Research paper

Process intensification of esterification reaction for the production of propyl butyrate by pervaporation

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Abstract

Pervaporation is a membrane separation process vastly used for purification in chemical and allied industries. Esterification reaction can be intensified and enhanced by coupling with pervaporation reactor (PVR). Polyvinyl alcohol (PVA)/polyethersulfone (PES) composite membrane was used for the pervaporation coupled esterification reaction study. Esterification of butyric acid with n-propanol was taken as a model reaction for the study and to test the performance of pervaporation reactor. Catalyst p-toluenesulfonic acid was used for the esterification reaction. The effects of various reaction parameters on conversion of butyric acid such as reaction temperature, initial molar ratio of n-propanol to butyric acid, catalyst loading and reaction time were studied. Experimental results show that the increase of temperature, initial molar ratio, and catalyst concentration enhance the conversion of butyric acid considerably. The highest conversion of 96.41% was obtained at temperature 353 K, molar ratio of 2 and catalyst loading of 2.5%w/w at reaction time of 420 minutes. PVA/PES membrane used in the experiments shows the good activity and hydrophilicity and plays a vital role for enhancing the conversion by selectively removing water. Pervaporation coupled esterification shows the better choice over the conventional route for the production of esters. This technique is environment friendly and energy intensified approach as it reduces pollution and energy requirement.

1. Introduction

Energy consumption in the world increased tremendously over the recent years because of human being and population's and daily needs. For sustainable development, there must be minimum energy consumption giving maximum benefits to human life and environment. This can be achieved by using clean, green, and renewable energies in industries and can be minimizing energy consumption by using process intensification, hybrid technology, novel equipments, and techniques that can be transformed energy into clean, safer, and environmental friendly energy [1]. The separation and purification technology has the advantages to produce useful products or to recover useful materials from the waste by the separation processes like reactive extraction, adsorption, and pervaporation [2–7]. These separation processes contribute in major areas of separation in chemical and its allied industries. Esters are very important class of chemicals used in human day to day life as it contains aroma. Organic esters have many important applications in chemical and allied industries such as in food industries for flavor and fragrance, as solvents, plasticizer in polymer industries, as insulator in power industries [8–10]. Esters are formed by esterification reaction between acids and alcohols in presence of homogeneous catalyst such as H_2SO_4, HI, HCl or heterogeneous catalyst such as Amberlyst, Dowex resins [8,11–15]. Esters can be produced in batch, semibatch and continuous mode of operation [16,17]. Esters were also produced in various designed reactors and processes such as conventional distillation, reactive distillation (RD), micro reactor and packed bed reactor (PBR) [18–20]. Distillation and packed bed reactors consumed high energy depend on vapor–liquid equilibria of the system and required number of separation units for the product separation and handling the azeotrope. Alternative to these methods, pervaporation was used for ester production because of simple design, less energy consumption

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Nomenclature

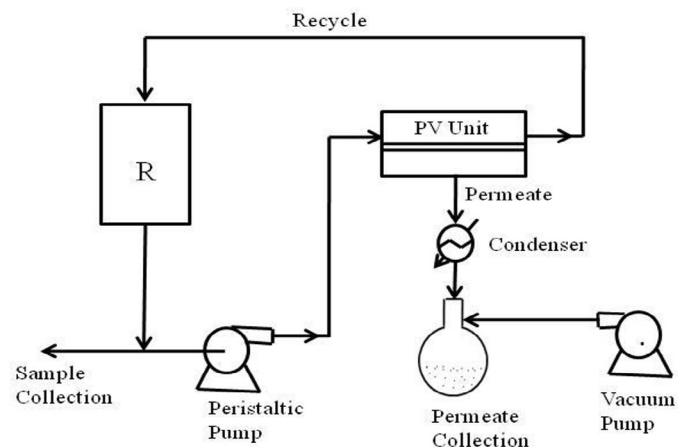|	
A	Butyric acid
B	n-Propanol
E	n-Propyl butyrate
W	water
k_1	forward reaction rate constant (lit.mol^{-1}.hr^{-1})
k_2	backward reaction rate constant (lit.mol^{-1}.hr^{-1})
J	flux through the membrane (Kg.m^{-2}.hr^{-1})
W_P	weight of water collected (Kg)
A_P	effective membrane area (m^2)
Δt	time interval difference (hr)
MR	molar ratio (n-Propanol/Butyric acid)
CL	catalyst loading (wt%)
T	temperature (K)
BR	batch reactor
PVR	pervaporation reactor
PVA/PES	polyvinyl alcohol/polyethersulfone
[BA]	concentration of butyric acid (mol.lit^{-1})
[PB]	concentration of n-propyl butyrate (mol.lit^{-1})
C_W	concentration of water (mol.lit^{-1})

