

가교된 PVA 분리막을 이용한 1, 2 hexanediol/water 혼합물의 투과증발 탈수 특성 연구

시브샹카 샤우드하리 · 조 세 옥 · 손 민 영[†]

국립부경대학교 공업화학 · 고분자공학부 공업화학전공
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Assessing the Dehydration Pervaporation Performance for Purification of Industrially Significant 1, 2 Hexanediol/Water Mixtures Using Crosslinked PVA Membrane

Shivshankar Chaudhari, Se Wook Jo, and Min Young Shon[†]

Department of Industrial Chemistry, Pukyong National University, Busan 48513, Republic of Korea

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요약: 본 연구에서는 에너지 소모가 큰 기존 진공 증류 공정의 대안으로 친환경이면서 에너지 효율적인 투과증발 분리 공정을 이용하여 1,2 hexane diol/water (1,2 HDO/water) 혼합물에서 물을 분리하는 데 적용되었다. 사용한 분리막은 glutaraldehyde (GA)로 가교된 PVA를 알루미늄 중공사 막(Al-HF) 내부에 코팅하여 사용하였다. 1,2 HDO/water 투과증발 분리 공정에서는 PVA/GA 비율, 경화 온도 및 투과증발 분리 공정 운전 조건에 대한 막의 최적화를 연구하였다. 장기 안정성 시험에서 PVA/GA (몰 비율 = 0.08, 경화 온도 = 80°C) 로 코팅된 Al-HF 막이 공정 온도 40°C에서 1.90~2.16 kg/m²h 범위의 투과도를 보였으며, 투과용액의 수분 함량은 99.5% (separation factor = 68) 이상이었다.

Abstract: In this study, the alternative to the energy-intensive conventional vacuum distillation process, an eco-friendly and energy-efficient pervaporation separation was employed in 1,2 hexane diol/water (HDO/water) mixture. The crosslinked PVA-glutaraldehyde was coated inside the alumina hollow fiber membrane (Al-HF). In the HDO/IPA pervaporation separation, optimization of the membrane concerning PVA/GA ratio, curing temperature, and pervaporation operating condition were performed. In the long-term stability test, the sustainable pervaporation separation performance giving flux in the range of 1.90~2.16 kg/m²h, and water content in permeate was higher than 99.5% (separation factor = 68) was obtained from the PVA/GA (molar ratio = 0.08, curing temperature = 80°C) coated Al-HF membrane from HDO/water (25/75, w/w, %) mixture at 40°C. Therefore, this work provides potential and inspiration for PVA-based membranes to mitigate excessive energy requirements in HDO/water separation by pervaporation.

Keywords: 1,2 Hexane diol, polyvinyl alcohol, alumina hollowfiber, composite membrane

1. Introduction

The compound 1,2-hexanediol, which contains two hydroxyl groups per molecule, plays a crucial role in various industries such as petroleum, cosmetics, and pharmaceuticals. It is considered environmentally friendly as it can be synthesized from bioresources like lignin, making it a renewable material[1,2]. The syn-

thesis of 1,2-hexanediol (HDO) involves the dehydrogenation of hexane to 1-hexene, followed by the oxidation of the double bond in 1-hexene using hydrogen peroxide to produce 1,2-HDO[3,4]. In the final stages of the synthesis process, the separation, purification, and concentration steps are essential to obtain a pure 1,2-HDO product. Typically, a vacuum distillation method is employed to remove excess water used in

[†]Corresponding author(e-mail: myshon@pknu.ac.kr; <https://orcid.org/0000-0002-9068-6952>)

the 1,2-HDO production process. However, the formation of 1,2-HDO bubbles in the mixture poses a challenge to purify 1,2-HDO via vacuum distillation spatially in where a diluted 1,2 HDO solution (75/25, w/w, % HDO/water). This process not only consumes significant amounts of energy but also requires a larger facility area. On the contrary, pervaporation is a membrane-based clean, eco-friendly separation technique that requires a relatively small facility area[5]. It operates based on the solution and diffusion of materials through a membrane[6,7]. Consequently, separating 1,2-HDO/water using pervaporation proves to be an effective and energy-efficient method[8].

