

## Pervaporation Separation of Ethanol-Water Mixtures Using Nylon 4 and Its Blended Membranes

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나일론 4와 이의 블렌드 막을 이용한 에탄올-물 혼합물의 투과 증발분리

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**Abstract:** The application of the pervaporation process in biotechnology is rapidly growing. A two stage pervaporation process can be applied to the downstream processing of ethanol fermentation. In this paper, the second stage process in which the water-ethanol composition was 50:50 wt.% was investigated in more detail by using Nylon 4 and its blended membranes containing poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA). Nylon 4 membranes were tested for compositions at 25, 30, and 35 °C. Nylon 4 membranes had a separation factor of 4.18 with a permeability of 0.69 kg/m<sup>2</sup> hr at water-ethanol composition of 50:50 wt.%, while nylon 4-PVA blended membranes crosslinked by 5 Mrad gamma-ray irradiation showed a higher separation factor of 10.56 with permeability 0.55 kg/m<sup>2</sup>hr at the same composition. Nylon 4 also showed a high separation factor 27.8 at the ethanol-water azeotropic composition among the homopolymer membranes.

**요 약:** 생물공학에의 투과증발공정의 응용은 성장 중에 있다. 2단계 투과증발공정이 에탄올 발효의 분리공정에 적용되어질 수 있다. 본 논문에서는 물-에탄올의 조성이 50 : 50wt.%가 되는 두번째 투과분리공정을 나일론 4와 폴리비닐알코올 및 폴리아크릴산을 포함하는 나일론 4블렌드 막을 이용하여 조사하였다. 나일론 4막은 25, 30, 35°C에서 에탄올의 조성 변화에 따라 실험이 수행되어졌다. 나일론 4막은 물-에탄올 조성이 50 : 50wt.%에 대해 선택도 4.18 그리고 투과도 0.69kg/m<sup>2</sup>hr을 얻은 반면에 5Mrad의 감마선에 의해 가교된 나일론 4-PVA 블렌드 막은 선택도 10.56, 투과도 0.55kg/m<sup>2</sup>hr을 얻었다. 또한 나일론 4 막은 물-에탄올 혼합물의 공비점에서 호모폴리머 중 27.8의 높은 선택도를 얻을 수 있었다.

### 1. Introduction

The dependence on traditional petrochemical energy resources for meeting the world's chemical and energy needs will lead to worldwide energy shortages in the future. This situation has accelerated in-

terest in the production of organic solvents from biomass to be used as a fuel or chemical feedstock. The traditional separation techniques, such as, distillation, adsorption, and liquid-liquid extraction, etc., are still responsible for the greatest part of the energy costs.

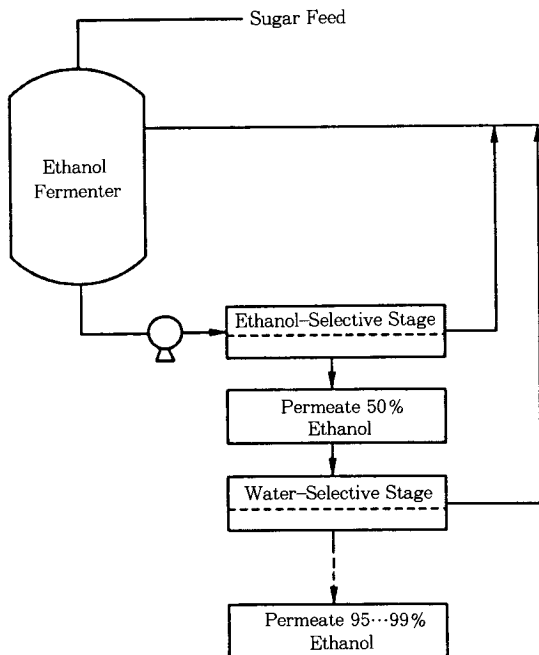


Fig. 1. Schematic diagram of the coupled fermentation.

