

Integrated production of polymer-grade lactide from aqueous lactic acid by combination of heterogeneous catalysis and solvent crystallization with ethanol

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Abstract—Lactide, a six-membered dimeric cyclic ester of lactic acid, is a key building block of polylactic acid, a representative bio-based biodegradable polymer. As an alternative to the conventional lactide production process of a two-step polymerization and depolymerization from lactic acid, we developed a novel continuous and one-step synthesis of optically pure lactide from lactic acid under atmospheric conditions with SnO₂-SiO₂ nanocomposites as heterogeneous catalyst. In this catalytic process, lactide was obtained in vapor phase together with water vapor and the unreacted lactic acid. After optimization of crystallization process using ethanol solvent, lactide crystals with 99 wt% purity and a lactide yield of 78 wt% were obtained. Based on these results, an integrated process for high-yield polymer-grade lactide production from aqueous lactic acid could be constructed by combination of the heterogeneous catalysis and crystallization with ethanol, which is more environmentally friendly as compared to the conventional two-step prepolymer process.

Keywords: Lactic Acid, Lactide, Catalysis, Crystallization, Ethanol

INTRODUCTION

Recently, much attention has been paid to bioplastics derived from natural plants from the viewpoint of renewability and climate change [1-3]. Polylactic acid (PLA) is regarded as a representative bio-based biodegradable polymer with potential applications in packaging, fibers, coatings, and biomedical fields [4-6]. Lactide (LT) is a six-membered dimeric cyclic ester of (usually L-) lactic acid (LA), and it is a building block of PLA. Lactide is industrially produced by a two-step polymerization and depolymerization from lactic acid or alkyl lactate under high-vacuum conditions [7-11] (Scheme 1). However, it is difficult to produce optically pure lactide at high yields using this prepolymer route, since it requires a long residence time (>10 h) at a high reaction temperature, and the chemical stability of L-LT is very low [12,13].

Recently, as an alternative to the conventional lactide production, we developed a continuous and one-step synthesis of optically pure lactide from lactic acid under atmospheric conditions [14]. The conventional Brønsted acidic catalysts such as ZSM-5 and beta zeolite showed a limitation on the high-yield L-LT from L-LA due to unselective acid-catalyzed condensation of LA to oligomer. Interestingly, SnO₂-SiO₂ nanocomposite prepared by simple precipitation-deposition of aqueous SnCl₄ on colloidal SiO₂ particles in NaOH was very effective for selective formation of L-LT from L-LA

due to the strong interaction between LA and the SnO₂ surface. The new catalytic system gave a record high lactide yield of 94 mol% with almost 100 mol% enantioselectivity and excellent long-term stability from aqueous LA at a reaction temperature of 240 °C and weight hourly space velocity of 1.0 h⁻¹.

In this catalytic process, lactide was obtained in vapor phase together with water vapor and the unreacted lactic acid. Water promotes the hydrolysis of PLA and lactic acid impurity interferes with the ring-opening polymerization of lactide, thereby lowering the PLA molecular weight [15]. Hence, water and lactic acid should be removed from the crude lactide before polymerization to PLA.