Fig. 1. Lab scale experimental set up of esterification reaction coupled with pervaporation reactor.

1.7 and 2), catalyst loading (1, 1.5, 2 and 2.5%w/w) and reaction time on conversion of butyric acid were studied.

2. Materials and methods

2.1. Chemicals and reagents

Butyric acid (99% purity) and oxalic acid (99.8% purity) was supplied by S. D. Fine Chem Ltd., Mumbai, India and n-propanol (99% purity), p-toulenesulfonic acid (98% purity), sodium hydroxide pellets (EMPARTA) and phenolphthalein indicator were supplied by Merck India Ltd., Mumbai, India. In this study, p-toulenesulfonic acid is used as catalyst which is white solid in nature. It is a strong acid having sulfonic group attached to the ring. p-Toluenesulfonic acid is soluble in water, most of the alcohols and other polar solvents. Polyvinyl alcohol (PVA)/ Polyethersulfone (PES) composite membrane was supplied by Permionics Membranes Pvt. Ltd., Baroda, India. All purchased chemicals and reagents were used without pretreatment and purification.
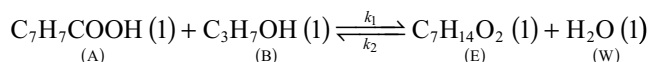
2.2. Experimental set up

Esterification reactions of butyric acid with n-propanol coupled with pervaporation reactor and without pervaporation were carried out in batch mode of operation. Experimental set up of the reaction is shown in Fig. 1. Reactor (R) made up of stainless steel (MOC, SS-316) surrounded by jacket having capacity of three liter volume was used as a batch reactor. Heating was provided by heating coil placed at the bottom of the reactor, and temperature of the reaction was sensed by the sensor and controlled by the PID (Proportional-Derivative-Integral) controller. The resolution of temperature is 0.1°C and accuracy of temperature controller is ±0.5°C. Reactor (R), peristaltic pump, pervaporation (PV) unit, vacuum pump and condenser (with attached chiller) were the major components of the experimental set up. Pervaporation coupled esterification experiments were conducted in batch reactor and pervaporation reactor (PVR). Reactor (R) served both as batch reactor and pervaporation reactor. By switching off peristaltic pump and vacuum pump, reactor acted as a batch reactor and by switching

and can operate beyond vapor–liquid equilibrium and can easily handle azeotropes [21–23].

Pervaporation is extensively used in chemical industries for separation of chemicals. Pervaporation coupled with esterification reaction is energy intensified approach as it uses less energy consumption compared to conventional distillation, reactive distillation column (RDC) and packed bed reactor (PBR). Nowadays, membrane reactors played vital role in separation and purification process because of high selectivity of membrane and it does not depend on vapor–liquid equilibrium [24]. Esterification is reversible and equilibrium limited reaction and hence conversion of reactants was limited because esterification reaction is thermodynamically equilibrium in nature. Pervaporation could drive the equilibrium reaction such as esterification, synthesis of methylisobutyl ketone and etherification [25–27]. Pervaporation can enhance the conversion of acid because of one of the product (water or ester) of the esterification reaction continuously removed by the membrane [28,29]. Polyvinyl alcohol (PVA) and its composite catalytic membranes have several advantages in pervaporation for esterification and dehydration of solvents because of high hydrophilicity, high flux and less swelling [30–33].

