Al-Khwarizmi
Engineering
Journal

Al-Khwarizmi Engineering Journal, Vol. 8, No. 4, PP 106-117 (2012)

Dehydration of Ethanol Using Pervaporation Separation with Nanoporous Hydrophilic Silica Ceramic Membrane

Ameel Mohammed Rahman Al-Mayah* **Zyad Rafaa Zair****
Maha Hadi Al-Hassani***
*,** *Department of Biochemical Engineering /Al-Khwarizmi College of Engineering/University of Baghdad*
*** *Department of Chemical Engineering /College of Engineering/University of Baghdad*

(Received 31 January 2012; accepted 30 December 2012)

Abstract

The pervaporation using a commercial hydrophilic ceramic membrane supplied from PERVATECH was conducted. The dehydration of ethanol/ water system was used as a model for the pervaporation study. Pervaporation experiments of ethanol/water system were carried out in the temperature range of 303-343K, ethanol concentration in the feed 10-90 vol. % and the feed flow rate in the range of 0.5-10 L/min. In this work, the effect of operation parameters on permeates fluxes as well as permeates separation factors have been studied. The Water flux is strongly dependent on the temperature; it increased with increasing in temperature, which in turn decreased the selectivity of membrane to water molecules.

In addition water flux was decreased with increasing of ethanol concentration and increased with increasing feed flow rate. The optimal operational conditions of pervaporation process are: T=333 K, feed flow rate 6 L/min, and 90 vol.% ethanol concentration in the feed. High values of water flux and separation factor were obtained. The final results agreed well with other studies reported in the literature.

Keywords: *Pervaporation, ethanol dehydration, bioethanol, hydrophilic ceramic membrane, silica.*

---

1. Introduction

The increase concern for negative impact of gaseous emissions from fossil fuel on the environmental as well as needs for alternative fuels has put great pressure on our society to find renewable friendly fuel alternatives. One of the most common renewable biofuel is bioethanol which is the dominated biofuel in the global energy market and produced from biomass by fermentation [1-3].

In bioethanol fermentation process, one of the major challenges associated with biofuel development and application is the availability of efficient separation and purification technique, which typically accounts for at least 40% (up to 80%) of the total process cost [1]. Ethanol/ dehydration is a cost effective task due to the formation of ethanol/water azeotrope. Separation azeotropic mixtures by conventional methods are expensive and consume large energy. Among these numerous separation methods, ethanol dehydration by pervaporation is the most widely used and promising technology. Pervaporation technology and their applications in the industrial separation processes has been grown considerably during the last three decades, and during the last few years becomes the most exciting aspects of separation [3-9].

Pervaporation is energy save, environmental, high selectivity and low operational cost method of separating close boiling point mixtures consists of heat sensitive compounds. In pervaporation process, the dehydration is achieved by permselective membrane. Water molecules pass the membrane (water-permselective membrane) whereas the impermeable molecules refluxed to the system. The permselective membrane materials play an essential role in dehydration process. Pervaporation dehydration performance can be improved by adjusting the hydrophilic and hydrophobic properties of a membrane material [5].

There are two types of pervaporation membranes used for ethanol/water mixture, the water permselective and ethanol-permselective membranes [7]. The mechanism of transport through the permselective membrane is solution-diffusion mechanism and it considered to be three step process consisting of: (i) sorption of the permeants at the liquid upstream side of the membrane, (ii) diffusion of the permeants through the membrane and (iii) desorption at the low-pressure side of the membrane. Therefore, the permeation rate is a function of solubility and diffusivity. In fact, the membrane selectivity is affected by both solubility, which is a thermodynamic property and diffusivity, which is a kinetic property [10].

A good pervaporation membrane material should have high permeation flux and separation factor for the pervaporation dehydration of alcohol. Polymeric and inorganic membranes are highly selective and permeable have been reported for dehydration of ethanol/ water systems [11]. Silica membranes are class of inorganic membranes. Silica or silicabased membranes are highly selective to permeation of smaller molecules and are relatively inexpensive and quite stable in acidic solutions [12].

The present study aimed to evaluate the performance of PREVATCH HybSi commercial ceramic silica membrane for dehydration of ethanol by pervaporation. Ethanol/water binary system separation is a well known system and therefore it was chosen as the model for this study. The effect of operating parameters (feed flow rate, ethanol concentration in the feed and operating temperature) on the membrane permeate fluxes and separation factors were explored in laboratory scale pervaporation unit which was developed locally. The thermodynamic properties were also discussed. Finally, the final results were also compared with the other reported researches present in the literature.

2. Experimental Work

2.1. Materials

Ethanol of analytical grade (obtained from Sigma-Aldrich Company) and Deionized water were used in the preparation of ethanol/water mixtures for pervaporation experiments.

2.2. Membrane

Commercial hydrophilic silica membrane supplied by Pervatech BV (The Netherlands) was used. The membrane is available in the form of cylindrical tube consisted of an α-alumina support tube, with 7 mm internal diameter and 50 cm length , and a γ-alumina intermediate layer on the internal face of the tube. The silica layer was placed on top of the intermediate layer. The active area per tube is 0.01 m^2. This membrane is essentially a dehydration membrane and is used for removal of water from feed streams.

2.3. Pervaporation Unit

Pervaporation experiments with the ceramic membrane were performed on a laboratory scale pervaporation unit. The unit was developed locally and the schematic of the pervaporation experimental setup is shown in Fig. 1. The unit is designed so that the pervaporation experiments can be performed on the cylindrical tube membrane. This unit is consist of booster feed pump (magnetic drive), feed flask of 1 L (glass type), vapour condenser, heating mantel of 1L size, pervaporation module, pressure gage, vacuum pressure gage, flow meter, two vapour traps and vacuum pump.

The membrane unit is a tubular, lab scale module had to be designed locally to conduct pervaporation experiments on the ceramic membrane. The schematic of this module is like the form of a double pipe heat exchanger; the HybSi ceramic membrane forms the inner pipe and the outer shell is made up of a stainless steel pipe. The feed is circulated on the inner side of the membrane tube whereas the permeate is drawn from the annual side of the module.