Polyvinyl alcohol (PVA) is a commonly used material for preparing dehydration membranes due to its high hydrophilicity, chemical, thermal, and mechanical resistance, as well as its film-forming characteristics[9, 10]. The abundance of hydroxyl groups on PVA membranes results in a high affinity for water compared to 1,2-HDO. However, in water-rich feed systems, PVA-based membranes tend to swell[11,12,13,14], leading to a decrease in pervaporation selectivity. Therefore, this study employed glutaraldehyde (GA) to crosslink the PVA chain, resulting in a dense and compact structure[15]. The 1,2-HDO and water molecules exhibit significant differences in molecular size. Exploiting this difference in size facilitates the permeation of smaller molecules (such as water) during pervaporation, leading to high water selectivity.

As an alternative to traditional vacuum distillation, the separation of 1,2 HDO/water was conducted using the pervaporation technique in this work. The PVA-GA solution was coated onto alumina hollow fibers (Al-HF). Polymeric support with lower mechanical strength, such as PVDF needs to be hydrophilized prior to coating[14] therefore, Al-HF was selected for its inherent hydrophilicity, ensuring good compatibility with PVA and providing high mechanical and chemical resistance to the composite membrane. Pervaporation tests were conducted to investigate the impact of crosslinking agent content, crosslinking temperature, and operating conditions on the separation process. The opti-

mized membrane was then subjected to long-term stability testing to assess its industrial applicability developed in this study.

2. Experimental Sections

2.1. Material

PVA with hydrolysis degrees of approximately 99% and a molecular weight ranging from 88,000 to 97,000 g/mol was purchased from Alfa Aesar (USA). Porous alumina hollow fiber (Al-HF) supports were obtained from the Korea Research Institute of Chemical Technology (South Korea), and their characterization was detailed in our previous report[16]. Hydrochloric acid (HCl, 36.0% w/w) was supplied by Dae-Jung Chemicals & Metal Co, Korea. GA in a 25% aqueous solution and 1,2-hexanediol (95%) were purchased from Alfa Aesar (USA). Deionized water (Puris, RO system) was used for all experiments.

2.2. Preparation of PVA-Al-HF membranes

The PVA-Al-HF membrane was prepared as follows: 4 g of PVA powder was dissolved in 96 g of water by stirring on a hot plate at 90°C for 5 h. Subsequently, the solution was allowed to cool to room temperature. A glutaraldehyde crosslinker at varying PVA/GA ratios (ranging from 0.06 to 0.25) was added, and an HCl catalyst was then added. The coating solutions were thoroughly mixed by stirring at room temperature for 1 h. The resulting PVA/GA solution was coated inside the Al-HF using a syringe pump (Longer Pump, LSP02-2B). The coating conditions included an infusion injection volume of 2 mL, a holding time of 30 seconds, and a 0.5 mm/min withdrawing speed. The coated membranes were subsequently allowed to dry at room temperature and then transferred to an oven with a preset temperature range of 40 to 120°C. The resulting PVA-Al-HF membrane was employed for pervaporation separation of 1,2-HDO/water solutions. The active layer thickness was observed using a field emission scanning electron microscope (Teskan, Czech, Vega II, and LSU) according to the number of coating layers.

