CHEMICAL ENGINEERING TRANSACTIONS

VOL. 64, 2018

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Enrico Bardone, Antonio Marzocchella, Tajalli Keshavarz

ISBN 978-88-95608- 56-3; **ISSN** 2283-9216

DOI: 10.3303/CET1864069

Conceptual Design and Scale Up of Lactic Acid Production from Fermentation-Derived Magnesium Lactate

Boonpradab Daengpradab, Panarat Rattanaphanee*

School of Chemical Engineering, Institute of Engineering, Suranaree University of Technology, Muang, Nakhon Ratchasima, 30000, Thailand.
panarat@sut.ac.th

A process for production of purified lactic acid from fermentation-derived magnesium lactate is conceptually designed and simulated using Aspen Plus simulator equipped with RADFRAC module. The process employs two reactive distillation columns: one, the RD column, for esterification of acidified magnesium lactate solution, and the other, the HY column, for hydrolysis of the produced ethyl lactate back to lactic acid. Series of fractional distillation columns are used in order to increase purity of the final product. The process design is a 2000-fold scale up based on experimental results obtained from a laboratory scale fermenter producing 50 L of the fermentation broth containing magnesium lactate resulted from neutralization of lactic acid by magnesium oxide. Key operating variables, such as total number of stage, distillate rate, reflux ratio and feed location, are optimized in order to maximize the production yield. Under the optimal conditions, conversion of lactic acid in the RD column is found to be 97.25 %, while the recovery of the produced ethyl lactate before it is subjected to hydrolysis is 99.86 %. The final product is received as an aqueous solution with the acid concentration of 59.52 mol% or 88.01 w/w%. The acid production rate is found to be 4.11 kmol/h or 370.39 kg/h with the energy consumption of 31.11 kJ/kg of lactic acid produced.

1. Introduction

Lactic acid is an organic acid containing both hydroxyl and carboxylic acid functional group in its molecule. Due to its versatile properties, the acid is considered to be one of the most valuable organic acids that becomes very attractive as a green building block for various industries especially those concerning green solvent, food, cosmetic, pharmaceutical and lactic-based biodegradable polymer (Martinez et al., 2013). Currently, over 90 % of lactic acid is produced via fermentation, which is more preferable than its chemical synthesis counterpart, because high selectivity and stereoisomer of lactic acid can be achieved (Joglekar et al., 2006). However, separation and purification of lactic acid from complex fermentation broth is very complicated as various kinds of impurities including nutrients, cell mass, hydrophilic salts and ions are presented. Multi-step purification processes are normally needed, which can lead to high production cost of the acid, which has been estimated to be about 50 % of the total production cost for highly purified lactic acid production (Abdel-Rahman et al., 2013).

Reactive distillation is one of the promising processes for purification of lactic acid. It is a unit operation that combines both chemical reaction and separation within the same unit. It can employ simultaneous removal of products during reactions proceeding to increase both reactant conversion and product selectivity. Thus, the reactive distillation is a very high potential process for carrying out the reversible reactions which limited by equilibrium limitation such as esterification (Gao et al., 2007 and Komkrajang et al., 2014).

The preliminary design of reactive distillation process for ethyl lactate production from fermentation-derived magnesium lactate is previously presented (Deangpradab and Rattanaphanee (2015a, 2015b)). In this study, conceptual design for purification of lactic acid from the fermentation-derived magnesium lactate using reactive distillation technique is proposed. Aspen Plus simulator equipped with RADFRAC module is used for process simulation. Operating conditions and column specifications of reactive and non-reactive distillation columns are optimized to maximize lactic acid production rate. Yield of lactic acid is satisfactorily achieved under the proposed process scheme and operating conditions.