Soukop[1] presented the economic analysis for a pervaporation plant with a daily production of 6,000 L of pure ethanol. The cost of a combined pervaporation-distillation plant is 2-3 times lower than that of a traditional plant, while the running costs are reduced by a factor of 1.5-2.5. Membrane applications in biotechnology can be regarded as an economical alternative, since the biomass and the nutrients can be reduced and the product inhibition problem can be reduced under the continuous operation.

In principle, a two stage pervaporation process can be applied for the concentration of ethanol from the fermentation broth. Gudernatch et al.[2] introduced the direct application of a pervaporation unit to a fermentation reactor by using poly(dimethylsiloxane) hollow fiber membranes. They showed that permeation rate was typically  $0.6\text{kg}/\text{m}^2\text{hr}$  and the separation factor reached up to 5.5 (e/w), which means that the ethanol concentration of permeate could be 50 wt.% because most of ethanol produced from fermentation contains 5 to 13 wt.%

ethanol.

Fig. 1 gives the process scheme of the coupled fermentation pervaporation unit with ethanol-selective membrane, such as, poly(dimethylsiloxane) (PDMS), in the first stage and water-selective membrane in the second stage. During the continuous operation, the produced ethanol can be concentrated in the first downstream, so that the product inhibition effect can be reduced and the cells are returned to the fermenter. Mulder et al.[3] have checked the selectivities of PDMS membrane for 5 wt.% ethanol in water with D-glucose and sodium chloride. PDMS membrane showed complete rejection of D-glucose and sodium chloride. As a result, ethanol can be purified up to 99% or more in the second stage.

In this paper, the second separation stage is investigated in more detail by using Nylon 4 and its blended membranes containing PVA and PAA. Nylon 4 membranes were also tested for the total range of compositions at 25, 30, and 35°C

## 2. Experimental

### 2. 1. Materials

Nylon 4 polymers were synthesized in our laboratory by the  $\text{CO}_2$ -initiated polymerization of 2-pyrrolidone using potassium 2-pyrrolidonate as the catalyst and the  $\text{CO}_2/\text{KOH}/18\text{-Crown-6}$  ether catalyst system[4]. The intrinsic viscosities of Nylon 4 used in this study varied from 2.23 to 6.07. Nylon 6 with molecular weight 42,000 and poly(acrylic acid) with molecular weight 150,000 (in 25 wt.% aqueous solution) were obtained from Polysciences Inc. Fully hydrolyzed poly(vinyl alcohol) of 72-60 grade was obtained from Du Pont. The solvents used in the present study were of analytical grade.

### 2. 2. Membrane preparation

#### 2. 2. 1. Nylon 4 membrane

The casting solution with 8 wt.% Nylon 4 polymer was prepared from 90% formic acid. The mem

brane was cast onto a clean glass plate using a Gardner knife with predetermined drawdown thickness. The membrane was predried for 5 min. at room temperature and was then heated in thermostatted oven for 1 hr. at 60°C and then cooled for 10 min. The formed film on a glass plate was soaked in deionized water for at least 24hr. The membrane was then peeled off and stored in deionized water for further use.

#### 2. 2. 2. Blended Nylon 4-PAA membrane

A 8wt.% Nylon 4 in 90 % formic acid and 10 wt.% aqueous solution of PAA were mixed together by varying each component composition to form a homogeneous solution. The membrane was then prepared following the same procedure as the case of Nylon 4. The prepared film was then crosslinked in a 10 wt.% aluminum nitrate crosslinking bath for 30 hrs., then immersed in deionized water for 24 hrs. with frequent water changes.

