

# Effect of Recycle and Feeding Method on Batch Reactive Recovery System of Lactic Acid

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**Abstract**—Reactive batch distillation coupling esterification and hydrolysis was studied for the recovery of lactic acid. The analysis of the dynamic behavior of the system showed drastic change of esterification reaction rate in the reboiler due to the difference of volatility and component boilup rate of each species. Methanol recycle and feeding method were investigated as the factors which could control the component boilup rate of each species and rate of esterification reaction. The flow rate and composition of methanol recycle stream was controlled by the temperature of the partial condenser. A temperature slightly higher than the methanol boiling point is optimum as the temperature of the partial condenser. When the temperature of the partial condenser was increased in the initial part of whole batch time and decreased in the latter part, the performance of the system was enhanced, compared with when the partial condenser temperature remained constant. Semibatch operation was compared with batch operation. Continuous feeding of methanol enhanced the recovery system performance while continuous feeding of lactic acid aqueous solution deteriorated, compared with batch operation.

Key words: Lactic Acid, Batch Reactive Distillation, Esterification, Hydrolysis

## INTRODUCTION

Lactic acid is of interest as the raw material of biodegradable polymer and green solvent as well as for use in the food, pharmaceutical and cosmetic industries. Recently, fermentation has been preferred to the conventional chemical synthetic process because of the production of a desired stereoisomer. However, it becomes a major challenge to reduce the cost of acid recovery and purification and to produce heat-stable lactic acid.

Purification of lactic acid obtained from fermentation is rather difficult due to such characteristics as strong affinity to water and low volatility. There have been several alternatives for the recovery of lactic acid from dilute aqueous solution such as precipitation [Datta, 1995], membrane process [Mani, 1991; Timmer et al., 1994; Husson, 1998], ion exchange process [Husson, 1998], adsorption [Husson, 1998], and extraction [Kertes and King, 1986; Hong and Hong, 1999; Han et al., 2000; Han and Hong, 1998]. In addition to these processes, high quality lactic acid can be obtained by the combined process of reaction and distillation composed of esterification of lactic acid, distillation of the lactate and hydrolysis of the distilled lactate [Vickloy, 1985; Cockrem and Johnson, 1993]. This process uses the selectivity of esterification to carboxylic acid against various salts and, thereby, can produce highly pure lactic acid. Lactic acid produced by this process is heat stable. However, this process contains multiple steps of several reactions and distillations. In addition, esterification of lactic acid is highly-equilibrium-controlled reaction with low reaction rate.

In order to enhance the economics and efficiency of this recovery process of lactic acid, the concept of reactive distillation, the hybrid process of reaction and distillation could be applied [Choi and Hong, 1999; Seo et al., 1999]. In reactive distillation, the conversion of the limiting reactant can be substantially increased by continuous removal of the products from the reacting mixture in terms of reaction [Guttinger and Morai, 1999]. In terms of separation, a nonreactive azeotrope and distillation boundary can often be overcome [Sundmacher et al., 1994].

In previous research, batch reactive distillation of lactic acid was investigated in terms of the feasibility of the system and the effect of operation parameters [Seo et al., 1999; Choi and Hong, 1999]. Esterification part and hydrolysis part were operated simultaneously with interconnecting streams, and cation exchange resin was used as acid catalyst. Operation was performed at batch mode to ensure sufficient residence time of lactic acid in reaction medium.

In this study, dynamic behavior of reactive batch distillation of lactic acid was analyzed in terms of the instantaneous reaction rate of esterification. To increase this rate, the boilup rate and residence time of each species were controlled during operation by the change of methanol recycle stream's condition and feeding mode.

## EXPERIMENTAL

### 1. Materials

L-Lactic acid [20% (w/w) Acros, USA] and methanol (Merck, Germany) were used without further purification. A strongly acidic cation exchange resin, DOWEX-50W in the H<sup>+</sup> (SIGMA, USA) was used as the solid catalyst. For pretreatment, new fresh resins were washed with deionized water. And then the dehydration of resins was performed in a vacuum oven at 348 K for 12 hr.

### 2. Experimental Procedure

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<sup>‡</sup>This paper is dedicated to Dr. Youn Yong Lee on the occasion of his retirement from Korea Institute of Science and Technology.

