Jurnal Teknologi, 39(A) Keluaran Khas. Dis. 2003: 55–64

PERVAPORATION SEPARATION OF ISOPROPANOL-WATER MIXTURES USING CROSSLINKED CHITOSAN MEMBRANES

MOHD GHAZALI BIN MOHD NAWAWI[1] & HASHIM BIN HASSAN[2]

Abstract. Chitosan membranes were prepared from local shrimp shells. Membranes were prepared as homogeneous (unmodified) and crosslinked chitosan. Chitosan membranes were modified via chemical crosslinking technique. The extent of crosslinking were determined by its crosslinking time. The pervaporation performances of the unmodified and the modified chitosan membranes were investigated in the pervaporation isopropanol-water systems. From the pervaporation experiments, it showed that chitosan membranes exhibited preferential permeation to water. The modified chitosan membranes showed a lower permeation flux but a higher separation factor than the unmodified membranes. The modified chitosan membrane had a better pervaporation performance than the unmodified membranes in terms of pervaporation separation index.

Keywords: pervaporation, chitosan, membrane, crosslinking, isopropanol-water mixtures.

Abstrak. Membran kitosan telah dihasilkan daripada kulit udang tempatan. Membran kitosan yang dihasilkan adalah membran homogen (tanpa ubah suai) dan membran terangkai-silang (terubah suai). Darjah perangkaisilangan adalah ditentukan oleh masa rangkai-silang itu sendiri. Prestasi bagi membran yang dihasilkan tanpa ubah suai dan membran yang terubah suai telah dikaji dalam pemisahan penelapsejatan bagi sistem campuran air-isopropanol. Daripada ujikaji penelapsejatan, membran yang dihasilkan daripada kitosan telah memberikan keutamaan dalam penelapan kepada air. Membran terubah suai menunjukkan penurunan dalam fluks tetapi terdapat peningkatan dalam faktor pemisahan berbanding dengan membran tanpa ubah suai. Daripada segi indeks pemisahan penelapsejatan (PSI) pula didapati membran terubah suai telah menunjukkan prestasi yang lebih baik berbanding membran tanpa ubah suai.

Kata kunci: penelapsejatan, kitosan, membran, terangkai-silang, campuran isopropanol-air.

1.0 INTRODUCTION

The separation of organic liquid mixtures using pervaporation membranes has received increasing attention in the chemical industries. The advantages of low cost, simplicity and capability of separating azeotropic mixtures make it a very promising separation process particularly in the separation of alcohol-water mixtures. Since the commercialisation of the GFT (Gesellschaft fur Trenntechnil) membranes in the separation of the ethanol-water mixtures using crosslinked poly (vinyl alcohol)-

[1,2] Chemical Engineering Department, Faculty of Chemical & Natural Resources Engineering Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia. *hashim@fkkksa.utm.my,

polyacrylonitrile composite membranes, many research works have been conducted in this area [1-6]. For the dehydration of alcohol mixtures, membrane materials, which contain hydrophilic groups in the polymer structure are preferred.

In the past few years, chitosan (CS) was found to be very attractive material for the preparation of hydrophilic membranes. Chitosan, the partially-deacetylated form of chitin can be found in the crustacean shells such as crab and shrimp. Recently many investigations [7-11] have been directed to chitosan as a pervaporation membrane material due to its favorable permselectivity and solvent stability, good film forming properties, highly hydrophilic, good chemical resistant properties and functional groups which are easy to modify. However, due to its high swelling properties in aqueous system, the modification of the chitosan membranes are inevitable. One of the widely used technique to improve the stability of the membrane is called chemical crosslinking. Besides the membranes stability, the separation efficiency of the membrane could also be enhanced through crosslinking.

In this study, homogeneous chitosan membrane and chitosan membrane crosslinked with aluminum nitrate solution were prepared and tested in the pervaporation separation of isopropanol-water mixtures. The effects of crosslinking time and the feed concentration on the permeation flux and separation factor were studied.

2.0 EXPERIMENTAL PROCEDURE

2.1 Materials

Chitosan were extracted from domestic shrimp shells. Reagent grade sodium hydroxide, ethanol and isorpopanol, hydrochloric acid fuming 37%, acetic acid and aluminium nitrate were purchase from various vendors. Deionized distilled water was used in this study.