#### 2. 2. 3. Blended Nylon 4-PVA membrane

A 8wt.% Nylon 4 solution in 90% formic acid and a 8wt.% PVA solution in water were blended together with various compositions to form a homogeneous solution. Then the membranes was prepared following the same procedures of the above Nylon 4 membranes, gamma-ray irradiation technique was used for crosslinking. First, the formed Nylon 4-PVA blended film was immersed in an aqueous solution of 40 vol.% methanol and allowed to equilibrate for 24 hrs. Then nitrogen gas was bubbled through the solution to remove the dissolved oxygen. The bottle containing the solution and film was capped and irradiated at room temperature with dose ranges of 1-10 Mrad. The source employed was a Cobalt-60 Gamma-Cell 220 irradiation unit (Atomic Energy of Canada, Ltd.).

#### 2. 2. 4. Blended Nylon 4-Nylon 6 membrane

The casting solutions with 8wt.% Nylon 4 and Nylon 6 polymer, respectively, were prepared from

90% formic acid and then mixed together with various compositions to form a homogeneous solutions. The membrane was then cast onto a clean glass plate using a Gardner knife with predetermined drawdown thickness. The membrane was prepared following the same procedures of the above Nylon 4 membranes.

#### 2. 2. 5. Blended Nylon 6-PVA membrane

A 8wt.% Nylon 6 in 90% formic acid and a 8wt.% PVA solution in water were blended together with various compositions to form a homogeneous solution. Then the membrane was prepared following the same procedures of the above Nylon 4-PVA blended membranes.

#### 2. 2. 6. Apparatus and experimental procedure

Details about the permeation cell, the pervaporation apparatus and experimental procedure have been reported elsewhere [5]. The necessary vacuum in the downstream was maintained by a vented exhaust. The vacuum was measured by a Fisher, close end, Bennet type vacuum manometer in the vacuum line near the cell and was always kept below 2mmHg. The analysis of the permeate was done using a Anton-Paar DMA 60 digital densitometer.

### 3. Results and Discussion

In membrane material science, it is difficult to select a polymer which is suitable for separating polar-polar mixture systems, such as the water-ethanol mixture because of complex interactions between the membrane material and the feed mixture to be separated. The basic idea presented in this paper is that the water solubility for a given mixture could be increased by adding hydrophilic polymer, so that, as a result, the ethanol selectivity is decreased.

The separation factor,  $\alpha$ , calculated in the present work is defined as

$$\alpha = (Y_{\text{water}}/Y_{\text{ethanol}})/(X_{\text{water}}/X_{\text{ethanol}})$$

**Table 1.** Permeability and Selectivity of Nylon 4-Nylon 6 Blended Membranes<sup>a</sup>

Nylon 4-Nylon 6 Blending Ratio	25°C		30°C		35°C	
	$\alpha_{w/e}$	$p^b$	$\alpha_{w/e}$	P	$\alpha_{w/e}$	P
5:5	1.23	0.425	1.16	0.570	1.19	0.622
6:4	2.66	0.450	2.26	0.632	2.33	0.721
8:2	3.14	0.549	2.61	0.735	2.44	0.876
Nylon 4	4.18	0.687	2.85	0.760	2.33	0.964

<sup>a</sup> Feed mixture composition, 50 wt.% ethanol in water<sup>b</sup> Permeability, kg/m<sup>2</sup>hr**Table 2.** Permeability and Selectivity of Nylon 6-PVA Blended Membranes<sup>a</sup>

Nylon 6-PVA Blending Ratio	25°C		30°C		35°C	
	$\alpha_{w/e}$	$p^b$	$\alpha_{w/e}$	P	$\alpha_{w/e}$	P
9:1	2.02	0.37	2.21	0.45	2.07	0.62
8.5:1.5	4.11	0.19	3.84	0.46	3.71	0.61
8:2	3.25	0.22	2.51	0.48	2.45	0.70

<sup>a</sup> Feed mixture composition, 50 wt.% ethanol in water. $\gamma$ -ray dose, 1 Mrad.<sup>b</sup> Permeability, kg/m<sup>2</sup>hr

where  $Y_i$ 's are the weight fraction of permeates and  $X_i$ 's are those of the feeds, respectively.

