TITLE: ETHYL ACETATE SYNTHESIS BY CHITOSAN/ POLY(VINYLPYRROLIDONE) BLEND MEMBRANE IN PERVAPORATION MEMBRANE REACTOR

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PAGES: 25-38

JOTCS Journal of the Turkish Chemical Society Section: B Chemical Engineering
TURKISH CHEMICAL SOCIETY

(This article was initially submitted to the UKMK 2016 (National Chemical Engineering Congress) and finally evaluated by the JOTCSB editorial staff).

Ethyl Acetate Synthesis by Chitosan/ Poly(Vinylpyrrolidone) Blend Membrane in Pervaporation Membrane Reactor

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Abstract: In this study, polymeric blend membranes were prepared for using the esterification reaction. Aluminum potassium sulfate dodecahydrate was used as catalyst. Chitosan and poly(vinylpyrrolidone) polymers were utilized for blend membrane solution. The membrane was prepared by solution casting method. The reaction of ethanol and acetic acid was chosen as a model reaction. Effect of the temperature, amount of catalyst, and initial molar ratio of reactants on the conversion of acetic acid, pervaporation flux, and selectivity were investigated and interpreted. When 10% of conversion value was obtained in batch reactor, 49.76% of conversion was obtained in pervaporation membrane reactor under the same reaction conditions (65 ^oC, catalyst amount of 5 wt.%, M =6 :1). Compared to the batch reactor, conversion values show the performance of the pervaporation membrane reactor. Pervaporation membrane reactor displayed higher performance with regard to the batch reactor.

Keywords: Ethyl acetate; chitosan; pervaporation membrane reactor; poly(vinylpyrrolidone).

Submitted: September 22, 2016. **Revised:** October 17, 2016. **Accepted:** November 08, 2016.

Cite this: Ünlü D, Hacıoğlu A, Hilmioğlu N. Ethyl Acetate Synthesis by Chitosan/ Poly(Vinylpyrrolidone) Blend Membrane in Pervaporation Membrane Reactor. JOTCSB. 2017;1(1):25–38.

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INTRODUCTION

The increment of industrial application of pervaporation is related to the advantages of this membrane separation technology. Hybrid process "pervaporation membrane reactor" (PVMR) is a combined reaction and separation and one of the pervaporation technology. Pervaporation membrane reactors are membrane-aided processes and reaction and separation occur simultaneously. The membrane permits the selective permeability of one of the products from the reaction mixture. Therefore, membrane reactors provide an increment of conversion values in the thermodynamic equilibrium limited reactions (1).

Esterification reactions have an important position in the industry (2). Esterification reactions are reversible equilibrium reactions. Generally, two methods are used for shifting the reaction equilibrium: One of the reactants is used as excess or one or more of the products are removed by reactive distillation. The usage of excess reactant increases the cost of operation and causes the formation of undesirable byproducts. The reactive distillation is not a suitable process for the close-boiling-point mixtures and azeotropes. The use of membrane reactor becomes an attractive option for these reasons. High conversion values can be obtained by the use of minimum reactants under the mild operating conditions in the membrane reactor. Thus, both reaction yield increases and cost of operation reduces. Also, compared to conventional batch reactor, reaction time decreases by using membrane reactor for achieving maximum conversion in esterification (3).

Separation efficiency of PVMR is not limited by relative volatility, it relies on sorption and transport properties of the membrane (4-5). When the feed solution contacts with upper surface of the membrane, one of the components is adsorbed by it. This component diffuses through the membrane, and then collected as vapors on the bottom side of the membrane. Vacuum or gas purge is used to obtain a partial pressure difference in the diffusion of molecules (3, 6).

Reaction and separation mechanism of the pervaporation membrane reactor takes place as follows. Selective membrane is placed in the reactor. One of the reaction products is removed through the membrane during the reaction and the reaction equilibrium changes towards the products. Therefore, both conversion increases and purification occurs (7).

