
Design and optimization of lactic acid purification process by reactive distillation with isoamyl alcohol

Abstract

A reactive distillation process to purify lactic acid by esterification with isoamyl alcohol and hydrolysis was designed and simulated by Aspen. Five columns were included in the process: esterification column, purification column, hydrolysis column, dehydration column and recovery column. Effects of process parameters (operating pressure, feed composition, feed position, number of reaction and separation stages, and reboiler duty) of the esterification column on the yield and purity of lactic ester was evaluated. Further evaluation was carried out to reveal the effects of process parameters of the hydrolysis column on the yield and purity of lactic acid. The total annual cost of the whole process was calculated. Simulation studies are carried out using Aspen Plus RADFRAC module. It was shown that under the optimized condition, the concentration of lactic acid can reach up to 82.4 wt%, and the organic acid impurities were less than 3 ppm. Compared with the traditional usage of methanol and butanol, the isoamyl alcohol process can save about 20% of the total annual cost at the same output of lactic acid.

Keywords: lactic acid; esterification; hydrolysis; reactive distillation; purification

1. Introduction

Lactic acid (2-hydroxypropionic acid, CAS 50-21-5) is a naturally occurring low-molecular-weight organic acid [1]. It is generally recognized as one of the simplest and most versatile hydroxyl carboxylic acids, with a broad range of applications in the food, cosmetic, textile, chemical, polymer and pharmaceutical industries [2]. Currently, the demand for lactic acid has grown dramatically due to its use as a monomer in the production of poly-lactic acid (PLA) and its potential as a feedstock to produce green solvents [3]. The worldwide demand for lactic acid was approximately 714.2 kilo tons in 2013, and it is estimated to increase annually by 15.5% [4].

Lactic acid can be produced by microbial fermentation or chemical synthesis, and the former is more prevailing. Currently, about 90% of the global lactic acid is produced by

Comment [L1]: The purpose of the study should be determined in abstract

Comment [L2]: You should write your recommend end of this study

fermentation [5]. Purification of lactic acid from fermentation broth is considered to be challenging because lactic acid has an affinity for water, a high normal boiling point and self-polymerization tendency [6]. There are various ways to purify lactic acid, including precipitation [7], adsorption [8], electro dialysis [9], ultrafiltration [10], extraction [11], and reactive distillation [12]. However, most of them suffer from the drawbacks, such as environmental pollution, high energy consumption and equipment corrosion, which limits their industrial applications. Reactive distillation is found to be the most promising method for the purification of lactic acid with a relatively high yield and purity [13].

Reactive distillation is a hybrid process that integrates reaction and separation. This technique can break the reaction equilibrium by removing products, and thereby high selectivity and conversion can be obtained. The purification process of lactic acid can be realized by a two-step reaction (esterification and hydrolysis). In the first step, the lactic acid contained in the fermentation broth reacts with alcohol of low molecular weight to form lactate, and then the obtained lactate is purified by distillation. In the second step, the high purity lactate is hydrolyzed to recover lactic acid. This technology was first discussed in a U.S. patent [14]. Research on reactive distillation has developed quickly in recent years. Liu et al. [15] and Gudena et al. [16] proposed a reactive distillation process for the hydrolysis of methyl lactate. Kumar et al. [17] discussed a continuous reactive distillation process for the recovery of lactic acid with n-butanol. Su et al. [14, 18] compared the different design and control schemes of the purification of lactic acid by reactive distillation with C1 ~ C4 alcohols. They found that the methanol and butanol were more attractive. C5 alcohols are also proposed for the esterification of lactic acid because the alcohol and the formed ester can form a low boiling heterogeneous azeotrope with water [16, 19]. Removal of water (aqueous layer) from the azeotropic composition and recycling back the alcohol through the organic layer to the reaction mixture leads to an enhancement in the conversion of esterification. In our previous work, two efficient catalysts were designed and the reaction kinetics of esterification and hydrolysis of isoamyl Lactate was also studied, which is necessary for accurate design of reactive distillation (RD) process.

The purpose of this work is to design a reactive distillation process for the purification of lactic acid using isoamyl alcohol. Vapor-liquid-liquid equilibria were simulated by Aspen Plus. Furthermore, steady state design was carried out with the aid of Aspen Plus RADFRAC. Effects of process parameters such as operating pressure, feed ratio, feed position, number of reaction and separation stages, and reboiler duty were evaluated based on the yield and purity of target products. At last, the capital and operating costs were estimated and compared with the traditional process.

2 Reaction kinetics and thermodynamic models

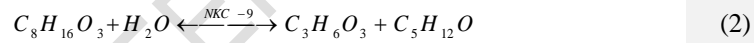
2.1 Reaction kinetics

The purification process of lactic acid involves two reversible reactions (esterification and hydrolysis), and the reactions can be described by equation (1) and equation (2).

Esterification:



Hydrolysis:



Jiang et al. [19] reported the kinetics of the esterification of isoamyl alcohol with lactic acid catalyzed by $NaHSO_4 \cdot Silica$. Xu [20] disclosed the hydrolysis kinetics of isoamyl lactate catalyzed by ion-exchange resin NKC-9. The kinetic parameters obtained by Jiang et al. [19] and Xu [20] were shown in Table 1. The kinetic models were catalyst-weight-based, and the catalysts weight was indispensable. It can be supposed that catalysts occupied 50% of the tray holdup volume [14], and the densities of $NaHSO_4 \cdot Silica$ and NKC-9 were 1000 kg m^{-3} and 830 kg m^{-3} , respectively.

Table 1. Parameters of the kinetic models

reaction	k_c^0 ($\text{kmol kg}^{-1} \text{ min}^{-1}$)	$E_{A,e}$ (kJ mol^{-1})
esterification	1.66×10^5	54.1
hydrolysis	5.35×10^4	59.22

2.2 Thermodynamic models

To account for nonideal vapor-liquid equilibrium (VLE) and vapor-liquid-liquid equilibrium (VLLE) for the system, a suitable thermodynamic model is necessary for

the process simulation. It can be confirmed that NRTL-HOC model has a more accurate prediction for similar systems (lactic acid, alcohol, water and ester) [21]. Therefore, NRTL-HOC model would be used for the next studies. Table 2 showed the binary interaction parameters and the way to obtain them for the isoamyl lactate system (lactic acid (Lact), isoamyl alcohol (iAmOH), water and isoamyl lactate (iAmLc)). Fig. 1 provides the ternary phase diagrams of Lact / iAmOH / water / iAmLc mixture simulated by Aspen plus. From Fig. 1, a two-liquid-phase region was obtained by Aspen simulation, indicating that pure water can be easily collected by liquid phase separation, and the decanter can be considered in the top of reactive distillation column. The normal boiling point (N.B.P.) of pure components and azeotropes was given in Table 3. The azeotropic point of isoamyl alcohol and water obtained by aspen simulation was 368.5 K, which was close to the literature value 368.2 K. Hence, we believe that the simulation results were credible.

