

## PERVAPORATION OF ETHANOL/WATER MIXTURE USING POLYMERIC MEMBRANE

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Pervaporation is the selective evaporation and separation of one component of liquid stream by membrane, which is in direct contact with liquid mixture. This makes pervaporation more energy efficient process. For this study pervaporation apparatus was designed and developed in line with criteria presented in the literature on the subject. Polymeric membrane obtained from Shanghai Megavision, China was used in the membrane cell. The membrane unit can also be used for reverse osmosis, gas separation, ultra and nano filtration by simply replacing membrane with other membrane compatible for the selected process. Experiments were performed to separate water from amixture of water/ ethanol. Change in concentration of retentate (feed stream going back to feed tank from membrane cell) with time at different temperatures 60°C, 70°C and 80°C was observed. Moreover, effect of temperature on flux was also studied.

**Keywords** : Polymeric membrane, Pervaporation

### 1. Introduction

Ethanol is commonly produced by fermentation processes, wherein the ethanol product is found in a water mixture. The production of fuel-grade ethanol requires that the fermentation product is to be dried beyond the azeotrope. The usual drying process of distillation requires a significant amount of energy. Therefore, it is desirable to separate ethanol from fermentation beers by a more economical method, such as by membrane separation, pervaporation process [1].

Pervaporation is a membrane process for liquid separation [2,3], a polymeric or zeolite membrane [4–6] usually serves the separating barrier for the process. When a membrane is in contact with a liquid mixture, one of the components can be preferentially removed from the mixture due to its higher affinity with, and/or quicker diffusivity in the membrane. As a result, both the more permeable species in the permeate, and the less permeable species in the feed, can be concentrated. In order to ensure the continuous mass transport, very low absolute pressures are usually maintained at the downstream side of the membrane, removing all the molecules migrating to the face, and thus rendering a concentration difference across the membrane. As a variant, the use of a sweeping gas [7,8] in the downstream side of the membrane

is also a feasible alternative for the generally used vacuum operation. It is well known that the phase change from liquid to vapor takes place in pervaporation. Processes involving phase changes are generally energy-intensive, and distillation is a notorious example of them. Pervaporation cleverly survives the challenge of phase change by two features. (1) Pervaporation deals only with the minor components (usually less than 10 wt.%) of the liquid mixtures, and (2) pervaporation uses the most selective membranes. The first feature effectively reduces the energy consumption of the pervaporation process. Compared with the distillation, because of the characteristics of pervaporation operation, it is essentially true that only the minor component in the feed consumes the latent heat. The second feature generally allows pervaporation the most efficient liquid-separating technology.

In the case of separation of isopropanol/water mixtures, the water content in the feed is 10 wt.%, the maximum single plate separation factor (isopropanol to water) in distillation is about 2, however, a pervaporation membrane can normally offer an one-through separation factor (water over isopropanol) of 2000–10,000 [9–11]. Furthermore, combination of these two features ranks pervaporation the most cost-effective liquid separation technology [12,13]. In addition,

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pervaporation also demonstrates incomparable advantages in separating heat sensitive, close-boiling, and azeotropic mixtures [14–17] due to its mild operating conditions, no emission to the environment, and no involvement of additional species into the feed stream. More recently, the hybrid processes [13,18–20] integrating pervaporation with other viable liquid-separating technologies, and processes are gaining momentum. With these developments, we have more reasons to believe that pervaporation will play even more important roles in the future.

To date, pervaporation has found viable applications [21] in the following three areas: (i) dehydration of organic solvents (e.g., alcohols, ethers, esters, acids); (ii) removal of dilute organic compounds from aqueous streams (e.g., removal of volatile organic compounds, recovery of aroma, and biofuels from fermentation broth); (iii) organic–organic mixtures separation (e.g., methyl *tert*-butyl ether (MTBE)/methanol, dimethyl carbonate (DMC)/methanol). Among them, dehydration of organic solvents is best developed.