First, Nylon 4-Nylon 6 blended membranes were tested by varying the polymer content of each. As can be seen in Table 1, the permeation rate and the separation factor increase with increasing Nylon 4 content as expected. Next we have tested the Nylon 6-PVA blended membranes. As shown in Table 2, the separation factors go up to 4.11 and then decrease with more hydrophilic polymer, PVA, content. This can be explained in terms of the hydrophilic/hydrophobic balance of the membranes, i.e., the Nylon 6-PVA membrane with the blending ratio of 8.5:1.5 has the best balance at 50:50 wt.% of water-ethanol mixture. The results shown in Table 1 and Table 2 are not good in terms of the separation efficiency, however, both of Nylon 4-Nylon 6 and Nylon 6-PVA blended membranes good examples which strongly support the hydrophilic/hydrophobic balance mentioned earlier.

**Table 3.** Permeability and Selectivity of Nylon 4-PAA Blended Membranes<sup>a</sup>

Nylon 4-Nylon 6 Blending Ratio	25°C		30°C		35°C	
	$\alpha_{w/e}$	$p^a$	$\alpha_{w/e}$	P	$\alpha_{w/e}$	P
Nylon 4	4.18	0.69	2.85	0.76	2.33	0.96
9:1	4.21	0.52	3.77	0.68	3.40	0.91
8:2	9.36	0.23	5.78	0.43	4.40	0.63

<sup>a</sup> Feed mixture composition, 50 wt.% ethanol in water<sup>b</sup> Permeability, kg/m<sup>2</sup>hr**Table 4.** Permeability and Selectivity of Nylon 4-PVA Blended Membranes<sup>a</sup>

Nylon 4-PVA Blending Ratio	25°C		30°C		35°C	
	$\alpha_{w/e}$	$p^b$	$\alpha_{w/e}$	P	$\alpha_{w/e}$	P
Nylon 4	4.18	0.69	2.85	0.76	2.33	0.96
9:1	4.06	0.87	3.58	1.04	2.88	1.30
8:2	4.50	0.81	3.94	0.92	3.23	1.03

<sup>a</sup> Feed mixture composition, 50 wt.% ethanol in water. $\gamma$ -ray dose, 1 Mrad.<sup>b</sup> Permeability, kg/m<sup>2</sup>hr**Table 5.** Effect of  $\gamma$ -Irradiation on Permeability and Selectivity of Nylon 4-PVA (8:2) Blended Membranes at 25°C<sup>a</sup>

Mrad	$\alpha_{w/e}$	$P^b$
1	4.50	0.81
2	5.48	0.78
5	10.56	0.55
10	5.64	0.84

<sup>a</sup> Feed mixture composition, 50 wt.% ethanol in water<sup>b</sup> Permeability, kg/m<sup>2</sup>hr

Table 3 shows the permeation rate and the separation efficiency of Nylon 4-PAA blended membranes. As can be seen, the separation factors increase with increasing PAA content. The wet technique[6] was chosen as the crosslinking method of PAA. A good quality membrane can be prepared from this technique because the presence of Nylon 4 in the membrane slows down the fast diffusion problem of metal ion into membrane during crosslinking. In this case 20 wt.% of PAA is the optimum content.

Table 4 shows the permeation rate and the selectivity of Nylon 4-PVA blended membranes. One

