가교된 PVA/PAA 막을 이용한 MTBE-Methanol 혼합물에 대한 투과증발분리

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Pervaporation Separation of MTBE-Methanol Mixtures Using PVA/PAA Crosslinked Membranes

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요 약 : 옥탄가상승제 및 대기오염 저감물질로 잘 알려진 메틸터셔리부틸에테르(MTBE)를 투과증발분리 공정을 이용하여 메탄올로 부터 분리하는 실험을 수행하였다. 물과 알코올계에 성공적으로 적용된 바 있는 폴리비닐알코올(PVA)과 폴리아크릴산(PAA)이 서로 가교된 막을 이용하여 폴리아크릴산의 양을 폴리비닐알코올에 대하여 5, 10, 15, 20, 25 wt% 변경하면서 조업온도 30, 40, 50℃, 공급혼합물액의 조성 메탄올 5, 10, 20 wt%에 대하여 투과증발 실험을 수행하였다. 공급액온도 50℃의 MTBE/MeOH=80/20 용액에 대하여 PVA/PAA=85/15 막을 사용하였을 때 투과도 10.1 g/m^2hr 및 선택도 약 4000을 얻었다. 또한 공급액온도 40℃의 MTBE/MeOH=90/10 용액에 대하여 같은 막을 사용했을 경우 투과도 8.5 g/m^2hr 및 선택도 약 6000의 우수한 결과를 얻었다. 또한 사용된 막과 투과도 및 선택도와의 관계에는 막의 hydrophilic/hydrophobic balance가 현재의 MTBE/MeOH 계의 분리에 중요한 역할을 하고 있다는 것을 알 수 있었다.

Abstract : Pervaporation separation of methyl tert-butyl ether (MTBE) and methanol (MeOH) mixture, of which the former compound is well known as the octane booster was carried out. Poly(vinyl alcohol) (PVA) membranes crosslinked with poly(acrylic acid) which have been successfully applied on the water-alcohol mixtures were used in this study. The PVA/PAA ratio in the crosslinked membranes was 95/5, 90/10, 85/15, 80/20, and 75/25 by weight. The operating temperatures were 30, 40, and 50℃, and the compositions of MTBE and MeOH to be separated were 95/5, 90/10, and 80/20 (MTBE/MeOH) solutions. PVA/PAA=85/15 membrane showed the separation factor $\alpha_{MeOH/MTBE}$=4000 and the permeation rate of 10.1 g/m^2hr for MTBE/MeOH=80/20 solution at 50℃. When the same membrane was used, the separation factor and permeation rate for MTBE/MeOH=90/10 solution at 40℃ were $\alpha_{MeOH/MTBE}$=6000 and 8.5 g/m^2hr, respectively. Also, the hydrophilic/hydrophobic balance of the membranes would take an important role in the relationships between the membranes and separation performances in terms of the flux and the separation factor.

1. Introduction

Increasing environmental pollution problems and the subsequent emergence of more strict regulations on fuel exhaust gases led to progressive changes in gasoline compositions. Among these changes, the amount of lead additive in gasoline, which is enhancing the octane ratings and showing the poisonous effects on exhaust catalytic mufflers, indicates the reduction trend. This demands petroleum refiners to increase the contents of other hydrocarbon components having high octane numbers such as benzene/toluene/xylene mixtures and to look for other new octane enhancers. However, due to the toxicity of aromatic compounds, their levels will rather be reduced than increased limitations of the available options[1,2].

Oxygenated compounds like alcohols or ethers have also high octane numbers. It has been reported that the addition of oxygenated compounds into gasoline led to reduce the emissions of carbon monoxide and unburned hydrocarbons. One of oxygenated fuel additives, methyl tertbutyl ether (MTBE) has been extensively tested if this could be more suitable than other alcohols as octane enhancer. As a result, it has been proven that MTBE could meet the requirement of the Clean Air Act amendments of the United States government[3,4].

