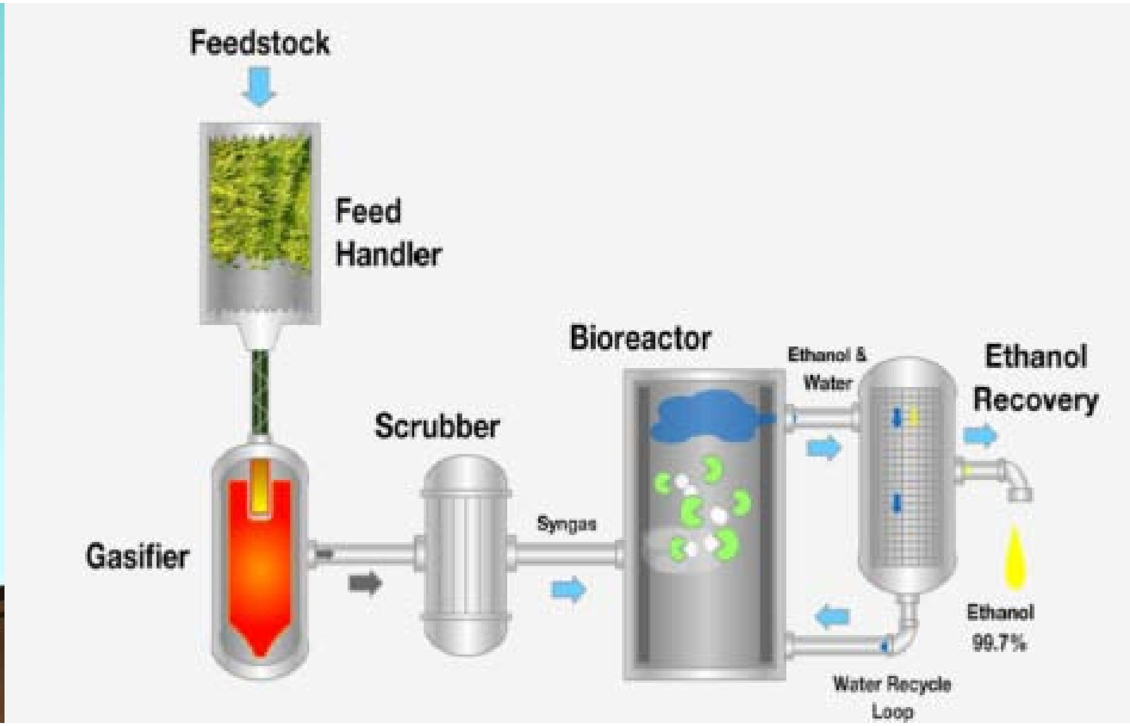
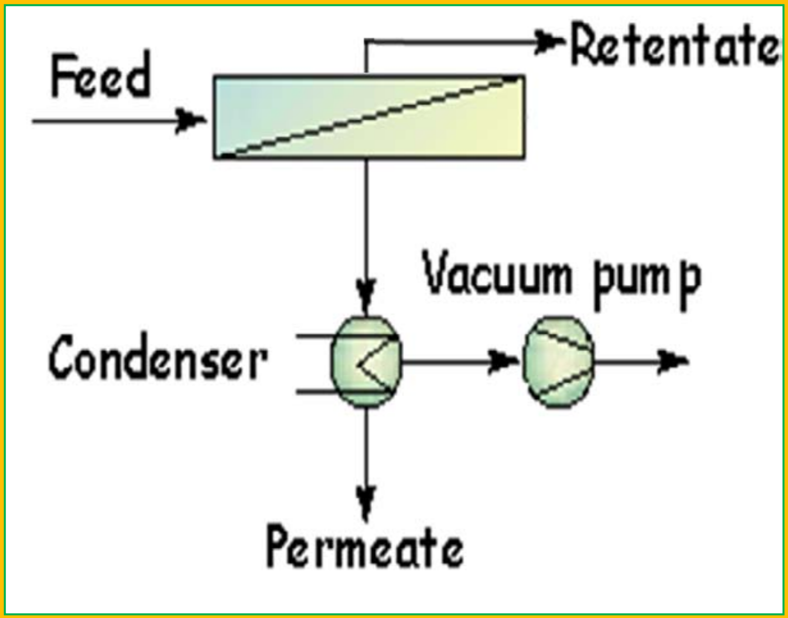
Pervaporation for ethanol concentration