In the present study, butyric acid and n-propanol were taken as model system for esterification reaction coupled with pervaporation. Polyvinyl alcohol (PVA)/Polyethersulfone (PES) composite membrane was used for the study. Esterification reaction was catalyzed by using catalyst p-toluenesulfonic acid. Effect of various parameters such as reaction temperature (323 K, 333 K, 343 K and 353 K), molar ratio (n-propanol/butyric acid = 1, 1.3,

on both the pumps, reactor acted as pervaporation reactor. Pervaporation unit consists of membrane test cell where polyvinyl alcohol (PVA)/polyethersulfone (PES) composite type membrane was used in membrane test cell (size of test cell: 240 mm × 180 mm × 25 mm, and MOC of test cell SS-316) with effective membrane area 0.0155 m². Liquid esterification reaction was pumped by using peristaltic pump to the pervaporation unit. Vacuum was applied at the permeate side of the membrane by using vacuum pump and condenser was used to condense the permeate vapors.

2.3. Reaction and analysis

Pervaporation aided esterification of butyric acid with n-propanol was carried out in batch and pervaporation coupled reactor (PVR). Required amount of butyric acid and catalyst p-toulenesulfonic acid were charged to the reactor (R) and heated to the desired temperature of the reaction. Then required amount of n-propanol was added to the reactor. Liquid exit from the reactor having butyric acid, n-propanol, propyl butyrate and water was continuously pumped by the peristaltic pump at constant speed of 80 RPM to the pervaporation unit (PV unit) of membrane test cell. Water was continuously removed from the reaction by the PVA/PES composite membrane and the recycle containing butyric acid, n-propanol and propyl butyrate was sent back to the reactor. Permeate side pressure was 300 mmHg. Chiller temperature was set at 7°C. The permeate vapor was condensed by liquid water flowing at 7°C through the condenser. Overall esterification reaction is described as:

$$\underset{(A)}{C_7H_7COOH\,(1)} + \underset{(B)}{C_3H_7OH\,(1)} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{(E)}{C_7H_{14}O_2\,(1)} + \underset{(W)}{H_2O\,(1)}$$

where k_1 and k_2 are the forward and backward reaction rate constants. Sodium hydroxide (NaOH) solution of normality 0.125 N was made and standardized with 0.1 N oxalic acid. Shimadzu (model AW220) weighing balance was used to weigh solid NaOH with an accuracy of 0.1 mg. Reaction sample of 3 ml was withdrawn from the reactor at each specified time interval in 10 ml vial and immediately placed in ice bath to prevent further reaction. Permeate sample was collected and withdrawn at every hour of time. Each sample was then titrated thrice with 0.125 N NaOH and average value was taken for the calculation of conversion of butyric acid. The conversion of butyric acid at any time was calculated by using the following equation:

$$Conversion(\%) = \frac{C_{A0} - C_A}{C_A} \tag{1}$$

where C_{A0} and C_A are the initial concentration and concentration at reaction time 't' of butyric acid. The equilibrium conversion of the reaction was calculated by withdrawing the sample after 10 hours where the reaction is almost in equilibrium. The performance of PVA/PES membrane is expressed in terms of water flux (J) by the following equation:

$$J = \frac{W_P}{A_M \Delta t} \tag{2}$$

where W_P is the weight of permeate collected in time Δt and A_M is the effective area of the membrane.

3. Results and discussion

Following the discussion provides the detailed study of the effect of various reaction parameters such as temperature (T), initial molar ratio (MR) of the reactants and catalyst loading (CL) on the conversion of butyric acid.

3.1. Effect of reaction temperature

The study of the effect of temperature on conversion is one of the important parameters of esterification reaction. Fig. 2 shows the variation of conversion with temperature. Reaction is carried out with different temperatures ranging from 323 K to 353 K at initial molar ratio (MR = n-propanol to butyric acid) of 1.7:1 and catalyst loading (CL) of 2.5%w/w. Results show that the higher the temperature, the greater is the conversion of butyric acid. The rate of reaction is the function of temperature and the forward reaction is faster than the backward reaction. Increasing the temperature increases the rate of reaction, therefore yields the higher conversion. Conversion of 92.94% is obtained at temperature 353 K, molar ratio of 1.7:1, catalyst loading of 2.5%w/w, and reaction time of 420 minutes.

