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Synthesis of ethyl lactate from ammonium lactate solution by coupling solvent extraction with esterification

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ABSTRACT

Ethyl lactate was synthesized selectively from aqueous ammonium lactate by coupling solvent extraction with esterification with ethanol. When ammonium lactate reacted directly with ethanol without solvent, the ethyl lactate yield was very low due to significant formation of byproducts such as oligomer and lactamide (Conv. 70%, Sel. 10% at 10 h). The significant improvement in ethyl lactate yield was obtained when lactic acid was extracted from ammonium lactate in tributyl phosphate and then it reacted with ethanol, where oligomer formation was decreased greatly (Conv. 78%, Sel. 95% at 10 h).

Compared with the traditional method including acidulation of calcium lactate, extraction, and esterification, the present technique is potentially more economical since it enhances not only the productivity of lactic acid fermentation but also the efficiency of overall process from fermentation broth to ethyl lactate.

1. Introduction

Recently ethyl lactate has received much attention as a green solvent due to its nontoxic, biodegradable properties as well as excellent solvent properties [1]. It is a very versatile building-block molecule for degradable plastic polymers such as propylene glycol, acrylates, and propylene oxide as well as specialty product derivatives [2]. It could also be used for the composition of common household products, such as packaging and biodegradable plastics as well as semiconductor chips in computers and consumer electronics.

Ethyl lactate can be synthesized by reactive distillation of lactic acid with ethanol. When the concentrated (88 wt% in water) lactic acid was used as a feedstock with 40% excess ethanol, 95% conversion of lactic acid was obtained with some byproduct lactate oligomer esters and acids [3]. But, its price has been too high until now to allow it to compete with lower-priced chemicals economically. The high cost of ethyl lactate is mainly due to the high production cost of lactic acid since the current fermentation-based method is not competitive compared with conventional chemical solvents.

The primary technology barriers to cost-effective production of lactic acid by fermentation methods are in separation and purification. In industrial fermentation, excess calcium carbonate is generally added to fermentor to neutralize the lactic acid produced since lactic acid fermentation is inhibited by acid concentration, which produces calcium lactate, not free lactic acid just after fermentation. The broth containing calcium lactate is filtered to remove cells, carbon treated, evaporated, and acidified with sulfuric acid to convert the salt into lactic acid and insoluble calcium sulfate, which is removed by filtration. The filtrate is further purified by carbon columns and ion exchange and evaporated to produce technical and food-grade lactic acid [4–6].

However, the conventional purification process is not only costly (about 50% of total production costs) but also environmental unfriendly as it consumes a huge amount of lime and sulfuric acid and it also produces a large quantity of calcium sulfate, gypsum as a waste [7].

Hence many studies have been focused on finding a technically and economically competitive process with the conventional gypsum-generating process. The genetically engineered *Lactobacillus* has been reported to produce protonated lactic acid directly at a low pH of 2.8–3.0 [8,9]. Its productivity was reported to too low to be economic for a commercial process (30 g/L and 0.7–0.9 mol per mole of dextrose). Recent advances in membrane-based purification technology such as ultrafiltration and electrodialysis, have been used for lactic acid production without gypsum waste [10–13]. However, this membrane technology does not seem to

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be currently practical on a commercial scale since it has a problem of membrane fouling, which requires frequent cleaning of the dialyzer. Moreover, dialysis units with large-volume, even greater than the volume of the fermentor vessel, are required in a commercial-scale and large amounts of salts from the ion-exchange regeneration are also formed as by-products [14].

The utilization of ammonium lactate as a feedstock for ethyl lactate can be very promising route since post-treatment steps such as acidification and filtration can be removed and thus the cost of ethyl lactate can be reduced greatly. However, only alcohols with high boiling point like butanol were reported to be successful, where the reaction temperature could be increased above 100 °C and thus, the removal of ammonia as well as water is facilitated [15,16].

If ammonia produced by dissociation of ammonium lactate is not removed rapidly, the reaction rate is very low and undesired lactamide could be generated. In order to facilitate the decomposition rate of ammonium lactate into lactic acid, the sulfuric acid was added in the reaction medium. However, in this process the basic salt of sulfuric acid should be crystallized to precipitate and then it should be filtered out. [17].

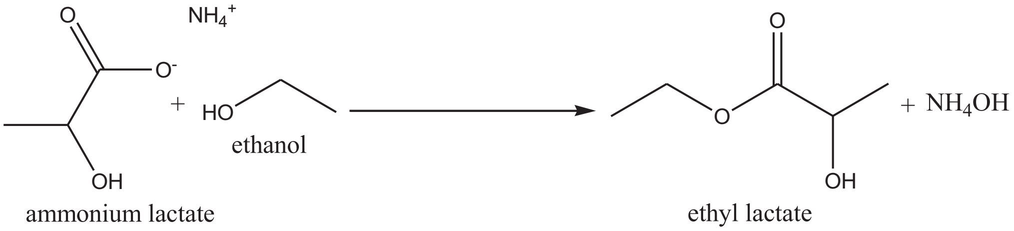
Although the competing species could be eliminated rapidly by the utilization of a chemically inert carrier gas during refluxing and the use of a drying agent to remove water, the reaction rate was quite low (only 45% conversion after 96 h) [18].

