Process simulation for the recovery of lactic acid using thermally coupled distillation columns to mitigate the remixing effect

Sung Young Kim, Dong Min Kim, and Bomsock Lee†

Dept. of Chemical Engineering, Kyung Hee University, 1732 Deogyeong-daero, Yongin 17104, Korea **Abstract**−The objective of this study was to find process simulations of the plant-wide scale lactic acid recovery pro-(Received 30 March 2016 • accepted 2 February 2017)

cess using thermally coupled distillation columns to mitigate the remixing effect. The remixing effect has been widely discussed because in a conventional column arrangement it induces a need for a significant amount of energy for repurification in lactic acid recovery processes. One way to overcome high energy consumption is by using thermally coupled distillation columns. This paper suggests and compares two types of thermally coupled distillation columns applied to the plant-wide scale lactic acid recovery process for removing the remixing effect considering a heavy organic impurity and lactic acid oligomerization in the process. The equilibrium stage model based on the RADFRAC module of Aspen Plus was employed for simulating the thermally coupled distillation columns. Simulation results showed that thermally coupled distillation columns can eliminate the remixing effect and reduce energy consumption compared to conventional lactic acid recovery processes.

Keywords: Lactic Acid Recovery Process, Thermally Coupled Distillation, Aspen Plus

INTRODUCTION

Over the last few decades, much of the chemical process research has focused on process intensification to save energy. Process intensification, which uses an integrated multifunctional unit to replace single function units in chemical processes, has two general approaches. The first is the heat integration method in which the hot process streams exchange heat with cold process streams by increasing pressure at one part of the column. Examples of the heat integration method include multi-effect distillation [1-4], vapor recompression columns [5,6] and dividing wall column [7,8]. The

† To whom correspondence should be addressed. E-mail: bslee@khu.ac.kr

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necting several towers. When streams are mixed at the feed, top, and bottom of conventional column arrangements, problems exist in terms of the inefficiency produced by thermodynamic irreversibility [9]. This is called the remixing effect. It is defined by an occurrence when the concentration profile for one component reaches into its highest purity in some tray and it starts to dilute because of an increase in concentration of the other component (presented in Fig. 1) [10]. Thus, a large amount of energy is consumed during the re-separation process. This phenomenon occurs when separating more than a ternary mixture. The remixing effect could be solved by using thermal coupling between columns without a reboiler and condenser. If thermally coupled distillation columns are applied to a process, the operating costs can be reduced by increasing the

other approach uses a thermally coupled distillation column by con-

Fig. 2. Comparison of (a) a conventional sequence and (b) a thermally coupled distillation system [11].

energy efficiency. Fig. 2 shows why thermally coupled distillation columns are more efficient than conventional column arrangements. Thermally coupled distillation columns prevent the need for repeated separations, as shown in Fig. 2 [11]. The types of thermally coupled distillation columns include partially thermally coupled distillation columns and fully thermally coupled distillation columns. Studies have shown that the thermally coupled distillation columns can achieve energy savings of 30% greater than conventional column arrangements [12-14].

