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Effects of Operation Variables on the Recovery of Lactic Acid in a Batch Distillation Process with Chemical Reactions

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Abstract–In this study, the feasibility of recovery of lactic acid by batch reactive distillation using cation exchange resin as a catalyst was investigated. For the recovery of lactic acid, two reactions, esterification and hydrolysis, are involved and hence, an apparatus with two distillation columns was developed and operated in a batch mode to ensure enough residence time in the reboiler and column. The effects of operation variables such as catalyst loading, reactant mole ratio, feed concentration, type of alcohols and partial condenser temperature on the yield were studied. In this study, the reaction products of the esterification (methyl lactate and water) were distilled to the hydrolysis part to be recovered into pure lactic acid. The yield of lactic acid increased as catalyst loading in the esterification part increased and reactant mole ratio and feed lactic acid concentration decreased. Methanol as a reactant gave higher yield than any other alcohols. The yield of recovered lactic acid was as high as 90%. The yield of lactic acid was closely related to the boiling temperature of the reaction mixture in the esterification part

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Key words : Batch Reactive Distillation, Lactic Acid, Cation Exchange Resin, Esterificaiton, Hydrolysis

INTRODUCTION

Lactic acid, $CH_3CHOHCOOH$, is a naturally occurring organic acid. As the world's crude oil resources diminish and the prices of petroleum products continue to increase, the production of chemicals by biological processes is becoming more competitive. High purity and heat stable lactic acid, which was mainly available from synthetic manufacture, is now being produced by fermentation. About 85% of the estimated 50,000 tons/yr of lactic acid produced worldwide is used in the food industry. The rest is used in pharmaceutical, cosmetics, textile, and leather industries. These markets are projected to grow at 2-4%/yr [Evangelista and Nikolov, 1996]. The use of polylactic acid (PLA) for biodegradable polymers, controlled-release drugs and pesticides can transform lactic acid into a commodity chemical [Lipinsky and Sinclair, 1986]. The commercial success of PLA, however, depends on the cost of producing heat stable lactic acid. Therefore, the development of economic and effective recovery process of lactic acid is essential.

The recovery of lactic acid is rather difficult due to its chemical behavior. Lactic acid has a strong affinity to water and low volatility which renders its separation by solvent extraction or distillation difficult [Lipinsky and Sinclair, 1986].

High purity lactic acid can be prepared by esterification with alcohols, distillation of the ester, hydrolysis of the distilled lactate ester to yield the alcohol and lactic acid, and distillation of the alcohol from the regenerated lactic acid [Vickroy, 1985; Cockrem and Johnson, 1993]. This recovery process produces a highly pure product, which is water white and heat stable. But this process is very complex and needs expensive equipment. Therefore, in this study reactive distillation which simultaneously performs chemical reaction and multistage separation is proposed. Reactive distillation is applied specifically to reversible chemical reactions in the liquid phase, in which reaction equilibrium limits conversion of the reactants. Lower capital investment, higher conversion and lower energy consumption make reactive distillation an attractive alternative to conventional processes [Bessling et al., 1998].

The reaction of esterification or hydrolysis is generally catalyzed by homogeneous catalyst such as sulfuric acid, anhydrous hydrogen chloride and many other mineral acids. However, the use of a solid ion exchange resin as a catalyst has several advantages over homogeneous catalysts: low corrosion, ease of separation for the reaction mixture and no side reactions [Helfferich, 1962].

Two reactions, esterification and hydrolysis, are involved in this system. Hence, for the recovery of lactic acid by reaction and distillation, enough residence time in the reboiler and column is needed. For this reason the process was operated in a batch mode. In the previous research, batch reactive distillation with one column was investigated for the recovery of lactic acid [Choi and Hong, 1999]. In this study, the feasibility of recovery of lactic acid by batch reactive distillation with two columns using cation exchange resin as a catalyst was investigated. The effects of operation variables such as catalyst loading, reactant mole ratio, feed concentration, type of alcohols and partial condenser temperature on the yield were studied.