Ethyl acetate, which is commonly used in the chemical industry, is produced by the esterification reaction of ethyl alcohol and acetic acid. Ethyl acetate is mostly synthesized by the reactive distillation in the industry. Ethyl acetate, water and waste ethanol are obtained at the end of the reaction. Double or triple azeotropes are formed in this case. It is not possible to separate the azeotrope with conventional distillation. Therefore, azeotropic distillation or extractive distillation processes should be used for the purification of ethyl acetate. Both processes consume relatively high energy and require large investment costs. Pervaporation is used for separation of the azeotrope and close boiling point mixture. Pervaporation has low energy consumption and it is also an environmentally friendly membrane technology (8).

In this study, ethyl acetate was synthesized by chitosan/poly(vinylpyrrolidone) blend membrane in the presence of aluminum potassium sulfate dodecahydrate catalyst in the pervaporation membrane reactor. There are similar PVMR studies for the esterification reaction of ethanol and acetic acid, but different membranes and catalysts are used. Chitosan/PVP blend membranes were used only for dehydration by pervaporation. There is no PVMR application by using chitosan/PVP membrane in the literature. Also, aluminum potassium sulfate dodecahydrate catalyst was not used in esterification. The effect of reaction parameters such as temperature, amount of catalyst, and molar feed ratio was examined on reaction conversion, flux, and selectivity.

MATERIALS AND METHODS

Chemicals

In this study, chitosan (CS) and poly(vinylpyrrolidone) (PVP) polymers and high purity grade of ethanol, acetic acid, sulfuric acid, and acetone were used and all of these chemicals were supplied from Sigma-Aldrich and Merck.

Experimental procedure

Chitosan/PVP blend membrane preparation: Dense, nonporous membrane prepared by solution casting method. The 2 wt.% solution of CS and the 2 wt.% solution of PVP were mixed separately. The blend of PVP/CS (20 wt%/80 wt%) was prepared by physically mixing both solutions. The blend polymeric solution was stirred for 24 hours. The prepared polymeric solution was poured onto poly(methyl methacrylate) surface by solution casting techniques and dried in room conditions. Crosslinking process is applied to improve physical and chemical resistance of the membrane. Membrane had been treated with 0.005 M sulfuric acid in 50 vol.% acetone-50 vol.% water solution for crosslinking. After the membrane was immersed in the crosslinking bath for 5 min, the blend membrane was washed with distilled water and dried at room conditions. Chitosan/PVP blend membrane was characterized by FTIR.

Synthesis of Ethyl Acetate in PVMR: Esterification of ethyl alcohol and acetic acid was carried out by chitosan/PVP blend membrane in the pervaporation membrane reactor. Reactants of ethanol and acetic acid and catalyst of aluminum potassium sulfate dodecahydrate catalyst were placed into three-necked reactor and reaction mixture was transferred to the membrane cell by the feed pump.

A thermocouple is used for temperature control of the reactor, a heating magnetic stirrer is used for the mixing and heating and the condenser is used to avoid solvent losses. Hydrophilic chitosan/PVP blend membranes were placed in the membrane cell. Vacuum is applied to the underside of the membrane cell and product is collected in a Dewar flask. The PVMR experiment system is shown in Figure 1.

