

Dehydration of Isopropanol and Ethanol by Pervaporation Technique

J R Khan*, Shah Muhammad and Waseem Ahmed

Department of Chemical Engineering, University of Engineering and Technology, Lahore.

Corresponding Author: drjrabbani@yahoo.com

Abstract

Pervaporation is an energy efficient process/technique for the evaporation of a selective component from the liquid mixture using membrane, in direct with the liquid stream. In present study an experimental setup was developed using a Pervatech Silica Based Single Tube Pervaporation Module. Experiments were performed and data was collected for the change in concentration of retentate as well as variation of permeate flux at different temperature, like 40 C and 77 C for two different alcohols ,i.e., isopropanol and 2-ethylhexanol. Vacuum on permeate side and velocity of retentate to membrane module were kept constant during all experiments. It was concluded that pervaporation process can be economically utilized for the production of dehydrated ethanol to be used in gasohol and other alcohols, replacing energy intensive and complicated azeotropic or extractive distillation processes.

Key Words:

1. Introduction

Purification of chemical feedstock and separation of valuable components is widely required in process industries. Requirement of Separation of solvent from its mixture with water and other liquid is increasing because of its utility for multiple applications. To explore the techniques for ease of separation and economical solution is the essential feature and responsibility of the professionals. The conventional methods of separation e.g. Distillation/evaporation have some limitations like degree of purity, cost of separation and it is a high energy intensive methodology. Azeotropes formation is major hurdle to get purify the alcohols and other solvents.

The novel/latest separation techniques are expensive but better solution. However the implementation of the membrane base separation technique provides an economical alternative as compared to the simple distillation. Different polymeric membranes are under investigation for purification of alcohol from its mixture with water. The selective properties that is the solubility, osmotic pressure etc. plays a vital role in this context. During the reverse osmosis process, the maintenance of the permeate below its vapor pressure enhances the

degree of purity.

Pervaporation separation of a single component from a liquid stream is an opportunity and is an optimized technique for industrial scale application, specifically for close boiling liquid mixtures (azeotropes) and organic solvents. Generally pervaporation can be classified into two categories. Separation due to equilibrium distribution and separation due to variation in transport rate. The transport rate depends on driving forces, such as gradient in Pressure, Temperature, Concentration, and Electric field applied over the membrane.

2. Scope of Work

An experimental set up was developed and experiments were performed for the wide range of operating conditions. Following were the main objectives of present research:

- Development of experimental setup for Pervaporation
- To study the effect of temperature on rate of dehydration and flux for two types of different alcohols.

In separation process, the desired objectives are to obtain high purity products along with high

percentage recovery. Using conventional distillation technique, both of these objective can be achieved, but at the cost of considerable energy consumption rate. Contrary to this, membrane is capable of producing a high purity product but percentage of recovery is significantly decreases. The reduced percentage recovery indicates the use of multistage membrane system which requires additional numbers of compressors.

Hybrid system (Combination of distillation and membrane Technologies) is a feasible alternative which can achieve the both aspects i.e. high purity along with the enhanced percentage of recovery.

3. Literature Review

Escalating energy costs and increased environmental awareness has necessitated designing and developing energy efficient processes in the industrial sector. Compared to the traditional separation operations (like distillation), membranes separation operations are energy efficient, low cost and easy to operate and are highly appreciated in industrial and energy/environmental fields. Pervaporation, a relatively new membrane based technique has received much attention in the last decades to separate liquid mixtures, especially organic liquids mixtures of close boiling liquids or liquid mixture sensitive to heat treatment.[1]. Removal of water from organic solvents is the main field that has widely used pervaporation [2, 3].

Various membranes materials and geometries are reported in literature that is used for dehydration by pervaporation. Previous researches indicate that hollow fibers having large surface area per volume ratio, high packing density, good flexibility, easy operation and self-contained mechanical support are mostly used [4,5,6,7]. However, thin dense skin, mechanical strength and resistance to feed- induced swelling are still the major challenges to produce commercially workable hollow fibers for pervaporation dehydration [8]. Polymer material, like polyimides are selected by some commercial fiber producers because of their easy processing, with relatively mechanically stronger thin skin and better chemical and thermal stability that is more suitable for corrosive and high temperature environment commonly, exists in pervaporation[9,10,11].