The membranes used in pervaporation processes are classified according to the nature of the separation being performed. Hydrophilic membranes are used to remove water from organic solutions. These types of membranes are typical made of polymers with glass transition temperatures above room temperatures. Polyvinyl alcohol is an example of a hydrophilic membrane material. Organophilic membranes are used to recover organics from solutions. These membranes are typically made up of elastomer materials (polymers with glass transition temperatures below room temperature). The flexible nature of these polymers make them ideal for allowing organic to pass through. Examples include nitrile, butadiene rubber, and styreneButadiene rubber[22].

The following sections cover the transport mechanism in polymeric membranes, development of pervaporation apparatus and membrane cell design, experimental work, results and discussion and conclusion drawn from the study

## 2. Transport Mechanism in Polymeric Membranes

Graham first proposed “Solution diffusion theory” [23] based on his extensive research on

gas permeation through homogeneous membranes. It is held that gas permeation through a homogeneous membrane consists of three fundamental processes :

1. Solution of gas molecules in the upstream surface of the membrane.
2. Diffusion of the dissolved species across the membrane matrix.
3. Desorption of the dissolved species in the downstream face of the membrane.

These three fundamental processes also govern the mass transport across pervaporation membranes [24]. Membrane transport is a rate-controlling process, which is generally governed by the Fick’s first law [23]:

$$N = -D \frac{dC_m}{d\delta} \quad (1)$$

Where  $N$  is the permeation flux of a species through the membrane,  $D$  the diffusion coefficient of the species in the membrane, and  $\delta$  is the position variable. By introducing the partition coefficient  $K$  of the species at the membrane/feed, and membrane/ permeate interface, the concentrations of a species in the faces of the membrane can be expressed in its concentrations in the feed and the permeate, respectively, and the Fick’s first law thus becomes:

$$N = -DK \frac{\Delta C}{\delta} = \frac{DK}{\delta} \Delta C \quad (2)$$

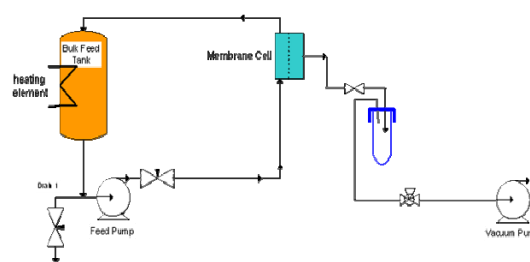


Figure 1. PFD of Apparatus for the Pervaporation process.

The ideal separation factor of a membrane for species  $i$  and  $j$  can thus be defined as:

$$\alpha_j^i = \frac{P_i}{P_j} = \frac{D_i K_i}{D_{jj} K_j} = (\alpha_j^i)_D (\alpha_j^i)_K \quad (3)$$

Research efforts in pervaporation were thus devoted to seeking the right membrane materials to maximize the differences in these parameters

(diffusion coefficient  $D$ , partition coefficient  $K$ , and thus permeability  $P$ ) so that the desired separation can be carried out in an efficient manner. Experimentally, the permeation flux, and the separation factor can be obtained, respectively by:

$$N = \frac{Q}{A\Delta t} \quad (4)$$

$$(\alpha_j^i)^{\text{Permselectivity}} = \frac{Y_i/Y_j}{X_i/X_j} \quad (5)$$

where  $Q$  is the quantity (in gram or moel) of the permeate collected in a time interval “ $t$ ”,  $A$  is the membrane area used for the test, and  $X$ , and  $Y$  represent the fractions of the components in the feed and the permeate, respectively.

### 3. Apparatus and Methods

Pervaporation apparatus having the capacity to handle 2 liters of ethanol/water feed with purity achievable more than 99% ethanol was developed according to PFD (Process flow diagram) given in Figure 1. The Pervaporation apparatus consists of a 2.5 liters feed tank with heating arrangement, circulation centrifugal pump, K-type thermocouple with temperature controller, pressure gauge needle valves. All aggregates are assembled ready for operation on a mild steel structure. The membrane laboratory unit can be equipped with different type of membrane t est cells and modules as available.



Pervaporation Rig Comprising Membrane Cell Fabricated and Assembled as part of MS Research Projects.

Figure 2. A snape shot of pervaporation rig.