Lactic acid (2-hydroxypropionic acid) is the most widely occurring hydroxy-carboxylic acid. It is used in various industrial fields, including biodegradable polymers and plant growth regulators, and is a common chemical intermediate. In addition, lactic acid has significant potential as a platform chemical. The yearly production of lactic acid is expected to exceed 259,000 metric tons [15]. Generally, lactic acid can be produced by chemical synthesis or fermentation. Lactic acid obtained from chemical synthesis is cheap but is mixed with D and L type lactic acid. Mixed lactic acid is not useful in the production degradable polymers like polylactic acid (PLA) and other applications. PLA is environmentally friendly and biocompatible. It can replace non-degradable plastics such as polyethylene, polystyrene and polypropylene. For these reasons, demand for PLA is expected to increase [16]. The useful form of PLA is the L-lactic acid form. Since both the L and D isomers of lactic acid are formed via non-biological chemical synthesis routes, fermentation is the more favorable method by which to produce lactic acid, because only one type of lactic acid isomer is produced. Fermentation, however, has some drawbacks. Undesired byproducts are produced, such as calcium sulfate [17] and other organic acids, after fermentation step, which requires removal of these byproducts. Extraction, ultrafiltration, reverse osmosis and adsorption are used for purification processes of lactic acid [17]. However, these processes result in low lactic acid recovery and have the following limitations. In solvent extraction [18], a relatively large amount of solvent is required and high purity lactic acid is difficult to obtain. Ultrafiltration [19] and osmosis [20] are not suitable for a large amount of raw material, and efficiency declines in parallel with a fall in membrane performance. Adsorption [21] has several problems, including particle selectivity, capacity, and regeneration. Reactive distillation, described as follows, has been proposed to alleviate these limitations. First, the lactic acid is reacted with methanol and methyl lactate is produced. Methyl lactate can be more easily purified by distillation. Then methyl lactate is sent to a hydrolysis column and recovered by the hydrolysis reaction. The advantages of this purifi-

Fig. 3. Block diagram of the lactic acid recovery process described in U.S. patent [22].

cation method are the ability of handling large capacities of raw materials and achieving high lactic acid recovery [17]. The block diagram of this method is described in Fig. 3 [22].

In this study, we extended the lactic acid recovery process to plant-wide scale configurations from previously presented thermally coupled distillation columns [23]. Thermally coupled distillation system has one condenser and reboiler only in the second column (Fig. 2(b)). This system provides choices of special interest for the separation of ternary mixtures because of their potential energy savings [24]. Total capital costs of the lactic acid recovery process using the thermally coupled distillation columns may be reduced because it uses fewer pieces of major equipment than the conventional columns [24]. Thermally coupled distillation columns can be more efficient to supply the feed at saturated liquid phase because of heat degradation and save total annual cost more than other configurations [25]. We added two more columns for removing water and methanol from the previous design [23], and we also considered a heavy organic impurity and lactic acid oligomerization. Partially thermally coupled distillation columns and fully thermally coupled distillation columns were applied for eliminating the remixing effect and reducing energy consumption in the process and compared to see which is appropriate for the lactic acid recovery process. Vapor-liquid and vapor-liquid-liquid equilibria were calculated using Aspen Plus with UNIQUAC.

PROCESS STATEMENT

1. Conventional Column Arrangements

More than 95% of the petrochemical and refining processes consists of a distillation process that consumes a significant amount of

Fig. 4. (a) Direct sequence, (b) indirect sequence, (c) prefractionator arrangement, and (d) distributed sequence [28].

energy in the evaporation/condensation process [26]. The operating cost of a distillation column is one of the important factors that determines the profitability of distillation processes. Shah and Agrawal suggest that by rearranging the distillation sequence, it is possible to reduce the energy cost by millions of dollars every year [27]. It is necessary to understand the arrangement of various distillation columns and select the appropriate distillation column arrangement to reduce the energy cost. Direct sequence, indirect sequence, distributed sequence and prefractionator arrangement are generally used in conventional column arrangements. These configurations are shown in Fig. 4 [28]. Direct sequence separates light component at top of the first column. Intermediate boiling point components and heavy component are sent to next columns and heavy component is separated. The indirect sequence is the opposite type of direct sequence, as it separates heavy component at bottom of the first column. Intermediate boiling point components and light component are sent to next columns and light component is separated. Prefractionator arrangement and distributed sequence are similar to each other. They do not completely separate one component at the first column, and then two split streams are sent to next columns from the first column. After separating in first column, distributed sequence send streams to two different columns while prefractionator arrangement sent components to one column. The advantage of these arrangements is that low-quality energy can be used because they do not separate mixtures to high purity at the first column. However, distributed sequence needs additional column and heat exchanger compared with the other arrangements.