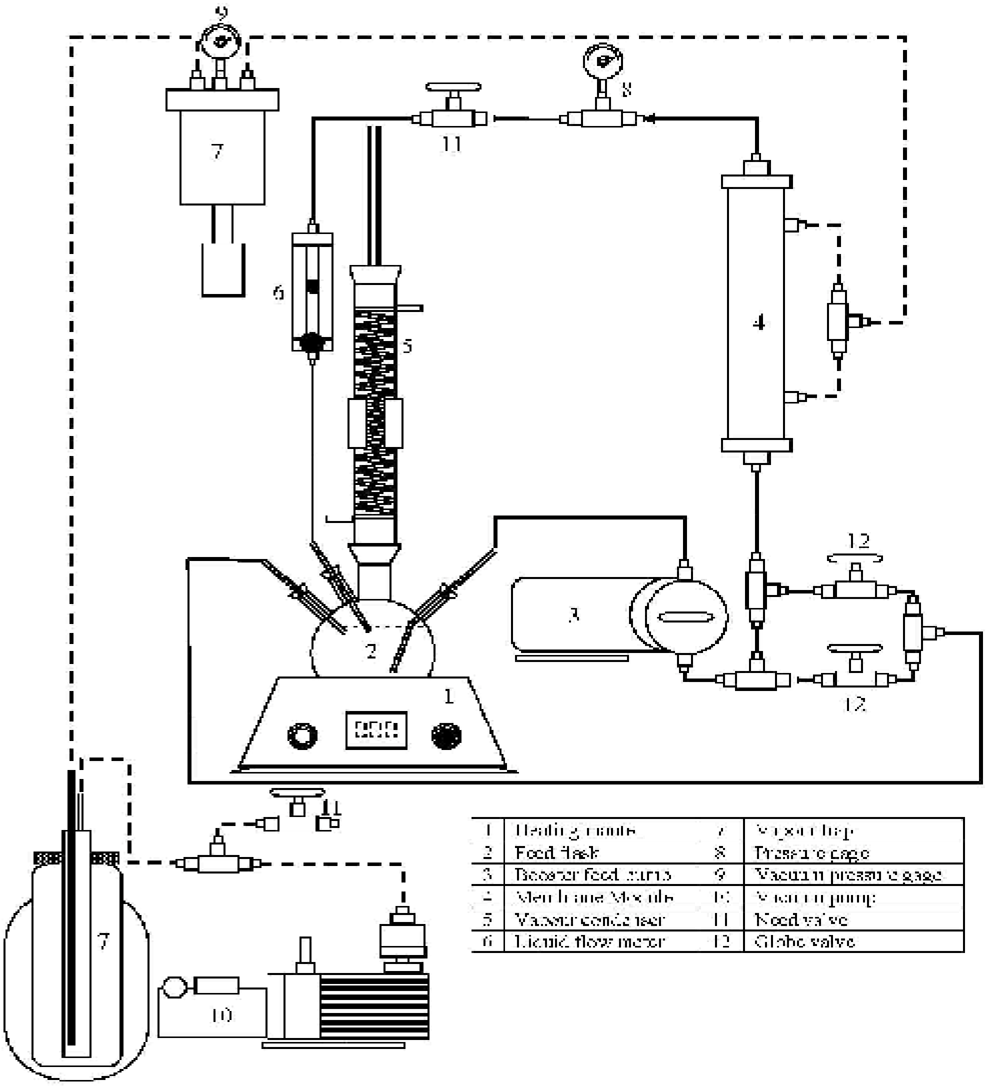

Fig. 1. Schematic Diagram of a Laboratory Scale Pervaporation Unit.

2.4. Pervaporation Experiments

Pervaporation experiments were conducted in a batch way. 10, 30, 60 and 90 vol. % of alcohol-water systems were used over a broad range of operating conditions. Experiments were carried out in the temperature range of 30-70°C, feed flow rate of 0.5-10 L/min, whereas the vacuum permeate pressure was kept nearly constant at 10 mbar. During the experimental work, liquid nitrogen was used as a cooling medium in the permeate trap in order to condensate the permeated vapour. An additional trap has been used in the unit for safety purposes.

The feed pressure was kept constant at 3.5 bar. It was circulated at a pre-specified flow rate, from a feed tank through the inside of the ceramic membrane tube; also the feed is continuously recycled back to the feed tank. The outside of the ceramic membrane tube was evacuated by using vacuum pump. The stainless steel membrane module was heated with tab heater. The feed in the tank was heated to about 5°C higher than the membrane surface. The permeate was condensed in a cold traps. In all experiments, the weights of the collected permeate (with ceramic membrane) was less than 1% of the weight of the feed charged to the tank. This means that the feed composition remains constant during the duration of the experiment. The samples were taken from the unit at the end of every 20 min time intervals from the feed and permeate to determine the partial, total fluxes and separation factors.

The total flux J and separation factor (α) were calculated from the following equations [13]:

$$J = \frac{Q}{A.t} \qquad ...(1)$$

Where Q(g) is the total mass of permeate collected in t hours, and A(m^2) denoted the effective area of the membrane [14].

$$a = \frac{Y_A.X_B}{X_A.Y_B} \qquad ...(2)$$

Where X_A and X_B represent the ethanol and water concentration (wt.%) in the feed solution respectively, Y_A and Y_B represent the ethanol and water concentrations (wt.%) in the permeate.
The sorption capacity was (SC) defined as [15]:

$$SC = \frac{W_s - W_d}{W_d} \qquad ...(3)$$

where W_d and W_s are the weight of the dry and swollen membrane samples, respectively.

2.5. Pervaporation Experimental Analysis

The collected feed and permeate pervaporation samples were analyzed to determine the composition. The analysis were performed using a gas chromatography (GC) measurement (Shimatzu 2010A).

