

## Pervaporation (PV) Separation of Methanol/Methyl Tert-butyl Ether Mixtures in Low Permeate Pressure Conditions

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### ABSTRACT

Recently, pervaporation separation processes have gained much attention in the separation of azeotropic and close boiling point organic-organic mixtures due to its high separation efficiency, economy, safety, and energy saving potentials. In this work, the effects of experimental factors such as feed composition and operating temperature on the performance of a commercial poly vinyl alcohol membrane in the separation of methanol/methyl tertiary butyl ether (MTBE) mixtures at low permeate side pressures (1-20 mmHg) were evaluated. Separation factor and methanol flux significantly increased by decreasing permeate side pressure, especially to less than 5 mmHg. Therefore, the reduction of pressure from 20 to 1 mmHg at 45 °C at a feed methanol concentration of 5 wt.% increased methanol flux and separation factor from 248 to 412 g/hm<sup>2</sup> and 73 to 211 respectively. In addition, the results indicate that by increasing feed temperature and methanol concentration in the feed, methanol flux is increased, while separation factor dropped.

**Keywords:** Pervaporation, Separation, Permeate Pressure, MTBE, Methanol

### INTRODUCTION

In recent years, methyl tertiary butyl ether has been extensively used as a lead free octane enhancer [1]. It has been shown that the addition of 10-15 wt.% MTBE to gasoline increases the octane number by 2-5 [2]. MTBE is also used as a reagent in fine chemical production. It is manufactured by reacting isobutene with excess methanol over a sulfonic ion exchange resin. The excess methanol then has to be separated from the products by distillation. The operation requires a high capital expenditure and

is not energy efficient because of the formation of methanol and MTBE azeotrope [1].

Pervaporation (PV), which is a more energy efficient and cheaper process, is one of the most developing membrane technologies, which has attracted much attention in the separation of azeotropic organic-organic mixtures [3-4]. PV is derived from combining permeation and evaporation, the two mechanisms involved in the process. In this process, the components of a liquid feed permeate through a dense membrane and evaporate into downstream

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at different rates. The difference in vapor pressure between the feed liquid and permeate vapor is the driving force for the process [5].

Considering the similar nature of methanol and water, hydrophilic membranes are used for the separation of methanol from MTBE. On this basis, extensive research has been performed to find an optimized membrane material to maximize separation performance in terms of separation factor, flux, and stability [6]. Membrane materials studied included poly vinyl alcohol (PVA) [7], poly vinyl alcohol/cellulose acetate [8], cellulose acetate-poly(N-vinyl-2-pyrrolidone) [9], and poly (ether ether ketone) [10]. The characterization of pervaporation process is usually considered with regards to the changes in different operational variables such as feed composition, temperature, and permeate pressure. Although much research has been conducted in this area [11-12], the studies have mostly been performed at low vacuum, and the effect of pressure on the separation of methanol from MTBE at high vacuum has not considerably been investigated. Permeate pressure is an important operating parameter as high vacuum corresponds to high energy cost. Thus, for the optimization of PV, the investigation of the effects of operating parameters on membrane performance at low permeate pressures seems necessary. In the present work, the separation of methanol-MTBE mixtures by pervaporation using a commercial membrane has been dealt with.

## EXPERIMENTAL PROCEDURES

In the pervaporation experiments carried out, the feed mixture was circulated from the feed tank in a temperature range of 20-45 °C and in a permeate pressure range of 1-20 mmHg through the cell using a peristaltic pump at a flow rate of 1.2 L/min. The volume of feed tank was 7 L, which was very big compared with the permeation volume. Therefore,

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the variation of the feed concentration during the experimental period was negligible. The permeate was condensed and collected in cold traps made of Pyrex glass, immersed in liquid nitrogen. Before starting the PV experiments, the test membrane was equilibrated for about 4 hrs with feed solutions. Figure 1 shows the experimental set-up used.

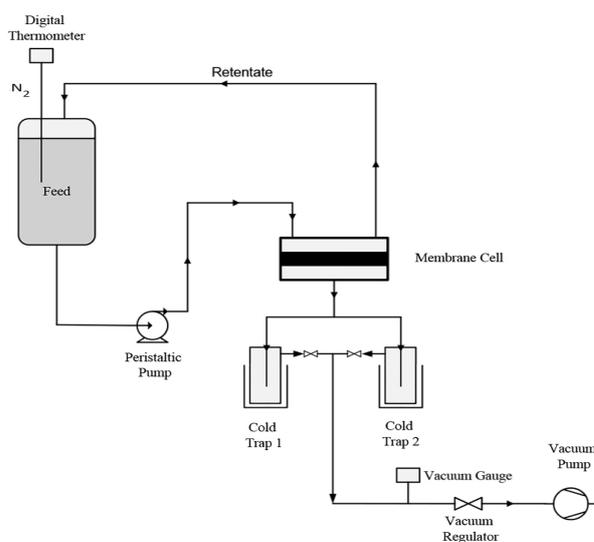


Figure 1: A schematic diagram of experimental apparatus.