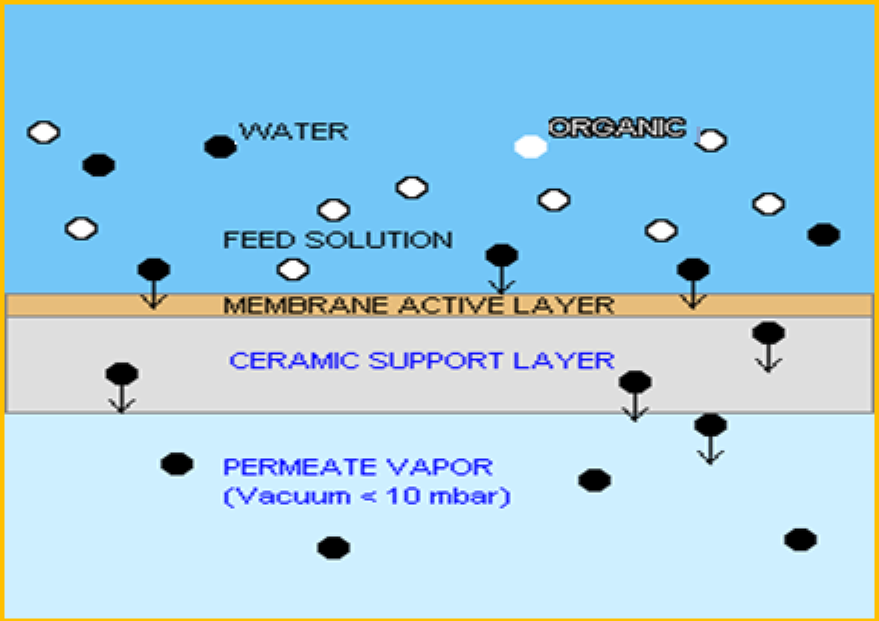
Introduction

- Anhydrous ethanol(99.5% purity) is used for blending with gasoline



Pervaporation





- **Pervaporation**

The driving force is the partial pressure difference of the feed and the permeate side.

- **Mechanism of pervaporation**

Selective sorption,
Selective diffusion through the membrane,
Desorption into a vapor phase on the permeate side

Membrane

- Preparation in poly(acrylonitrile-co-acrylic acid(AA)) membrane
- Pervaporation characteristics of ethanol/water mixtures
- Effect of the AA content in the membrane on flux and separation factor
- Effect of the ethanol content in feed on flux and separation factor

Experimentals

Chemicals

Acrylonitrile (AN), N,N-dimethylformamide(DMF), benzoyl peroxide(BPO), Acrylic acid(AA)

Copolymerization

AN	80 ℃ +	DMF	희석액
AA		BPO	개시제

C-membrane : 0.306 mole fraction of AA (Acrylic Acid)

