Using PERVAP® 2201 Membrane in Vapor Permeation Facilitated Isopropyl Propionate Production through Esterification Reaction

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Abstract

A commercial flat polymeric membrane (PERVAP® 2201) was employed in vapor permeation process to selectively remove water from the reaction atmosphere during the synthesis of isopropyl propionate from iso-propanol and propionic acid. The reaction was carried out in a bench scale batch reactor at three different values of alcohol/acid molar ratio (1:1, 1.5:1 and 3:1) with 3 wt% para toluene sulfonic acid (with respect to acid) as catalyst.. The polymeric membrane was in contact with only the volatile components, namely water and isopropanol, for a long period of time with no detectable defect. The conversion of the reversible esterification reaction was enhanced by simultaneous employing of the chemical reaction and the vapor permeation process, where in a set of experiments almost complete conversion was achieved after only 140 minutes. Also, results revealed that initial molar ratio of the reactants had strong effects on the acid conversion and water permeation flux through the membrane.

Keywords: *Esterification, Membrane Reactor, Isopropyl Propionate, Polymeric Membrane*

1. Introduction

Today, the use of membranes coupled with chemical reaction processes is attracting much attention. In recent years many investigations have been done on the application of water-permeable membranes to improve liquid-phase reactions. Since membranes consent selective permeation of a component from a mixture, these can enhance the conversion of thermodynamically or kinetically limited reactions through controlled removal of usually one of the product species from the reaction mixture.

In recent years pervaporation (PV) and vapor permeation (VP have become promising techniques, potentially useful in applications such as dehydration and removal/recovery of organic compounds from aqueous solutions and reactant mixture, as well as the separation of organic mixtures. The concept of using pervaporation to remove by-product

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species from reaction mixtures was suggested in the early stage of research on pervaporation by Jennings and Binning [1]. Processes for pervaporation membrane reactor (PVMR) application contain the production of ethyl and butyl acetate, ethyl and n-butyl oleate, diethyltartrate, dimethyl urea, ethyl valerate, isopropyl and propyl propionate, and methylisobutylketone, just to name a few. These few examples are intended to show that PVMR is attracting attention, and they have found industrial applications. However, reported research regarding studies on vapor permeation membrane for liquid-phase reactions is not as much as those on the pervaporation process. So, the majority of the studies on membrane reactor are in the field of pervaporation. Therefore, in this work an experimental investigation on vapor permeation facilitated esterification of isopropyl propionate from isopropyl alcohol and propionic acid was conducted. To this aim a commercial polymeric membrane (PERVAP$^®$ 2201) was used to withdraw water from liquid phase reaction media, in which para toluene sulfonic acid was used.

2. Experimental
2.1. Chemicals
Propionic acid (99 % purity) and iso-propyl alcohol (99.8% purity) were purchased from Merck. Initial esterification reaction feed mixture was prepared by adding 0.125 gmole propionic acid (9.25 g) to 0.125, 0.18 and 0.35 gmoles (7.5 g, 10 g, and 20 g) iso-propanol, to give iso-propanol to propionic acid molar ratios of 1:1, 1.5:1, and 3:1, respectively. Then, 3 wt. % (with respect to

propionic acid) of para toluene sulfonic acid catalyst was added to the reactants mixure.

2.2. Membrane and module
The experiments with polymeric membrane, PERVAP$^®$ 2201, were conducted in a flat shaped module. The membrane had a cross-linked PVA selective layer and a porous PAN supporting layer cast on a polyphenylene sulfide (PPS) nonwoven fabric. The selective layer, PVA, had strong interactions with water through hydrogen bonding because it is a strong hydrophilic material with highly polar groups. In this module a flat membrane was placed on a polymeric mesh to support the membrane to avoid deforming the thin flat membrane under vacuum force. The flat module was made of Teflon and the active surface area of the membrane was equal to 5x12.5 cm^2. A silicon rubber gasket was used to prevent vapor leakage between the two sides of the membrane, feed and permeate sides. A simple schematic of this module is illustrated in Fig. 1(a).

