

Esterification of acrylic acid with ethanol using pervaporation membrane reactor

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(Received 13 December 2016 • accepted 22 March 2017)

Abstract—Esterification of acrylic acid with ethanol was carried out using an in-situ reactor with an integrated pervaporation assembly (IPAE) made of polyvinyl alcohol (PVA) membrane and was compared with a non-integrated (NIE) system. Effect of reaction temperature (T_r), catalyst loading (C_c), molar ratios of reactants (MR) and ratio of effective membrane area to unit volume of reaction mixture (S/V_o) on kinetics of esterification reaction were studied. Conversions achieved in IPAE were found to be distinctly higher than the NIE. The highest conversion of acrylic acid was obtained as 83.3% at $T_r=60^\circ\text{C}$, $M_R=3:1$, $C_c=2\%$ and $S/V_o=14.1\text{ m}^{-1}$. Equilibrium conversion of acrylic acid in NIE was obtained as 55.1% at 60°C , 1:1 in 7 h, while using IPAE conversion enhances to 67.6%. Esterification of acrylic acid and ethanol with presently studied operating parameters provides a new approach to existing literature reported esterification-pervaporation system.

Keywords: Pervaporation, Acrylic Acid, Esterification, Kinetics, Equilibrium

INTRODUCTION

Merging a reactor with a separation unit has become a recent trend in the chemical industry in order to increase the process efficiency and lower the energy consumption [1]. Combining a chemical reactor, executing equilibrium limited reaction, with a membrane based pervaporation unit could result in achieving higher conversion due to selective removal of the product from the reacting mixture. In addition, the integration leads to lower production cost (product concentration is achieved by-product removal). Pervaporation membrane separation technology has gotten a global reorganization in application for dehydrating organic mixtures [2-5]. Esterification reactions are reversible with the products being ester and water. The dehydrating potential of hydrophilic membranes employed in pervaporation units could provide a solution to lower yield of the esterification reaction. The integration of per-

vaporation unit to esterification reactor could overcome the thermodynamic equilibrium barrier due to the simultaneous removal of side-product (water) continuously with a subsequent reactant reflux to shift the chemical equilibrium towards the greater production of desired product (ester).

Esters of acrylic acid have many industrial uses and hence the esterification of acrylic acid with different alcohols (methanol, ethanol, n-butanol) has been widely investigated [6,7]. Out of these, ethyl acrylate is a useful ester that is used as a reactive building block to produce coatings and inks, adhesives, sealants, textiles, plastics and elastomers. Integration of pervaporation with esterification has been explored in the last few decades for its possibility to intensify conversion of esterification reactor. In this regard, pervaporation membrane reactors assisted with esterification have been studied for acetic acid and iso-propanol [8], acetic acid and iso-butanol [9], acetic acid and ethanol [10], lactic acid and ethanol [11,12],

Table 1. A few literature studies on effect of process parameters for the esterification-pervaporation process of carboxylic acids with alcohol

System (acid and alcohol)	Catalyst	Membrane	Parameter studied	Reference
Acetic acid and isopropanol	<i>p</i> -Toluenesulfonic acid	Hydrophilic membrane PERVAP 1005 (GFT)	T_r , S/V_o , M_R , C_c	[8]
Acrylic acid and n-butanol	Amberlyst 131	Hydrophilic membrane, PERVAP 2201	T_r , S/V_o , M_R , C_c	[7]
Lactic acid and n-butanol	Sulphuric acid	Hydrophilic Polyvinyl alcohol-polyether sulfone (PVA-PES) composite type membrane	T_r , S/V_o , M_R , C_c	[15]
Lactic acid and ethanol	Amberlyst 15	CS-TEOS hybrid membranes	Membrane casting solution recipe, T_r , M_R , C_c	[16]
Acetic acid and ethanol and n-butanol	H_2SO_4	Acid-stable mordenite membrane	T_r , M_R , C_c	[17]
Propionic acid and ethanol	Strong-acid ion exchange resin 002CR	T-type zeolite membrane	T_r , S/V_o , M_R	[18]

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lactic acid and iso-propanol [13], acrylic acid and n-butanol [7], oleic acid and ethanol [14] and many more studies. Table 1 summarizes some studies performed with the parameters and conditions investigated. The studies have focused on the effect of operating conditions, membrane types and membrane dynamics. Polymeric and ceramic membranes have shown to have potential in the selective separation of water from the product of esterification reaction. Out of these hydrophilic polymeric based membranes (such as PVA, polyethersulfone, polyetherimide) have been more commercially a success owing to having high hydrophilicity and stable under acidic conditions. A very few works related to pervaporation-cum-esterification reactors for esterification of acrylic acid with ethanol have been available on literature. Truong et al. [2] used both polymer and zeolite based membrane to improve the synthesis of acrylic esters. They observed that polymeric base membrane performed better than the zeolite membrane. Additionally, chemical stability of these membranes was also investigated.

In the present work, we investigated esterification of acrylic acid and ethanol in esterification reactor integrated pervaporation in-situ unit (IPAE) and compared the non-integrated esterification unit (NIE). PVA membrane was used in the pervaporation unit. Employing an in-situ membrane unit could result in reduction of material cost and time to recycle the reaction and hence prove to be better against the loop assemblies. Effects of different operating parameters such as reaction and pervaporation temperature (T_r), ratio of membrane area to initial reaction liquid (S/V_0), catalyst concentration (C_C) and initial molar ratio of reactants (M_R) on the esterification pervaporation aided process were investigated.