2. Nonconventional Column Arrangements

Many studies have tried to reduce the operating cost of distillation columns by a variety of methods. For example, there are multieffect columns [1-4] and heat pump-assisted distillation columns [5,6]. Recent research into thermally coupled distillation columns has increased. Thermally coupled distillation columns are accomplished by direct contact of materials flowing between the columns [29]. The thermally coupled distillation columns are shown in Fig. 5 [28] and are designated as the side rectifier, side stripper and Petlyuk column. The side rectifier and side stripper are connected to the side of the main column. The side columns do not have a reboiler or condenser. These columns are called partially thermally coupled distillation columns. The Petlyuk column is similar to the distributed sequence or prefractionator arrangement, and does not have a reboiler or a condenser at the first column. Vapor and liquid streams are exchanged between the first column and second column. Since one column is completely connected to the other without a reboiler and a condenser, this column is called a fully thermally coupled distillation column.

3. Design Method of Distillation Systems

Conventional arrangements have the number of stages, reflux ratio and heat load of the reboiler as design parameters, but thermally coupled distillation columns have more design parameters than conventional arrangements. The reason is that in thermally coupled distillation columns two or more columns are connected to each other. Liquid split ratio, vapor split ratio and side-product flow rate are variables needed additionally when thermally coupled distillation columns are used. Thermally coupled distillation columns have more degrees of freedom than conventional arrangements, but the initial design procedures are similar.

For design of thermally coupled distillation columns, some initial estimates are used based on a conventional arrangement. The total number of stages is the same or less than the conventional arrangement. Total duties of reboiler are about 70% compared to conventional arrangement. Vapor and liquid splits are equal. These rules are for initial convergence. For the optimization, much adjustment is needed. Some of the shortcut methods are introduced below.

The Fenske equation is used for calculating the minimum theoretical number of stages at the condition of total reflux [28], and the Underwood equation is used for calculating the minimum reflux ratio for multicomponent distillation [28]. The feed location is decided using an empirical equation developed by Kirkbride [28]. V_{min} diagram method simply shows how the minimum energy consumption is related to the feed-component distribution [28]. This method is introduced by Halvorsen and Skogestad [30]. It is based on Underwood equations with assumptions of constant molar flows, constant relative volatilities and infinite number of stages. V_{min} is calculated by using feed composition, liquid fraction of feed, Kvalues and, recovery of component. It can present a V_{min} as a function of vapor flow rate per feed flowrate (V/F) and flowrate of the top product per feed flowrate (D/F) using each of the points where recovery of component is 1 or 0. We found the initials from the above methods and optimized by varying one variable with fixing others from the initials.

Fig. 5. Partially thermally coupled distillation system [28] (a) side stripper, (b) side rectifier and, (c) fully thermally coupled distillation system Petlyuk column.

System	Kinetic model
Methyl lactate [31]	$r = m_{cat}$ (ka _{LAC} a _{MeOH} – k _a _{MeLC} a _{H₂O)} $k_f = 2.98 \times 10^4 \exp(-51300/RT)$ $k = 2.74 \times 10^2$ exp(-47200/RT)
Dilactate [32]	$r = m_{cat} (k_{A_{LAC}}x_{LAC} - k_{r}x_{L2}x_{H2O})$ $k_f = 1.1 \times 10 \exp(-52000/RT)$ $k_r = 5.54 \times 10 \exp(-52000/RT)$
Trilactate [32]	r=m _{cat} (k x_{L2} x _{LAC} -k _r x _{L3} x _{H₂O)} $k_f = 4.56 \times 10^{-4}$ exp(-50800/RT) $k_r = 2.28 \times 10 \exp(-50800/RT)$

Table 1. Kinetic data for the esterification and oligomerization reactions

PROCESS SIMULATION

Esterification, hydrolysis with methanol and oligomerization reaction of the lactic acid can be represented by the following reaction sequence:

