EFFECT OF OPERATING CONDITIONS ON THE DEHYDRATION OF TOLUENE BY PERVAPORATION USING A POLYVINYL ALCOHOL MEMBRANE

Ghasem Khatinzadeh[1]*, Mohammad Mahdyarfar[2], and Ali Mehdizadeh[1]

[1] Chemical Science and Technology Research Division, Research Institute of Petroleum Industry (RIPI), P.O. Box 14665-1998, Tehran, Iran

[2] Gas Research Division, Research Institute of Petroleum Industry (RIPI), P.O. Box 14665-1998, Tehran, Iran

ABSTRACT

The effects of operating parameters such as feed temperature and permeate-side pressure on the performance of a commercial PVA membrane in the dehydration of toluene by a pervaporation (PV) membrane system is studied in the present work. The results obtained indicate that increasing temperature in the range of 40 to 70 °C and reducing permeate pressure in the range of 1 to 10 mmHg increase membrane flux and selectivity, which consequently leads to the considerable modification of membrane performance in the reduction of water content of the feed.

Keywords: Pervaporation, Membrane, Toluene, Dehydration, Polyvinyl Alcohol, Processing Parameters

INTRODUCTION

In chemical processing industries, it is often necessary to remove water from solvents in order to avoid the deactivation of catalysts and/or the corrosion of equipment. Toluene is a widely used industrial aromatic solvent due to its capability of dissolving paints, rubbers, adhesives, and many chemical reagents. Some industrial uses of toluene include dealkylation to benzene and disproportionation to a mixture of benzene and xylene. When oxidized, toluene yields benzaldehyde and benzoic acid, two important chemical intermediates.

Adsorption and distillation techniques are usually used to remove water from toluene down to ppm ranges [1]. However, there are disadvantages associated with these processes including high energy consumption due to the regeneration of adsorbent and operation difficulties. In the past few decades, pervaporation has been developed as an alternative, promising separation technology for the dehydration of organic solvents including alcohols [2-4], especially ethanol [5-7], and other common organic solvents [8-9]. This process has characteristics such as high separation efficiency, simplicity of setting up and operation, and little energy consumption, making it favorable compared with other conventional methods.

In PV processes, the feed liquid contacts one side of a membrane through which a mixture enriched with one of the feed components

permeates. The separation in PV occurs because of the different rates of sorption and diffusion of the feed components through the membrane [10]. The permeate enriched in this component is removed as a vapor from the other side of the membrane. The vapor pressure difference between the feed liquid and permeate vapor is the driving force for the process. In the dehydration of various solvents by PV, hydrophilic polymers are selected as the membrane materials because water molecules are easily sorbed by such membranes [11]. In fact, the dehydration of aromatic solvents such as benzene using hydrophilic polymeric membranes in a pervaporation system has already been reported [12]. The study was performed at a constant temperature and pressure. However, the effects of feed temperature and permeate pressure, as two of the most important operating parameters which significantly influence the membrane performance, were not studied. Thus, it seems necessary to study the effect of these parameters on the optimization of PV processes [13].

In the present work, the influence of temperature and pressure on the performance of a hydrophilic polyvinyl alcohol membrane in the dehydration of toluene using pervaporation has been investigated.

EXPERIMENTAL

The schematic diagram of the experimental set up is shown in Figure 1. In the pervaporation experiments carried out, the feed (toluene) was pumped from a feed tank to the shell side of a 177 cm^2 Pervap 2201 membrane (Sulzer Chemtech). The membrane was a composite with a top layer of PVA (thickness=2 µm) on a polyacrylonitrile (PAN) porous support (thickness=80 µm) housed in a plate and frame module. Reduced pressure gradient was then applied using a vacuum pump maintained by a regulator and monitored using a vacuum gauge.
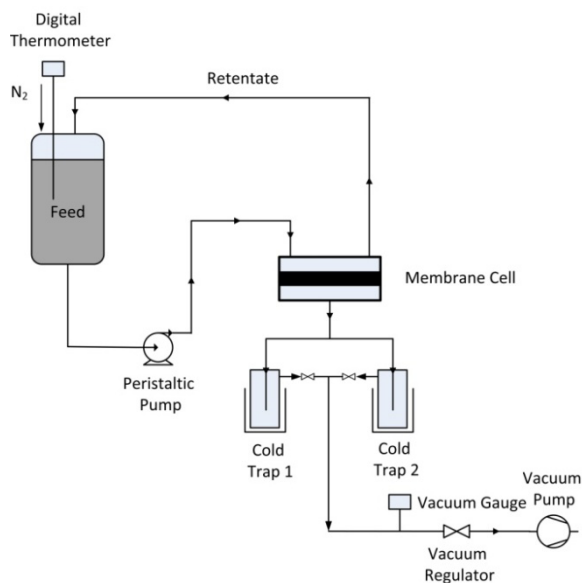