A typical MTBE production can be obtained from the reaction of pure MeOH and isobutylene. The excess MeOH in MTBE reaction must be removed for recycle to the reactors and for high purity ether products and C_4 to C_7 raffinates. The effluent of the reactor contains, mainly, the MTBE produced and the untreated excess of MeOH. The effluent mixtures is first splitted in the debutanizer into a bottom MTBE product and a near azeotropic mixture of MeOH and MTBE, whose composition is 14.3 wt% MeOH at 760 mmHg. This mixture is then separated by water washing after which MeOH and water mixture is distilled to recycle MeOH to the reactor[1,5]. However, it is well known that this conventional separation process is both energy- and capital-intensive.

Pervaporation has been considered as an alternative separation process. Doghieri et al.[6] studied the pervaporation separation of MeOH-MTBE mixtures through modified poly(phenylene oxide) membranes under the various operating conditions. In the cases where the MeOH concentrations in feed varied from 1.1 to 20.9 wt%, the selectivities showed from 23.4 to 7.7 while the MTBE transmembrane flux decreased from 232 to 120 g/m^2hr when the alcohol concentration in the feed increased from 0 to 3.2 %; then it decreased up to 210 g/m^2hr for 21 % MeOH. Park et al.[2] and Park[7] investigated the pervaporation separation of MTBE-MeOH mixture using poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA) blended membranes. As the contents of PVA in the blend increased, the selectivity toward MeOH increased. They showed that the selectivity of about 300 at the composition of 10% MeOH was obtained for 20 wt% PAA membrane in the blend. Chen et al.[8] at Air Products & Chemicals Inc. developed the Total Recovery Improvement for MTBE (TRIM) process which is an improved esterification process for ether production, especially MTBE by incorporating one or more pervaporation membrane steps in the purification section downstream of the esterification reactors to remove alcohol from the product stream using cellulose acetate membranes. The separation factors ranged from 14 to 400 over a wide range of feed MeOH concentration, temperature, and membrane type in the MTBE/MeOH binary system. Pasternak et al.[9] at Texaco Inc. developed the PVA membranes crosslinked with glutaraldehyde and the fluorinated resins to separate MTBE and MeOH mixtures. The PVA membranes showed the separation factor of 233 (99.9 wt% in permeate) with the permeation rate of 0.43 kg/m^2hr for MeOH 81.1 wt% in feed. The fluorinated membranes, however, were exposed to the lower MeOH concentration, 11 to 16 wt%, in feed. In this case the separation factors of 4.7 to 50.9 were obtained while the flux were 0.02 to 0.23

kg/m^2hr. Therefore, they concluded that PVA membranes would be preferred for a high concentration of MeOH and the preferred membranes for a low concentration may be ion exchange membranes. Craig[10] developed the composite poly(4-vinyl pyridine) membranes crosslinked with dibromobutene mounted onto polyacrylonitrile for the purpose of the separation of MTBE/MeOH/C₅ mixture. Typically the separation factor 442 and the flux 2.06 kg/m^2hr were obtained when the feed concentrations of MTBE/MeOH/C5 were 19.8, 12.1 and 67.9 wt%, respectively. Park et al.[2,7] investigated the separation of MTBE and MeOH mixtures using PVA/PAA blended and crosslinked membranes with gradual increasing of PVA contents. When the feed concentration of MeOH was 20 %, PAA/PVA=70/30 blended membrane showed the selectivity of about 170 and the flux of about 0.3 kg/m^2hr while the crosslinked membrane with the same composition gave almost the same results with those of the blended membranes. Lee et al.[11] investigated the application of polymer membranes, cellulose acetate(CA), poly-arylate(PA), and polycarbonate(PC), to the catalytic decomposition of MTBE. It was revealed that all the membranes showed larger permeability of MeOH than that of MTBE. The perm-selectivity of MeOH/MTBE was in the order of CA>PC>PA. As a result, the membrane reactor showed better performance than the corresponding fixed bed reactor.