2.3. Pervaporation experimental setup

Pervaporation experiments for separating 1,2-HDO/water was conducted using the PV setup designed in our previous study[16]. The PVA-Al-HF membranes (3) were cut into 5 cm lengths with an inner diameter of 0.22 cm and fixed into the stainless-steel HF membrane module. The 1,2 HDO/water feed mixture was circulated at a rate of 80 mL/min through the inner side of the HF, and a vacuum (less than 1 torr) was applied to the outer side. The outer side of the membrane was connected to a tube immersed in liquid nitrogen. After a 1 h experiment, the permeated solution collected in traps was melted and weighed using an electronic balance. For the evaluation of the exact water and HDO content in the feed and permeation solutions, a gas chromatograph (GC, DS Sci. DS7200) equipped with a Flame Ionization Detector was utilized. Equations 1 and 3 were employed to calculate flux and separation factor after each pervaporation experiment. The reported values represent the average obtained from three successive tests, with standard deviations less than 2 for flux and 5 for the separation factor.

$$Flux(J) = Q/A \times t \quad (1)$$

Here, J is the permeation flux ($\text{kg m}^{-2} \text{h}^{-1}$), Q stand for mass of the permeated solution collected in the cold trap (kg) with respect to the effective area A (m^2) over time t (h). Effective area was calculated according equation 2, where r and h are the radius and height of inside coated hollowfiber.

$$Effect\ area\ of\ Al-HF(\text{m}^2) = 2 \times \pi \times r \times h \quad (2)$$

$$Separation\ Factor(\alpha) = \frac{P_{(j)}/P_{(i)}}{F_{(j)}/F_{(i)}} \quad (3)$$

Where, symbols $P_{(i)}$, $P_{(j)}$, $F_{(i)}$, and $F_{(j)}$ are the weight fractions of water or IPA and the 1,2 HDO in permeate and feed solutions respectively.

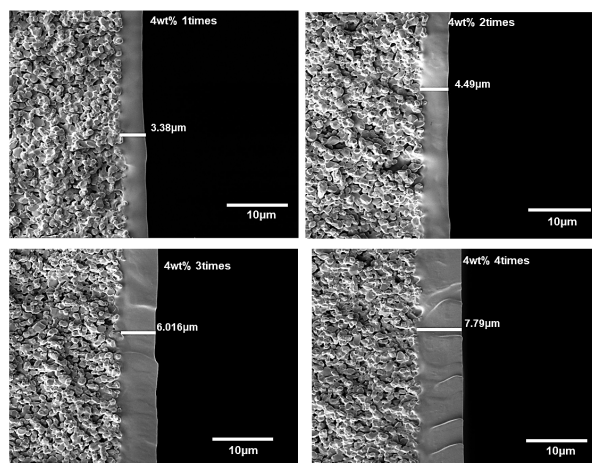


Fig. 1. Cross-sectional micrographs for the different PVA-Al-HF membranes.

3. Results and Discussion

3.1. Morphology of PVA coated Al-HF membrane

Fig. 1 illustrates the cross-sectional micrographs of the PVA-Al-HF membranes. The alumina support exhibits spherical grains organized loosely, presenting a sponge-like porous morphology. The PVA selective layer demonstrates good compatibility with the Al-HF support, attributed to the hydrogen bonding between the alumina hydroxyl groups and those of the PVA polymer[16]. No apparent delamination of the selective layer was observed, and the thickness of the coating layer increased with the coating time of the PVA layer. A thin active layer is likely to yield high pervaporation performance; therefore, a membrane thickness of approximately 3 μm was selected for all subsequent optimization tests.

3.2. Effect of PVA/GA molar crosslinking ratio

Fig. 2 illustrates the impact of the molar ratio of PVA/GA on flux and separation factor in a feed containing a 1,2-HDO/water solution (25/75 w/w %) at 40°C. As the GA content increased in the coating solution, the total flux decreased from 3.64 to 0.60 $\text{kg/m}^2\text{h}$, while the separation factor increased from 20 to 912. This phenomenon can be attributed to the reduction of hydroxyl moieties due to crosslinking with

