Korean J. Chem. Eng., **28**(7), 1593-1598 (2011)
DOI: 10.1007/s11814-010-0532-9

Incorporation of vapor permeation process to esterification reaction of propionic acid and isopropanol for performance improvement

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(*Received 19 October 2009 • accepted 29 December 2010*)

Abstract−A commercial tubular zeolite membrane (NaA) was employed in a vapor permeation system to dehydrate the reaction mixture during the esterification of propionic acid with isopropanol. The reaction was performed in a batch reactor, using Amberlyst 15 as a catalyst with different weight fractions relative to propionic acid. Experiments were conducted to investigate the effect of the alcohol-to-acid molar ratio on the performance of the hybrid process. The integration of the chemical reaction with the vapor permeation process significantly enhanced the conversion of the reversible esterification reaction. It was observed that contrary to the effect of increasing alcohol-to-acid molar ratio from 1 : 1 to 1.5 : 1, the acid conversion and the permeated water flux decreased when the reactants molar ratio increased from 1.5 : 1 to 3 : 1. This effect was due to the reducing effect of reaction mixture composition on the boiling point and reaction and evaporation rates during the hybrid process. Also, increasing catalyst loading had noticeable influence on the acid conversion and the permeated water flux.

Key words: Esterification, Isopropyl Propionate, Membrane Reactor, Vapor Permeation, Zeolite Membrane

INTRODUCTION

Esterification is an equilibrium reaction in which water and relatively non-volatile esters are often produced. In practice, an excess of one reactant can be used to shift the equilibrium, and/or water is continuously removed by adsorption on drying agents or by codistillation with such entrainers as benzene to overcome the kinetics equilibrium. Also, water can be separated from the reaction media by a hydrophilic membrane applied in a membrane reactor.

In the last decade, membrane processes such as pervaporation (PV) and vapor permeation (VP) have proven to be energy efficient and highly selective separation processes for the dehydration of organic chemicals and the separation of volatile products. Therefore, the productivity and the conversion rate of equilibrium-limited reactions such as esterification can be significantly enhanced when the reaction is coupled with vapor permeation or pervaporation processes.

In recent years, several theoretical and experimental studies concerning the integration of pervaporation/vapor permeation and condensation reactions have been conducted. Detailed reviews on this subject have been reported by Lipnizki et al. and Lim et al. [1,2].

Among different types of the membranes used in the mentioned processes, the zeolite membranes, having high porosities and well-defined pore sizes in the range of 3-12A°, are noticeably proper candidates for use in membrane reactors. In membrane reactors, since the membrane separation process is affected by the hydrophilicity/hydrophobicity of the membrane, zeolite membranes have the advantage that their hydrophilic/hydrophobic nature can be adjusted by changing the Si/Al ratio in their structure during the membrane synthesis process.

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NaA type zeolite membrane is the first zeolite membrane which has been used in a large-scale pervaporation plant for alcohol dehydration [3]. Also, type-A zeolite membranes are nearly ideal membranes for organic dehydration due to their high hydrophilicity and their XRD pore diameter (0.4 nm), which is smaller than the kinetic diameter of almost all organic molecules but larger than that of water molecules.

However, other zeolite membranes have shown their potential for widespread PV/VP applications. For example, a membrane reactor using an H-ZSM5 membrane was employed by Bernal et al. to study the acetic acid/ethanol esterification reaction [4]. In their work, an equimolar ethanol/acetic acid liquid mixture was fed into the feed side of the membrane module, while the membrane itself acted as the catalyst for the reaction. Tanaka et al. used T-type and NaA-type zeolite membranes in a pervaporation membrane reactor (PVMR) and vapor permeation membrane reactor (VPMR) for esterification reactions [5]. The T-zeolite membrane, which was in direct contact with the reaction mixture, was more stable under acidic conditions and proved to be capable of being used for esterification in a PVMR. On the other hand, by using the NaA membrane in the esterification of oleic acid in a VPMR at 383 K, water removal from the reaction mixture led to complete conversion.