Please cite this article as: Daengpradab B., Rattanaphanee P., 2018, Conceptual design and scale up of lactic acid production from fermentation-derived magnesium lactate, Chemical Engineering Transactions, 64, 409-414 DOI: 10.3303/CET1864069

2. Research methodology

2.1 Process description

Overall process schematic for purification of lactic acid from fermentation-derived magnesium lactate is displayed in Figure 1. This process is divided into two major parts: the first part is esterification of lactic acid with ethanol in the RD column, and the second part is hydrolysis of the produced ethyl lactate back into its acid form in the HY column. Three fractional distillation columns (DIS1-DIS3) are used to separate and purify the produced ethyl lactate before it is subjected as a feed for hydrolysis in the HY column. Major duty of the last fractional distillation column (DIS4) is to concentrate the purified lactic acid to achieve its target value. All the columns in this process are designed as tray-type column and operated under atmospheric pressure. Equilibrium stages of each column are numbered down from top to bottom. Hence, condenser and reboiler of each column are always the first and the N^{th} stage, respectively.

A solution obtained from acidification of fermentation-derived magnesium lactate powder with 1 M sulfuric acid is used as the feed of this process. Procedure for preparation of this solution has been described in detail in our previous work (Daengpradab and Rattanaphanee, 2012). In short, the powder is completely mixed with stochiometric amount of 1 M sulfuric acid solution. All the non-dissolvable solid residues are filtrated by vacuum filtration. Some of water content in the clear solution obtained after filtration is evaporated out in order to reduce its interference in esterification reaction. The feed solution containing lactic acid and soluble impurities is mixed with concentrated sulfuric acid, a catalyst for esterification, before it is charged into the RD column via feed steam F1. Ethanol is fed via feed steam F2. The compositions of both feed streams are analyzed and tabulated in Table 1.

The present process is an extension of the ethyl lactate production process previously proposed in Deangpradab and Rattanaphanee (2015a). In this work, the process is scaled up 2000 fold in order to achieve higher production rate. Reaction zone in the RD column extends between the two feed stages. Synthesized ethyl lactate and unreacted ethanol are vaporized out at the top of the RD column via the top product stream, TP. Details of three fractional distillation columns for ethyl lactate purification are discussed and explained in Deangpradab and Rattanaphanee (2015a). Ethyl lactate, in form of aqueous solution in stream EL, is then fed into the HY column where it is hydrolyzed back to lactic acid. This column is designed to be the tray-type column containing Amberlyst 15 cation exchange resin as a hydrolysis catalyst. Amount of catalyst presented in the column is evaluated by multiplying the resin density by 50 % of tray hold-up volume and total number of the reactive stages. The final product is received as the purified lactic acid solution in stream LA with desired concentration of about 88 w/w%.

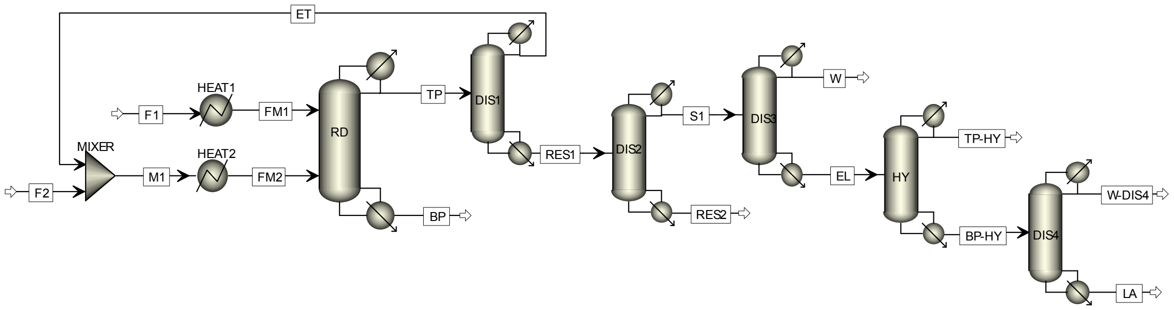


Figure 1: Proposed process schematic for lactic acid production.

Table 1: Composition and molar flow rate of feed streams.