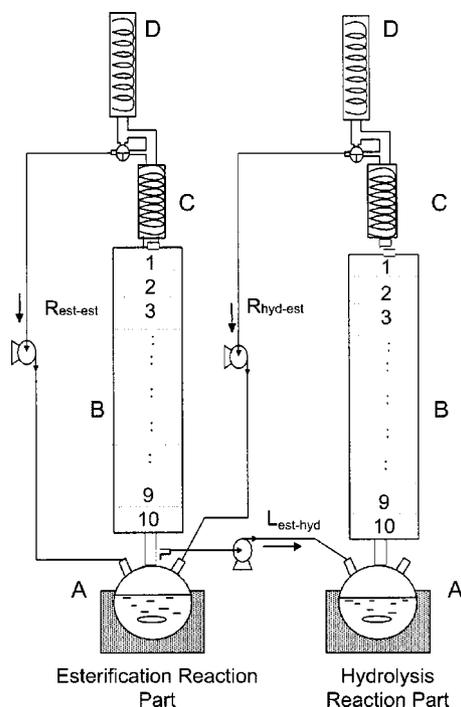


Fig. 1. Schematic diagram of reactive experimental apparatus for batch distillation.

A. Reboiler  
B. Oldershaw column  
C. Partial condenser  
D. Total condenser

A schematic diagram of the experimental apparatus is shown in Fig. 1. The experimental system consists of two parts: the esterification part and the hydrolysis part. The glass Oldershaw columns with vacuum jacket were used for each part.

Reactions in the reboilers are as follows:



The forward reaction of (1) occurs in the esterification part and the backward reaction occurs in the hydrolysis part.

The residuals in the reboilers of both parts consist of the four components in Eq. (1). However, boilups from the reboilers have only three components (methyl lactate, methanol and water) since lactic acid has little volatility and decomposes before vaporization. Methanol-rich vapor flow (distillate) and methyl lactate-rich liquid flow are formed from this boilup by fractionation in the column. Methanol-rich vapor flow is transported through partial and total condensers and recycled into the reboiler of the esterification part (through  $R_{\text{est-est}}$  and  $R_{\text{hyd-est}}$ ). Lactate-rich liquid flow in the column of esterification part is moved into the reboiler of hydrolysis part (through  $L_{\text{est-hyd}}$ ) and liquid flow in the column of hydrolysis part is refluxed into the reboiler. Methyl lactate in the reboiler of the hydrolysis part is converted into the final product, pure lactic acid solution. Water was used as the solvent of lactic acid in the initial feed and was produced from reaction.

The operation procedure was as follows. The starting point of operation was taken as the moment that the initial mixture started to boil up by preheating in the reboiler of esterification part. Time until the point that dewes appeared in total condenser from starting point was taken as startup period. The residual in the reboiler was

stirred well with a magnetic stirrer during the whole operation.

### 3. Analysis Methods

The concentration of lactic acid was titrated by 0.1 N NaOH solution using phenolphthalein as an indicator. Formation of dimer or oligomer of lactic acid by self-esterification could be ignored under this condition [Troup and Kobe, 1950]. Total ester content of a sample was measured by using saponification of ester. Excess base added into the sample and the remaining base was back-titrated with 0.1 M HCl [Kolah et al., 1996]. Water content in the reboiler was determined by Karl Fischer titration with coulometric K-F titrimeter model 447.

The performance of the system was represented as yield, loss, production efficiency and energy consumption. These terms were defined as follows.

- (1) Yield: amount of produced lactic acid [g]/amount of lactic acid in feed [g]
- (2) Loss: amount of residual lactic acid and lactate in the reboiler of esterification part after operation [mole]/amount of lactic acid in feed [mole]
- (3) Production efficiency [%/hr]: yield/operation time of esterification part
- (4) Energy consumption [kJ/g lactic acid]: heat applied into the reboilers [kJ]/amount of produced lactic acid [g]

## RESULTS AND DISCUSSION

### 1. Dynamic Characteristic of Operation

In Fig. 2, the behavior of the system with time is shown. The reaction rate was calculated from the experimental values of compositions and temperatures with Eq. (2)

$$\frac{dC_{ML}}{dt} = (k_0 + k_c C_C) \exp\left(-\frac{E}{RT}\right) (C_{LA} C_{MeOH} - C_{ML} C_{H_2O} / K) \quad (2)$$