Table 2. Binary Interaction Parameters and Source

Comp. <i>i</i>	Water	Lact	Lact	Lact	Water	iAmOH
Comp. <i>j</i>	iAmOH	Water	iAmOH	iAmLc	iAmLc	iAmLc
source	Aspen built-in	UNIFAC	UNIFAC	UNIFAC	UNIFAC	VLE-HOC
a_{ij}	0	0	0	0	0	0
a_{ji}	0	0	0	0	0	0
b_{ij}	1846.1022	-363.3481	277.2152	206.3739	2130.48	761.13 [22]
b_{ji}	-8.4445	823.7980	25.3204	585.2386	83.2168	993.42 [22]
c_{ij}	0.3	0.3	0.3	0.3	0.3	0.3

Table 3. The normal boiling point of pure components and azeotropes

component	Azeotropic Composition (mole %)	N.B.P. (K)
W		373
L		490
IA		404
IL		475
W : IL	98.49:1.51	372.8

W : IA	84.36:15.64	368.5
L : IL	29.51:70.49	469.3

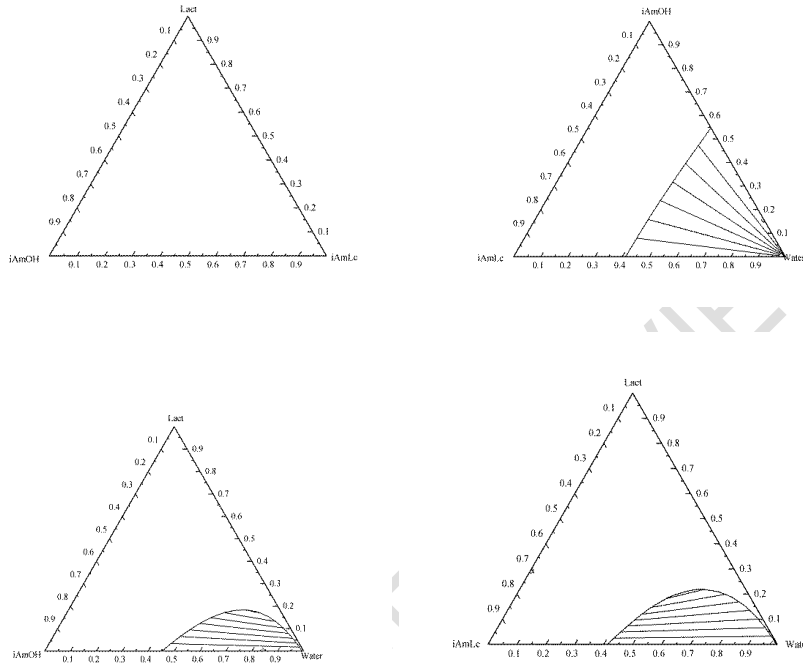


Fig. 1. Ternary diagrams for Lact/iAmOH/water/iAmLc mixture system

3 Process design and simulation

The reactive distillation process for purification of lactic acid should be designed taking into consideration the presence of other organic acids. Succinic acid is selected as a representative heavy impurity existing in fermentation broth. Because the organic acid impurities are present in relatively small amount, their esterification are not considered and their affects on vapor-liquid equilibrium are also ignored in this work, which will make the continuous reactive distillation system much simpler.

As illustrated in Fig. 2, the process included five columns: esterification column (RD-E), purification column (PUR), hydrolysis column (RD-H), dehydration column (DW) and recovery column (REC). The lactic acid solution containing a certain amount of succinic acid were fed to the top of reactive zone of the esterification column, and reacted with pure isoamyl alcohol which was introduced at the bottom of the reactive

zone. The top stream of the column was condensed into two-phase mixture in a decanter. Water was removed continuously and the organic phase was recycled back to the column. Isoamyl lactate along with the nonvolatile organic acid and the possibly formed heavy oligomers were taken out from the bottom and were sequentially separated in the second column. In the following step, the purified isoamyl lactate was placed on the top of reactive zone of the hydrolysis column to react with the water which was introduced on the lowest reactive stages. The top stream of the hydrolysis column was the mixture of water, isoamyl alcohol and unhydrolyzed lactate. With a decanter, the top mixture was divided into aqueous layer and organic layer, pure water was refluxed and the organic layer was taken out to the following recovery system. The high purity lactic acid, as the final product, could be obtained at the bottom of the hydrolysis column. Finally, the top organic layer entered a dehydration column and a subsequent recovery column. The recovered isoamyl alcohol was delivered to the esterification column and high purity isoamyl lactate could be collected as a by-product at the bottom.

The esterification and hydrolysis are the key section of this five-column purification process, and the characteristics and the design variables should be identified and investigated. Preliminary simulations have been performed for the proposed flow sheet of the esterification and hydrolysis column.

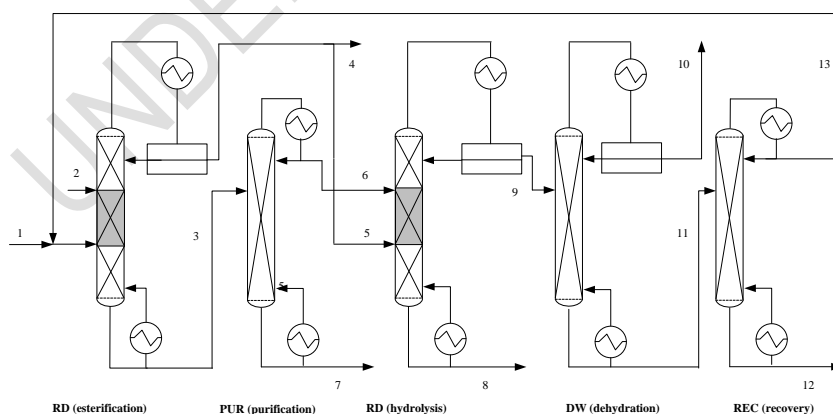


Fig. 2. Reactive distillation process for purification of lactic acid

3.1 Preliminary simulation

The esterification and hydrolysis column reflux were determined by the natural flow of organic and water phase from the top decanter, respectively. Therefore, the design variables were the operation pressure (P), the number of reactive (N_{rxn}) and separation (rectifying N_R and stripping N_S) stages, feed position (NF), feed molar ratio (FR) and the reboiler duty (Q_R). The effects of the variables on the yield and the purity of target products were investigated by simulation.