Stream	Component	Molecular weight (kg/kmol)	Normal boiling point (°C)	Mole fraction	Molar flow rate (kmol/h)
F1	Lactic acid	90.08	216.63	0.077	4.234
	Water	18.02	100.02	0.859	47.052
	Magnesium sulfate	120.36	N/A	0.050	2.739
	Sulfuric acid	98.08	340	0.014	0.750
F2	Ethanol	46.06	78.31	1.000	12.700

2.2 Reaction kinetics

The kinetic parameters for esterification of lactic acid in acidified magnesium lactate with ethanol using sulfuric acid as homogenous catalyst are obtained from Daengpradab and Rattanaphanee (2012). The reactive mixture containing lactic acid (LA), ethanol (EtOH), ethyl lactate (EtLA), water (W) and magnesium sulfate resulted from magnesium lactate acidification is definitely a non-ideal solution. The reaction rate for esterification ($-r_{LA}$) is expressed in the term of activity (a_i) instead of concentration as in Eq(1). The reaction rate constants for forward (k_1) and backward (k_{-1}) reaction as a function of reaction temperature are presented in Eq(2) and Eq(3), respectively.

$$-r_{LA} = k_1(a_{EtOH}\alpha_{LA}) - k_{-1}(\alpha_{EtLA}\alpha_W) \tag{1}$$

$$k_1 = 13{,}300 exp\left(\frac{-30{,}400\,\frac{J}{mol}}{RT}\right) \tag{2}$$

$$k_{-1} = 0.799 exp\left(\frac{-7{,}022.67\,\frac{J}{mol}}{RT}\right) \tag{3}$$

Where R is the universal gas constant (8.314 J/mol.K) and T is temperature (K).
The reaction rate of ethyl lactate hydrolysis ($-r_{EtLA}$) is expressed in term of the component mole fractions as shown in Eq(4), are extracted from Asthana et al. (2006), where m_{cat} is the catalyst mass (kg). The reaction rate constants for forward (k_2) and backward (k_{-2}) reactions of hydrolysis are given in Eq(5) and Eq(6), respectively.

$$-r_{EtLA} = m_{cat}k_2(x_{EtLA}x_W) - m_{cat}k_{-2}(x_{EtOH}x_{LA}) \tag{4}$$

$$k_2 = 2{,}720 exp\left(\frac{-48{,}000\,\frac{J}{mol}}{RT}\right) \tag{5}$$

$$k_{-2} = 6{,}520 exp\left(\frac{-48{,}000\,\frac{J}{mol}}{RT}\right) \tag{6}$$

2.3 Phase equilibrium

In all columns of this process, vapor-liquid equilibrium (VLE) of the reactive mixture at constant low pressure and temperature is assumed and given by Eq(7).

$$\phi_i y_i P = \gamma_i x_i P_i^{sat} \phi_i^{sat} \tag{7}$$

Here, γ_i and ϕ_i are activity coefficient and fugacity coefficient of component *i*, respectively, x_i and y_i is mole fraction of component *i* in liquid and vapor phase, respectively, P_i^{sat} is vapor pressure of component *i* at temperature *T*, and ϕ_i^{sat} is fugacity coefficient of pure component *i* as a saturated vapor at corresponding *T* and P_i^{sat}. Presence of magnesium sulfate in the solution could significantly alter the VLE behavior of the quaternary mixture inside the RD column. However, the VLE data of this mixture containing magnesium sulfate is not available. Therefore, the activity coefficients of all components in the liquid phase are computed from UNIQUAC model with binary interaction parameters obtained from Delgado et al. (2007). The vapor phase is assumed to be an ideal, and the fugacity coefficients of all the gaseous components are unity.

2.4 Process simulation

Aspen Plus simulator equipped with RADFRAC module is used as a tool for process simulation and optimization. Sensitivity analysis and optimization of interested process variables are studied. The interested manipulated variables of all the distillation columns are total number of stage, distillate rate, reflux ratio, feed location. Influences of feed temperature in the RD column are also investigated. The main target of the RD column is to maximize conversion of lactic acid ($\%C_{LA}$), recovery of ethyl lactate ($\%R_{EtLA}$), and yield of ethyl lactate ($\%Y_{EtLA}$) achieved from esterification reaction. After ethyl lactate is produced from the RD column, it is purified by fractional distillation columns. In the HY column, ethyl lactate produced from esterification is hydrolyzed back to lactic acid. The manipulated variables of the HY column are optimized in order to maximize the conversion of produced ethyl lactate ($\%C_{EtLA}$), recovery ($\%R_{LA}$) and yield of purified lactic acid ($\%Y_{LA}$) obtained in the process.