Figure 1: Schematic diagram of experimental set up

Before starting each PV experiment, the test membrane was equilibrated for about 3 hrs with feed solutions. Upon reaching the steady state, the permeate samples were condensed and collected in cold traps immersed in a liquid nitrogen bath. Toluene used in these experiments was provided by Isfahan Petrochemical Complex and contained 150 ppm of water. A heater and a temperature controller were used to keep the feed at a constant temperature. A temperature probe was attached to the feed tank and used to monitor the temperature during each run. The feed was circulated through the membrane at a feed flow rate of 1.1 l/min using a peristaltic pump. The water content in the retentate (product) was determined by the Karl Fisher method. Permeate fluxes were determined at different temperatures and permeate pressures by weighing the permeate obtained during a certain period of time by using Equation 1:

$$J = \frac{Q}{A.t} \tag{1}$$

where, J is the permeate flux (g/hm^2); Q, A, and t stand for permeate weight (gr), membrane area (m^2), and operation time (hr) respectively. Separation factor (α) was evaluated using Equation 2:

$$\alpha = \frac{Y_W / Y_T}{X_W / X_T} \qquad (2)$$

where, α is the separation factor and X and Y are the mass fractions of the feed and permeate respectively. Subscripts W and T stand for water and toluene respectively.

The pervaporation separation index (*PSI*) (g/hm^2) was used to evaluate the overall PV efficiency [14]. This was calculated using Equation 3:

$$PSI = J(\alpha - 1) \qquad (3)$$

All experiments were carried out under a blanket of nitrogen gas in order to prevent moisture from entering the system.

RESULTS AND DISCUSSION

Effect of Feed Temperature

PV experiments were performed at various operating temperatures in the range of 40 to 70 °C using feed mixtures containing 150 ppm water in order to investigate the effect of feed temperature on the membrane performance in the dehydration of toluene. The feed flow rates and pressures were kept constant at 1.1 l/min and 3 mmHg respectively for all the runs. Figure 2 shows water flux and the relative selectivity of the membrane to water as a function of temperature. As this figure clearly shows, water flux increases as the temperature rises.

Mass fluxes through the membrane are highly dependent on temperature. They increase exponentially according to the empirical Arrhenius law [15].

$$J = J_0 \exp\left(\frac{E_p}{RT}\right) \qquad (4)$$

where, J_0 is permeability constant; E_P represents activation energy, and T and R are the feed temperature and gas constant respectively. This

may result from the increase in the diffusion coefficient of the solute as the temperature rises. In fact, the thermal motion of the polymer chains of the membrane increases by raising temperature, which may facilitate the permeation of the adsorbed molecules through the membrane. Furthermore, as the operating temperature rises, the vapor pressure at the feed side increases while the vapor pressure at the permeate side does not significantly change. Therefore, the vapor pressure at the feed and permeate sides of the membrane increases and consequently the permeation of the permeating components through the membrane becomes easier. Additionally, as shown in Figure 2, the selectivity increases at higher temperatures, indicating that an increased operating temperature favors the permeation of water rather than toluene.
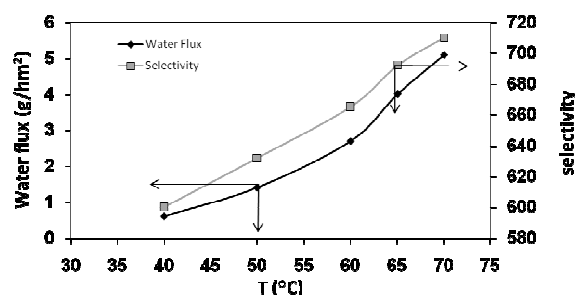