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EXPERIMENTAL

1. Materials

Methanol, ethanol, 2-propanol of 99.8% purity (Merck) and aqueous lactic acid solution with a content of 20 wt% acid (Acros) were used without further purification. A strongly acidic cation exchange resin, DOWEX-50W in the H^+ form, was purchased from SIGMA Co. and used as a solid catalyst. This ion exchange resin was a gel form and consisted of a sulfonated styrene crosslinked with 8% divinylbenzene. Its total exchange capacity was 4.8 meq/g. Before the experiment, new fresh resins were washed with deionized water and kept at 75 °C in a vacuum oven overnight to remove moisture completely. The properties of ion exchange resin are shown in Table 1.

2. Apparatus

The distillation columns are glass packed columns whose diameter is 1 inch with a height of 60 cm for the esterification part and 90 cm for the hydrolysis part. The packing materials were 3 mm×3 mm stainless steel helices. The capacity of the reboiler is 500 ml. The schematic diagram of reactive distillation process is shown in Fig. 1. Columns and joints were well insulated.

3. Procedures

Table 1. Properties of DOWEX-50W

Degree of crosslinking (%)	8
Type	gel form
Mesh size	16-40
Total exchange capacity (meq/g)	4.8
Ionic form	H^+

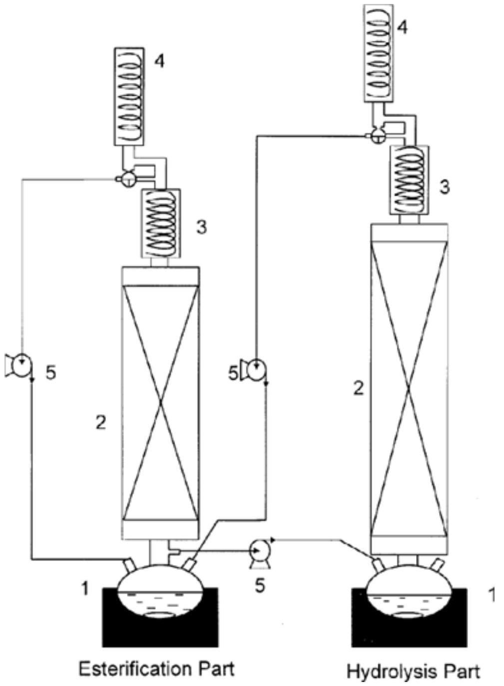

Fig. 1. Schematic diagram of the reactive distillation process.

1. Reboiler	4. Total condenser
2. Packed column	5. Pump
3. Partial condenser	

Table 2. The boiling point of reactants and products

Reactants and products	Molecular weight	Boiling point (at 760 mmHg)
Lactic acid	90.08	122 °C at 14 mmHg
Methanol	32.04	64.7 °C
Water	18.02	100 °C
Methyl lactate	104.11	144-145 °C

For the recovery of lactic acid, two reactions are involved:

Esterification : Lactic acid + Methanol→Methyl lactate + Water
Hydrolysis : Methyl lactate + Water→Lactic acid + Methanol

The volatilities of reactants and products play an important role in the design of a reactive distillation process. The order of volatilities of reactants and products involved in this experiment is as follows: methanol >water>methyl lactate>lactic acid (Table 2). Lactic acid is almost non-volatile under atmospheric pressure. The apparatus was designed considering two reactions and volatility. In this experiment, both reactions go on in the state of boiling. Formation of dimer or oligomer of lactic acid by self-esterification could be ignored because lactic acid solution of low concentration (20 wt%) was used [Troup and Kobe, 1950].