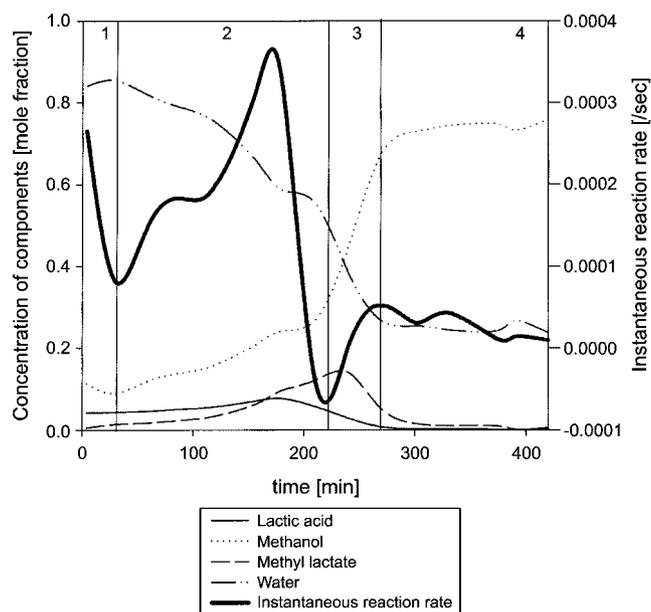


Fig. 2. Analysis of dynamic behavior of system in the reboiler of esterification part.

The equation of reaction rate and constant values were obtained from Seo and Hong [Seo and Hong, 2000].

Component boilup rate of each species was determined by the relative volatility of each species. The order of volatility is as follows: methanol (b.p at 1 atm, 64.7 °C) > water (100 °C) > methyl lactate (144 °C) > lactic acid (not volatile). The change of instantaneous reaction rate with time can be explained by the difference in component boilup rate of each species. According to that, whole batch time was divided into the subparts.

Part 1: Initially, the instantaneous rate of esterification decreased. This was due to the rapid boilup of methanol (the lightest boiler) and to the production of methyl lactate.

Part 2: Reaction rate increased in this part. It is caused by decreasing of water content in reaction mixture. Through a recycle stream, loss of methanol during the previous part was compensated to a certain extent.

Part 3: Reaction rate decreased abruptly, again mainly because of the accumulation of methyl lactate (the heaviest boiler).

Part 4: Reaction rate increased due to the removal of methyl lactate. However, this value did not increase much. Residual lactic acid is converted into lactate completely by excess amount of methanol through the recycle stream.

In this system, two cases of overheating in the reboiler of the esterification part occurred. In Case 1, reaction rate was too low, compared with boilup rate. A large amount of unconverted lactic acid accumulated in the reboiler, which resulted in the abrupt increase of temperature due to the nonvolatility of lactic acid. Because of high temperature, methanol required for the conversion of residual in reboiler could not have sufficient residence time. If heat was applied continuously into the reboiler, unconverted lactic acid was decomposed and resin was deactivated. In this case, loss of lactic acid in feed happened. In Case 2, mainly in the latter part of whole batch time, reaction rate increased quickly due to almost complete removal of water, and large amount of methyl lactate was produced during a short time interval. Temperature did not increase more than to the limiting temperature of resin. However, methyl lactate boiled up more rapidly than methanol recycled into the reboiler. And residual in the reboiler disappeared temporarily.

## 2. Effect of Methanol Recycle

Distillate from the esterification part was the lightest-boiler methanol (reactant)-rich flow while reflux flow is water-methyl lactate (product)-rich flow. Therefore, to operate the esterification part appropriately, distillate flow should be used for recycle of methanol and simultaneously product in reflux flow should be removed from the reboiler of the esterification part. These two flows could be controlled by a partial condenser. The temperature and capacity of the partial condenser could affect the composition and the flow rate of two streams.