3. Results and Discussion

3.1. Effect of Feed Concentration on Membrane Performance

The effect of feed concentration on the membrane performance at different temperatures is shown in Figs. 2 - 4. In the whole range of ethanol concentration (10-90vol. %), it can be observed that ethanol flux increased with increasing of ethanol concentration while water and the total fluxes decreased. This can be attributed to the fact that the decreasing in water flux might be related to the presence of the association equilibrium between water and ethanol molecules. At low ethanol concentrations, water molecules are in excess of ethanol molecules, it can be expected that water molecules would still be predominantly present in the form of isolated water molecules. Therefore, the permeation of water is less influenced by the presence of association equilibrium. At higher concentrations, however, ethanol molecules are in excess of water molecules. The decreasing in the concentration of isolated water molecule might be responsible for decreasing of water flux.

The effect of feed concentration on separation factors can be observed in Figs. 5 and 6. Ethanol separation factor decreased with increasing of ethanol concentration in the feed, while water separation factor increased over the same range of ethanol concentration. The decreasing of ethanol concentration facilitates water sorption on the surface of the membrane and, in turn, increases the swelling of the membrane, which enhances water molecules permeation. Moreover, water molecules smaller than ethanol and this increases the diffusion rate of water which in turn decreases the separation factor of water at low ethanol concentration and increases the separation factor of ethanol and vice versa. The same observations were reported by other studies [1, 2, 16-20].

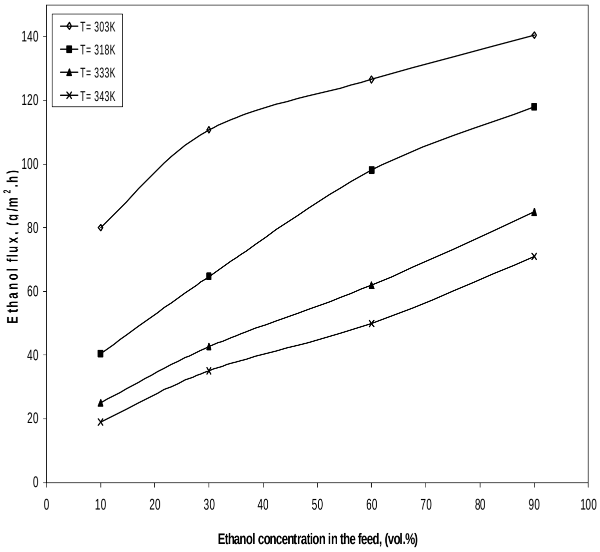

Fig. 2. Effect of Ethanol Concentration in the Feed on Ethanol Flux at Different Temperatures.

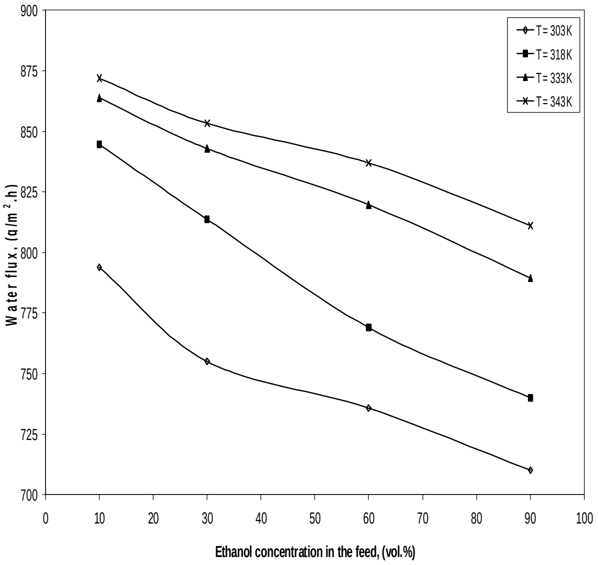

Fig. 3. Effect of Ethanol Concentration in the Feed on Water Flux at Different Temperatures.

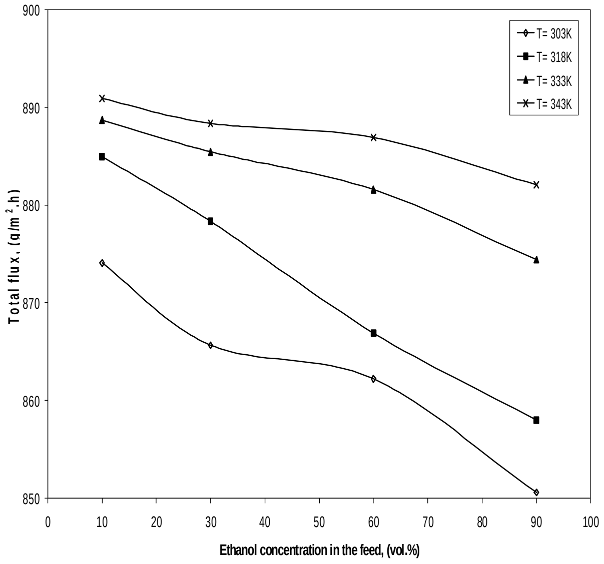

Fig. 4. Effect of Ethanol Concentration in the Feed on Total Flux at Different Temperatures.

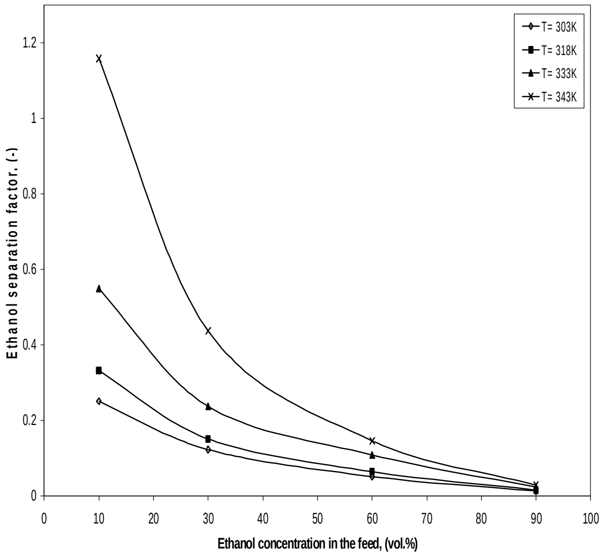

Fig. 5. Effect of Ethanol Concentration in the Feed on Ethanol Separation Factor at Different Temperatures.