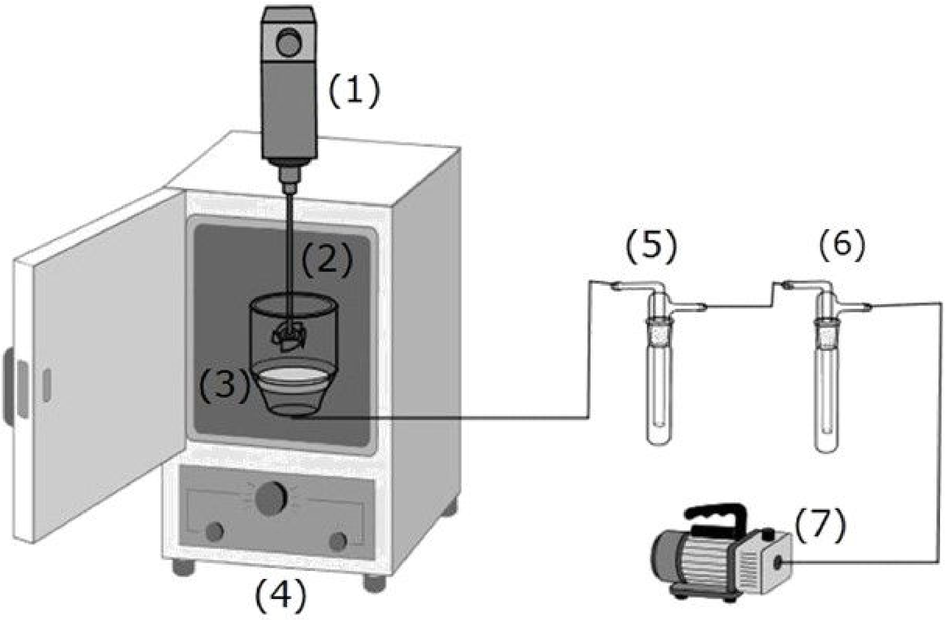

Figure 1. PVMR process (1) Mixer (2) Reactor (3) Membrane (4) Drying oven (5), (6) Cold trap (7) Vacuum pump.

Samples of permeate and reaction mixture were injected to gas chromatography at every hour of analysis. GC-7820A installed with TCD and HP-FFAP capillary column was used to analyze concentrations. Detector and column temperatures were 280 and 220 °C, respectively. Conversion, flux, and selectivity values were calculated.

Conversion values were calculated using Equation 1.

$$x = \frac{N_{Ao} - N_A}{N_{Ao}} \quad \text{(Eq. 1)}$$

In this equation, N_{Ao} is the number of moles of acetic acid at t = 0, N_A is the number of moles of acetic acid at any time of the reaction (9).

Flux is defined as the mass of the collected permeates in the cold trap. Flux is determined as mass amount per unit time, per unit area of the membrane. Flux (J) (kg/m^2.h) and selectivity (α) values are calculated by Equations 2 and 3.

$$J = \frac{m}{A.t} \qquad \text{(Eq. 2)}$$

$$\alpha = \frac{Y_a / Y_b}{X_a / X_b} \qquad \text{(Eq. 3)}$$

In these equations, t is the time (h), A is the membrane area (m^2), m is the amount of sample taken from traps (kg). X and Y are the weight fractions of feed and permeate streams, respectively. Parameter a is the component of selectivity of membrane, b represents all of the other materials. Selectivity is a unitless parameter.

RESULTS AND DISCUSSION

Membrane characterization by FTIR spectroscopy

Figure 2 shows the FTIR spectra of PVP/CS blend membrane.