CH₃CH(OH)COOH₊ CH₃OH
\n(lactic acid) (method)
\n
$$
\xleftarrow{k_{f,1}} C H_3CH(OH)COOCH_3 + H_2O
$$
\n(20014)
\n(300)
\n
$$
CH_3CH(OH)COOH + CH_3OH(OH)COOH
$$

$$
\frac{k_{32}}{\left(\text{lactic acid}\right)} \qquad \text{(lactic acid)} \tag{9}
$$
\n
$$
\frac{k_{33}}{\left(\text{dilactate}\right)} \qquad \text{(lactic acid)} \tag{9}
$$

$$
C_6H_{10}O_5 + CH_3CH(OH)COOH
$$
\n(dilactate)
\n
$$
\xrightarrow[k_{53}]{L_{53}H_{14}O_7} + H_2O
$$
\n
$$
\xrightarrow[k_{53}]{L_{53}H_{14}O_7} + H_2O
$$
\n
$$
\xrightarrow[k_{53}]{(trilactate)}^{(10)}
$$
\n(10)

Reactions only occurred in reactive sections with catalysts. To simulate these reactions, kinetic parameters in Table 1 were obtained from data using solid catalysts. Kinetic equations are represented

Table 2. Boiling point temperatures

	Estimated value	Experimental value	
Component	Boiling point $({}^{\circ}C)$		
Methanol	64.53	64.7	
Water/Methyl lactate	99.86	99	
Water	100.02	100	
Methyl lactate	144.84	144-145	
Lactic acid	120.7 (@ 12 mmHg)	122 (@ 12 mmHg)	

Table 3. Composition and conditions of the feed stream

in pseudo homogeneous form. Table 1 shows the esterification and oligomerization reaction kinetic rate. The oligomerization reaction can occur in the reactive sections the same as the esterification. All reaction kinetics are represented as a function of the catalyst-weight (m_{cat}) . When using Aspen Plus, a commercial process simulator, we assumed that the solid catalyst occupies 50% of the tray holdup volume and that the density of the catalyst is 770 kg/m³, which was used to calculate the holdup volume [17].

To calculate the equilibrium composition of the vapor-liquid and vapor-liquid-liquid, the UNIQUAC activity coefficient model was used. If parameters were not in the database, they were calculated by the UNIFAC model. The Hayden-O'Connell second virial coefficient was used for the vapor phase. Association parameters in Aspen Plus were used to calculate fugacity coefficients. Table 2 shows the normal boiling point components calculated from the binary interaction parameters. The conventional lactic acid recovery process is expressed in Fig. 6. A feed stream produced by fermentation was fed into the preconcentrator. The excess water hindered esterification and as did impurities included in the feed (Table 3 shows compositions of the feed stream.). In the preconcentrator, excess water was removed and left in the top product, while lactic acid and the heavy impurity were sent to the esterification column. The temperature of the bottom product stream was

Fig. 6. Modeling of the conventional process [17] by Aspen Plus.

Partially thermally coupled		
Trays	88, 21	
Feed stage	23, 10	
Recycle stage	1, 10	
Condenser type	Total	
Reboiler type	Kettle	
Pressure	1	
Fully thermally coupled		
Trays	91	
Feed stage	8	
Liquid recycle stage	89	
Vapor recycle stage	24	
Condenser type	Total	
Reboiler type	Kettle	
Pressure	ı	

Table 4. Conditions of the design of thermally coupled distillation columns

lower than 80 °C to prevent the production of oligomers. The lactic acid, which was sent to the esterification column, was esterified with methanol and the heavy impurity was removed at the bottom of the esterification column. The methyl lactate, i.e., esterified lactic acid, was hydrolyzed with water in the hydrolysis column, and a mixture of water and lactic acid were obtained as bottom products. Water and methanol were sent to the recovery column and the methanol was recycled into the esterification column. Fig. 6 shows the process flow diagram of the lactic acid recovery process simulated using Aspen Plus [17]. Energy inefficiencies caused by the remixing effect are the focus of this paper. Energy consumption for the entire process was 1,762.601kW, and the portion of the hydrolysis and recovery column of energy consumption was 48.2%. In the upper section of the hydrolysis column, the mole fraction of water went through a maximum then decreased in the distillate. Large energy consumption was required due to the re-separating mixture. Thermally coupled distillation columns were applied to the hydrolysis column and the recovery column to mitigate the remixing effect.