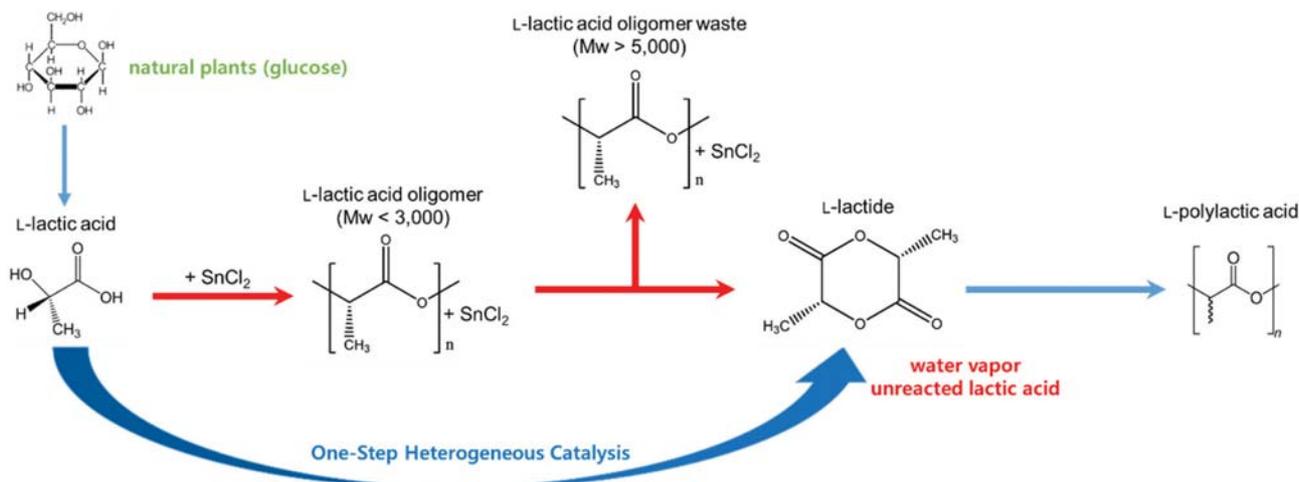
Generally, these impurities are removed from the crude lactide by distillation under vacuum, which is useful for purification of the crude lactide synthesized by the conventional two-step process [7]. However, lactic acid and lactide easily undergo thermal polymerization and hydrolysis, respectively, during distillation at high temperatures (>100 °C) [16]. In addition, distillation of lactide needs high-vacuum conditions (<10 torr) and purification of a high yield of crude lactide to the polymer-grade by this method is difficult.

Low-temperature solvent crystallization is widely used for the purification of heat-sensitive chemicals such as dihydroxystearic acid [17] and γ -linolenic acid [18], stigmasterol, and β -sitosterol [19], which are difficult to purify by high-temperature distillation. In this regard, solution or solvent crystallization is desirable for the purification of lactide because of the lower energy consumption [20,21]. In our one-step heterogeneous catalytic process, crude lactide with impurities of lactic acid and water vapor is produced at the atmospheric condition, and thus the solvent crystallization method is

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Scheme 1. Lactide production routes from natural plants-derived lactic acid. Conventional two-step batch homogeneous catalysis under vacuum (red) vs. one-step continuous heterogeneous catalysis under atmospheric pressure (blue).

more desirable than vacuum distillation.

In this study, we investigated the feasibility of solvent crystallization for the as-synthesized crude lactide with water and lactic acid as impurities, which were obtained from the one-step catalytic dehydration of lactic acid. In addition, an integrated process scheme from aqueous lactic acid to polymer-grade lactide is suggested based on the heterogeneous catalysis and crystallization using ethanol.

EXPERIMENTAL

1. Materials

L-lactic acid (90 wt%, Aldrich) and L-lactide (99.9 wt%, Purac) were used as feedstock for lactide production and as the standard material, respectively. Ethanol (99.8 wt%, Aldrich) and γ -butyrolactone (GBL, 99 wt%, Aldrich) were used as received.

2. Catalytic Reaction

The lactic acid dehydration reaction was performed in a fixed-bed reactor with continuous flow of aqueous L-lactic acid (75 wt%). Typically, the reaction temperature was maintained at 240 °C and 101.3 kPa with a weight hourly space velocity (WHSV) of 1.0 h⁻¹ under N₂ carrier gas with a flow of 250 ml min⁻¹.

3. Lactide Crystallization

Mixtures of the crude lactide sample (50.0 g) and ethanol at various ratios (w/w) were individually heated to 50 °C and maintained at this temperature for 30 min so that the crude lactide crystals could be solubilized in ethanol. The respective solutions obtained were then cooled and maintained at different temperatures (0 °C, 10 °C, 15 °C, 20 °C and 30 °C) for the recrystallization of pure lactide. The recrystallized lactide was filtered and then dried at 30 °C for the removal of residual ethanol. The dried lactide was weighed and analyzed by acid and Karl-Fischer titration to check the lactide purity.