The three key parameters in process optimization are defined as in Eq(8) to Eq(10).

$$\%C_i = \frac{\text{Mole of } j \text{ produced in the unit}}{\text{Mole of } i \text{ in feed stream}} \times 100\% \tag{8}$$

$$\%R_j = \frac{\text{Mole of } j \text{ in product stream}}{\text{Mole of } j \text{ produced in the unit}} \times 100\% \tag{9}$$

$$\%Y_j = \frac{\%C_i \times \%R_j}{100\%} \tag{10}$$

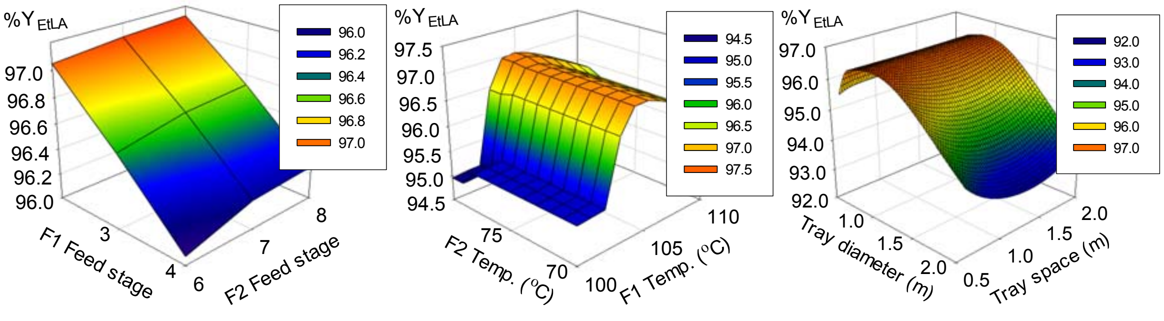
where *i* and *j* is the reactant and the desired product of each unit, respectively.

Production rate of lactic acid in term of kilograms of lactic acid produced per hour of the operation is considered for overall process efficiency. Energy consumption per unit mass of lactic acid is also evaluated.

3. Results and discussions

3.1 Optimization of esterification of acidified magnesium lactate

Influence of operating variables and column specifications on yield of ethyl lactate obtained from esterification is studied using a sensitivity analysis and the process optimization. Initial distillate rate and reflux ratio of the RD column are 63 kmol/h and 0.001, Initial temperature of feed stream F1 and F2 are 110 and 75ºC, respectively. Column specifications, such as tray diameter, tray space and weir height, are initially set at 1 m. For the fractional distillation columns, DIS1-DIS3, the initial total number of stage, feed location and manipulated variables are initially received from results of DSTWU module of individual unit. Then, the obtained values are applied with the RADFRAC module and connected to the RD column for the process optimization. In order to distinctively compare, the dimension of all the columns in this process are fixed to be the same as the optimum dimension of the RD column. The operating variables are simultaneously optimized with the specified objective function as maximum yield of ethyl lactate obtained from esterification process. Some results from sensitivity analysis are examined in Figure 2 while optimization results are tabulated in Table 2.



(a) (b) (c)

Figure 2: Sensitivity analysis of the RD column: (a) effect of feed location, (b) effect of feed temperature, and (c) effect of tray space and diameter ethyl lactate yield.

The optimum total number of stage for the RD column is found to be 9 with feed location at the first and the last stage of the reactive zone. Longer reactive zone of the RD column increases contact time between two reactants and results in higher conversion and product selectivity. The optimal distillate rate and reflux ratio of the RD column are found to be 75.513 kmol/h and 0.3814, respectively. The DIS3 column is found to be the tallest column due to highest total number of stage requirement for completely removal of unreacted ethanol from the desired product.

Table 2: Optimal column specifications and operating variables of all unit operations in the proposed process.