MATERIALS AND METHODS

1. Materials

Hydrophilic PVA membrane was supplied by Permionics Membranes Pvt. Ltd., India. For the esterification reaction sulfuric acid (homogeneous catalyst) was used as catalyst. Reactants, acrylic acid, ethanol and catalyst were of analytical grade with purity higher than 99% and obtained from Merck India and were used without further purification.

2. Experimental Procedure

The IPAE experimental set-up used for the experiments is shown in Fig. 1. The operation was in-situ batch mode. The membrane was placed just below the reactor in a particularly designed stainless steel permeation cell, which provided an effective membrane area (78.5 cm^2) in contact with the feed mixture. One reactant was added to the reactor together with catalyst and heated to the desired reaction temperature. Other reactant was heated separately, and after reaching the reaction temperature was added to the reactor. At the same time, the stirrer was started at 300 rpm speed for the proper mixing of reaction mixture, and the time was taken as the initial time for the experiment. A thermostat was used to maintain the temperature within an accuracy of $\pm 1^\circ \text{C}$ during the reaction. With the help of hydrophilic membrane (PVA), water was separated from the feed mixture simultaneously. The pressure on the permeate side was held constant at 5 mbar using a vacuum pump and permeates (water rich vapor stream) were condensed and collected using a chiller with temperature maintained at -5°C .

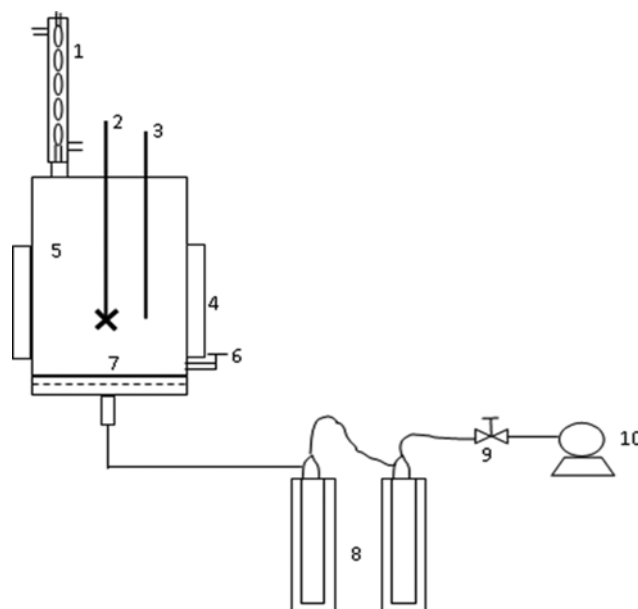


Fig. 1. Schematic diagram of the pervaporation-esterification integrated system.

- | | |
|-----------------------|----------------------|
| 1. Condenser | 6. Sampling point |
| 2. Stirrer | 7. Membrane |
| 3. Temperature sensor | 8. Chiller/cold trap |
| 4. Heater | 9. Valve |
| 5. Reactor | 10. Vacuum pump |

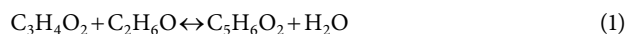
During the experiment, samples were withdrawn from the reactor at regular intervals. The permeate flux was obtained from the mass of permeate collected, which in turn was obtained gravimetrically.

3. Sample Analysis

Samples collected from the reactor and the permeate were analyzed by NUCON series gas chromatography with oven temperature programmed as 180°C equipped with a thermal conductivity detector (TCD). The GC column was a porapak column (id 2 mm, od 1/8", length 2 m) and hydrogen gas taken as carrier gas with flow rate 60 ml/min.

THEORETICAL DEVELOPMENT

The esterification of acrylic acid (A) with ethyl alcohol (B) to produce ethyl acrylate (E) and water (W) can be represented as an elementary second-order reversible reaction as well as first-order reaction with respect to each reagent and is presented as [19]:



The rate expression for second-order reversible reaction in the presence of catalyst can be written by considering the catalyst concentration as C_C :

$$-r_A = \frac{-dC_A}{dt} = k_1 C_A C_B C_C - k_{-1} C_E C_W C_C \quad (2)$$

where C_A , C_B , C_E , C_W and C_C represent the concentration (mol/m^3) of acrylic acid, ethanol, ethyl acrylate, water and catalyst, respectively. k_1 and k_{-1} are the rate constants of forward and backward reaction and t is the reaction time.