In the reboiler of the esterification part, lactic acid solution was first charged. After lactic acid solution was heated to the desired temperature, methanol and a given amount of catalyst were added. The total amount of feed (lactic acid solution and methanol) in the esterification part was 350 g for all the experiments. As esterificaiton of lactic acid with methanol proceeds in the reboiler, water and methyl lactate which have midway volatilities are produced. Produced methyl lactate, water and unreacted methanol are distilled upward through the distillation column, then water and methyl lactate are removed in the bottom of the column after being condensed in the partial condenser and simultaneously transferred to the reboiler of the hydrolysis part. Methanol is recycled to the reboiler of the esterification part through the partial and total condenser. Hydrolysis of methyl lactate and water in the column of the esterification part was not observed.

In the hydrolysis part, methyl lactate is hydrolyzed into lactic acid. Recovered lactic acid and water stay in the reboiler of the hydrolysis part. Produced methanol is recycled to the reboiler of the esterification part by distillation. Hydrolysis also occurred in the column of the hydrolysis part.

The samples from the reboilers of the esterification and hydrolysis part were weighed and titrated with 0.1 N standard sodium hydroxide solution using phenolphthalein as an indicator. The products from the top and bottom of the columns were analyzed by Gas Chromatography (HP 5890 II series) equipped with TCD. The yield is defined as the amount of recovered lactic acid in the reboiler of the hydrolysis part to that of lactic acid initially charged in the reboiler of the esterification part.

RESULTS AND DISCUSSION

1. Comparison of Reactive Distillation with Batch Reaction

Esterification of lactic acid with methanol is a representative

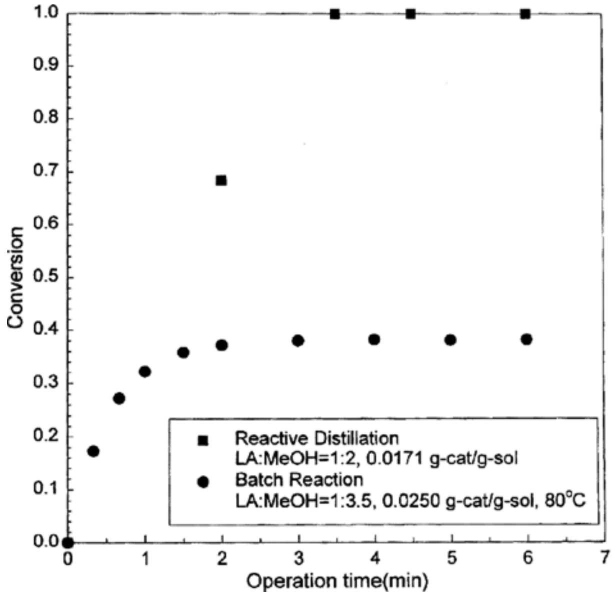

Fig. 2. Comparison of the results with and without removal of products.

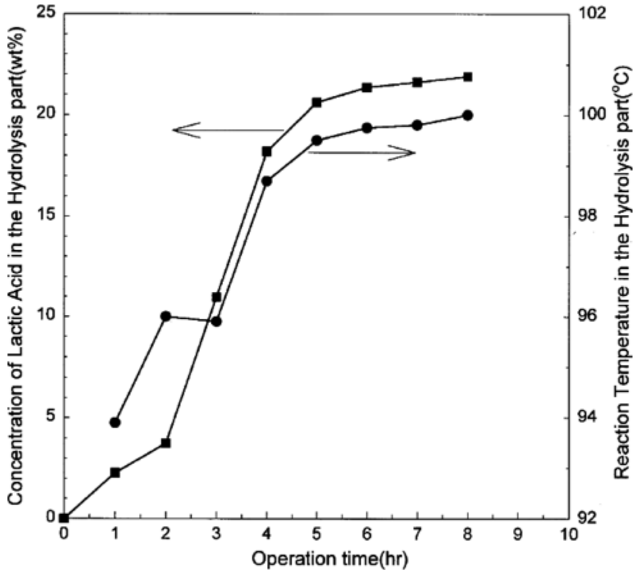

Fig. 4. The concentration and temperature changes in the hydrolysis part.
20 wt% Lactic acid, LA : MeOH=1 : 2, est.resin=0.00857 g-cat/g-sol, hyd.resin=3 g