3.2. Effect of initial molar ratio of the reactants

Esterification of butyric acid with n-propanol is an equilibrium limited reaction. Conversion of butyric acid can be increased by the use of excess n-propanol. Reactions are conducted at temperature 353 K and catalyst loading of 2.5%w/w by varying initial molar ratio from 1:1 to 2:1. Fig. 3 shows the effect of initial molar ratio on conversion of butyric acid. In liquid phase esterification reaction, changing the initial molar ratio of the reactants (butyric acid and n-propanol) can disturb the equilibrium composition of products (n-propyl butyrate and water) and hence increasing the molar ratio resulted higher conversion. Highest conversion of 96.41% is obtained at molar ratio of 2, temperature 353 K, catalyst loading of 2.5%w/w, and for reaction time of 420 minutes.
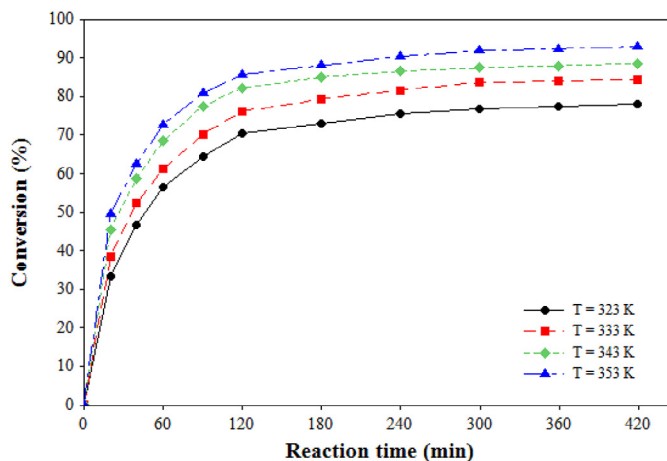

Fig. 2. Effect of reaction temperature on the conversion of butyric acid (MR = 1.7, CL = 2.5 wt %).
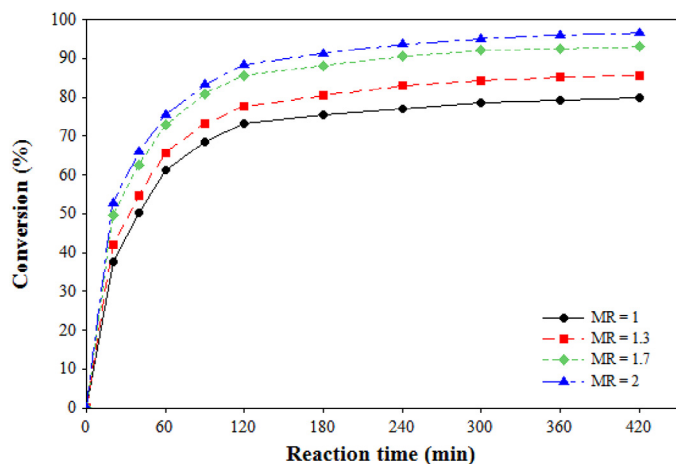
Fig. 3. Effect of initial molar ratio (MR) of the reactants on the conversion of butyric acid (T = 353 K, CL = 2.5 wt %).

Fig. 5. Comparison of esterification reaction in batch reactor (BR) and pervaporation reactor (PVR) (T = 353 K, MR = 1.7 and CL = 2.5 wt %).

3.3. Effect of catalyst loading

Esterification reactions were carried out by varying catalyst concentration from 1 to 2.5%w/w at temperature 353 K and molar ratio of 1.7:1. The results are shown in Fig. 4. The conversion of butyric acid is increased with increasing catalyst concentration. The higher conversion may be obtained with increasing catalyst concentration because of more availability of H^+ ions in the solution which ultimately increase the rate of reaction. The esterification reaction reaches faster at the higher catalyst concentration than the lower value of catalyst concentration. Esterification rate is increased from catalyst loading 1%w/w to 2.5%w/w which resulted in an increase in conversion from 71.61% to 92.94%.