From material balance, the change in concentration of acrylic acid, ethyl alcohol, ester and water can be represented as

$$r_i = \frac{-dC_A}{dt} = \frac{-dC_B}{dt} = \frac{dC_E}{dt} = \frac{dC_W}{dt} = k_1 C_A C_B C_C - k_{-1} C_E C_W C_C \quad (3)$$

Eq. (3) can be written as

$$-r_i = \frac{d(C_i)}{dt} = k_1 C_C \left(C_A C_B - \frac{C_E C_W}{K_{eq}} \right) \quad (4)$$

where, the equilibrium constant (K_{eq}) can be calculated by the following equation:

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{C_E C_W}{C_A C_B} \quad (5)$$

By combining pervaporation with esterification, the change of concentration can be written as follows:

$$\frac{d(C_i)}{dt} = r_i - \frac{S}{V_o} J_i \quad (6)$$

The effective surface area of the membrane (S) and total flux of the membranes is determined by:

$$J = W/(S \cdot t) \quad (7)$$

where W , S and t denotes the permeate amount, effective membrane area and reaction time, respectively. The partial flux of components (J_i) is the function of total flux and weight fraction of the component in permeate (x_i).

$$J_i = J x_i \quad (8)$$

In the present work, a hydrophilic PVA membrane was used and thus the partial fluxes of acrylic acid, ethanol and ethyl acrylate were neglected ($J_{Ethanol} \sim J_{Acid} \sim J_{ester} \sim 0$) [7,20].

RESULTS AND DISCUSSION

In this study, experiments involved a laboratory-scale reactor with and without pervaporation unit. The effect of the various operating parameters such as reaction temperature, molar ratio of the reactant, catalyst concentration, ratio of effective membrane area and unit volume of reaction mixture on reaction as well as separation were studied. The results obtained in this study are discussed in the following sections.

1. Comparison of Esterification with Pervaporation and Without Pervaporation

Conversion of acrylic acid in the esterification process of acrylic acid and ethanol mixture was studied using NIE and IPAE system. The obtained results are shown in Fig. 2 and 3. Fig. 2 presents the conversion of acrylic acid at a T_r of 60 °C, C_C of 2% and with M_R of 1. The conversion in IPAE is distinctly higher than in NIE. This is attributed to the continuous water removal from the reaction mixture by the IPAE, which increased the yield of ethyl acrylate. Conversion of acrylic acid in the NIE was obtained to be 54.8% which increased to 67.6% with IPAE in 7 h time.

Since IPAE is responsible for the increase in conversion, a better view of the obtained results can be presented if water concentration is monitored with respect to time. Fig. 3 represents the con-

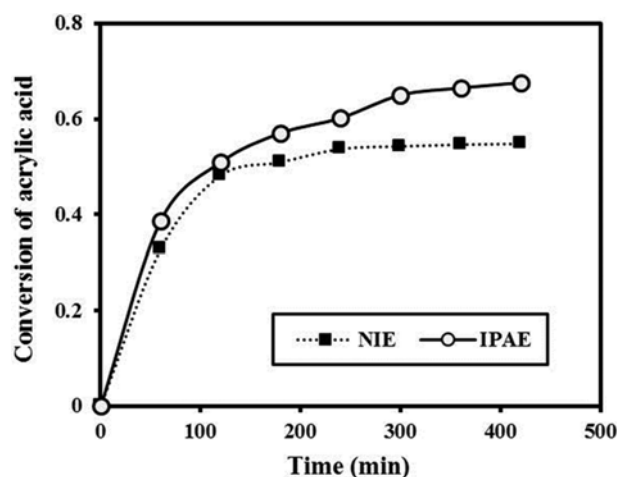


Fig. 2. Comparison of conversion of acrylic acid with time in esterification of acrylic acid with ethanol in IPAE and NIE system ($T_r=60^\circ\text{C}$, $M_R=1:1$, $C_C=2\%$, $S/V_o=14.1\text{ m}^{-1}$).

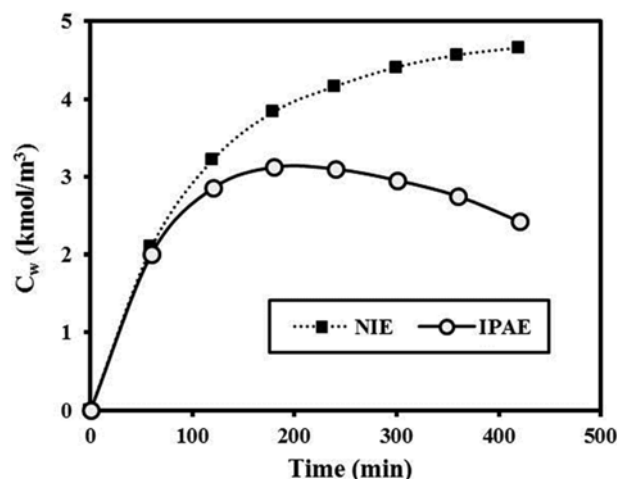


Fig. 3. Comparison of concentration of water with time in esterification of acrylic acid with ethanol in IPAE and NIE system ($T_r=60^\circ\text{C}$, $M_R=1:1$, $C_C=2\%$, $S/V_o=14.1\text{ m}^{-1}$).

centration profile of water in the reaction mixture for the pervaporation-esterification process, which shows that at the beginning the content of water increases until a maximum value has been reached. After this, the water concentration in the reactor decreases continuously due to the water removal by pervaporation from the reaction mixture, which in turn is much faster than its formation rate by esterification [8]. At $t=0$, there is no water present. At the start of reaction when t is slightly greater than 0, water starts forming but the concentration is not large so in both IPAE and NIE, the water is produced at the same rate till it attains a peak (maximum value). Thereafter in NIE, it continues to increase as the water starts building up. As the reaction is reversible, this leads to more or less stabilization of the conversion of acrylic acid as seen for time 180 min onwards in without pervaporation unit. Water concentration increases from 3.8 to 4.7 mol/m³ in time 180 to 420 min. On the other hand, in IPAE, water concentration in the reactor falls from 3.1 to 2.4 kmol/m³ which leads to the shoot.