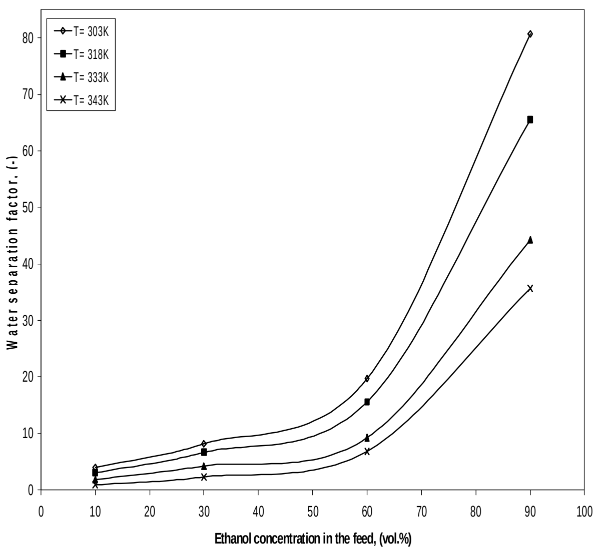

Fig. 6. Effect of Ethanol Concentration in the Feed on Water Separation Factor at Different Temperatures.

3.2. Effect of Temperature on Membrane Performance

The effect of pervaporation operating temperature on normalized ethanol and water fluxes and separation factors are shown in Figs. 7 - 11. Water and the total fluxes increased with increasing of temperature, while ethanol flux decreased over the same range of temperature. When the temperature increases, the membrane swells leading to an enlarge permeation flux and have more free volume and chain mobility as well as the vapour pressure difference is higher, which enhance the transport driving force. These two factors favor the diffusion of ethanol and water molecules through the membrane, leading to higher permeate flux. However, since water molecule is smaller than that for ethanol, the diffusion rate of water is faster, decreases the separation factor. This is agreed well with other studies reported in the literature [3, 10, 17-25].

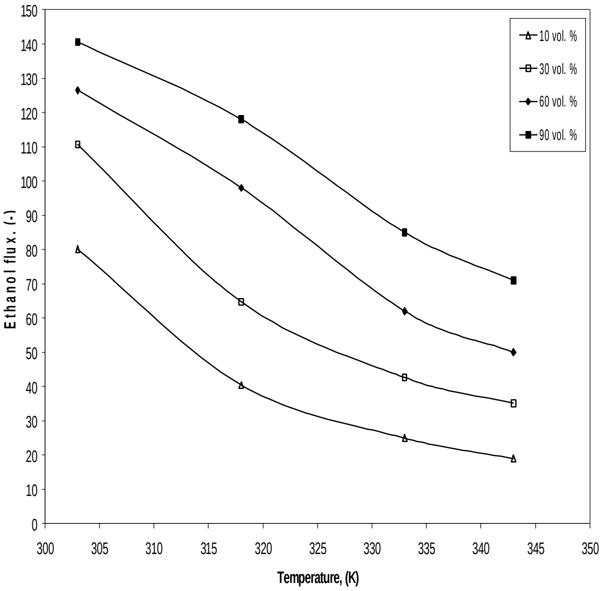

Fig. 7. Effect of Temperature on Ethanol Flux at Different Feed Concentration.

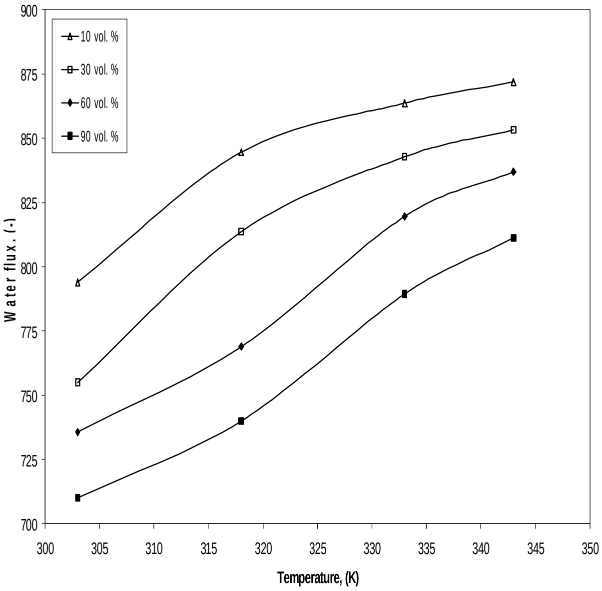

Fig. 8. Effect of temperature on water flux at different feed concentration.

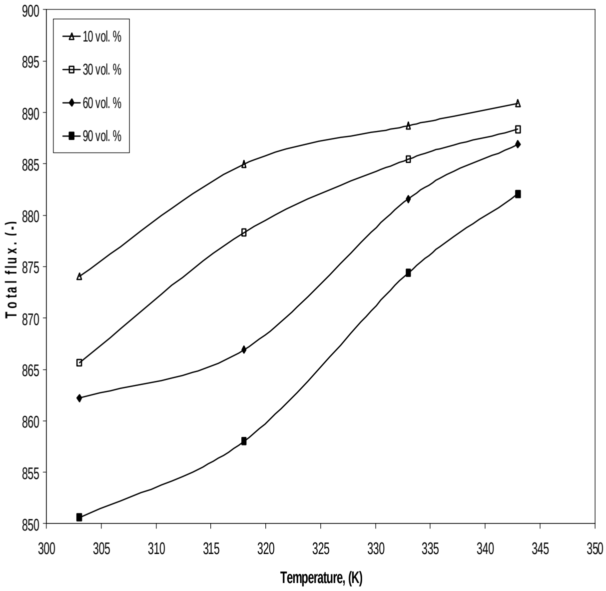

Fig. 9. Effect of Temperature on the Total Flux at Different Feed Concentration.