2.3. Experimental setup
A schematic layout of the experimental setup is shown in Fig. 1(b). Liquid phase esterification reaction was performed in a laboratory-scale glass-made batch reactor. The reactor was placed in oil bath and was simultaneously heated and stirred using an electrical heater and magnetic stirrer. The bath temperature was controlled and set at fixed value using a thermo-regulator connected to the heater. In the reactor, reaction and vaporization processes occurred simultaneously. So the vapor generated in the reactor rose toward the membrane module.

The module temperature was held at 90ºC during the separation process. The vacuum on the permeate side was maintained below 2mbar using a three stage diaphragm vacuum pump (Mod. MD1, Vacuubrand, GMBH, Germany). Two cold traps were set in parallel and collected the permeate over time. The retentate vapor in the module was passed through the shell and tube water cooling condenser, and then the condensed liquid was returned to the reactor.

2.4. Analysis

2.4.1. Determination of permeate composition

Samples taken from the permeate collected in the cold traps were screened for iso-propanol, propionic acid and isopropyl propionate content by HPLC (Jasco, Germany) equipped with an Amino HPX-87H column. RI detector operating at 40 ºC and UV detector working at a wave length of 210 nm were used for alcohol and acid detection,

respectively. The oven temperature for the HPLC was 60ºC and 0.005 M sulfuric acid was used as the eluent. The samples were twenty times diluted with 35Vol% aceto nitrile aqueous solution and the flow rate was 0.6 ml/min for HPLC tests.

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 80ºC for 3 minutes and then raised to 150ºC with ramp of 10ºC/min and kept at this temperature for 1 minute. Temperature of FID detector was 250ºC, and the injector temperature was adjusted to 150ºC.
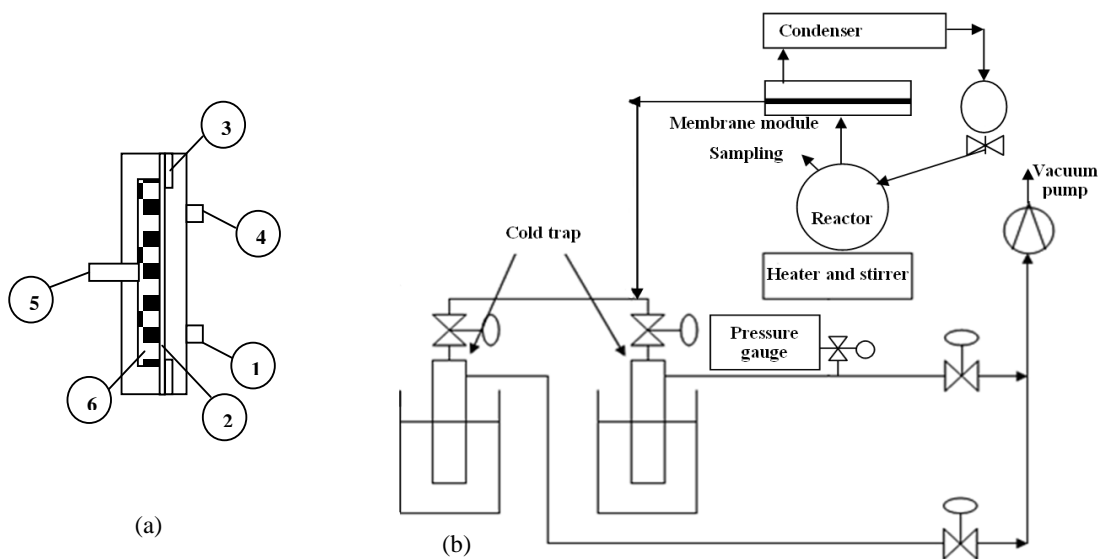

Figure 1: a) Flat PERVAP® 2201 Membrane Vapor Permeation Module.: 1– Feed inlet, 2– Membrane, 3– Silicon rubber, 4– Retentate outlet, 5– Permeate outlet, 6- Membrane support.
b) Schematic of the VP utilized reaction system.

