Jurnal Teknologi, 49(F) Dis. 2008: 159–166

PERVAPORATION OF ISOPROPANOL-W[illegible] USING POLY(VINYL) ALCOHOL-ZSM[illegible]

CHONG WOON CHAN[1*], MOHD GHAZALI M[illegible]
AZIATUL NIZA SADIKIN[3]

Abstract. The pervaporation separation of isopropanol-water m[illegible] poly(vinyl) alcohol (PVA) membrane incorporated with 0.2 wt% ZS[illegible] variables were feed temperature and feed concentration. Initially[illegible] dissolved in distilled water at 98 °C. The solution was stirred using[illegible] produce a homogenous solution. It was then cooled to room temperature before added with the zeolite. The PVA-zeolite solution was stirred for 24 hours at room temperature before it was casted on a porous support. The support layers were produced through phase inversion using casting solution of 12 wt% polysulphone, 11 wt% cellusolve and 77 wt% N,N-dimetil formamide (DMF). Finally, the modified composite membranes were produced by casting the PVA- zeolite solution on the porous polysulphone support layers. Pervaporation tests were conducted using SOLTEQ Pervaporation Bench Test Unit (Model: TR 12). The results showed the increase of water concentration in the feed and operating temperature, resulted in higher flux and lower selectivity. ZSM-5 filled PVA membrane showed potential as a separation medium for the pervaporation separation of isopropanol-water mixtures.

Keywords: Pervaporation; poly(vinyl) alcohol; ZSM-5 zeolite; polysulphone; composite membranes

Abstrak. Dalam eksperimen ini, keberkesanan membran komposit yang telah diubah suai dikaji bagi pemisahan larutan campuran isopropanol-air menggunakan proses pervaporasi. Pemboleh ubah dalam uji kaji ini adalah suhu operasi dan kepekatan larutan campuran. Membran poli(vinil) alkohol (PVA) yang diubah suai dengan 0.2 wt% ZSM-5 zeolite disediakan. Mulanya, 5 wt% serbuk PVA dilarutkan di dalam air suling. Ia dikacau sementara dipanaskan hingga 98 °C dan akhirnya disejukkan kepada suhu bilik. Untuk mengubah suai membran PVA, 0.2 wt% ZSM-5 zeolit dimasukkan ke dalam setiap larutan dan dikacau selama sehari. Lapisan sokongan membran komposit pula disediakan melalui proses songsangan fasa menggunakan larutan tuangan yang mengandungi campuran 12 wt% polisulfon, 11 wt% Metil Selusof dan 77 wt% N, NDimetil Formidamida (DMF). Akhirnya, membran komposit dihasilkan dengan menyalutkan larutan PVA campuran 0.2 wt% zeolit ke atas membran poros polisulfon. Proses pervaporasi telah dijalankan menggunakan SOLTEQ Pervaporation Bench Test Unit (Model: TR 12). Keputusan menunjukkan kedua-dua suhu operasi dan kepekatan larutan suapan mempengaruhi keberkesanan membran komposit dalam pemisahan larutan campuran isopropanol-air. Kebolehresapan (fluks) meningkat manakala kememilihan membran menurun apabila suhu operasi dan kuantiti air dalam larutan suapan meningkat. Data yang diperoleh telah menunjukkan membran PVA komposit campuran ZSM-5 merupakan satu medium yang sesuai untuk pemisahan larutan campuran isopropanol-air.

Kata kunci: Pervaporasi; poli(vinil) alkohol; ZSM-5 zeolit; polisulfon; membran komposit

[1,2&3] Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor Bahru, Malaysia
* Corresponding author: Email: chongwoonchan@gmail.com

1.0 INTRODUCTION

Membrane phenomena can be traced back to eighteenth century when Abbe Nollet invested the word "osmosis" to describe permeation of water through a diaphragm in 1748. Pervaporation is a process using membrane to separate mixtures of dissolved solvent through evaporation of volatile components through a non-porous selective membrane. The first paper was published by Kober, who discovered the potential of pervaporation. In early 1950s, pervaporation as a new separation method in industry was introduced. This was a milestone for the development of pervaporation which was initiated by Binning, Lee and co-workers at American Oil in separation of organic mixtures. After abundant of effort for years, Gesellschaft Fur Trennverfahren, GFT of Hamburg, West Germany, utilized membrane separation technology in their plant in 1982. With increasing experience and confidence in the new technology, more and more new membranes have been developing for separation of gases and liquids mixtures purpose via pervaporation [1].