The purpose of this work is to develop more efficient and ecologically sound pathway for ethyl lactate from fermentation product of lactic acid. In this paper, we propose a regenerative synthesis route for ethyl lactate from ammonium lactate by coupling solvent extraction with esterification reaction. It is believed that this technology would reduce the production cost of ethyl lactate greatly by simplifying process steps compared with the conventional method.

2. Experimental

2.1. Materials

Ammonium lactate solution (40 wt%, Wako Chemical), lactic acid (88 wt%, Kanto Chemical), tridecylamine (95%, Tokyo Chemical Industry), tributyl phosphate (97%, Wako Chemicals), ethanol (99.9 wt%, Samchun Chemical) and sulfuric acid (98 wt%, Samchun Chemical) were used in experiments without further treatment. The cation exchange resins (Amberlyst-15, Amberlite-IRP64 and Amberlyst-36) were obtained from Rohm and Haas. Aqueous lactic acid solutions (90 wt%, 50 wt%, and 20 wt%, Aldrich), ethyl lactate (99%, Lancaster Chemicals) and lactamide (99%, Aldrich) were used for calibration.



2.2. Esterification

For extraction of lactic acid from ammonium lactate, typically 12 g of ammonium lactate solution was mixed with 50 g of an organic solvent (tridecyl amine or tributyl phosphate) in a three-neck glass reactor with a volume of 100 ml. The reactor was equipped with a dean stark apparatus to collect water distilled off, which was connected with a reflux condenser and then vacuum pump. The reactor with a magnetic stirrer was placed in a temperature-controlled heating jacket. The temperature and vacuum pressure inside the reactor was continuously monitored by thermocouple and vacuum gauge, respectively.

The esterification reaction was carried out in the same reactor containing a mixture of lactic acid and organic solvent. The reactor equipped with a reflux condenser was placed in an oil bath and 0.5 g of ion-exchange resin as an acid catalyst was added to the reactor.

2.3. Analyses

The concentration of lactic acid, ethanol, ethyl lactate, lactamide in the reaction mixture was analyzed by gas chromatography (DONAM, DS6200) equipped with flame ionization detector (FID) using a DB-WAX column, (30 m × 0.53 mm). The column temperature program involved initially holding at 50 °C for 2 min, heating to 200 °C at 10 °C/min, followed by ramp up to 230 °C at 10 °C/min and holding for 4 min. Argon was used as a carrier gas with a flow rate of 3 ml/min. The injector and FID temperatures were maintained at 250 °C.

The concentrations of lactamide, lactic acid, ester, and oligomers were also quantitatively analyzed by HPLC (Younglin) using a reversed-phase symmetry C18 column (4.6 mm × 150 mm) at 40 °C equipped with UV detector (UV 730D) at 210 nm. Water/acetonitrile (ACN) mixtures buffered at pH = 1.3 were used as mobile phase with a flow rate of 1.0 ml/min in a gradient mode (0% ACN ($t = 0$) to 60% ACN ($t = 20$ min) to 90% ACN ($t = 25$ min) to 0% ACN ($t = 28$ min) [3].

The concentration of water was analyzed after extraction of lactic acid by Karl Fischer apparatus (METROHM, 784KFP). The conversion of ammonium lactate was determined from the analysis of ammonium ions in the extracted solutions by ion chromatography (METROHM, Metrosep C2 150 column).

3. Results and discussion

As a preliminary study, the esterification reaction of ammonium lactate with ethanol was investigated at 110 °C and 1 bar without refluxing ethanol in order to enhance the reaction rate by fast removal of water and ammonia. The molar ratio of ethanol to ammonium lactate or lactic acid was maintained to 10 by supplying ethanol continuously into the reactor using N_2 carrier gas.

As shown in Table 1, the direct esterification of commercial 40 wt% ammonium lactate with ethanol in the presence of 1 mol% of H_2SO_4 as catalyst gave the ethyl lactate yield of only 1.8% after 4 h. There was little difference in ethyl lactate yield between 70 wt% and 40% ammonium lactate, although the removal of water in esterification reaction has been reported to improve the reaction rate. When the sulfuric acid concentration increased from 1 mol% to 10 mol% for 70 wt% ammonium lactate, the ethyl lactate yield was increased a little to 4.7%. However, this reaction rate was negligible compared with lactic acid as a reactant, where almost equilibrium yield of 85% was obtained after 4 h in the presence of 1 mol% of sulfuric acid. It is notable that 16% of lactic acid was converted into ethyl lactate even without acid catalyst.

This slow rate of the reaction with ammonium lactate compared with lactic acid could be mainly due to the presence of