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Vapor-permeation-aided esterification of isopropanol/propionic acid using NaA and PERVAP® 2201 membranes

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A B S T R A C T

Two different commercial (tubular NaA zeolite and flat polymeric (PERVAP® 2201)) membranes were used in a vapor permeation process to remove water from the reaction atmosphere during the synthesis of isopropyl propionate. The reaction was carried out in a batch reactor using 3 wt.% (relative to propionic acid) of para toluene sulfonic acid as the catalyst. Effects of membrane type and initial alcohol/acid molar ratio on the performance of the combined process were investigated. Experiments were carried out with three different levels of alcohol/acid molar ratio. It was found that the coupled process was generally capable of enhancing the conversion of reversible esterification reaction. However, complete acid conversion was achieved in a shorter period of time with zeolite membrane than with polymeric membrane. In addition, initial molar ratio of the reactants had a strong effect on both acid conversion and on water flux through the membranes.

1. Introduction

Combination of reaction systems and membrane processes such as vapor permeation (VP), and pervaporation (PV) in general, improves the performance of these systems, giving rise to a number of new process concepts.

In recent years, membrane reactors have received much attention due to their high selectivity and independence from the vapor–liquid equilibrium. Membrane reactors have several advantages such as enhancement of reaction conversion, improvement of selectivity usually with respect to one of the species, close contact between reactants, and compactness and integration of the reaction and separation systems.

In a membrane reactor, the membrane can be applied as: (1) an extractor, (2) a distributor, and (3) an active contactor.

In the extractor configuration, membranes are used to remove selectively one of the products of an equilibrium-limited reaction to enhance reaction conversion by overcoming the equilibrium. In the previous studies, the performance of various kinds of organic and inorganic membranes, such as zeolite membranes, has been investigated [1–3]. Polymeric membranes have shown both high permselectivity and fast permeation properties in membrane reactors. However, their application has been limited in these systems due to their inadequacies, namely restricted resistance to temperature, solvents and corrosive environments.

A number of studies have been conducted on using polymeric membranes to improve the performance of esterification reactors [4–6]. Kita et al. used a pervaporation membrane reactor equipped with a flat polymeric membrane to investigate esterification of oleic and acetic acids with ethanol to find that the membrane improved the reactor conversion beyond equilibrium [4].

Pearse investigated a coupled membrane and the reaction process with flat PVA or Nafion membranes used for the esterification reaction of acetic acid with ethanol [7]. David et al. employed a membrane, prepared by embedding poly-styrene-sulfonic acid in a cross-linked PVA matrix, in a pervaporation process [8]. Matouq et al. applied a PVA membrane in the production of MTBE from methanol and tert-butyl alcohol [9].

Lately, Teresa Sanz and Gmehling have studied esterification of acetic acid with isopropanol coupled with pervaporation using the commercial PERVAP® 2201 membrane. In their work, they investigated the synthesis and hydrolysis of isopropyl acetate by using the commercial ion exchange resin Amberlyst 15 as the catalyst [10].

In addition to polymeric membranes, zeolite porous membranes have been recently used in pervaporation membrane reactor applications. Zeolite membranes present a class of sub-micron porous inorganic crystals with a high ratio of surface area to volume. Compared to organic membranes, they exhibit higher levels of mechanical strength, thermal stability, and resistance to chemical corrosion.

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Type-A zeolite membranes are more attractive for dehydrating organic compounds due to their high hydrophilicity which, in turn, stems from the fact that their pore diameter (0.4 nm) is smaller than the kinetic diameter of almost all organic molecules but larger than that of water. This type of membranes also has non-zeolite pores [11,12] that include hydrophilic silanol groups [13–15]. These properties considerably enhance water permeation over organic compounds and lead to high separation factors that are often over 1000 or even higher.

Besides applications in separation processes, zeolite membranes can be used in catalytic membrane reactors. One important example of this is the selective removal of water from equilibrium-limited esterification reaction systems by using different types of hydrophilic zeolite membranes (types A, T, and ZSM-5) [15–17].

Recently, Van Hoof et al. carried out a comparative study of the performance of tubular NaA zeolite membrane and several plate form commercial polymeric membranes such as Pervap®2216, Pervap®2201, and Pervap®2510 in a pervaporation system used for the dehydration of some organic solvents [18]. Over the last decade, the tubular zeolite NaA membranes have been used by several researchers to investigate their performance in alcohol dehydration processes and in equilibrium-limited esterification reactions. Jafar et al. synthesized a tubular zeolite NaA membrane on a carbon/zirconia support and used it for the removal of water from water/isopropanol and water/ethanol mixtures. They used their membrane in both pervaporation and vapor permeation processes and reported its high selectivity for water [19]. They also studied the esterification of lactic acid with ethanol to produce ethyl lactate in a batch reactor with the two different modes of using para toluene sulfonic acid (PTSA) as the catalyst and without a catalyst. They reported that using the zeolite A membrane in a vapor permeation system enhanced the yield.

Also, Mitsui Engineering & Shipbuilding Co., Ltd. (MES) used a NaA type zeolite membrane in the dehydration vapor permeation membrane process to facilitate the esterification reaction. In this work, the selective removal of water by vapor permeation separation shifted the equilibrium in favor of ester formation [20]. Another development by MES is a T-type zeolite membrane which is resistant to acids and exhibits good dehydration performance through the vapor permeation process. Tanaka et al. used this zeolite T membrane for vapor-permeation-aided esterification of lactic acid with ethanol. They achieved complete conversion within a short reaction time by removing water from the reaction mixture [21]. They further used the zeolite T membrane for pervaporation-aided esterification of acetic acid with ethanol at 343 K. In their experiments, nearly complete conversion was reached within 8 h with initial alcohol to acetic acid molar ratios of 1.5 and 2 [22].

Inoue et al. performed ester condensation from stoichiometric mixture of acetic acid and ethanol assisted by pervaporation via Merlinoite and ZSM-5 zeolite membranes [23].

NaA zeolite membranes have a hydrophilic top layer with a regular pore size which adsorbs water. Due to the open structure of this membrane, water can rapidly diffuse through the membrane, leaving larger molecules behind. In addition, the low Si/Al ratio in the framework of the NaA zeolite membranes provides excellent dehydration performance in pervaporation processes. However, its chemical stability diminishes in the presence of organic acid.

In the present work, the esterification reaction of isopropanol and propionic acid coupled with vapor permeation process was investigated. The vapor permeation process was used simultaneously for dehydration from the esterification reaction mixture to overcome the kinetic equilibrium of the reaction, which enhanced the conversion of the reversible reaction. For this purpose, a batch reactor was coupled with a vapor permeation membrane module and experiments were carried out in the batch mode.

Two different commercial membranes were used and compared for vapor permeation. Using vapor permeation system allowed avoiding the direct contact between used membranes, especially the zeolite one, and the organic acid (propionic acid). In this way, it was expected that the membranes would exhibit a good stability and a satisfactory performance despite the presence of an organic acid in the reaction mixture.

