Azeotropic Separation of Isopropanol-Water Mixtures By Pervaporation Using A Locally-produced Chitosan-Based Membrane

Mohd. Ghazali bin Mohd. Nawawi,
Hashim bin Hassan and Tan Soon Huat

Department of Chemical Engineering
Faculty of Chemical & Natural Resources Engineering
Universiti Teknologi Malaysia

81310 UTM Skudai, Johor Darul Ta'zim

ABSTRACT

Pervaporation, a membrane process for separation of liquid mixtures has been recognized as an energy efficient alternative to conventional separation methods especially when involves the separation beyond the azeotropic point. In this study, membranes were developed from chitosan. Chitosan were converted from chitin which was extracted from shrimps shell. The membrane were prepared in the form of homogeneous and composite. The performances of the pervaporation membranes were investigated in terms of the permeation flux and separation factor in the isopropanol-water system with emphasis on the breaking of azeotropic composition and the dehydration of high concentration of isopropanol . At ambient temperature, a total flux of 48.8 $(g/m^2.hr)$ and a separation factor of 261 were achieved for homogeneous membrane at 95 wt% isopropanol in feed. Composite chitosan membrane consisting of a dense skin layer and casted on a porous polysulfone were also developed for dehydration of isopropanol. A total flux of 139.1 $(g/m^2.hr)$ and a separation of 168 were obtained for dehydration of 95 wt% isopropanol solution. By comparison, composite chitosan showed higher Pervaporation Separation Index (PSI) than homogeneous chitosan at 95 wt% isopropanol in feed solution indicating that composite chitosan membrane has the potential to be commercialized and used as pervaporation membranes for the dehydration of organic mixtures especially for the separation beyond the azeotropic conditions.

Keywords. Pervaporation; Dehydration of isopropanol; Azeotropic; Chitosan; homogeneous; composite

INTRODUCTION

Pervaporation, a unique membrane process that is capable of separating organic liquid mixtures has gaining increased interest in recent separation technique especially in the separation of azeotropes or close boiling mixtures. In this process, the feed is introduced to one side of a membrane and the permeate is removed in the vapor state from the other side. The separation is governed by the chemical nature of the permeating species and the membrane material, the morphology of the membrane, and the process operation conditions.

Dehydration of organic solvents is the best developed areas in pervaporation. One of the very promising industrial application is the dehydration of isopropanol. Isopropanol forms azeotropes with water at about 87 wt % of isopropanol in the system. Since the separation is based on the relative permeation rates of different components, pervaporation is effective for the separation of azeotropic and close-boiling mixtures, which is difficult by thermodynamics-governed processed such as distillation. Hydrophilic polymers being the most suitable candidates as material for pervaporation dehydration membranes. One of the hydrophilic polymer that has attracted much attention in the development of pervaporation membrane material is chitosan.

Chitosan was chosen as the membrane material because of its favorable permselectivity and solvent stability, good film forming properties, highly hydrophilic, and good chemical resistant properties (Feng and Huang,1996; Kubota,1997 and Mohd. Ghazali,1997). In this study, Membrane were prepared in homogeneous and composite form. Both types of membranes have been investigated in the pervaporation dehydration of isopropanol-water systems.

EXPERIMENTAL

Materials

Polysulfone was purchased from Amocco and dimethyl formamide were of analytical grade. Reagent grade sodium hydroxide was purchased from All Chem, ethanol and isorpopanol from J. T. Baker, hydrochloric acid fuming 37 % from R & M Marketing and acetic acid from Merck. Deionized distilled water was used in this study.

Membrane Preparation

Chitosan, a deacetylated form of chitin is obtained from shrimp shells. First, protein is removed from ground shells by treating it with sodium hydroxide aqueous solution (NaOH) at 2-3 M at temperature 80-90 °C for 2 hours. Then it is washed thoroughly with distilled water. The shrimps shell is subsequently treated in 2M hydrochloric acid (HCL) aqueous solution for 24 hours to remove the 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.

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 onto a glass plate with the aid of casting knife, allowing the casting solvent to evaporate for 48 hours at room temperature.The formed membrane is 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 is air-dried at room temperature.

Composite membranes are consists of a dense skin top layer supported by a porous sublayer. In this study, the porous sublayer is prepared from polysulfone via phase inversion technique. First, a homogeneous casting solution is prepared from 12 wt% polysulfone, 11 wt% methyl cellosolve and 77 wt% N,N, Dimethyl Acetamide(DMAc). The casting solution was cast onto the backing material held on glass plate, and then the cast film was immediately immersed in a gel bath consisting 50 wt% DMF and deionized water at room temperature for 10 minutes. The porous polysulfone membrane thus obtained was washed with deionized water for 24 hours and air-dried at room temperature.

The composite membrane was prepared by coating with 1.0 wt% chitosan onto the porous polysulfone with the aid of dropper and glass rod adjusting to the appropriate thickness. Then the coated membrane was dried at room temperature for 24 hours, treated in an alkaline solution containing 3 wt% NaOH aqueous solution, and 50 wt% iso-propanol for another 24 hours, washed thoroughly in deionized water and dried in air at room temperature.