Figure 2: Water flux (♦) and selectivity (■) as a function of feed temperature (permeate pressure is set at 3 mmHg)

This is shown more clearly in Figure 3, showing the influence of temperature on the ratio of water to toluene flux. It can be observed that the ratio of water to toluene flux rises by increasing temperature. In other words, water concentration in the permeate is higher at high temperatures. Hence, increasing temperature leads to increased flux and selectivity, and thereby enhancing membrane performance in toluene dehydration by a PV system according to Equation 3.

Effect of Permeate Pressure

Water flux and selectivity are plotted versus

permeate pressure in Figure 4. According to the results, by varying permeate pressure from 1 to 10 mmHg, the membrane exhibits a considerable decrease in flux from 6.9 to 1.1 (g/hm^2) as well as a reduction in selectivity from 1122 to 153. Flux reduction depends on the thermodynamic properties of organic constituents such as saturated vapor pressure and activity coefficient.
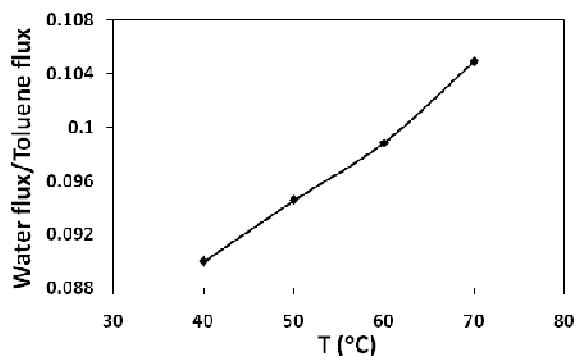

Figure 3: Variation in the ratio of water to toluene flux as a function of feed temperature (permeate pressure is set at 3 mmHg)

Drawing on this fact and according to Fick's law, increasing permeate pressure (lower vacuum) raises the activities of both permeants dissolved in the downstream layer of the membrane. Therefore, activity gradients across the thickness of the membrane decline and permeation flux drops [15]. Furthermore, increasing permeate pressure lowers the driving force, which slows down the desorption rates of the sorbed molecules. In such cases, the membrane relative selectivity to water is governed by the vapor pressures of the two components of the feed mixture. Toluene, which has a higher vapor pressure, permeates competitively with water, and thereby lowering the concentration of water in the permeate. On this basis, at pressures below 10 mmHg, reducing permeate pressure causes increased flux and selectivity and hence improves membrane performance.

The separation performance of the membrane is evaluated by calculating PSI, which shows the combined effect of selectivity and flux. As shown in Figures 5 and 6, dropping permeate side pressure and increasing feed temperature considerably raises PSI; in other words, the performance of a PV membrane system in the dehydration of toluene improves.
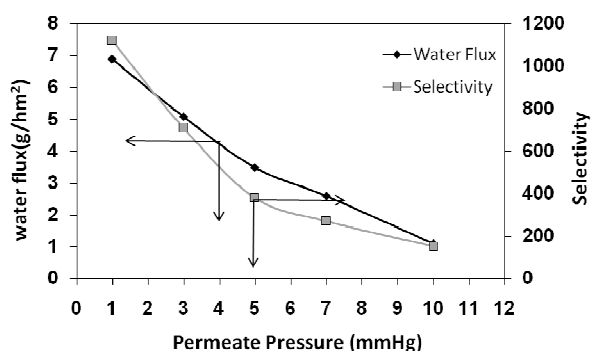

Figure 4: Effect of permeate pressure on membrane selectivity (■) and water flux (♦) (temperature is set at 70 °C).