2.2 Chitosan Preparation

Chitosan, a deacetylated form of chitin was obtained from shrimp shells. First, protein is removed from ground shells by treating it with sodium hydroxide aqueous solution (NaOH) of 2 – 3 M and at temperature of 80 – 90°C for 2 hours. Then it was washed thoroughly with distilled water. The shrimp shells are subsequently treated in 2 M hydrochloric acid (HCL) aqueous solution for 24 hours to remove calcium from the shells. The chitin thus obtained is washed with distilled water and dried under the sun. The chitin flakes is then subsequently deacetylated in 50% NaOH solution at a temperature of 90 – 110°C for 3 hours to produce chitosan. Then the chitosan flakes are washed with distilled water, dried under the sun for three hour and is further dried at room temperature for a week.

2.3 Membrane Preparation

A preweighed quantity of chitosan was first dissolved in 10 wt% acetic acid solution at room temperature for 24 hours to produce a casting solution consisted of 2 wt% of chitosan. Then, the polymer solution is first filtered to remove impurities and undissolved chitosan to give a clear homogeneous casting solution. The resulting casting solution was cast into a petri dish, allowing the casting solvent to evaporate for 48 hours at room temperature. The formed membrane was peeled off from the plate before being immersed in a coagulation bath containing 3 wt% NaOH, 47 wt% ethanol and 50 wt% water for 24 hours at room temperature, then washed thoroughly with deionized water to completely remove NaOH and finally was air-dried at room temperature. Membranes were then immersed in 0.01 wt% aluminum nitrate solution at 25°C with crosslinking time varying from 10 to 30 min. After crosslinking, membranes were thoroughly rinsed with deionized water and were allowed to dry at room temperature.

2.4 Swelling Experiment

The dry membrane samples were weighed and subsequently immersed in a isopropanol-water mixtures for 72 hours at room temperature. The swollen samples were weighed immediately after careful blotting. The degree of swelling is calculated using the following equation:

$$DS = \frac{W_s - W_d}{W_d} \tag{1}$$

where W_s and W_d are the weight of the dry and swollen membranes respectively.

2.5 Pervaporation Experiment

Pervaporation experiments were conducted in a continuous pervaporation unit with an effective membrane area of 52.8 cm^2. The permeation cell consisted of two detachable stainless steel parts. The glass feed tank has a feed solution capacity of 1000 ml. The feed solution was well mixed by a magnetic stirrer. From the feed tank, the feed mixture is circulated through the cell by a Masterflex peristaltic pumps. The permeate side of the membrane was connected to a cold trap immersed in liquid nitrogen, followed by a vacuum pump to supply the required driving force for pervaporation. During pervaporation, the permeate pressure was maintained at about 3 – 5 mm Hg. The permeate collected in the cold trap was weighed and analysed to determine the permeation flux and the separation factor.

The pervaporation properties are characterised by the permeation flux (J) and the separation factor. Permeation fluxes were determined by measuring the weight of

liquid collected in the cooling trap at a predetermined period of time after a steady state condition was reached. The separation factor (α) is defined by

$$\alpha = \left(\frac{Y}{1-Y}\right)\left(\frac{1-X}{X}\right) \tag{2}$$

where X and Y are the weight fraction of the more permeable component in the feed and permeate, respectively.

The separation ability of a membrane can be expressed in terms of permeation flux and separation factor which usually take place in the opposite way, that is, when one factor increases, the other decreases, but both of them are important parameters in the separation process. A pervaporation separation index (PSI) can be defined as a new measure of the separation ability of a membrane[12] as:

$$PSI = J(\alpha - 1) \tag{3}$$

3.0 RESULTS AND DISCUSSION

3.1 Degree of Swelling

The swelling behavior of a preferential component affects the pervaporation membrane performance . This property depends on the nature of membrane material and the membrane preparation conditions. The swelling property for the unmodifed and the modified chitosan membrane are given in Figure 1. It is clearly seen that for both membranes, the degree of swelling of the membrane decreases with increasing concentration of isopropanol in the feed solution. By comparison, the modified membranes have a degree of swelling lower than that of unmodified membranes. Modification of the chitosan membrane via chemical crosslinking resulted in a more compact structure and therefore the membrane aquire less affinity and less sorption ability.