The Pervaporation apparatus developed as shown in Fig. 2 on the basis of PFD as presented in Figure 3.

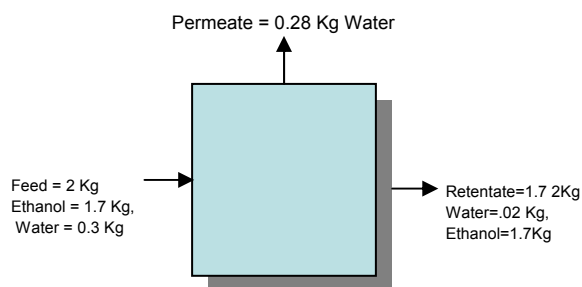


Figure 3. Material Balance on Membrane Cell. Table 1: Operating conditions.

Table 1. Operating conditions.

Feed (85% ethanol, 15% water )	2Kg
Density of feed, $\rho$ (25°C)	804 Kg/m <sup>3</sup>
Viscosity of feed, $\mu$ (25°C)	0.47 mNs/m <sup>2</sup>
Specific heat of feed	2.5 KJ/Kg-K
Velocity in pipe	2-3 m/s
Recommended Reynold number in membrane cell, $Re=\rho uD/\mu$	2000-5000
Recommended pressure on permeate side	10-100 m bar.

Using design conditions in Table 1, area of membrane cell can be calculated by flux equation given below

$$J_i = \frac{Q_i}{At} \quad (6)$$

where  $J_i$  is Flux of water (moles/hr-sq-m),  $Q_i$  is moles of water permeated in time  $t$  and  $A$  is effective membrane surface area. From literature at 15% water content, the flux is 2.1 Kg/hr-m<sup>2</sup> or 0.11 moles/hr-m<sup>2</sup> [1]. Area of membrane cell is estimated by using equation 6, for 1 hr operation , area required is  $0.015/0.117 = 0.12$  m<sup>2</sup>. Thus area required for 10 hrs is 0.012 m<sup>2</sup>

So we designed circular membrane cell having diameter 114.3 mm(4.5 inch.) and having area 0.0.1 m<sup>2</sup>. Water permeated in time  $t$  is 0.28 Kg.

#### 3.1. Membrane cell design

Membrane cell as shown in Figure 1 was fabricated with Stainless Steel SS-304. SS-304 is compatible with our operating conditions (operating temp. max. 90 °C, operating pressure max. 4bar.)

Membrane cell is divided into two compartments feed side and permeate side. A perforated Teflon disc is placed between two

compartments, which act as support. Polymeric membrane obtained from China is placed on this support. Then the membrane and support was bolted between two compartments.

### 3.2 Materials

The water and ethanol binary system was selected as the subject to investigate in this experiment. Commercial grade ethanol was used. The ethanol is a colorless liquid with characteristic odor and is highly flammable with a boiling point of 78°C at 1 atmosphere. It forms an azeotropic mixture with water weight concentration of 95%. It has a very good solubility in water and is fully miscible in water at ambient conditions. Polymeric membrane obtained from Shanghai Megavision, China was used in pervaporation experiments for dehydration of ethanol.

### 3.3 Pervaporation experiments

A water/ethanol binary mixture contains 0%-20% water in weight was used as the feed. The pervaporation experiments were conducted on pervaporation apparatus developed as shown in Figure 1. The flat sheet membranes were put into a stainless steel test cell with an inner diameter of 4.5 inch and the estimated surface area as 100 cm<sup>2</sup>. The water and ethanol solvent mixture (2 litre) was fed into the tank, which has a maximum volume of 2.5 liter, heated by a heating coil and re-circulated with a centrifugal pump. The flow rate was set to 10 liter/min. according to the unit specifications. The temperature was selected ranging from 60°C to 80°C and it can be adjusted by the temperature controller. The concentration change in feed and the water permeate flux were investigated at different temperatures to evaluate the membrane performance. On the permeate side, a vacuum was applied and the permeates were condensed to ensure complete collection of the permeates. Feed samples were collected for analysis in a fixed interval (normally one hour) after achieving stability of the system. The flux was determined by weighing the permeate sample mass divided by the product of sample time and the known membrane area. The separation factor  $\alpha$  is thus estimated by using its definition.

$$\alpha = \frac{Y_i / Y_j}{X_i / X_j} \quad (8)$$

Where Y and X are the weight fractions of components in the permeate and feed, respectively, and the subscripts i and j represent the two components in the binary system, respectively.