example of an equilibrium-limited reaction. The reversible reaction of lactic acid and methanol yields water and methyl lactate. As excess of water was present in the reaction mixture, the conversion was greatly restricted by the equilibrium limitation. As can be seen from Fig. 2, only up to 40% conversion of lactic acid (mole ratio 1 : 3.5) was achieved in batch reactions. If one of the products can be efficiently removed from the reaction mixture, then it would be possible to achieve very high conversions of the limiting reactant. The reaction was very efficiently carried out in reactive distillation wherein simultaneous reaction and distillation caused to shift the equilibrium in forward direction, which led to very high conversions of the limiting reactant at relatively low mole ratios [Chopade and Sharma, 1997]. Fig. 2 shows that reactive distillation gives much higher conversion than batch reaction although the mole ratio and catalyst loading are lower.

2. Progress of Reaction and Separation

Fig. 3 and Fig. 4 show the temperature and concentration profiles in the esterification and hydrolysis part, respectively. In the esterification part, lactic acid was removed by reaction, so the concentration continuously decreased and temperature also decreased. In the end part of the experiment, the reboiler of the esterification part became filled with almost methanol and hen-

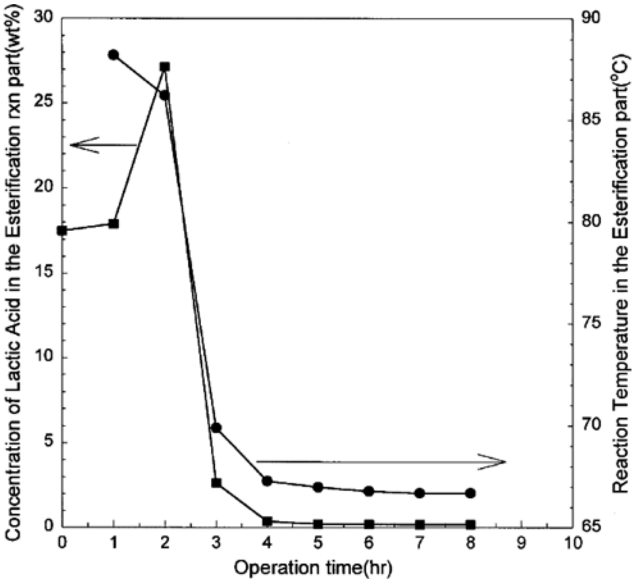

Fig. 3. The concentration and temperature changes in the esterification part.
20 wt% Lactic acid, LA : MeOH=1 : 2, est.resin=0.00857 g-cat/g-sol, hyd.resin=3 g

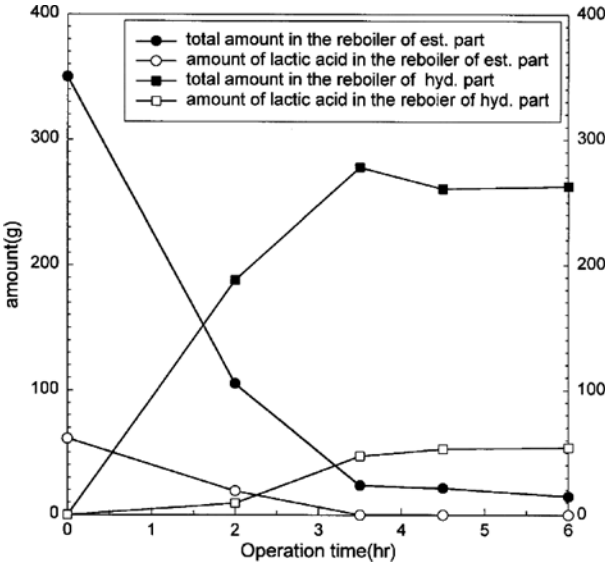

Fig. 5. The progress of reaction and separation of lactic acid in the reactive distillation process.
20 wt% Lactic acid, LA : MeOH=1 : 2, est.resin=0.0171 g-cat/g-sol, hyd.resin=3 g

ce, the boiling temperature of the reaction mixture was just above the boiling point of methanol (64.7 °C). At the initial period the concentration was temporarily increased because more unreacted methanol and water in the reactant was removed by distillation than that of produced methyl lactate. In the hydrolysis part, methyl lactate was hydrolyzed into lactic acid, so the concentration of lactic acid and the temperature increased with operation time.

