLA are decreased, leading to deterioration and, consequently, limiting its applicability. Therefore, to achieve high enantiopurity of recovered lactic acid, it is important to investigate its racemization mechanism under hydrothermal conditions. Moreover, although recovery of lactic acid from various wastes such as fish meat[2] and sludge[3] under hydrothermal conditions have been studied intensively in the past, analysis of the underlying racemization reaction has not been discussed.

Recent studies involving reactions of lactic acid with high temperature water include dehydration[4], hydrolysis and oxidation[5]. Their attention has been largely focused on derived products as well as decomposition pathways. However, the racemization of lactic acid under hydrothermal conditions has not been reported. To date, racemization of alanine, leucine and phenylalanine has also been reported to occur at 225–275°C[6]. In this study, the racemization mechanism of lactic acid under hydrothermal conditions is proposed and the reaction conditions for the recovery of high purity of lactic acid are also discussed. The obtained information is useful to increase the yield of L-lactic acid in a hydrothermal depolymerization process of PLLA as well as in the recovery of lactic acid from wastes under hydrothermal conditions.

EXPERIMENTAL

In this study, L-lactic acid (99%+) and pyruvic acid (99%+) were used as the test materials. A continuous flow tubular reactor was used. The experimental setup has been described in detail elsewhere[7] and only a brief description is given below. The reactor and all connecting parts are made of SUS 316. The water and the sample solution were delivered separately using two HPLC pumps (PU-1580, JASCO Corp.). To minimize the transition in temperatures during the reaction, the water passed through a preheating tube (O.D.: 1/16 inch, I.D.: 0.5 mm, length: 40 m, volume: 7.9 cm^3) before mixing with the sample and before entering the main reactor tube (O.D.: 1/16 inch, I.D.: 0.25 mm, length: 5 m, volume: 0.25 cm^3). The mixing ratio of sample solution used was sample : water as (1 : 2) resulting in 10 mmol/L solution was used. After passing the reactor tube, the reaction effluent was quenched in the cooling unit (Model LC-101, ADVANTEC) at 5°C to cease the reaction. The pressure in a system was adjusted by a back-pressure regulator (SCF-Bpg, JASCO Corp.). Organic acids were analyzed using organic acid analyzer (LC-10A, Shimadzu Corp.) consisting of ion exclusion column (Shim-Pack SCR-102H) and electroconductivity detector (CDD-6A, Shimadzu Corp.). Lactic acid enantiomers were analyzed using the AS-2050 plus (JASCO Corp.) HPLC system, equipped with a Sumichiral OA-5000 column (Sumika Chemical Analysis Service Ltd., Japan) and multiwavelength detector (MD 1510, JASCO Corp.).

RESULTS AND DISCUSSION

Fig. 1 shows the chromatograms of HPLC analysis of L-lactic acid and pyruvic acid after reaction at 250°C and 10 min. Pyruvic acid and acetic acid were produced from L-lactic acid hydrolysis. A more complex product generated from hydrolysis and oxidation of lactic acid in near critical water has been discussed by Li *et al.*[5] Tsujino *et al.*[8] also reported that the oxidation of lactic acid at 90°C with the presence of $Pb/Pd/CaCO_3$ (Lindlar catalyst) and $Pb/Pd/Al_2O_3$ yielded

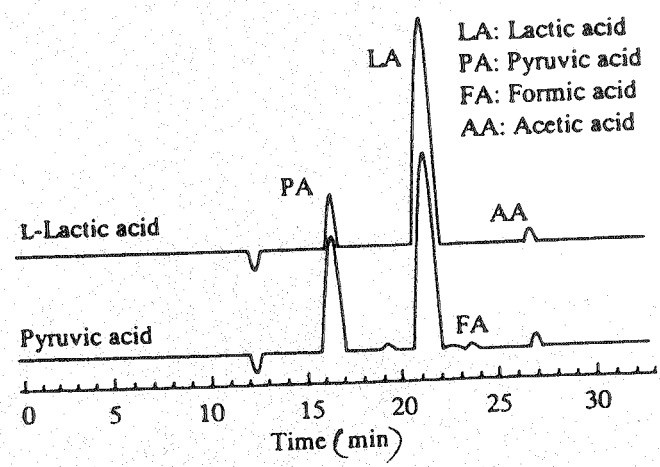

Fig. 1. HPLC chromatograms for L-lactic acid and pyruvic acid after reaction at 250°C and 10 min. (Column: Ion exclusion SCR-102H, Mobile phase: 5 mM *p*-toluenesulfonic acid Detector: electroconductivity CDD-6A, Flow rate: 0.8 mL/min, Temp.: 40°C)