Hasanoglu et al. [10] observed that by using pervaporation membrane system the conversion of acid increased from 57.5% to 65.8%, Han et al. [1] found from 56.3 to 70.0% increase, Ameri et al. [21] obtained from 49.0 to 59.0% increase and Zhang et al. [18] observed from 82.6% to 90.8% increase on other acids. The obtained results agree with literature in pervaporation aided system of various acid and alcohol.

2. Effect of Reaction Temperature

Esterification of acrylic acid+ethanol mixture was studied at various reaction temperatures in an in-situ membrane reactor of IPAE and NIE system with constant M_R (1.0), C_C (2%) and S/V_o (14.13

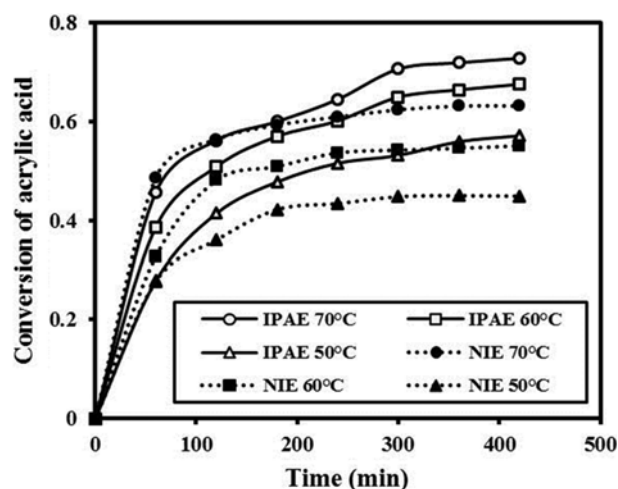


Fig. 4. Effect of the reaction temperature on the conversion of acrylic acid in the esterification of acrylic acid and ethanol mixture ($M_R=1:1$, $C_C=2\%$, $S/V_o=14.1 \text{ m}^{-1}$).

m^{-1}). Fig. 4 shows the variation of conversion of acrylic acid versus time at different temperatures. Both reaction rate and permeation rate are influenced by the reaction temperature. It can be seen from Fig. 4 that while increasing reaction temperature from 50 to 70 °C the conversion also increases from 57.2 to 72.9% and the IPAE unit significantly increases the conversion of acrylic acid from 45.0% to 57.2%, from 55.1% to 67.6% and from 63.2% to 72.9% at temperatures of 50, 60, and 70 °C, respectively. Higher temperature is appropriate for the increase in rate of the forward reaction compared to backward reaction [22–24].

With increasing temperature, the permeation rate through the

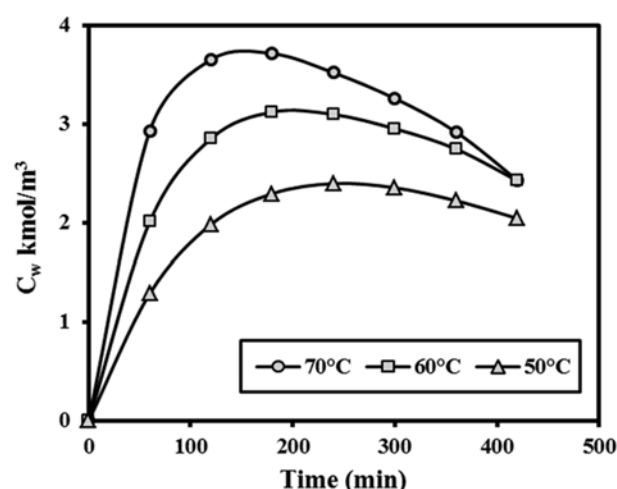


Fig. 5. Effect of the reaction temperature on water concentration in the esterification of acrylic acid and ethanol mixture using IPAE system ($M_R=1:1$, $C_C=2\%$, $S/V_o=14.1 \text{ m}^{-1}$).

Table 2. Overview of effect of temperature on the conversion of acrylic acid of the pervaporation-aided esterification process and Comparison of results of esterification reaction with and without pervaporation process

System	Operating conditions		Conversion of acid (%)		Intensification (%)	Reference
	Constant parameters	T_r (°C)	Without pervaporation	With pervaporation		
Acrylic acid and ethanol	$M_R=1:1$, $C_C=2\%$, $S/V_o=14.1 \text{ m}^{-1}$, $t=420 \text{ min}$	50	44.9	57.2	27.3	Present work
		60	55.1	67.6	22.6	
		70	63.2	72.9	13.3	
Propionic acid and ethanol	$M_R=2:1$, $S/V_o=0.1059 \text{ m}^2 \cdot \text{kg}^{-1}$, $t=420 \text{ min}$	70	79.9	83.4	4.2	[18]
		80	83.3	92.0	9.4	
		90	85.3	97.4	12.4	
Acetic acid and ethanol	$M_R=1:1$, $C_C=5 \text{ g}$, Amberlyst 15/100 g acetic acid, $t=360 \text{ min}$	50	47.8	51.7	7.5	[10]
		60	51.0	65.1	21.7	
		70	66.0	71.3	7.4	
Acetic acid and ethanol	$M_R=1:1$, $C_C=1 \text{ g}$ sulfuric acid/100 g acetic acid, $S/V_o=13.3 \text{ m}^{-1}$, $t=360 \text{ min}$	60	65.3	70.6	8.1	[10]
Acrylic acid and n-butanol	$M_R=4$, $C_C=10 \text{ g/L}$, $t=360 \text{ min}$	65	36.5	68.8	46.9	[7]
		75	54.3	86.0	36.9	
		85	71.5	93.5	23.5	
Oleic acid and ethanol	$M_R=15:1$, $t=420 \text{ min}$	80	56.3	70.0	19.6	[1]
	$M_R=15:1$, $t=1440 \text{ min}$	80	84.2	87.2	3.4	