Lan Ying Jiang et al [12,13] developed matrimid polymer hollow fiber for the separation of water-Isopropanol mixture and studied the impact of chemical crosslinking thermal harden in on the separation process. Their observations show that the separation factor significantly increases with degree of crosslinking whereas it has a negative effect on flux. The thermal annealing alone has no effect on pervaporation performance perhaps due to cracks produced by shrinking in heating process. They further added that combine thermal annealing and cross-linking improve performance of hollow fibers independent of their initial status.

Polyethylene glycol (PEG) based polyether urethane membranes with increasing molecular weight and increase in chain length were examined by S. Das and co-workers [14], for the dehydration of methanol, ethanol and isopropanol. They concluded that membranes selectivity towards water increases with molecular weight as well as with increase in polymer chain length of membrane.

The problem of feed induced swelling was studied by Yan Wang and is co-workers l [15]. They fabricated a unique polyamide (PAI) and polyetherimide (PEI), hollow fiber membrane using two layers spinning technology for the separation of C_1 to- C_4 alcohols, with the objective to analyze their order of fluxes and performance. Their conclusions were, that for the dual layer hollow fiber membrane the separation performance is highest (separation factor > 50,000 and flux > 700 gm/m².h) for the hollow fibers spun at an air gap of 2-cm apart and hardened at 75°C temperature. also it adores a good stability for a longer period that is up to 200 h, it is perhaps because of their fully porous inner layer and less water intakes that favours less swelling characteristics of (PEI) layer. Zeolite T enjoying both hydrophilic and good acid resistance properties are good candidate to produce, membranes have great potential for liquid pervaporation/ gas separation. Zhang Xiaoliang et al [16], developed a Zeolite T membrane to study the effect of molecular ratios of SiO_2/Al_2O_3 and H_2O/SiO_2 , alkalinity, blending temperature, as well as crystallization time over membrane growth/permeation performance and found that pervaporation process performance is strongly affected especially, by alkalinity of clear solution. In recent years membranes made of hybrid

materials consisting of organic and inorganic compounds, are considered in various fields. A.A. Kittur et al [17] prepared a hybrid membrane using poly vinyl alcohols (PVA) and tetraethylorthosilicate (TEOS, to study the swelling effect and found a significant decrease in swelling with increase in concentration of (TEOS), most likely because of hydrogen and covalent bonds formed in membrane matrix. In addition to this they found that membranes containing higher amount of TEOS display higher separation performance.

In present work Pervatech Single Tube Silica Based membrane was selected to perform experiment for the dehydration of two alcohols i.e. 2-ethyl hexanol and Isopropanol One liter of volume of known composition of each alcohol was taken for every experiment.

4. Theoretical Development

The separation factor α (i.e. ratio of concentration of 'i' and 'j' components in permeate as compared to feed) is a key parameter to determine the efficiency of membrane process. It is defined as:

$$\alpha = \left(\frac{y_i/x_i}{y_j/x_j} \right) \quad (1)$$

Where, x and y represent the fractions of components 'i' and 'j' in the permeate and feed, respectively.

Two methods are frequently given in literature to illustrate the pervaporation process, (1) pore flow model (2) adsorption-diffusion model. Pore flow model presume 'pervaporation' as the liquid permeation over the membrane and then convective flow of permeate through the pores, with a phase change that takes place where the pressure within the membrane decreases below the vapour pressure.

In adsorption - diffusion model the membrane is considered to be so compact that the process through the membrane is diffusion not the convective process. Fluid flows through the membrane by three successive steps. Initially, the permeate sorption over the membrane surface from feed mixture followed by the diffusion through the membrane and finally desorption as vapours on the opposite side of membrane. The permeate flux is computed as the

mass of permeate/surface area of membrane $\times$ time interval.

The present work is a humble effort to explore the pervaporation through a microporous silica membranes and applying the adsorption-diffusion model, to explain the effect of temperature and nature of permeating species on the change in concentration of retentate as well as permeate flux for the selected binary mixtures.