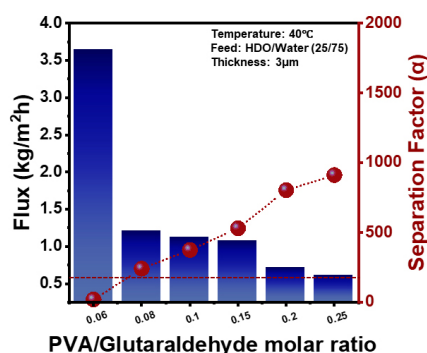


Fig. 2. Effect of PVA/GA crosslinking ratio on flux and separation factor in 1,2 HDO/water separation.

aldehyde groups, forming acetal moieties in the membrane. This effect becomes more pronounced with higher GA content. The increased crosslinking density in the coating solution leads to forming a dense and compact membrane structure during curing, thereby reducing the free volume in the membrane[17]. Consequently, the pervaporation permeation of molecules occurs at a slower rate. On the other hand, the molecular size of 1,2-HDO is more significant than that of water molecules[18]. Therefore, permeation of 1,2-HDO becomes increasingly difficult with a more compact membrane structure, leading to an increase in the separation factor with higher GA content in the membrane. The PVA/GA membrane, with a molar ratio of 0.08, delivered comparatively high performance (giving flux =1.2 kg/m²h and water content in permeate 99.81%) and additionally, with increase of GA content, the flux has significantly reduced to 0.60 kg/m²h (PVA/GA (0.25)). Therefore, PVA/GA (0.08) was optimized condition for the subsequent investigation of the curing temperature effect and the data for the above PVA/GA (0.08) molar ratio has not been considered.

3.3. Effect of curing temperature effect

The impact of curing temperature on the crosslinking degree in the coating layer and its subsequent effects on flux and separation were examined for a (25/75 w/w %) 1,2-HDO/water feed mixture at 40°C. Below

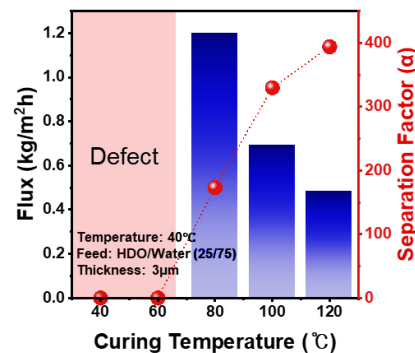


Fig. 3. Effect of curing temperature on flux and separation factor in 1,2 HDO/water separation.

60°C, defects were observed, while an increase in curing temperature from 80°C to 120°C resulted in a linear decrease in flux (from 1.2 kg/m²h 0.48 kg/m²h) and a monotonous increase in separation factor (Fig. 3). In the lower temperature range, a lower degree of crosslinking produces a membrane with an abundance of hydroxyl moieties, leading to a higher likelihood of swelling. As a result, the PVA selective layer of the membrane tends to dissolve during the pervaporation test. Conversely, at higher curing temperatures (100 and 120°C), the intramolecular condensation of OH groups and hydroxyl and aldehyde crosslinking leads to a higher packing density in the selective layer[19]. As increased of curing temperature from 80°C to 120°C results in 1/3-fold reduction in flux, therefore, based on pervaporation performance considerations, a curing temperature of 80°C was identified as optimal for all further tests.

3.4. Effect of feed temperature

The boiling point of 1,2 HDO and water is 223°C and 100°C respectively. The 1,2 HDO and water is not formed azeotropic mixture in any mixing ratio. In term of energy saving perspective, it can be beneficial if membrane delivering the decent performance in lower feed temperature range. Therefore, feed temperature ranges from 30 to 70°C was selected to observe the pervaporation output by elevation of from 30 to 70°C. Fig. 4a illustrates the effects of feed solution temper-

ature on flux and separation factor during the separation of 1,2 HDO/water (25/75 w/w, %). As the feed solution temperature increased from 30 to 70°C, the total flux significantly rose from 1.31 to 2.51 kg/m²h, while the separation factor linearly decreased from 533 to 130.