3. Results and discussion

3.1. Effect of the membrane

Variation of propionic acid conversion as a function of time under various conditions, 1) with no membrane (condensed vapors directly returned into the reactor) and 2) facilitated with vapor permeation process using polymeric membrane is shown in Fig. 2. This set of experiments was carried out with iso-propanol to propionic acid molar ratio of 1.5:1.

Fig. 2 shows that the additional enhancement in conversion was achieved by simultaneous employment of the membrane dehydration process. This proves that selective removal of the produced water from the reaction mixture can break the limiting equilibrium and therefore complete conversion can be achieved over a short time. In the experiments carried out without membrane, the reaction reached to equilibrium after 140 minutes and the final conversion was limited to 69%, whereas using membrane system increased this value and complete conversion was obtained at the same time.
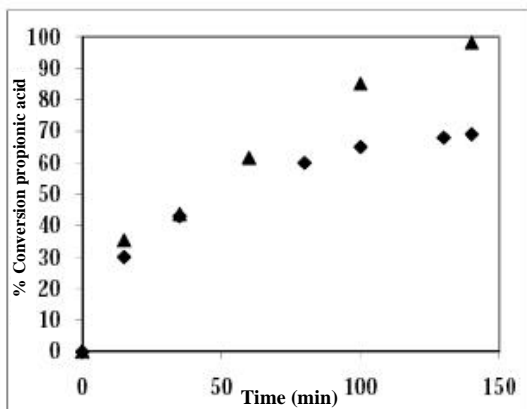
It is worth mentioning that due to low reaction conversion in the first 30 minutes of the reaction, the mass of the water produced and accumulated in the reactor was small. As a result, the difference between reaction conversion values of two processes, with and without membrane, was not significant. But with the progress in the reaction, in the case of the process without membrane accumulation of water in the reactor limited the reaction. So the effective membrane dehydration can be more distinctly observed in the longer times of the process.

3.2. Effect of alcohol/acid molar ratio on propionic acid conversion

The esterification reaction was conducted with the initial molar ratio of isopropanol to propionic acid changing from 1:1 to 3:1. As shown in Fig. 3 the equilibrium conversion was enhanced with increasing the initial reactant molar ratio from 1:1 to 1.5:1. From this figure, in the experiment with the initial molar ratio of 1:1 the equilibrium conversion of 65% was reached after 40 minutes, whereas the conversion was enhanced to 98% when the reactants molar ratio increased to 1.5:1.
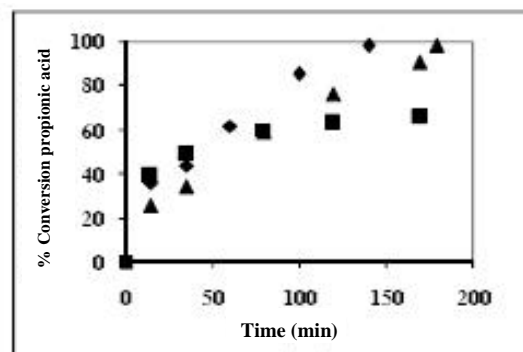

Figure 2. Conversion of propionic acid vs time: with polymeric membrane (▲) and without membrane (♦).

Figure 3. Effect of isopropanol to propionic acid molar ratio on the conversion of propionic acid in the coupled process for the initial reactant molar ratio of 1:1 (■), 1.5:1 (♦) and 3:1 (▲).

The same finding has been reported by some other researchers. It was observed that the conversion of acid in different esterification reactions without using membrane can be enhanced with increasing the alcohol to acid molar ratio [2-4].