This article deals with the separation of MTBE-MeOH mixtures using PVA/PAA membranes by pervaporation technique. The operating temperatures, MeOH concentration in feed mixtures, and the PAA concentration in PVA/PAA membranes will be varied to investigate the separation performance of PVA/PAA membranes and the optimum separation characteristics.

2. Experimental

## 2.1 Materials

Fully hydrolyzed PVA with a molecular weight of 50,000 and PAA with a molecular weight of 2,000 (25 wt % in water) were purchased from Showa Chemical Co. (Tokyo, Japan) and Aldrich Co.(Milwaukee, USA), respectively. MTBE were analytical grade from Aldrich Co. The ultrapure water used was the ultrapure water produced from the SK system.

2.2 Membrane preparation[12]

Aqueous 10 wt % PVA solutions were prepared by dissolving preweighed quantities of dry PVA in ultrapure water and heating at 90℃ for at least 6 h. Aqueous 25 wt % PAA solutions were diluted to 10 wt % solutions. Then two polymer solutions (in case of PVA/PAA=95/5, PVA 95 g and PAA 5 g were mixed together since each polymer solution had 10 wt.% polymer concentration) were mixed together by varying each component composition to form a homogeneous solution for at least 1 day at room temperature. Homogeneous membranes were cast onto a Plexiglass plate using a Gardner knife with predetermined drawdown thickness. The membranes were allowed to dry in air at room temperature, and completely dried membranes were then peeled off. The dried and blended membranes were then heated in a thermosetted oven at 150℃ for 1 h. The thickness of the resulting membranes showed 15~20 μm. The prepared membranes were then stored in solutions, such as 10 and 20 wt.% of MeOH, to be separated for further use.
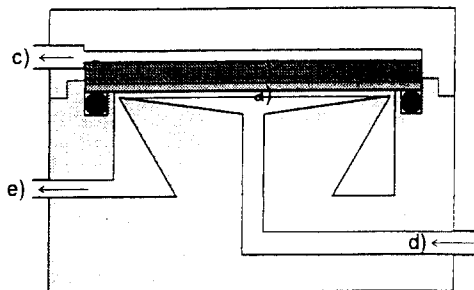
2.3 Pervaporation

The experimental apparatus and the membrane cell used in this study are illustrated in Fig. 1. The pervaporation separation experiments were performed employing two stainless steel pervaporation cell (Fig. 2). The detailed descriptions can be found in ref. [13]. The pervaporation experiments of MTBE-MeOH mixtures were conducted at 25, 35 and 45℃. Upon reaching steady-state flow conditions, product samples were collected with timed intervals, isolated from the vacuum system, and weighed. During the experiments, the downstream pressure, 0.3~1 torr, was maintained.
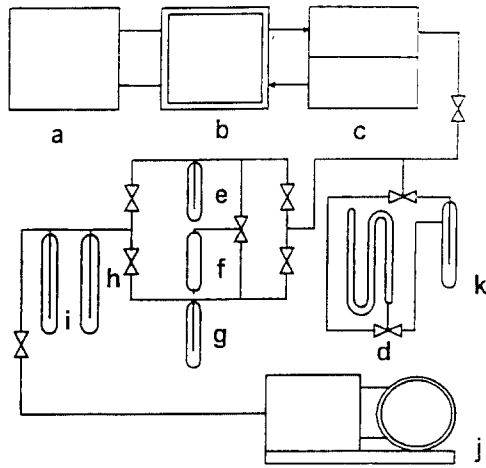
a – Temperature Controller
b – Feed tank
c – Permeation cell
d – Vacuum manometer
e, g – Cold traps for collecting samples
f – Drying tube
h, i – Cold traps
j – Vacuum pump
k – Trap

Fig. 1. Schematic diagram of pervaporation appa-
ratus used in this study.

a) membrane
b) porous support
c) permeate
d) feed mixture in
e) feed mixture out

Fig. 2. Configuration of the pervaporation cell
used in this study.

