

Recovery Process of Lactic Acid Using Two Distillation Columns

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Abstract Lactic acid is of interest as the raw materials of polylactide that is a biodegradable polymer. For an effective purification of lactic acid, batch distillation with the simultaneous reactions was used. Two Oldershaw columns and reboilers were used for fractionation of methanol and reactions. Esterification reaction of lactic acid with methanol produced methyl lactate and water. The products of the esterification reaction, methyl lactate and water were transported to the reboiler of the hydrolysis part. In hydrolysis part, reaction of methyl lactate and water reproduced lactic acid and methanol. Methanol produced in the hydrolysis part and unreacted methanol in the esterification part were separated by distillation and recycled to the reboiler of the esterification part so that the esterification reaction would be stimulated. Thus, pure lactic acid solution remained in the reboiler of the hydrolysis part. The effect of the number of stages in column on the recovery yield was also investigated. In the operation with columns the recovery yield of lactic acid was improved. It is due to the fact that the columns improved the fractionation of components and stimulated the reactions in two parts.

Keywords. lactic acid, reactive batch distillation, esterification, hydrolysis

INTRODUCTION

Lactic acid (2-hydroxypropanoic acid, 2-hydroxypropionic acid) has been an intermediate-volume specialty chemical (world production-50,000 tons/yr) used in food processing and other industrial applications. Lactic acid has the potential to become a very large volume, commodity-chemical intermediate produced from renewable carbohydrates to be used as feedstocks for biodegradable polymers, oxygenated chemicals, environmentally friendly green solvents, plant growth regulators, and specialty chemical intermediates [1].

Lactic acid can be manufactured by either chemical synthesis or carbohydrate fermentation. Recently, for a fermentation-based lactic acid process to be economically attractive for the production of specialty and commodity chemicals, the development of low cost fermentation must be combined with low cost and effective product recovery and purification methods.

However, the purification of lactic acid obtained from fermentation is difficult to be achieved due to low vapor pressure of lactic acid, its self-esterification, and other impurities such as glucose and amino acid. The conventional methods for the recovery of pure lactic

acid are crystallization [2], solvent extraction [3,4], and filtration-carbon treatment-evaporation [5]. Some of these processes are not effective due to the high cost and the low purity. Smith and Claborn (1959) proposed the esterification of lactic acid with alcohol to obtain the highly purified lactic acid [6]. The lactate ester produced by the esterification of lactic acid with alcohol was separated by distillation, and the distilled lactate ester was hydrolyzed into lactic acid. However, these processes were complex for recovery of pure lactic acid and the capital cost of equipment is high [7]. To overcome these disadvantages the batch distillation with simultaneous reactions was proposed [7].

In this study the recovery of lactic acid through reactive batch distillation was investigated based on the optimum design and effective operation. The experimental apparatus consisted of two columns for fractionation of reactants and two reboilers for esterification reaction and hydrolysis reaction. Batch operation mode was used for the sufficient residence time of the reactants for the recovery of pure lactic acid.

MATERIALS AND METHODS

Twenty%(w/w) L-lactic acid solution was obtained from Acros Organics, in USA and methanol from Merck in Germany. These were used without further purification. A strongly acidic cation exchange resin, Dowex-

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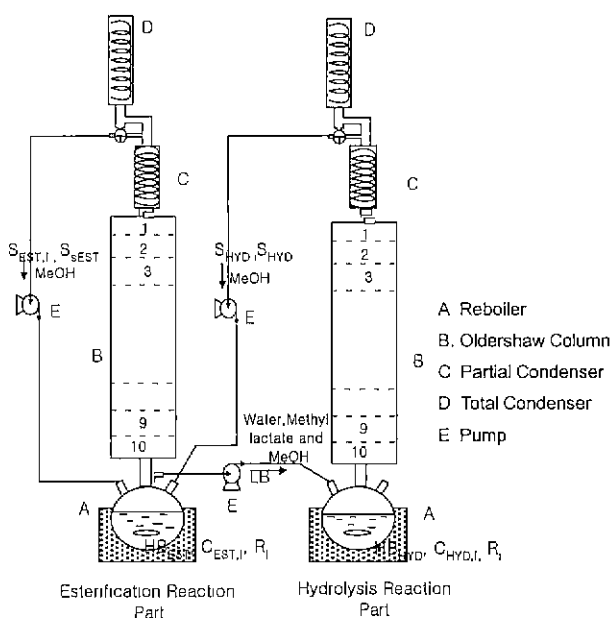


Fig. 1 A Schematic diagram of the experimental apparatus.