60% of pyruvic acid. Fig. 1 also shows that the product of pyruvic acid hydrolysis was mainly lactic acid. Acetic and formic acids may come from hydrogen abstraction of lactic acid followed by hydroxylation. At temperature higher than 300°C, the hydrolysis of lactic acid extends to acetaldehyde, acrylic acid, propionic acid and acetic acid as reaction intermediate prior to complete degradation to H_2O and CO_2[5].

The effect of reaction time and temperature on hydrothermal degradation of pyruvic acid was further investigated. Fig. 2 shows that at a temperature of 250°C, L and D-lactic acids could be observed from 0.5 min of reaction time, then increased with increasing reaction time. Acetic and formic acids were observed in trace amounts. Similar trends were also observed when the temperature of 300°C was used however, acetic acid slightly increased. The remaining might be gaseous product; such as CO and CO_2 that could not be analyzed. According to these results, lactic acid would be the major product in the hydrothermal treatment of pyruvic acid in the temperature range of 250–300°C and a period of 10 min.

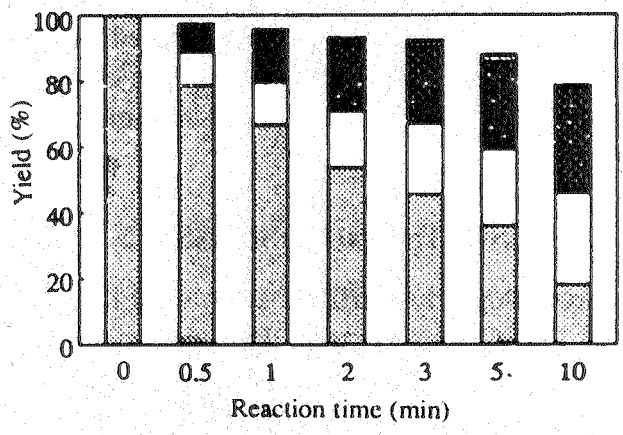

Fig. 2. Effect of reaction time on hydrothermal degradation of pyruvic acid at 250°C (▨ Pyruvic acid, □ L-lactic acid, ■ D-lactic acid, ▨ Acetic acid, ■ Formic acid)

The proposed pathways of racemization of L-lactic acid under hydrothermal conditions are shown in Fig. 3. This mechanism requires the intermediate

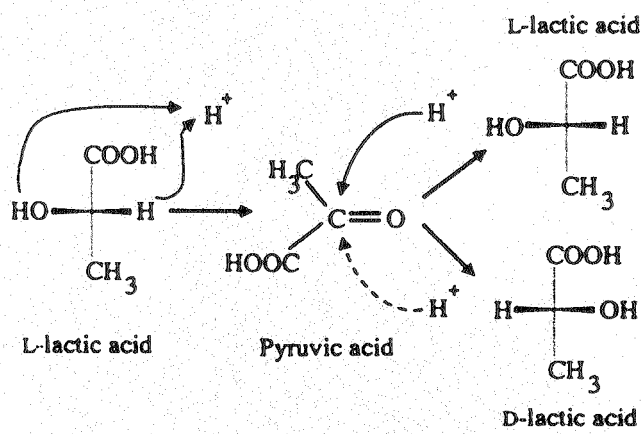

Fig. 3. Proposed pathways of racemization of L-lactic acid under hydrothermal conditions

formation of pyruvic acid. This route begins with the hydrogen abstraction on asymmetric carbon atom of L-lactic acid, followed by the formation of double bond with oxygen producing pyruvic acid. It is speculated that proton (H^+) attacks the carbonyl carbon atom of pyruvic acid allowing the formation of L and D-type of lactic acids. This has been confirmed by the experiment with pyruvic acid showing the formation of a considerably high amount of L-lactic acid and D-lactic acid (Fig. 2). The above results suggest the hydrothermal racemization of L-lactic acid consisting of consecutive-reversible reactions (*i.e.*, L-lactic acid ↔ pyruvic acid ↔ D-lactic acid). This pathway also occurs through chemo-enzymatic process as proposed by Oikawa *et al.*[9]