The composition analysis of the permeate was
done using gas chromatography. The following
relationship was used to calculate the separation

factor :

$$\alpha_{i/j} = (y_i/y_j)/(x_i/x_j)$$

where x is the feed composition, y is the
permeate composition, and component i is the
preferentially permeating component.

3. Results and Discussion

The resulting PVA/PAA crosslinked mem-
branes have been successfully applied to the per-
vaporation separations of water-alcohol mixtures.
The separation factors for water-ethanol mixtures
showed much higher than those of water-MeOH
mixtures [13,14]. In other words, the permeation
rate of MeOH was much higher than that of
ethanol through the membranes in question. This
could be interpreted in terms of the hydrogen
bonding forces, i.e., that the hydrogen bonding
forces between water and polymer materials such
as PVA and PAA are stronger than those
between organic chemical and the same polymers,
since PVA and PAA shows the preferential water
permeation rather than that of organic component
in the feed mixture. According to the previous
works[13,14] and Yoshikawa's studies [15], the
hydrogen bonding abilities toward the functional
groups in polymers, hydroxyl and carboxyl
groups decreased in the following order : water
> MeOH > ethanol > acetonitrile. This implies
that the mixture to be separated in this study
would show the more permeation of MeOH rather
than that of MTBE. Park et al. [2] showed the
same trends when the blended and the
crosslinked membranes of PVA and PAA were
used for the same feed mixture in question.

First, the PVA/PAA=75/25 membrane which
showed the highest separation efficiency for
water-alcohol mixtures as mentioned above[13,14]
was demonstrated to investigate the effect of the
operating temperatures for MTBE/MeOH=80/20.
This results are illustrated in Fig. 3. Generally
speaking as the crosslinking density in a polymer
increases, the resulting membrane has a more
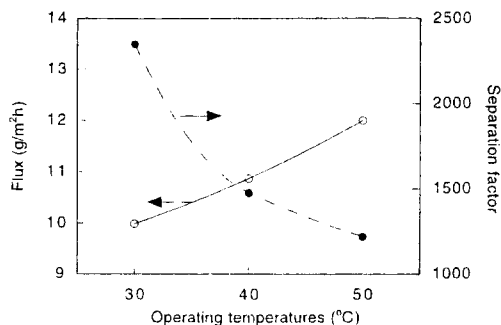compact network, resulting in less chain mobility.

Fig. 3. Effect of the operating temperatures for MTBE/MeOH=80/20 using PVA/PAA= 75/25 membrane on the permeation rate and the separation factor.
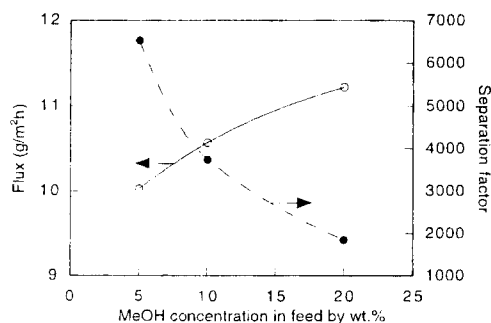

Fig. 4. Effect of the feed composition using PVA/ PAA=80/20 membrane on the permeation rate and the separation factor at 30℃.

Therefore, the free volume in the polymer decreased. As a result, the solubility of the liquid mixtures declines and the diffusivity, which is governed by the free volume, decreases due to the rigidity of the polymer chains. This might cause the permeation rate through the membrane to decrease as the operating temperature is lowered. Furthermore, since the interaction ability between the each component and the membrane becomes stronger as the operating temperatures are lowered, the flux decreases. As can be seen in Fig. 3, the permeation rate increases while the separation factor increases as the operating temperature decreases. This figure shows the

typical trend of the pervaporation experiments. At 30℃, the separation factor and the permeation rate show 2350 and 10 g/m^2hr, respectively.