3.2 Permeation Flux of Unmodified Membrane

The partial permeation flux of the unmodified chitosan membrane is shown in Figure 2. As the isopropanol concentration in the feed increases, the permeation flux for water decreases more significantly resulting the decrease in the total permeation flux. Since, the total permeation flux of water is almost identical to that of the total permeation flux, a decrease in the water flux leads to a decrease in the total flux for the entire feed composition of water- isopropanol mixtures. Due to its high hydrophilicity, chitosan membrane has high affinity to water. At high water weight fraction in the feed, the armophous region of the membrane swell more significantly resulting the polymer chain to become more flexible, thus decreasing the energy required for diffusive

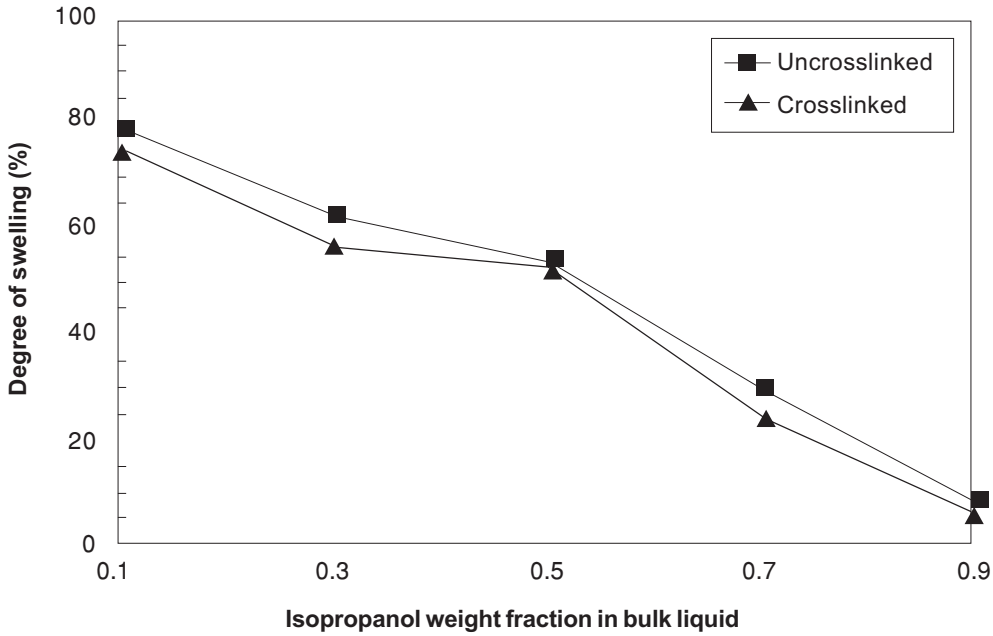

Figure 1 Degree of swelling versus isopropanol weight fraction in bulk liquid (20 min crosslinking time. Temperature 30°C)

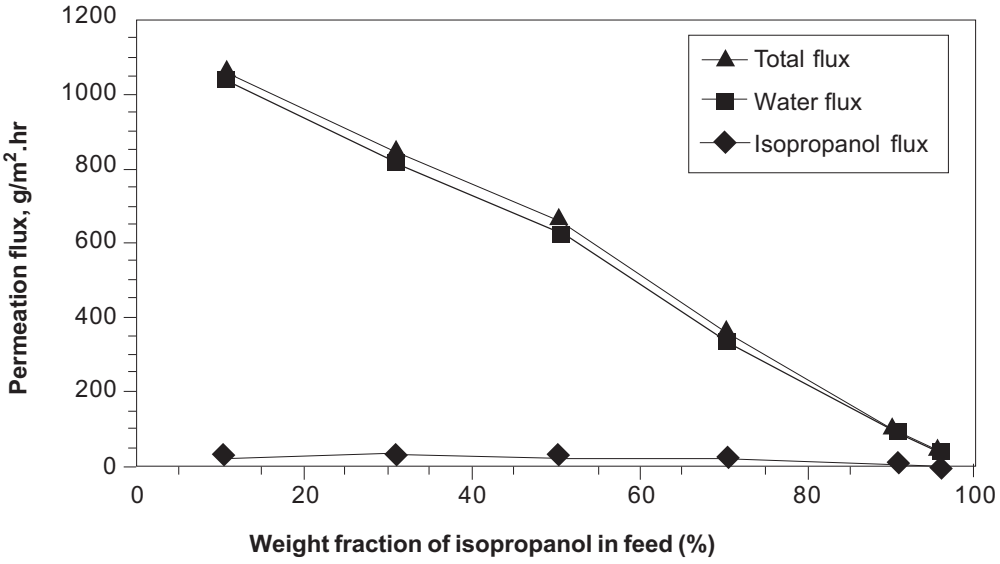

Figure 2 Effect of feed concentration on the individual permeation flux for the unmodified chitosan membrane (Temperature: 30°C)