### 3.3 HPLC analysis

Sample of ethanol/water mixture was run in HPLC (instrument of Perkin Elmer equipped with C-18 column and UV detector). Two peaks were observed, larger peak at 1.3 minute retention time and smaller peak at 1.83 minute retention time, as sample was enriched in ethanol so larger peak at retention time 1.3 minute was of ethanol and smaller peak at retention time 1.83 minute was of water. Retention time of ethanol and water was confirmed by running distilled water. Single peak at retention time 1.83 minute appeared.

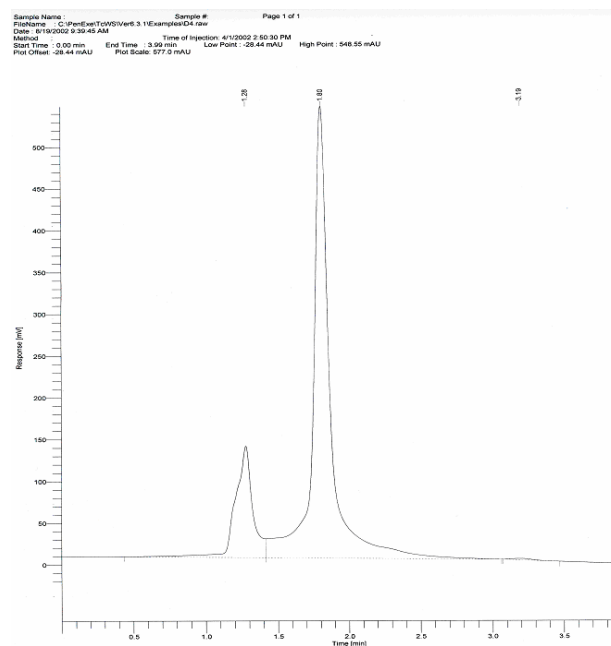


Figure 4. HPLC Analysis of Permeate

## 4. Results and Discussion

The membrane is marked for the dehydration of solvents. It is applied for operation in an environment of less than 100 °C and with feed water concentrations less than 20%. The water concentration in the retentate was monitored after stable time and the results are shown in Figure 6.

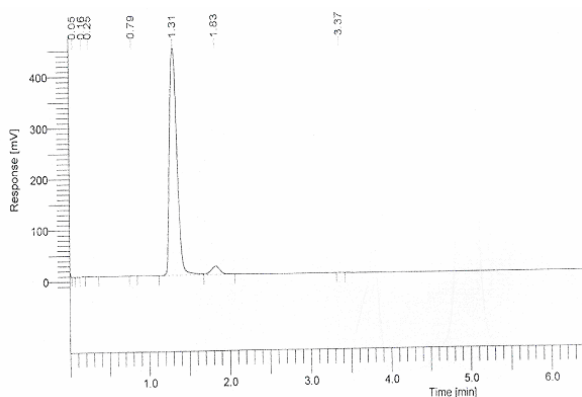


Figure 5. HPLC analysis of product.

The water concentration in the retentate was experiment time because of the permeate water being continuously removed during the experiment. Since the water flux at 80°C is quite high, the water concentration in the retentate decreases a lot after stabilized one hour as shown in Figure 6.