membrane as well as the water production rate by esterification increases. As a result, water concentration has a higher maximum value for a higher reaction temperature (Fig. 5). At earlier stage of the reaction the water content went through its maximum value, due to a slower backward reaction rate; after water content reached the maximum value, it decreased faster due to a higher backward reaction rate.

Vapor pressure of permeating components in the upstream side of the membrane was increased, when operating temperature increased. Due to vapor pressure difference between the upstream and downstream side of the membrane the transport driving force was enhanced. As a result, with increasing temperature attained higher molecular diffusivity; so, the mass transport was faster. Moreover, polymer chains became more flexible and accommodated larger available free volume of the polymer matrix for diffusion, as temperature was increased, which allowed easier water transfer across membrane [16].

Comparative statement of different literature reported esterification reaction system using IPAE and NIE unit is given in Table 2. Conversion and percentage intensification in the reported systems do vary from the present work due to many changes in the esterification-pervaporation operating conditions in those systems. However, our results are comparable and better than many literatures' reported work.

The Arrhenius plot of water flux versus temperature for esterification of acrylic acid+ethanol system is illustrated in Fig. 6. An increase in temperature increases the flux of water. Activation energy of water permeation across the PVA membrane is 17.5 kJ/mol, which reveals high energy requirement for water permeation through the PVA membrane. Sert and Atalay, [7] reported the need of 36.5 kJ/mol activation energy for Pervap 2201 membrane for acrylic acid+n-butanol system. Similarly, Yun et al. [25] also reported the Arrhenius relationship between temperature and water flux for water/organic separation. Activation energies for water permeation in binary water/organic systems were reported to be 9.1, 13.5, and 4.4 kJ/mol for water/n-butanol, water/n-butyl acetate and water/acetic acid, respectively.

3. Effect of Catalyst Concentration

For this study, experiments were performed at a constant T_r of 60 °C and with an M_R of 1. The effect of C_C was investigated by

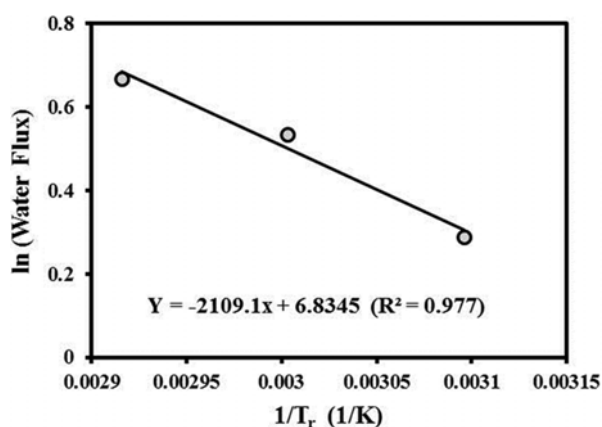


Fig. 6. Arrhenius plot of water flux vs. temperature.

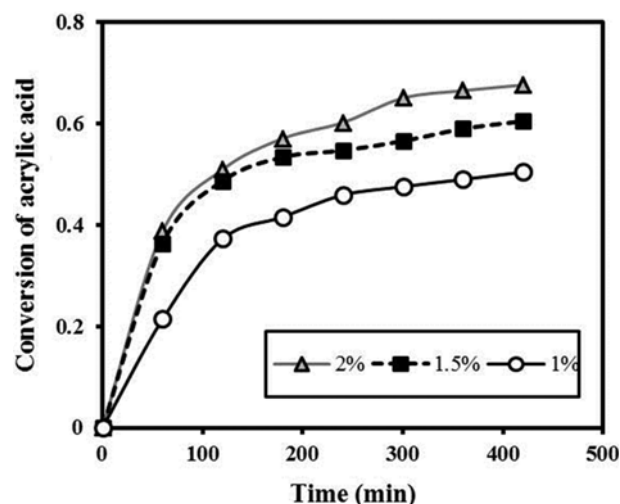


Fig. 7. Effect of the catalyst loading on the conversion of esterification of acrylic acid and ethanol in IPAE ($T_r=60\text{ }^{\circ}\text{C}$, $M_R=1:1$, $S/V_o=14.1\text{ m}^{-1}$).