Specification	Unit Name							
	HEAT1	HEAT2	RD	DIS1	DIS2	DIS3	HY	DIS4
Type of unit operation	Heater	Heater	Reactive distillation	Fractional distillation	Fractional distillation	Fractional distillation	Reactive distillation	Fractional distillation
Temperature (ºC)	104.9	77.72	-	-	-	-		
Total number of stages	-	-	9	8	13	31	19	9
Feed stage	-	-	2 and 8	7	11	21	8	8
Tray diameter (m)	-	-	0.7818	0.7818	0.7818	0.7818	0.7818	0.7818
Tray space (m)	-	-	0.9304	0.9304	0.9304	0.9304	0.9304	0.9304
Weir height (m)	-	-	0.3656	0.3656	0.3656	0.3656	0.3656	0.3656
Distillate rate (kmol/h)	-	-	75.513	11.5326	63.9088	10.0000	46.1376	0.8563
Reflux ratio	-	-	0.3814	8.2331	0.5000	12.0390	0.3930	0.5268
Condenser heat duty (kW)	-	-	1,217.20	1,162.42	1,113.25	1,420.86	743.69	15.02
Reboiler heat duty (kW)	-	-	973.42	1,165.94	1,113.72	1,434.44	696.40	15.68
Total heat duty (kW)	425.16	25.51	2,190.61	2,328.36	2,226.97	2,855.30	1,440.09	30.70

Under the optimal operating operation, $\%C_{LA}$ in the RD column is found to be 97.25 % with 99.86 % of produced ethyl lactate is recovered in the product stream EL. Ethyl lactate is synthesized in form of aqueous solution with the concentration of 7.712 mol% or 35.42 w/w%. The production rate of ethyl lactate is found to be 4.157 kmol/h or 491.11 kg/h. The produced ethyl lactate is further fed as the reactant for hydrolysis reaction in the HY column, where it would be converted into lactic acid in the HY column. The compositions of each stream are presented in Table 3.

Table 3: Stream composition in the proposed process.

Description	Stream								
	FM1	FM2	BP	TP	ET	RES1	S1	RES2	W
Temperature (°C)	104.90	77.72	319.66	84.65	78.26	88.08	88.04	217.03	78.19
Molar flow rate (kmol/h)	54.78	24.23	3.49	75.51	11.53	63.98	63.91	0.07	10.00
Mole fraction									
Ethanol	0	0.9105	0.0001	0.2371	0.8118	0.1335	0.1336	0	0.8540
Lactic acid	0.0773	0	0.0012	0.0009	0	0.0011	0	0.9763	0
Ethyl lactate	0	0	0.0008	0.0551	0	0.0650	0.0651	0.0003	0
Water	0.8590	0.0895	0	0.7069	0.1882	0.8004	0.8013	0.0001	0.1460
Sulfuric acid	0.0137	0	0.2143	0	0	0	0	0.0233	0
Magnesium sulfate	0.0500	0	0.7837	0	0	0	0	0	0

Table 3 (Cont.): Stream composition in the proposed process.

Description	Stream				
	EL	TP-HY	BP-HY	W-DIS4	LA
Temperature (°C)	99.41	87.08	111.23	100.02	114.29
Molar flow rate (kmol/h)	53.91	46.14	7.77	0.86	6.91
Mole fraction					
Ethanol	0	0.0893	0	0	0
Lactic acid	0	0.0001	0.5296	0	0.5952
Ethyl lactate	0.0771	0.0008	0	0	0
Water	0.9229	0.9098	0.4704	1.0000	0.4048
Sulfuric acid	0	0	0	0	0
Magnesium sulfate	0	0	0	0	0

3.2 Optimization of hydrolysis to produce lactic acid

The total number of stage of the column is optimized by varying the total number of stage in the column with feed location is initially fixed at the 2nd stage. The column dimensions in hydrolysis process are set to be the same as the column in esterification process. Initial distillate rate of the HY column is evaluated based on completely conversion of produced ethyl lactate into lactic acid which is found to be about 45.75 kmol/h. Initial reflux ratio of the column is 0.001. The objective functions for optimization of the hydrolysis process are the maximum yield of purified lactic acid produced in the HY column and recovery of lactic acid in the final product stream, LA. The optimization results of the HY column and DIS4 column are also tabulated in Table 2. The HY column requires 19 stages of total number of stage to achieve higher than 80 % yield of lactic acid with highest conversion of ethyl lactate. The optimal distillate rate and reflux ratio of the HY column are found to be 46.1376 kmol/h and 0.3930, respectively. Moreover, it is found that, the DIS4 column requires 9 stages for purification of produced lactic acid to achieve its desired concentration about 88 w/w%.