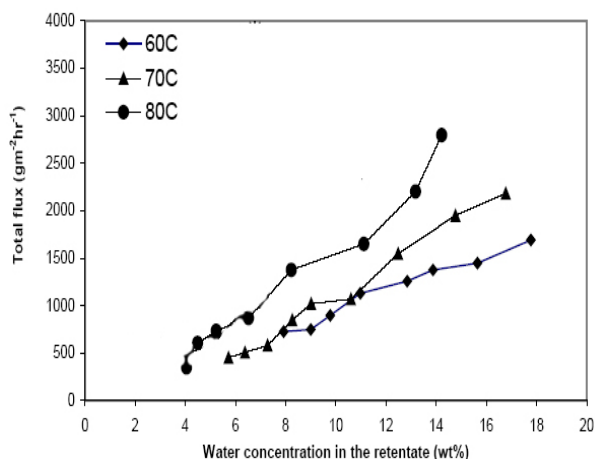


Figure 6. Water concentration in the retentate vs. time for the dehydration of a ethanol/water mixture with polymeric membrane.

The flux and concentration change in feed were monitored in the experiments and plotted as a function of water concentration in the retentate at different temperatures. The results are shown in the Figures 6 and 7 individually. It can be observed that the flux increases with increasing water concentration in the retentate. These phenomena can be explained by the interaction between the polymer molecules and permeates. Membrane used is hydrophilic membrane, which normally has a relatively high polarity groups that have a strong

interaction with water by hydrogen bonding. As the water concentration is higher, more water molecules interact with membrane molecules and this causes the membrane to become more swollen. Therefore, the permeate molecules are able to pass through the membrane more easily and the permeate flux increases.

According to Figure 7, as the experimental temperature increases, the slope of the increasing total flux curve becomes sharper as well. It can be explained by both the free volume theory and temperature-dependent diffusion process. The randomly thermal motion of polymer chains in the amorphous regions produces the free volume. As the temperature increases, the thermal motion of polymer chain becomes more violent, thus leading to the larger free volume of the membrane. In addition, the increasing thermal motion of the permeate molecules contributes to their diffusing more quickly through the larger free volume of the membrane. As a result of all the effects mentioned above, the permeate flux increases sharply with increasing temperature.

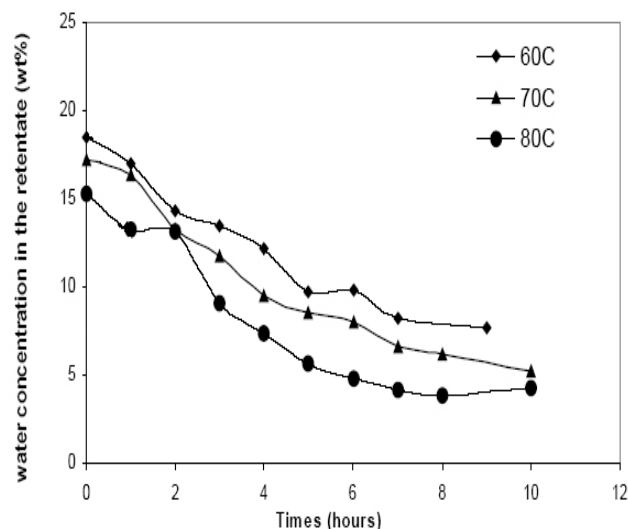


Figure 7. Total flux vs. water concentration in the retentate for the ethanol/water mixture Polymeric membrane

The effect of concentration and temperature on both the total flux across the polymeric membrane and the change in feed concentration are illustrated in Fig. 7. The total flux increases with an increase in water concentration. This may arise from the fact that increasing water concentration also causes the membrane further swelling, thus



resulting in a higher flux . Moreover, the flux and change in feed concentration appear to have the same uprising trend as the temperature goes up. elsewhere , The membrane have a lower flux and concentration change at the same water concentration, which may probably be attributed to the different cross link component of the active layer, different support layer, dense layer thickness and the morphology discrepancy of this membrane.

## 5. Conclusions

Experiments performed on designed pervaporation apparatus gave promising and encouraging results. Study shows that separation and flux is better at 80°C than at 70°C and 60°C, means that with rise in temperature, flux and separation considerably increases. Dehydration of ethanol using polymeric membrane obtained from Shangai Megavision China, successfully performed. The pervaporation process is very simple, energy efficient and environment friendly. Ethanol fuel is also environment friendly. Pervaporation apparatus can easily scaled up and fuel grade ethanol can be produced from low grade ethanol , abundantly available in Pakistan, from sugar industry.

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