3.4. Comparison of batch reactor and pervaporation coupled reactor

The comparison of esterification reaction of butyric acid with n-propanol coupled with pervaporation and without pervaporation is show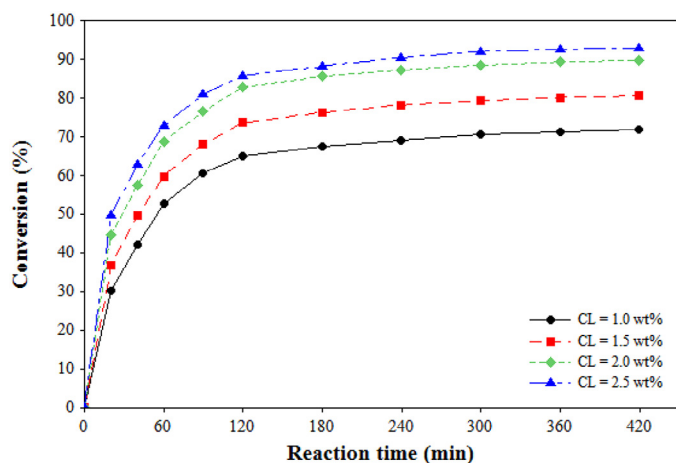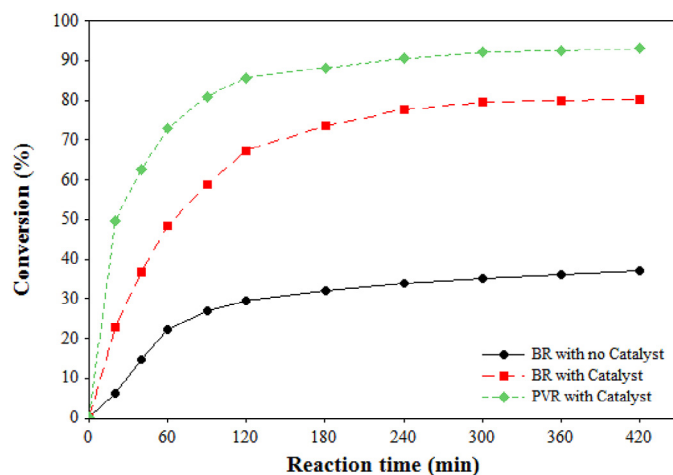n in Fig. 5. The comparable values for batch reactor without catalyst, batch reactor with catalyst and pervaporation reactor with catalyst were presented in Table 1. The results show that the conversion of butyric acid coupled with pervaporation is greater than the without pervaporation for same reaction parameters. Conversion of butyric acid without pervaporation was 80.12% but it increased to 92.94% for pervaporation coupled esterification reaction at conditions of temperature 353 K, molar ratio of 1.7:1, catalyst loading of 2.5%w/w and 420 minutes of reaction time. When esterification reactions were conducted in batch reactor (BR) without catalyst, batch reactor (BR) with catalyst and in pervaporation reactor (PVR) with catalyst, the corresponding conversions were obtained as 35.11%, 80.12% and 92.94%. Concentration profile for butyric acid (BA) and n-propyl butyrate (PB) is shown in Fig. 6. Pervaporation coupled esterification could drive the equilibrium due to the continuous removal of one of the product, here, water from the reaction mixture. PVA/PES membrane is hydrophilic and shows good affinity toward water. It shows that the pervaporation coupled esterification can enhance the conversion of butyric acid and production of esters. In this case, enhancement in conversion was 16%.

The variation of water concentration in reaction mixture is shown in Fig. 7. For batch reactor, water content was continuously increased as there is no removal or separation of water from the reaction mixture. More water production rate with no removal of water created resistance to forward reaction resulting lower conversion of acid and yield of ester. The concentration profile of water in the reaction mixture for pervaporation coupled esterification shows that the water content increased in initial period of

Fig. 4. Effect of catalyst loading (CL) on the conversion of butyric acid (T = 353 K, MR = 1.7).

Table 1
Comparison of batch reactor (BR) and pervaporation reactor (PVR).