To accelerate the esterification reaction, PTSA was used as the catalyst and the effect of initial molar ratio of alcohol to acid was studied in the experiments. Three different values of 1:1, 1.5:1, and 3:1 were chosen for this ratio based on findings reported by other researchers on the effect of alcohol/acid molar ratio on the reactants conversion during esterification reactions [24–27].

2. Materials and methods

2.1. Chemicals

Propionic acid and isopropyl alcohol (both with purity levels of 99.8%) were purchased from Merck. To run esterification experiments, synthetic mixtures were prepared by adding 0.125 gmole of propionic acid to 0.125, 0.18, and 0.35 gmole of isopropanol to obtain alcohol to acid molar ratios of 1:1, 1.5:1, and 3:1, respectively. Depending on the initial molar ratio of the reaction mixture, the initial volume of the mixture varied between 19 and 38 mL. 3 wt.% of PTSA from Merck (relative to propionic acid) was added to the mixture to catalyze the reaction.

2.2. Membranes and modules

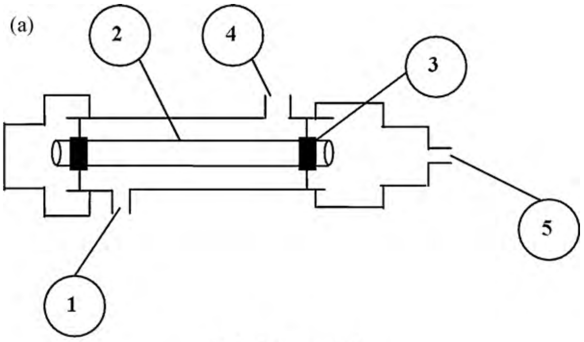
Tubular nanoporous NaA zeolite membrane was supplied by Mitsui Engineering and Shipbuilding, Japan. The active layer of the membrane was a 30 μm thickness hydrothermally synthesized NaA zeolite layer on a kaolin support. The porous support was made of mullite with 65 wt% alumina content. The average pore size and porosity of the membrane were 1 μm and 40%, respectively. The membrane's ID and OD were 10 and 12.5 mm, respectively, with an active length of 18 cm [28].

The tubular module was designed and made in the form of a double pipe with proper inlet and outlet connections, where the inner pipe was the zeolite membrane and the outer shell was made of Teflon as shown in Fig. 1(a).

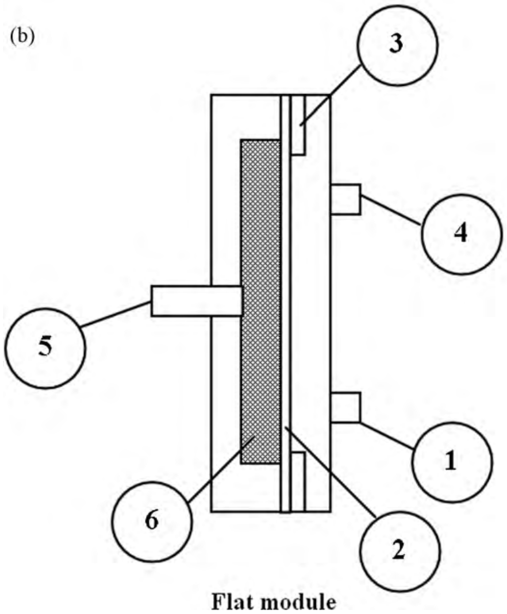
The experiments with polymeric membrane were conducted using PERVAP® 2201 (supplied by Sulzer) in a different module with a flat geometry. Similar to the tubular module, the flat module was made of Teflon and the active surface area of the membrane was equal to 5 cm × 12.5 cm. A schematic diagram of this module is illustrated in Fig. 1(b).

2.3. Experimental setup

A schematic layout of the experimental setup is shown in Fig. 2. Liquid phase esterification reaction was performed in a laboratory scale glass batch reactor. The reactor was placed in an oil bath which was simultaneously heated and stirred using an electrical heater and a magnetic stirrer. A temperature regulator connected to the heater was used to control and maintain temperature at the appropriate level. In the reactor, reaction and vaporization occurred simultaneously and the vapor generated in the reactor was fed to the membrane module via a connection. The temperature of the module was maintained at reaction temperature in order to avoid vapor condensation in the module during the separation process. The tubular and flat modules were sealed by solvent resistant Teflon O-rings and silicon rubber gaskets, respectively. The vacuum on the permeate side was maintained at 2mbar using a three-stage diaphragm vacuum pump (Mod. MD1, Vacuubrand,



Tubular module



Flat module

Fig. 1. (a) Tubular zeolite membrane vapor permeation module: (1) feed inlet, (2) membrane, (3) Teflon O-ring, (4) retentate outlet, and (5) permeate outlet, (b) flat PERVAP® 2201 membrane vapor permeation module: (1) feed inlet, (2) membrane, (3) silicon rubber, (4) retentate outlet, (5) permeate outlet, and (6) membrane support.

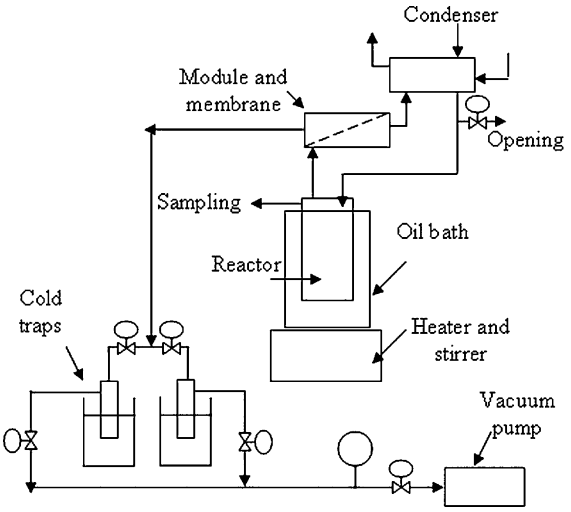


Fig. 2. Schematic diagram of the experimental setup.

GMBH, Germany). The permeate was collected over time using two cold traps set in parallel. The part of the vapor which did not pass through the membrane, called retentate vapor, was passed through a shell and tube water cooling condenser to be totally condensed before being recirculated into the liquid phase of the reactor. A small opening was made at the top of the condenser outlet to prevent pressure buildup in the reactor so that the reaction occurred at ambient pressure (about 0.84 bar). The whole setup was tested for leakage by some test runs on a water/ethanol mixture and mass balances were made on both components after each run.

2.4. Analysis

2.4.1. Determination of permeate composition

The permeate samples were screened for their isopropanol, propionic acid, and isopropyl propionate content by HPLC (Jasco, Germany) equipped with an Amino HPX-87H column. RI detector (operated at 40 °C) and UV detector (worked at a wavelength of 210 nm) were used for alcohol and acid detection, respectively. Oven temperature for HPLC was adjusted at 60 °C and 0.005 M sulfuric acid was used as the eluent. The samples were twenty times diluted with 35 vol.% acetonitrile aqueous solution and the injection rate was 0.6 ml/min.