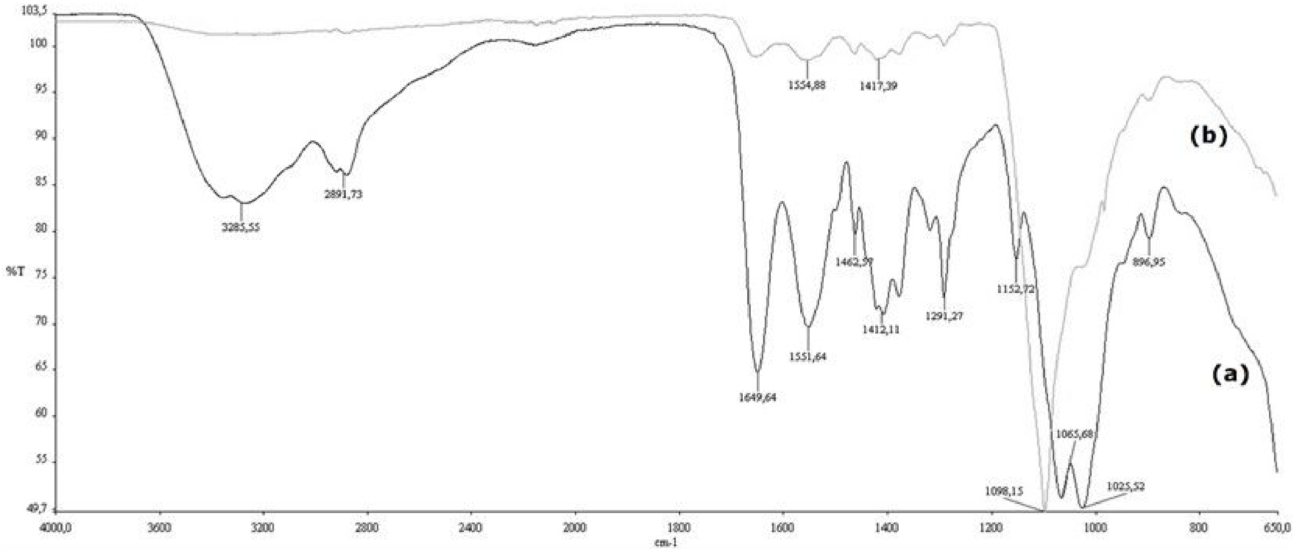

Figure 2. FT-IR spectra of PVP/CS blend membrane (a) uncross-linked (b) cross-linked.

Spectrum a in Figure 2 represents the uncross-linked blend membranes. The characteristic O−H peak can be seen between 2800-3500 cm^{-1}. FTIR spectra shows the functional groups of polymers. The peak around 1649.64 cm^{-1} shows a single carbonyl band of CS/PVP blend. This bond is formed between amine groups of CS and carbonyl group of PVP. The peak at 1291.27 cm^{-1} is assigned to the absorbance of C-N bonds. The peak at 1551.64 cm^{-1} is assigned to the specific absorbance of N–H bonds in NH_3^+ groups. Spectrum a of Figure 2 represents the cross-linked blend membranes. For the PVP/CS blend, crosslinked with H_2SO_4, the appearance of a new peak at 1554.88 cm^{-1} and 1417.39 cm^{-1} is due to crosslinking with sulfuric acid. This could be due to the crosslinking reaction occurring between amino groups of chitosan and sulfate ions of sulfuric acid (Zhang *et al.,* 2009 and Devi *et al.,* 2006 and Caetano *et al.,* 2013).

Degree of swelling

Figure 3 presents how the swelling degree of membrane in water varies with time. When the cross-linking degree of the membrane is good, the mobility of polymer chains decreases. In this experiment, H_2SO_4 was used as crosslinking agent. As seen in Figure 3, membrane had low swelling degree, because H_2SO_4 had high crosslinking properties. Rigidity of the membrane increased by using H_2SO_4 as a crosslinking agent. Therefore, diffusivity of membrane decreased and swelling degree of membrane was lower.

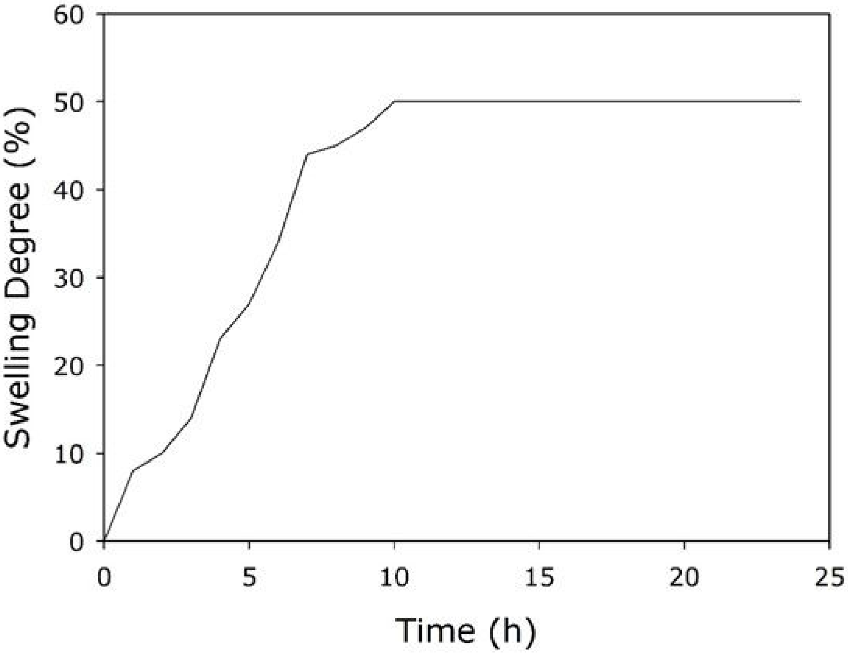

Figure 3. Swelling degree of membrane in water.