Experimental Setup

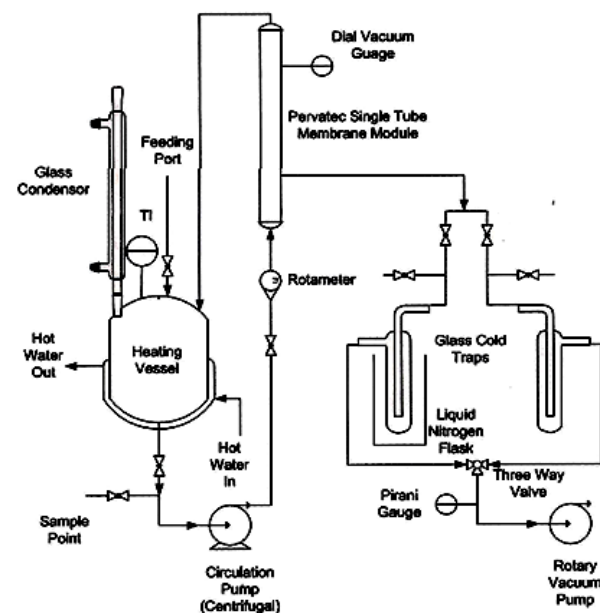


Fig. 2 Layout of Experimental Setup

A laboratory scale pervaporation unit was fabricated, installed and tested. Flow meter and gauge to monitor the vacuum on permeate side were calibrated. Experiments for test runs were performed.

Test Procedure

Feed of known composition (alcohol/water) is filled in the heating vessel and the valve is closed. Hot water is circulated through the jacket of heating vessel to heat the feed to the desired temperature. Circulation pump is switched on to circulate the feed/retentate through membrane modules and the heating vessel and a feed flow rate of 0.5 liter/min is maintained. Liquid Nitrogen is poured into vacuum flask and the vacuum pump was started to create vacuum on the permeate side. A vacuum < 5 mbar is maintained throughout the experiments.. Glass cold

trap is switched on after equal intervals to collect samples of retentate and permeate and to measure the flux. Samples are collected after every one hour.

Following two alcohols were selected for pervaporation experiments:

1. 2. Ethyl hexanol (2-EH)
2. Isopropanol (IPA)

Result, Conclusion & Recommendation

Two sets of experiments, one for each type of alcohol were performed. Experiments were conducted for three different temperatures i.e., 40C, 55C and 70C. Following parameters were studied during experimentation and the data is presented in graphical form.

1. Variation of water concentration in retentate with temperature and time.
2. Variation of permeate flux with temperature and time