3.1.1 Operation pressure

The temperature profile is correlated with the operation pressure of the column. Temperature on reactive trays must be lower than 393 K to avoid catalyst degradation and lactic acid oligomerization [14]. Therefore, the effect of operating pressure on temperature profile of the esterification column was discussed under the condition that the other design variables such as the number of reactive stages ($N_{rxn}=15$), the number of rectifying stages ($N_R=7$), the number of stripping stages ($N_S=8$), the feeding position of lactic acid ($NF_{Lact}=N_R+1$), the feed position of isoamyl alcohol ($NF_{iAmOH}=N_R+N_{rxn}$), the feed molar ratio of isoamyl alcohol to lactic acid ($FR_{iAmOH/Lact}=1.0$), and the reboiler duty ($Q_R=1700$ KW) were kept constant. Fig. 3 showed that the temperature of the last two reactive trays was higher than 393 K at the operation pressure of 1 bar. This means that lower pressure was needed in the esterification column. According Fig. 3, the temperature of all reactive trays can be kept below 373 K when the pressure was fixed at 0.3 bar.

The temperature profile of the hydrolysis column at the operation pressure of 1 bar was simulated when the other design variables such as N_{rxn} ($N_{rxn}=40$), N_R ($N_R=5$), N_S ($N_S=5$), $FR_{Water/iAmLc}$ ($FR_{Water/iAmLc}=3.0$), NF_{iAmLc} ($NF_{iAmLc}=N_R+1$), NF_{Water} ($NF_{Water}=N_R+N_{rxn}$), and Q_R ($Q_R=1500$ KW) remained constant. The result was shown in Fig. 4 and the maximum temperature of hydrolysis column was 388 K. Therefore, the operating pressure of the hydrolysis column was 1 bar.

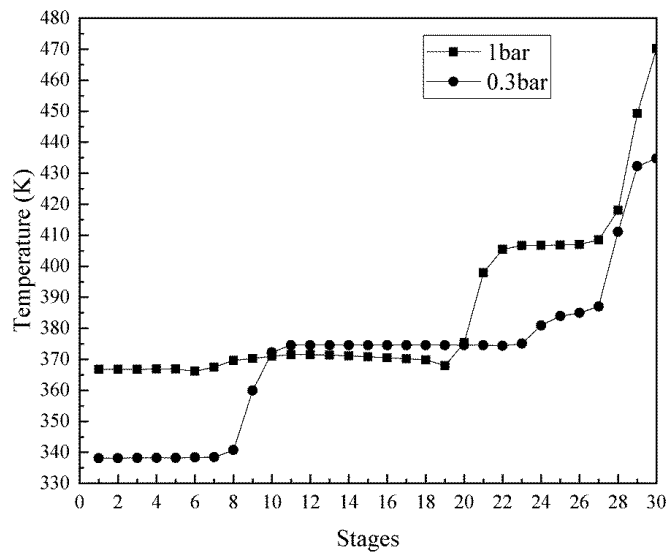


Fig. 3. Temperature profile of the esterification column at 0.3 bar and 1.0 bar
 ($N_R=7$, $N_{rxn}=15$, $N_S=8$, $Q_R=1700$ KW, $FR_{iAmOH/Lact}=1:1$)

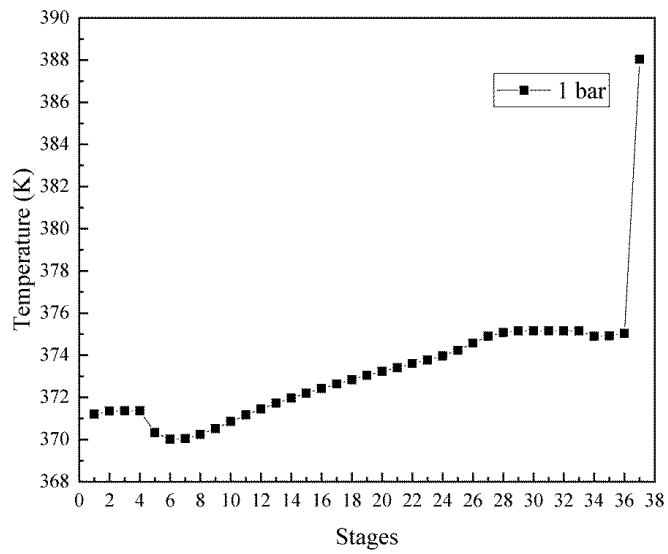


Fig. 4. Temperature profile of the hydrolysis column at 1.0 bar
 ($N_R=5$, $N_{rxn}=40$, $N_S=5$, $Q_R=1500$ KW, $FR_{Water/iAmLc}=3:1$)

3.1.2 Number of stages

The yield and purity of target product was improved with the increase in the number of reactive stages. However, the increase in reactive stages will lead to the increase in capital and operating costs. Consequently, it is very important to optimize the number of reactive stages. The effects of the number of reactive stages on the yield and purity of isoamyl lactate of esterification column were discussed when operating pressure was 0.3 bar ($P=0.3$ bar), $N_R=7$, $N_S=8$, $NF_{Lact}=N_R+1$, $NF_{iAmOH}=N_R+N_{rxn}$, $FR_{iAmOH/Lact}=1.0$, and $Q_R=1700$ KW. The results were shown in Fig. 5. From Fig. 5, the yield and purity of isoamyl lactate could reach up to 99.90 % when the number of reactive stages was five. However, there were no significant changes in the yield and purity of isoamyl lactate with a further increase in the number of reactive stages.