transport through the membrane. As a result, the water permeation flux increases with an increase in water weight fraction in the feed. Higher affinity of chitosan to water and the fact that water has a molecular size smaller than that of isopropanol would make the chitosan membrane more selective to water.

3.3 Pervaporation Performance of Modified Membrane

In pervaporation process, it is desired that membrane should have high permeation flux and good selectivity. However, the polymeric membranes generally exhibit a trade-off phenomenon between flux and separation factor. One of the widely used techniques to improve the separation factor is crosslinking. The extent of the degree of crosslinking were determined by its crosslinking time. In the present study, the chitosan membranes were crosslinked from 10 to 30 minutes with 0.01 wt% aluminum nitrate solution.

Figure 3 shows the influence of crosslinking time on permeation fluxes and separation factors at 30°C for pervaporation of isopropanol-water mixtures at 90 wt% isopropanol in the feed solution. The results show that permeation fluxes decrease with crosslinking time. Once the crosslinking took place, the crosslinking density would increase with time to make the zone more compact and rigid. At higher crosslinking degree, the resulting membrane has a more compact network structure and less chain mobility, which reduces the solubility and diffusivity of the permeating molecules. Thus, the permeation flux decreases with crosslinking time. However, initially the separation factor increases and has a maximum at crosslinking time of 20 minutes. Further

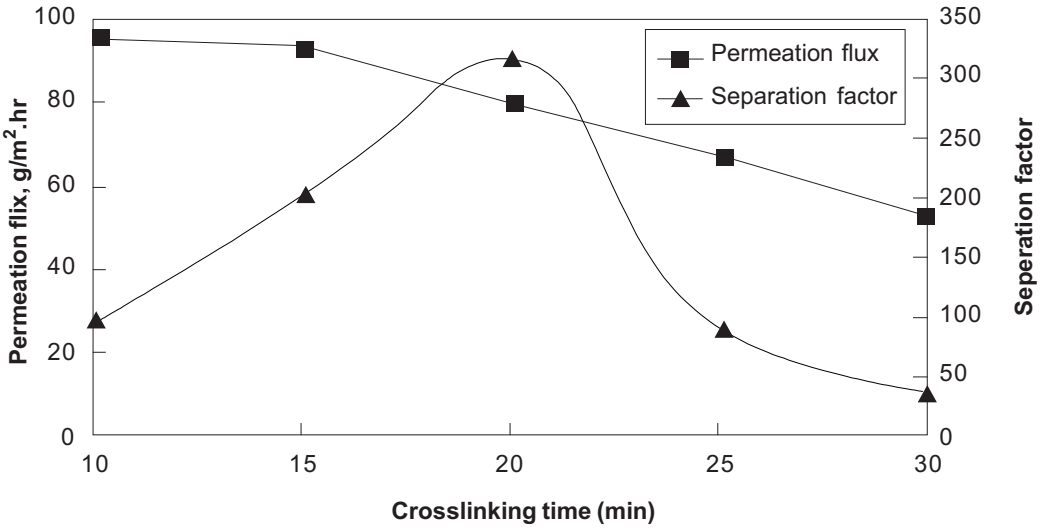

Figure 3 The pervaporation data of the crosslinked membranes as a function of crosslinking time. Feed isopropanol concentration: 90 wt%

crosslinking results in the decrease of separation factor. This is due to the excess in the crosslinking agent: the membrane structure thus formed allows more isopropanol to permeate through membrane and as a result the separation factor decreased. Similar trend has also been reported [8,13].

In this study, membrane crosslinked at 20 minute was chosen for further investigation of pervaporation performance in isopropanol-water separation. The effect of feed concentration on the permeation flux and the separation factor were investigated and the results were presented in Figure 4. The permeation flux decreases with increasing isopropanol concentration in feed solution while the separation factor increases and has a maximum at 90 wt% isopropanol. Again, the tradeoff phenomenon between permeation flux and separation factor is shown by the crosslinked membranes.