Tanaka et al. used T-type zeolite membrane to study esterification of lactic acid with ethanol coupled with the vapor permeation process. They achieved complete conversion within a short reaction time by removing water from the reaction mixture [6]. In another work, they used the same type of zeolite membrane for esterification of acetic acid with ethanol at 343 k. They reported complete conversion of acid within 8 h at two different initial alcohol-to-acetic acid molar ratios of 1.5 and 2 [7].

Inoue et al. conducted ester condensation from stoichiometric mixture of acetic acid and ethanol, where the reaction was aided by pervaporation using Merlinoite and ZSM-5 zeolite membranes

[8]. They succeeded in preparing a hydrophilic zeolite membrane with good resistance to acidic environment.

In most of the studies, esterification reactions have been integrated with pervaporation systems [4,5,7,8]. In such types of coupled processes, the reaction should be carried out at temperatures below the boiling point of the reaction mixture, which can in turn have negative effect on the reaction rate. In contrast, in conventional methods esterification reactions are carried out at a relatively high temperature, which leads to boiling of the reaction mixture and hence higher reaction rate.

The purpose of the present work is to investigate the effect of coupling an NaA membrane facilitated vapor permeation system with the esterification reaction of isopropanol with propionic acid catalyzed by Amberlyst 15 cation-exchange resin. By this means, the produced water was separated from the vapor phase evolved from liquid phase of the reaction media while it was boiling during the reaction. Therefore, a positive effect of high reaction temperature on the reaction rate was achieved. It is worth noting that as NaA zeolite membranes are usually unstable in acidic environments, direct contact between the membrane and acidic reaction mixture was avoided by using the membrane in the vapor permeation system.

Ion exchange resins have proven to be suitable catalysts for esterification reactions [9-12]. Recently, sulfuric acid has been replaced by ion-exchange resins as dictated by the environmental regulations. Therefore, in this work Amberlyst 15 was used as catalyst for the esterification reaction. Also, to achieve a complete profile, the effects of different parameters such as catalyst loading and alcohol-to-acid molar ratio on propionic acid conversion and water permeation flux were investigated.

EXPERIMENTAL PROCEDURE

1. Materials

Propionic acid (99% purity) and isopropanol (99.8% purity) were purchased from Merck. To run the experiments, synthetic mixtures consisting of 0.125 gmole propionic acid (9.25 g solution) and 0.125, 0.18 and 0.35 gmole isopropanol (7.5 g, 10 g and 20 g solution) provided the isopropanol-to-propionic acid molar ratios of 1 : 1, 1.5 : 1 and 3 : 1, respectively. The strong acidic ion-exchange resin, Amberlyst 15, with an exchange capacity of 4.75 mequiv H^+/g of dry catalyst (Rohm & Haas) was used as catalyst. The resin was washed several times before use with distilled water, and dried at 353.15 K until a constant mass was achieved for a volume of the resin.

2. Membrane

NaA zeolite membrane was supplied by Mitsui Engineering and Shipbuilding, Japan. This membrane was in the form of cylindrical tubes with 10 and 12.5 mm ID and OD, respectively, and 20 cm in length. The active layer of the membrane was a hydrothermally synthesized NaA zeolite layer of 30 μm thickness on a kaolin support. The porous tubular support was made by hydrothermal synthesis of mullite containing 65 wt% alumina. The support had an average pore size of 1 μm and a porosity of about 40% [13].

The tubular module, as shown in Fig. 1, was in the form of a double pipe, where the zeolite membrane was the inner pipe and the outer shell was made of Teflon.

3. Setup

The reaction/separation experimental setup is shown in Fig. 2.

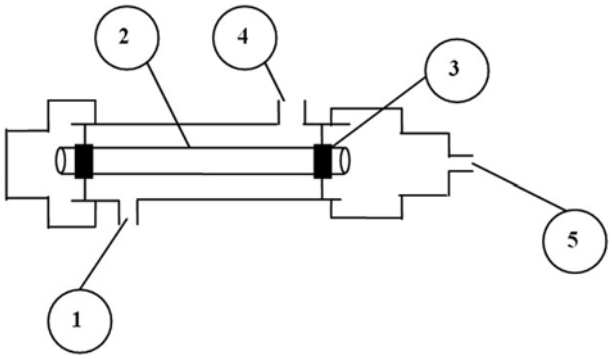

Fig. 1. Schematic diagram of tubular vapor permeation module.
1. Feed inlet
2. Membrane
3. Teflon O-ring
4. Retentate outlet
5. Permeate outlet