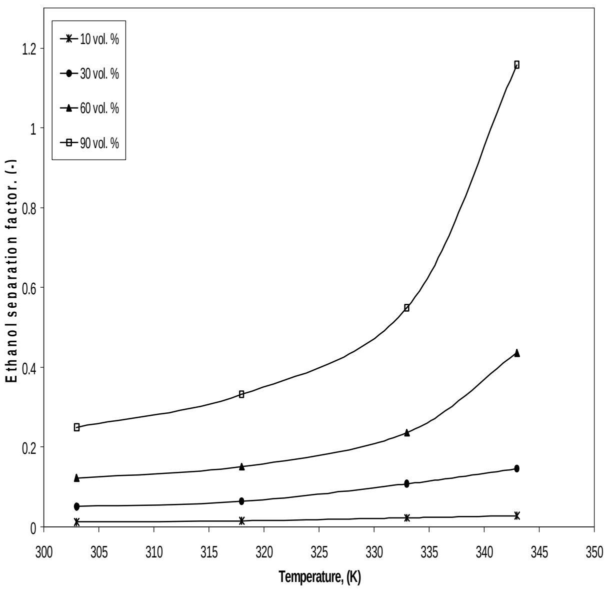

Fig. 10. Effect of Temperature on Ethanol Separation Factor at Feed Concentration.

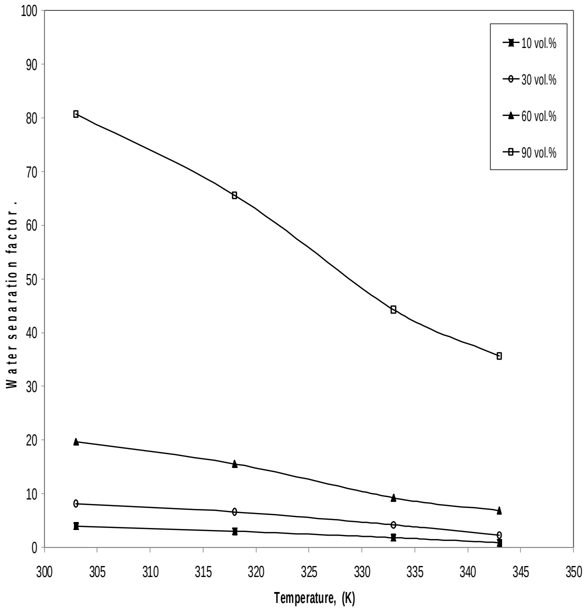

Fig. 11. Effect of Temperature on Water Separation Factor at Different Feed Concentration.

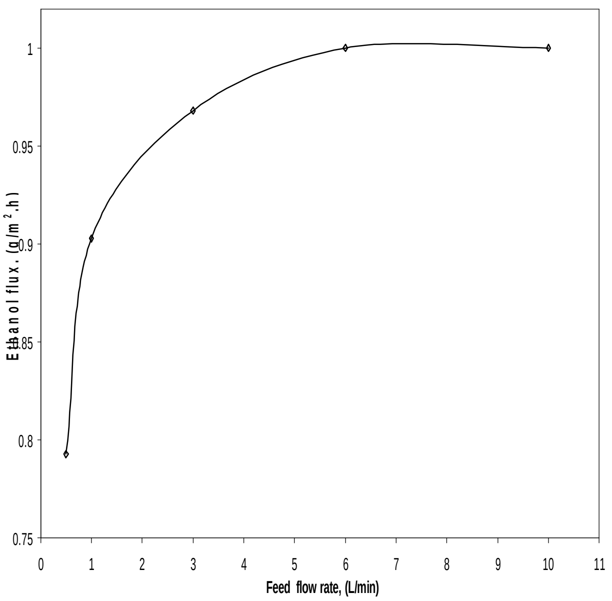

Fig. 12. Effect of Feed Flow Rate on Ethanol Flux (60 vol. % Ethanol and T=333K).

3.3. Effect of Feed Flow Rate on Membrane Performance

Figures 12 to 14 show the effect of feed flow rate on the partial and total fluxes for ethanol and water. All fluxes increased with increasing of feed flow rate. As the feed flow rate increases up to 6 L/min, the thickness of the liquid boundary layer and mass transport resistance lowered, so the fluxes increased. A very slight change can be observed when the flow rate increases greater than 6 L/min and become unaffected.

The effect of feed flow rate on normalized ethanol and water separation factor is shown in Fig. 15. The rate of change of water separation factor decreases with increasing feed flow rate and the change continue up to 6 L/min after that a very slight change can be observed due to the slight change in the fluxes. The same trends were observed by other studies in the literature [10-25].

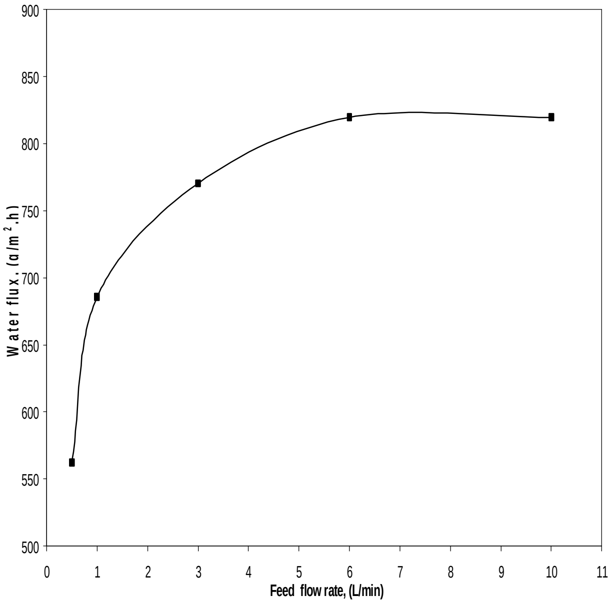

Fig. 13. Effect of Feed Flow Rate on Water Flux (60 vol. % Ethanol and T=333K).