Fig. 5 shows the progress of reaction and separation of lactic acid in the reactive distillation process. From these figures, it can be found that most of the lactic acid and water in the reboiler of the esterifcation part was removed within 3 hours of operation, and in the reboiler of the hydrolysis part, most of lactic acid was recovered by hydrolysis after 4 hours of operation. After 6 hours of operation, no more yield of lactic acid could be obtained.

3. The Effect of Catalyst Loading

In this study, cation exchange resin was used as the solid catalyst. The kinetics of lactic acid with methanol catalyzed by cation exchange resin was already studied [Choi et al., 1996; Seo and Hong, 1999].

The effect of catalyst loading in the esterification part on the yield of lactic acid was investigated (Fig. 6). The yield increased with catalyst loading up to 0.0171 g-cat/g-sol. With the increase in catalyst loading, the surface area and the total number of active sites increase. Therefore, the production rate of methyl lactate which is hydrolyzed into lactic acid in the reboiler of hydrolysis part increased and thus, the final yield of lactic acid also increased.

Fig. 7 shows the effect of catalyst loading in the hydrolysis part on the yield of lactic acid. In a 3 hour experiment, the result was similar to that in the esterification part. That is, the yield of lactic acid increased with the increment of the catalyst loading. But in the 6 hour experiment, it can be seen that the yield of lactic acid was less influenced by the catalyst loading. As the hydrolysis of methyl lactate and water proceeds, the effect of catalysis becomes decreased because of the removal effect of the reaction product, methanol.

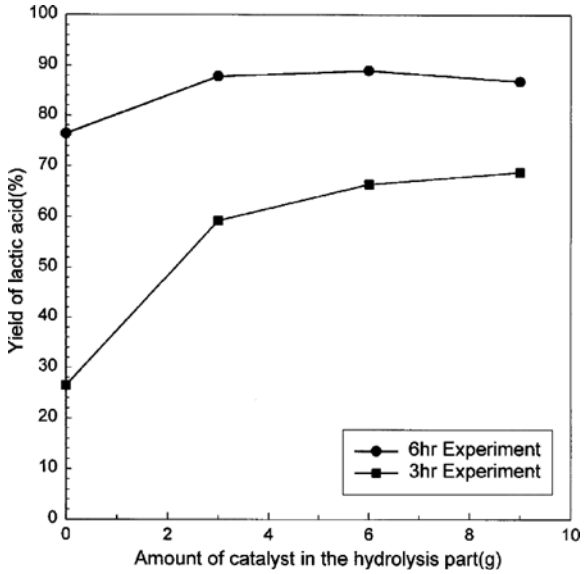

Fig. 7. The effect of catalyst loading in the hydrolysis part on the yield.
20 wt% Lactic acid, LA : MeOH=1 : 2, est.resin=0.0171 g-cat/g-sol

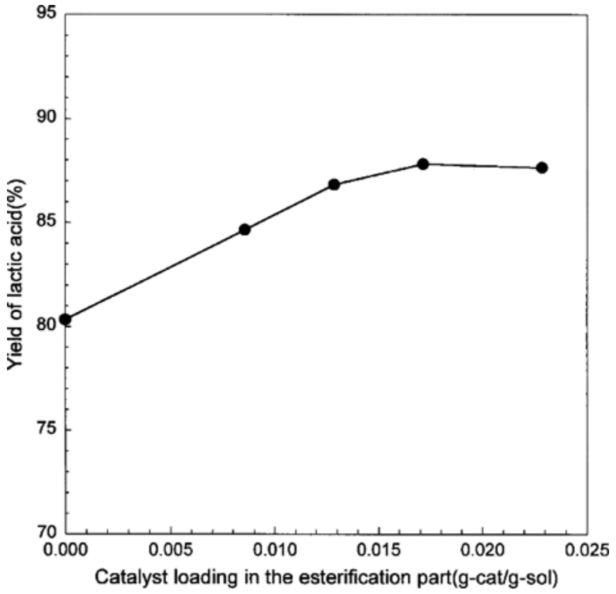

Fig. 6. The effect of catalyst loading in the esterification part on the yield.
20 wt% Lactic acid, LA : MeOH=1 : 2, hyd.resin=3 g

