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# Effects of Permeate Pressure and Feed Flow Rate on Benzene Dehydration by Pervaporation

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## ABSTRACT

Membrane-based pervaporation (PV) has attracted much attention in the dehydration of organic solvents. Permeate pressure and feed flow rate are two important parameters, which affect membrane performance in pervaporation. The effects of these two parameters on the performance of a commercial poly (vinyl alcohol) membrane in the dehydration of benzene have been investigated in this work. The experiments have been carried out at a constant temperature of 60°C, and pressure and feed flow rate range from 1 to 20 mmHg and from 200 to 1200 ml/min respectively. The results indicate that variations in vacuum, especially in permeate pressures of less than 10 mmHg, greatly affect flux and selectivity so that water flux and separation factor increase from 0.98 to 2.63 (gr/hm$^2$) and from 160 to 310 respectively by decreasing permeate pressure from 10 to 1 mmHg. Furthermore, increasing flow rate improves membrane performance only at rates of below 1000 ml/min, and no changes are observed at higher feed flow rates.

**Keywords**: Pervaporation, Dehydration, Permeate Pressure, Benzene, Feed Flow Rate

## INTRODUCTION

Benzene is widely used as a solvent and raw material. Some industries use benzene to make other chemicals, which are used to make plastics, resins, nylon, and synthetic fibers. Benzene is also used to make some types of rubbers, lubricants, dyes, detergents, drugs, and pesticides [1]. However, during the application of benzene in chemical processing industries, it is often necessary to remove water from it in order to avoid the deactivation of the catalyst and/or corrosion of equipment. For example, in the production of long, straight chain alkyl benzene, the water content of benzene must be lower than 20 ppm for either hydrogen fluoride or crystalline silica aluminate as catalysts [2]. Distillation and adsorption are the traditional processes for the dehydration of hydrocarbon liquids [3]. However, distillation suffers from complexity, and there are drawbacks associated with adsorption including high energy consumption due to the regeneration of adsorbent. Membrane-based pervaporation technique is considered a promising alternative for conventional energy intensive technologies, given the economical and safety aspects as well as the simplicity of setting up and operation [4]. In this process, a liquid stream containing two or more components is placed in contact with one side of a dense membrane

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(upstream) and the permeated product is removed as a vapor from the other side (downstream) by applying low pressure. The difference in vapor pressure between the feed liquid and permeate vapor is the driving force for the process. The separation of the mixture takes place as a result of the different rates of sorption and diffusion of the feed components through the membrane [5]. The dehydration of solvents has been considered a common application of PV. Although the dehydration of solvents such as dioxane and acetone using PV has been investigated over the past few years [6-7]; alcohols, especially ethanol and isopropanol, have been more extensively studied in this regard [8-9]. Hydrophilic polymers are selected as membrane materials in the dehydration of various solvents by PV because polar water molecule is easily sorbed by such membranes [10]. Such membranes as polybenzimidazole and polyimide membranes have recently been modified by various techniques to improve their performance [11-12]. The improvement in hydrophilic characteristics of membranes using nano compounds has also been of great interest in recent years [13]. Among aromatic compounds, the dehydration of benzene using pervaporation has been focused on. Yu Lixin et al. have used PVA hydrophilic membrane in benzene dehydration at a temperature of 70°C and a pressure of 800 Pa [14]. In addition, Gutch et al. have used aromatic polyamide membranes for the same purpose [15]. Li et al. have studied benzene dehydration in laboratory and pilot scales using modified hydrophilic membranes in 2002 [16]. The work has been carried out at a constant temperature and pressure and the effects of parameters such as pressure and feed flow rate have not been considered. Therefore, it seemed necessary to study the effects of these parameters on the optimization of the PV process. Although the investigations have been performed on toluene dehydration [17], the difference in the polarity and molecular structure of benzene and toluene causes different interactions with the membrane and thus different membrane selectivity toward these two molecules. In the present work, the influence of feed flow rate and pressure on the performance of a hydrophilic poly (vinyl alcohol) membrane in benzene dehydration using the pervaporation method has been investigated.

## EXPERIMENTAL PROCEDURES

The schematic diagram of the experimental apparatus is shown in Figure 1.