According to Fig. 3, at a partial condenser temperature of slightly higher (67 °C) than the boiling point of methanol, better performance could be obtained than at other temperatures. At higher temperatures than this temperature, production efficiency decreased and energy consumption increased rapidly, while at lower temperatures of the partial condenser, a large amount of unconverted lactic acid remained in the reboiler of the esterification part after 5-hr operation.

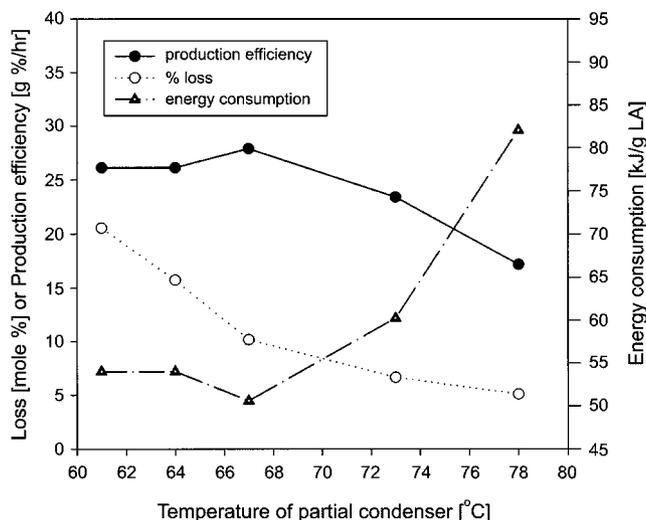


Fig. 3. Effect of temperature of partial condenser on the performance of system.

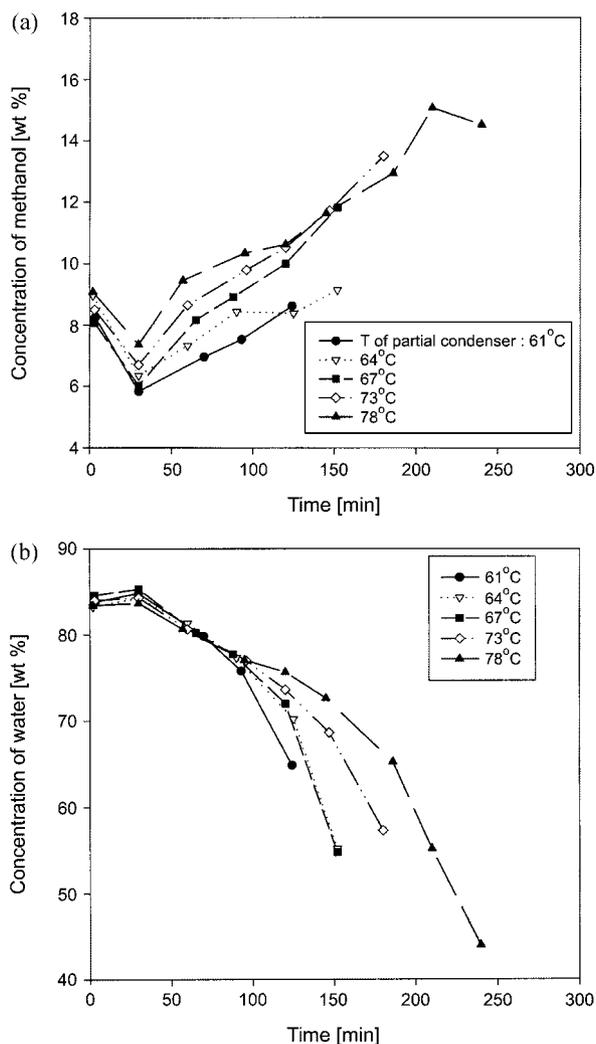


Fig. 4. Behavior of reaction mixture in the reboiler of esterification part with time.