2.4.2. Determination of the reaction mixture composition

The reaction mixture samples, after dewatering, were analyzed by GC (P-4410, Philips) operated with an OV1 packed column. The column temperature programming was given by the following plan:

The initial temperature was held at 80 °C for 3 min to be later increased to 150 °C at a rate of 10 °C/min and kept at this temperature for 1 min. The FID detector temperature was 250 °C and the injector temperature was adjusted at 150 °C.

2.5. Determination of separation factors

The separation factor of water with respect to alcohol was calculated as follows:

$$\alpha = \frac{y_{\mathrm{w,p}}/y_{\mathrm{al,p}}}{y_{\mathrm{w,v}}/y_{\mathrm{al,v}}}$$

in which, $y_{\mathrm{w,v}}$ and $y_{\mathrm{al,v}}$ represent mole fractions of water and alcohol in the vaporous feed of the membrane module, respectively. Also $y_{\mathrm{w,p}}$ and $y_{\mathrm{al,p}}$ are mole fractions of these components in the permeate, respectively. As already explained in Section 2.4.1, the mole fractions in the permeated phase were determined by HPLC analysis. For the components in the vapor phase, however, their determination had to be based on the equilibrium between liquid and vapor phases in the reactor. For this purpose, the mole fractions of the components in the liquid phase were determined by the results from GC analysis for organics and mass balance for water. Subsequently, the vapor composition was determined by applying UNIFAC and Ideal Gas equations for the liquid and vapor phases, respectively.

To make the mass balance for water, the total mass of water in the permeated phase was determined from the results of the HPLC analysis. On the other hand, the number of moles of water produced was obtained using the results of GC analysis for samples taken from the reaction mixture and the mole number of ester. Finally, since the system was sealed with no leaks, the mass balance for water was used to obtain the amount of water in the reaction mixture.

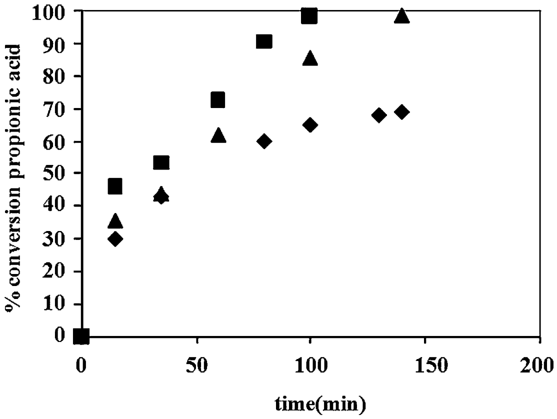


Fig. 3. Variation of acid conversion with time for an alcohol/acid ratio of 1.5:1 with the three different systems: VP and zeolite membrane (■); VP and polymeric membrane (▲); without membrane (◆).

3. Results and discussion

3.1. Effect of membrane type

Fig. 3 depicts the variation in acid conversion with time in the experiments carried out with an alcohol to acid ratio of 1.5:1. These experiments were performed in three different modes: without simultaneous separation or facilitated by the vapor permeation process using either zeolite or polymeric membranes.

Fig. 3 shows that in the experiments facilitated by the vapor permeation system, selective removal of the produced water from the reaction mixture could break the limiting equilibrium and, thus, a complete conversion could be achieved over a short period of time. In the experiment without membrane separation, the conversion achieved after 140 min was 69% and the equilibrium conversion reached after 200 min was nearly 72%.

It should be noted that during the initial 30 min, the amount of water produced and accumulated in the reactor was low, indicating that water removal by the membrane process had no significant effect on the reaction conversion. Hence, no considerable difference was observed between acid conversion values in the processes with or without a membrane. In the case of the process without a membrane, further progress in the reaction with time was limited by the equilibrium due to the accumulation of water in the reactor. So the effect of membrane dehydration can be more distinctly observed over longer process times.

3.2. Effect of initial alcohol/acid molar ratio

To investigate the effect of the reactants' molar ratio, the initial molar ratio of isopropanol to propionic acid was varied in the range of 1:1 to 3:1. As seen in Fig. 4, at a molar ratio of 1:1, ultimate conversions achieved by polymeric and zeolite membranes were 65% and 68%, respectively. This value increased to 98% for a molar ratio of 1.5:1 for both types of membrane.

This finding was in agreement with those obtained by other researchers who reported that acid conversion in different esterification reactions without a membrane separator could be enhanced by increasing the alcohol to acid molar ratio [24–27]. However, a different trend was observed in both membrane types when the alcohol to acid molar ratio was further increased to 3:1. Results show that acid conversion declined when the molar ratio increased from 1.5:1 to 3:1. This observation can be explained by considering the effect of the alcohol content of the feed mixture on the reaction mixture boiling point. The boiling points for different mixtures are given in Table 1. Increasing the alcohol content of the reaction mixture as the result of increasing the alcohol to acid molar ratio from 1.5:1 to 3:1 led to a reduction of boiling point by nearly 5 °C and, thereby, to the reduced reaction temperature of the mixture. As a result, the rate of reaction declined and a lower level of acid conversion was achieved for higher alcohol content in the feed solution. This explanation for the effect of molar ratio is in agreement with previous investigations of esterification reactions [29–34]. With the rise in isopropanol concentration in the initial reaction mixture, more alcohol was evaporated during the reaction process which, in turn, caused alcohol concentration to increase in the vapor in contact with the membrane. This had two effects on the separation process. The first involved more sites being occupied by alcohol molecules on the membrane surface with increasing isopropanol concentration in the vapor phase. In this situation, the contact between water molecules and the membrane surface decreased, led to reduced water permeation through the membrane. The second effect was due to the increase in alcohol concentration in the feed mixture and, thereby, in the vapor phase. This effect reduced the water partial pressure in the vapor in contact with the membrane. Table 2 presents the mole fractions of all the components in both liquid and vapor phases in the reactor as well as the permeated phase in the experiments carried out with

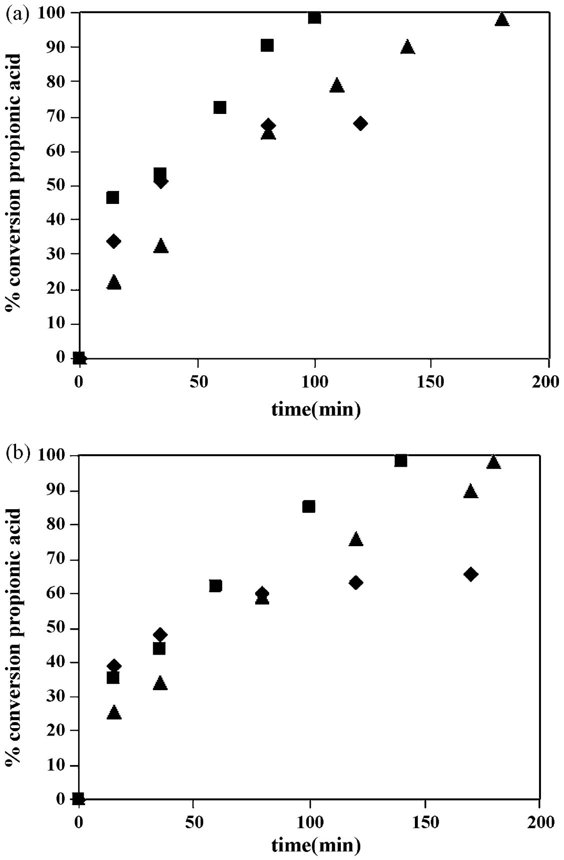


Fig. 4. Effect of isopropanol to propionic acid initial molar ratio on the conversion of propionic acid with (a) NaA zeolite membrane and (b) PERVAP® 2201 membrane, for initial reactant molar ratios of: 1:1 (◆), 1.5:1 (■), and 3:1 (▲).