varying the catalyst amount to 1, 1.5 and 2 (vol) % of initial reaction mixture (Fig. 7). Increasing catalyst amount obviously increases the reaction rate because reaction rate is proportional to catalyst concentration and water production rate. Consequently, an increase in the amount of catalyst leads to an increase in the water production rate and thus increases in water permeation flux. Less amount of catalyst (up to 2%) was considered for experiments because of its corrosive nature. Conversions of acrylic acid were obtained as 50.4% and 67.6% after 7 h for the lowest and highest values of catalyst concentration, respectively, which indicates that catalyst concentration had significant effect on the reaction. Both forward and backward reaction rate was varied with the change of catalyst concentration, and thus increasing the catalyst loading favors the formation and removal of water. The concentration of water in the reactor was higher for a higher catalyst loading, and it increased at initial stage during the reaction and reached a maximum value

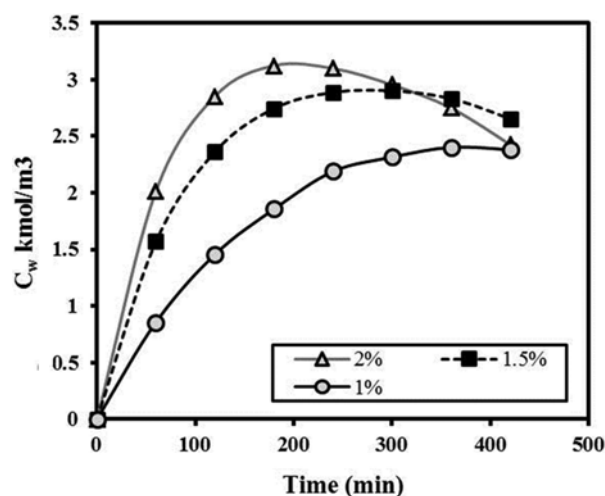


Fig. 8. Effect of the catalyst loading on the concentration of the water of esterification of acrylic acid and ethanol in IPAE ($T_r=60\text{ }^{\circ}\text{C}$, $M_R=1:1$, $S/V_o=14.1\text{ m}^{-1}$).

Table 3. Overview of effect of catalyst concentration on the conversion of acrylic acid of the pervaporation-aided esterification process

System	Operating conditions		Conversion of acid (%)	Reference
	Constant parameters	C_C		
Acrylic acid and ethanol	$T_r=60^\circ\text{C}$, $M_R=1:1$, $S/V_o=14.1\text{ m}^{-1}$, $t=420\text{ min}$	1	50.4	Present work
		1.5	60.4	
		2 vol%	67.6	
Acrylic acid and n-butanol	$T_r=85^\circ\text{C}$, $M_R=4:1$, $t=360\text{ min}$	10	89.0	[7]
		15	92.1	
		20 g/L	95.5	
Lactic acid and iso-propanol	$T_r=90^\circ\text{C}$; $M_R=1.4$; $S/V_o=15.2\text{ m}^{-1}$, $t=8\text{ h}$	0.1	68.5	[13]
		0.2	77.7	
		0.3	82.7	
		0.4	85.8	
		0.5 kmol/m ³	87.6	
Lactic acid with n-butanol	$T_r=90^\circ\text{C}$; $M_R=1.4$; $S/V_o=15.2\text{ m}^{-1}$, $t=480\text{ min}$	0.1	75.1	[15]
		0.2	80.3	
		0.3	84.9	
		0.4	87.6	
		0.5 kmol/m ³	88.9	
Acetic acid and benzyl alcohol	$T_r=80^\circ\text{C}$; $M_R=0.66$, $t=180\text{ min}$	0	18.0	[26]
		2.1	33.0	
		4.1	46.0	
		11 mol/m ³	49.0	

and beyond that it decreased with time (Fig. 8). In case of 1% catalyst concentration the water removal rate was much less in comparison to production rate; therefore, water concentration tended to increase with time. But at higher catalyst concentration, water concentration in the reactor dropped beyond 180 min. Higher partial pressure of water was created in the vapor phase due to increase in water production rate in reactor while passing through the membrane, which resulted in increase in water permeation [21]. Table 3 reviews the results in terms of conversion obtained by researchers by using various IPAE. Similar kinds of results have been reported as obtained by experiments and showed that conversion of acid increased with increasing amount of catalyst.

4. Effect of Molar Ratio of Ethanol to Acrylic Acid

The effect of initial M_R of ethanol to acrylic acid (EOH:AA) was investigated over a range of 1:1 to 3:1. All the experiments were in an IPAE reactor at 60°C and 2% catalyst loading of initial reaction mixture. Using excess amount of one reactant (generally alcohol) did ensure higher conversions. It is evidence from Fig. 9 that the initial rate of increase of conversion of acrylic acid was more for high M_R 3:1 as compared to other M_R (2:1 and 1:1). The conversion of acrylic acid increased from 67.6% to 83.3% at 7 h when the initial molar ratio of ethanol to acrylic acid increased from 1:1 to 3:1 due to increased excess ethanol. Table 4 summarizes related studies to the effect of M_R on the IPAE and shows that acid conversion increased with the increase M_R .