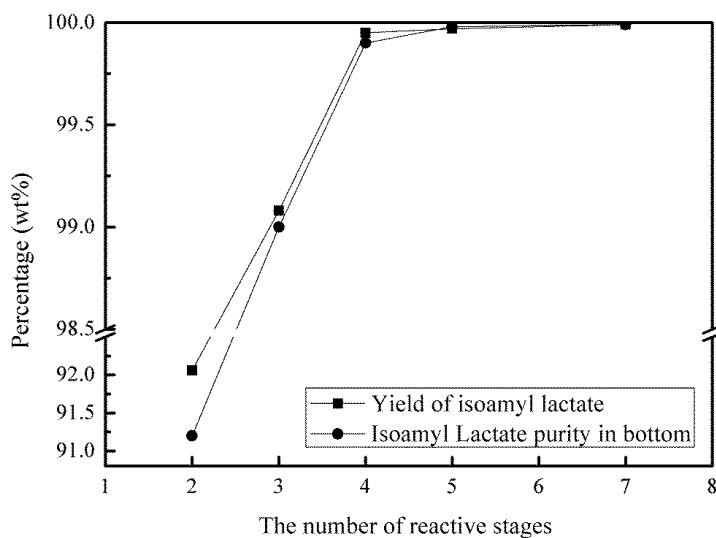


Fig. 5. Effect of reactive stages on the yield and the purity of bottom isoamyl lactate in esterification column

($P=0.3$ bar, $N_R=7$, $N_S=8$, $Q_R=1700$ KW, $FR_{iAmOH/Lact}=1:1$)

The effects of the number of reactive stages on the yield and purity of lactic acid of hydrolysis column were also discussed when $P=1.0$ bar, $N_R=5$, $N_S=5$, $NF_{iAmLc}=N_R+1$, $NF_{Water}=N_R+N_{rxn}$, $FR_{Water/iAmLc}=3.0$, and $Q_R=1500$ KW. The results were shown in Fig. 6. It showed that the yield of lactic acid increased from 17.48 % to 78.49 % and the

purity of lactic acid increased from 11.2 wt% to 74.5 wt% as the number of reactive stages increased from 3 to 24. There were no significant changes in the yield and purity of lactic acid when the reactive stages was more than 24. However, Fig 7 showed that the impurity content decreased from 1.05 wt% to 0.01 wt% as the number of reactive stages increased from 24 to 32. Therefore, the number of reactive stages of hydrolysis column was determined to be 32.

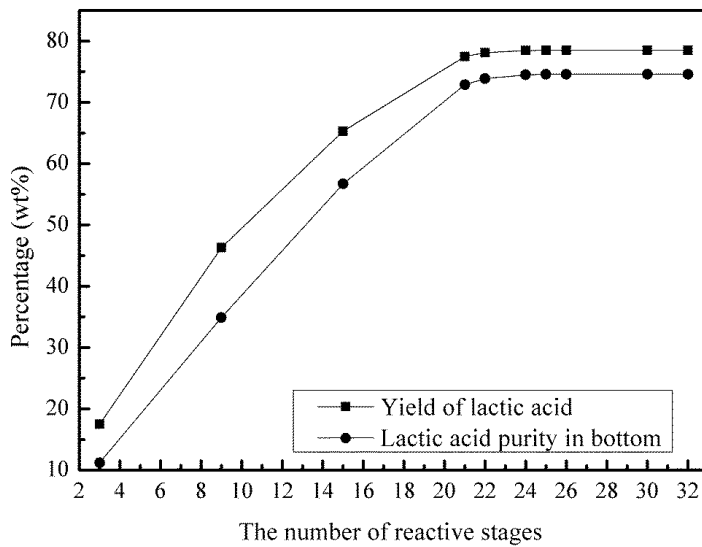


Fig. 6. Effect of reactive stages on the yield and purity of bottom lactic acid in hydrolysis column
($P=1.0$ bar, $N_R=5$, $N_S=5$, $Q_R=1500$ KW, $FR_{Water/iAmLc}=3:1$)

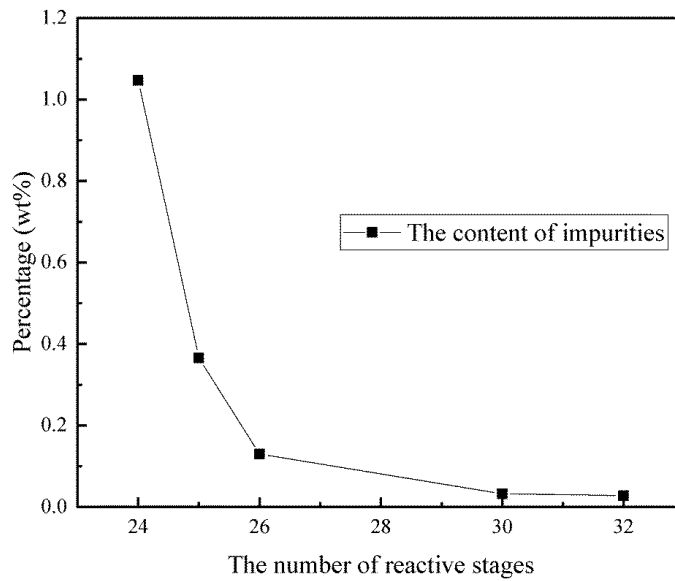


Fig. 7. Effect of reactive stages on the content of bottom impurities in hydrolysis column

($P=1.0$ bar, $N_R=5$, $N_S=5$, $Q_R=1500$ KW, $FR_{Water/iAmLc}=3:1$)

The effects of the number of rectifying stages and stripping stages on the purity of top water and bottom isoamyl lactate of esterification column were discussed when $P=0.3$ bar, $N_{rxn}=15$, $N_R+N_S=15$, $NF_{Lact}=N_R+1$, $NF_{iAmOH}=N_R+N_{rxn}$, $FR_{iAmOH/Lact}=1.0$, and $Q_R=1700$ KW. The results were listed in Table 4. Table 4 showed that the increase of the number of rectifying stages and stripping stages of esterification column had no obvious influence on separation. It is because of the large differences in boiling points of the related components.

