RAPID COMMUNICATION

Application of hollow fiber supported liquid membrane as a chemical reactor for esterification of lactic acid and ethanol to ethyl lactate

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Abstract–Hollow fiber supported liquid membrane was applied as a reactor to synthesize ethyl lactate from lactic acid. Lactic acid in the feed solution was extracted by tri-n-octylamine (TOA) and stripped by ethanol with p-toluene sulfonic acid acting as the catalyst to form ethyl lactate. Central composite design (CCD) was used to determine the significant factors and their interactions. The response surface was applied for optimization. An optimized yield of 30% was predicted and its validity was evaluated by comparison with experimental results at different concentrations of lactic acid in the feed solution, with good agreement achieved.

Keywords: Liquid Membrane, Hollow Fiber, Ethyl Lactate, Lactic Acid, CCD

INTRODUCTION

Liquid membrane processes have been promising methods for metal ion and organic compound separation. They have received considerable attention due to the advantages of combining extraction and stripping processes in one stage, as well as non-equilibrium mass transfer and up-hill effect, where the solute can move from low-to-high concentration solutions [1]. Many researchers have separated metal ion using various kinds of liquid membrane, namely bulk liquid membrane [2], emulsion liquid membrane [3,4], flat sheet supported liquid membrane [5] and hollow fiber supported liquid membrane [6,7]. Among these processes, hollow fiber supported liquid membranes (HFSLM) show considerable advantages, including lower capital and operating costs, lower energy consumption, low solvent use and high selectivity [8,9]. In our previous studies, the separation of several kinds of metal ions, as well as pharmaceutical product by a hollow fiber supported liquid membrane, has been reported [10-15].

Conversely to other liquid membrane works, a hollow fiber module was applied as a reactor to synthesize ethyl lactate from lactic acid by a liquid membrane mechanism. Basically, ethyl lactate is an ester of lactic acid that is a transparent, colorless liquid possessing a characteristic odor, and is nontoxic and biodegradable. Ethyl lactate is commonly used for the production of food, medicine and cosmetics, mainly due to its favorable hygroscopic and emulsifying properties [16]. It is used as a solvent for nitrocellulose, cellulose acetate, cellulose ethers and a co-solvent to produce suitable conditions for the formation of aryl aldimines [17]. It is also a diverse building-block molecule for degradable plastic polymers such as propylene glycol, acrylates, and propylene oxide [18].

Ethyl lactate is generally synthesized from esterification of lactic

acid and ethanol because both can be produced in large quantities by fermentation. The esterification between lactic acid and ethanol is an equilibrium-limited reaction. Higher yields of ethyl lactate can be obtained by shifting the reaction towards products by hybrid processes, such as pervaporation-aided reactor and reactive distillation instead of using a large excess of reactants. However, these processes are energy intensive since some products and/or reactants need to be vaporized. Our work illustrates the use of HFSLM to synthesize ethyl lactate. The benefit of the process is the use of low concentration of lactic acid and ethanol. With low concentration of reactants, the yield of ethyl lactate is expected to be very low in the conventional reactor. The concentration of lactic acid was kept at low concentration both in feed (dilute by water) and in extract phase (dilute by TOA) solution; therefore, oligomerization of lactic acid rarely occurs.

In the present work, our concept is to use esterification as a driving force to separate lactic acid from the feed solution. The synthesis of ethyl lactate by hollow fiber supported liquid membrane with catalyst was also performed. Ethyl lactate can be produced simultaneously, which is unlimited by equilibrium limitation. Tri-n-octylamine (TOA) was found to be an efficient carrier for the separation of organic lactic acid [19-21]. The stripping agent was ethanol. Ethyl lactate was the product from the stripping reaction by using p-toluene sulfonic acid as the catalyst. Central composite design (CCD) was employed to determine the magnitude of the effects of these factors, namely the concentration of TOA, concentration of ethanol, temperature and their interaction on the yield of ethyl lactate. A second-order polynomial regression equation to predict the yield in different concentrations of lactic acid was determined from CCD. Consequently, optimization was determined by response surface.