Fig. 10 represents the water concentration profile in reacting mixture during the reaction. Similar kind of trend line was observed for all three molar ratios of reactants. However, water concentration was max for low M_R and it was low for high M_R . When the

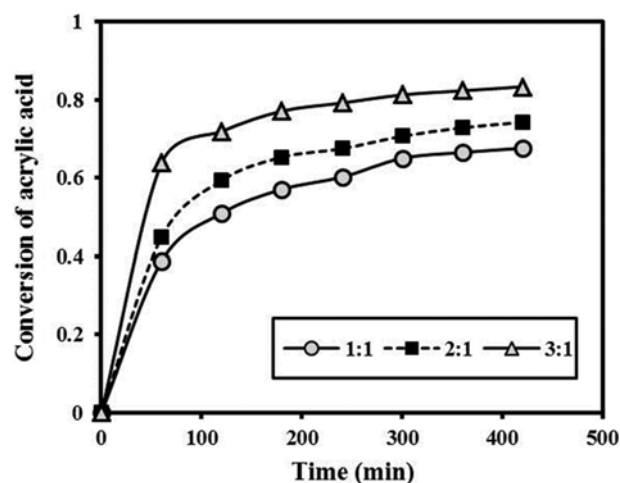


Fig. 9. Effect of the initial alcohol/acid molar ratio on the conversion of the esterification of acrylic acid and ethanol in IPAE ($T_r=60^\circ\text{C}$, $C_C=2\%$, $S/V_o=14.1\text{ m}^{-1}$).

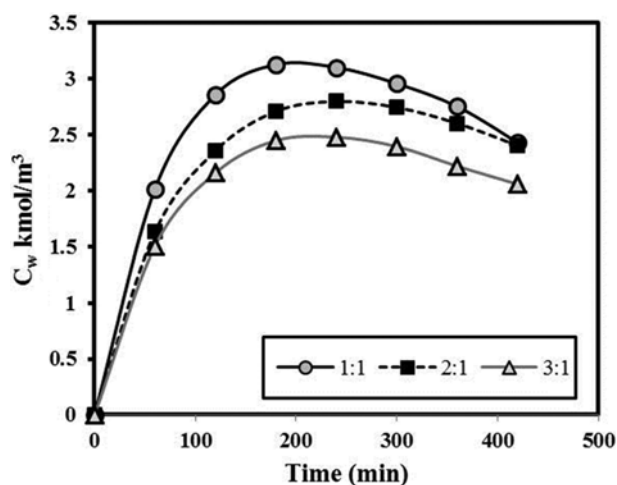
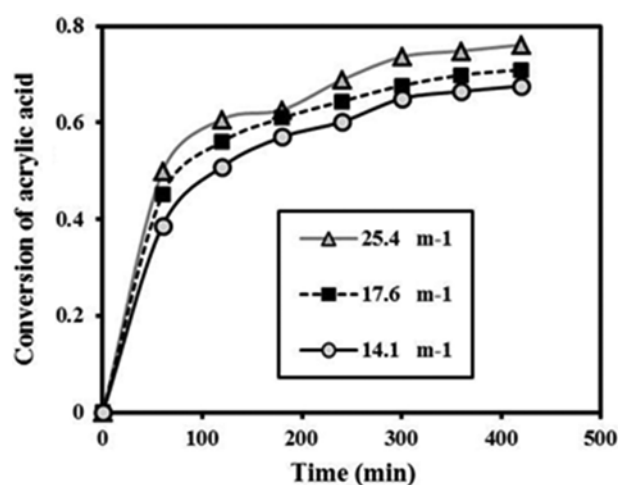
EOH:AA ratio increased, the water production rate decreased, which led to decrease in maximum water content. Initial molar ratio of reactant had an effective role in reaction rate, but exerted no effect on pervaporation kinetics [16]. In the study of esterification pervaporation coupled process, similar behavior has been depicted in the literature [8,27].

5. Effect of the Membrane Area to Initial Solution Volume Ratio (S/V_o)

S/V_o ratio has significant impact on pervaporation process due

Table 4. Overview of effect of initial molar ratio (M_R) on the conversion of acrylic acid of the pervaporation-aided esterification process

System	Operating conditions		Conversion of acid (%)	Reference
	Constant parameters	M_R (alcohol : acid)		
Acrylic acid and ethanol	$T_r=60^\circ\text{C}$, $C_C=2\text{ vol}\%$, $S/V_o=14.1\text{ m}^{-1}$, $t=420\text{ min}$	1 : 1	67.6	Present work
		2 : 1	74.2	
		3 : 1	83.3	
Propionic acid and ethanol	$T_r=90^\circ\text{C}$, $S/V_o=1059\text{ cm}^2\cdot\text{kg}^{-1}$, $t=420\text{ min}$	1 : 1	84.4	[18]
		1.5 : 1	93.6	
		2 : 1	96.3	
Acrylic acid and n-butanol	$T_r=85^\circ\text{C}$, $C_C=10\text{ g/L}$, $t=360\text{ min}$	3 : 1	97.5	[7]
		4 : 1	90.7	
		6 : 1	93.6	
Acetic acid and ethanol	$T_r=60^\circ\text{C}$, $C_C=1\text{ g sulfuric acid/100 g acetic acid}$, $t=360\text{ min}$	8 : 1	95.6	[10]
		1 : 1	70.7	
Acetic acid and ethanol	$T_r=60^\circ\text{C}$, $C_C=5\text{ g Amberlyst 15/100 g acetic acid}$, $t=360\text{ min}$	1.5 : 1	79.7	[10]
		1 : 1	64.0	
Lactic acid and ethanol	$T_r=75^\circ\text{C}$, $S/V_o=23\text{ m}^{-1}$, $C_C=2\text{ wt}\%$	1.5 : 1	70.0	[11]
		1 : 1	68.2	
		2 : 1	86.5	
		3 : 1	89.6	