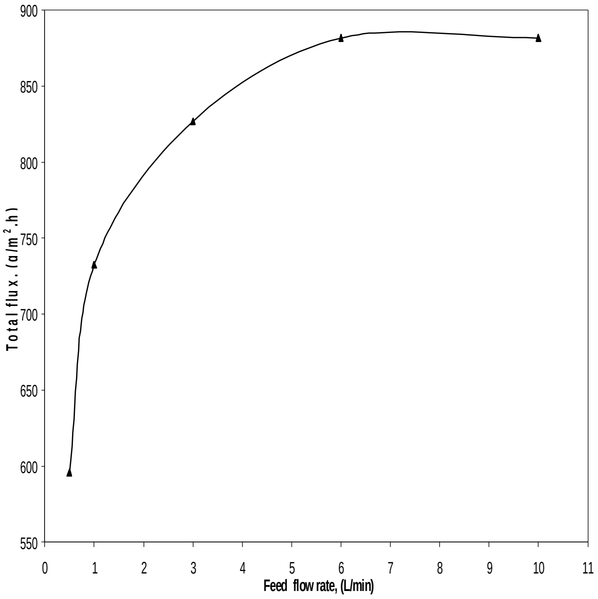

Fig. 14. Effect of Feed Flow Rate on the Total Flux (60 vol. % Ethanol and T=333K).

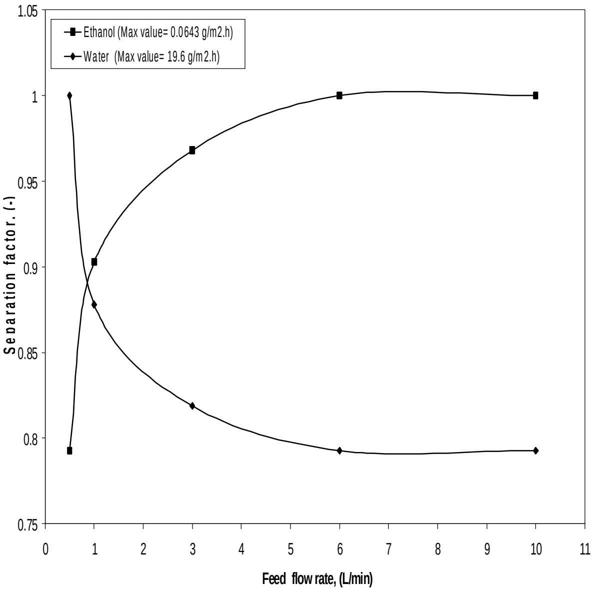

Fig. 15. Effect of Feed Flow Rate on Ethanol and Water Separation Factor (60 vol. % Ethanol and T=333K).

3.4. Activation Energy for Pervaporation Membrane

The activation energy for ethanol/water mixture pervaporation was calculated. The pervaportaion experimental data were treated with Arhenius equation [15]:

$$J = J_o \exp\left(\frac{-E_{app}}{RT}\right), \qquad \ldots(4)$$

where E_{app} apparent activation energy of the transport in pervaporation, J and J_o denote the fluxes, R is the gas constant and T is temperature (K).

A plot of ln(J) vs. (1/T) and as shown in Figs. 16 and 17 gives straight lines with slopes equal to ($-E_{app}$/R), from which the activation energy was calculated. The final results of calculations of activation energies were drawn in Figs. 18 and 19 for ethanol and water respectively.

It can be observed from Fig. 18 that the activation energy is not constant and increases with increasing of ethanol concentration in the feed. Higher activation energy means the diffusion of the water molecules is more restricted through the membrane. As the concentration increases, membrane swelling decreases and hence diffusion of water through the active layer is hindered. Therefore, the activation energy of permeation increases, and vice versa for ethanol, as it is observed in Fig. 19. These observations were also reported by various researchers in this field [1, 5, 16-25], and the results are agreed well with the reported trend in literature.

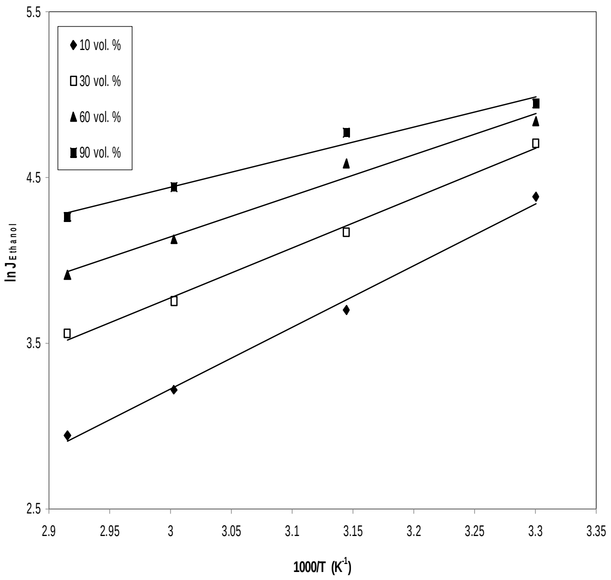

Fig. 16. Arrhenius Plots of Ethanol Flux at Different Feed Concentration.

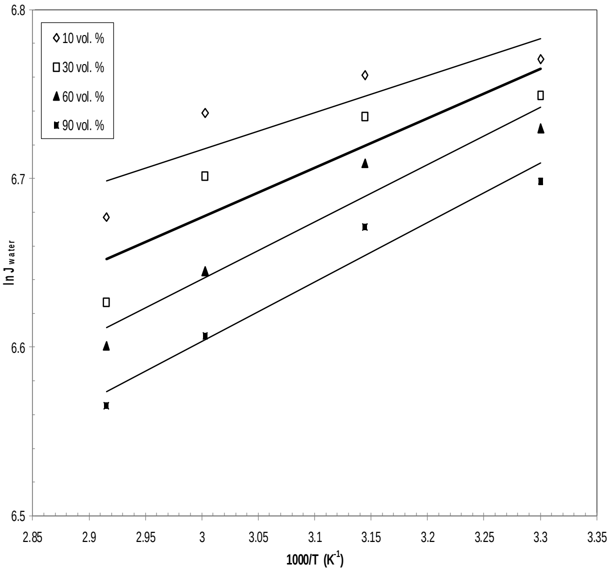

Fig. 17. Arrhenius Plots of Water Flux at Different Feed Concentration.