4. The Effect of Reactant Mole Ratio

To investigate the effect of reactant mole ratio on the yield of lactic acid, the mole ratio of LA : MeOH was increased from 1 : 2 to 1 : 4 (Fig. 8). As the reactant mole ratio decreased, the yield of lactic acid increased. This result is opposite to that of the batch reaction [Seo, 1999]. This is due to the characteristics of the system which includes two coupled reactions (esterification and hydrolysis) and is operated in a batch mode. The de-

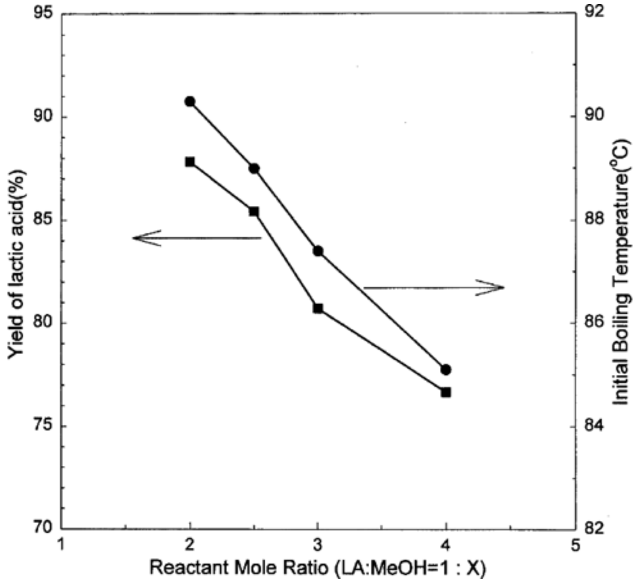

Fig. 8. The effect of reactant mole ratio on the yield.
20 wt% Lactic acid, est.resin=0.0171 g-cat/g-sol, hyd.resin=3 g

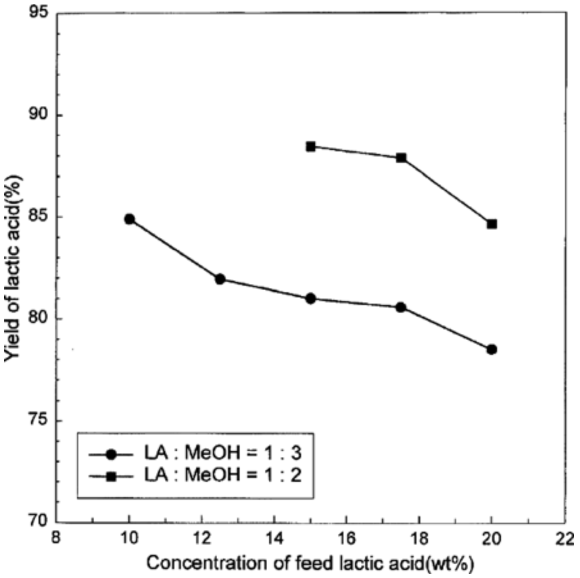

Fig. 9. The effect of feed lactic acid concentration on the yield.
est.resin=0.00857 g-cat/g-sol, hyd.resin=3 g