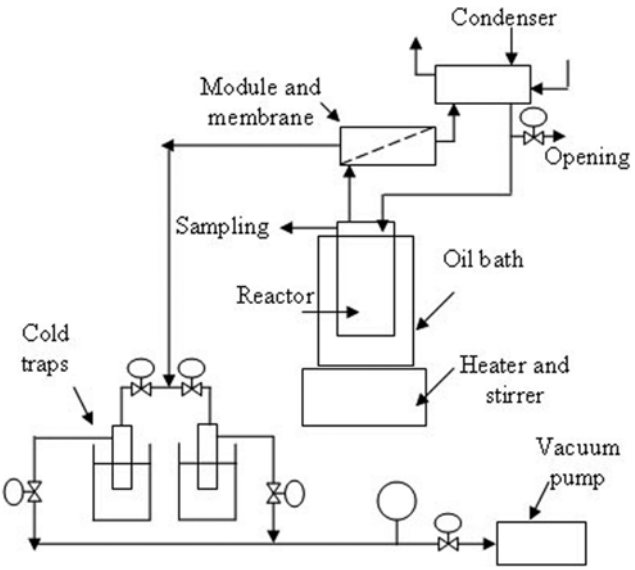

Fig. 2. Schematic diagram of the experimental set-up.

The liquid phase esterification reaction was carried out in a glass batch reactor, placed in an oil bath. A coupled electrical heater and magnetic stirrer were used for heating and mixing the reaction mixture. The bath temperature was controlled during the process by using a temperature regulator connected to the heater. In the reactor, both reaction and vaporization processes occurred simultaneously. Therefore, the vapor generated in the reactor rose into the membrane module, in which the vapor was in contact with the zeolite membrane. The module temperature was held at 90 °C during the separation process. The two sides of the membrane placed in the module were sealed by using solvent-resistant Teflon O-rings. A three-stage diaphragm vacuum pump (Mod. MD1, Vacuubrand, GMBH, Germany) was used to keep the permeated side pressure as low as 2 mbar. Two cold traps were set in parallel to collect the permeated stream during the experiments. The part of the vapor which did not permeate through the membrane, namely retentate vapor, passed through a shell and tube water cooling condenser to be totally condensed before recycling to the liquid phase of the reactor. There was a small opening at the top of the condenser outlet to pre-

vent pressurizing of the reactor, and therefore, the reaction took place at the ambient pressure (about 0.84 bar). The whole setup was tested for leakage by some test runs on water/ethanol mixture and making mass balance on both components after each run.

ANALYSIS

1. Determination of the Permeated Composition

The permeated samples were analyzed for isopropanol, propionic acid and isopropyl propionate content by HPLC (Jasco, Germany) equipped with an Amino HPX-87H column. RI detector worked at 40 °C for isopropanol monitoring, and UV detector wave length was adjusted at 210 nm for acid and ester screening. The oven temperature was set at 60 °C and the eluent was 0.005 M sulfuric acid solution. The samples were injected into the column after twenty times of dilution with 35 vol% acetonitrile aqueous solution, and the flow rate was 0.6 ml/min.

2. Determination of the Reaction Mixture Composition

The reaction mixture samples were analyzed after dewatering. For this purpose, a GC instrument (P-4410, Philips), working with an OV1 packed column, was used. The column temperature was arranged as follows:

The initial temperature was set at 80 °C for 3 minutes and then was increased to 150 °C with a heating rate of 10 °C/min and finally was fixed at this temperature for 1 min.

The working temperatures of the FID detector and the injector were set at 250 °C and 150 °C, respectively.

RESULTS AND DISCUSSION

1. Effect of the Membrane

The variations of propionic acid conversion with time under two conditions, with and without simultaneous vapor permeation process, are shown in Fig. 3. This set of experiments was carried out with alcohol-to-acid molar ratio of 1.5 : 1, where 10 wt% of Amberlyst 15 (with respect to propionic acid) was used as catalyst.