4. Analysis

The moisture content in each lactide sample was measured using a Metrohm Karl Fischer Titrator (831 KF Coulometer). 1.0 g of lactide sample was dissolved in 1.0 g solvent (GBL), and then, 50 mg aliquots of the prepared samples were titrated with the analyte

(HYDRANAL @ Coulomat AG, Fluka Chemicals). For quantification of acid concentration, 2.0 g of lactide sample was dissolved in 20 ml of absolute methanol. Then the solution was titrated with the solution of 0.01 N KOH in methanol with phenolphthalein as the indicator. Differential scanning calorimetry (DSC) profiles were obtained from 0 °C to 400 °C at a ramping rate of 10 °C/min under N₂ flow of 50 mL/min, using a TA instrument DSC Q1000 V9.9. ¹H Nuclear magnetic resonance of lactide samples were dissolved in CDCl₃ from Aldrich containing TMS at 0.05%. ¹H NMR spectra were obtained at 500 MHz at room temperature using a Bruker ULTRASHIELD TM 300 spectrometer. TMS was used as the internal reference.

RESULTS AND DISCUSSION

First, we fabricated the crude lactide by one-step continuous heterogeneous catalysis. In this process, the SnO₂-SiO₂ nanocomposite catalyst (SSO-80) gave a lactic acid conversion of 94 mol% and L-lactide selectivity of 99.5 mol% from 75 wt% aqueous L-lactic acid at 240 °C, with a weight hourly space velocity of 1.0 h⁻¹ under N₂ carrier gas [14]. The composition of the vapor-phase product after the catalytic reactor was 56.1 wt% L-lactide, 0.3 wt% meso-lactide, 4.5 wt% L-lactic acid, and 39.1 wt% H₂O. This vapor stream was condensed to a mixture of liquid and solid phases by allowing it to flow through the sample collector maintained at 5 °C. During this quenching process, the crude lactide and the unreacted lactic acid could be separated as a crystalline phase and liquid phase, respectively. After 24 h of the catalytic reaction, the crude lactide crystals were separated from aqueous lactic acid solution by vacuum filtration. The crude lactide crystals contained 82.6 wt% L-lactide, 0.3 wt% meso-lactide, 3.7 wt% L-lactic acid, and 13.4 wt% H₂O. The acid concentration was determined to be 1,394 meq/kg by NaOH titration (Fig. 1). We purified the lactide crystals using various easily available solvents to remove the lactic acid and H₂O impurities.

Before crystallization of lactide, we investigated the solubility of lactide (L-form) in various solvents and at different dissolution

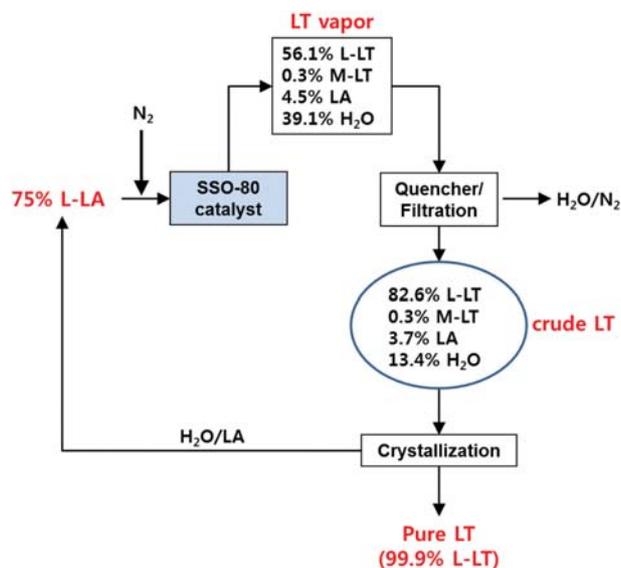


Fig. 1. Process flow for lactide production from aqueous lactic acid by vapor-phase heterogeneous catalysis and the stream composition. L-lactide (L-LT); meso-lactide (M-LT); L-lactic acid (LA).