Effect of the temperature in PVMR

The effect of temperature on the PVMR process was investigated in the temperature of 55 °C, 65 °C, and 75 °C. The change of the conversion of acetic acid with temperature is given in Figure 4.

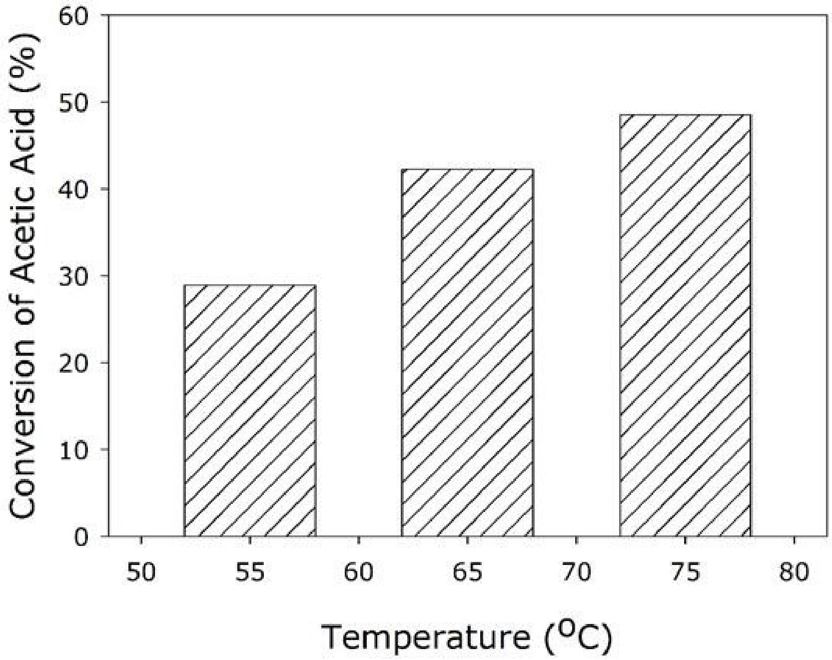

Figure 4. Effect of the different temperatures on the conversion (catalyst amount of 5 wt.%, M = 6: 1).

Conversion increased with increasing reaction temperature. The temperature has an important effect on both of pervaporation performance and the reaction kinetics (13). Increasing the reaction temperature led to an increase in the rate constant and the rate of reaction (14). Relation between temperature and reaction rate constant can be explained by the Arrhenius' equation. The activation energy, which is needed to start a reaction, is provided by the kinetic energy of the reactants. Therefore, increment of the reaction temperature resulted in the high kinetic energy of the reactant molecules hence reaction rate is increased. Esterification of acetic acid with ethanol is an endothermic reaction. Increment of the temperature shifts the equilibrium in the direction of the products and conversion increases.

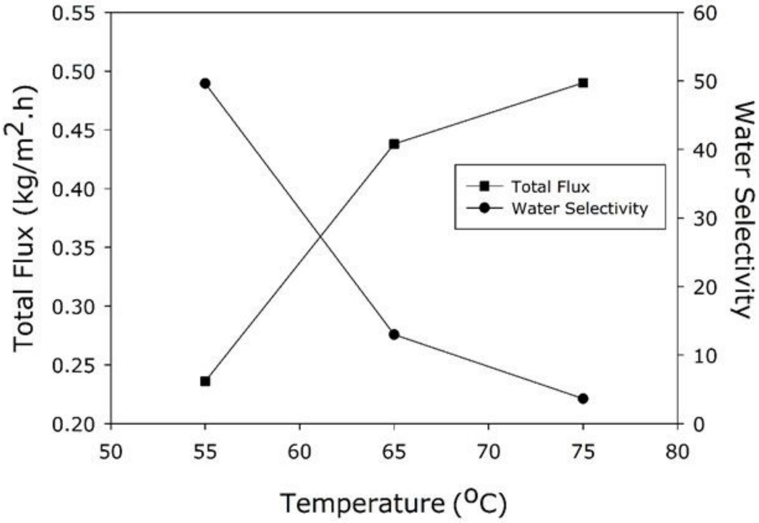

Figure 5. Effect of the different temperatures on flux and selectivity (catalyst amount of 5 wt.%, M = 6: 1).