According to this figure, the acid conversion was significantly limited for the experiment without membrane separation process, e.g., conversion was 49% after 240 minutes. On the other hand, as expected, utilizing the reaction with the membrane separation process led to enhancement in the acid conversion (59% in 180 minutes) by selectively removing water from the reaction mixture.

In general, water molecules have a very strong affinity for cation-exchange resins such as Amberlyst 15. So, adsorption of water by the resins is more than the other species presented in the reaction mixture. This is shown by Song et al. [14]. In their work on the esterification of methyl acetate over Amberlyst-15, they measured and compared the adsorption of different components present in their system. It was found that water was adsorbed more strongly than the other species. As a result, high water adsorption on the catalyst decreases the interaction between reactants and resins, which in turn leads to lower acid conversion through the reaction process with Amberlyst 15 as catalyst. When the reversible esterification reaction is coupled with the membrane separation process, this effect is weakened by selectively removing water from the reaction mixture, and thus, high acid conversion is achieved in a coupled reaction/separation system [14].

Also, it is seen that with the progress of reaction time the difference between the acid conversion values for the two processes, with and without membrane separation process, became greater. This can be explained by considering the fact that in the initial time interval of the reaction the mass of the water produced and accumulated in the reactor was low. Therefore, reaction progress and acid conversion were not significantly affected by the water held up in the reaction. This caused a small difference for acid conversion between the two processes. However, as the reaction progressed with time, enhancement of the water mass in the reactor (in the absence of the membrane separation process) limited the reaction progress and caused more difference between acid conversions obtained for the two modes of operation.

2. Effect of Catalyst Loading on Acid Conversion

The effect of catalyst loading is shown in Fig. 4. The catalyst loading was expressed as the weight percentage of the Amberlyst 15

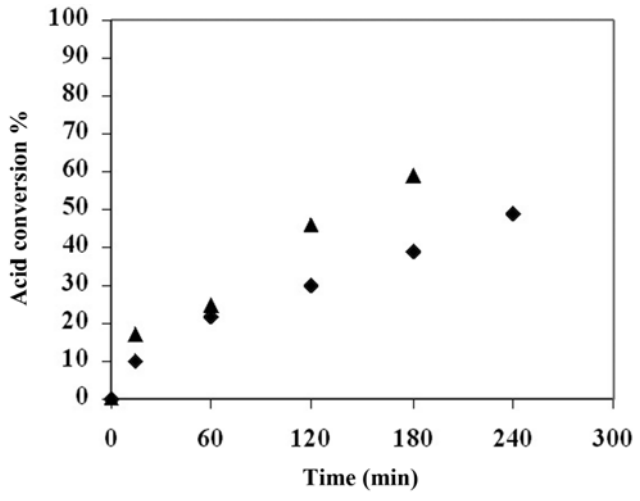

Fig. 3. Variation of the acid conversion with time for alcohol to acid molar ratio of 1.5 : 1 and using 10 wt% Amberlyst 15 catalyst, with membrane (▲) and without membrane (◆).

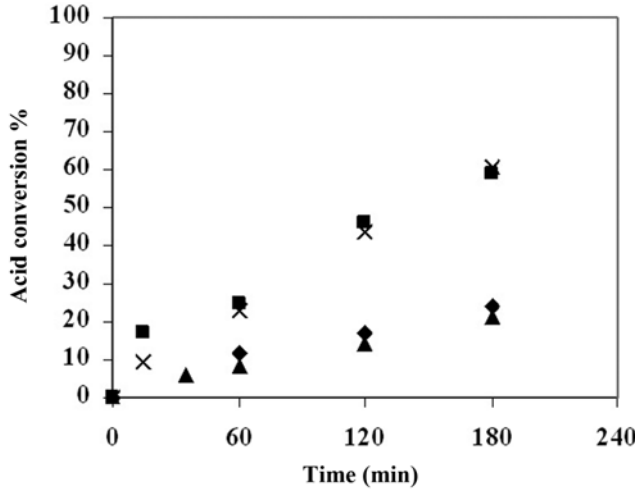

Fig. 4. Effect of catalyst loading on the variation of acid conversion with time for the initial reactants molar ratio of 1.5 : 1, at 3 (▲), 4 (◆), 10 (×) and 12 (■) weight percent of Amberlyst 15.

relative to the initial weight of propionic acid, and was varied from 3 to 12 wt%. The experiments were conducted with the alcohol-to-acid molar ratio of 1.5 : 1 for this purpose. Fig. 4 shows that the acid conversions were 20% and 61% after 180 minutes for the lowest and highest values of catalyst loading, respectively. This means that the amount of catalyst loading had significant effect on the acid conversion.