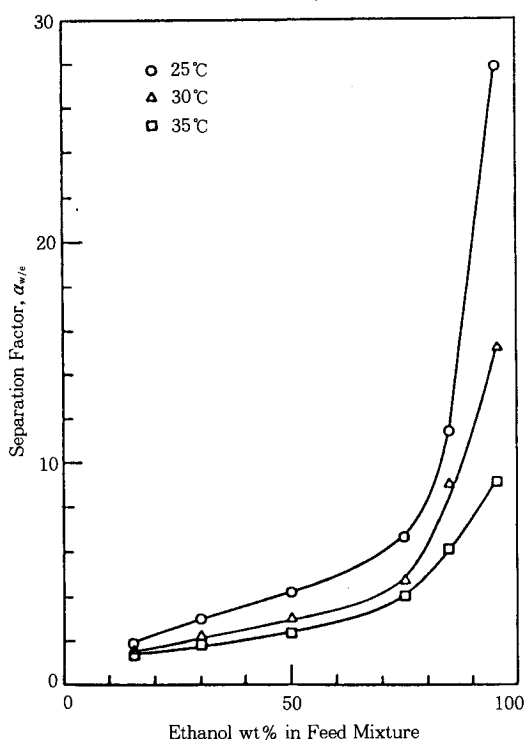


Fig. 2. Separation factor of Nylon 4 membrane.

can see that the separation factor does not increase much even though hydrophilic PVA polymer is added gradually. Therefore it was attempted to control the hydrophilic/hydrophobic balance of the membrane by changing the crosslinking degree. The control of the hydrophilic/hydrophobic balance could arise from the chemical and physical changes of the polymer, i.e., (i) changes of the chemical structure in the polymer; the resulting selectivity is dependent on the crosslinking agent (ii) changes of the chain mobility; in this case the resulting selectivity depends on the sizes of the mixture to be separated.

Table 5 shows the effect of gamma-irradiation on the permeability and separation efficiency for the Nylon 4-PVA with blending ratio of 8:2 which presents the best selectivity. According to Katz and Wydeven[7], PVA membrane swelling ratio in water indicated a steep decrease with dose below 10 Mrad whereas beyond 10 Mrad, it changed only

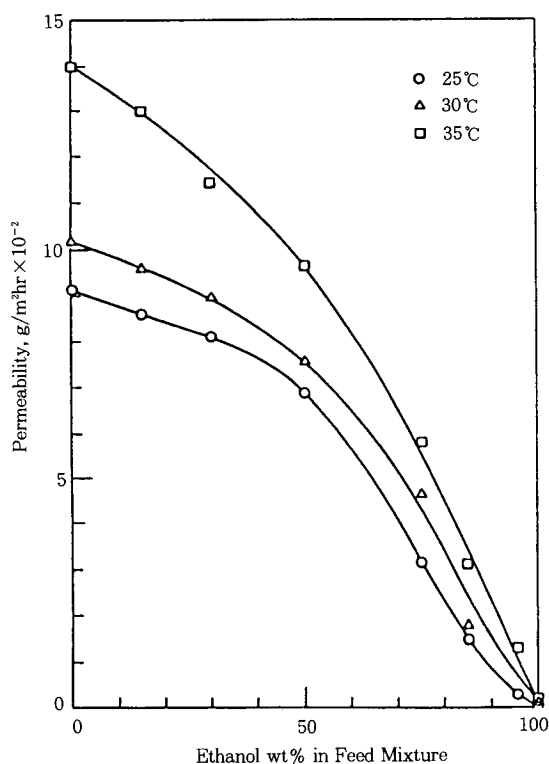


Fig. 3. Permeation rates of Nylon 4 membrane.

slightly with dose. Thus we checked the radiation dose of the membrane up to a dose of 10 Mrad. Table 5 shows that the maximum separation factor, 10.56, was observed at the dose of 5 Mrad. Consequently, the optimum hydrophilicity/hydrophobicity balance is the membrane with the blending ratio of 8:2 and crosslinking dose of 5Mrad in this system. From these result, it should be recognized that the affinity of the polymer towards water must not be too high because this leads to extensive swelling, resulting in sorption increase of ethanol. Thus crosslinking the polymer plays an important role in control of the balance between the hydrophilicity and swelling.