The increase in temperature not only affects the reaction rate but also the pervaporation rate. As the reaction rate is increased, water amount in the reaction mixture rises. In this study, chitosan and PVP were chosen as membrane materials. Chitosan and PVP have hydrophilic structure interacting with water. Therefore, water was removed from the reaction mixture by the chitosan/PVP blend membrane. Removal of water changed the reaction equilibrium towards the products and conversion is increased. PVMR has higher conversion values than the batch reactor.

Polymer molecules also had a more flexible structure at the higher temperature, the diffusion rate of components increased. The reaction equilibrium shifted towards the product side by the increment of diffusion of water. Increasing the diffusion rate caused an increase of free volume of the membrane. Flux increased with free volume and this free volume also facilitated the transport of other components and consequently the selectivity of water was decreased (15). Figure 5 presents the flux and the selectivity for chitosan/PVP membrane for different reaction temperatures. As seen in Figure 5, while total flux increased, water selectivity decreased with the temperature.

Effect of the amount of catalyst in PVMR

To determine the effect of the catalyst amount on conversion, 2.5 wt.%, 5 wt.%, and 7.5 wt. % of catalyst was added into the reaction mixture. The change of the conversion of acetic acid with amount of catalyst is given in Figure 6.

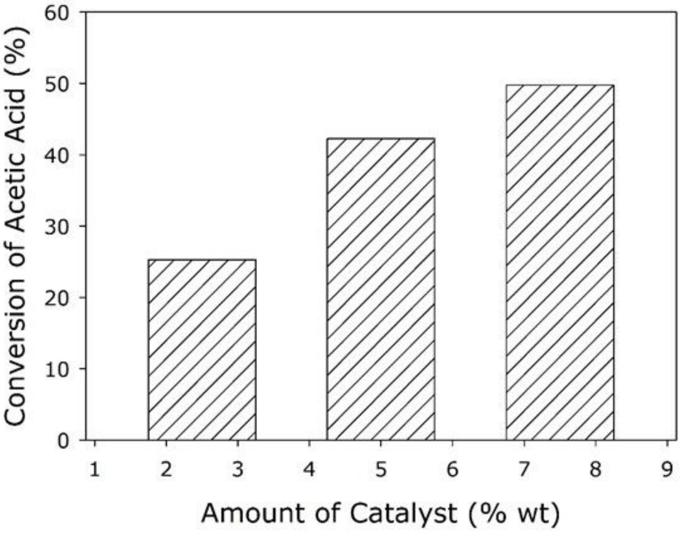

Figure 6. Effect of the different catalyst amounts on the conversion (65°C, M = 6: 1).

Conversion increased with increasing amount of the catalyst. The reaction rate is directly related to the number of active groups in the catalyst. Conversion increased with increasing amount of the catalyst. The reaction rate is directly related to the number of active groups in the catalyst. The number of the active groups was increased by increasing catalyst amount in the reaction medium. Reactants easily contact with active groups of the catalyst and acetic acid conversion increased. The catalyst amount based on the weight of acetic acid varied as 2.5%, 5%, and 7.5 %, respectively.