It is worth mentioning that the difference between acid conversions for experiments with 10 wt% and 12 wt% catalyst loading was not considerable. So, it was concluded that using 10 wt% catalyst loading is preferable from an economical point of view.

3. Effect of Initial Reactants Molar Ratio

The effect of initial alcohol to acid molar ratio was investigated by varying this ratio from 1 : 1 to 3 : 1 (with catalyst loading of 12 wt%). This effect is shown in Fig. 5. As seen in this figure, increasing the reactant molar ratio from 1 : 1 to 1.5 : 1 enhanced the conversion of propionic acid. Therefore, after 3 hours from the beginning of the reaction, the conversion of propionic acid for the experiment with alcohol to acid molar ratio of 1.5 : 1 was approximately 14% more than that of the case with the molar ratio of 1 : 1.

The same finding has been reported by some other researchers. Yadav and Thathagar, Yadav and Kulkarni, Sami et al. and Delgado et al. studied different esterification reactions without membrane, and showed that acid conversion increased with increasing the alcohol to acid molar ratio [12,15-17].

In the present work, by further increasing the alcohol-to-acid molar ratio from 1.5 : 1 to 3 : 1 a reduction was seen in the acid conversion. This different behavior can be explained by considering the effect of mixture boiling point. The boiling point of isopropanol is much less than that of propionic acid, and therefore, decreasing the alcohol content in the initial reaction feed mixture causes the boiling point of the mixture to rise. As the reaction mixture had been boiling during the process, increasing the reaction temperature (for reactants molar ratio of 1.5 : 1) caused more effective contact between reactants. These effective contacts with sufficient activation energy led to increase in the reaction rate, and therefore, higher acid conversion. This was in agreement with the previous investigations done on esterification by other researchers, who studied different esterification reactions without separation process and found that higher reaction temperature causes more conversions [18-23]. The same trend was observed for other catalyst loadings (3, 4, and 10 wt%) used in this work.

4. Effect of Catalyst Loading on the Flux of Permeated Water

The effect of catalyst loading on the permeated water flux for three different catalyst loading values of 3, 4, and 12 wt% is shown in Fig. 6. The water flux increased proportionally with increase in the catalyst loading. As expected, increase in the catalyst loading means more available active sites for the reaction, which results in higher reaction rate and more produced water in the reactor. The variation of water flux and produced water with time, for two experi-

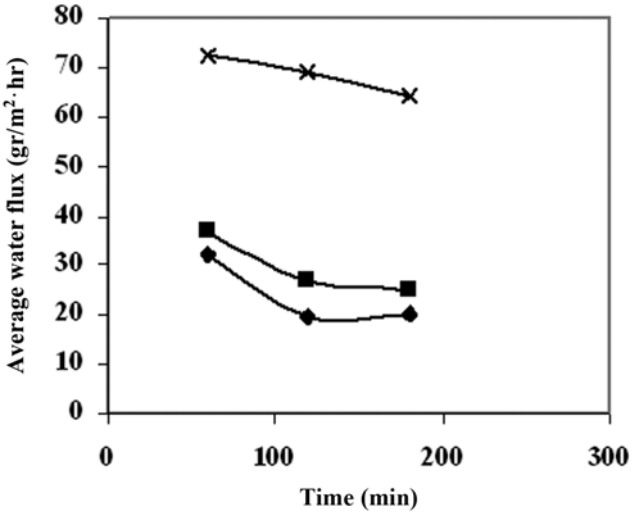

Fig. 6. Effect of catalyst loading on the variation of permeated water flux with time for the initial reactants molar ratio of 1.5 : 1 at: 3 (◆), 4 (■) and 12 (×) weight percent of Amberlyst 15.