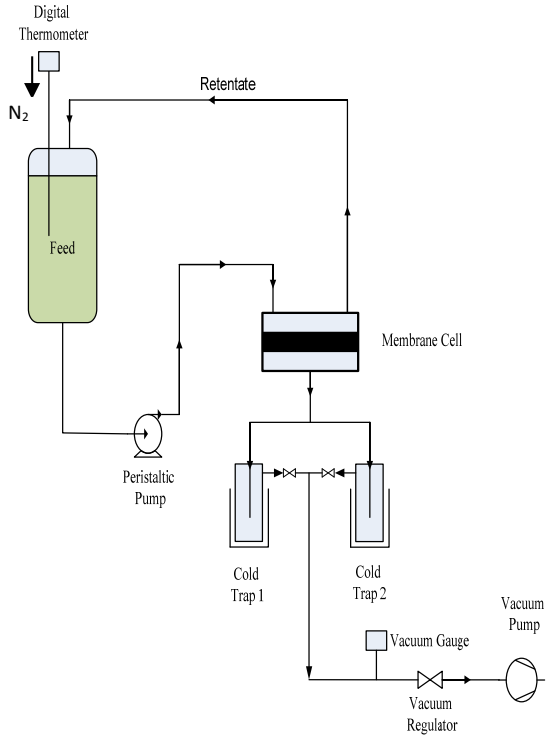


**Figure 1: A schematic diagram of experimental apparatus.**

The membrane used was supported on a porous stainless steel disc with an effective membrane area of 177 $cm^2$ embedded in a stainless steel plate and frame module from Sulzer Chemtech. In all the experiments, the membranes of Sulzer Chemtech were used (Pervap 2201). The membrane was a composite one with a top layer of PVA (thickness=2 μm) on a polyacrylonitrile (PAN) porous support (thickness=80 μm). Benzene used in these experiments was provided by Isfahan Petrochemical Complex and contained 150 ppm of water. Before starting each PV experiment, the test membrane was equilibrated for about 3 hr with feed solutions.

In the pervaporation experiments, the feed (benzene) was circulated over the membrane using a peristaltic pump (Heidolph, model PD5206). The volume of feed tank was 7 lit., which was very big compared with the permeation volume. Therefore, the variation of the feed concentration during the experimental period was negligible. All the experiments were performed at a constant temperature (60°C) and a permeate pressure of 1-20 mmHg obtained using a model BS2212 Edward vacuum pump. A temperature probe attached to the feed tank was used to monitor the temperature during each run. The feed flow rate was changed using a feed pump from 200 to 1200 ml/min. Feed flow rates for the experiments concerning permeate pressure were fixed at 1.1 lit/min. The permeate was condensed and collected in cold traps made of Pyrex glass (height: 30 cm, diameter: 4 cm), immersed in liquid nitrogen. The PV experiments were repeated three times to check for repeatability, expressed as relative standard deviation and ranged between 2.2 and 4.3%. Permeate fluxes (gr/hr.m$^2$) were calculated by weighing the permeate obtained during a certain period of time using Equation 1:

$$J = \frac{Q}{A.t} \quad (1)$$

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

$$\alpha = \frac{Y_W / Y_B}{X_W / X_B} \quad (2)$$

where α is the separation factor, and $X$ and $Y$ are the mass fractions of the feed and permeate respectively. Subscripts $W$ and $B$ stand for water and benzene respectively. All the experiments were carried out in an $N_2$ atmosphere in order to prevent moisture from entering the system. The water content in the samples was determined by Karl Fisher method.

## RESULTS AND DISCUSSION

Permeate pressure and feed flow rate are two of the most important operating parameters, which influence the membrane performance significantly. Because of this, for the optimization of PV processes, it is necessary to study the effect of these process parameters.

### Permeate Pressure Effect

Figure 2 shows the effect of the permeate pressure on the water flux at 60°C and a feed flow rate of 1100 ml/min. As shown, by varying permeate pressure from 1 to 20 mmHg, the membrane exhibits a considerable decrease in water flux from 2.6 to 0.8 (gr/hr.m$^2$).