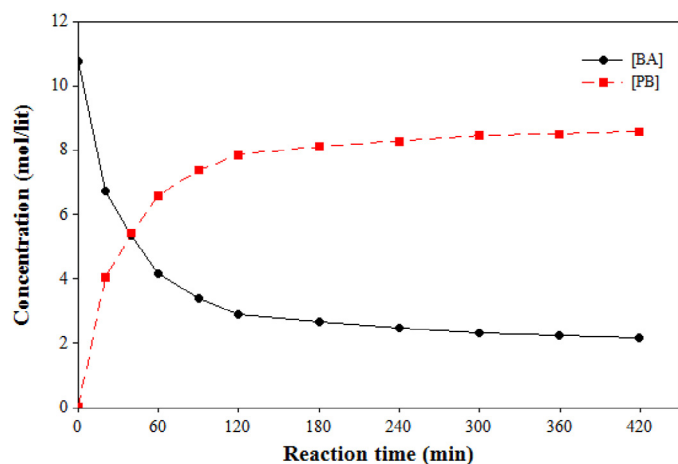| Parameter conditions	% Conversion in BR without catalyst	% Conversion in BR with catalyst	% Conversion in PVR
Temperature 353 K Molar ratio 1.7 Catalyst loading 2.5 wt%	35.11	80.12	92.94

Fig. 6. Concentration profile for butyric acid [BA] and n-propyl butyrate [PB] with reaction time (T = 353 K, MR = 1, CL = 2.5 wt%).

reaction and then decreased later with time. This occurred because of continuous removal of water by the membrane. In the initial reaction time, the water production rate was higher than the water removal rate because of low water content in the reaction mixture. Water concentration increased continuously and reached maximum value at 180 minutes of reaction time, where its production rate and removal rate was equal. After 180 minutes of reaction time, the water removal rate was higher than its production rate, which resulted in the decrease of water content in the reaction mixture. Because of continuous removal of water, the conversion of reaction and yield of ester was enhanced considerably. Pervaporation easily breaks the azeotrope formed in reaction mixture by alcohol and water without using separate unit for handling azeotrope. In conventional esterification reaction, multiple separation units including distillation column have been used for product separation and handling azeotropes. Also, one of the reactants used in excess because of equilibrium controlled reaction. Therefore, cost and energy perspective, pervaporation is intensified approach for production of esters.
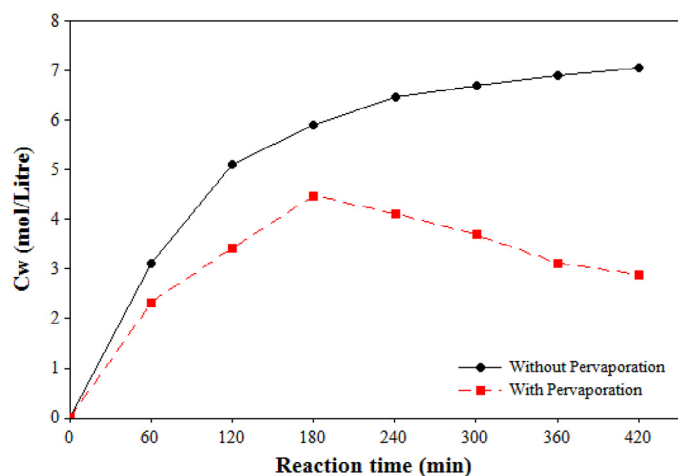

Fig. 7. Variation of water concentration in batch and pervaporation coupled reactor.