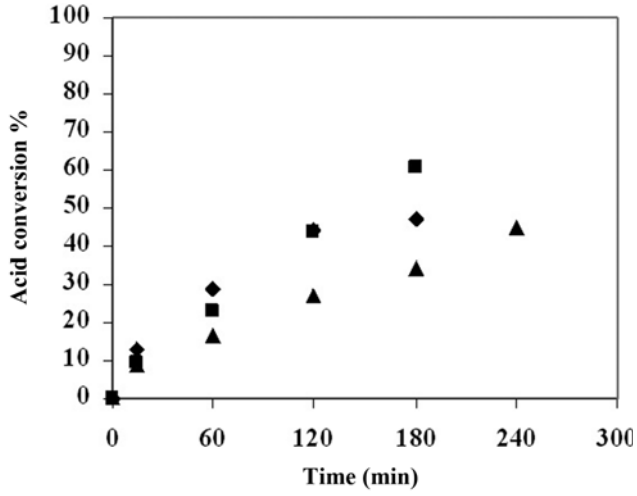

Fig. 5. Effect of alcohol to acid molar ratio on the variation of acid conversion with time, using 12 wt% of Amberlyst 15, for the initial reactants molar ratios of 1 : 1 (◆), 1.5 : 1 (■) and 3 : 1 (▲).

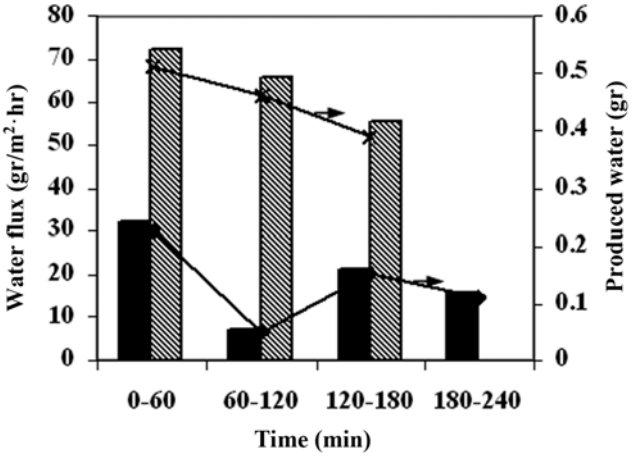

Fig. 7. Variations of the water flux (bar charts) and produced water (line curves) with time at the initial reactants molar ratios of 1.5 : 1, for two different experiments: dashed bar and (◆) for 3 wt% and filled bar and (×) for 12 wt% of Amberlyst 15.

ments using 3 and 12 wt% catalyst loading, are compared in Fig. 7. As expected, an increase in the amount of the produced water in the reaction mixture led to higher partial pressure of water in the vapor phase passing through the membrane module, and therefore, an enhancement in the water permeation was seen.

5. Effect of Alcohol-to-acid Molar Ratio on the Flux of Permeated Water

The effect of alcohol-to-acid molar ratio on the average flux of permeated water is shown in Fig. 8. The average flux was obtained by considering the total mass of the permeated water determined for each time. This effect was investigated for three different catalyst loadings of 3, 4 and 12 wt%. This figure shows that the average flux was reduced with time for all initial reactants molar ratios and catalyst loadings. As previously seen in Fig. 5, the rate of increase in acid conversion became smaller with time, and this led to a reduction in the rate of water generation during the reaction process. This effect caused a lesser amount of water in the vapor to evolve from the reaction mixture, and therefore, the average flux of permeated water was reduced. To support the above discussion, the variations of permeated water flux and produced water with time, for two alcohol/acid molar ratios of 1.5 : 1 and 3 : 1, using 12 wt% catalyst loading, are shown in Fig. 9.