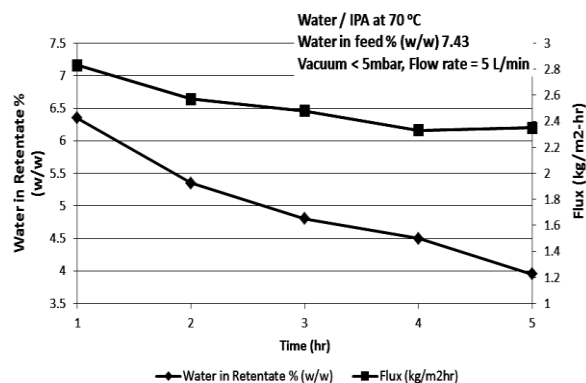


Fig.2 Water/IPA system at 70C

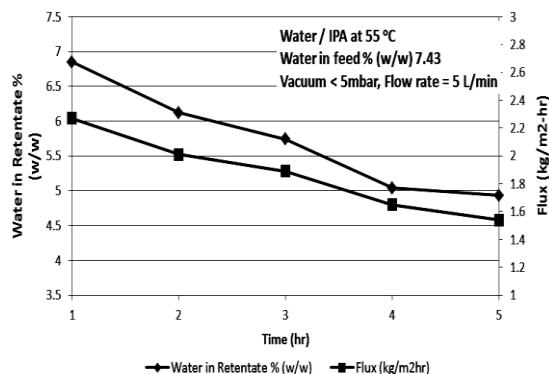


Fig.3 Water/IPA system at 55C

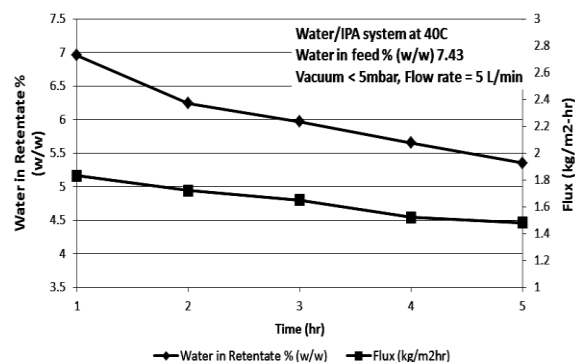


Fig. 4 Water/IPA system at 40C

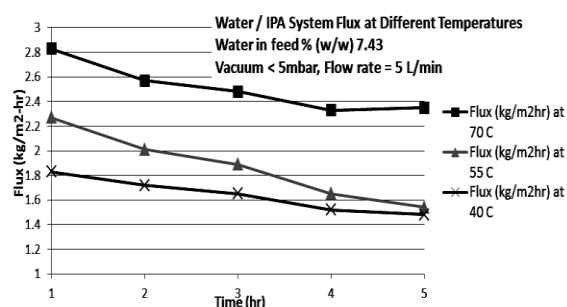


Fig. 5 Water/IPA system flux at different temperature

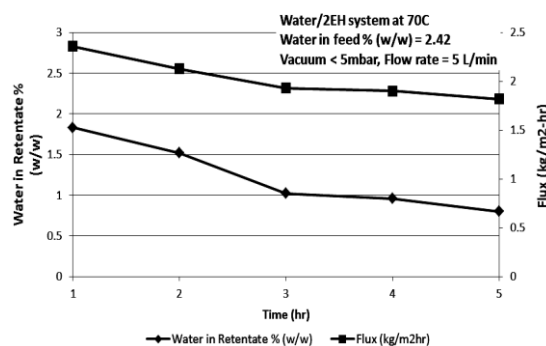


Fig. 6 Water/2EH system at 70C

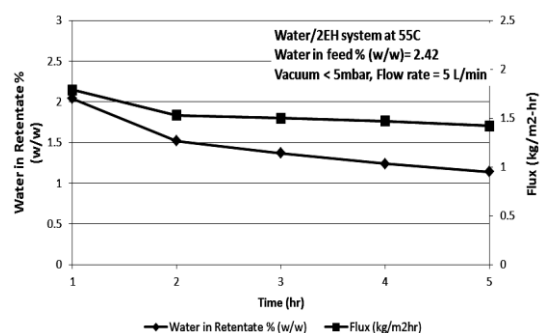


Fig. 7 Water/2EH system at 55C

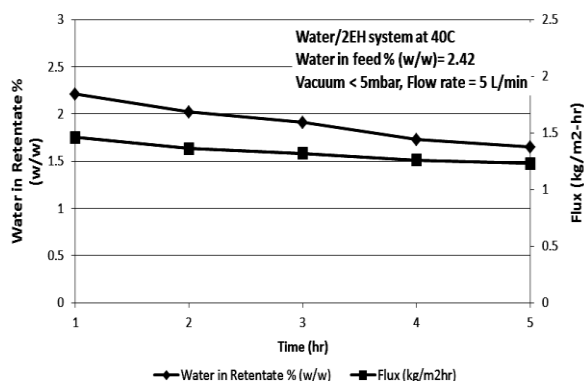


Fig. 8 Water/2EH system at 40C

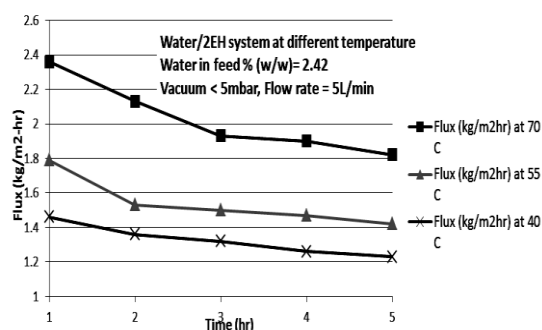


Fig. 9 Water/2EH system flux at different temperature

Result

Effect of Time

Figures 2 – 4 (in case of IPA), demonstrate that concentration of water gradually decrease with time in retentate while the rate of dehydration gradually decreases with time. This supports the theoretical background of pervaporation process. Same phenomenon has been observed in case of 2EH through as shown in figure 6 to 9.

Effect of Temperature on Flux

Figure 5 (in case of IPA), indicates, that permeate flux increases with the increase in retentate temperature and has maximum value at highest temperature i.e. at 70C while at lowest temperature i.e. at 40C flux is minimum. Same effect has been observed in case of 2EH.

Conclusions

1. Permeate flux increases with the increase in retentate temperature and decreases with time, in a batch process pervaporation.

2. During this study it has been concluded that pervaporation dehydration is a feasible process at high temperature, with reasonable flux.

Recommendations

1. As the fuel prices are escalating due to the international situation, pervaporation being the less energy intensive process for high purity solvents has become the only choice.
2. Pakistan is agriculture based country and largely depends on the import of oil. The local production of ethanol to promote the use of ethanol as gasoline blending constituent can be of greater advantageous to escalates its economy.