But in our work a different trend in acid conversion was observed by increasing the alcohol to acid molar ratio from 1.5:1 to 3:1. Results showed that acid conversion became smaller when the molar ratio increased from 1.5:1 to 3:1. This observation refers to the rise of the reaction mixture temperature. As the reaction mixture was boiling during the process, increasing the alcohol content in the initial feed of the reactor in the case of molar ratio 3:1 led to a lower boiling point of the mixture. Boiling at lower temperature caused low reaction rate. In general, this effect causes less contact between reactants molecules. The reduced number of contacts with insufficient energy (activation energy) caused a smaller number of reactions between reactants and achieving lower values of conversion of propionic acid. This interpretation on the effect of molar ratio is in agreement with previous investigations on esterification reactions [5-7]. However, by further increase in the isopropanol concentration of the initial reaction mixture, more alcohol was evaporated during the reaction process, which in turn increased the concentration of the alcohol in the vapor in contact with the membrane. This had two effects on the separation process. At first, isopropanol concentration increases in the vapor causes more coverage of the membrane surface by alcohol vapor. So the contact between water molecules and the membrane surface is decreased, reducing water

permeation through the membrane. The second effect by increasing the alcohol concentration in the feed mixture and therefore in the vapor contacting with the membrane is less partial pressure of water in the vapor contacted with the membrane which decreases the driving force for water permeation through the membrane. These two effects finally lead to low acid conversion, due to water accumulation in the reaction mixture based on the Loshatolie's law.

3.3. Effect of alcohol/acid molar ratio on water flux

The effectiveness of the PERVAP® 2201 membrane in removing water during the esterification reaction by vapor permeation process for all alcohol/acid molar ratios experimented in this work are shown in Fig. 4(a, b).

High retentate water mass for alcohol/acid molar ratio of 1.5:1 shows the membrane can not extract the large amount of the generated water from the reactor. This figure also reveals that, this membrane succeeded in water permeation in the experiment with alcohol/acid molar ratio of 3 with less conversion and less produced water.

It is also shown that the highest value of retentate water in the reactor was for the molar ratio of 1:1. The reason for this observation can be explained as follows. In this case, at the initial 30 minutes of the reaction the acid conversion has the highest values (see Fig. 2). So the generated water will be more in this duration of time and the membrane cannot extract all of the generated water in the reactor. In addition, due to the

boiling point rise of the mixture, the evaporation rate will be smaller in this case. This reduction in evaporation rate decreases the contacts between water molecules and the membrane and causes low water permeation by vapor permeation.
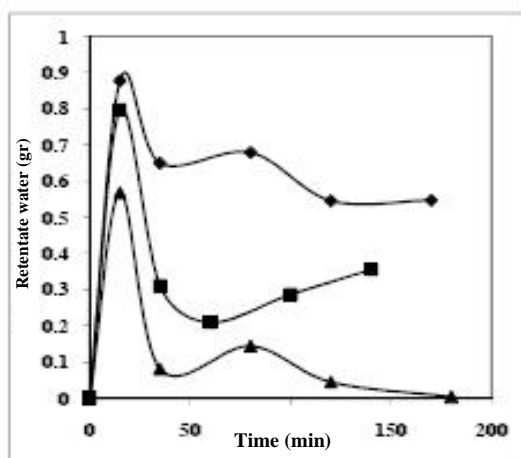

(a)
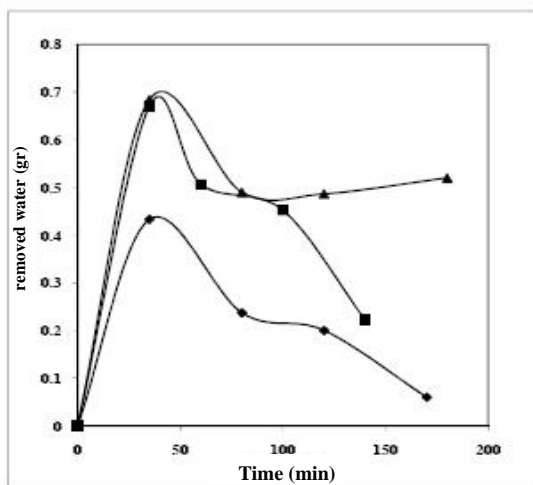
(b)

Figure 4. Variation of water mass (gr) with time in a) reaction mixture and b) permeate, for the initial reactants molar ratio of 1:1 (♦), 1.5:1 (■) and 3:1 (▲).