Pervaporation

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 5 mm Hg. The permeate

collected in the cold trap was weighed and analyzed to determine the permeation flux and the separation factor.

Membrane Performance Characterization

The pervaporation properties are characterized by the permeation flux and the separation factor. Permeation fluxes (J) 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

$$\alpha = (\frac{Y}{1-Y})(\frac{1-X}{X})$$

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(Huang and Feng, 1993):

$$PSI = J.(\alpha - 1)$$

RESULTS AND DISCUSSION

Figure 1 shows the total permeation flux and individual fluxes as a function of isopropanol weight percent in feed solution. As the concentration of isopropanol increases, the total permeation flux and the water permeation flux decreases while the isopropanol permeation flux increased to a maximum at 30 wt % and then decrease back. At high water concentration in the feed solution, the armophous region of the membrane became more swollen resulting the polymer chain to be more flexible and thus provides more space for diffusion to occur. At this condition, less energy is required for diffusive transport resulting the water flux to increase with an increase in water concentration in feed. In the entire composition range, the water permeation flux is identical to the total permeation flux suggesting that water is preferentially permeable through the membrane. Chitosan is a highly hydrophilic polymer. The permselectivity of chitosan membrane to water is believed to be due to stronger affinity of chitosan to water molecules and smaller molecular size of water as compared to isopropanol.

Figure 2 shows the total permeation flux and separation factor versus weight percent of isopropanol in feed. There is a trade-off relationship between permeation flux and separation factor. The increase in the permeation flux will lead to the decrease in separation factor and vice-versa. Interestingly, high separation factors for water removal is observed at high feed isopropanol concentrations. Hence, the membranes is effective for the dehydration of high concentrations of isopropanol. Separation factors of 197 and

261 were achieved for the dehydration of isopropanol solutions at 90 wt % and 95 wt %, respectively.
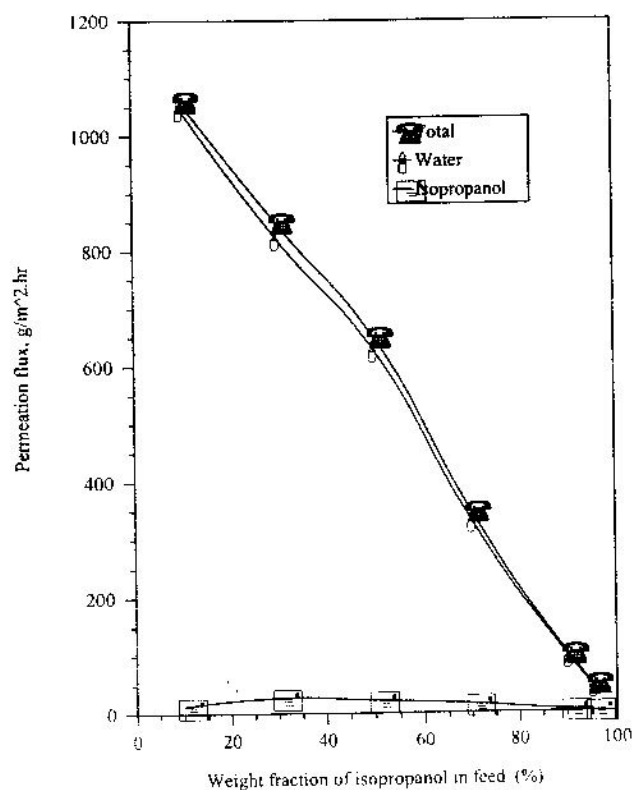

Figure 1 Effect of feed concentration on the individual permeation flux for homogeneous chitosan membrane. Operating temperature 30 °C.