The effect of the feed composition using PVA/ PAA=80/20 membrane is shown in Fig. 4. As the MeOH concentration in the feed decreases, the flux decreases while the separation factor increases. When the membrane has less chances to contact with the more preferential composition, MeOH, in the feed, the membrane swells less and, as a result, the permeation rate becomes less. Typically the PVA/PAA=80/20 membrane shows the permeation rate, 11.2 g/m^2hr, and the separation factor, 1850, for MTBE/MeOH=80/20 feed composition at 30℃. Fig. 5 illustrates the effect of the amount of the crosslinking agent, PAA, on the pervaporation characteristics for MTBE/MeOH=80/20 solution at 50℃. As the amount of PAA decreases, the separation factor increases up to 15 % of PAA and then decreases while the permeation rate shows *vice versa*. Park et al.[2] investigated the pervaporation separation of MTBE/MeOH mixtures using both blended and crosslinked PVA membranes with PAA. However, the major composition of their blended or crosslinked PVA/PAA membranes was PAA while ours is PVA. According to their results, the selectivities increased monotonously with increasing the PVA composition. The selectivities of the blended membranes ranged from 50~150 whereas the crosslinked membranes showed the separation factor of 100~200 when both kinds of membranes were exposed to MTBE/MeOH=80/20 solutions at 35℃. From their results, it could be expected that the selectivities increase as the more PVA to the membranes is added. This could imply that the PVA has a more important role than PAA, in other words, the hydroxyl group in PVA is more efficient to separate the MTBE/MeOH mixture than the carboxyl group in PAA. In fact, the hydroxyl group in PVA can form stronger hydrogen bonding abilities with both MeOH and MTBE than the carboxyl group in PAA as can be seen in Table 1. Therefore, it could be interpreted that the flux increases while
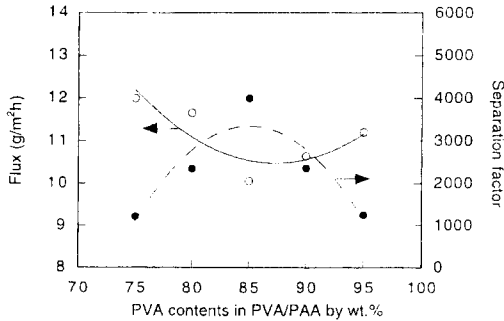
Fig. 5. Permeation rate and separation factor for MTBE/MeOH=80/20 mixtures with varying PAA contents at 50℃.

the separation factor decreases since the membrane network is not much compact due to the less addition of crosslinking agent of PAA and the larger contribution of the hydroxyl group is applied on above the ranges of 85 wt.% PVA concentration.

However, this analysis would not be fit below 85 wt.% of PVA. The next Fig. 6 illustrates the individual flux of MeOH and MTBE for the results of Fig. 5. The MTBE flux is almost constant with varying the PAA concentration while the flux of MeOH shows the same shape of total flux illustrated in Fig. 5. It could be considered that MTBE flux is independent on the effects of the crosslinking degree and of PAA concentrations. The MeOH flux decreases slightly as the PVA is more added up to 85 wt.%. even

Table 1. Solubility parameters of polymers and feed components used in this study.

	δ_d	δ_p	δ_h	δ_t	V
MeOH	7.4	6.0	10.0	14.5	40.7
MTBE*	7.6	1.7	2.4	8.1	119.0
PVA*	16.0	14.3	23.9	32.1	35.0
PAA*	20.2	9.6	15.1	27.0	43.6**

* Solubility parameters ($cal^{1/2}/cm^{3/2}$) calculated by the group contribution method proposed by van Krevelan[16]