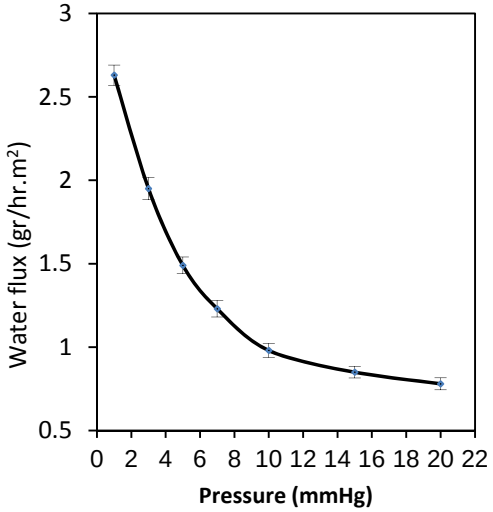


**Figure 2: Effect of permeate pressure on water flux (temperature: 60°C, feed flow rate: 1100 ml/min).**

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. In pervaporation processes, the driving force is provided by the vapor pressure difference between the feed and permeate sides of the membrane. Reducing permeate pressure leads to increased driving force and consequently enhances total flux. Increasing the permeate

pressure decreases the diving force and thus reduces permeation rate because the maximum diving force is obtained at zero permeate pressure. This was also mathematically described and experimentally confirmed [18]. In addition, according to Fick's law, increasing permeate pressure (lower vacuum) increases the activities of both permeates dissolved in the downstream layer of the membrane. Therefore, activity gradients across the thickness of the membrane decline and permeation flux drops [19]. Selectivity can be either increased or decreased by raising permeate pressure depending on the relative vapor pressure of the permeating components [20]. As shown in Figure 3, selectivity decreases by increasing permeate pressure. Diffusion through the membrane is a rate-determining step at reduced pressure in PV. The diffusing water molecules will thus experience a larger driving force, which would enhance the desorption rate at the downstream side of the membrane. The driving force, however, decreases by lowering vacuum (high pressure), thus lowering 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. Benzene, which has a higher vapor pressure, permeates competitively with water, and thus the concentration of water in the permeate reduces. A considerable point is that pressure variations at ranges below 10 mmHg influence the variables affecting membrane performance more greatly. Reducing pressure, especially below 3 mmHg, remarkably increases water flux and membrane selectivity to water, and it hence improves membrane performance in the dehydration of benzene by pervaporation.

## Feed Flow Rate Effect

The variations in permeation flux with respect to the feed flow rate are shown in Figure 4. The results show that flux increases with increasing feed flow rate.

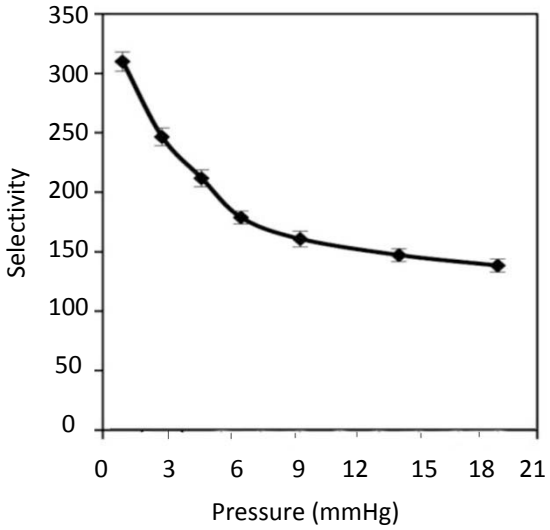


**Figure 3: Effect of permeate pressure on selectivity (temperature: 60°C, feed flow rate: 1100 ml/min).**

This can be related to the diminishing of concentration polarization effect. In benzene dehydration using PV, since water molecules penetrate more quickly into the membrane, benzene concentration in the membrane boundary increases compared with that in the bulk phase of the membrane. This concentration gradient between the more concentrated boundary solution and less concentrated bulk is termed as "concentration polarization" [21].

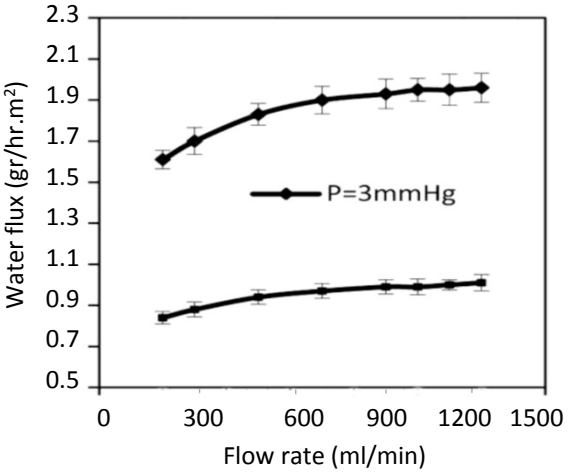


**Figure 4: Effect of Feed flow rate on water flux (temperature: 60°C).**

The concentration polarization is directly related to the thickness of boundary layer, which is of importance to the separation efficiency and may result in decreasing the process performance.