Membrane separation became one of the significant method for mixtures separation due to its potential in separating variety of mixtures and it is energy saving. The most important solvent to be treated are the light alcohols, ethanol, propanols and butanols. Today, the technology is regarded as a reliable state-of-the-art process and in numerous applications, is even an integrated part of a production process.

Pervaporation is not an "ideal" technology, but just a new unit operation which is attractive when weighed against other competitive processes [2]. The problems of pervaporation technology that are highlighted are selectivity and reliability [3].

Isopropanol is widely used as cleaning agent and solvent in the industry as well as producing household product and cosmetic. Hydrophilic membrane is mainly used for removal of water from organic solvents and solvent mixtures, with an emphasis on azeotropic mixtures. PVA is a suitable material used for the dehydration of aqueous organic mixtures owing to its good thermal stability, film forming and high hydrophilicity. However, it exhibits a high degree of swelling due to high hydrophilic. Thus, it is always corporated with hydrophobic zeolite to improve the performance of membrane by allowing certain molecules to enter the pores while reject the too large molecules. As self-standing zeolite layer is fragile, polyacrylonitrile, polyetherimide and polysulfone with high resistance against chemical attack, good thermal and mechanical properties are those used to form porous support [4].

In this research, the performance of pervaporation was investigated through permeation flux and separation factor. However, the two parameters are always contradicted. The main objectives of the study are to investigate the effect of feed concentration and feed temperature on the ability of liquid separation and permeation rate towards the pervaporation dehydration of isopropanol (IPA) using zeolite ZSM-5 filled PVA membranes.

2.0 EXPERIMENTAL

2.1 Materials

In this work, polyvinyl alcohol (PVA) powder and ZSM-5 zeolite came from Fluka BioChemika, N,N-dimethylformamide (DMF) from Labscan Asia Co. Ltd., solid polysulphone was provided by Amoco and methyl cellosolve ethylene glycol from Krass. Besides, the equipments required were SOLTEQ Pervaporation Bench Test Unit (Model: TR 12) in Makmal Teknologi Zarah, Fakulti Kejuruteraan Kimia Universiti Teknologi Malaysia.

2.2 Methods

2.2.1 Preparation of PVA-ZSM-5 Zeolite Solution

Preweighed 5 g PVA was first dissolved in 95 mL distilled water, then stirred and heated until all the PVA dissolved, with reaching temperature 98 °C. It was then left to cold to room temperature. 0.2 wt% quantity of ZSM-5 was added and left to keep stirring for overnight.

2.2.2 Preparation of PVA-polysulphone Composite Membranes

Initially, 12% weight of polysulphone, 11% weight of cellosolve and 77% weight of N,N-dimetil formamida(DMF) were mixed together. It was then heated for around 15 minutes until all the polysulphone dissolved. The solution was left to cold in room temperature. It was then poured onto a drawing paper which was sticked on a glass plate. Immediately, the product was immersed into 50% weight dimetyl formamide in distilled water for 10 min. The polysulfone support layer was then immersed in distilled water for 24 hours. Finally, it was dried at room temperature. Then, the support was topped zeolite-filled PVA solution and left to dried at room temperature for 24 hours.

2.3 Pervaporation Test

An ordinary technique was used to carry out the permeation of isopropanol-water mixture through membranes using SOLTEQ Pervaporation Bench Test Unit. Membrane was first kept inside the pervaporation cell. The temperatures needed to be adjusted and waited to achieve the desired values before starting the pervaporation process. For temperature test, 3 L of 90 wt% IPA isopropanol-water mixture was directed to the feed stream. On the other hand, for concentration test, the concentration of feed should be changed each time according to the need. Meanwhile, the experiment was done in the room temperature which was around 27.5 °C. The permeate pressure was always maintained at 720 mmHg under vacuum and the feed rate was kept constant. The permeate was condensed in a cold trap using ice.