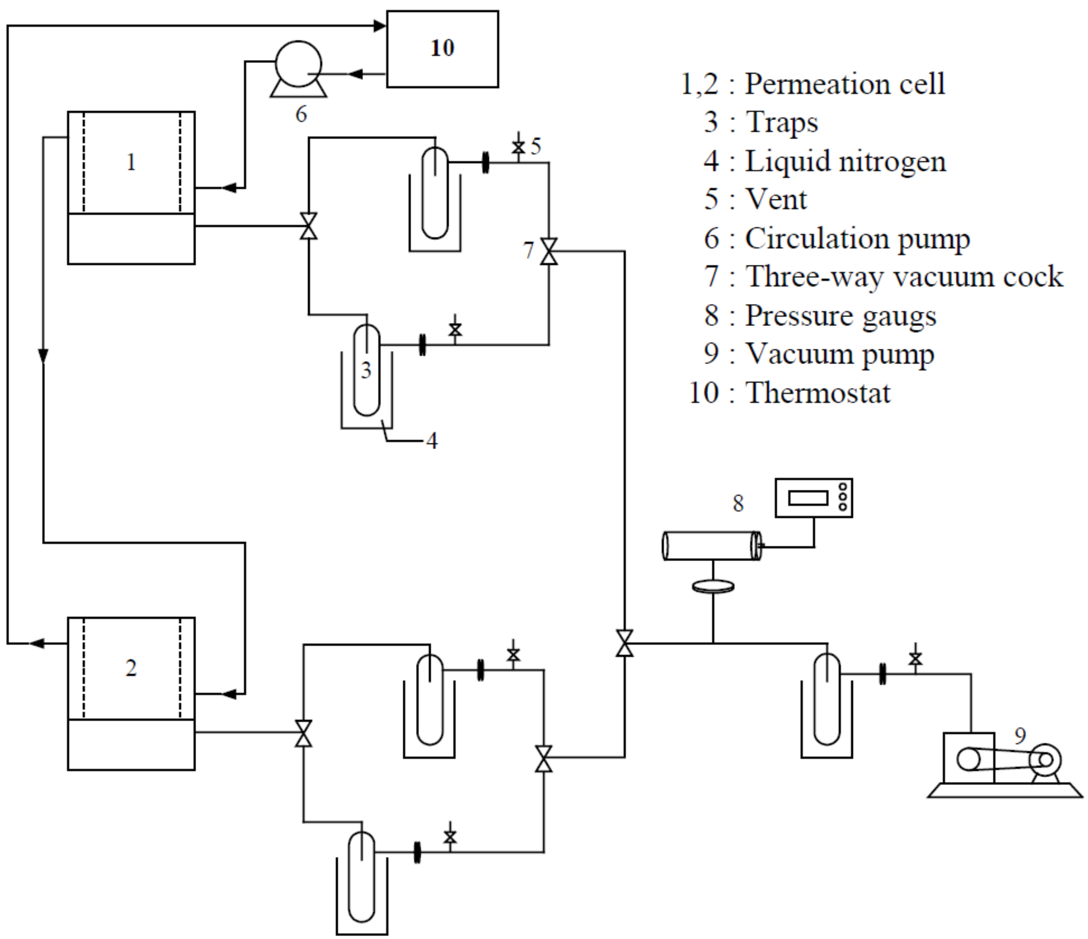
D-membrane : 0.370 mole fraction of AA (Acrylic Acid)

E-membrane : 0.424 mole fraction of AA (Acrylic Acid)

Film casting

copolymer solution	5 wt%.% poly (acrylonitrile-co-acrylic acid) in DMF
cast	3 mm solution
evaporation	At 70 ℃ in the 3 mmHg vacuum
Peeling	From the PE film
storage	In desiccator
measurement	Fischer Permascope →

Apparatus



1,2 : Permeation cell
3 : Traps
4 : Liquid nitrogen
5 : Vent
6 : Circulation pump
7 : Three-way vacuum cock
8 : Pressure gaugs
9 : Vacuum pump
10 : Thermostat

Fig. 1. Schematic diagram of the pervaporation apparatus.

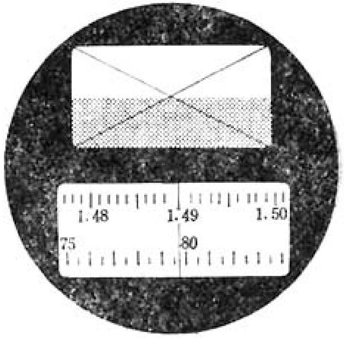
EtOH analysis

Refractive index

A calibration curve of refractive index versus ethanol weight percentage in solution was plotted by accurately weighing out mixture of the two liquids for each binary solution.

Approximate intervals of 10 wt.% were used for the calibration, and 11 points were plotted.

An Abbey refractometer manufactured by Bausch and Lomb was used. The refractometer prisms were maintained at 20 ± 0.5℃.



Results

Table 1
Molecular characteristics and permeate flux of pure water and ethanol

Components	L^a (Å)	V/L^a (Å^2)	δ^b (cal/cm^3)
	molecular length	cross section area	
Water	1.5	19.4	43.4
EtOH	4.2	23.1	12.7

Components	J_i^0 (g/(m^2 h))		
	C-membrane	D-membrane	E-membrane
Water	6.66	10.24	11.15
EtOH	64.85	78.29	86.24

이론

The permeate flux increased as the molecular length decreased for alcohols of similar cross section area.

실험

Water gives the smallest permeation flux among these permeating substances.