temperatures for choosing the best solvent and crystallization conditions. The lactide solubility depended strongly on the solvent type and it increased with dissolution temperature [22]. The lactide solubility at room temperature was much higher in acetone and ethyl acetate than in isopropanol and ethanol. Thus, in terms of the lactide crystal yield at room temperature, ethanol and isopropanol are more advantageous than acetone and ethyl acetate. However, the solvent vapor pressure should also be considered, so that the solvent adsorbed on the lactide crystals can be removed easily after crystallization. Solvents with high vapor pressure, such as methanol and ethanol, are more advantageous than those with low vapor pressure, such as isopropanol and toluene. Ethanol is regarded as the most preferable solvent in terms of lactide solubility and vapor pressure. In addition, ethanol is a renewable and green solvent [23],

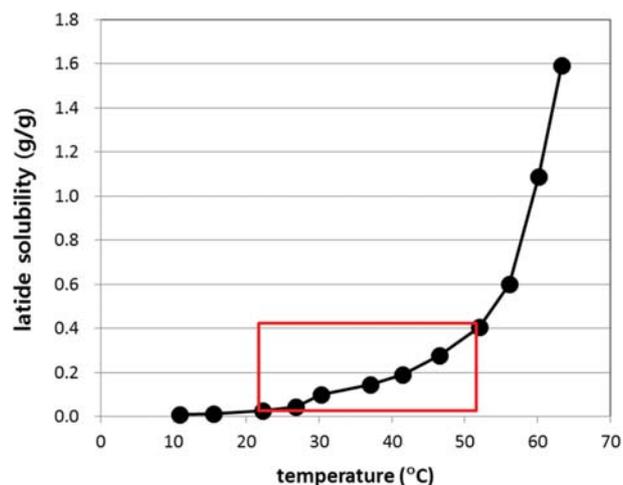


Fig. 2. Lactide solubility in ethanol with temperature. The data were reorganized using the data in Ref. [22].

which can be easily obtained from biomass fermentation; hence, we chose this solvent for the crystallization of lactide. The lactide solubility in ethanol was as high as 0.41 g/g at 52 °C but negligible (0.03 g/g) at 22 °C (Fig. 2). This indicates that lactide yields exceeding 90 wt% can be obtained by crystallization at room temperature after complete dissolution at around 50 °C in ethanol.

Next, we investigated the operational variables (ethanol to crude lactide ratio, crystallization temperature, and crystallization time) on the lactide crystallization efficiency (lactide yield and purity) when using ethanol (Table 1). To verify the effect of the weight ratio of ethanol to crude lactide, the crude lactide was solubilized at 50 °C for 30 min, and then, the mixture was cooled to 20 °C and maintained for 60 min. The acid and H₂O concentration drastically decreased from 1,394 meq/kg and 13.47 wt% to 280 meq/kg and 0.13 wt%, respectively, after crystallization at the weight ratio of ethanol to crude lactide of 1.25. The lactide crystal yield was as high as 97 wt% under these crystallization conditions. The crystallization efficiency depended markedly on the weight ratio of etha-

Table 1. The lactide crystallization efficiency on the operational variables

Amount ratio of ethanol to crude lactide (g/g)	Crystallization temperature (°C)	Crystallization time (min)	Acid concentration (meq/kg)	H ₂ O concentration (wt%)	Lactide yield (crystal amount/ crude lactide amount, wt%)
1.25	20	60	280	0.13	97
1.50	20	60	138	0.09	94
1.75	20	60	96	0.07	93
2.00	20	60	40	0.04	90
2.50	20	60	18	0.01	87
3.00	20	60	8	0.00	78
2.00	0	60	28	0.34	96
2.00	10	60	26	0.04	94
2.00	15	60	30	0.04	93
2.00	30	60	288	0.76	88
2.00	20	10	210	1.59	80
2.00	20	30	78	0.73	89
2.00	20	90	48	0.04	91