This trend aligns with findings in the literature regarding pervaporation separation in polymer-based membrane systems[20]. This phenomenon occurs for two primary reasons. Firstly, with increased feed temperature, the vapor pressure on the feed side rises. In contrast, the pressure on the permeated side remains constant due to the vacuum, thereby enhancing the driving force for permeation. Secondly, the elevated feed temperature induces thermal agitation in polymer chains, creating random free volume in the membrane. This, in turn, facilitates the faster permeation of associated feed molecules, resulting in an increase in flux and a decrease in the separation factor. The temperature dependence of flux can be mathematically expressed using an Arrhenius-type equation, as provided below[16].

$$Flux(J_i) = A_p \times e^{-E_p/RT} \quad (4)$$

Where J_i (kg m⁻² h⁻¹) is the flux of component i , which corresponds water or HDO; T (K) denotes absolute temperature in kelvin; R (J mol⁻¹ K⁻¹) represents the universal gas constant; and A_p (kg m⁻² h⁻¹) and E_p (kJ mol⁻¹) pertain to the pre-exponential factor and the apparent activation energy for permeation, respectively. Individual fluxes of 1,2 HDO and water was calculated using equation 5.

$$(j_i) = \frac{(J) \times P_i}{100} \quad (5)$$

where j_i is the flux of component i (kg m⁻² h⁻¹) and J (kg m⁻² h⁻¹) is total flux, P_i stands for weight fraction of component i (1,2 HDO or water) in the permeate solution.

A linear plot of the natural logarithm of individual

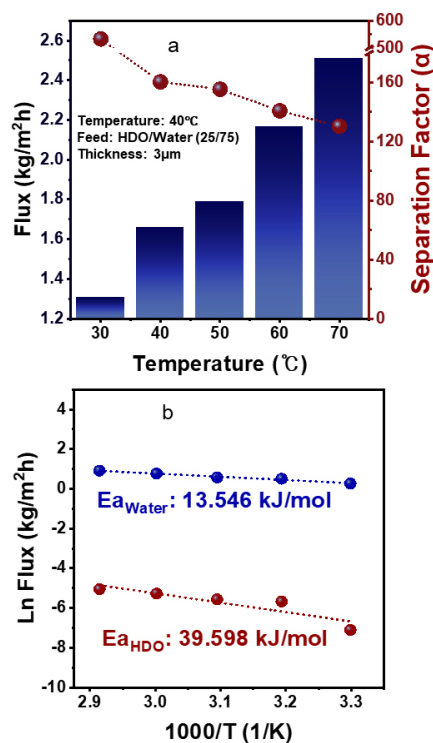


Fig. 4. Effect of feed temperature on flux and separation factor in 1,2 HDO/water separation (a) Natural logarithm of individual fluxes of water and 1,2 HDO as a function of temperature (b).

fluxes of 1,2 HDO and water as a function of temperature was generated by plotting (Fig. 4b). From the slope of this plot, the apparent activation energies (E_a) for the permeation of water and 1,2 HDO were determined. The E_a value for 1,2 HDO (39.598 kJ/mol) was found to be higher than that for water (13.546 kJ/mol), indicating a higher water permselectivity for the membrane produced in this study. Furthermore, it was observed that the permeation of 1,2 HDO is more sensitive to changes in feed temperature, leading to a significant decrease in the separation factor with increasing operating feed temperature.

3.5. Effect of Feed concentration

To assess the effect of the feed composition ratio of the 1,2 HDO and water feed mixture on pervaporation performance, the water content in the feed was adjusted from 5 to 95 wt.% relative to 1,2 HDO. While

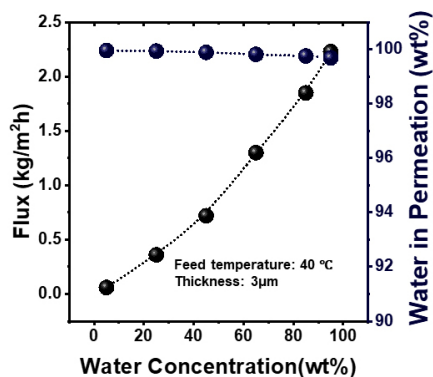


Fig. 5. Effect of water/1,2 HDO ratio in feed on flux and separation factor in HDO/water separation.