Composition and conditions of the lactic acid product were maintained to compare the energy consumption of the conventional process, and two types of thermally coupled distillation columns (side stripper and Petlyuk column) were applied to the process to show

Fig. 8. Modeling of fully thermally coupled distillation system by Aspen Plus.

which is more suitable for the process. The conditions of the design are shown in Table 4. The reactive zone was placed in 2-20 stages in the esterification column and 5-67 stages in the hydrolysis column in the partially thermally coupled distillation system, in 30- 90 stages in the esterification column and 1-66 stages in the hydrolysis column in the fully thermally coupled distillation system.

RESULTS AND DISCUSSION

The equilibrium stage model based on the RADFRAC module of Aspen Plus was used to simulate the conventional process and two types of thermally coupled distillation columns. Either condenser or reboiler was removed and a hydrolysis column and recovery column were connected via vapor and liquid streams. Locations of product streams of the partially thermally coupled distillation columns were the same as with the conventional process. In the fully thermally coupled distillation columns, methanol, lactic acid and water were obtained from the top (stream no. 11), bottom (stream no. 8) and side product (stream no. 10), respectively (process flow diagrams are shown in Figs. 7 and 8). A comparison of the product streams (which contain lactic acid) of the conventional process, the partially thermally coupled distillation columns and the fully thermally coupled distillation columns are shown in Table 5. The mole fraction of lactic acid in the product stream of fully thermally coupled distillation columns was 0.578 and was lower than the conventional process. The mole fraction of lactic acid in the product stream of the partially thermally coupled distillation columns was 0.580 and was similar to the conventional process. This result was affected by the composition of the stream which was sent

Fig. 7. Modeling of partially thermally coupled distillation system by Aspen Plus.

Component	Conventional	Partially thermally coupled	Fully thermally coupled
Lactic acid	0.580	0.580	0.578
Dilactate	0.01	0.01	0.01
Methyl lactate	0.002	0.002	0.002
Water	0.408	0.408	0.408

Table 5. Composition of product streams

to the hydrolysis column (stream no. 6). Hydrolysis was disturbed in the hydrolysis column due to a higher purity of methanol than the conventional column in stream no. 6. Therefore, the purity of lactic acid in the product stream (stream no. 8) was slightly lower than the conventional column. The mole fraction of methanol in stream no. 6 is shown in Table 6. Results of each stream for the conventional process and partially and fully thermally coupled distillation columns are shown in Tables 7, 8 and 9.

Results of each column for the conventional system, the partially thermally coupled distillation system and the fully thermally coupled distillation system are shown in Table 10. Energy consumptions of these systems were compared in Table 11. The reboiler duty of the hydrolysis column and recovery column in partially thermally coupled distillation columns was 612.793 kW, which was 27.8% lower than the conventional process. The reboiler duty of hydrolysis column and recovery column in the fully thermally coupled distillation columns was 560.776 kW, which was 34.0% lower than the conventional process. Two types of thermally coupled distillation columns reduced the energy consumption by about 30% compared to the conventional columns. Energy consumption was

shown to be more efficient when using thermally coupled distillation columns. Mitigation of the remixing effect is the same as operating with a reversible split. In conventional columns, the reflux flow must be in equilibrium with the vapor flow leaving from the top stage to operate a reversible split. Equilibrium was impossible unless the liquid product flow rate was zero in the conventional column. Thermally coupled distillation columns made streams in equilibrium. Due to these results, thermodynamic inefficiencies were removed and energy consumption was reduced (conventional columns and thermally coupled distillation columns are compared in Fig. 9). In the beginning of stages on Fig. 9, we highlighted that components were completely separated in the beginning of stages of the thermally coupled column and were diluted in the conventional column. This showed that the remixing effect was removed when the thermally coupled columns applied.