With increasing flow rates, the thickness of boundary layer remarkably decreases. This situation causes mass transfer resistance of the boundary layer on the upstream of membrane to decrease, which in turn leads to increased permeation flux.

The effect of feed flow rate on the boundary layer has been schematically shown in Figure 5 [22].

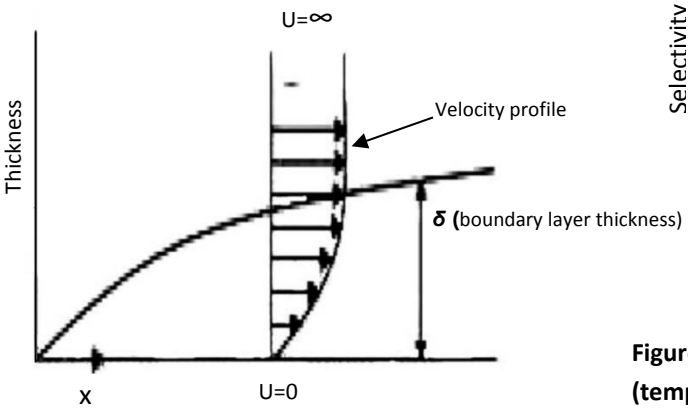


**Figure 5: Effect of feed velocity on boundary layer thickness.**

Furthermore, the permeating constituents need some energy to transfer into vapor phase and this is provided by the feed. This decreases feed temperature around the membrane (temperature polarization). Increasing feed flow rate diminishes temperature polarization effect and therefore increases total flux [23]. A reduction of temperature polarization means that the temperature difference between the membrane surface and bulk phase has decreased. Figure 6 shows the effect of feed flow rate on selectivity at 60°C and a permeate pressure of 3 and 10 mmHg. As observed, by increasing feed flow rate, membrane selectivity increases. In fact, increasing flow rate causes water concentration near membrane boundary phase to get close to that in the bulk phase, leading to the increased penetration of water molecules, and thereby enhancing membrane selectivity toward water. However, as the results indicate, the variations in flow rate affect membrane performance only at flow rates below 1000 ml/min and increasing flow rate beyond 1000 ml/min does not appreciably change flux and selectivity. Therefore, at higher flow rates, the effect of concentration polarization becomes very small or insignificant due to the close concentrations of components in the membrane boundary and bulk phases.

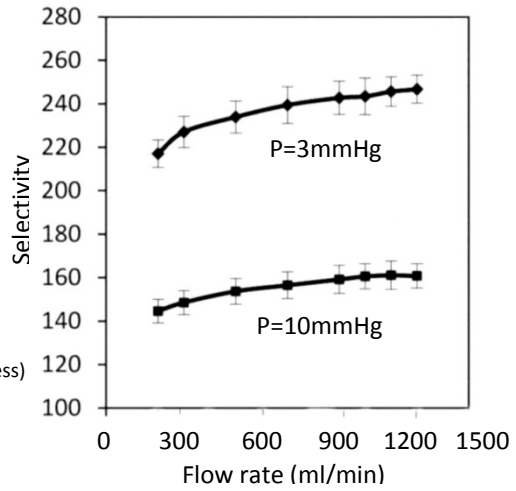


**Figure 6: Effect of feed flow rate on selectivity (temperature: 60°C).**

## CONCLUSIONS

The PVA membrane used here is selective to water compared to benzene and its performance is highly affected by permeate pressure and feed flow rate. Decreased pressure (increasing vacuum) and increased feed flow rate lead to increased water flux and membrane selectivity toward water and thus increased membrane performance in the dehydration of benzene using PV. However, increased feed flow rate in the ranges below 1000 ml/min affects membrane performance, especially at low pressures (3 mmHg). This observation shows that besides a membrane resistance, an additional resistance, originally from the boundary layer at the membrane interface, dominates the pervaporation performance in the process at lower feed flow rates. In addition, the results indicate that pressure variations affect membrane performance much more considerably compared with feed flow rate, and reduced pressure causes flux and selectivity to increase greatly. However, the process at low pressures is highly expensive and the selection of optimal conditions requires more work. Obtaining

supplementary data together with mass, energy, and equipment cost calculation in order to optimize conditions are the objectives of future works.

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