- (a) Content of methanol in reboiler of esterification part  
(b) Content of water in reboiler of esterification part

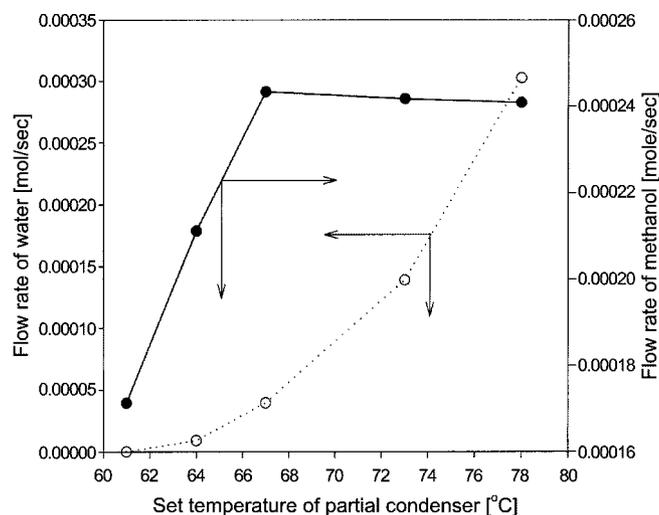


Fig. 5. Effect of temperature of partial condenser on the properties of recycle stream.

In Fig. 4, the changes of composition in the reboiler of the esterification part with time are given. Concentrations of methanol and water in the reboiler of esterification part increased with increasing temperatures of the partial condenser. Especially, the concentration of water in the reboiler for each temperature of the partial condenser was similar in the initial part of the whole batch time. However, that became different significantly during the latter part of the batch. According to this figure, at lower temperatures of the partial condenser than the methanol boiling point, loss of methanol could not be compensated sufficiently by methanol recycle stream. At higher temperature, the accumulation of water after part 2 delayed the removal of the product from the esterification part and more heat was consumed for the removal of water.

Operation results in Figs. 3 and 4 were explained by the characteristics of recycle streams shown in Fig. 5. When the temperatures of the partial condenser were above the boiling point of methanol, the water flow rate increased almost linearly while methanol flow rate did not change or decrease slightly after a certain extent of increase. This figure confirms the accumulation of water at higher temperatures of the partial condenser and loss of methanol at lower temperatures of the partial condenser.

In Table 1 and Fig. 6, operation results of each methanol recycle mode were presented. Similar operation results were obtained at temperature of the partial condenser, 67 °C (mode 1) and at 71 °C (mode 2) as in Table 1. However, as shown in Fig. 6, the dynamic behaviors at these two modes were different. At 71 °C, the time at which concentrations of lactic acid and methyl lactate become decreased (at part 2-part 3) was delayed. Fig. 6(c) represents the instantaneous reaction rate at each mode. In part 1, the instantaneous reaction rate at 71 °C was higher than at 67 °C. However, at 71 °C, part 2 and part 3 where the instantaneous reaction rate increased and decreased, respectively, started later than at 67 °C. According to this result, it can be said that, at the temperature of the partial condenser, 71 °C, the conversion of limited reactant, lactic acid is larger in the initial part (part 1) of whole batch time due to relative rapid recovery of methanol (the lightest boiler). However, more accumulation of water after that part at 71 °C delayed the proceeding of esterification and the boilup of methyl lactate.

Modes 1 and 2 were modified by changing the temperature of the partial condenser during the operation (mode 3 and mode 4). Operation results of mode 3 at which the temperature of the partial condenser changes from 67 °C to 71 °C were worse than those of mode 1 and mode 2 (modes at constant temperature of partial condenser). However, for the case of mode 4 at which the temperature of the partial condenser changes from 71 °C to 67 °C, the performance of the system was enhanced over that for the case of mode 1 and mode 2.

At mode 3, temperatures of partial condensers changed from 67 °C to 71 °C at part 3. At part 3, methyl lactate (the heaviest boiler) was produced and accumulated in the reboiler of the esterification part and the reaction rate decreased abruptly. Increase of partial condenser temperature in this period decreased removal rate of methyl lactate due to more rapid supply of light boilerwater and methanol through recycle stream. Accordingly, the instantaneous reaction rate after the change of partial condenser temperature decreased even into negative values as in Fig. 6.