At the optimal conditions, $\%C_{EL}$ in the HY column is found to be 99.08 %. The final product is in form of an aqueous solution with concentration of 88.01 w/w%. The lactic acid production rate is found to be 4.11 kmol/h or 370.39 kg/h. Compositions of process streams are also exhibited in Table 3.

3.3 Energy consumption

Heat requirement for each unit operation in the proposed process is displayed in Table 2. The total heat requirement of the proposed process can be evaluated from summation of total heat duty of all columns including two heaters. The total energy requirement is found to be 11,523 kW. Therefore, the energy consumption per unit mass of lactic acid produced in this process is 31.11 kJ/kg.

4. Conclusions

The process for purification of lactic acid from fermentation-derived magnesium lactate is designed and optimized using Aspen Plus simulator. Two reactive distillation columns, RD and HY column, are used for esterification of acidified magnesium lactate and hydrolysis of ethyl lactate back to its acid form. The operating variables and column specifications are optimized with the main target of maximizing lactic acid production rate. As the optimization results, $\%C_{LA}$ in the RD column is found to be 97.25 % with $\%R_{EtLA}$ of 99.86 %. The produced ethyl lactate is further hydrolyzed in the HY column to produce purified lactic acid. At the optimum conditions, the lactic acid production rate is found to be 370.39 kg/h which its concentration is 88.01 w/w%. The energy consumption per mass of lactic acid produced in the proposed process is found to be 31.11 kJ/kg.

Reference

Abdel-Rahman M.A., Tashiro Y., Sonomoto K., 2013, Recent advances in lactic acid production by microbial fermentation processes, Biotechnology Advances, 31, 877-902.

Asthana N.S., Kolah A.K., Vu D.T., Lira C.T., Miller D.J., 2006, A kinetic model for the esterification of lactic acid and its oligomers, Industrial & Engineering Chemistry Research, 45, 5251-5257, DOI:10.1021/ie0531604

Daengpradab B., Rattanaphanee P., 2012, Kinetic study of ethyl lactate synthesis from magnesium lactate, Engineering Transaction, 15, 84-90.

Daengpradab B., Rattanaphanee P., 2015a, Process intensification for production of ethyl lactate from fermentation-derived magnesium lactate: A preliminary design, International Journal of Chemical Reaction Engineering. 13, 407–412, DOI: 10.1515/ijcre-2014-0133

Daengpradab B., Rattanaphanee P., 2015b, Efficiency comparison of different design schemes of reactive distillation process for ethyl lactate production from fermentation-derived magnesium lactate, Computer Aided Chemical Engineering, 37, 1079-1084.

Delgado P., Sanz M.T., Beltran S., 2007, Isobaric vapor liquid equilibria for the quaternary reactive system: Ethanol+water+ethyl lactate+lactic acid at 101.33 kPa, Fluid Phase Equilibria, 255, 17–23.

Gao J., Zhao X.M., Zhou L.Y., Huang Z.H., 2007, Investigation of ethyl lactate reactive distillation process, Transactions of the Institution of Chemical Engineers, Part A, 85, 525–529.

Joglekar H.G., Rahman I., Babu S., Kulkarni B.D., Joshi A., 2006, Comparative assessment of downstream processing options for lactic acid, Separation and Purification Technology, 52, 1-17.

Komkrajang T., Kheawhom S., Paengjuntuek W., Arpornwichanop A., 2014, Design of model predictive control for butyl acetate production in reactive distillation, Chemical Engineering Transactions, 39, 427-432, DOI:10.3303/CET1439072.

Martinez F.A.C., Balciunas E.M., Salgado J.M., González J.M.D., Converti A., Oliveira R.P.D.S., 2013, Lactic acid properties, applications and production: a review, Trends in Food Science & Technology, 30, 70–83.