The effects of the number of rectifying stages and stripping stages on the purity of top isoamyl alcohol and bottom lactic acid of hydrolysis column were discussed when $P=1$ bar, $N_{rxn}=21$, $N_R+N_S=19$, $NF_{iAmLc}=N_R+1$, $NF_{Water}=N_R+N_{rxn}$, $FR_{Water/iAmLc}=3.0$, and $Q_R=1500$ KW. The results were shown in Table 5. It showed that the increase of the number of rectifying stages and stripping stages of hydrolysis column had no obvious influence on separation.

Table 4. Effect of rectifying stages and stripping stages on the purity of top water and bottom isoamyl lactate in esterification column

(P=0.3 bar, $N_{rxn}=15$, $N_R+N_S=15$, $Q_R=1700$ KW, $FR_{iAmOH/Lact}=1:1$)

N_R	N_S	$x_{D, Water}$ (wt%)	$x_{B, iAmLc}$ (wt%)
2	13	57.90	98.30
4	11	57.90	98.20
6	9	57.80	98.10
7	8	57.80	98.10
8	7	57.80	98.10
10	5	57.80	98.10
12	3	57.80	98.10

Table 5. Effect of rectifying stages and stripping stages on the purity of top isoamyl alcohol and bottom lactic acid in hydrolysis column

(P=1 bar, $N_{rxn}=21$, $N_R+N_S=19$, $Q_R=1500$ KW, $FR_{Water/iAmLc}=3:1$)

N_R	N_S	$x_{D, iAmOH}$ (wt%)	$x_{B, Lact}$ (wt%)
2	17	24.40	57.90
4	15	24.40	57.90
6	13	24.40	57.90
8	11	24.40	57.90
12	7	24.40	57.90
14	5	24.40	57.90
16	3	24.40	57.90

3.1.4 Molar feed ratio

The effects of initial molar ratio of isoamyl alcohol to lactic acid ($FR_{iAmOH/Lact}$) on the yield and purity of isoamyl lactate of esterification column were discussed when P=0.3 bar, $N_{Lact}=N_R+1$, $N_{iAmOH}=N_R+N_{rxn}$, $N_R=2$, $N_{rxn}=7$, $N_S=3$, and $Q_R=1700$ KW. The results were shown in Fig. 8. It was found that the yield of isoamyl lactate kept substantially high (99.90 %) when $FR_{iAmOH/Lact}$ varied from 1.01 to 1.03. However, the the purity of bottom isoamyl lactate dropped off obviously with a slight increase in

$FR_{iAmOH/Lac}$. Therefore, the molar ratio of isoamyl alcohol to lactic acid was determined to be 1.01.

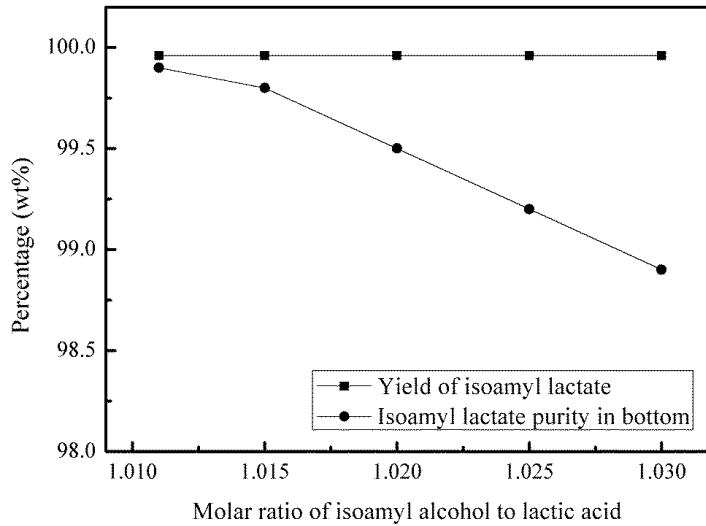


Fig. 8. Effect of $FR_{iAmOH/Lact}$ on the yield and purity of bottom isoamyl lactate in esterification column

($P=0.3$ bar, $N_{rxn}=7$, $N_R=2$, $N_S=3$, $Q_R=1700$ KW)

The effects of initial molar ratio of water to isoamyl lactate ($FR_{Water/iAmLc}$) on the yield and purity of bottom lactic acid of hydrolysis column were discussed when $P=1.0$ bar, $N_R=2$, $N_{rxn}=21$, $N_S=3$, $NF_{iAmLc}=N_R+1$, $NF_{Water}=N_R+N_{rxn}$, and $Q_R=1700$ KW. The results were shown in Fig. 9. $FR_{Water/iAmLc}$ has little effect on the the yield of lactic acid and the highest yield of lactic acid was obtained when $FR_{Water/iAmLc}$ was 2.5. However, the purity of bottom lactic acid decreased obviously with an increase in $FR_{Water/iAmLc}$. Therefore, the molar ratio of water to isoamyl lactate was desired to be 2.5.

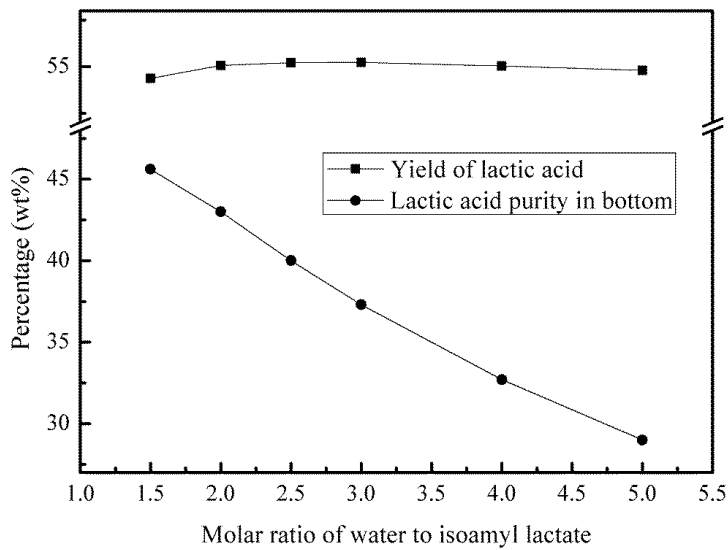


Fig. 9. Effect of $FR_{\text{Water/iAmLc}}$ on the yield and purity of bottom lactic acid in hydrolysis column

($P=1$ bar, $N_{\text{rxn}}=21$, $N_{\text{R}}=2$, $N_{\text{S}}=3$, $Q_{\text{R}}=1700$ KW)