50W in the H^+ form, was purchased from Sigma Chemical Co in USA and used as the solid catalyst. This ion exchange resin was a sulfonated styrene cross-linked with 8% divinylbenzene. For pretreatment, new fresh resins were washed with deionized water and kept at 348 K in a vacuum oven for 12 h for the removal of moisture in the resins.

A schematic diagram of the experimental apparatus is shown in Fig. 1. The experimental apparatus consisted of two parts, the esterification part and the hydrolysis part. The glass Oldershaw columns with vacuum jacket were used. The properties of reactants and products in this study are shown in Table 1. The volatility of the reactants and products in this experiment decrease in the order of methanol > water > methyl lactate > lactic acid.

Experimental procedure are as follows: First, lactic acid, methanol and the catalyst, ion exchange resin were charged into the reboiler of the esterification part. The reaction mixture was sufficiently stirred throughout the whole process. The liquid stream of esterification part consisting of water, methanol and methyl lactate was transported to the reboiler of the hydrolysis part by metering pump. Unreacted methanol in vapor stream of esterification part was recovered from the partial condenser at 65.5°C and the total condenser.

In the hydrolysis part, liquid stream from esterification part was collected and hydrolyzed. Methanol produced in this part was also recycled to the esterification part reboiler. And lactic acid produced from hydrolysis part was remained in the reboiler of this part.

In this study, the batch reactive distillation system was developed to allow sufficient residence time for two reactions (esterification and hydrolysis) and distillation

Table 1. The boiling point of the reactants and products

Reactants and products	Molecular weight	Boiling point (at 760 mmHg)	Company
Lactic acid	90.08	* 217°C	Acros
Methanol	32.04	64.7°C	Merk
Water	18.02	100°C	
Methyl lactate	104.11	144-145°C	

* Value is hypothetical due to decomposition before boiling [11].

Table 2 Analysis conditions of gas chromatography

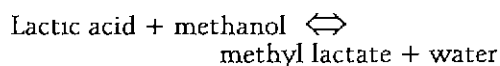
	MeOH/Water system	MeOH/Water/Methyl lactate system
Detector type	TCD	TCD
Detector	210	220
Temperature (°C)		
Injector temperature (°C)	200	210
Oven temperature (°C)	180	190
Column	Porapak Q	Porapak Q
Carrier gas	Helium	Helium
Carrier flow rate (mL/min)	42.9	42.9

was performed for the recovery of pure lactic acid with a high recovery yield. The yield was defined as the amount of recovered lactic acid in the hydrolysis reactor to that of lactic acid initially charged into the esterification reactor.

The samples taken from the reboilers of the esterification and hydrolysis reaction parts were titrated with 0.1N standard NaOH solution using phenolphthalein as an indicator. Troupe and Kobe (1950) reported that the formation of dimer or oligomer of lactic acid by self-esterification could be ignored when the concentration of lactic acid was lower than 30%(w/w) [8]. The products from the top and bottom of the columns were analyzed by gas chromatography (HP 5890 II series, USA) equipped with TCD. The analysis conditions of GC are shown in Table 2.

RESULTS AND DISCUSSION

In this study, reactions in the reboilers are as follows:



The residuals in the reboilers of both parts consisted of the four components in above reaction. But boilups from the reboilers had only three components - methanol, water and methyl lactate since lactic acid has little volatility and decomposes before vaporization in the case of L-lactic acid. The experimental apparatus

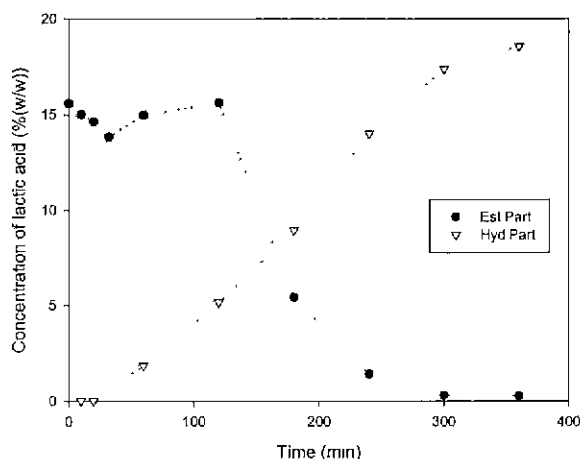


Fig. 2. Concentration changes of lactic acid in both reboilers ((E10H10) LA MeOH = 1:4, DOWEX-0.0250 g-cat/g-sol).
* esterification part : 10 stages/hydrolysis part : 10 stages.

was designed to split methanol and methyl lactate in boilup from reboilers and then transport methanol into the esterification part and methyl lactate into the hydrolysis part. And in this experiment, water used as the solvent of lactic acid in the initial feed and produced from reaction. This water mainly moved into the hydrolysis part since it has boiling point above partial condenser temperature. The residual water in hydrolysis part can be removed to some extent by further distillation in only hydrolysis part.