Table 1
Boiling points of the reaction mixture at different initial alcohol/acid molar ratios.

Alcohol/acid molar ratio	Boiling point (°C)
1:1	92
1.5:1	86
3:1	81

Table 2
Mole fractions of the reaction components in the liquid and vapor phases (x and y, respectively) and in the permeated phase ($y_{i,p}$); for the experiments with the NaA zeolite membrane and two initial alcohol/acid molar ratios: (a) 1.5:1 and (b) 3:1.

(a)

Time (min)	Alcohol			Acid		
	x	y	y_p	x	y	y_p
0	0.60	0.94	0.00	0.40	0.06	0.00
15	0.61	0.85	–	0.14	0.01	–
35	0.48	0.77	0.53	0.20	0.02	0.00
60	0.44	0.70	0.47	0.14	0.02	0.00
80	0.39	0.62	0.47	0.06	0.01	0.00
100	0.34	0.57	0.72	0.00	0.00	0.00

(a)

Time (min)	Ester			Water		
	x	y	y_p	x	y	y_p
0	0.00	0.00	0.00	0.00	0.00	0.00
15	0.13	0.09	–	0.13	0.04	–
35	0.22	0.17	0.00	0.10	0.03	0.47
60	0.37	0.27	0.00	0.05	0.01	0.53
80	0.53	0.37	0.00	0.02	0.00	0.53
100	0.65	0.43	0.00	0.01	0.00	0.28

(b)

Time (min)	Alcohol			Acid		
	x	y	y_p	x	y	y_p
0	0.75	0.97	0.00	0.25	0.03	0.00
15	0.68	0.91	–	0.20	0.02	–
35	0.68	0.90	0.78	0.18	0.02	0.00
80	0.65	0.83	0.61	0.10	0.01	0.00
110	0.65	0.80	0.52	0.07	0.01	0.00
140	0.59	0.76	0.60	0.04	0.00	0.00

(b)

Time (min)	Ester			Water		
	x	y	y_p	x	y	y_p
0	0.00	0.00	0.00	0.00	0.00	0.00
15	0.06	0.05	–	0.06	0.02	–
35	0.08	0.07	0.00	0.06	0.02	0.22
80	0.19	0.14	0.00	0.05	0.01	0.39
110	0.27	0.20	0.00	0.00	0.00	0.48
140	0.33	0.23	0.00	0.06	0.02	0.40

zeolite membrane at two different molar ratios. It is seen that a smaller mole fraction was obtained for alcohol in the vapor phase in the experiment carried out at a molar ratio of 1.5:1. This was contrary to the relative mole fractions of water for two different molar ratios, where the mole fraction of water was smaller for a molar ratio of 3:1. These different relative situations of the mole fractions led to a decreased driving force for water permeation at greater molar ratios (3:1). These two effects resulted in a low acid conversion due to the water accumulation in the reaction mixture and according to the Loshatolie's law.

Comparison of acid conversions for the two membrane types revealed the superior performance of zeolite membrane. Indeed, the properties of the zeolite membrane led to a higher acid conversion during esterification facilitated by vapor permeation process for different initial alcohol/acid molar ratios.

3.3. Effectiveness of the zeolite membrane

The effect of the NaA zeolite membrane on water removal by vapor permeation during the esterification reaction is shown in Fig. 5.

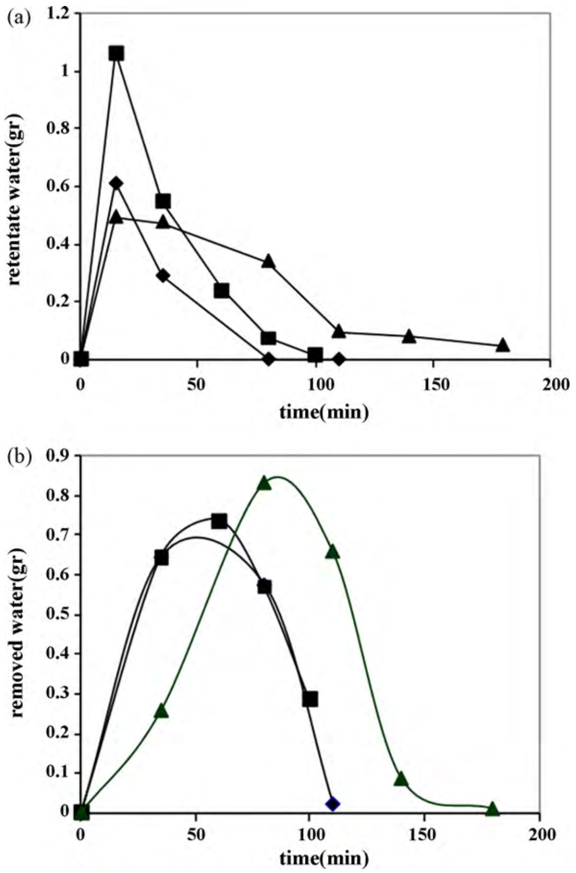


Fig. 5. Variation of water mass (g) with time in the system equipped with the NaA zeolite membrane in (a) reaction mixture and (b) permeated phase, for the initial reactant molar ratios of 1:1 (♦), 1.5:1 (■) and 3:1 (▲).

Fig. 5(a) shows the variation in the mass of water remaining in the reaction mixture with process time for three different alcohol/acid molar ratios. At all molar ratios, a rapid reaction rate in the early stages of the process caused a rapid increase in the water remaining in the reaction mixture, which was followed by a reduction due to the vapor permeation process. The reaction rate and the amount of water produced in each time interval are given in Table 3 for the experiments carried out at a molar ratio of 1.5:1. According to the data given in this table, a high reaction rate and, hence, a high amount of water obtained during the first time interval. This was due to the high initial concentration of the reactants. In addition, the rate of water removal from the vapor phase was lower than that of water production, indicating that the membrane process was not capable of removing water as fast as it was produced. Thus, water accumulated in the reactor. The high water accumulation affected reaction rate due to the equilibrium nature of the reaction, leading to a sharply reduced amount of water production in the second time interval. Water removal from the reaction media by the membrane module led to small increases

Table 3
Instantaneous water production and reaction rate for the system equipped with the NaA zeolite membrane at an initial alcohol/acid molar ratio of 1.5:1.