THEORY

1. Ethyl Lactate Synthesis by Liquid Membrane Mechanism

The liquid membrane system consists of an aqueous feed con-

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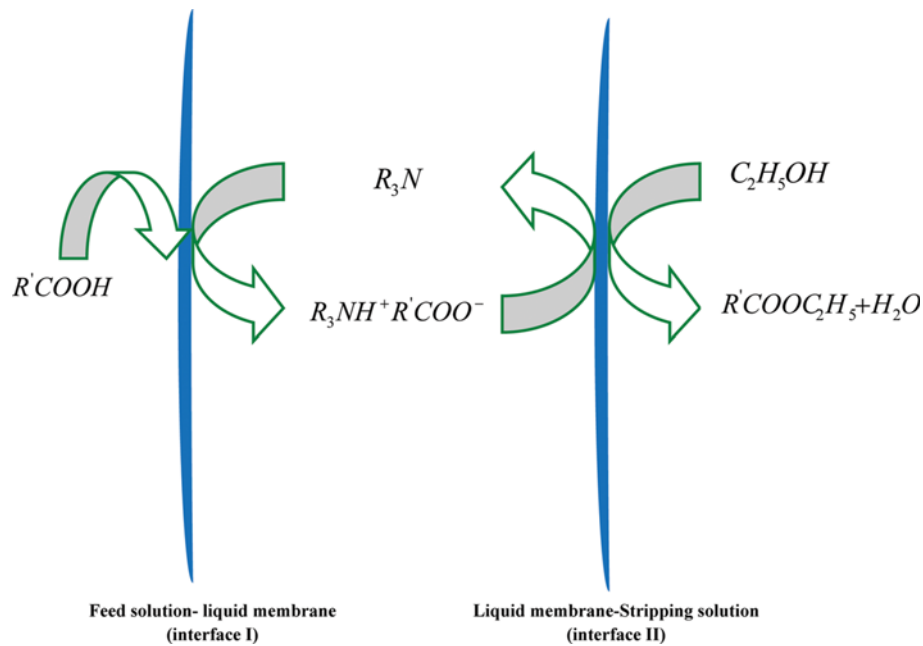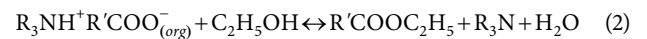E-mail: ramakul_p@su.ac.th

Fig. 1. Mechanism of extraction of lactic acid to synthesize ethyl lactate.

taining lactic acid and a stripping solution containing ethanol. The liquid membrane is between the feed and stripping phases, containing tri-n-octylamine as an organic extractant. As shown in Fig. 1, the lactic acid molecule reacts with tri-n-octylamine (R_3N) at the interface between the feed and liquid membrane to form complex species by the extraction reaction in Eq. (1).

$$R'COOH_{(aq)} + R_3N_{(org)} \leftrightarrow R_3NH^+R'COO^-_{(org)} \qquad (1)$$

After that, the complex species diffuse across the organic liquid membrane to the stripping solution at the opposite interface. Ethyl lactate is formed by the reaction between complex species and etha-

nol in a stripping phase at the interface between the liquid membrane and stripping phase by Eq. (2). Finally, the complex species reverts to the original form of tri-n-octylamine (R_3N) and diffuses back to react with the lactic acid molecule in a new cycle. The transport is driven by the hydrogen ion concentration gradient between the feed and stripping phases [22].

$$R_3NH^+R'COO^-_{(org)} + C_2H_5OH \leftrightarrow R'COOC_2H_5 + R_3N + H_2O \qquad (2)$$