In all the experiments, the commercially available PERVAP 2256 membrane from Sulzer Chemtech consisting of PVA active layer (thickness=2  $\mu\text{m}$ ) and polyacrylonitrile (PAN) (thickness=80  $\mu\text{m}$ ) support has been used.

The membrane module used in this study was of plate and frame type, which was made of stainless steel and supported on a porous disc with an effective membrane area of 177  $\text{cm}^2$ . The feed side of the membrane was at atmospheric pressure and permeate side was maintained in a desired pressure range using a vacuum pump. The PV experiments were repeated three times to check for repeatability. Repeatability is expressed as relative standard deviation, ranged between 2 and 4.5%. Permeate fluxes ( $\text{g/h m}^2$ ) were gravimetrically determined at different temperatures and pressures using Equation 1:

$$J = \frac{M}{A \cdot t} \quad (1)$$

where,  $J$  is the permeate flux, and  $M$  is permeate mass (g);  $A$  ( $m^2$ ) represents the membrane area and  $t$  (h) is operation time. Separation factor was calculated using Equation 2:

$$\alpha = \frac{Y_{Me} / Y_M}{X_{Me} / X_M} \quad (2)$$

where,  $\alpha$  is separation factor, and  $X$  and  $Y$  are the concentrations of components in feed and permeate respectively. Subscripts Me and M represent methanol and MTBE respectively. The analyses of samples were performed using a Varian 3800 gas chromatograph equipped with an FID detector and a capillary column.

## RESULTS AND DISCUSSION

### Effect of Feed Methanol Concentration

The methanol flux and pervaporation selectivity values are presented as functions of methanol concentration in the feed in Figures 2 and 3. As observed, a rise in methanol concentration from 1 to 10 wt.% in a pressure range of 3-20 mmHg, causes a considerable increase in methanol flux, for example, from 51 to 670  $g/hr.m^2$  at 3 mmHg, while separation factor (membrane selectivity to methanol) decreases from 254 to 108 at the same pressure. Feed composition influences the pervaporation performance of a membrane by varying the membrane microstructure, which in turn results in different sorption and diffusion behaviors. Because of a strong interaction between methanol and the membrane, by increasing methanol concentration in the feed, the membrane becomes more swollen. As a result, polymer chains become more flexible and there will be more free volume leading to higher methanol flux [7]. In addition, decreasing separation factor by increasing feed methanol concentration due to the interaction forces of permeating molecules increases the concentration of MTBE molecules compared with methanol in permeate [13].

In any events, as observed in Figures 2-3, within this concentration range, pressure variations in the range of 3-10 mmHg are more effective on flux and selectivity, and thus on membrane performance, than the corresponding variations in the range of 10-20 mmHg.

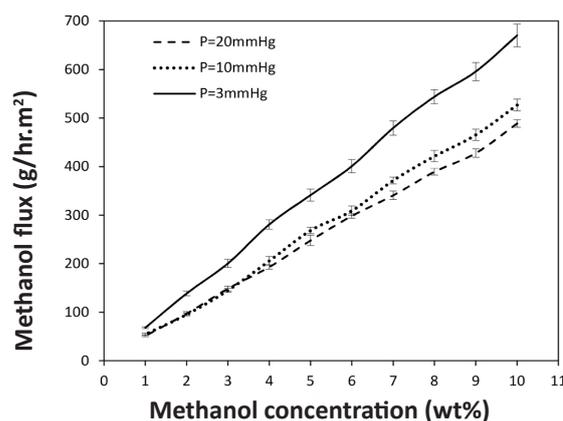


Figure 2: Methanol flux as a function of methanol concentration in the feed (MTBE-methanol mixture) (Temperature: 45°C, Feed flow rate: 1200 mL/min).