Comparison of the Effects of Temperature and Pressure on PSI

It should be noted that PSI variations as a function of permeate side pressure 167-7735 (g/hm^2) are more considerable compared with the PSI variations resulting from temperature changes 335-3616 (g/hm^2). In other words, pressure variations have a greater influence on the membrane performance in toluene dehydration than temperature changes do. This is the result of the drastic influence of permeate side pressure on the membrane selectivity towards water molecules in the organic solvent.
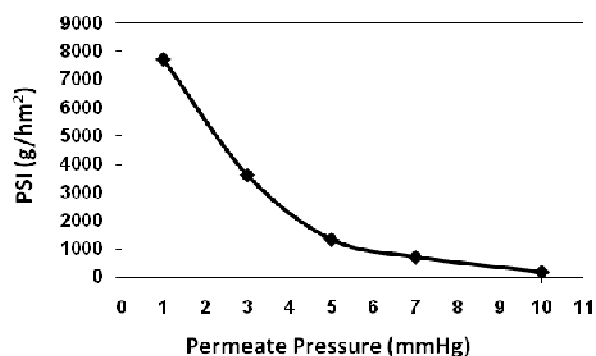

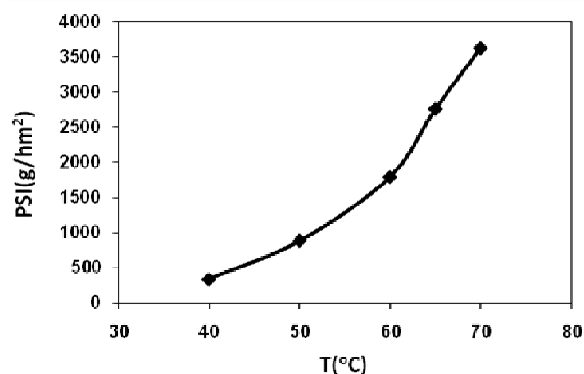**Figure 5: Effect of permeate pressure on PSI (temperature is set at 70 °C)**

http://jpst.ripi.ir

**Figure 6: Effect of feed temperature on PSI
(permeate pressure is set at 3 mmHg)**

Investigation of PVA Membrane Performance in the Dehydration of Toluene

Figure 7 shows the variation of the water content as a function of time in the retentate (dried toluene) at various operating temperatures and a fixed permeate pressure of 3 mmHg. It can be observed that the final water content in toluene may experimentally drop to below 50 ppm. Therefore, the water content of toluene can be reduced to very low values by the application of polymeric membranes in a pervaporation system. It is well known that the separation characteristics of a membrane depend upon the interaction between the solvent to be separated and the membrane matrix [16]. Hydrophilic membranes such as PVA can develop hydrogen bonding interactions with water, leading to the preferential sorption and diffusion of water through the barrier membrane. The observation that the water content of the product cannot be further reduced to concentrations lower than 50 ppm indicates that water permeation into the membrane is remarkably decreased in such concentrations.

Furthermore, extending the process time lowers the amount of water remaining in the retentate only down to 40-50 ppm; nevertheless, longer process times do not appreciably affect water content reduction. This also depends on the degree of the interaction of water molecules with the membrane and its very negligible

penetration at low concentrations. However, the reduction of water content to about 50 ppm shows the great potential of this process for the preparation of anhydrous toluene.
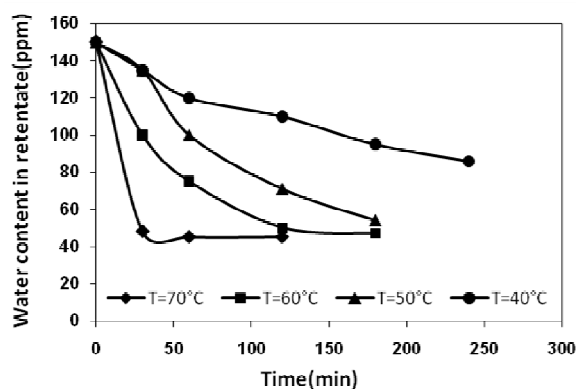

**Figure 7: Variation of water content in the retentate against time at various operating temperatures
(permeate pressure is set at 3 mmHg)**

CONCLUSIONS

The water content of toluene can be reduced from 150 to below 50 ppm using a pervaporation system. Feed temperature and permeate pressure are two of the most important operating parameters, significantly influencing the membrane performance. Permeate flux and selectivity are enhanced by increasing feed temperature and dropping permeate pressure. This modifies the membrane performance and as a result favors the dehydration of toluene. Also, the effect of permeate pressure on PSI is more considerable than that of temperature. However, high temperatures can typically be reached more easily and/or economically than low permeate pressures do. Therefore, the optimization of permeate pressure based on balancing membrane performance and operational costs is necessary.