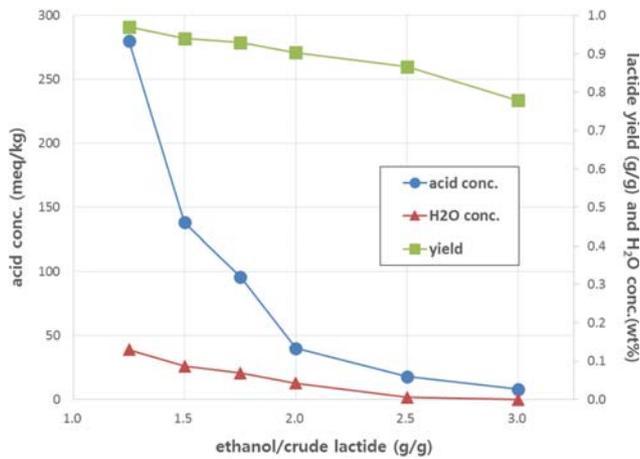


Fig. 3. Effect of ethanol amount to crude lactide on crystallization efficiency. Crystallization temperature, 20 °C; crystallization time, 60 min.

nol to crude lactide (Fig. 3). The acid concentration decreased gradually from 280 meq/kg to 8 meq/kg as the weight ratio of ethanol to crude lactide was increased from 1.25 to 3.0. The slope of acid concentration with respect to ethanol/crude lactide in the range 1.25 to 2.0 was two-times higher than that in the range 2.0 to 3.0. The H₂O concentration and lactide crystal yield also decreased from 0.13 wt% to 0.00 wt% and from 97 wt% to 78 wt%, respectively, as the ethanol/crude lactide ratio increased from 1.25 to 3.0. From these results, it is concluded that adding a greater amount of ethanol to crude lactide could enhance the lactide purity; however, the loss of lactide yield was inevitable due to the increased solubility at higher ethanol concentrations.

Next, the effect of crystallization temperature was investigated at the ethanol/crude lactide weight ratio of 2.0, where the lactide yield and lactide purity were high (Fig. 4). The acid and H₂O concentrations were very high at 288 meq/kg and 0.76 wt%, respectively, when the crude lactide was recrystallized at 30 °C. At this high crystallization temperature, lactic acid might also be crystallized

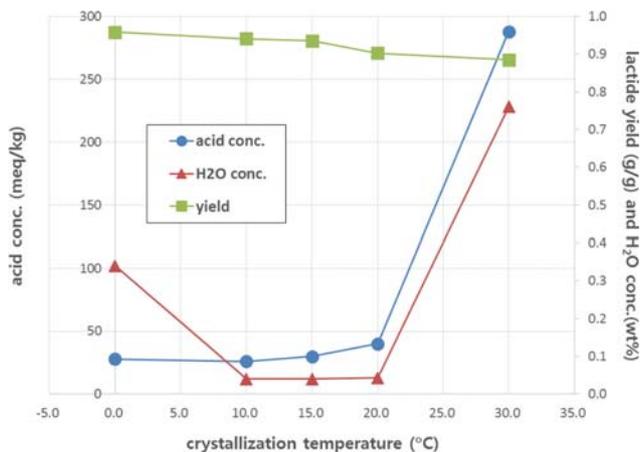


Fig. 4. Effect of crystallization temperature on crystallization efficiency. Ethanol to crude lactide ratio, 2.0 (g/g); crystallization time, 60 min.