Figure 3 shows the total permeation flux and separation factor versus the isopropanol weight percent in feed solution of composite chitosan membranes. In the whole concentration range, the pervaporation properties is similar to that of homogeneous membranes. Again, the trade-off relationship between the separation factor and the total permeation flux was observed. It is interesting to note that, the separation factor is increased with the increase in isopropanol concentration in the feed solution. A separation factor of 168 was obtained at 95 wt % of isopropanol in the feed solution. This is necessary for a membrane in order to be used effectively in the pervaporation dehydration of azeotropic separation i.e. isopropanol-water systems
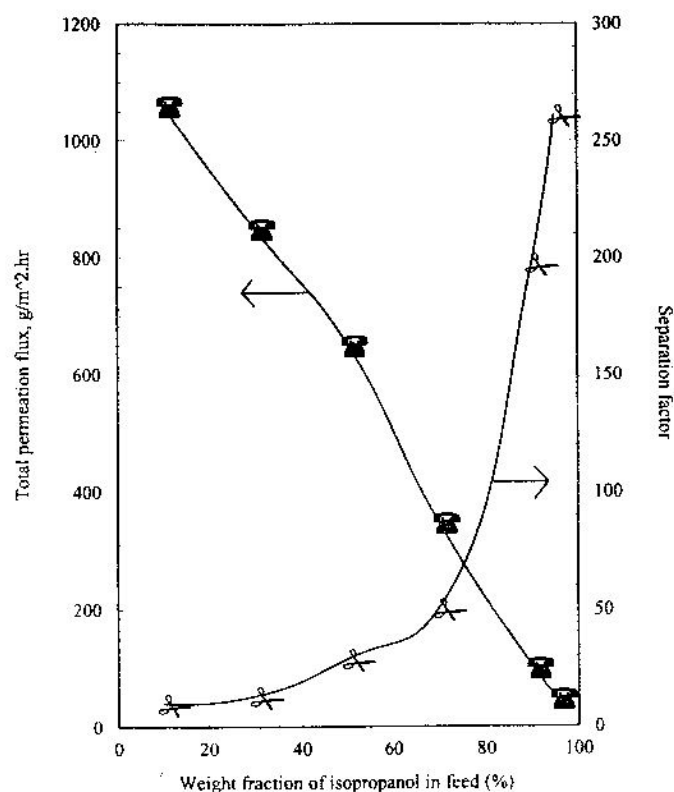
Figure 2   Effect of feed concentration on the separation factor and total
permeation flux for homogeneous chitosan membrane
Operating temperature 30°C

In light of the permeation flux-separation factor trade-off, the pervaporation separation index (PSI) may be used as a composite parameter to evaluate the pervaporation performance. The PSI for both homogeneous and composite membranes are plotted as a function of isopropanol weight fraction in feed solutions as shown in Figure 4. It is shown that the PSI for both membranes tends to increase with increasing feed isopropanol concentration and the decreases back when the weight percent of isopropanol is above 90. The PSI for homogeneous membranes is larger than that of composite membranes especially at isopropanol weight fraction below 70 %. At higher isopropanol weight fraction, the PSI for composite membrane become larger than that of homogeneous membranes. It means that the composite membranes is more effective for feed at high isopropanol weight fraction while homogeneous membranes is more effective to be used at dilute aqueous isopropanol solutions.
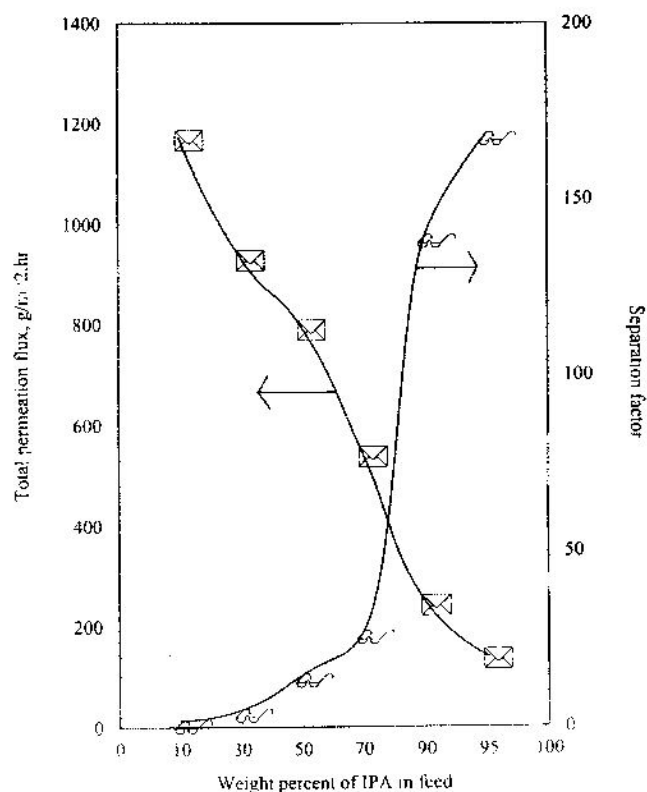
Figure 3   Separation performance for the composite chitosan
membrane as a function of weight percent of IPA in feed.
Temperature 30 °C.

CONCLUSIONS

Homogeneous and composite chitosan membranes were prepared and investigated for the pervaporation dehydration of isopropanol. The following conclusions can be drawn from the observations made in this study.

1. Chitosan based membranes prepared from locally available shrimp shell were water selective and were applicable for the dehydration of aqueous isopropanol solutions.

2. High separation factor was achieved for both homogeneous and composite chitosan membranes at high isopropanol feed concentration.

3. The PSI shows that the composite membrane was more effective for dehydration of isopropanol at high concentration than homogeneous membrane.

ACKNOWLEDGEMENTS

REFERENCES

Feng, X. and Huang, R.Y.M. (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.

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

Kubota, N. (1997). "Note: Permeability Properties of Chitosan Transition Metal Complex Membranes." *Journal of Applied Polymer Science.* **64**. 819-822.

Mohd. Ghazali Mohd. Nawawi (1997). "Pervaporation Dehydration of Isopropanol-Water Systems Using Chitosan Membranes." Ph.D Thesis, University of Waterloo.