4. Conclusions

In this work, esterification of butyric acid with n-propanol was studied with catalyst p-toulenesulfonic acid. The effect of different reaction parameters such as temperature, molar ratio and catalyst concentration was studied for batch reactor and pervaporation coupled esterification reaction. Increasing the temperature of the reaction (323 K to 353 K), molar ratio (1 to 2) and catalyst loading (1 to 2.5%w/w) increases the conversion of butyric acid. The conversion of butyric acid significantly enhanced by the pervaporation coupled esterification than batch reactor without pervaporation from 80.12% to 92.94%. The highest conversion of 96.41% was obtained at temperature 353 K, molar ratio of 2 and catalyst loading of 2.5%w/w at reaction time of 420 minutes. Study shows that experimental conversion achieved by pervaporation is higher than batch reactor for the same experimental conditions. Polyvinyl alcohol (PVA)/polyethersulfone (PES) membrane used in the experiments shows the good activity and hydrophilicity and plays a vital role for enhancing the conversion by selectively removing water. In conventional esterification process such as distillation, demands high energy because of liquid feed evaporation. Replacing distillation by the pervaporation or combining the two processes, large energy savings are possible. Though pervaporation separation process is similar for esterification reaction, the use of different systems (acid+alcohol) resulted in significant variation in conversion. Also the use of alcohol chain length (linear and branched) with carboxylic acid is affected on the conversion of acid.

References

[1] A.I. Stankiewicz, J.A. Moulijn, Process intensification: transforming chemical engineering, Chem. Eng. Prog. (2000) 22–34.
[2] K.L. Wasewar, A. Keshav, S. Chand, Equilibrium and kinetics of reactive extraction of propionic acid using aliquat 336 and Tri-n-butyl phosphate in n-hexanol, Int. J. Chem. React. Eng. 7 (2009) A35.
[3] K.L. Wasewar, D.Z. Shende, Equilibrium for the reactive extraction of caproic acid using Tri-n-butyl phosphate in methyl isobutyl ketone and xylene, J. Chem. Eng. Data 56 (8) (2011) 3318–3322.
[4] M. Ganesapillai, P. Simha, The rationale for alternative fertilization: equilibrium isotherm, kinetics and mass transfer analysis for urea-nitrogen adsorption from cow urine, Resour. Effic. Technol. 1 (2015) 90–97.
[5] M. Ganesapillai, P. Simha, K. Desai, Y. Sharma, T. Ahmed, Simultaneous resource recovery and ammonia volatilization minimization in animal husbandry and agriculture, Resour. Effic. Technol. 2 (2016) 1–10.
[6] M. Ganesapillai, A.S.P. Simha, Separation processes and technologies as the mainstay in chemical, biochemical, petroleum and environmental engineering: a special issue, Resour. Effic. Technol. 2 (2016) S1–S2.
[7] B.K. Datta, W. Ji, S.K. Sikdar, Pervaporation: principles and applications, Sep. Purif. Rev. 25 (1996) 131–224.
[8] S.H. Ali, A. Tarakmah, S.Q. Merchant, T. Al-Sahhaf, Synthesis of esters: development of the rate expression for the Dowex 50Wx8-400 catalyzed esterification of propionic acid with 1-propanol, Chem. Eng. Sci. 62 (2007) 3197–3217.
[9] A. Chakrabarti, R. Filler, B.K. Mandal, Borate ester plasticizer for PEO-based solid polymer electrolytes, J. Solid State Electrochem. 12 (2008) 269–272.
[10] G. Feng, Y. Hu, B. Xu, Y. Zhou, Synthesis and characterization plasticizer epoxy acetyl polyglycerol ester, J. Forest Prod. Ind. 3 (2014) 100–105.

[11] R. Ronnback, T. Salmi, A. Vuori, H. Haario, J. Lehtonen, A. Sundqvist, et al., Development of a kinetic model for the esterification of acetic acid with methanol in presence of homogeneous catalyst, Chem. Eng. Sci. 52 (1997) 3369–3381.

[12] Y. Liu, E. Lotero, J.G. Goodwin, Effect of water on sulfuric acid catalyzed esterification, J. Mol. Catal. A Chem, 245 (2006) 132–140.

[13] J. Lilja, D. Murzin, T. Salmi, J. Aumo, P. Maki-Arvela, M. Sundell, Esterification of different acids over heterogeneous and homogeneous catalysts and correlation with the Taft equation, J. Mol. Catal. A Chem, 182–183 (2002) 555–563.

[14] W.T. Liu, C.S. Tan, Liquid-phase esterification of propionic acid with *n*-Butanol, Ind. Eng. Chem. Res. 40 (2001) 3281–3286.