Concentration changes of lactic acid in the reboilers of the esterification part and the hydrolysis part are shown in Fig. 2. Since the esterification reaction rate was fast at the beginning of operation, the concentration of lactic acid in the reboiler of the esterification part decreased for a little while. After that period concentration of lactic acid in the esterification part increased from 30 to 120 min. This increase was due may be to the fact that the evaporation rate of methanol and water production in the reboiler was faster than the disappearance rate of lactic acid by esterification reaction. After two-hour operating time, the concentration of lactic acid in the reboiler of the esterification part decreased abruptly. The fast disappearance of lactic acid is due to the sufficient supply of methanol from the recycled stream from the top of the hydrolysis reaction part. Concentration of lactic acid in the reboiler of the hydrolysis part increased as the hydrolysis reaction proceeded owing to continuous removal of methanol. The recovery yield of lactic acid was 84% after 6 h.

Temperature changes of the reboiler and of several stages in the esterification part are shown in Fig. 3. As the operation proceeded, the temperature of the reboiler decreased from the boiling point of the initial reaction mixture near to the boiling point of pure methanol. After three hours, the temperature of the remaining mixture was near the boiling point of methanol, showing

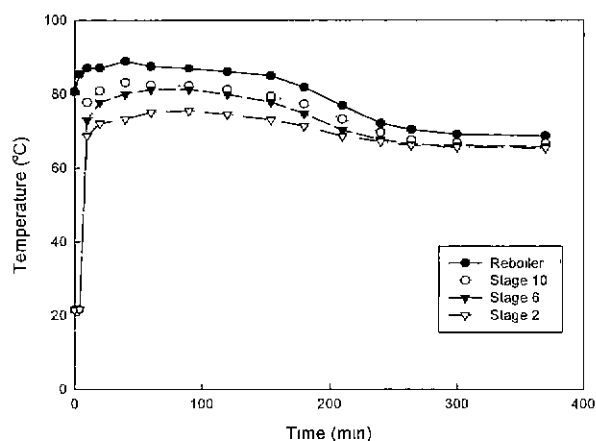


Fig. 3. Temperature changes at each stage in the esterification part ((E10H10) LA:MeOH = 1:4, DOWEX-0.0250 g-cat/g-sol).

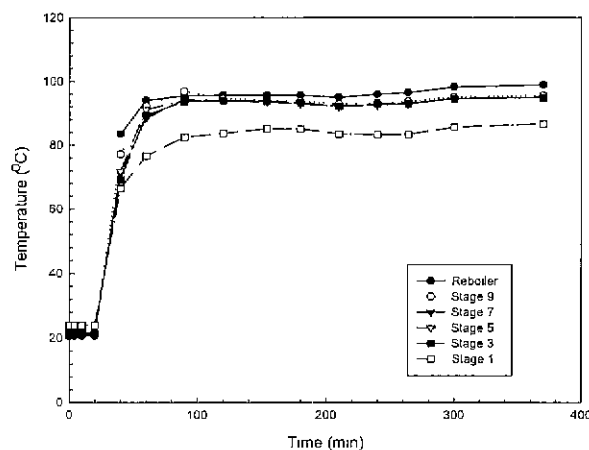


Fig. 4. Temperature changes at each stage in the hydrolysis part ((E10H10) LA MeOH = 1:4, DOWEX-0.0250 g-cat/g-sol).

transition into the methanol rich phase in the reboiler of the esterification part. Temperature changes of the reboiler and of the several stages in the hydrolysis part are shown in Fig. 4. As the operation proceeded temperature of the reboiler of the hydrolysis part increased with the increasing concentration of lactic acid in the reboiler.

Sufficient time was needed to obtain high-purity lactic acid since this system needed two reactions and distillation process for separation. From these results, it is concluded that 6 h operating time was sufficient as one batch time.

Fig. 5 shows the effect of the number of stages in the columns on the concentration of lactic acid in both reboilers. Effective recovery was accomplished by increasing the number of the stages. Table 3 represents the recovery yields of lactic acid according to the number of stages of columns.