원인

" Water clusters "

Effect of AA contents

Table 2
Activation energies of pure water and ethanol through poly (acrylonitrile-co-acrylic acid)

Components	Activation energy (kcal/mol)		
	C-membrane	D-membrane	E-membrane
Water	6.08	4.23	3.82
EtOH	3.58	2.13	2.01

Membrane E, with the highest AA content had the smallest energy barrier, followed by membrane D, and then membrane C with the highest energy barrier.

It suggests that increasing the AA content in the copolymer structure and thus increases the size or number of holes formed in the copolymer membrane matrix available for the pervaporation of water or ethanol.

Meanwhile, increasing the AA content in copolymer also considerably lowers The degree of aggregation and H-bonding.

원인

"Reduce the tightness of the polymer structure"

Permeation flux

Total permeate flux

$$J = \gamma_{EtOH} C_{EtOH}^{feed} J_{EtOH}^{0} + \gamma_{H_2O} C_{H_2O}^{feed} J_{H_2O}^{0}$$

J_{EtOH}, J_{H_2O} : the permeate flux of pure ethanol and pure water.

C_{EtOH}^{feed}, $C_{H_2O}^{feed}$: the weight concentration in feed

γ_{EtOH}, γ_{H_2O} : the coefficients of deviation from ideal permeation behavior

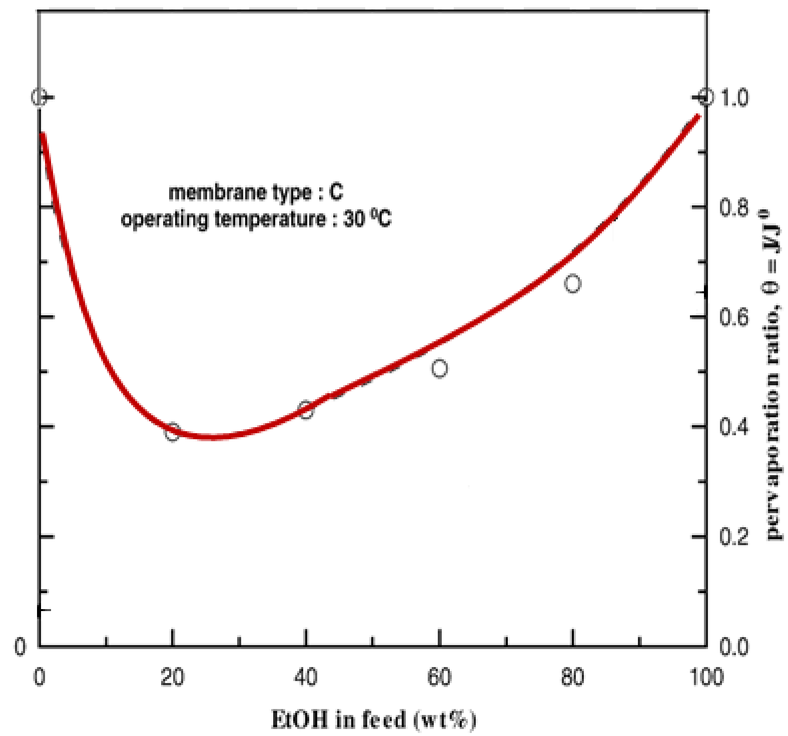


Fig. 3. Permeate flux and separation factor of ethanol aqueous solution through C-membrane at 30 °C.

$$\gamma_{EtOH} = \frac{J C_{EtOH}^{permeate}}{J_{EtOH}^{0} C_{EtOH}^{feed}} \qquad \gamma_{H_2O} = \frac{J C_{H_2O}^{permeate}}{J_{H_2O}^{0} C_{H_2O}^{feed}}$$

The total permeate flux of ethanol aqueous solution deviate negatively from the ideal permeation behavior.