Time interval (min)	Instantaneously produced water (g)	Reaction rate (mole/h g catalyst)
0–15	1.07	0.85
15–35	0.13	0.08
35–60	0.43	0.21
60–80	0.40	0.24
80–100	0.23	0.07

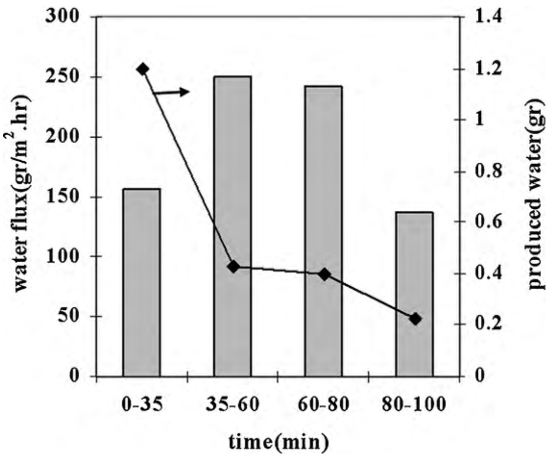


Fig. 6. Variation of water flux and the amount of produced water during different time periods at the initial reactant molar ratio of: 1.5:1 in the system equipped with the NaA zeolite membrane.

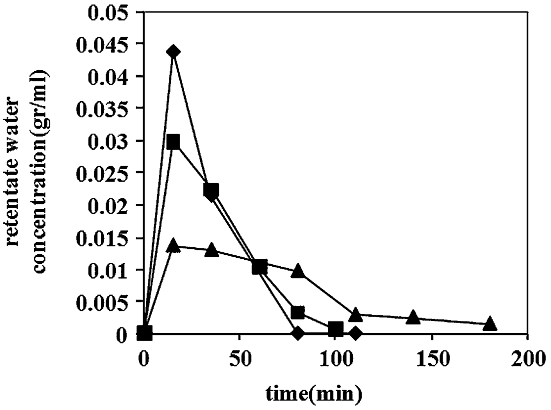


Fig. 7. Water concentration in the reaction mixture versus time in the system equipped with the NaA zeolite membrane and for the initial reactant molar ratios of: 1:1 (♦), 1.5:1 (■), and 3:1 (▲).

in both reaction rate and water production during the following time interval. However, reaction rate significantly dropped during the last time interval (80–100 min) due to the consumption of the reactants. The water flux through the membrane and the amount of water produced for a molar ratio of 1.5:1 over different time intervals are graphically shown in Fig. 6, which confirms the above explanation suggested for the variation in the amount of water produced and the action of the membrane module. The curves for the behavior of the remaining water indicate successful water removal by the zeolite membrane from the reaction mixture. This conclusion is confirmed by the negligible amounts of water in the reaction mixture at the final stages of the process, as also shown in Fig. 5(a).

It is also seen in the figure that the amount of remaining water at the initial stages of the process was higher for an alcohol/acid molar ratio of 1.5:1 than that for the other two molar ratios. As mentioned earlier, decreasing the alcohol/acid molar ratio from 1.5:1 to 1:1 or increasing it from 1.5:1 to 3:1 led to lower acid conversion and water production in the reaction mixture (as also seen in Fig. 4(a)). This effect caused more water to be produced in the early stages of the process (before 40 min) for the alcohol/acid molar ratio of 1.5:1. Together with the fact that the separation process was the controlling step in the whole process (due to limited membrane surface area), consequently, more water was accumulated in the reaction mixture for the experiment with the reactants' molar ratio of 1.5:1. When enough time has passed, the experiment tends toward termination and the amount of remaining water also diminishes. However, the experiment carried out at a molar ratio of 3:1 is not yet complete at this stage and more water is, therefore, accumulated in the reaction mixture than that in the experiment with a reactants' molar ratio of 1.5:1.

The effect of reaction conversion rate on water permeation rate can be seen in Fig. 5(b). At the early stages of the process, the rate of water production is high and the amount of water removed (permeated), therefore, increases with time. As reaction proceeds toward its completion, less water is produced and, in turn, a reduction is observed in the amount of water permeated. This can be easily understood by examining the curves in Figs. 4(a) and 5(b) for one specific molar ratio, e.g. 1.5:1. It is seen that the slope of the curve for this molar ratio in Fig. 4(a) is initially high but it takes a milder slope as the reaction draws near its completion. The reduced acid conversion leads to less water produced at each interval. As a result, a reduction is observed in the amount of water removed (permeated). This state of affairs gives rise to a maximal curve for the amount of removed water, as seen in Fig. 5(b). This behavior is seen with some delay for the experiment with a reactants' molar ratio of 3:1. This delay is due to the lower conversion rate of this experiment compared to the other two so that less water was produced and permeated through the membrane at the initial stages of the process. After sometime, however, at the time when other experiments reached their final points and the amount of permeated water diminished, this value for the experiment with a reactants' molar ratio of 3:1 reached its maximum to subsequently drop to lower values.

The variation in water concentration in the reaction mixture and the water flux through the membrane with time is shown in Figs. 7 and 8, respectively, for all alcohol/acid molar ratios. It is clear in Fig. 7 that water concentration increased and then decreased with time during the coupled reaction/separation process which can be explained by the same reasoning used to explain the variation in the amount of remaining water. This behavior affected the amount of water flux through the membrane.

Examination of Fig. 8 reveals that decreased water concentration in the reaction mixture and in the vapor produced from this mixture leads to a corresponding reduction in water flux. This is due to the lessened driving force for water molecules to pass through the membrane. Another reason for the flux drop at low water concentrations may be the increased alcohol concentration in the vapor in contact with the membrane. With increasing isopropanol concentration in the vapor phase, higher fractions of the membrane surface come into contact with alcohol molecules, decreasing the chance for water molecules to meet membrane pores. This can reduce water flux through the membrane.

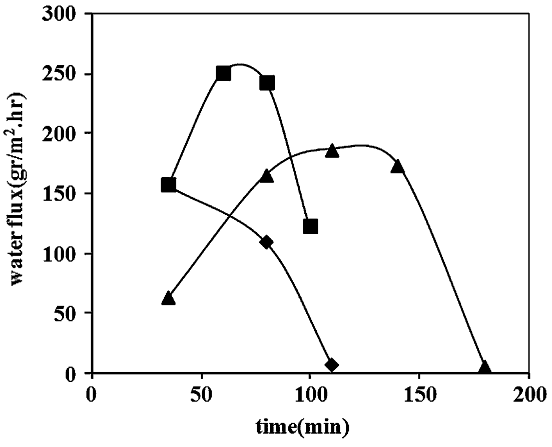


Fig. 8. Variation of water flux through the NaA zeolite membrane versus time for the initial reactant molar ratios of: 1:1 (♦), 1.5:1 (■) and 3:1 (▲).

Table 4
Calculated separation factors for different alcohol/acid molar ratios for the NaA zeolite membrane.