Fig. 6 shows the effect of the number of stages in the columns on the temperature of the reboiler of the hydrolysis part. The temperature increased as the

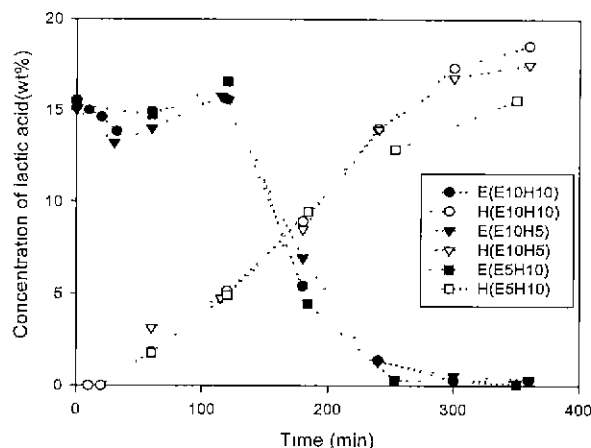


Fig. 5. Effects of the number of stages (E10H10, E10H5 and E5H10) on the concentrations of lactic acid in both reboilers (LA:MeOH = 1.4, DOWEX-0.0250 g-cat/g-sol).

Table 3. Recovery yields of lactic acid according to the number of stages of the columns

Number of stages of columns		Recovery yield of lactic acid (%)
Esterification part	Hydrolysis part	
0	0	75.7
(E5H10) 5	10	77.8
(E10H5) 10	5	84.0
(E10H10) 10	10	85.6

concentration of lactic acid in the reboiler increases. In the column with more stages, the temperature in the reboiler was higher, resulting in higher concentration of lactic acid.

The effect of existence of column is shown in Fig. 7 plotting the concentrations of lactic acid in the reboiler of the hydrolysis part. In this case without column, methanol was separated only by means of condensers. The yield with the columns was 85.6% whereas that without column was much less with 75.8%. The recovery yield of lactic acid was enhanced by 10% using 10-stage columns in both reaction parts.

The increase of yield with columns is due to the fact that columns have role of fractionating the boilups from the reboilers. In details, column made the lightest boiler, methanol richer in vapor flow and the others in liquid flow. The vapor stream was condensed and recycled into the reboiler. So column made recycle stream of purer methanol and prevent methanol to remain hydrolysis part. Ultimately, these effects of columns stimulated the reactions in both reboiler by improving the recycle of methanol as reactant in esterification part and the removal of methanol as product in hydrolysis part. Therefore the recovery yield with columns was improved. The fact that the yield of E10H5 was larger than that of E5H10 means that this effect of columns was more significant in the esterification part.

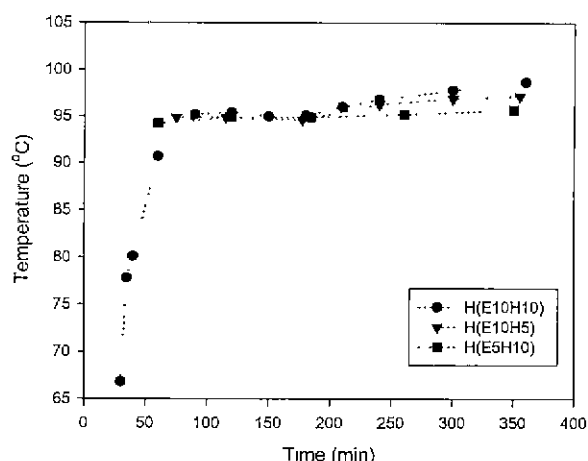


Fig. 6. Temperature of the reboiler in the hydrolysis part with varying number of stages in the columns (LA:MeOH = 1.4, DOWEX-0.0250 g-cat/g-sol).

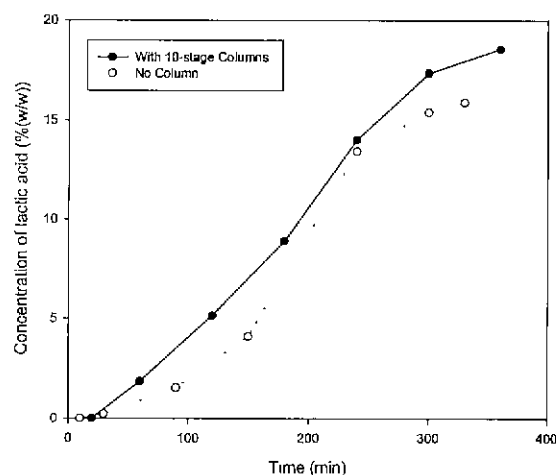


Fig. 7. Effect of existence of a column in the hydrolysis part (LA:MeOH = 1:4, DOWEX-0.0250 g-cat/g-sol).