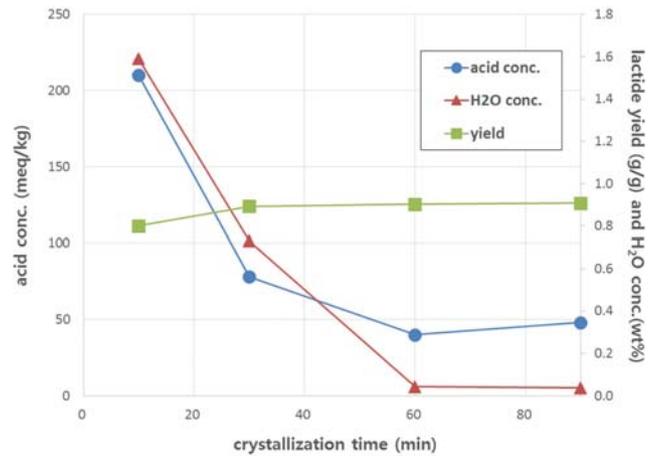


Fig. 5. Effect of crystallization time on crystallization efficiency. Ethanol to crude lactide ratio, 2.0 (g/g); crystallization temperature, 20 °C.

with lactide because of the low crystallization rate of the latter. The acid and H₂O concentrations decreased drastically to 40 meq/kg and 0.04 wt%, respectively, when the crude lactide was recrystallized at 20 °C. The acid concentration decreased further to 26 meq/kg at a crystallization temperature of 10 °C. However, at 0 °C, the acid concentration did not show any notable change from the abovementioned value, while the H₂O concentration increased to 0.34 wt% because of ice formation. The crystal yield increased almost linearly from 88 wt% to 96 wt% as the crystallization temperature decreased from 30 °C to 0 °C, which was consistent with the lactide solubility.

Crystallization time also affected the crystallization efficiency (Fig. 5). In this experiment, the crude lactide was solubilized at 50 °C for 30 min, and then, the mixture was cooled to 20 °C and maintained at this temperature for a specific time. The acid and H₂O concentrations was very high, i.e., 210 meq/kg and 1.59 wt%, respectively, when the crude lactide was recrystallized for 10 min. The crystal yield was as low as 80 wt% under these conditions. These results indicated that 10 min was not sufficient for lactide crystallization in ethanol at 20 °C. The acid and H₂O concentra-

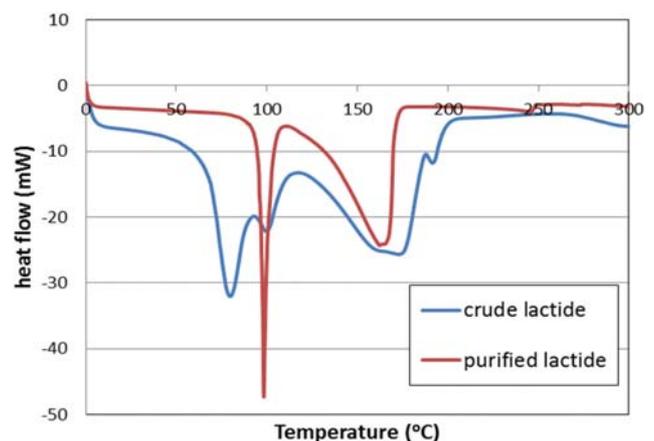


Fig. 6. DSC curves for lactide crystals before and after crystallization.

tions decreased drastically to 40 meq/kg and 0.04 wt%, respectively, when the crude lactide was recrystallized for 60 min, but did not change much when the crystallization time was increased to 90 min. The lactide crystal yield increased slightly from 89 wt% to

91 wt% as the crystallization time was increased from 30 min to 90 min.

Lactide crystals with the lowest acid concentration of 8 meq/kg, which corresponds to a lactide purity of 99.9 wt%, were obtained