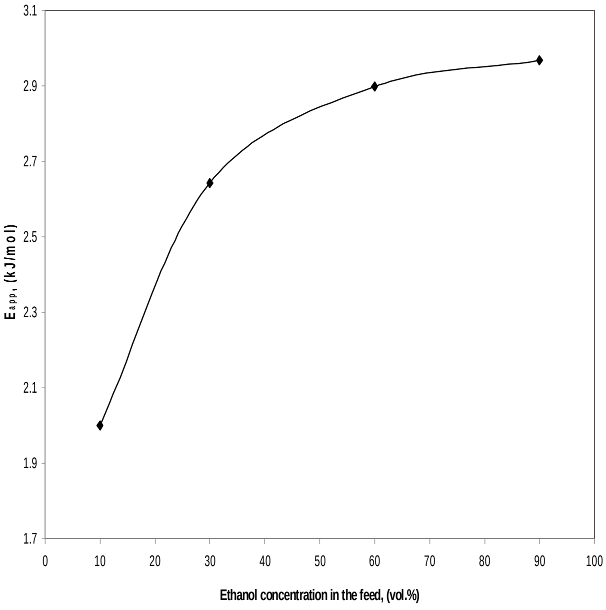

Fig. 18. Effect of Ethanol Concentration in the Feed on Water Apparent Activation Energy.

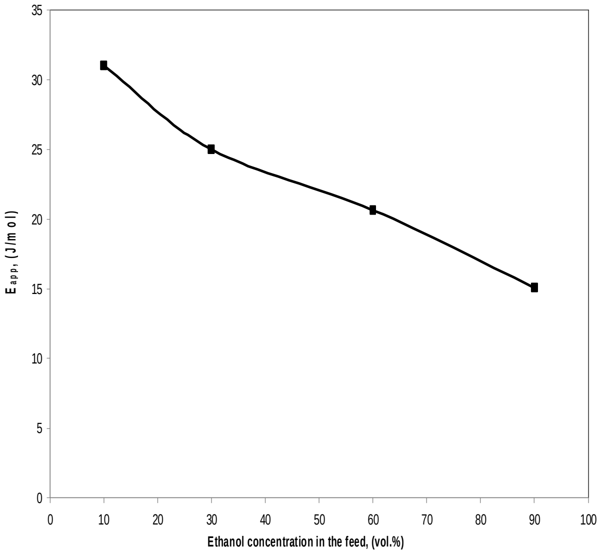

Fig. 19. Effect of Ethanol Concentration in the Feed on Ethanol Apparent Activation Energy.

4. Conclusions

In the present study, the dehydration of ethanol/water system was performed using commercial hydrophilic silica pervaporation membrane in a lab scale pervaporation unit in a batch operation. The following conclusions have been stated:

1- The proposed membrane is water perm-selective membrane, and has a high flux and a high selectivity for water compared to ethanol.
2- The present study indicates that the membranes have no major imperfections since the total flux and water selectivity is barely affect by the feed concentration.
3- Water flux is strongly dependent on the operating temperature and, the separation factor decreased with increasing the operating temperature. Water flux increases with increasing in temperature, which in turn decrease the selectivity of membrane to water molecules.
4- In the whole range of feed flow rate, the partial and total fluxes increases with the increase in feed flow rate up to 6 L/min, after that the fluxes does not affected by the increase in feed flow rate.
5- The optimal operational conditions of pervaporation process are: T=333k, feed flow rate 6 L/min, 90 vol.% ethanol concentration in the feed. Under these conditions the high values of both responses, i.e. total water flux

and separation factor, have been established simultaneously.

5. References

[1] L. L Ngoc., W. Yan, and C. Tai-Shung, "Pebax/POSS mixed matrix membranes for ethanol recovery from aqueous solutions via pervaporation", *Journal of Membrane Science*, vol. 379, no. 1-2, pp. 174 – 183, 2011.

[2] Z. Haoli, S. Yi, C. Xiangrong, and W. Yinhua, "Separation of acetone, butanol and ethanol (ABE) from dilute aqueous solutions by silicalite-1/PDMS hybrid pervaporation membranes", Separation and Purification Technology, vol. 79, pp. 375 – 384, 2011.

[3] W. Jinhui, and T. Toshinori, "Cobalt-doped silica membranes for pervaporation dehydration of ethanol/water Solutions", Journal of Membrane Science, vol. 369, pp. 13–19, 2011.

[4] W. Jinhui, M. Yu, and T. Toshinori, "Prediction of pervaporation performance of aqueous ethanol solutions by nanopermporometry characterization", Separation and Purification Technology, vol. 74, pp. 310–317, 2010.

[5] K. Jelan, S. Stevia, G. Jorge, G. Joachim, and K. Freek, "Performance and stability of multi-channel MFI zeolite membranes detemplated by calcination and ozonication in ethanol/water pervaporation", Journal of Membrane Science, vol. 339, pp. 261–274, 2009.

[6] K. Swayampakula, S. Biduru, S. Sundergopal, and K. Abburi, "Pervaporation separation of ethanol–water mixtures through sodium alginate membranes", Desalination, vol. 229, pp. 68–81, 2008.

[7] C. Shih-Hsiung, L. Rey-May, H. Ching-Shan, C. Dong-Jong, Y. Kuang-Chang, C. Chia-Yuan, "Pervaporation separation water/ethanol mixture through lithiated polysulfone membrane", Journal of Membrane Science, vol. 193, pp. 59–67, 2001.

[8] G. S. Luo, M. Niang, P. Schaetzel, "Pervaporation separation of ethyl tert-butyl ether and ethanol mixtures with a blended membrane", Journal of Membrane Science, vol. 125, pp. 237–244, 1997.

[9] D.N. Theodorou, U.W. Suter, Atomistic modeling of mechanical properties of polymeric glass, Macromolecules vol. 19, pp. 139–146, 1986.

[10] M. Khayet, C. Cojocaru, G. Zakrzewska-Trznadel, "Studies on pervaporation separation of acetone, acetonitrile and ethanol from aqueous solutions", *Separation and Purification Technology*, vol. 63, pp. 303–310, 2008.