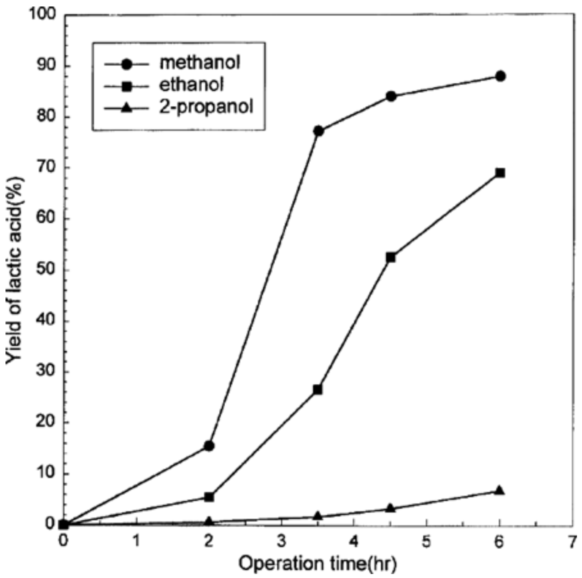

Fig. 10. The effect of alcohols as reactants on the yield.
20 wt% Lactic acid, LA : Alcohol=1 : 2, est.resin=0.0171 g-cat/g-sol, hyd.resin=3 g

crease in reactant mole ratio resulted in the decrease of the unreacted methanol, which increased the boiling temperature of reaction mixture. Higher boiling temperature enables more amount of methyl lactate produced in the reboiler of the estrification part to be transferred to the reboiler of the hydrolysis part by distillation. As can be seen from Fig. 8, the boiling temperature of reaction mixture was closely related to the yield of lactic acid in this system.

5. The Effect of Feed Lactic Acid Concentration

The purification and separation of lactic acid from fermentation broth using reactive distillation can be realized after pretreatment through electrodialysis and other filtration methods (nano-, ultra, micro-filtration etc.). The concentration of lactic acid varies according to the methods of pretreatment. Hence, the effect of feed lactic acid concentration on the yield was studied (Fig. 9). As the concentration of feed lactic acid decreased, the yield of lactic acid increased. This result was similar to that of the effect of reactant mole ratio. The amount of methanol in the reaction mixture decreases with the decrease in the concentration of lactic acid. This caused an increase in the boiling temperature of the reaction mixture which resulted in the higher yield of lactic acid.

6. The Effect of Alcohols

Methanol, ethanol and 2-propanol were used as reactants to investigate the effect of alcohols on the yield of lactic acid (Fig. 10). The properties of alcohols used as reactants are given in Table 3. Alcohols of which boiling point was lower than that of water were used in this experiment, because this process used partial condensers whose temperature was controlled by water from circulators.

Fig. 10 shows methanol as a reactant gave higher yield than other alcohols. Methanol has the lowest boiling point and molecular weight. In the experiment of constant mole ratio and fixed total amount of reaction mixture, when methanol was used as a reactant, the proportion of alcohol in the reaction mixture was smaller than when other alcohols were used. Therefore, the boiling temperature of reaction mixture including methanol becomes higher, even though the boiling point of methanol is lower than that of other alcohols. Moreover, because the boiling point of ester formed by methanol is lowest, a larger amount of ester can be distilled and removed to the reboiler of the hydrolysis part.

Table 3. The properties of alcohols

Alcohols	Molecular weight	Boiling point (°C)	Boiling point of formed ester (°C)	Initial boiling point of reaction mixture (°C)
Methanol	32.04	64.7	144	90.3
Ethanol	46.07	78.5	154	88.8
2-propanol	60.10	82.3	167	86.8

7. The Effect of Partial Condenser Temperature

The effect of partial condenser temperature on the yield is shown in Fig. 11. As the temperature of partial condenser increased, the condensation efficiency of methyl lactate and water from the top of the column was lowered and, therefore, the yield of lactic acid was lowered.

In the esterification part, as the partial condenser temperature increases, the amount of methyl lactate and water uncondensed by the partial condenser increases. Therefore, the uncondensed methyl lactate and water are recovered to the reboiler of the esterification part through the total condenser and, thus, are not removed to the reboiler of the hydrolysis part. This can be confirmed by Fig. 12. At 81 °C, the yield of lactic acid dropped abruptly because at such a high temperature, a larger amount of methyl lactate was recovered to the reboiler of the esterification part without being condensed by partial condenser.