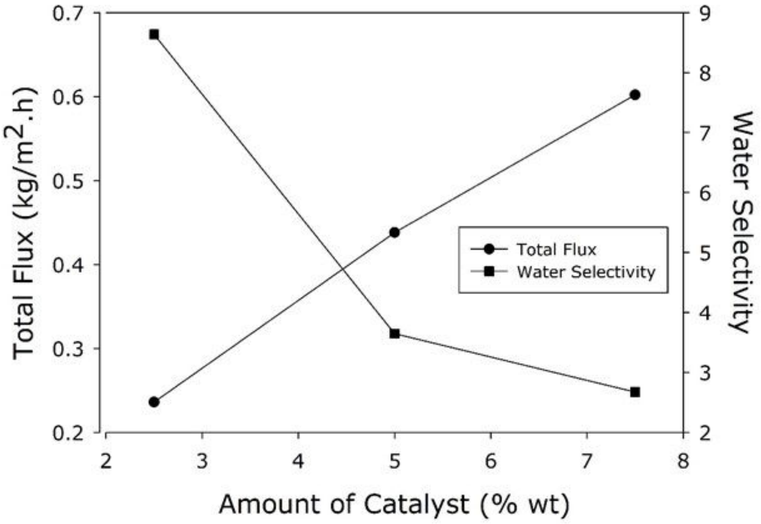

Figure 7. Effect of the amount of catalyst on flux and selectivity (65°C, M = 6: 1).

As the conversion of the acid increased, the amount of product (ethyl acetate and water) increased too. Increment of water amount resulted in the increase of concentration gradient. The driving force of the PVMR process is concentration gradient. High concentration gradient facilitated the diffusion of water and flux of water increased. Esterification of acetic acid and ethanol is a kind of reversible reaction. If water is removed from the reaction mixture, reaction equilibrium shifts towards the products and thus leads to an increased conversion of acetic acid (18). Chitosan/PVP membrane is swollen by high amount of water. The other components with water diffused through the membrane and water selectivity decreased. Figure 4 shows the change of flux and selectivity with the amount of catalyst.

Effect of the initial molar ratio in PVMR

Three different alcohol / acid initial molar ratios were studied in PVMR, M = 3: 1, M = 6: 1, and M = 9: 1. Figure 8 shows the effect of the initial molar ratio on conversion values.

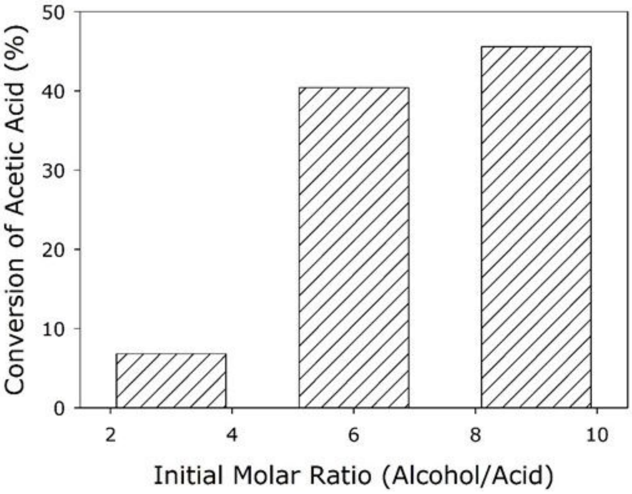

Figure 8. The effect of different initial molar ratios on conversion (65°C, catalyst amount of 5 wt.%).

Usage of excess reactant or removal of one of the products are two methods for increment of conversion. The use of excess reactant is conventional and favored method for obtaining higher conversion values in the reversible reaction. As seen in Figure 5, conversion increased with increasing initial molar ratios. High conversion values are obtained with respect to Le Châtelier's principle when excess amount of one of reactants is used in the esterification, because the usage of excess reactant shifts the reaction equilibrium towards the products [19].