2. Inside a Hollow Fiber Module

A hollow fiber module is composed of an outer shell, which is a single nonporous material through which the components inside
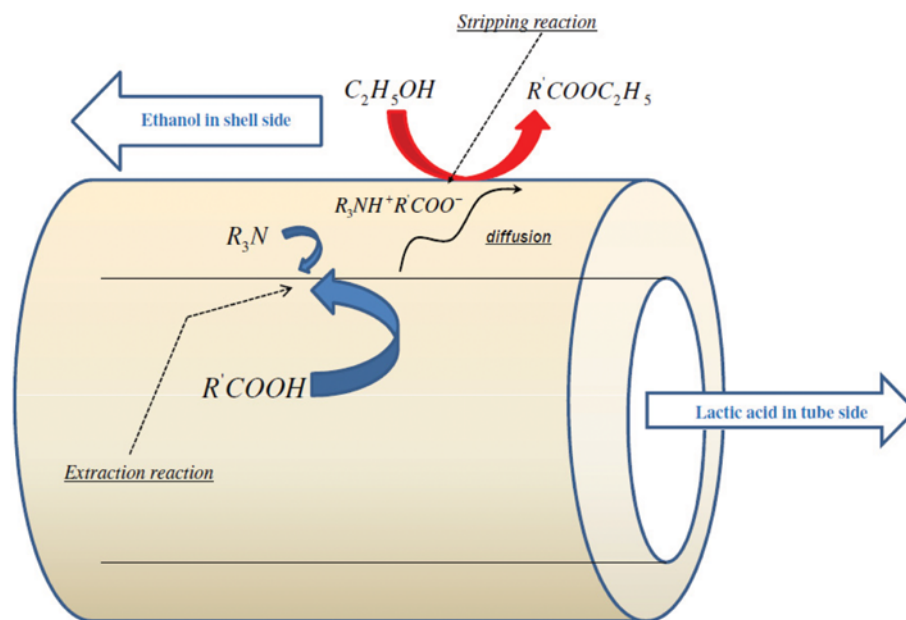

Fig. 2. Flow pattern in the hollow fiber supported liquid membrane module.

cannot be transported. Inside that shell are multiple thin fibers running the length of the shell, all in nice, neat rows.

Fig. 2 shows a hollow fiber which supports the liquid membrane and a close-up of the cross section of a single hollow fiber. The liquid membrane phase fill in the pores of fibers and trapped in hydrophobic micropores due to capillary force [23]. The liquid membrane phase acts as a barrier between the feed and stripping solutions. The extraction and stripping reactions occur at the interfaces (feed/membrane and membrane/stripping interface).

EXPERIMENTAL

1. Feed and Chemicals

The lactic acid and p-toluene sulfonic acid were purchased from Sigma-Aldrich (Germany). Tri-n-octylamine (TOA), kerosene and ethanol (C_2H_5OH) were supplied by Merck. All chemicals were AR grade.

2. Apparatus

• A Liqui-Cel® Laboratory Liquid/Liquid Extraction System (composed of two gear pumps, two variable speed controllers, two rotameters and four pressure gauges) was used.

• A Liqui-Cel® Extra-Flow module (Celgard, Charlotte, NC; formerly Hoechst Celanese) was used as a support material. This module uses Celgard® microporous polyethylene fibers that are woven into a fabric and wrapped around a central tube feeder that supplies the shell-side fluid. The woven fabric allows more uniform fiber spacing, which in turn leads to higher mass transfer coefficients than those obtained with individual fibers. The properties of the hollow fiber module are shown in Table 1. The fibers are potted into a solvent-resistant polyethylene tube sheet with a polypropylene shell casing.