The weight of the cold trap was measured using a digital electronic balance and the permeate composition was analysed by taking its refractometric index, *nD*. The permeation performances were indicated in terms of permeate weight and permeation concentration. Meanwhile, the permeation concentration was used to find the value of separation factor, *a* and the permeate weight was used for the flux calculation as shown in equations below.

$$\text{Separation Factor, } \alpha = \frac{y_i / y_j}{x_i / x_j} \tag{1}$$

Where x and y are the weight fraction of feed and permeate respectively while i and j are water and isopropanol respectively.

$$\text{Flux, } J = \frac{W}{Axt} \tag{2}$$

Where W is the permeate weight, A is contacting area and t is period of pervaporation process in hour.

2.4 Refractomeric Index, *nD* Test

Refractomeric index test was done by using refractometer in Makmal Unit Operasi to get the refractomeric index for concentration of isopropanol-water mixtures for the purpose of getting the permeation selectivity.

3.0 RESULTS AND DISCUSSION

3.1 The Permeation Flux of 0.2 wt% ZSM-5-filled Membranes for Different Feed Concentration at Room Temperature

Refering the result in Figure 1, the amount of permeates obtained increased as the composition of water in the feed increased until 30 wt%. Then, the permeate flux started to decreased continuously.

When the amount of permeate rate molecules in the feed increased, the partial pressure of permeating molecules increased, created a gradient of pressure between feed and permeate side. Besides, when the concentration decreased, the membrane was swollen and the polymer chain segments become more mobile. Thus, the energy required for diffusive transport through the membranes decreased. Therefore, more permeate are being absorbed into the ZSM-5 filled membrane and the permeation rate increases. However, at certain point, adverse response will occur.

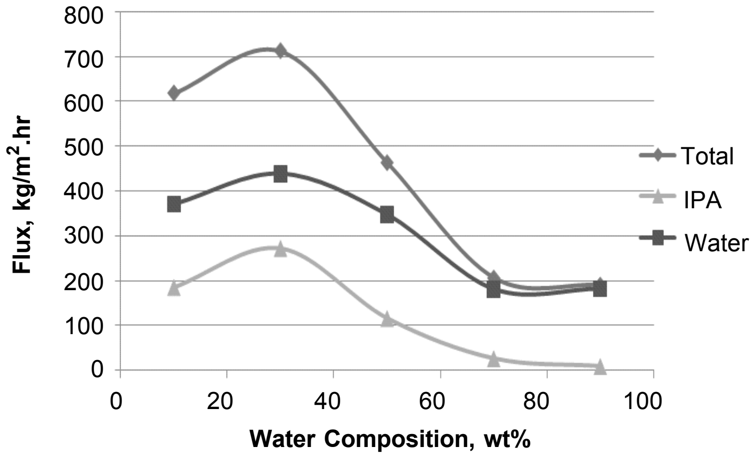

Figure 1 Effect of feed concentration on IPA and water permeate fluxes at room temperature

This was caused by the formation of cluster water molecules at high concentration of water in the feed [4].

This can be concluded that the permeation rate depends on the vapor pressure and also concentration of the feed.

3.2 The Separation Factor and Pervaporation Separation index of 0.2 wt% ZSM-5-filled Membranes for Different Feed Concentration at Room Temperature

Referring to Figure 2 and 3, the result showed the greatest separation performance was at 10 wt% composition of water in the mixture where the separation factor was