3.1.4 Feeding position

Feeding position plays an important role in the purification of lactic acid. The feed position affected the distribution of the concentration of reactants which affected the heat and mass transfer process. From the previous discussion, it was found that the yield of isoamyl lactate in the esterification column could reach up to 99.90 % when lactic acid was fed at the top of reaction zone and isoamyl alcohol was introduced into the bottom of reaction zone. Therefore, the following research was only focused on the hydrolysis process. Table 6 illustrated the influence of feed position on hydrolysis process when $P=1$ bar, $N_{\text{R}}=2$, $N_{\text{S}}=3$, $N_{\text{rxn}}=32$, $Q_{\text{R}}=1700$ KW, and $FR_{\text{Water/iAmLc}}=2.5$. Considering the purity of bottom lactic acid of the hydrolysis column, the optimum way was to introduce water at the bottom of reaction zone and place isoamyl lactate on the top of reaction zone.

Table 6. Effect of feed position on the yield and purity of bottom lactic acid in hydrolysis column

(P=1 bar, $N_R=2$, $N_S=3$, $N_{rxn}=32$, $Q_R=1700$ KW, $FR_{Water/iAmLc}=2.5:1$)

	$N_{F_{iAmLc}}$	$N_{F_{Water}}$	yield of Lact (wt%)	$x_{B, Lact}$ (wt%)	$x_{B, iAmLc}$ (wt%)
A	3	34	78.58	82.40	trace
B	4	34	78.86	82.60	trace
C	5	34	79.17	82.70	0.002
D	6	34	79.50	82.80	0.012
E	7	34	79.81	82.90	0.083
F	9	34	80.10	83.00	0.115
G	3	3	71.90	71.10	0.009
H	4	3	72.00	69.30	0.032
I	5	3	70.72	66.60	0.060
J	7	3	67.06	60.40	0.121
K	8	3	62.70	53.90	0.184

3.1.5 Reboiler duty

The reflux ratio cannot be adjusted due to the use of decanter, therefore, the reboiler duty was specified as the dominant operating variable. The effects of reboiler duty on the yield and purity of bottom isoamyl lactate of esterification column were discussed when $P=0.3$ bar, $N_R=2$, $N_{rxn}=7$, $N_S=3$, $N_{F_{Lact}}=3$, $N_{F_{iAmOH}}=9$, and $FR_{iAmOH/Lact}=1.01$. The results were shown in Fig.10. The yield and purity of isoamyl lactate increased obviously with the increase of reboiler duty and reached close to 100% when the reboiler duty was 1500 KW.

The effects of reboiler duty on the yield and purity of bottom lactic acid of hydrolysis column were also discussed when $P=1.0$ bar, $N_R=2$, $N_{rxn}=32$, $N_S=3$, $N_{F_{iAmLc}}=3$, $N_{F_{Water}}=34$, and $FR_{Water/iAmLc}=2.5$. The results were shown in Fig. 11. It showed that the yield and purity of lactic acid increased gradually with the increase of reboiler duty in the range of 1200 KW to 1700 KW. However, an excessive reboiler duty would lead to the decrease of the yield and purity.

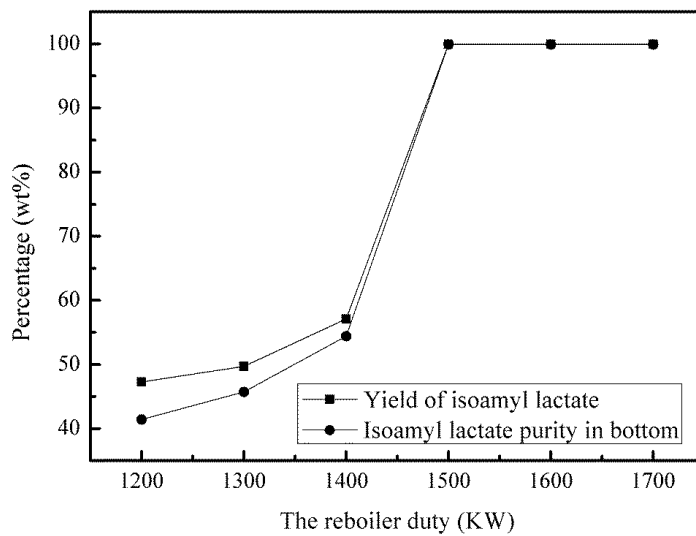


Fig. 10. Effect of the reboiler duty on the yield and purity of bottom isoamyl lactate in esterification column

($P=0.3$ bar, $N_{rxn}=5$, $N_R=2$, $N_S=3$, $FR_{iAmOH/Lact}=1.01:1$)

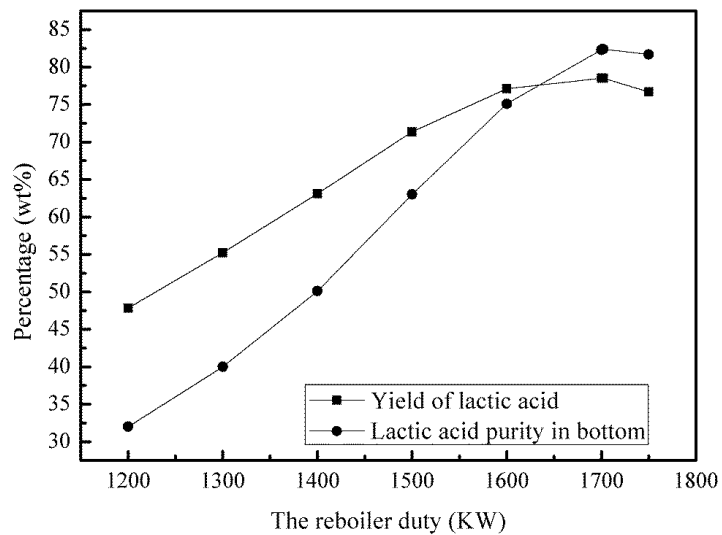


Fig. 11. Effect of the reboiler duty on the yield and purity of bottom lactic acid in hydrolysis column

($P=1$ bar, $N_{rxn}=32$, $N_R=2$, $N_S=3$, $FR_{Water/iAmLc}=2.5:1$)