Mode 4 showed different dynamic behavior. At this mode, the instantaneous reaction rate remained higher than at modes 1 and 2. During part 1, loss of lightest methanol and decrease of reaction rate was mitigated, compared with modes 1 and 3. Lowering the temperature of partial condenser from part 2 enhanced the removal rates of light boilers, especially water. At mode 4, methanol recycle

Table 1. Operation results of each methanol recycle modes using temperatures of partial condenser - 67 °C and 71 °C

No. of mode	Yield (%)	Corrected yield (%)	Production efficiency	Energy consumption	% loss
Mode 1	86.1	99.9	14.35	48.33	0.14
Mode 2	87.1	95.3	14.52	47.77	3.77
Mode 3	82.2	95.1	13.70	50.62	3.57
Mode 4	89.3	97.8	17.86	38.83	2.17

Mode 1: constant temperature of partial condenser 67 °C during whole batch time (6 hr)

Mode 2: constant temperature of partial condenser 71 °C during whole batch time

Mode 3: change of temperature of partial condenser from 67 °C to 71 °C at Part 3 (in Fig. 2)

Mode 4: change of temperature of partial condenser from 71 °C to 67 °C at Part 1

operating condition: feed mixture - 20 wt% lactic acid aqueous solution 306.27 g

moles of methanol : moles of lactic acid = 3 : 1

catalyst: DOWEX 50W(HCR-2) 4 g

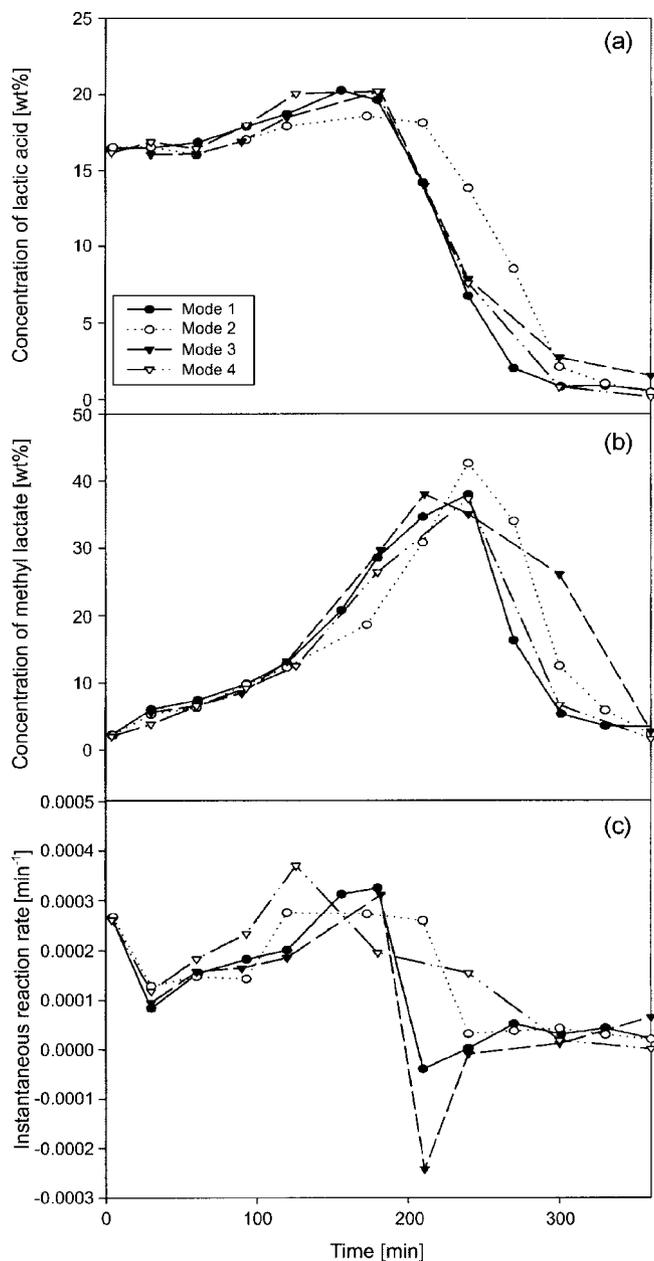


Fig. 6. Comparison of dynamic behaviors for each methanol recycle mode.