Fig. 2 shows the separation factors at various temperatures for the entire range of the feed composition. Fig. 3 shows the relation of the permeation rate to the feed composition at various temperatures by Nylon 4 membrane. The increase of the

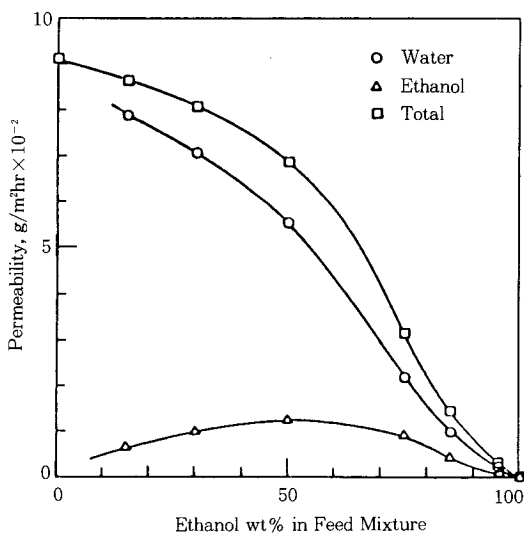


Fig. 4. Individual permeation rate of Nylon 4 membrane at 25°C.

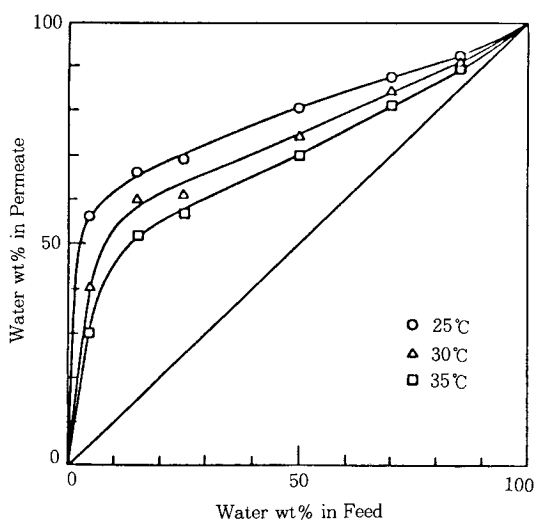


Fig. 5. X-y diagram.

water content in the feed mixture causes the permeation rate to become greater and the same trends are noted at other temperatures.

Individual permeation rates of water and ethanol at 25°C are illustrated in Fig. 4. Even if pure ethanol permeation rate is very small, the ethanol permeation rate increases with the increase of the

water content and shows a maximum rate at 50 wt. % ethanol in feed mixture. This could be due to the coupling effect, i.e., the presence of water facilitates the ethanol permeation rate. According to our sorption and diffusion studies of water and ethanol in Nylon 4 membranes, the sorption capacity is not much different from each other, i.e., the diffusion rate of ethanol in Nylon 4 membrane is much slower than that of water[8]. The separation factors increase exponentially for Nylon 4 membrane with the change in feed composition. At azeotropic composition the Nylon 4 membrane gives higher separation factor when compared with that of other homopolymer membranes while at 50 wt.% of ethanol in feed mixture, moderately high separation factor is obtained. This is also illustrated in the x-y diagram in Fig. 5.

#### 4. Conclusions

It has been demonstrated that the separation efficiencies can be enhanced by controlling the hydrophilicity/hydrophobicity balance based on the changes of the blending ratio of two polymers and the crosslinking degree. Nylon 4-PAA membranes with the blending ratio of 8:2 showed the highest separation factor of 9.36 at 50 wt.% ethanol concentration in the feed. Nylon 4-PVA membrane with the blending ratio of 8:2 crosslinked  $\gamma$ -irradiation with the dose rate of 5 Mrad showed the highest separation factor of 10.56 at 50 wt.% ethanol concentration in the feed. At azeotropic composition, Nylon 4 gave a higher separation factor of 27.8 when compared with that of other homopolymer membranes while at 50 wt.% of ethanol in feed, a moderate high separation factor was obtained.

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