3.2 Steady state design

The reactive distillation process for the purification of lactic acid was shown in Fig. 2. The process included five columns: esterification column, purification column, hydrolysis column, dehydration column and recovery column. The optimization of the five-column process has a large number of design variables, in order to reduce the number of design variables, the following specification and assumption are made: (1) the feed rate of the crude lactic acid is fixed at 2500 kg h^{-1} , it contains 40 wt % lactic acid and 4 wt% succinic acid; (2) The design specifications of the esterification column were the yield and purity of bottom isoamyl lactate; and the design specifications of the hydrolysis column were the yield and purity of bottom lactic acid; (3) The design specifications of the purification column was that the recovery of isoamyl lactate was over 95%, and the concentration of succinic acid was less than 0.01 wt%. (4) The design specifications of the dehydration and recovery column was that the recovery of isoamyl alcohol and isoamyl lactate was over 95 wt%, and the purity of isoamyl alcohol and isoamyl lactate was over 99.5 wt%. Simulation are carried out using Aspen Plus RADFRAC module. Fig. 12 and Table 7 showed the steady-state operating conditions and results.

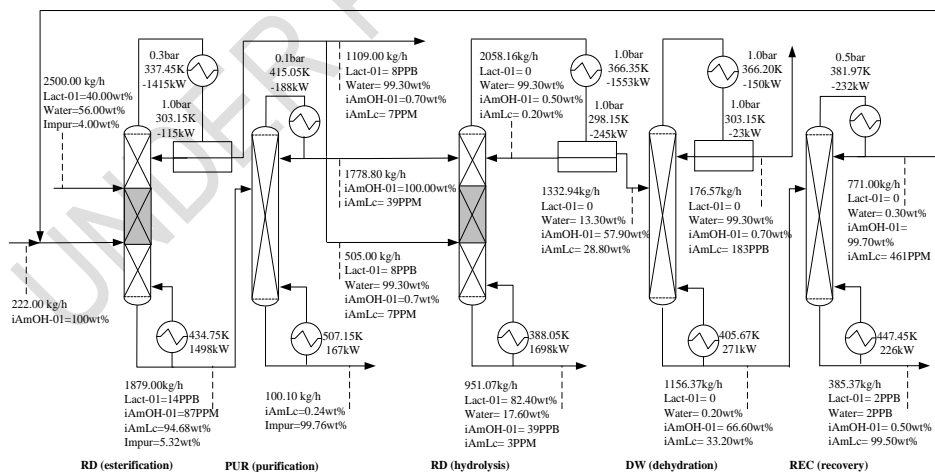


Fig. 12. Simulation results for steady process of the system

Table 7. Simulation results of column configuration

Column Configuration	Esterification	Purification	Hydrolysis	Dehydration	Recovery
Total no. of trays including the reboiler	10	10	37	12	10
No. of trays in rectifying section (N_R)	2	10	2	12	10
No. of trays in reactive section (N_{rxn})	5	-	32	-	-
No. of trays in stripping section (N_S)	3	-	3	-	-
Operating pressure at the top (bar)	0.3	0.1	1.0	1.0	0.5
Column diameter (m)	1.42	0.80	0.78	0.41	0.50
Feed flow rate of heavy component (kg/h)	2500.0	1879.0	1778.8	1332.9	1156.4
Feed flow rate of light component (kg/h)	222.0	-	505.0	-	-
Top product flow rate (kg/h)	1164.0	1778.80	1332.9	176.5	771.00
Bottom product flow rate (kg/h)	1879.0	100.10	951.07	1156.4	385.37
Distillate composition (wt %)					
Lactic acid	8 PPB	-	-	-	-
Water	99.3	-	13.3	99.3	0.3
Isoamyl alcohol	0.7	-	57.9	0.7	99.7
Isoamyl lactate	7PPM	1.00	28.8	183PPB	461PPM
Succinic acid	-	39PPB	-	-	-
Bottom composition (wt %)					
Lactic acid	14 PPB	-	82.4	-	2PPB
Water	-	-	17.6	0.2	2PPB
Isoamyl alcohol	87 PPM	-	39 PPB	66.6	0.5
Isoamyl lactate	94.68	0.24	3 PPM	33.2	99.5
Succinic acid	5.32	99.76	-	-	-
Condenser temperature (K)	337.45	415.05	366.35	366.20	381.97
Reboiler temperature (K)	434.75	507.15	388.0	405.7	447.4
Condenser duty (KW)	-1415	-188	-1553	-150	-232
Decanter duty (KW)	-115	-	-245	-23	-
Reboiler duty (KW)	1498	167	1698	271	226
Conversion (%)	99.99	99.98	78.40	-	99.80

3.3 Total annual cost

Total annual cost (TAC) is a combination of the annual capital investment and operating cost. The equation of calculating TAC was expressed as follows:

$$TAC = \frac{\text{capital cost}}{\text{payback year}} + \text{operating cost } t \quad (3)$$

In this work, the payback period was assumed to be 8 years [14, 21]. The capital cost includes the cost of heat exchangers, trays and column, and the operating cost covers the cost of cooling water, steam [14]. The detailed formulas for calculating TAC were given in equations (4) to (8), and the TAC was determined to be 656.1 (\$1000/year). It

can save about 20% of total annual cost compared with butanol and methanol reported in the literature [14].

capital investment:

$$\text{column cost } [\$] = \frac{1461 \cdot 3}{280} \times 101.9 \times D_c^{1.066} \times L_c^{0.802} \times (2.18 + 3.67) \quad (4)$$

$$\text{tray cost } [\$] = \frac{1461 \cdot 3}{280} \times 4.7 \times D_c^{1.55} \times L_c \times (1 + 1.8 + 1.7) \quad (5)$$

$$\text{heat exchanger cost } [\$] = \frac{1461 \cdot 3}{280} \times 101.3 \times (A_R^{0.65} + A_C^{0.65}) \quad (6)$$

operating cost:

$$\text{cooling water cost } [\$] = \frac{\$0.03}{1000 \text{ gal}} \left(\frac{1 \text{ gal}}{8.34 \text{ lb}} \right) \left(\frac{Q_C}{30} \right) \left(8150 \frac{\text{h}}{\text{year}} \right) \quad (7)$$

$$\text{steam cost } [\$] = \frac{\$3.4}{1000 \text{ lb}} \left(\frac{Q_R}{\lambda_v} \right) \left(8150 \frac{\text{h}}{\text{year}} \right) \quad (8)$$

Where D_C is the column diameter; L_C is the column height; A_R is the reboiler heat transfer area; A_C is the condenser heat transfer area; λ_v is latent heat of stream.