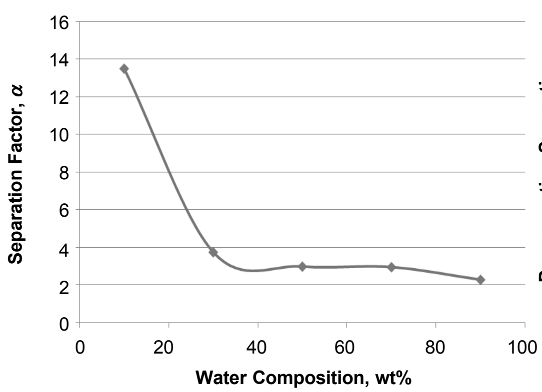

Figure 2 Effect of feed concentration on separation factor at room temperature

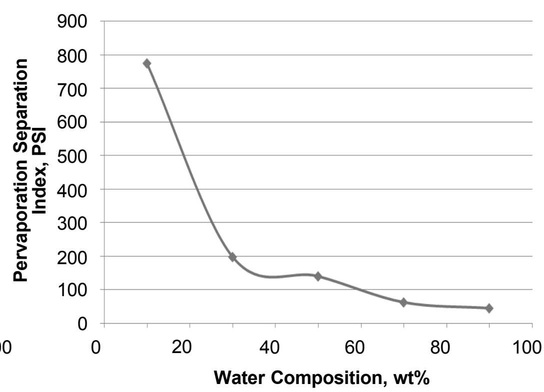

Figure 3 Effect of feed concentration on pervaporation separation index at room

the highest. The separation factor decreased drastically up to 50 wt% of water composition. Then the trend remained almost constant, showing not much variation beyond 50 wt% of water composition in the feed. Water molecules diffused through the amorphous regions in the polymer matrix and the zeolite pores in the membranes. Although the pore size of the water molecules is smaller than IPA molecules, the water and IPA molecules diffuses more frequently through the ZSM-5 filled membranes as the vapour pressure increased. Solution of 90 wt% IPA feed concentration of IPA appears to possess the best separation performance for the membrane in pervaporation test.

The performance of the membranes in different conditions can be clearly differentiated through pervaporation separation index. 90 wt% IPA feed concentration was the best condition of 0.2 wt% ZSM-5 filled membrane as it owned the highest PSI.

3.3 The Permeation Flux of 0.2 wt% ZSM-5-filled Membranes for Different Feed Temperatures

The result showed the permeation flux increased with increasing temperature in Figure 4. The water fluxes were always greater than IPA fluxes. According to Arrhenius relationship shown, if the activation energy is positive, the permeation flux increase with increasing temperature. This is indeed the case in most of the PV

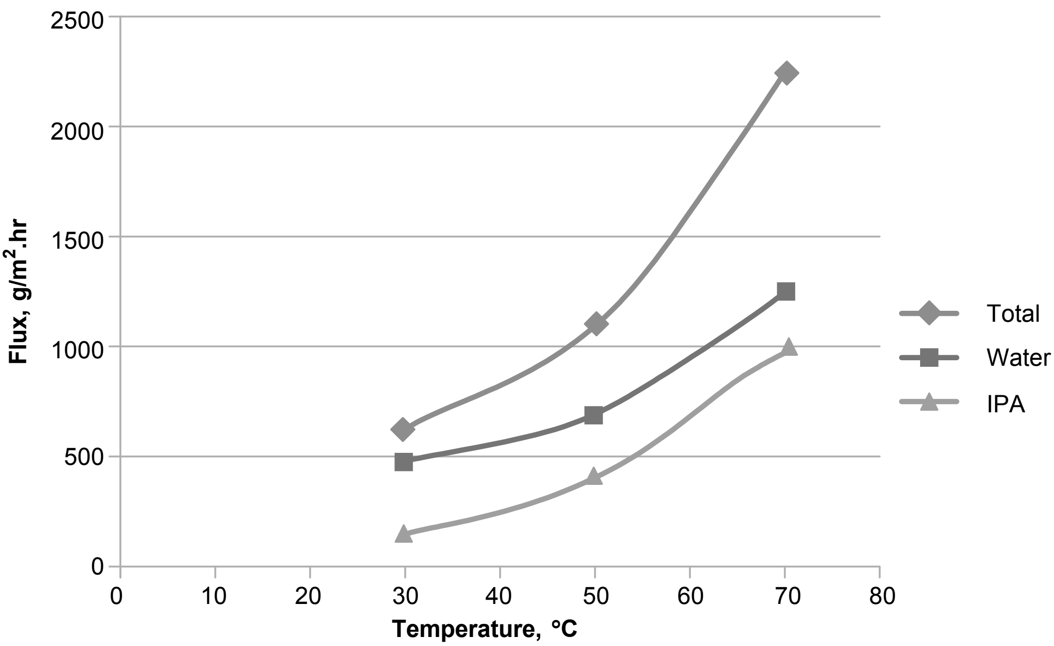

Figure 4 Effect of temperature on 90 wt% IPA and water mixture permeate fluxes

experiment. As the temperature of the feed increased the vapour pressure of the feed side increased too. However, the vapour pressure at the permeation side maintained not affected. This increased the driving force between the different sides of the membrane. Besides, when heat was applied to the process, the free volume in the polymer matrix would expanse. Water molecules tended to show plasticizing effect. (Kittur, 2003) Therefore, permeating molecules could absorb into the ZSM-5 filled membrane easier.

$$J_p = J_{po} \exp\left(\frac{-E_p}{RT}\right) \quad (3)$$

Here, J_p is permeation flux, J_{po} is preexponential factor, E_p is activation energy, R is gas constant and T is temperature in Kelvin. The result obeyed the theory that the greater the feed temperature, the higher the permeate flux result.