[11] W. Jinhui, and T. Toshinori, "Cobalt-doped silica membranes for pervaporation dehydration of ethanol/water Solutions", Journal of Membrane Science, vol. 369, pp. 13–19, 2011.

[12] O. Inmaculada, A. Pedro, and U. Ane, "Pervaporation of azeotropic mixtures ethanol/ethyl lert-butyl ether: influence of membrane conditioning and operation variables on pervaporation flux", Desalination, vol. I49, pp. 67-72, 2002.

[13] W. B. Richard, "Membrane technology and applications", 2nd Ed., John Wiley & Sons Ltd., 2004.

[14] C. P. Mark, "Handbook of industrial membrane technology", Noyes Publications, 1990.

[15] D. Enrico and G. Lidietta, "Comprehensive membrane science and engineering: Vol. 1-Basic aspects of membrane science and engineering", Elsevier B.V., 2010.

[16] P. Kaewkannetra, N. Chutinate, S. Moonamart, T. Kamsan, and T.Y. Chiu, "Separation of ethanol from ethanol–water mixture and fermented sweet sorghum juice using pervaporation membrane reactor", Desalination, vol. 271, pp. 88–91, 2011.

[17] S. Claes, P. Vandezande, S. Mullens, R. Leysen, K. De Sitter, A. Andersson, F.H.J. Maurer, H. Van den Rul, R. Peeters, and M.K. Van Bael, "High flux composite PTMSP-silica nanohybrid membranes for the pervaporation of ethanol/water mixtures", Journal of Membrane Science, vol. 351, pp. 160–167, 2010.

[18] L. Gongping, W. Wang, W. Hao, D. Xueliang, J. Min, and J. Wanqin, "Pervaporation performance of PDMS/ceramic composite membrane in acetone butanol ethanol (ABE) fermentation–PV coupled process", Journal of Membrane Science, vol. 373, pp. 121–129, 2011.

[19] K. Dacho, R. Thirasak, A. Pavadee, K. Neeranut, A. Duangduen, K. Santi, and W. Sujitra, "Performance of sodium A zeolite membranes synthesized via microwave and autoclave techniques for water–ethanol

separation: Recycle-continuous pervaporation process", Desalination, vol. 269, pp. 78–83, 2011.

[20] S. Zereshki, A. Figoli, S. S. Madaenib, F. Galiano, and E. Drioli, "Pervaporation separation of ethanol/ETBE mixture using poly (lactic acid) /poly (vinyl pyrrolidone) blend membranes", Journal of Membrane Science, vol. 373, pp. 29–35, 2011.

[21] D. Patricia, T. S. María, B. Sagrario, and A. N. Luis, "Ethyl lactate production via esterification of lactic acid with ethanol combined with pervaporation", Chemical Engineering Journal, vol. 165, pp. 693–700, 2010.

[22] B. Ben, v. Adrian, M. v. v. Henk, V. Carlo, D. Jan, and V. D. B. Bart, "Pervaporation of binary water–alcohol and methanol–alcohol mixtures through microporous methylated silica membranes: Maxwell–Stefan modeling", Computers and Chemical Engineering, vol. 34, pp. 1775–1788, 2010.

[23] S.M. P. Carla, M.T.M. S. Viviana, P. P. Simão, and E. R. Alírio, "Batch and continuous studies for ethyl lactate synthesis in a pervaporation membrane reactor", Journal of Membrane Science, vol. 361, pp. 43–55, 2010.

[24] M. Jing, Z. Minhua, L. Lianyu, Y. Xin, C. Jing, and J. Zhongyi, "Intensifying esterification reaction between lactic acid and ethanol by pervaporation dehydration using chitosan–TEOS hybrid membranes", Chemical Engineering Journal, vol. 155, pp. 800–809, 2009.

[25] C. Cojocaru, M. Khayet, G. Zakrzewska-Trznadel, and A. Jaworska, "Modeling and multi-response optimization of pervaporation of organic aqueous solutions using desirability function approach", Journal of Hazardous Materials, vol. 167, pp. 52–63, 2009.

فصل الماء عن الكحول الاثيلي بتقنية التبخير الجزئي باستعمال غشاء نانو سيلكا hydrophilic السيراميكي

*** اميل محمد رحمن المياحي ** زياد رافع زائر *** مها هادي الحسني**
*،** قسم الهندسة الكيميائية الأحيائية/ كلية الهندسة الخوارزمي/ جامعة بغداد
***قسم الهندسة الكيمياوية/ كلية الهندسة/ جامعة بغداد

الخلاصة

فصل الماء عن الكحول الاثيلي بطريقة التبخر الجزئي باستعمال غشاء hydrophilic سيراميكي تجاري من شركة PERVATECH. تم استعمال نظام الكحول/الماء كموديل لدراسة التبخير الجزئي. اجريت التجارب المختبرية بدرجات حرارة تراوحت بين ٣٠٣-٣٤٣ كلفن، تركيز الايثانول في اللقيم ١٠-٩٠ % (نسبة حجمية) ومعدل جريان اللقيم ٥,٠-١٠ لتر/ دقيقة. تمت دراسة تاثير الظروف التشغيلية على معدل تدفق المواد، معامل الفصل للمواد النافذة، في هذا العمل. وجد ان معدل تدفق الماء يتأثر بشدة بدرجة الحرارة، اذ يزداد بزيادة درجة الحرارة ومعدل جريان اللقيم ويقل بزيادة تركيز الايثانول.

كما وجد ان معدل تدفق الماء يقل مع زيادة تركيز الايثانول ويزداد مع زيادة معدل جريان اللقيم. ان افضل الظروف التشغيلية لعملية الفصل بالتبخرير الجزئي هي درجة حرارة ٣٣٣ كلفن ومعدل جريان اللقيم ٦ لتر/دقيقة و ٩٠% نسبة حجمية لتركيز الايثانول وقد تطابقت هذه النتائج مع دراسات كثيرة بمراجع مختلفة.