maintaining a constant feed temperature of 40°C, the flux exhibited a linear increase with the rising water content in the feed (Fig. 5). In contrast, the water content in the permeated solution showed a marginal reduction. The hydrophilic nature of the PVA-based membrane, attributed to the abundance of OH moieties on its surfaces, led to increased membrane swelling with higher water content in the feed, inducing plasticization in the polymer chain [20]. Moreover, the elevated water content enhanced the fugacity of water molecules, consequently increasing the driving force for permeation. As a result, flux increased with higher water content in the feed composition. However, it is plausible that the plasticization effect led to an increased spacing in the PVA polymer chain.

This, in turn, facilitated the transportation of associated molecules such as HDO and water, resulting in a decrease in the separation factor.

3.6. Long term membrane stability

The membrane developed in this study was designed with industrial applications in mind. A continuous 250-hour pervaporation test was conducted, with intermittent sampling to assess flux and water content in the permeation solution. Throughout the stability test, a feed composition 25/75 (w/w%, 1,2 HDO/water) was maintained, and the membrane (PVA/GA = 0.08, curing temperature = 80°C) was affixed in the membrane cell. Fig. 6 illustrates the results of the long-term per-

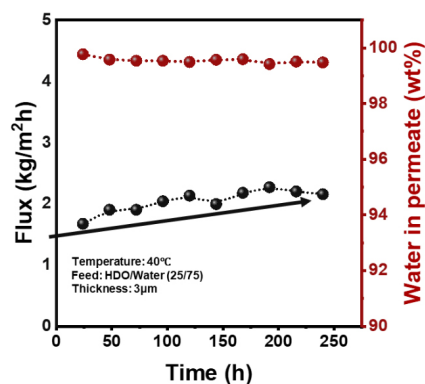


Fig. 6. The long-term pervaporation results for (PVA/GA=0.08, curing temperature= 80°C) coated on Al-HF membrane.

formance evaluation during the extended pervaporation operation. Throughout the test, the flux showed a marginal increase (from 1.90 to 2.16 kg/m²h), while the water content in the permeation consistently remained above 99.5%. The observed increase in flux over time can be attributed to the relaxation and conditioning effect of the polymer chain with the feed solution, a phenomenon commonly observed in PVA-based membranes[21,22]. Based on these findings, it can be concluded that the membrane developed in this study demonstrates robust performance and can effectively separate 1,2 HDO/water over an extended period.

4. Conclusion

A composite membrane comprising a hydrophilic PVA layer inside a 3µm-thick coating of Al-HF was developed for the pervaporation separation of 1,2 HDO/water mixtures. The conditions for the coating layer were optimized based on the GA crosslinker content and curing temperature. Pervaporation tests were conducted using a (25/75 w/w%) 1,2 HDO/water feed mixture. The flux exhibited a decreasing trend (from 3.64 to 0.60 kg/m²h) with an increase in crosslinker content (PVA/GA ratio of 0.06 to 0.25) and curing temperature (from 40 to 120°C). Conversely, the separation factor increased linearly, reaching values from 20 to 911 and 172 to 394, respectively. Under elevated operating conditions in the pervaporation test, the flux

increased with feed temperature and water content in the feed composition, while the water content in the permeated solution was slightly reduced. In a 240-hour long-term pervaporation operation, the developed membrane demonstrated stable separation performance, yielding a flux of 1.9 to 2.16 kg/m²h, with the water content in the feed consistently maintained above 99.5%. In conclusion, implementing a hydrophilic pervaporation dehydration method utilizing a PVA-Al-HF composite membrane offers a straightforward and highly efficient strategy to significantly enhance energy conservation in the purification process of industrially crucial 1,2 HDO/water mixtures.

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