The effect of reaction times on the change of optical purity of L-lactic acid at various temperatures is shown in Fig. 4. It can be seen that the optical purity decreased with increasing reaction time and temperature. As expected, at low temperature of 230°C, the optical purity only decreased slightly as reaction time progressed. However, the optical purity decreased remarkably when the temperature was raised to 300°C. The result is consistent with a previous study, in which the yield of L-lactic acid formed from PLLA hydrolysis decreases with increasing reaction time and temperature[1]. Similar results were also observed when the pressure was varied (from 10–30 Mpa), and thus pressure does not play a significant role in the enantioselection.

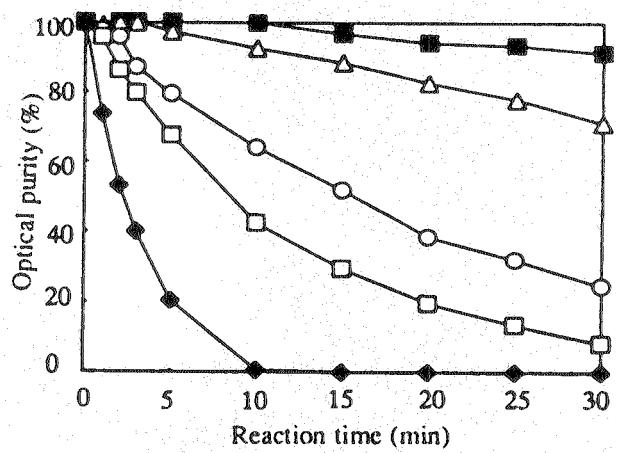

Fig. 4. Effect of reaction time on optical purity of L-lactic acid at various temperatures (■ 230°C Δ 250°C, ○ 270°C, □ 280°C, ◆ 300°C)

Further, the effect of NaOH as an additive was investigated. Fig. 5 shows the hydrolysis of L-lactic acid at a temperature of 250 and 270°C for a period of 30 min with and without addition of NaOH. The result shows that the addition of NaOH increased the purity of L-lactic acid to about 15 and 30% at temperature of 250 and 270°C, respectively. Probably, the presence of OH from NaOH limited the formation of D-lactic acid resulting in the increase of L-lactic acid. This result suggests that L-lactic acid was favourable under basic conditions. In addition, pyruvic acid as intermediate product also slightly increased with the presence of NaOH (data not shown here).

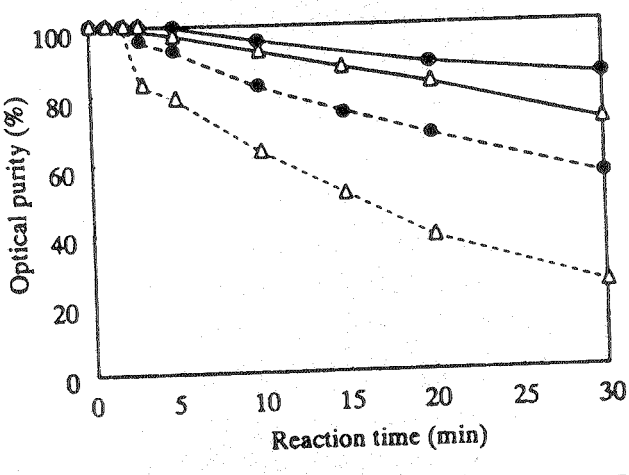

Fig. 5. Effect of NaOH on optical purity of lactic acid at 250 and 270°C (● W/O NaOH, Δ NaOH (pH: 10.8), —— 250°C, ------ 270°C)

Conclusions

Based on the above results, it can be suggested that in the hydrothermal depolymerization of PLLA, temperature below 230°C with reaction time longer than 30 min and addition of suitable additives are necessaries to control the purity. The proposed mechanism could suggest the suitable reaction conditions on the improving of enantioselectivity of L-lactic acid. This finding also adds to multiple reaction possibilities that may occur under hydrothermal conditions.

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