A series of simple balance equations was used to calculate the concentration changes of lactic acid in the reboiler of the esterification part. In these equations, the vapor-liquid equilibrium between the vapor flows from the reboilers and liquid holdups in the reboilers was assumed. The nomenclatures in these equations are shown in Fig. 1. The mass balance equations used in the calculation are as follows:

Total balance equations :

$$\frac{dHB_{Est}}{dt} = -LB + S_{Est} + S_{Hyd} \tag{1}$$

$$\frac{dHB_{Hyd}}{dt} = -LB - S_{Hyd} \tag{2}$$

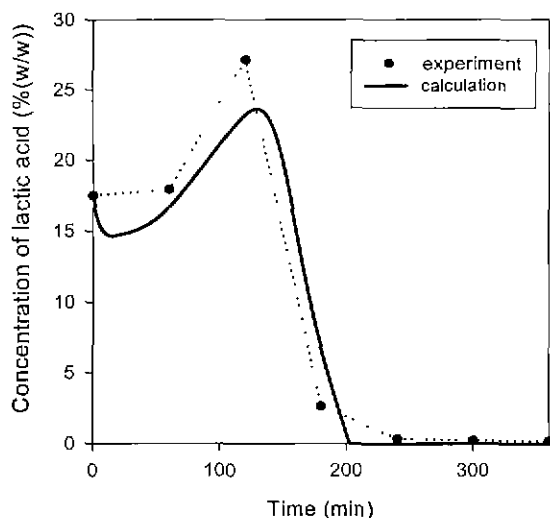


Fig. 8. Concentration of lactic acid in the reboiler of the esterification part. - Comparison of calculated values and experimental values for the packed column

Component balance equations :

$$\frac{d(HB_{Est}C_{Est,i})}{dt} = -LB_i - R_i HB_{Est} + S_{Est,i} + S_{Hyd,i} \quad (3)$$

$$\frac{d(HB_{Hyd}C_{Hyd,i})}{dt} = LB_i - R_i HB_{Hyd} - S_{Hyd,i} \quad (4)$$

Reaction rate equation:

$$\frac{dC_{ML}}{dt} = (k_0 + k_c C_c) \exp\left(-\frac{E}{RT}\right) (C_{LA} C_{MeOH} - C_{ML} C_{H_2O} / K) \quad (5)$$

The reaction rate equation and its constants were obtained from the work by Seo and Hong [10]. They interpreted the kinetics of lactic acid esterification over ion exchange catalysts using a pseudo-homogeneous model. Fig. 8 compares the calculated values with the experimental values. The calculated values for the concentration of lactic acid in the esterification part show a temporary increase at the initial period as in the experimental values.

This process was designed as the final purification step followed by the treatment with conventional recovery processes such as filtration and electrodialysis. Lactic acid feed went through these pretreatment steps contains less than 1% glucose and trivial amino acids. These components are not volatile like lactic acid but cannot react with methanol. So this process have selectivity to lactic acid compared with the other components.

Under the above consideration, this investigation was focused on the optimum design and the effective operation based on the higher yield and less operating time. The investigation on the effect of the other impurities such as glucose and amino acid is in progress

CONCLUSION

The reactive batch distillation by two Oldershaw columns for the recovery of the high purity lactic acid was performed. Concentration and temperature profiles in the reboilers and on each stage were investigated throughout the operation. 6 h operating time was required for the high purity lactic acid.

The effect of columns on the recovery yield was investigated. The column improved the fractionation of the boilups from the reboilers. More effective fractionation in columns allowed vapor stream in columns to contain more methanol and liquid stream to contain less methanol. Thereby, methanol-concentrated recycle flow was obtained more effectively and methanol was prevented to remain hydrolysis part. That resulted in the more effective reaction in both reboilers and improved the yield of system.

NOMENCLATURE

C_i	Concentration of each component [mol/g]
C_c	Concentration of catalyst [g-cat./g-sol.]
E	Activity energy [J/mol]
HB	Holdup of reboiler [g]
k	Reaction constant
K	Reaction equilibrium constant
LB	Flow rate of the stream transported from the esterification part to the hydrolysis part [mol/sec]
R	Reaction rate [mol/g sec]
S	Flow rate of the recycle stream from the top of the esterification part or the hydrolysis part [mol/sec]
t	Time [sec]

Subscripts

i	Index of components
Est	Esterification reaction part
Hyd	Hydrolysis reaction part

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