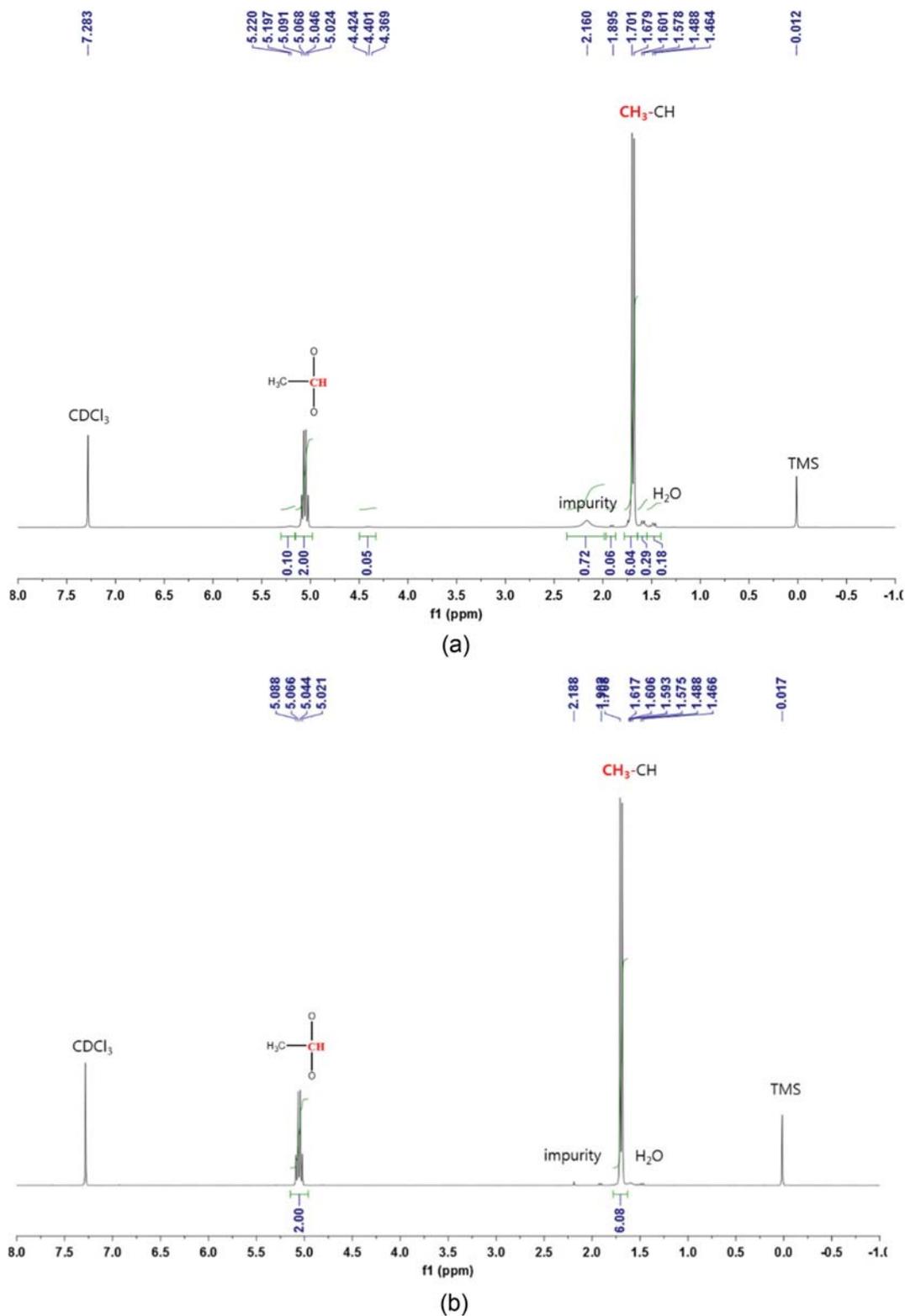


Fig. 7. ¹H NMR spectrum of lactide crystals after crystallization. (a) Before crystallization; (b) after recrystallization.

under the following optimized conditions: ethanol/crude lactide weight ratio, 3 : 1; crystallization temperature, 20 °C; crystallization time, 60 min. Although the lactide crystal yield was not the highest, this crystallization condition was chosen as the optimum condition, because the pure lactide with acid concentration less than 10 meq/kg was necessary to synthesize PLA of high molecular weight higher ($M_w > 100,000$) [7].