REFERENCES

[1] Joshi S., Fair J. R., "Adsorptive Drying of Toluene", *Ind. Eng. Chem. Res*. **1988**, 27, 2078-2085.

[2] Rachipudi P. S., Kariduraganavar M. Y., Kittur A. A., "Synthesis and Characterization of

Sulfonated-polyvinyl alcohol Membranes for Pervaporation Dehydration of Isopropanol", *J. Membr. Sci*, **2011**, 383, 224-234.

[3] Jiang L. Y., Chung T. S., "Homogeneous Polyimide/ Cyclodextrin Composite Membranes for Pervaporation Dehydration of Isopropanol", *J. Membr. Sci*. **2010**, 346, 45-58.

[4] Tang Y., Widjojo N., Shi G. M., Chung T. S., "Development of Flat-sheet Membranes for C1–C4 Alcohols Dehydration Via Pervaporation from Sulfonated Polyphenylsulfone (sPPSU)", *J. Membr. Sci*, **2012**, 415-416, 686-695.

[5] Lieu Le N., Wang Y., Chung T. S., "Synthesis, Cross-linking Modifications of 6FDA-NDA/DABA Polyimide Membranes for Ethanol Dehydration Via Pervaporation", *J. Membr. Sci,* **2012**, 415-416, 109-121.

[6] Bolto B., Hoang M., Xie Z., "A Review of Membrane Selection for the Dehydration of Aqueous Ethanol by Pervaporation", *J. Membr. Sci*, **2011**, 503, 227-235.

[7] Hyder M. N., Huang R. Y. M., Chen P., "Pervaporation Dehydration of Alcohol–water Mixtures: Optimization for Permeate Flux and Selectivity by Central Composite Rotatable Design" *J. Membr. Sci,* **2009**, 326, 343-353.

[8] Chapman P. D., Tan X., Livingston A. G., "Dehydration of Tetrahydrofuran by pervaporation Using a Composite Membrane" *J. Membr. Sci*, **2006**, 268, 13-19.

[9] Singha N. R., Parya T. K., Ray S. K.,

"Dehydration of 1,4-dioxane by Pervaporation Using Filled and Crosslinked Polyvinyl Alcohol Membrane" *J. Membr. Sci.* **2009**, 340, 35-44.

[10] Neel J., "Introduction to Pervaporation" in: Huang R. Y. M. (Ed.), "Pervaporation Membrane Separation Processes", **1991**, 36-37.

[11] Devi D. A., Smitha B., Sridhar S., Aminabhavi T. M., "Pervaporation Separation of Dimethylformamide/ Water Mixtures Through Polyvinyl alcohol/ Poly(acrylic acid) Blend Membranes" *Sep. Purif. Technol*. **2006**, 51, 104-111.

[12] Li J., Chen C., Han B., Peng Y., "Laboratory and Pilot-scale Study on Dehydration of Benzene by Pervaporation" *J. Membr. Sci*. **2002**, 203, 127-136.

[13] Lin L., Kong Y., Yang J., "Scale-up of Pervaporation for Gasoline Desulphurization, Part 1, Simulation and Design*" J. Membr. Sci.* **2007,** 298, 1-13.

[14] Nawawi M. G., Huang R. Y. M., "Pervaporation Dehydration of Isopropanol with Chitosan Membranes" *J. Membr. Sci*. **1997**, 124, 53-62.

[15] Cabasso I., Grodzinski J. J., Vofsi D., "Polymeric alloys of Polyphosphonates and Acetyl Cellulose: Sorption and Diffusion of Benzene and Cyclohexane", *J. Appl. Polym. Sci*. **1974**, 18, 2117-2136.

[16] Shao P., Huang R. Y. M., "Polymeric Membrane Pervaporation" *J. Membr. Sci.* **2007**, 287, 162-179.