4. Conclusion

In this paper, a novel lactic acid purification process by reactive distillation with isoamyl alcohol was proposed and simulated by Aspen plus. Operational and structural variables of the reactive distillation column like number of theoretical stages, feed location, feed molar ratio, and reboiler duty were investigated and optimized. Under optimized conditions, the concentration of lactic acid can reach up to 82.4 wt%, and the organic acid impurities were less than 3 ppm. The TAC was estimated to be 656.1 (\$1000/year). It can save about 20% of total annual cost compared with butanol and methanol reported in the literature.

References

- 1 Datta R, Henry M. Lactic acid: recent advances in products, processes and technologies - a review. *J Chem Technol Biotechnol*. 2006; 81:1119-1129.
- 2 Ouyang J, Ma R, Zheng Z, Cai C, Zhang M, Jiang T. Open fermentative production of L-lactic acid by *Bacillus* sp. strain NL01 using lignocellulosic hydrolyzates as low-cost raw material. *Bioresour Technol*. 2013; 135:475-480.

Comment [L3]: You should be discussed your study results with other study results

Comment [L4]: Positive or negative results of the study should be given.

- 3 Abdel-Rahman MA, Tashiro Y, Sonomoto K. Recent advances in lactic acid production by microbial fermentation processes. *Biotechnol Adv.* 2013; 31:877-902.
- 4 Abdel-Rahman MA, Sonomoto K. Opportunities to overcome the current limitations and challenges for efficient microbial production of optically pure lactic acid. *J Biotechnol.* 2016; 236:176-192.
- 5 Kadam SR, Patil SS, Bastawde KB, Khire JM, Gokhale DV. Strain improvement of *Lactobacillus delbrueckii* NCIM 2365 for lactic acid production. *Process Biochem.* 2006; 41:120-126.
- 6 Sun X, Wang Q, Zhao W, Ma H, Sakata K. Extraction and purification of lactic acid from fermentation broth by esterification and hydrolysis method. *Sep Purif Technol.* 2006; 49:43-48.
- 7 Joglekar HG, Rahman I, Babu S, Kulkarni BD, Joshi A. Comparative assessment of downstream processing options for lactic acid. *Sep Purif Technol.* 2006; 52:1-17.
- 8 Aljundi IH, Belovich JM, Talu O. Adsorption of lactic acid from fermentation broth and aqueous solutions on Zeolite molecular sieves. *Chem Eng Sci.* 2005; 60:5004-5009.
- 9 Hábová V, Melzoch K, Rychtera M, Sekavová B. Electrodialysis as a useful technique for lactic acid separation from a model solution and a fermentation broth. *Desalination.* 2004; 162:361-372.
- 10 González MI, Alvarez S, Riera F, Alvarez R. Economic evaluation of an integrated process for lactic acid production from ultrafiltered whey. *J Food Eng.* 2007; 80:553-561.
- 11 Alkaya E, Kaptan S, Ozkan L, Uludag-Demirer S, Demirer GN. Recovery of acids from anaerobic acidification broth by liquid-liquid extraction. *Chemosphere.* 2009; 77:1137-1142.
- 12 Komesu A, Martinez PFM, Lunelli BH, Filho RM, Maciel MRW. Lactic acid purification by reactive distillation system using design of experiments. *Chem Eng Process.* 2015; 95:26-30.
- 13 Kamble SP, Barve PP, Joshi JB, Rahman I, Kulkarni BD. Purification of Lactic Acid via Esterification of Lactic Acid Using a Packed Column, Followed by Hydrolysis of Methyl Lactate Using Three Continuously Stirred Tank Reactors (CSTRs) in Series: A Continuous Pilot Plant Study. *Ind Eng Chem Res.* 2012; 51:1506-1514.
- 14 Su CY, Yu CC, Chien IL, Ward JD. Plant-Wide Economic Comparison of Lactic Acid Recovery Processes by Reactive Distillation with Different Alcohols. *Ind Eng Chem Res.* 2013; 52:11070-11083
- 15 Liu M, Jiang ST, Pan LJ, Zheng Z, Luo SZ. Design and control of reactive distillation for hydrolysis of methyl lactate. *Chem Eng Res Des.* 2011; 89:2199-2206.
- 16 Gudena K, Rangaiah GP, Lakshminarayanan S. Modeling and Analysis of Hybrid Reactive Stripper-Membrane Process for Lactic Acid Recovery. *Ind Eng Chem Res.* 2013; 52:2907-2916.

-
- 17 Kumar R, Mahajani SM. Esterification of Lactic Acid with n-Butanol by Reactive Distillation. *Ind Eng Chem Res.* 2007; 46(21):6873-6882.
 - 18 Su CY, Yu CC, Chien IL, Ward JD. Control of Highly Interconnected Reactive Distillation Processes: Purification of Raw Lactic Acid by Esterification and Hydrolysis. *Ind Eng Chem Res.* 2015; 54:6932-6940.
 - 19 Jiang Z, Xu J, Zeng Z, Xue W, Li S. Kinetics of the Esterification between Lactic Acid and Isoamyl Alcohol in the Presence of Silica Gel-Supported Sodium Hydrogen Sulphate. *Can J Chem Eng.* 2018; 96:1972-1978.
 - 20 Xu JM. Studies on Kinetics, Thermodynamic and Reactive Distillation Simulation of the Esterification and Hydrolysis Reactions for Lactic Acid Purification. Ph.D. Thesis. 2020.
 - 21 Dai SB, Lee HY, Chen CL. Design and Economic Evaluation for the Production of Ethyl Lactate via Reactive Distillation Combined with Various Separation Configurations. *Ind Eng Chem Res.* 2019; 58:6121-6132.
 - 22 Xu JM, Li ST, Zeng ZX, Xue WL. Isobaric Vapor-Liquid Equilibrium for Binary System of Isoamyl DL-Lactate and Isoamyl Alcohol at 25.0, 50.0, and 101.3 kPa. *Ind Eng Chem Res.* 2020; 65:81-87.

UNDER PEER REVIEW