The structure of this lactide crystal was confirmed by DSC and NMR analyses. The DSC curve of the purified lactide crystal showed two sharp endothermic peaks at approximately 100 and 180 °C, corresponding to the melting and evaporation of L-lactide, respectively (Fig. 6). The ^1H NMR spectrum of the purified lactide sample had two characteristic peaks at 1.68 and 5.05 ppm [24], corresponding to the methyl ($-\text{CH}_3$) and methine ($-\text{CH}$) groups, respectively (Fig. 7). Thus, it was confirmed that polymer-grade L-lactide was successfully obtained by simple crystallization of crude lactide with ethanol.

Based on these results, an integrated process for lactide production from aqueous lactic acid can be developed, as shown in Fig. 8. First, aqueous lactic acid (~20 wt%) in a feed tank (FT) is passed through a thin film evaporator (WE) for removal of H_2O . The concentrated lactic acid (~75 wt%) is then introduced into the packed-bed reactor (CR) containing the SSO-.80 catalyst. After the catalytic reaction, a vapor-phase mixture of lactide/lactic acid/ H_2O is obtained. This mixture is introduced into the lactide quencher (LQ), where the lactide vapors are crystallized and the uncrystallized lactic acid/ H_2O is continuously filtered out to prevent dissolution of the lactide crystals. The filtrate (lactic acid/ H_2O) is then transferred to the lactic acid FT for recycling. Polymer-grade lactide crystals are obtained in the lactide crystallizer (LC) by dissolution of the lactide/lactic acid mixture in ethanol, followed by crystallization. The filtrate containing ethanol with the residual

lactic acid enters the ethanol distillation column (ED), where ethanol is separated from lactic acid, which are then recycled to the lactide crystallizer and lactic acid feed tank, respectively. In summary, the entire process for high-yield polymer-grade lactide production from aqueous lactic acid can be integrated by using simple and conventional unit processes based on green chemistry principles such as heterogeneous catalysis, no waste, environmentally friendly solvents, and high energy efficiency.

CONCLUSION

Among the various solvents investigated for lactide crystallization, ethanol was found to be the most suitable from the viewpoint of lactide solubility, vapor pressure, and renewability. Lactide crystals with 99.9 wt% purity and a lactide yield of 78 wt% could be obtained under the optimized crystallization conditions: ethanol to crude lactide weight ratio of 3 : 1, crystallization temperature of 20 °C, and crystallization time of 60 min. The purified lactide crystals were confirmed to be polymer-grade by DSC and NMR analyses. Thus, by combination of heterogeneous catalysis with crystallization in ethanol, polymer-grade lactide could be produced from aqueous lactic acid. The process herein described is more environmentally friendly as compared to the conventional two-step prepolymer process.

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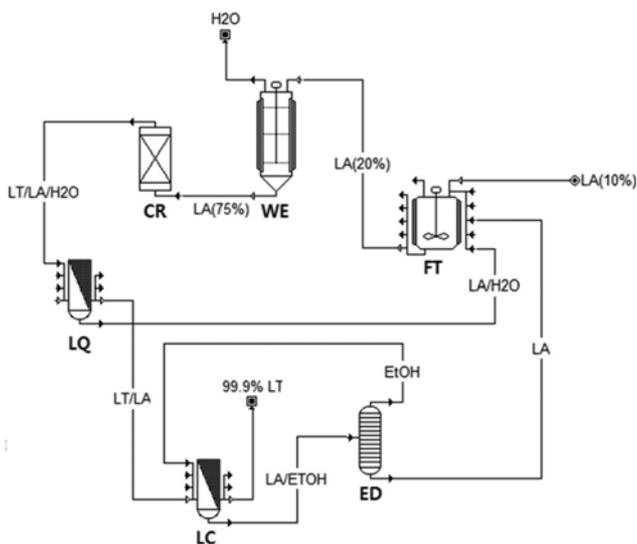


Fig. 8. An integrated process flow for lactide production from aqueous lactic acid using heterogeneous catalysis (LA: lactic acid, LT: lactide, EtOH: ethanol, FT: feed tank, WE: water evaporator, CR: catalytic reactor, LQ: lactide quencher, LC: lactide crystallizer, ED: ethanol distillation column).

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