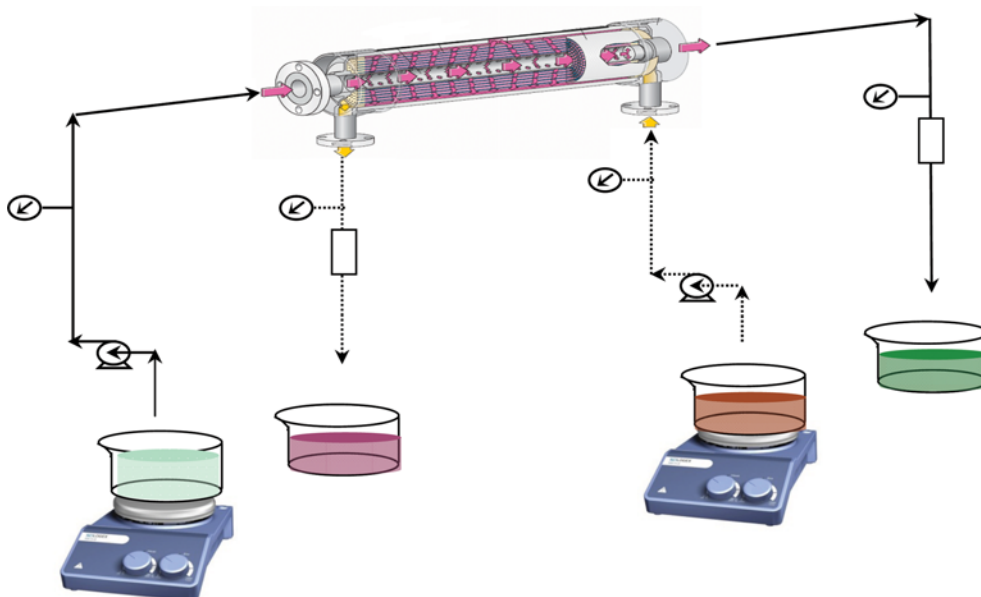**Table 1. Properties of the hollow fiber module**

Properties	Description
Materials	Polypropylene
Dimension of module (diameter x length)	6.3×20.3
Inside diameter of a hollow fiber	240 mm
Outside diameter of a hollow fiber	300 mm
Number of hollow fiber	35,000
Size of pore	0.05 μm
Effective surface area	1.39 m^2
Porosity	30%
Area per unit volume	29.3 cm^2/cm^3

3. Procedures

The feed solution was 0.001 mol/L of lactic acid solution. Tri-n-octylamine (TOA) was dissolved in kerosene and circulated in the tube and shell sides of the hollow fiber membrane for 20 min in order to become embedded in the pores. The experiment was started by introducing the feed solution into the tube side. Simultaneously, ethanol solution with 3% (w/w) p-toluene sulfonic acid was countercurrently pumped into the shell side. The flow rates of feed and stripping solution were 100 mL/min and a once-through mode was operated. The flow diagram is shown in Fig. 3. The outlet of the stripping solutions was sampled and analyzed by gas chromatography (GC) to measure the concentration of lactic acid and ethyl lactate.

The %yield of ethyl lactate can calculated from Eq. (3).

$$\text{Yield of ethyl lacatate (\%)} = \frac{C_{EL,st}}{C_{LA,f}} \times 100 \qquad (3)$$

Fig. 3. Schematic counter-current flow diagram for one-through-mode operation in a hollow fiber supported liquid membrane.

1. Inlet feed solution reservoir	4. Outlet pressure gauges	7. Hollow fiber module
2. Gear pump	5. Flow meters	8. Inlet stripping solution reservoir
3. Inlet pressure gauges	6. utlet stripping solution reservoir	9. Outlet feed solution

Table 2. Actual levels and central composite design levels

Factors	Factor level					Unit
	−1.68	−1	0	1	1.68	-
Conc. of TOA (X_1)	2.32	3	4	5	5.68	% (v/v)
Conc. of ethanol (X_2)	2.32	3	4	5	5.68	mol/L
Temperature (X_3)	43.2	50	60	70	76.8	°C

Where $X_1 = (\alpha_1 - 4)/1$, $X_2 = (\alpha_2 - 4)/1$, $X_3 = (\alpha_3 - 60)/10$ and α means actual value

where $C_{LA,f}$ and $C_{EL,st}$ are the concentrations of lactic acid in the feed solution and the outlet concentration of ethyl lactate in the stripping solution, respectively.