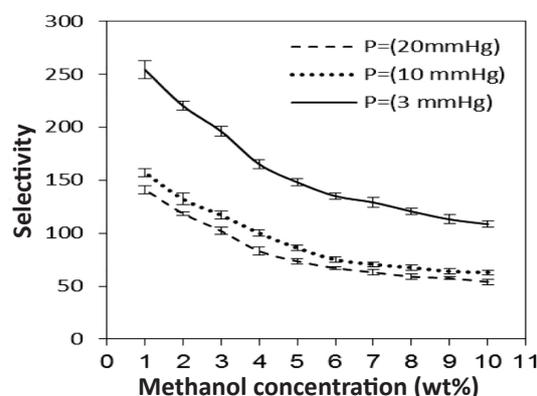


Figure 3: Selectivity as a function of methanol concentration in the feed (MTBE-methanol mixture) (Temperature: 45°C, Feed flow rate: 1200 mL/min).

### EFFECT OF PERMEATE PRESSURE

Figure 4 shows the effect of permeate pressure on methanol flux at 45 °C and at feed compositions of 1 and 5 wt.% of methanol. By lowering permeate pressure, flux remarkably increases. The main contribution to the driving force is the activity gradient of the components in the membrane. Since the permeate pressure is directly related

to the activity of the components at the permeate side of the membrane, the permeate pressure has a strong influence on the pervaporation performance. Reducing permeate pressure increases the driving force on the diffusing molecules in the membrane and will result in the component being swept out rapidly from downstream side and consequently in higher permeate flux [14].

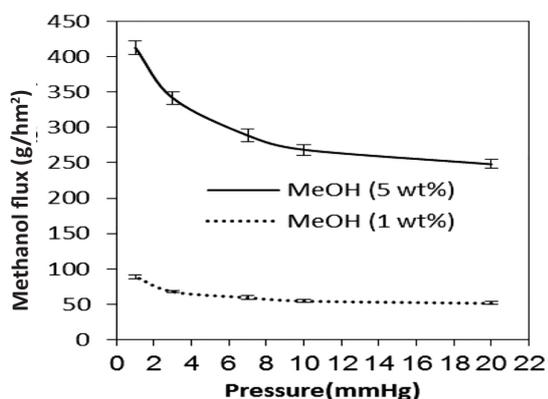


Figure 4: Effect of permeate pressure on methanol flux (Temperature: 45°C, Feed flow rate: 1200 mL/min).

In addition, as shown in Figure 5, the separation factor considerably drops at higher permeate pressures, especially at permeate pressures of over 10 mmHg. In fact, diffusion through the membrane is a rate-determining step at reduced pressures in PV. The selectivity of the membrane to methanol indicates the larger driving force and desorption rate of methanol molecules compared with MTBE. Increasing permeate pressure lowers the driving force and results in slowing down the desorption rates of the sorbed molecules. In this case, vapor pressures of the two components of the feed mixture govern the membrane selectivity [15]. Therefore, as shown in Figure 5, since methyl tertiary butyl ether has a higher vapor pressure compared with methanol, increasing pressure reduces membrane selectivity to methanol.

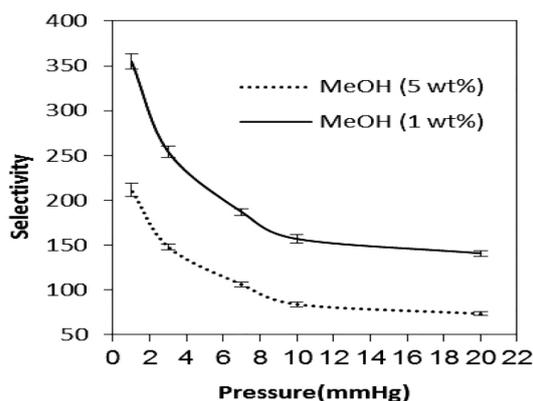


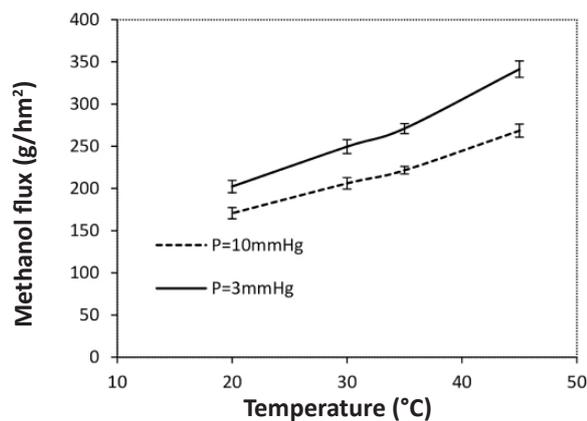
Figure 5: Effect of permeate pressure on membrane selectivity (Temperature: 45°C, Feed flow rate: 1200 mL/min).