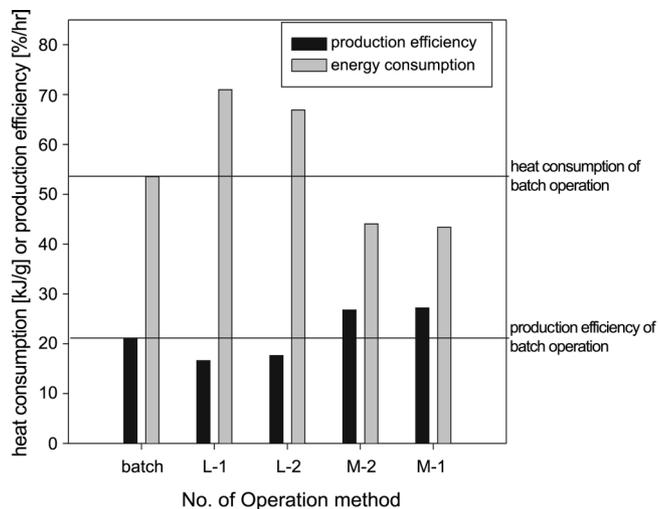


Fig. 7. Results of operations for each feeding mode.

cle stream was controlled according to the characteristic features of each subpart of whole batch time and this resulted in the enhancement of the operation results.

### 3. Effect of Feeding Method: Semibatch Operation Mode

The specifications of each semibatch policy are given in Table 2. Semibatch operation modes were divided into modes of continuous feeding of methanol (M mode) and continuous feeding of lactic acid (L mode). When only methanol was residual in the reboiler, it boiled up completely before lactic acid solution was supplied sufficiently. Therefore, at L mode, residual mixtures in the reboiler contained a small amount of lactic acid.

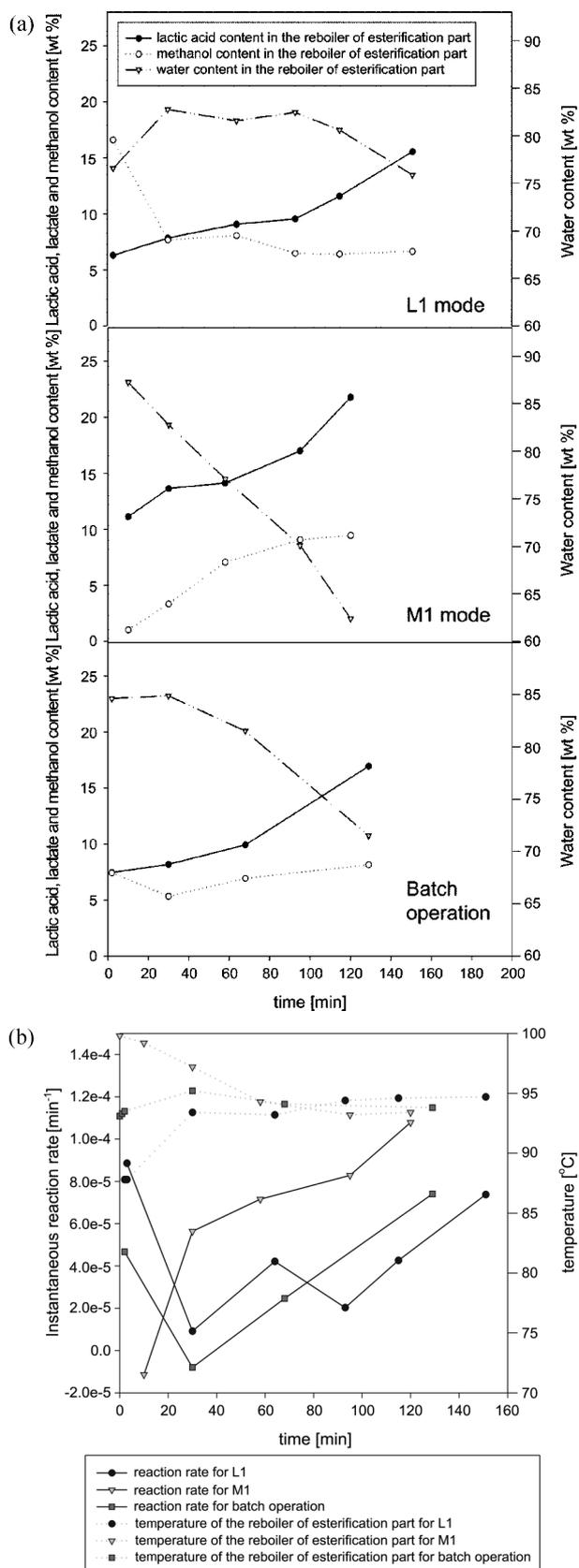
Fig. 7 shows the result of operation for each feeding mode. For M mode operation, higher production efficiency and lower energy consumption could be obtained than for batch operation. In the case of L mode, performance of system was deteriorated, compared with batch operation.