4. Central Composite Design

Central composite design (CCD) [24] was used as the methodology of experimental design for modeling and optimization of the synthesis of ethyl lactate from lactic acid by hollow fiber supported liquid membrane. The effect of three factors (TOA concentration, ethanol concentration and process temperature) and their interactions was also analyzed. The central composite design combines the vertices of the hypercubes, whose coordinates are given by a 2^n factorial design [24,25].

According to the design of the experiment, each process variable was varied in five levels, as shown in Table 2, with α, $-\alpha$ being the axial points, +1, −1 being the factorial points and 0 being the central point. In this work, the α-value of the design was 1.68. The required number of experiments for estimation of the four factors was 20. Eight experiments were referred to the factorial points. The set of axial points included six experiments. The central point was

Table 3. Central composite design factors and the response

Exp. no.	Factors			Response
	X_1	X_2	X_3	Y
1	−1	−1	−1	0
2	+1	−1	−1	2
3	−1	+1	−1	15
4	+1	+1	−1	17
5	−1	−1	+1	8
6	+1	−1	+1	7
7	−1	+1	+1	21
8	+1	+1	+1	23
9	−1.68	0	0	17
10	1.68	0	0	19
11	0	−1.68	0	0
12	0	1.68	0	22
13	0	0	−1.68	7
14	0	0	1.68	17
15	0	0	0	20
16	0	0	0	18
17	0	0	0	19
18	0	0	0	19
19	0	0	0	19
20	0	0	0	19

repeated six times for estimation of a pure error sum of squares. In addition, a second-order polynomial regression model was used for modeling the %yield of ethyl lactate. The general equation of the second order polynomial model is presented in Eq. (4).
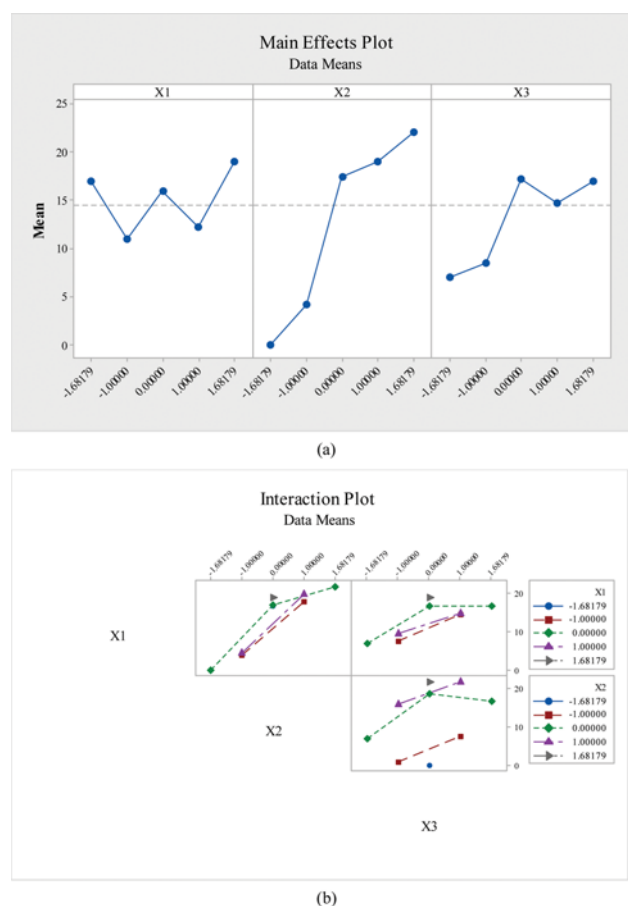
$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 \quad (4)$$

where, x_1, x_2, x_3 are the process factors, β_0 is the average value, β_1, β_2, β_3, β_{11}, β_{22}, β_{33}, β_{12}, β_{13}, β_{23} are the regression coefficients, and Y is the response. The response is the %yield of ethyl lactate. Minitab 17.0 software was used to calculate the coefficients of Eq. (4) and also to determine the significant factors and their interactions by using the analysis of variance (ANOVA). Consequently, optimization was performed by the response surface and regression model, which correlates with the significant factors.