The reboiler duty of the fully thermally coupled distillation columns was lower than the partially thermally coupled distillation columns because of the lower vapor flow rate in the hydrolysis column. Flowrates in the columns are compared in Table 12. Fully thermally coupled distillation columns reduced energy consumption in the reactive distillation since vapor and liquid streams between the hydrolysis column and the recovery column replaced reboiler and

Table 7. Stream results of the conventional system

Table 8. Stream results of the partially thermally coupled distillation system

Table 9. Stream results of the fully thermally coupled distillation system

condenser. Therefore, the reboiler duty of fully thermally coupled distillation columns was lower than the reboiler duty of the partially thermally coupled distillation columns.

CONCLUSION

An equilibrium stage model based on the RADFRAC model of

Conventional system				
	Preconcentrator	Esterification	Hydrolysis	Recovery
Distillate rate [kmol/hr]	39.834	26.464	33.658	16.662
Reflux ratio	0.1445	0.0815	0.2418	0.9517
Reboiler duty [kW]	583.439	330.098	520.453	328.611
Condenser duty [kW]	548.846	349.608	456.036	319.597
Partially thermally coupled distillation system				
	Preconcentrator	Esterification	Hydrolysis	Recovery
Distillate rate [kmol/hr]	39.834	26.464	43.658	16.662
Reflux ratio	0.1445	0.0814	0.2287	2.302
Reboiler duty [kW]	583.439	330.098	545.458	65.5766
Condenser duty [kW]	548.846	349.588		540.733
Fully thermally coupled distillation system				
	Preconcentrator	Esterification	Hydrolysis+Recovery	
Distillate rate [kmol/hr]	39.834	26.464	16.662	
Reflux ratio	0.1445	0.0831	2	
Reboiler duty [kW]	583.439	330.098	560.776	
Condenser duty [kW]	548.846	349.859	489.776	

Table 10. Column results of the conventional and nonconventional systems

Table 11. Comparison of reboiler duty

Aspen Plus was applied for process simulations of the plant-wide scale lactic acid recovery process by two types of thermally coupled designs considering a heavy organic impurity and lactic acid oligomerization. The UNIQUAC-HOC model was used to calculate the activity coefficient and fugacity coefficient. Two types of thermally coupled distillation systems reduced the energy consumption by more than 30% relative to the conventional column arrangement, and the fully thermally coupled distillation had the lowest energy consumption because the fully thermally coupled

Fig. 9. Comparison of conventional columns and thermally coupled distillation columns.

Partially thermally coupled		Fully thermally coupled		
Stage	Liquid flow rate (kmol/hr)	Vapor flow rate (kmol/hr)	Liquid flow rate (kmol/hr)	Vapor flow rate (kmol/hr)
	38.209	55.018	33.324	49.986
	37.972	54.871	33.323	49.986
4	37.594	54.634	33.323	49.985
	37,002	54.256	33.322	49.985

Table 12. Comparison of flowrate in the columns

distillation used vapor and liquid streams between the hydrolysis column and the recovery column instead of using reboiler and condenser, and had lower vapor flow rate in the hydrolysis column than the partially thermally coupled distillation. The reboiler duty of the fully thermally coupled distillation eliminated 34% of the energy consumption. The thermodynamic inefficiency of the remixing effect in the lactic acid recovery process was removed and energy consumption was reduced. An analysis of energy consumption showed that applying the thermally coupled distillation system for the plant-wide configurations of the lactic acid recovery process is more efficient than the conventional column arrangement.