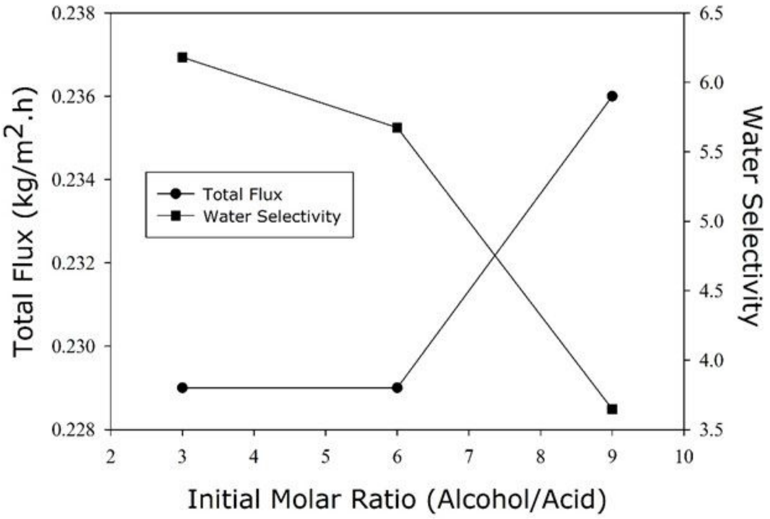

Figure 9. The effect of different initial molar ratios on flux and selectivity (65°C, catalyst amount of 5 wt.%).

Water formation increased with increment of conversion and hence the rate of water diffusion increased. In PVMR, water was removed from the reaction mixture by the hydrophilic chitosan/PVP membrane and conversion was increased. As a result of the increment of water amount, polymer transport channel expanded and flux increased, selectivity decreased, because of increment in free volume in the membrane [20]. The effect of the initial molar ratio on flux and selectivity values is shown in Figure 6.

CONCLUSIONS

The esterification of acetic acid with ethyl alcohol for the production of ethyl acetate and water was carried out under different operating conditions in PVMR. The effect of reaction temperature, the initial molar ratio of reactants and the amount of the catalyst on reaction conversion and pervaporation performance were investigated. The membrane which was prepared in the laboratory was used in the research. Chitosan/PVP blend membrane was preferred for good hydrophilic and high selectivity properties. Aluminum potassium sulfate dodecahydrate as a catalyst was used in PVMR and at the end of the reaction, 49.76% conversion was obtained. Under the same reaction conditions, 10% conversion value is obtained in batch reactor in previous studies [21]. The reaction performance of the PVMR and batch reactor was compared, and it can be seen that the PVMR displayed higher performance with regard to the batch reactor. These results indicate that the PVMR is a good alternative to the conventional batch reactor. The usage of the PVMR for the synthesis of ethyl acetate is economical and environmental technology.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from Kocaeli University, Scientific Research Projects Unit (Project No. 2014/076).

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Türkçe Öz ve Anahtar Kelimeler

Pervaporasyon Membran Reaktörde Kitosan / Poli(vinilpirolidon) Blend Membran ile Etil Asetat Sentezi

Derya Unlu, Aynur Hacıoglu, Nilufer Hilmioglu

Öz: Bu çalışmada, polimerik blend membranlar esterleştirme reaksiyonlarında kullanılmak için hazırlanmıştır. Alüminyum potasyum sülfat dodekahidrat katalizör olarak kullanılmıştır. Kitosan ve poli(vinilpirolidon) polimerleri blend membran çözeltisi için kullanılmıştır. Membran çözeltiden döküm yöntemiyle hazırlanmıştır. Etanol ve asetik asit tepkimesi model reaksiyon olarak seçilmiştir. Sıcaklık, katalizör miktarı ve reaktanların ilk molar oranının asetik asidin dönüşümü, pervaporasyon akısı ve seçicilik üzerindeki etkisi araştırılmış ve yorumlanmıştır. Kesikli reaktörde %10 dönüşüm elde edilirken pervaporasyon membran reaktördeki dönüşümün %49,76 olduğu bulunmuştur (tepkime koşulları aynıdır, 65 °C, ağırlıkça %5 katalizör ve M = 6:1). Kesikli reaktörle kıyaslandığında, dönüşüm değerleri pervaporasyon membran reaktörün performansını göstermektedir. Pervaporasyon membran reaktör, kesikli reaktöre göre daha yüksek performans göstermiştir.

Anahtar kelimeler: Etil asetat; kitosan; pervaporasyon membran reaktör; poli(vinilpirolidon).

Sunulma: 22 Eylül 2016. **Düzeltme:** 17 Ekim 2016. **Kabul:** 08 Kasım 2016.