RESULTS AND DISCUSSION

1. Central Composite Design and Analysis

The responses were evaluated in the central composite design and tabulated in Table 3. The results of three individual effects are shown in Fig. 4(a). It can be seen that the increasing of TOA concentration in the liquid membrane (X_1) results in slightly increas-

(a)

(b)

Fig. 4. Plot of the effects of concentration of TOA, concentration of ethanol and temperature on ethyl lactate yield by central composite design. (a) The main effect plots. (b) The interaction plots.

ing yield of ethyl lactate. When the ethanol concentration in the stripping solution (X_2) increased, the yield of ethyl lactate abruptly increased as well. The stripping reaction is expressed in Eq. (2). According to Le Chatelier's principle, as the ethanol concentration increases, more ethyl lactate is produced in the stripping solution [24]. In addition, the production rate of ethyl lactate increased with the increase of temperature (X_3). The increasing of temperature could accelerate the rate of esterification in the stripping solution. However, when the temperature was higher than 65 °C, %yield decreased because the liquid membrane in the hollow fiber microporous was destroyed and peeled out from micropore with feed and stripping solution.

The interactions between each factor are shown in Fig. 4(b). Minitab 16 software also calculated the coefficients that were used in the regression equation with the following expression.

$$Y = 19.055 + 0.612\, X_1 + 7.029\, X_2 + 3.062\, X_3 - 0.716\, X_1^2 - 3.191\, X_2^2$$
$$- 2.837\, X_3^2 + 0.375\, X_1 X_2 - 0.375\, X_1 X_3 - 0.125\, X_2 X_3 \quad (5)$$

The magnitude of coefficients represents the strength of the effect. The sign (+, −) means the way that it responds to the %yield of ethyl lactate. From the analysis of variance (ANOVA) in Table 4, the P-values of X_1, X_1^2, $X_1 X_2$ and $X_1 X_3$ were higher than 0.05. This means that these effects are not significant, with 95% confidence. Therefore, X_1, X_1^2, X_2^2, $X_1 X_2$, $X_2 X_3$ and $X_1 X_3$ terms can be removed from the regression model and the regression model that predicts the %yield of ethyl lactate was reduced as follows:

$$Y = 19.055 + 7.029\, X_2 + 3.062\, X_3 - 2.837\, X_3^2 \quad (6)$$

2. Optimization

The significant factors, namely the concentration of ethanol (X_2) and the temperature (X_3) for the synthesis of ethyl lactate by hollow fiber supported liquid membrane, were optimized using response surface. Figs. 5(a) and (b) show the response surface plot and contour plot, which were generated from Eq. (6). According to the observation of contour plots in Fig. 5(b), an acceptable compromise
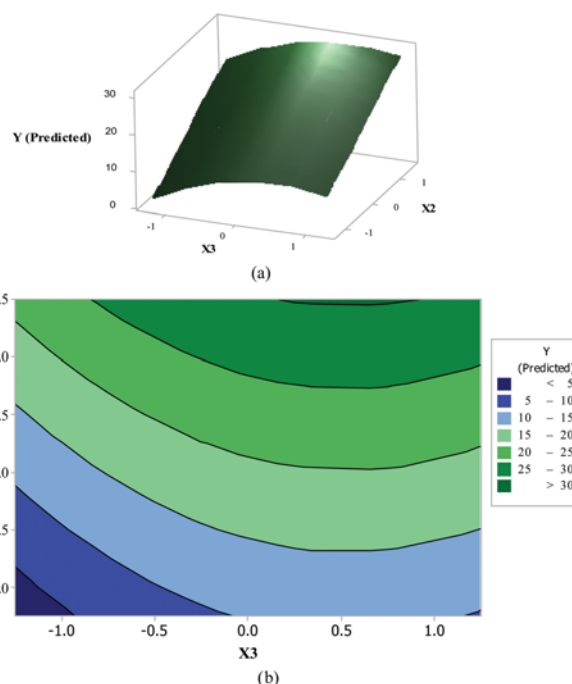

Fig. 5. Plots of the effects of ethanol concentration and temperature on the % yield of ethyl lactate (a) response surface, (b) contour plot.

was found by the criteria for %yield of ethyl lactate and operating temperature. The concentration of ethanol at 5.5 mol/L (X_2=1.5) and the temperature of 65 °C (X_3=0.5) was selected as the best operating condition because the highest yield of 30% was obtained.