** Molar volume (cm^3/mol) calculated by the group contribution method proposed by van Krevelan[16]
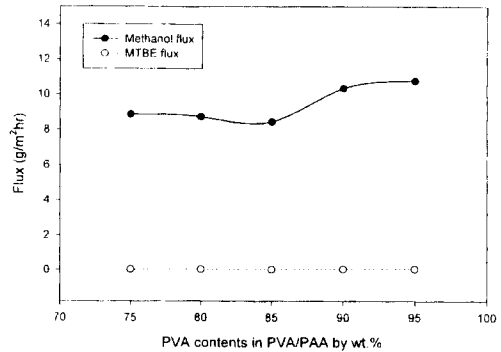

Fig. 6. Individual permeabilities of MTBE and MeOH for MTBE/MeOH=80/20 mixtures with varying PAA contents at 50℃.

though the MeOH flux would be expected to increase due to the less crosslinking degree. This phenomena seems to come from the carboxylic group effect in PAA with MeOH rather than the crosslinking effect. It has been studied the hydrophilic/hydrophobic balance of the blended membranes of Nylon 6/PVA and Nylon 4/PVA in terms of the flux and the separation factors for water-ethanol mixtures[17]. The addition of more hydrophilic polymer, PVA, to Nylon polymers showed the same trend with PVA/PAA membranes used in this study. Therefore, in this case, the hydrophilic/hydrophobic balance of the membranes contributes seriously to the membrane performances. Typically, the separation factor, about 4000, and the permeation rate, 10.1 g/m^2hr, were obtained when PVA/PAA=85/15 membrane was used.

The effect of the amount of the PAA in the membranes on the pervaporation characteristics for MTBE/MeOH=90/10 solution at 40℃ which composition is over the azeotropic point of 14.3 wt.% MeOH is illustrated in Fig. 7. The membrane characteristics showed the same trend with the previous results of Fig. 5. The separation factor of about 6000 with the permeation rate, 8.5 g/m^2hr can be found when PVA/PAA=85/15 membrane was used.
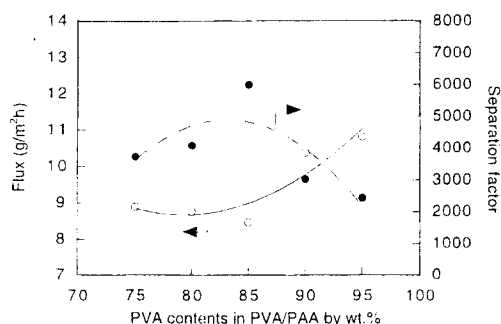
Fig. 7. Permeation rate and separation factor for MTBE/MeOH=90/10 mixtures with varying PAA contents at 40℃.

Even though the selectivities were obtained fairly good through the whole experiments, the flux was too small to apply to the commercial step. In order to increase the flux, the composite membrane has to be considered. However, the present crosslinking temperature is so high enough that the porous structure in the support layer could be possibly collapsed during the composite membrane preparation. Therefore, the alternative of the membrane preparation to lower the crosslinking temperature will be shown in the next paper.

4. Conclusion

The pervaporation separation of MTBE-MeOH mixture was carried out using crosslinked PVA membranes with PAA as the crosslinking agent. The experiments were conducted at 30, 40, and 50℃ for MTBE/MeOH=95/5, 90/10, and 80/20 mixtures. When the PAA concentrations in the PVA/PAA membranes are varied from 5 to 25 wt.%, the flux shows the concave curve while the separation factor the convex curve. Above the range of 85 wt.% of PVA, the crosslinking degree and the hydroxyl group in PVA are more dominant effect for the separation characteristics. However, below that concentration of PVA, the hydrophobic/ hydrophilic balance takes an important role for the separation performance. In this case, PVA/ PAA=85/15 membrane showed

the highest separation factor, $\alpha_{MeOH/MTBE}$=4000 with the permeation rate, 10.1 g/m^2hr, for MTBE/MeOH=80/20 solution at 50℃. When the same membrane was used, the separation factor and permeation rate for MTBE/MeOH=90/10 solution at 40℃ showed $\alpha_{MeOH/MTBE}$=6000 and 8.5 g/m^2hr, respectively.

Acknowledgment

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