Alcohol/acid molar ratio	Time (min)	Separation factor
1:1	35	118
1:1	80	163,847
1:1	120	3347
1.5:1	35	70
1.5:1	60	216
1.5:1	80	219,072
1.5:1	100	18,383
3:1	35	52
3:1	80	132
3:1	110	24,160
3:1	140	2

The data given in Table 2 were used to calculate the separation factors for the different alcohol/acid molar ratios of 1:1, 1.5:1, and 3:1 and reported in Table 4. It is seen that a high instantaneous separation factor of nearly equal to 220,000 can be achieved by using NaA zeolite membrane at proper reactant molar ratios. It is worth mentioning that the separation factor is a complicated function of reaction rate and separation process performance. Therefore, no specific trend can be seen in the variation of this factor.

3.4. Effectiveness of the polymeric membrane

Fig. 9 shows the variations in the amounts of remaining water and permeated water with time for the experiments with PERVAP® 2201 membrane and for all the alcohol/acid molar ratios used.

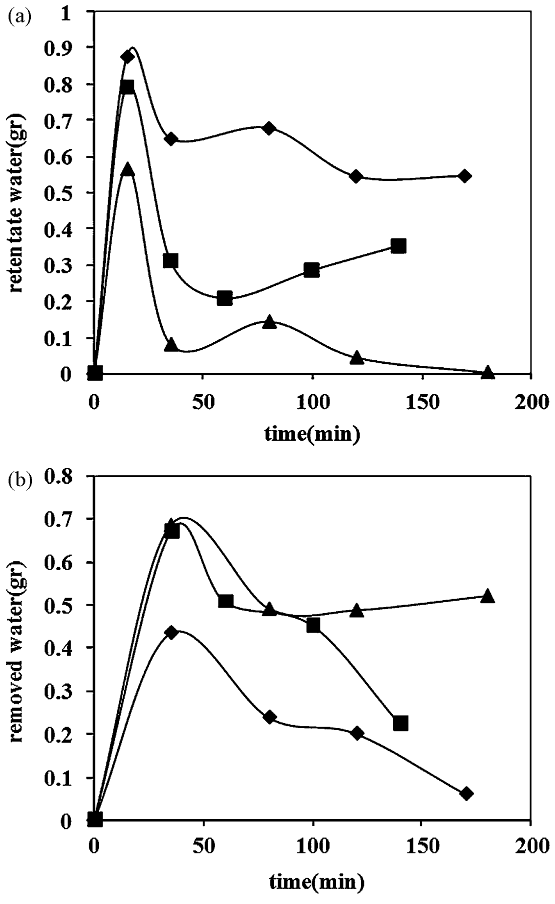


Fig. 9. Variation of water mass (g) with time in the system equipped with the PERVAP® 2201 membrane in (a) reaction mixture and (b) permeated phase, for the initial reactant molar ratios of 1:1 (♦), 1.5:1 (■) and 3:1 (▲).

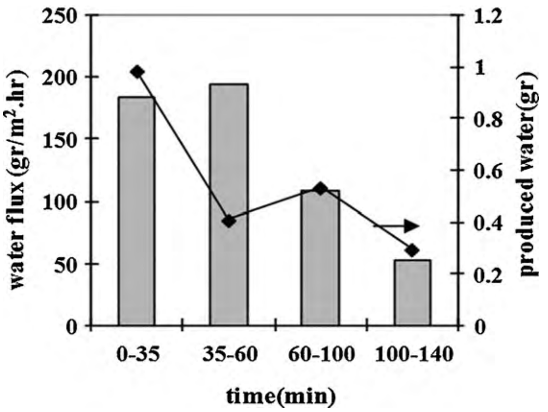


Fig. 10. Variation of water flux and the amount of produced water during different time periods at the initial reactant molar ratio of: 1.5:1 in the system equipped with the PERVAP® 2201 membrane.

It is seen that the curves in this figure represent a different general trend from that obtained for the zeolite membrane. This is due to the fact that the active surface area of the polymeric membrane (62.5 cm^2) was slightly smaller than that of the zeolite membrane (70.7 cm^2). The different natures of the membranes and the differences in active surface areas affect the quantitative contribution of the vapor permeation process to the overall result of the whole process.

This effect can be established by comparing the amount of water remaining in the reaction mixture for two experiments with reactant molar ratios of 1.5:1 and 3:1 in Fig. 9(a). Despite the higher acid conversion achieved in the reaction with a molar ratio of 1.5:1, the polymeric membrane was not able to remove all the water produced due to its smaller surface area so that the amount of remaining water was high. However, in the experiment with the molar ratio of 3:1, acid conversion and thereby the amount of water produced were lower; hence, less water remained in the reaction mixture. It should be noted that less acid conversion generally occurred with the polymeric membrane, which was due to the lower capability of the membrane in selective water removal.

Fig. 9(a) shows the highest values of remaining water in the reaction mixture for the molar ratio of 1:1. The reason for this can be understood by considering the effect of mixture alcohol content on the evaporation rate in the reactor. In the experiment carried out at this molar ratio, acid conversion was slightly higher during the first 30 min of the reaction than it was in the other two experiments (Fig. 4(b)). So, more water was generated during this time. In addition, lowering the alcohol content of the reaction mixture increased its boiling point and evaporation rate in the reactor was, therefore, lower in this case. This reduction in evaporation rate enhanced the amount of the water remaining in the reactor. Also, the lower evaporation rate led to reduced amounts of permeated water in this case, as seen in Fig. 9(b).

Fig. 10 shows the variations in water flux and amount of produced water over different periods during the experiments carried out at a molar ratio of 1.5:1. Similar to Fig. 6, some variation is again seen in both variables for which the same reasoning can be suggested as was used for the situation in Fig. 6.

The reaction rates and the amounts of water produced over each time period are presented in Table 5 for the experiment using the polymeric membrane and with the molar ratio of 1.5:1.

Variations in water concentration in the reaction mixture and the water flux through the membrane for different reactant molar ratios are plotted against time in Figs. 11 and 12, respectively. These figures show that the water flux reduced with decreasing water concentration in the reaction mixture. As already mentioned for the similar case of experiments with the zeolite membrane, this

Table 5
Instantaneous water production and reaction rate for the system equipped with the PERVAP® 2201 membrane with an initial alcohol/acid molar ratio of 1.5:1.

Time interval (min)	Instantaneously produced water (g)	Reaction rate (mole/h g catalyst)
0–15	0.80	0.63
15–35	0.18	0.11
35–60	0.40	0.19
60–100	0.53	0.16
100–140	0.30	0.09

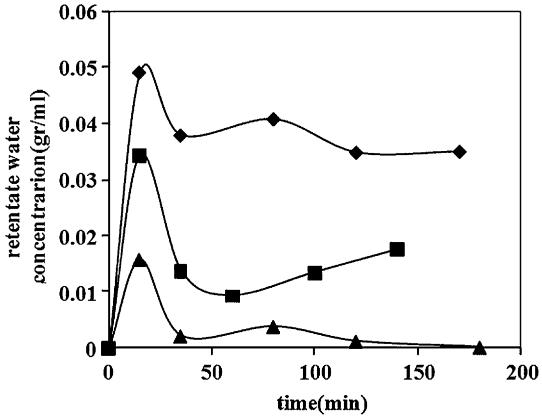


Fig. 11. Water concentration in the reaction mixture versus time in the system equipped with the PERVAP® 2201 membrane and for the initial reactant molar ratios of: 1:1 (♦), 1.5:1 (■), and 3:1 (▲).

behavior may be due to the effect of water and alcohol concentrations in the vapor phase in contact with the membrane.