3. Optimized Condition Validation

The optimized condition and yield predicted from Section 2 was validated. The concentrations of ethanol (X_2) and temperature (X_3) were fixed at optimized condition of 1.5 (5.5 mol/L) and 0.5 (65 °C), respectively, in different concentrations of TOA (X_1). Variations in

Table 4. Analysis of variance: (ANOVA)

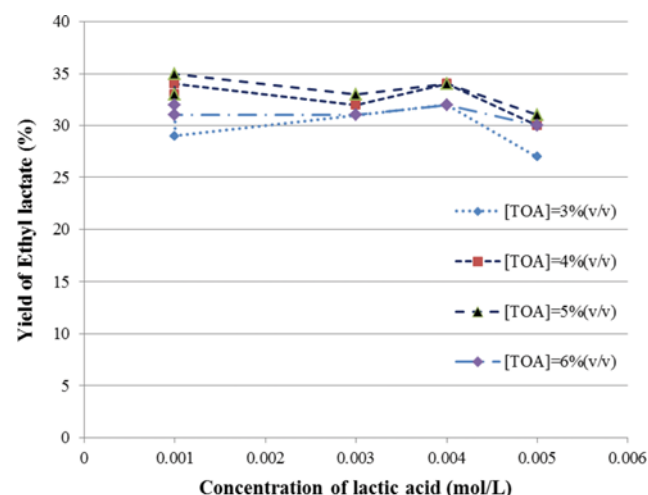| Source of variance	df	SS	MS	F	P-value
Model	9	1050.01	116.668	78.09	0.000
Linear	3	807.99	269.330	180.28	0.000
	1	5.12	5.122	3.43	0.094
	1	674.82	674.818	451.70	0.000
	1	128.05	128.048	85.71	0.000
Square	3	239.65	79.882	53.47	0.000
	1	7.39	7.391	4.95	0.580
	1	146.74	146.742	98.22	0.050
	1	116.03	116.027	77.66	0.000
Interaction	3	2.37	0.792	0.53	0.672
	1	1.13	1.125	0.75	0.406
	1	1.12	1.125	0.75	0.406
	1	0.13	0.125	0.08	0.778
Error	10	14.94	1.494		
Total	19	1064.95		R^2=0.986	

Fig. 6. Effect of concentration of lactic acid on yield of ethyl lactate while the concentration of ethanol (X_2) and temperature (X_3) were fixed at optimized condition of 5.5 mol/L and 65 °C, respectively.

the concentration of lactic acid at different concentrations of TOA are shown in Fig. 6. The results indicated that when the concentration of lactic acid increased from 0.001 to 0.005 mol/L, the yield of ethyl lactate was around 30%. This means that the optimized condition predicted by CCD and response surface is satisfactory. However, when the concentration of lactic acid exceeded 0.004 mol/L, the yield of ethyl lactate gradually decreased, unless increased the concentration of TOA.

CONCLUSIONS

The synthesis of ethyl lactate from lactic acid by using hollow fiber supported liquid membrane as the reactor was achieved. Low concentration of lactic acid was employed in the feed stream. Tri-n-octylamine (TOA) was employed as an extractor in the liquid membrane. Diluted ethanol and p-toluene sulfonic acid catalyst was co-fed in the stripping stream where esterification to ethyl lactate can occur. The experimental results were analyzed by using a central composite design (CCD), and the concentrations of ethanol and temperature were the significant factors. The optimized condition was predicted by a regression model and response surface of 5.5 mol/L and 65 $^{\circ}$C for concentrations of ethanol and temperature, respectively. Good agreement was obtained by comparing the experimental results.