**Fig. 10. Effect of the initial alcohol/acid molar ratio on the concentration of the water esterification of acrylic acid and ethanol in IPAE ($T_r=60^\circ\text{C}$, $C_C=2\%$, $S/V_o=14.1\text{ m}^{-1}$).****Fig. 11. Effect of the ratio of membrane area to initial volume on the concentration of the water of the esterification of acrylic acid and ethanol in IPAE ($T_r=60^\circ\text{C}$, $C_C=2\%$, $M_R=14.1\text{ m}^{-1}$).**

to its influence on water extraction rate. In the present work, esterification experiments were carried out using constant membrane area (78.5 cm^2) by changing the initial reaction volume and employing S/V_o as 14.1, 17.6 and 25.4 m^{-1} . The obtained results for various S/V_o ratios on acrylic acid conversion and concentration of water in esterification reaction are shown in the Fig. 11 and Fig. 12 while keeping the other operating parameters as constant (M_R (1 : 1), C_C (2%) and T_r (60°C)). The conversion of acrylic acid increased from 67.6 to 76.1% with increase of S/V_o ratio from 14.1 to 25.4 m^{-1} , respectively with equilibrium time period of 7 h (Fig. 11). Similarly, Sert and Atalay [7] obtained the conversion as 71.8,

79.1 and 83.0% by varying the S/V_o as 35, 52.5 and 70 m^{-1} . Zhang et al. [18] also reported the increase of conversion from 90.0% to 99.8% with membrane area to initial reaction liquid (S/m), ranging from 158.9 to $1,059\text{ cm}^2\cdot\text{kg}^{-1}$.

When membrane area per unit reaction volume was increased from 14.1 to 25.4 m^{-1} , the concentration of water in the reactor dropped drastically from 2.4 to 1.8 kmol/m^3 . The water removal rate decreased with the decrease of S/V_o ; however, water production rate was similar for various S/V_o . In this study, ratio of the membrane area and the reaction volume was selected based on economical point of view [28].

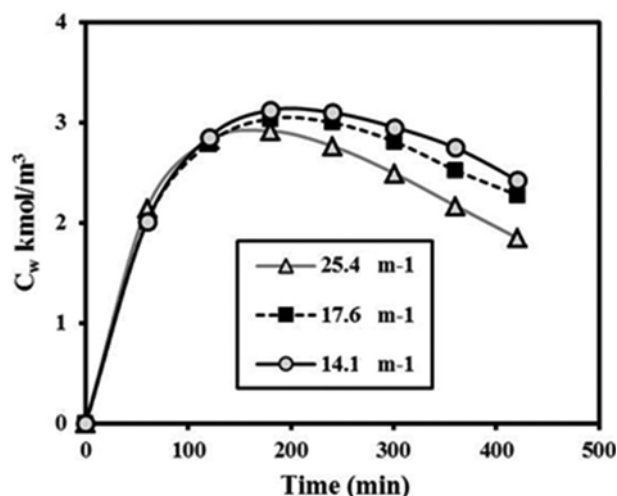


Fig. 12. Effect of the ratio of membrane area to initial volume on the concentration of the water of the esterification of acrylic acid and ethanol in IPAE ($T_r=60^\circ\text{C}$, $C_c=2\%$, $M_R=14.1\text{ m}^{-1}$).

CONCLUSIONS

Pervaporation-esterification integrated process was investigated thoroughly and effects of the important operating parameters on the coupling process were studied. The variations of conversion of acrylic acid and water concentration with reaction time at different T_r , different M_R , different C_c and different ratios of the S/V_o were studied. It can be concluded that the selection of the parameters has a significant effect on the performance of the esterification-pervaporation integrated reactor. Pervaporation and reaction rate both can be increased with increase in operating temperature. Compared to only esterification reaction, the conversion of esterification-pervaporation hybrid process gets intensified by 27.3, 22.6 and 13.3% at 50, 60 and 70°C , respectively. The ester rate formation increases significantly with increase in catalyst concentration. When the S/V_o ratio increases, higher ester conversions are obtained. It was also observed that final water content decreases with increase in the initial molar reactant ratio.

NOMENCLATURE

C_A	: concentration of acrylic acid [mol/m^3]
C_B	: concentration of ethyl alcohol [mol/m^3]
C_E	: concentration of ethyl acrylate [mol/m^3]
C_W	: concentration of water [mol/m^3]
C_C	: concentration of catalyst [mol/m^3]
k_1	: forward reaction rate constant [$(\text{m}^3)^2/\text{kmol}^2\cdot\text{min}$]
k_{-1}	: backward reaction rate constant [$(\text{m}^3)^2/\text{kmol}^2\cdot\text{min}$]
t	: reaction time [min]
T_r	: reaction temperature [$^\circ\text{C}$]
K_{eq}	: equilibrium constant
S	: membrane area [m^2]
J	: total flux [$\text{gm}/\text{m}^2\cdot\text{min}$]
R	: rate constant [$8.3\text{ J}/\text{mol K}$]
E_a	: activation energy [J/mol]
V_o	: volume of initial reaction mixture

M_R : initial molar ratio of alcohol to acid

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