Table 6
Mole fractions of the reaction components in the liquid and vapor phases (*x* and *y*, respectively) and in the permeated phase ($y_{i,p}$); for the experiments with the PERVAP® 2201membrane and an initial alcohol/acid molar ratio of 1.5:1.

Time (min)	Alcohol			Acid		
	x	*y*	y_p	*x*	*y*	y_p
0	0.60	0.94	0.00	0.40	0.06	0.00
15	0.45	0.78	–	0.26	0.04	–
35	0.47	0.78	0.38	0.26	0.04	0.00
60	0.44	0.71	0.22	0.20	0.02	0.00
100	0.33	0.60	0.25	0.09	0.01	0.00
140	0.23	0.48	0.07	0.01	0.00	0.00

Time (min)	Ester			Water		
	x	*y*	y_p	*x*	*y*	y_p
0	0.00	0.00	0.00	0.00	0.00	0.00
15	0.14	0.12	–	0.14	0.06	–
35	0.20	0.17	0.00	0.06	0.02	0.62
60	0.31	0.25	0.00	0.05	0.01	0.78
100	0.50	0.38	0.00	0.07	0.02	0.75
140	0.65	0.48	0.00	0.10	0.03	0.93

Table 7
Calculated separation factors for different alcohol/acid molar ratios for the PERVAP® 2201membrane.

Alcohol/acid molar ratio	Time (min)	Separation factor
1:1	35	243
1:1	80	131
1.5:1	35	230
1.5:1	60	753
1.5:1	100	338
1.5:1	140	680
3:1	35	9650
3:1	80	8678
3:1	120	10,746
3:1	180	1635

The mole fractions of all components in the liquid and vapor phases in the reactor as well as the permeated phase are given in Table 6 for the experiments carried out with the polymeric membrane and at the molar ratio of 1.5:1. Also, the separation factors of water with respect to alcohol for this set of experiments are presented in Table 7. The different values reported in this table for the separation factors with their considerable variations can be explained by referring to the fact that the amount of separation factor is affected by the two reaction and separation processes. In general, the concentrations of reactants and products in the reaction mixture and the vapor evolved from the reactor in such a coupled process change as the reaction and separation processes progress. Since the separation factor is a function of water and alcohol concentrations and because these are affected by such different parameters as reaction and evaporation rates for each experiment, an inconsistency is observed in separation factors for different alcohol/acid molar ratios.

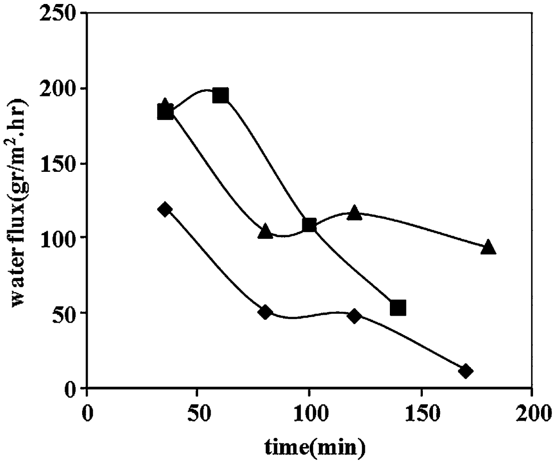


Fig. 12. Variation of water flux through the PERVAP® 2201 membrane versus time for the initial reactant molar ratios of: 1:1 (♦), 1.5:1 (■) and 3:1 (▲).

4. Conclusion

This paper studied the effect of vapor permeation process employed to improve reaction conversion rate in the esterification of propionic acid and isopropanol catalyzed with para toluene sulfonic acid. For this purpose, two different commercial membranes, namely a tubular NaA zeolite membrane and a flat polymeric membrane (PERVAP® 2201), were used to selectively remove water from the reaction atmosphere during the equilibrium esterification reaction. The vapor permeation process coupled with the reaction significantly increased acid conversion during the processes with both the zeolite and polymeric membranes. For the esterification reaction without facilitation by the membrane process, an acid conversion of 69% was achieved after 140 min at an alcohol/acid molar ratio of 1.5:1. The equilibrium conversion in this case was extrapolated to be about 72%. But, using the membrane process simultaneously for the selective removal of water from the reaction media yielded a complete acid conversion over a reasonably shorter time.

Investigation of the effect of alcohol/acid molar ratio with three different values of 1:1, 1.5:1 and 3:1 showed that this ratio had a considerable effect on acid conversion and on the amount of water remaining in the reaction mixture during the process. The highest reaction rate was observed for an alcohol/acid molar ratio of 1.5:1 with both types of membrane. In addition, complete reaction conversion could be achieved only at alcohol/acid molar ratios of 1.5:1 and 3:1 with both types of membrane used in this study.

The values obtained for permeated water flux showed that this flux was strongly influenced by acid conversion during the coupled process. On the other hand, at molar ratios of 1:1 and 3:1, acid conversion was low and alcohol was, therefore, the dominant component in the vapor due to the lower production of water in the reactor. These two effects led to reduced water flux through the membrane.

No specific trend was observed in the results of calculated separation factors. This was due to the fact that separation factor in the coupled process was affected by both reaction and separation processes, which are, in turn, influenced by such parameters as the rate of vapor production, the initial alcohol/acid molar ratio of the reactants, and its effect on the boiling point of the mixture, which are responsible for the large variation seen in the value of the separation factor.

Finally, NaA zeoilte membrane was successfully used in the proposed reaction and separation system without any defect by avoiding direct contact with propionic acid. As indicated by Tables 2 and 6, the mole fraction of propionic acid in the vapor phase was less than 6% in all the experiments. In fact, no significant amount of the acid was vaporized during the process due its high boiling point, from which it may be concluded that the zeolite membrane was not in great contact with the acid. This makes it possible to use zeolite membranes in membrane systems in conjunction with the esterification reaction, whereas it is almost impossible to use zeolite membranes in normal applications of the pervaporation system with this reaction system. This is due to the direct contact between the liquid acid and the membrane and o the negative effect of the acid on zeoilte membranes.

References

[1] S. Lauterbach, P. Kreis, Experimental and theoretical investigation of a pervaporation membrane reactor for a heterogeneously catalysed esterification, Desalination 199 (2006) 418–420.

[2] Ó. Iglesia, R. Mallada, M. Menéndez, J. Coronas, Continuous zeolite membrane reactor for esterification of ethanol and acetic acid, Chem. Eng. J. 131 (2007) 35–39.

[3] M.A. Salomón, J. Coronas, M. Menéndez, J. Santamaría, Synthesis of MTBE in zeolite membrane reactors, Appl. Catal. A: Gen. 200 (2000) 201–210.