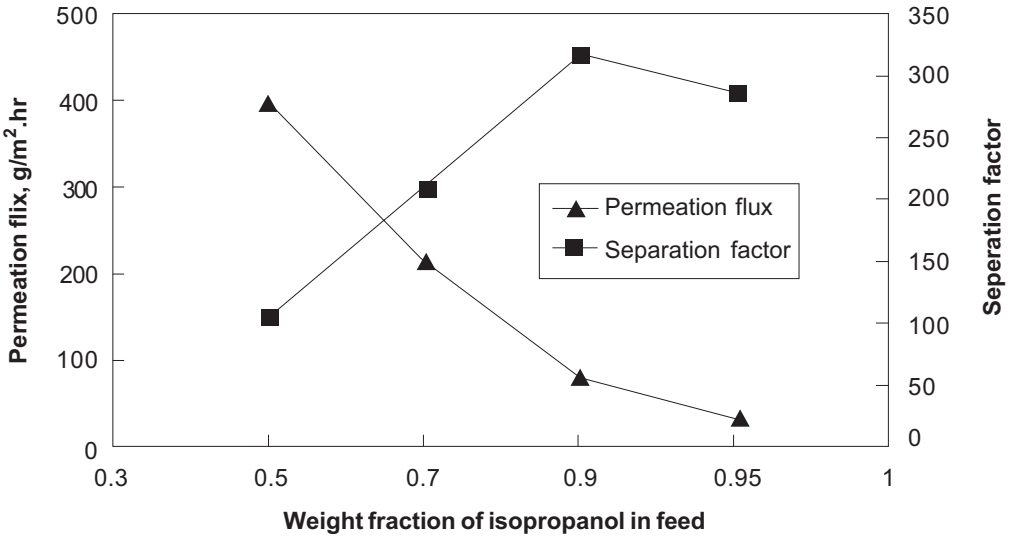

Figure 4 Effect of isopropanol weight fraction in feed on the permeation flux and separation factor

3.4 Modified versus Unmodified Membranes

By comparison, the modified membranes show a higher separation factor but a lower permeation flux than the unmodified membranes for the entire feed composition. The lower permeation flux of the modified chitosan membrane is in good agreement with the results for degree of swelling shown in Figure 1. In order to compare the performance between the modified and the unmodified membranes, the pervaporation separation index(PSI) was used [12]. The PSI for both membranes is plotted as a function of isopropanol concentration in the feed solution as shown in Figure 5. Membranes with modified structure show a higher PSI value up to 90 wt% isopropanol in the feed. The higher value of PSI was attributed to the increase in separation factor of the modified membranes as compared with the unmodified membranes since the PSI value is a

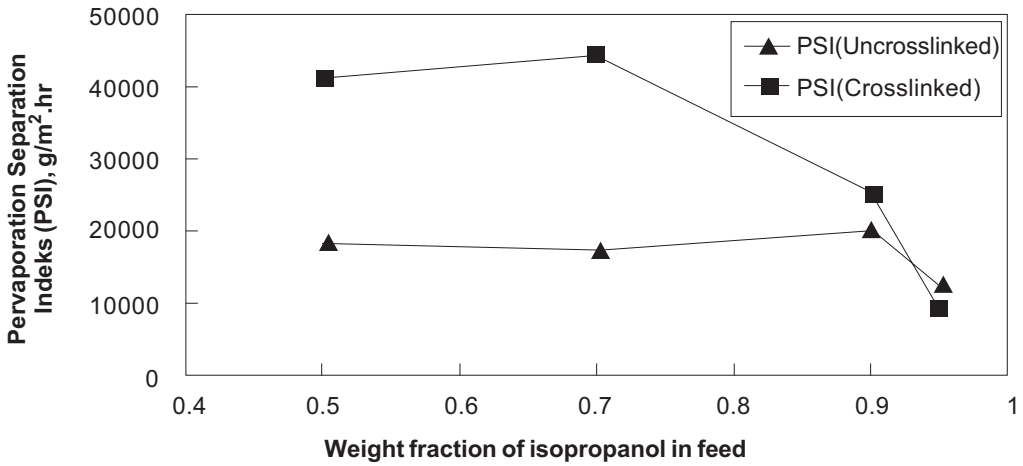

Figure 5 Perporation separation index (PSI) of the uncrosslinked and crosslinked membranes

product between the permeation flux and the separation factor. However, the PSI value of the modified membrane was slightly decreased at 95 wt% of isopropanol concentration due to the decrease in the permeation flux and the separation factor.