ACKNOWLEDGEMENTS

REFERENCES

1. G. Schultz, *Desalination.*, **68**, 191 (1988).
2. B. Schuur, J. G. M. Winkelman and H. J. Heeres, *Ind. Eng. Chem. Res.*, **47**, 10027 (2008).
3. B. Mokhtari and K. Pourabdollah, *Chin. J. Chem. Eng.*, **23**, 641 (2015).
4. R. N. Raja Sulaiman, N. Othman and N. A. Saidina Amin, *J. Ind. Eng. Chem.*, **20**, 3243 (2014).
5. M. Sekhar, M. Kamal, K. Bhatluri, P. Saha and A. K. Ghosha, *J. Membr. Sci.*, **447**, 325 (2013).
6. S. Chaturabul, T. Wannachod, V. Mohdee, U. Pancharoen and S. Phatanasri, *Chem. Eng. Process.*, **89**, 35 (2015).
7. R. Vijayalakshmi, S. Chaudhury, M. Anitha, D. K. Singh, S. K. Aggarwal and H. Singh, *Int. J. Miner. Process.*, **52**, 135 (2015).
8. A. Gabelman and S. T. Hwang, *J. Membr. Sci.*, **61**, 159 (1999).
9. N. M. Kocherginsky, Q. Yang and L. Seelam, *Sep. Purif. Technol.*, **171**, 53 (2007).
10. N. Leepipatpaiboon, U. Pancharoen, N. Sunsandee and P. Ramakul, *Korean J. Chem. Eng.*, **31**, 868 (2014).
11. U. Pancharoen, P. Ramakul and W. Pattaweekongka, *J. Ind. Eng. Chem.*, **11**(6), 926 (2005).
12. N. Sunsandee, N. Leepipatpiboon and P. Ramakul, *Korean J. Chem. Eng.*, **30**(6), 1312 (2013).
13. N. Sunsandee, P. Ramakul, U. Pancharoen and N. Leepipatpiboon, *Sep. Purif. Technol.*, **116**, 405 (2013).
14. N. Leepipatpiboon, U. Pancharoen and P. Ramakul, *Korean J. Chem. Eng.*, **30**(1), 194 (2013).
15. P. Ramakul, T. Supajaroon, T. Prapasawat, U. Pancharoen and A. W. Lothongkum, *J. Ind. Eng. Chem.*, **15**, 224 (2009).
16. C. Gao, C. Ma and P. Xu, *Biotechnol. Adv.*, **29**, 930 (2011).
17. J. S. Bennett, K. L. Charles, M. R. Miner, C. F. Heuberger, E. J. Spina, M. F. Bartels and T. Foreman, *Green Chem.*, **11**(2), 166 (2009).
18. S. P. Tsai, R. Datta, M. Henry, Y. Halpern and J. R. Frank, *Membrane Technol.*, **109**, 12 (1999).
19. D. Yankov, J. Molinier, J. Albet, G. Malmary and G. Kyuchoukov, *Biochem. Eng. J.*, **21**, 63 (2004).
20. A. Manzak and O. Tutkun, *Can. J. Chem. Eng.*, **89**, 1458 (2011).
21. C. Scholler, J. B. Chaudhuri and D. L. Pyle, *Biotechnol. Bioeng.*, **42**, 50 (1993).
22. M. C. Porter, *Handbook of Industrial Membrane Technology,* Noyes Publications, Park Ridge, New Jersey (1990).
23. Y. S. Mok and W. K. Lee, *Sep. Sci. Technol.*, **29**, 743 (1994).
24. D. C. Montgomery, *Design and Analysis of Experiments*, Wiley (2013).
25. D. Kavak, M. Demir, B. Başsayel and A. S. Anagün, *Des. Water Treat.*, **51**, 1712 (2013).