[4] H. Kita, S. Sasaki, K. Tanaka, K.I. Okamoto, M. Yamamoto, Esterification of carboxylic acid with ethanol accompanied by pervaporation, Chem. Lett. (1988) 2025–2028.

[5] K. Okamoto, T. Semoto, K. Tanaka, H. Kita, Application of pervaporation to phenol–acetone condensation reaction, Chem. Lett. (1991) 167–170.

[6] K. Okamoto, M. Yamamoto, Y. Otoshi, T. Semoto, M. Yano, K. Tanaka, H. Kita, Pervaporation aided esterification of oleic acid, J. Chem. Eng. Jpn. 26 (1993) 475–481.

[7] G.K. Pearse, Esterification process, European Patent, 0,210,055 (1987).

[8] M.O. David, T.Q. Nguyen, J. Neel, Pervaporation membranes endowed with catalytic properties, based on polymer blends, J. Membr. Sci. 73 (1992) 129–141.

[9] M. Matouq, T. Tagawa, S. Goto, Combined process for production of methyl tert-butyl ether from tert-butyl alcohol and methanol, J. Chem. Eng. Jpn. 27 (1994) 302–306.

[10] M. Teresa Sanz, J. Gmehling, Esterification of acetic acid with isopropanol coupled with pervaporation. Part I: kinetics and pervaporation studies, Chem. Eng. J. 123 (2006) 1–8.

[11] K. Okamoto, H. Kita, K. Horii, K. Tanaka, M. Kondo, Zeolite NaA membrane: preparation, single-gas permeation, and pervaporation and vapor permeation of water/organic liquid mixtures, Ind. Eng. Chem. Res. 40 (2001) 163.

[12] Y. Morigami, M. Kondo, J. Abe, H. Kita, K. Okamoto, The first large-scale pervaporation plant using tubular-type module with zeolite NaA membrane, Sep. Purif. Technol. 25 (2001) 251.

[13] M.A. Camblor, A. Corma, S. Iborra, S. Miquel, J. Primo, S. Valencia, Beta zeolite as a catalyst for the preparation of alkyl glucoside surfactants: the role of crystal size and hydrophobicity, J. Catal. 172 (1997) 76.

[14] H. Takaba, A. Koyama, S. Nakao, Dual ensemble Monte Carlo simulation of pervaporation of an ethanol/water binary mixture in silicalite membrane based on a Lennard–Jones interaction model, J. Phys. Chem. B 104 (2000) 6353.

[15] Y. Oumi, A. Miyajima, J. Miyamoto, T. Sano, Binary mixture adsorption of water and ethanol on silicalite, Stud. Surf. Sci. Catal. 142 (2002) 1595.

[16] X. Chen, Z.H. Ping, Y.C. Long, Separation properties of alcohol–water mixture through silicalite-I-filled silicone rubber membranes by pervaporation, J. Appl. Polym. Sci. 67 (1998) 629.

[17] S. Li, V.A. Tuan, J.L. Falconer, R.D. Noble, Properties and separation performance of Ge-ZSM-5 membranes, Micropor. Mesopor. Mater. 58 (2003) 137.

[18] V. Van Hoof, Ch. Dotremont, A. Buekenhoudt, Performance of Mitsui NaA type zeolite membranes for the dehydration of organic solvents in comparison with commercial polymeric pervaporation membranes, Sep. Purif. Technol. 48 (2006) 304.

[19] J.J. Jafar, P.M. Budd, R. Hughes, Enhancement of esterification reaction yield using zeolite A vapour permeation membrane, J. Membr. Sci. 199 (2002) 117–123.

[20] Y. Tadafumi, A. Jun, S. Etsuo, Development of membrane aided reactor, Mitsui Zosen Tech. Rev. 178 (2003) 115–120.

[21] K. Tanaka, R. Yoshikawa, C. Ying, H. Kita, K. Okamoto, Application of zeolite T membrane to vapor-permeation-aided esterification of lactic acid with ethanol, Chem. Eng. Sci. 57 (2002) 1577–1584.

[22] K. Tanaka, R. Yoshikawa, C. Ying, H. Kita, K. Okamoto, Application of zeolite membranes to esterification reactions, Catal. Today 67 (2001) 121–125.

[23] T. Inoue, T. Nagase, Y. Hasegawa, Y. Kiyozumi, K. Sato, K. Kobayashi, M. Nishioka, S. Hamakawa, F. Mizukami, Ester condensation from a stoichiometric mixture of a carboxylic acid and an alcohol at 313 K assisted by pervaporation via zeolite membranes, Chem. Lett. 35 (1) (2006).

[24] G.D. Yadav, H.B. Kulkarni, Ion-exchange resin catalysis in the synthesis of isopropyl lactate, React. Funct. Polym. 44 (2000) 153–165.

[25] G.D. Yadav, M.B. Thathagar, Esterification of maleic acid with ethanol over cation exchange resin catalysts, React. Funct. Polym. 52 (2002) 99–110.

[26] H.A. Sami, T. Alia, Q.M. Sabiha, A.S. Taher, Synthesis of esters: development of the rate expression for the Dowex 50 Wx8-400 catalyzed esterification of propionic acid with 1-propanol, Chem. Eng. Sci. 62 (2007) 3197–3217.

[27] P. Delgado, M.T. Sanz, S. Beltrán, Kinetic study for esterification of lactic acid with ethanol and hydrolysis of ethyl lactate using an ion-exchange resin catalyst, Chem. Eng. J. 126 (2007) 111–118.

[28] M. Kondo, M. Komori, H. Kita, K. Okamoto, J. Membr. Sci. 133 (1997) 133.

[29] K. Venkateswarlu, R. Sinha, R.J. Rao, Kinetics of esterification of n-butanol with propionic acid in a stirred tank batch reactor, Chem. Petrochem. J. (1976) 3–10.

[30] Y.V. Rao, M.S. Reddy, C.V. Rao, A study on the reaction kinetics of n-octyl alcohol esterification with acetic acid in the presence of aluminum sulphate catalyst, Chem. Petrochem. J. (1976) 27–35.

[31] P.S.T. Sai, Esterification kinetics of acetic acid with 1-butanol, J. Energy Heat Mass Transf. 10 (1988) 181–189.

[32] M.J. Lee, H.T. Wu, C.H. Kang, H.M. Lin, Kinetic behavior of amyl acetate synthesis catalyzed by acidic cation exchange resin, J. Chin. Inst. Chem. Eng. 30 (1999) 117–122.

[33] M.M. Awad, A.M. Salem, A.A. Swelam, Kinetics of catalyzed esterification of propionic acid with various alcohols using synthetic cation exchange resin, J. Indian Chem. Soc. 74 (1997) 467–469.

[34] S.H. Ali, S.Q. Merchant, Kinetics of the esterification of acetic acid with 2-ropanol: impact of different acidic cation exchange resins on reaction mechanism, Int. J. Chem. Kinet. 38 (2006) 593–612.