4.0 CONCLUSIONS

Based on the present study, chitosan membranes were successfully prepared from locally produced shrimp shells. The membranes show a preferential permeation to water and thus has the potential for the pervaporation separation of isopropanol-water mixtures. Chitosan membranes modified via a chemical crosslinking technique show a better pervaporation performance in terms of PSI values up to 90 wt% of isopropanol in the feed.

ACKNOWLEDGEMENTS

The financial support by the Ministry of Science, Technology and Environment of Malaysia through IRPA grant for funding this research is gratefully acknowledged.

REFERENCES

[1] Mochizuki, A., Y. Sato, H. Ogawara and S. Yamashita. 1989. "Pervaporation Separation of Water-Ethanol Mixtures Through Polysaccharide Membranes: The Permselectivity Neutralized Chitosan Membrane and the Relationshi ps Between its Permselectivity and Solid State Structure". *Journal Applied Polymer Science.* 37: 3358-3398.

[2] Kang, Y. S., S. W. Lee, U. Y. Kim and J. S. Shim. 1990. "Pervaporation of Water-Ethanol mixtures Through Crosslinked and Surface-Modification Poly(Vinyl Alcohol) Membrane". *Journal Membrane Science.* 51: 215-226.

[3] Lee, Y. M. and E. M. Shin. 1991. "Pervaporation Separation of Water-Ethanol Through Modified Chitosan Membrane. IV. Phosphorylated Chitosan Membranes". *Journal Membrane Science*. 64: 145-152.

[4] Uragami, T., T. Matsuda, H. Okuno and T. Miyata. 1994. "Structure of Chemically Modified Chitosan Membranes and Characteristics of Permeation and Separation for Aqueous Ethanol Solutions". *Journal Membrane Science*. 88: 243-251.

[5] Wang, X. P., Z. Q. Shen and F. Y. Zhang. 1996. "A Novel Composite Chitosan Membrane for the Separation of Alcohol-Water Mixtures". *Journal Membrane Science*. 119: 191-198.

[6] Huang, R. Y. M., R. Pal and G. Y. Moon. 2000. "Pervaporation Dehydration of Aqueous Ethanol and Isopropanol Mixtures Through Alginate/Chitosan Two Ply Composite Membranes Supported by Poly(vinylflouride) Porous Membrane". *Journal Membrane Science*. 167: 275-289.

[7] Mohd. Nawawi, M. G. and R. Y. M. Huang. 1997. "Pervaporation Dehydration of Isopropanol with Chitosan Membranes". *Journal of Membrane Science*. 124: 53-62.

[8] Lee, Y. M., S. Y. Nam and D. J. Woo. 1997. "Pervaporation of Ionically Surface Crosslinked Chitosan Composite Membranes for Water-Alcohol Mixtures". *Journal of Membrane Science*. 133: 103-110.

[9] Kubota, N. 1977. "Note: Permeability Properties of Chitosan-Transition Metal Complex Membranes". *Journal of Applied Polymer Science*. 64: 819-822.

[10] Huang, R. Y. M. and X. Feng. 1993. "Dehydration of Isopropanol by Pervaporation Using Aromatic Polyethermide Membrane". *Separation Science And Technology*. 28: 2035-2048.

[11] Goto, M., A. Shioshaki and T. Hirose. 1994. "Separation of Water/Ethanol Vapor Mixtures Through Chitosan and Crosslinked Chitosan Membranes". *Separation Science And Technology* 29. 14: 1915-1923.

[12] Feng, X. and R. Y. M. Huang. 1996. "Pervaporation With Chitosan Membranes. I. Separation of Water from Ethylene Glycol by a Chitosan/Polysulfone Composite Membranes". *Journal of Membrane Science.*116: 67-76.

[13] Zhao, X. P. and R. Y. M. Huang. 1990. "Pervaporation Separation of Ethanol-Water Mixtures Using Crosslinked Blended Polyacrylic Acid(PAA)-Nylon 66 Membranes". *Journal of Membrane Science*. 41: 2133-2145.