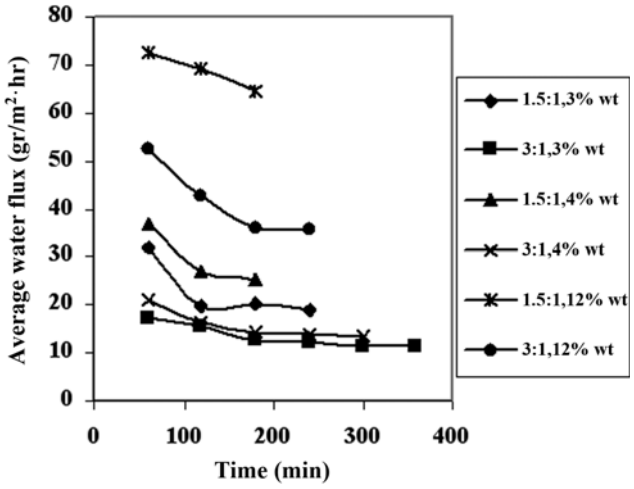

Fig. 8. Effect of the alcohol to acid molar ratio on the variation of average permeated water flux with time at different values of the reactants molar ratio and catalyst loading.

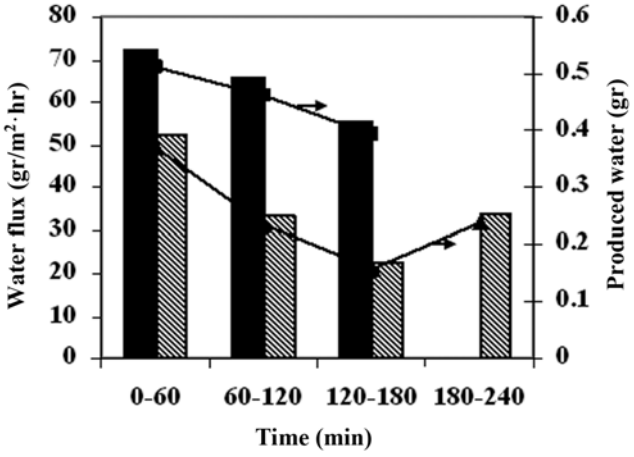

Fig. 9. Variations of the water flux (bar charts) and produced water (line curves) with time using 12 wt% of Amberlyst 15, for two different alcohol to acid molar ratios : dashed bar and (▲) for 3 : 1 and filled bar and (■) for 1.5 : 1 .

CONCLUSIONS

Effect of using a commercial tubular NaA zeolite membrane in vapor permeation process on the conversion of esterification reaction of propionic acid and isopropanol with Amberlyst 15 as catalyst was studied in this work. As expected, coupling of the membrane separation process with the equilibrium limited reaction had significant effect on the enhancement of the acid conversion. Similar to the findings of the other researchers, increasing the alcohol-to-acid molar ratio from 1 : 1 to 1.5 : 1 led to enhancement in the acid conversion from 47% to 61%. But surprisingly, increasing this ratio from 1.5 : 1 to 3 : 1 not only did not have a positive effect on the reaction conversion, but rather decreased it. A similar effect was seen for the permeated water flux. This effect was due to the influence of the reaction mixture composition on the mixture boiling point. Since this temperature influences both parameters of reaction and evaporation rates, it can cause lower acid conversion and permeated water flux for the reaction mixtures a lower boiling point.

Studying the effect of the catalyst, it was found that increasing catalyst loading had a significant positive effect on the acid conversion, which was found to be in agreement with the findings of other researchers.

In general, the results of the experiments prove that facilitating the esterification reaction with vapor permeation membrane process can be considered as a promising solution to overcome the equilibrium of the reaction. However, this hybrid process is influenced by different parameters, and further studies are required in future work. One important parameter is the reaction temperature and its effect on the reaction rate and evaporation of the species from the reaction mixture. From one point of view, increasing the initial alcohol-to-acid ratio in the reaction mixture is in the favor of more acid conversion. On the other hand, the existence of more alcohol in the reaction mixture reduces the boiling point of the mixture, which in turn leads to lower reaction rate and acid conversion. Also, this leads to lower evaporation and water removal. These effects make this hybrid process more complicated than when pervaporation process is coupled with the reaction. In this regard, one has to consider the effect of reactor pressure on the reaction temperature more accurately, which in turn is expected to have significant effects on both parameters of acid conversion and evaporation rates.

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