In the hydrolysis part, the amount of methyl lactate and water which were recovered to the reboiler of the esterification

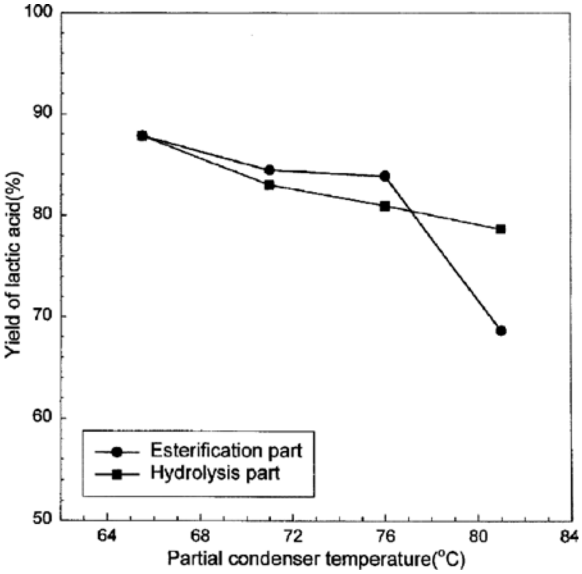

Fig. 11. The effect of partial condenser temperature on the yield.
20 wt% Lactic acid, LA : MeOH=1 : 2, est.resin=0.0171 g-cat/g-sol, hyd.resin=3 g

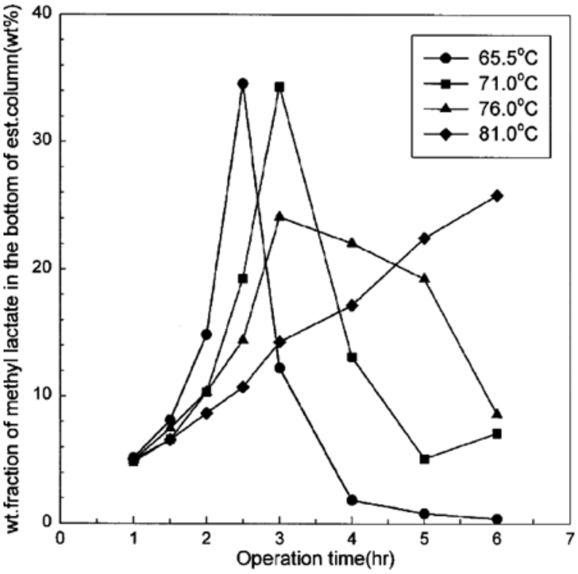

Fig. 12. The wt fraction changes of methyl lactate in the bottom of the esterification column according to partial condenser temperature of esterification column.
20 wt% Lactic acid, LA : MeOH=1 : 2, est.resin=0.0171 g-cat/g-sol, hyd.resin=3 g

part without being condensed by partial condenser also increased with an increase in the partial condenser temperature. However, the recovered methyl lactate and water were directly removed in the esterification column and transferred to the hydrolysis part. Therefore, even at a high temperature such as 81 °C, the yield of lactic acid was not much influenced.

CONCLUSION

In this study, a batch reactive distillation process of two columns considering both esterification and hydrolysis was developed and the feasibility of this process for the recovery of lactic acid was investigated. Cation exchange resin was used as a catalyst. The effect of catalyst loading, reactant mole ratio, feed lactic acid concentration, type of alcohols and partial condenser temperature on the yield was studied. The yield of lactic acid increased as catalyst loading in the esterification part increased and the reactant mole ratio and concentration of feed lactic acid decreased. Methanol as a reactant gave a higher yield. The yield of recovered lactic acid was as high as 90% in the optimum condition. The yield of lactic acid was closely related to the boiling temperature of reaction mixture in the esterification part.

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