[15] A.Q. Yaakob, S. Bhatia, Esterification of palmitic acid with methanol in the presence of macroporous ion exchange resin as catalyst, IIUM Eng. J. 5 (2004) 35–51.

[16] B. Srinivasan, S. Palanki, D. Bonvin, Dynamic optimization of batch processes I. Characterization of nominal solution, Comput. Chem. Eng. 27 (2003) 1–26.

[17] J. Chang, K. Chen, An integrated strategy for early detection of hazardous states in chemical reactors, Chem. Eng. J. 98 (2004) 199–211.

[18] J. Park, N.H. Lee, S.J. Park, J. Cho, Experimental and simulation study on the reactive distillation process for the production of ethyl acetate, J. Ind. Eng. Chem. 12 (2006) 516–521.

[19] A.A. Kulkarni, K.P. Zeyer, T. Jacobs, M. Kaspereit, A. Kienle, Feasibility studies and dynamics of catalytic liquid phase esterification reactions in a micro plant, Chem. Eng. J. 135S (2008) S270–S275.

[20] A.S. Simos, L. Ramos, L. Freitas, J.C. Santos, G.M. Zanin, H.F. Castro, Performance of an enzymatic packed bed reactor running on babassu oil to yield fatty ethyl esters (FAEE) in a solvent-free system, Biof. Res. J. 6 (2015) 242–247.

[21] Y. Zou, Z. Tong, K. Liu, X. Feng, Modeling of esterification in a batch reactor coupled with pervaporation for production of *n*-Butyl acetate, Chin. J. Cataly. 31 (2010) 999–1005.

[22] S. Korkmaz, Y. Salt, S. Dincer, Esterification of acetic acid and isobutanol in a pervaporation membrane reactor using different membranes, Ind. Eng. Chem. Res. 50 (2011) 11657–11666.

[23] D.J. Upadhyay, N.V. Bhat, Separation of azeotropic mixture using modified PVA membrane, J. Memb. Sci. 255 (2005) 181–186.

[24] E. Ameri, A. Moheb, S. Roodpeyma, Vapor-permeation-aided esterification of isopropanol/propionic acid using NaA and PERVAP® 2201 membranes, Chem. Eng. J. 162 (2010) 355–363.

[25] M.O. David, R. Gref, T.Q. Nguyen, J. Neel, Pervaporation–esterification coupling. Part-I. Basic kinetic model, Chem. Eng. Res. Des. 69 (1991) 335–340.

[26] C. Staudt-Bickel, R.N. Lichtenthaler, Integration of pervaporation for the removal of water in the production process of methylisobutyl ketone, J. Memb. Sci. 111 (1996) 135–141.

[27] B.L. Yang, S. Goto, Pervaporation with reactive distillation for the production of ethyl *tert*-butyl ether, Separ. Sci. Technol. 32 (1997) 971–981.

[28] W. Li, X. Zhang, W. Xing, W. Jin, N. Xu, Hydrolysis of ethyl lactate coupled by vapor permeation using polydimethylsiloxane/ceramic composite membrane, Ind. Eng. Chem. Res. 49 (2010) 11244.

[29] W. Li, W. Liu, W. Xing, N. Xu, Esterification of acetic acid and n-propanol with vapor permeation using NaA zeolite membrane, Ind. Eng. Chem. Res. 52 (2013) 6336–6342.

[30] Y. Zhu, H. Chen, Pervaporation separation and pervaporation-esterification coupling using crosslinked PVA composite catalytic membranes on porous ceramic plate, J. Memb. Sci. 138 (1998) 123–134.

[31] M.L. Gimenes, L. Liu, X. Feng, Sericin/poly (vinyl alcohol) blend for pervaporation separation of ethanol/water mixtures, J. Memb. Sci. 295 (2007) 71–79.

[32] R. Guo, X. Fang, H. Wu, Z. Jiang, Preparation and pervaporation performance of crosslinked PVA/PES composite membrane, J. Memb. Sci. 322 (2008) 32–38.

[33] G. Liu, W. Wei, W. Jin, N. Xu, Polymer/ceramic composite membranes and their application in pervaporation process, Chinese J. Chem. Eng. 20 (2012) 62–70.