References

- [1] Jonquieres, A., Clement, R., Lochon, P., Neel, J., Dresch, M., and Chretien, B., "Industrial state-of-the-art of pervaporation and vapour permeation in the western countries", *Journal of Membrane Science* 206, pp. 87-117, (2002).
- [2] Feng, X., and R.Y.M. Huang, "Liquid Separation by membrane pervaporation: a review", *Industrial and Engineering Chemistry Research* 36, pp. 1048-1060, (1997).
- [3] Smitha, B., Suhanya, D., Sridhar, S. and Ramakrishna, M., "Separation of organic-organic mixtures by pervaporation- a review". *Journal of membrane science* 241, 1-21, (2004).
- [4] Matsuura, T., "Synthetic membranes and membrane separation processes CRC Press Boca Raton", FL, pp. 314-315,(1994).
- [5] Tsuyumoto, M., Teramoto, A., and P. Meares, "Dehydration of ethanol on a pilot-plant Scale, using a new type of hollow fiber membrane", *Journal of Membrane Science* 133, pp. 83-94, (1997).
- [6] Xu, Z.K. Dai, Q.W., Liu, Z.M., Hou, R.Q., and y.y. Xu, "Microporous propylene hollow fiber membranes, II. Pervaporation separation of water/ethanol mixture by the Poly (acrylic acid) grafted membranes", *Journal of Membrane science* 214, pp. 71-81, (2003).

- [7] Seok, D.R., Kang, S.G., and S.T., Hwang, "Use of pervaporation for separation of azeotropic mixtures using two different hollow fiber membranes", *Journal of Membrane Science* 33, 71-81, (1987).
- [8] Liu, R.X., Qiao, X.Y., and T.S., Chung, "The development of high performance 84 co-polyimide hollow fibers for pervaporation dehydration of isopropanol", *Chemical Engineering Science* 60, pp. 6658-6673, (2005).
- [9] Clausi, D.T., and W.J. Koros, "Formation of defect-free polyimide hollow fiber membranes for gas separation", *Journal of Membrane Science* 167, pp. 79-89, (2000).
- [10] Li, D.F., Chung, T.S., and R. Wang, "Morphological aspects and structure contro of dual-layer asymmetric hollow fiber membranes form by a simultaneous co-extrusion approach", *Journal of Membrane Sc.*, 243, pp. 155-175, (2004).
- [11] Jiang, L.Y.Chung, T.S. and S. Kulprathipanja, "Fabrication of mixed matrix hollow fibers with intimate polymer zeolite interface for gas separation", *A.I.Ch.E. Journal* 52, pp. 2898-2908, (2006).
- [12] Jiang, L.Y., Chung, T.S., and R. Rajagopalan, "Dehydration of alcohols by pervaporation through polyimide Matrimid asymmetric hollow fibers with various modifications", *Journal of Chemical Engineering Sc.*, 63, pp. 204-216, (2008).
- [13] Koops, G.H., Nolton, J., Mulder, M.H.V., and C.A. "Smolders, Integrally skinned polysulfone hollow-fiber membranes for pervaporation", *Journal of Applied Polymer Science* 54, pp. 385-404, (1994).
- [14] Das, S., Sakar, S., Basak, P., and B. Adhikari, "Dehydration of alcohols by pervaporation using hydrophilic polyether urethane membranes", *Journal of Scientific and Industrial Research*, vol 67, March, pp. 219-227, (2008).
- [15] Wang, Y. Goh, S.H. Chung, T.S., and P. Na, "Polyamide-imide/ polyetherimide dual-layer hollow fiber membranes for pervaporation dehydration of C1-C4 alcholos", *Journal of membrance Science* 326, pp. 222-233, (2009).
- [16] Xiaoliang, Z., Xin, S., Lingfang, Q., Minzheng, D., Rongfei, H.N.Z., and C. Xiangshu, "Synthesis and pervaporation of highly reproducible zeolite membranes from clear solutions", *Chinese Journal of Catalysis* 34, pp. 542-547, (2013).
- [17] Kittur, A.A., Jeevankumar B.K., and Kariduraganavar, "Pervaporation separation of water-dioxane mixtures through poly (vinyl alcohol)-silicone based hybrid membranes "International Journal of current Engineering and Technology, Special Issue1, Sept, pp. 148-156, (2013).