Interference

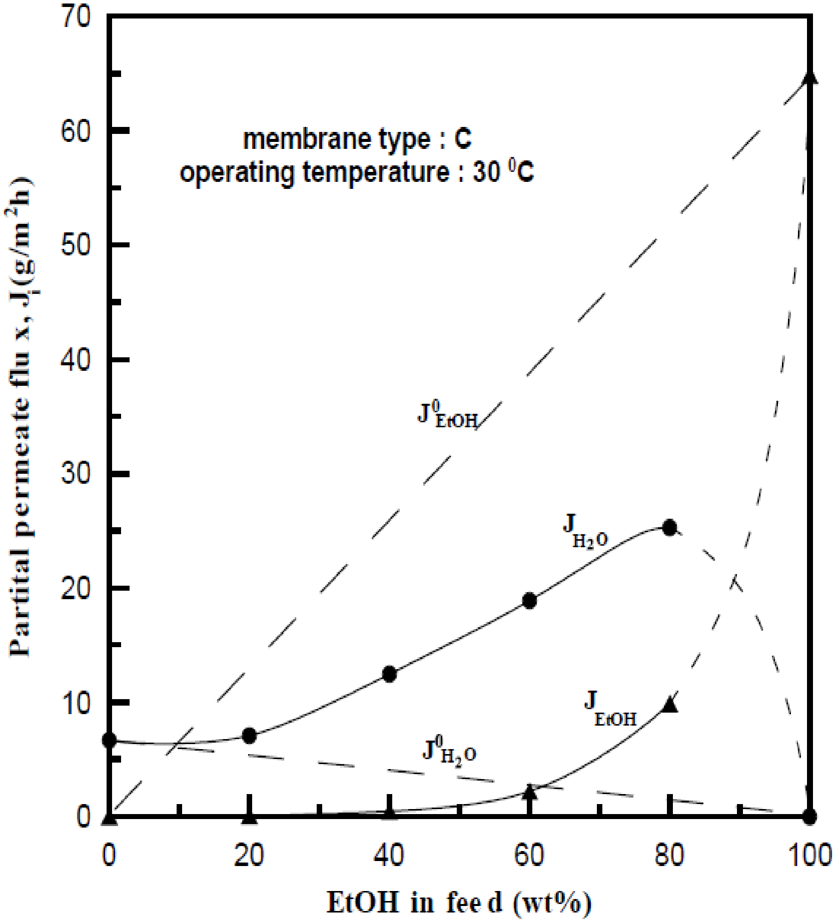


Fig. 4. The partial permeate flux of ethanol aqueous solutions through C-membrane at 30 °C.

The permeate flux of water in aqueous solution exceeds those of pure water,

The pervaporation of ethanol in aqueous solution through membrane is very much slower than that of pure ethanol pervaporation.

The ethanol molecules in the polymer membranes enhance the pervaporation of water, but on the contrary, water molecules in polymer membranes inhibit the permeation of ethanol molecules through these poly membranes.