The considerable point is the remarkable changes in flux and selectivity in pressures below 10 mmHg, especially those below 5 mmHg. Peivasti et al. [12] have investigated the effect of permeate pressure on the selectivity and flux of PVA membrane in the pressure range of 15-35 mbar in the separation of 10-30 wt.% methanol-MTBE mixtures. The results indicate slight changes in the membrane performance under conditions such as this pressure range, and the greatest variations occur in selectivity and flux from 52 to 60 and 650 to 680 g/h m<sup>2</sup> respectively. However, as Figures 4-5 show, pressure change from 10 to 1 mmHg strongly affects flux and selectivity, thereby improving membrane performance more effectively.

### Effect of Feed Temperature

The effects of the operating temperature ranging from 20 to 45 °C on the permeation flux and separation factor are presented in Figures 6-7. It is evident that permeation flux increases, while the separation factor decreases when the temperature rises. Mass fluxes through the membrane are highly dependent on temperature. They increase exponentially according to empirical Arrhenius law [16]. This may result from the rise in diffusion coefficient of the solute as the temperature increases. According to solution-diffusion

mechanism, increased temperature causes the solubility on the surface of membrane and diffusion rate in the membrane to increase. Furthermore, the increase of temperature produces a higher vapor pressure of the permeating components on the feed side of membrane, while the pressure on the downstream side remains unchanged. This situation enhances the driving force, leading to a rise in permeation flux.

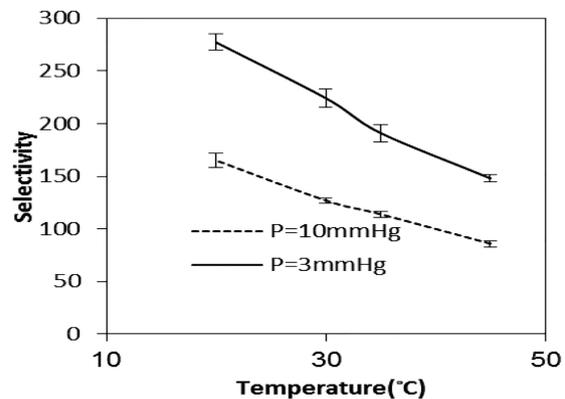


**Figure 6: Effect of feed temperature on methanol flux (Feed methanol concentration: 5 wt.%, Feed flow rate: 1200 mL/min).**

Additionally, decreasing membrane selectivity to methanol by increasing temperature shows that this parameter affects the diffusion of MTBE molecules into membrane more in comparison with methanol molecules. In other words, the transport of MTBE molecules through the membrane is more sensitive to the operating temperature and becomes easier at higher temperatures. Therefore, the separation factor decreases at an increased temperature.

However, as the results show, the reduction of pressure below 10 mmHg within a wide temperature range considerably improves membrane performance (as previously observed for concentration in the effect of feed methanol concentration), thereby reducing the required membrane area. Thus, given that the membrane is usually the most expensive component in the PV process, PV separation should be run at low permeate pressures in order to minimize the

membrane area. As a result, considering the high expense of the process at low pressures, the selection of optimal conditions requires mass, energy, and equipment cost calculation [17].



**Figure 7: Effect of feed temperature on membrane selectivity (Feed methanol concentration: 5 wt.%, Feed flow rate: 1200 mL/min).**

## CONCLUSIONS

Increasing methanol concentration in the feed enhances membrane swelling, which results in a rise in flux, but a reduction in selectivity. Both flux and selectivity increase by reducing permeate pressure due to increased driving force and higher volatility of MTBE compared with methanol. In addition, increasing feed temperature causes the enlargement of free volume inside the membrane resulting in a considerably higher flux and a reduction in selectivity. Decreasing pressure effectively increases flux and selectivity in a wide temperature range anyway. Overall, by decreasing permeate pressure, the membrane performance improves for the separation of methanol-MTBE mixture resulting in a reduced membrane area, especially at permeate pressures of less than 5 mmHg. Low permeate pressures mean high energy consumption; consequently, the key step in running a PV system is the determination of the optimum pressure to establish a balance between membrane area and required energy consumption to achieve the minimum expenses for the scale up

of the pervaporation system.

The experimental data obtained in this work can be used to obtain simulation equations, which will be useful in the simulations leading to the design of a scale-up unit. Obtaining supplementary data together with mass, energy, and equipment cost in order to calculate the total separation cost are the future objectives of this group.

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