Fig. 8(a) compares dynamic behaviors of L mode, M mode and batch operation in terms of concentration. At L1 mode, methanol content decreased rapidly at initial time of operation while water content did not decrease during operation. However, for M2 mode, methanol content increased and water content decreased more rapidly than for batch operation. For this mode, concentration of lactic acid remained at high level than for other operation policies.

Table 2. Specifications of semibatch operation modes

Mode no.	Residual feed in the reboiler of esterification part	Semi-feeding feed	Feeding rate
L mode: Feeding-of-lactic acid mode			
L1	all ME+1/3 LA solution (ME: methanol, LA: lactic acid)	2/3 LA solution	3 g/min
L2	all ME+1/3 LA solution	2/3 LA solution	1.5 g/min
M mode: Feeding-of-methanol mode			
M1	2/3 LA solution	all ME+1/3 LA solution	2.25 g/min
M2	2/3 LA solution	all ME+1/3 LA solution	1.5 g/min

\*Operation condition: feed mixture - 8 wt% lactic acid aqueous solution 450 g  
 moles of methanol : moles of lactic acid=3 : 1  
 catalyst: DOWEX 50W(HCR-2) 4 g  
 partial condenser temperature=67 °C



**Fig. 8. Time evolution in the reboiler of esterification part for each feeding mode.**

(a) Concentrations of components. (b) Reaction rate and temperature in reaction mixture of esterification part

In Fig. 8(b), instantaneous reaction and temperature are given. Slower loss of methanol and simultaneous more rapid removal of water for M1 mode resulted in steady and rapid increase of instantaneous reaction rate. For the case of L1 mode, reaction rate decreased rapidly during the initial time of operation as the case of batch operation and then increased more slowly than for batch operation. Temperature in the reboiler of esterification part could represent the thermodynamic conditions of residual in reboiler, which affects the component boilup rate of each species.

There were significant differences between feeding-of-methanol (excess reactant, lightest boiler) mode (M mode) and feeding-of-lactic acid (limited reactant, heaviest or not boiler) mode (L mode). At M mode, continuous feeding of methanol could compensate for the loss of methanol from the reboiler more rapidly than only recycle stream from the partial condenser. And, simultaneously, the removal of products of esterification reaction (water and methyl lactate) was faster since the residual in the reboiler of the esterification part did not contain excess methanol. At L mode, water was supplied continuously into the reboiler of the esterification part as solvent of lactic acid. This prevented the esterification of lactic acid. The boiling point of the residual mixture was too low to remove methyl lactate and water from the reboiler of the esterification part due to excess methanol. In addition, this policy decreased the residence time of limited reactant, lactic acid.

## CONCLUSION

In reactive batch distillation of lactic acid, the reaction is coupled with distillation. Therefore, residence time or boilup rate by distillation affects the reaction rate of esterification directly. Residence time of methanol should be sufficient to react with the limiting reactant, lactic acid, completely. Simultaneously, water and methyl lactate should be removed as fast as possible to enhance esterification reaction.

The flow rate and composition of methanol recycle stream could be controlled by the temperature of the partial condenser and affect the residence time of the light boilers (water and methanol). A temperature slightly above the boiling point of methanol was optimum according to operation results. The control of methanol recycle stream during operation, according to the characteristics of subparts, enhanced the performance of the recovery system. Methanol recycle should be controlled in the direction of mitigating the rapid loss of methanol sufficiently in initial part and enhancing the removal of product in the latter part. According to that, it is suitable that the temperature of the partial condenser increases at the initial part and then decreases at the latter part near the boiling point of methanol.

In semibatch operation mode, the residence time of each component in the reboiler could also be varied by feeding method. Continuous feeding of methanol (lightest reactant) compensated for the loss of methanol from the reactor and enhanced the removal of products of the esterification reaction.

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