Water cluster

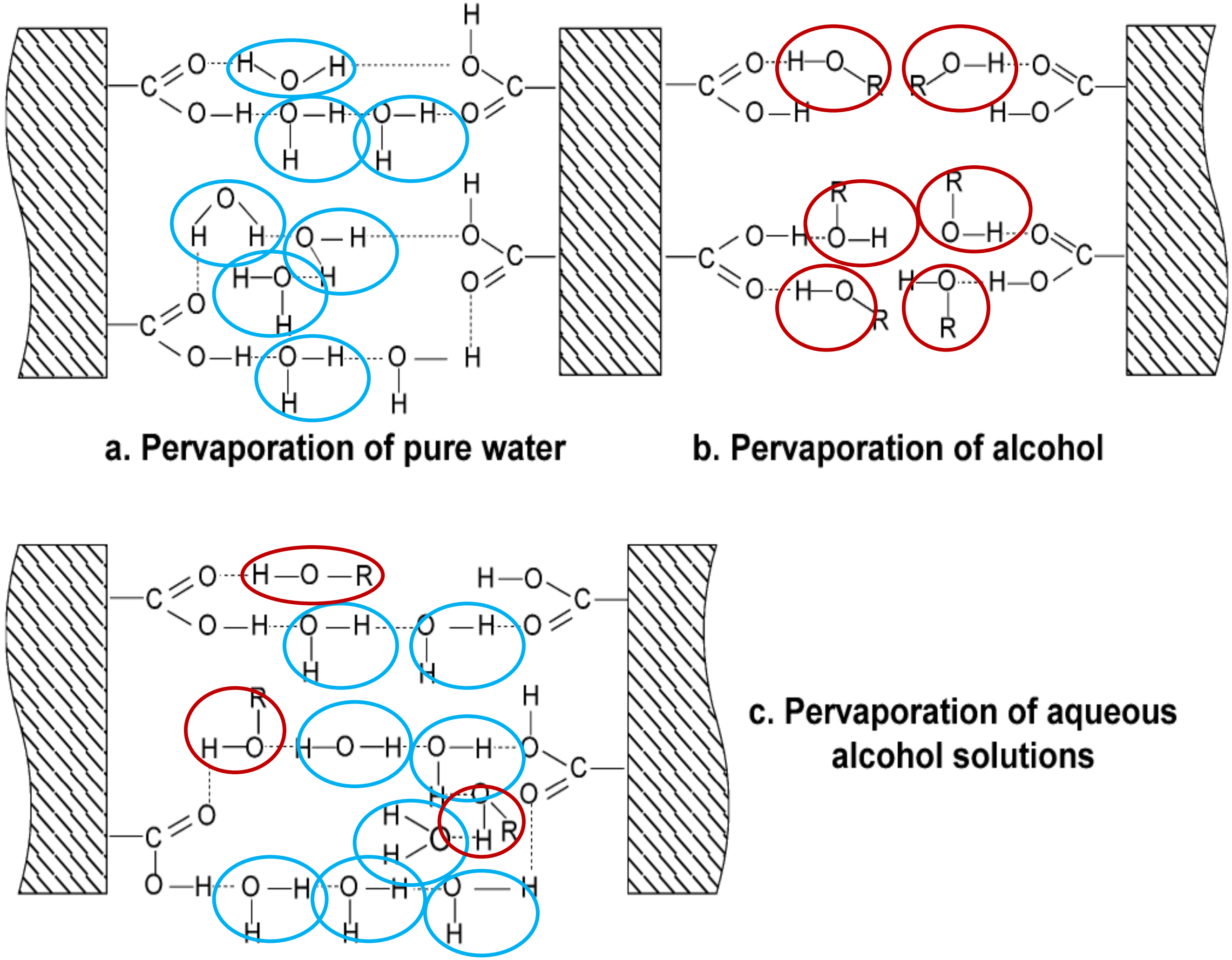


Fig. 5. Schematic picture for the interpretation of the possible interactions of the penetrating molecules within poly(acrylonitrile-co-acrylic acid) membranes.

Pervaporation equilibrium

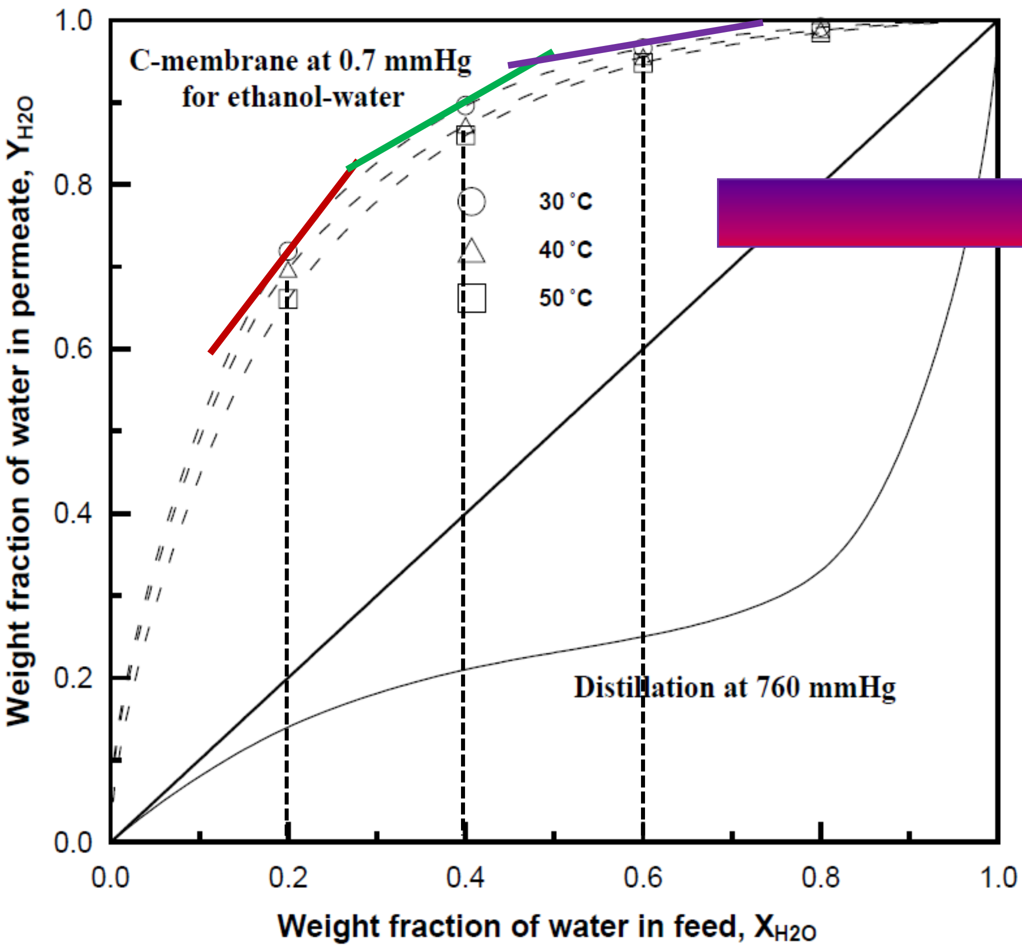
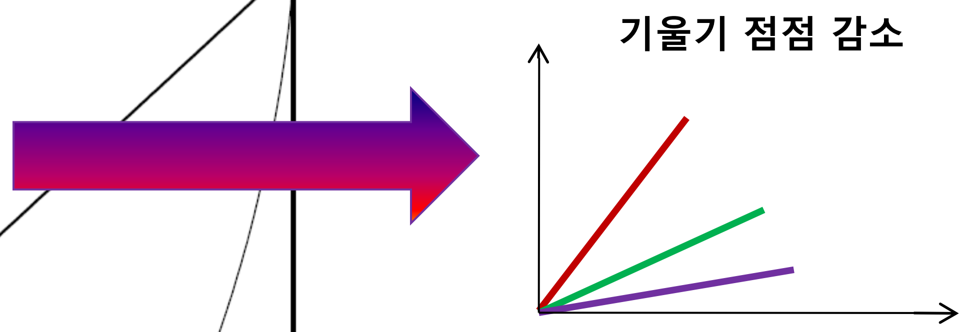