3.4 The Separation Factor and Pervaporation Separation Index of 0.2 wt% ZSM-5-filled Membranes for Different Feed Temperatures

The result in figure 5 shows the selectivity decreases with increasing of temperatures.

The higher the separation factor, the better the separation performance. The decrease of separation factor at high temperature is probably caused by the thermal motion of the feed components and the polymer chains in the membranes. As the temperature increases, the thermal agitation increases and creates more free volume in the polymer matrix. More molecules of water as well as IPA diffuse through the membranes. This leads to the increase of permeation flux and the decrease of separation factor. The values of separation factor show that the lower the feed

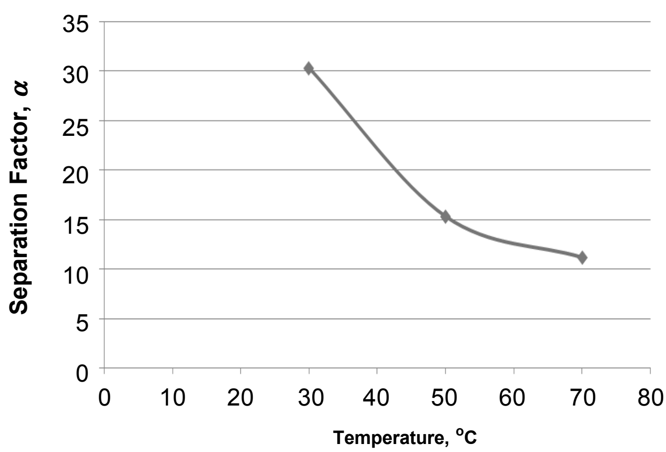

Figure 5 Effect of temperature on separation factor of 90wt% IPA-water mixture.

temperatures, the better the separation performance. The greatest performance of 0.2 wt% ZSM-5 filled membrane is at temperature of 70 °C. The flux is quite satisfied and separation factor is the highest. Thus it gives the highest PSI.

4.0 CONCLUSION

Performances of ZSM-5 filled membranes were analysed using different temperatures and feed concentration through dehydration pervaporation. After obtained the separation factor and fluxes, the pervaporation separation indexes, PSI of all membranes in both conditions are compared to find out the best separation conditions.

Concentration affects both permeation rate as well as flux of the zeolite-filled membrane. As the concentration of water in feed increases, the separation factor decreases as both water and IPA molecules diffuse more frequent through the pores. For IPA-water mixture separation, the preferred concentration of feed is 90% IPA which gives the highest PSI value. For another case where the temperature of feed increases, the permeation flux factor increases. However, the separation factor decreases. From the result shown, temperature of 70 °C shows the highest PSI value which means the best condition for the pervaporation test.

ACKNOWLEDGEMENTS

The authors would like to gratefully acknowledge MOSTI for their financial support for this research.

REFERENCES

[1] Baker, R. W. 2006. Membrane Technology in the Chemical Industry. (305-334). Germany: WILEY-VCH Verlag GmbH & Co.KGaA.

[2] Le, T. N. T. 2004. Pervaporation of Isopropanol Using Chitosan-Zeolite A Membrane: The Effects of Zeolite A Concentration. Master. University Technology Malaysia, Skudai.

[3] Rautenbach, R. and R. Albrecht. 1989. *Membrane Process*. John Wiley and Sons Ltd.

[4] Kittur, A. A., M. Y. Kariduraganavar, U. S. Toti, K. Ramesh, T. M. M. Aminabhavi. 2003. Pervaporation Separation of Water-Isopropanol Mixtures Using ZSM-5 Zeolite Incorporated Poly(vinyl alcohol) Membrane. *Journal of Applied Polymer Science*. 90: 2441-2448.