In Fig. 5 (a, b) the variation of water flux and retentate water concentration in the reactor versus time are shown for all reactant molar ratios. Observing these figures shows that, the permeate flux became smaller as the

water concentration of the reactor dropped down.

The separation factors which were achieved for vapor permeation during the esterification are shown in Table (1). The different values for the separation factors refer to the fact that the whole process is affected by two processes, reaction and separation. Moreover, concentrations of reactants and products in the reactor change with progress in both reaction and separation processes. Since the separation factor is a function of water and alcohol concentrations, these two effects make an inconsistency in separation factors with different alcohol/acid molar ratios.
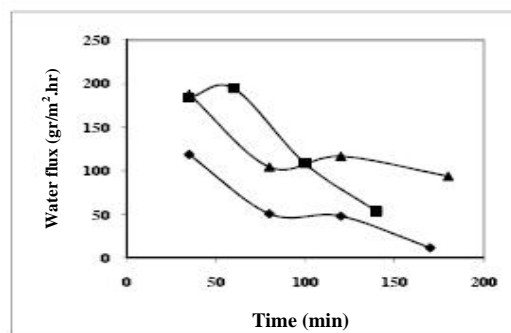
(a)
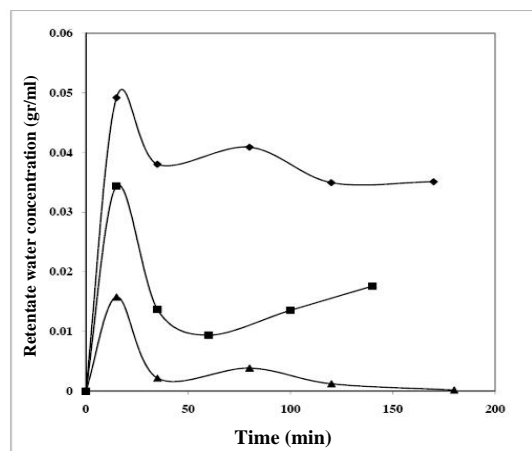
(b)

Figure 5. (a) Variation of water flux through PERVAP[®] membrane and (b) Water concentration (g/ml) in the reactor versus time with the initial reactants molar ratios of 1:1 (♦), 1.5:1 (■) and 3:1 (▲).

Table 1. Separation factor for 3 processes with different alcohol /acid molar ratio for PERVAP® 2201

Alcohol/acid molar ratio	Time(min)	Separation factor
1:1	35	50.3
1:1	80	26.4
1.5:1	35	40.8
1.5:1	60	109.1
1.5:1	100	43.2
1.5:1	140	92.5
3:1	35	1995.8
3:1	80	370.8
3:1	120	1796.2
3:1	180	1635.6

4. Conclusions

In this study the effectiveness of PERVAP® 2201 membrane in a simultaneous vapor permeation process for the esterification of propionic acid and iso-propanol to produce iso-propyl propionate was investigated. Utilizing the reaction with the vapor permeation process significantly increased reaction yield at different initial alcohol/acid molar ratio of the feed mixture, varying from 1:1 to 3:1. The complete reaction conversion was achieved by applying the polymeric membrane at two alcohol/acid molar ratios of 1.5:1 and 3:1.

Moreover, in this study the polymeric membrane worked stably for a long period of time due to contacting with only harmless components, namely water and isopropanol. This observation can be explained by the experimental data in the separation section. The data showed the selective permeation of water through the membrane during the hybrid process. On the other hand, if the membrane cracking was happening, the

selective removal of the water was not being observed during the separation process. In addition, the leakage tests for the membrane and module were performed several times and no membrane destruction was observed during the tests.

The effect of alcohol/acid molar ratio on the retentate water mass in the reactor and water flux was also investigated. The limiting surface area of the membrane led to incomplete separation during the reaction process and caused an increase in retentate water mass in the reactor during the process with high acid conversion. Accordingly, the retentate water mass accumulated in the reactor showed high values in the experiment with molar ratio of 1.5:1 with high acid conversion in comparison with the cases with two other alcohol/acid molar ratios. In addition, high values for water fluxes were observed for the experiments with high acid conversion.

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