REFERENCES

- 1. M. Han and S. Park, J. Process Control, **6**, 247 (1996).
- 2. S. Hasebe, M. Noda and I. Hashimoto, Comput. Chem. Eng., **23**, 523 (1999).
- 3. H. K. Engelien and S. Skogestad, Comput. Chem. Eng., **28**, 683 (2004).
- 4. A.H. Al-Elg and A. Palazoglu, Comput. Chem. Eng., **13**, 1183 (1989).
- 5. J. A. Ferre, F. Castells and J. Flores, Ind. Eng. Chem. Process Des. Dev., **24**, 128 (1985).
- 6. O. Annakou and P. Mizsey, Heat Recov. Syst. CHP, **15**, 241 (1995).
- 7. H. J. Cho, S. H. Choi, T. Y. Kim, J. Kim and Y. Yeo, Korean J. Chem. Eng., **32**, 1229 (2015).
- 8. Y. H. Kim, Korean J. Chem. Eng., **33**, 2513 (2016).
- 9. F. B. Petlyuk, V. M. Platonov and D. M. Slavinskii, Int. Chem. Eng., **5**, 555 (1965).
- 10. M. A. Schultz, D. G. Stewart, J. M. Harris, S. P. Rosenblum, M. S. Shakur and D. E. O'Brien, Chem. Eng. Prog., **98**, 64 (2002).
- 11. N. V. D. Long and M. Lee, Asia‐Pac. J. Chem. Eng., **7**, S71 (2012).
- 12. A. C. Christiansen, S. Skogestad and K. Lien, Comput. Chem. Eng., **21**, S237 (1997).
- 13. L. Królikowski, AIChE J., **33**, 643 (1987).
- 14. Z. T. Fidkowski and R. Agrawal, AIChE J., **47**, 2713 (2001).
- 15. F. A. C. Martinez, E. M. Balciunas, J. M. Salgado, J. M. D. González, A. Converti and R. P. D. S. Oliveira, Trends Food. Sci. Technol., **30**, 70 (2013).
- 16. S. C. Park, S. M. Lee, Y. J. Kim, W. S. Kim and Y. M. Koo, KSBB J., **21**, 199 (2006).
- 17. C. Y. Su, C. C. Yu, I. L Chien and J. D. Ward, Ind. Eng. Chem. Res., **52**, 11070 (2013).
- 18. W. Zihao and Z. Kefeng, Biotechnol. Bioeng., **47**, 1 (1995).
- 19. M. I. Gonzalez, S. Alvarez, F. Riera and R. Alvarez, J. Food Eng., **80**, 553 (2007).
- 20. M. K. H. Liew, S. Tanaka and M. Morita, Desalination, **101**, 269 (1995).
- 21. R. L. Evangelista and Z. L. Nikolov, Appl. Biochem. Biotechnol., **57**, 471 (1996).
- 22. M. C. M. Cockrem and P. D. Johnson, US Patent, 5,210,296 (1993).
- 23. D. S. Woo, Y. M. Cho, B. Kim, H. D. Hwang and M. Han, Korean Chem. Eng. Res., **48**, 342 (2010).
- 24. S. Hernandez and A. Jumenez, Comput. Chem. Eng., **23**, 1005 (1999).
- 25. M. Khalifa and M. Emtir, Clean. Techn. Environ. Policy, **11**, 107 (2009).
- 26. S. Hernández, J. G. Segovia-Hernández and V. Rico-Ramírez, Energy, **31**, 2176 (2006).
- 27. V. H. Shah and R. Agrawal, AIChE J., **56**, 1759 (2010).
- 28. R. Ashrafian, Using dividing wall columns (DWC) in LNG production, M.S. Thesis, Norwegian University of Science and Technology, Trondheim, Norway (2014).
- 29. K. A. Amminudin R. Smith, D. C. Thong and G. P. Towler, Chem. Eng. Res. Des., **79**, 701 (2001).
- 30. I. J. Halvorsen and S. Skogestad, Ind. Eng. Chem. Res., **42**, 596 (2003).
- 31. M. T. Sanz, R. Murga, S. Beltrán, J. L. Cabezas and J. Coca, Ind. Eng. Chem. Res., **43**, 2049 (2004).
- 32. N. S. Asthana, A. K. Kolah, D. T. Vu, C. T. Lira and D. J. Miller, Ind. Eng. Chem. Res., **45**, 5251 (2006).