Fig. 6. Comparison of the equilibrium line of ethanol–water solution obtained by the pervaporation method and by the distillation method.



The separation of water from ethanol solution may be attributed to the formation of water clusters within membrane.

Separation factor

Table 4
Pervaporation performance data of ethanol–water mixture

Membrane type	EtOH in feed (wt. %)	Water/EtOH separation factor, β		
		30 °C	40 °C	50 °C
C	20	31	30.58	15.87
	40	18.6	14.21	12.21
	60	12.89	10.21	9.21
	80	10.23	9.2	7.8
D	20	24.95	15.37	12.9
	40	16	11.4	10.1
	60	11.54	9.21	8.3
	80	9.6	8.12	6.66
E	20	19	14.03	11.06
	40	14.8	10.12	8.6
	60	10.04	8.56	7.06
	80	8.8	7.53	5.4

Separation factor

$$\beta = \frac{C_{H_2O}^{\text{permeate}} / C_{\text{EtOH}}^{\text{permeate}}}{C_{H_2O}^{\text{feed}} / C_{\text{EtOH}}^{\text{feed}}}$$

All obtained values of exceeded one, indicating that the ethanol content in ethanol solutions can be effectively increased using polymer membranes and pervaporation technique.

Temperature Effect

Table 3
Data for permeate flux of ethanol–water mixture

Membrane Type	Thickness (μm)	EtOH in feed (wt.%)	Permeate flux ($g/(m^2 h)$) 30 °C	40 °C	50 °C
C	12.5	0	6.66	8.56	12.5
	13.5	20	7.14	9.92	14.49
	13.0	40	12.89	16.85	23.35
	14.5	60	21.07	30.48	36.58
	13.5	80	35.14	46.92	59.13
	13.5	100	64.85	79.03	93.79
D	13.5	0	10.24	12.53	15.87
	13.5	20	14.38	16.14	18.73
	14.0	40	20.47	22.29	26.14
	15.5	60	32.24	35.36	40.02
	14.5	80	50.61	55.18	64.89
	14.5	100	78.29	89.12	97.49
E	13.5	0	11.15	13.84	16.53
	13.5	20	16.74	19.16	22.47
	16.5	40	25.13	30.94	32.68
	13.0	60	38.77	45.02	51.32
	12.5	80	57.12	65.47	72.43
	13.5	100	86.24	97.31	106.05

Increasing the pervaporation temperature increases the permeate flux.

Temperature Effect

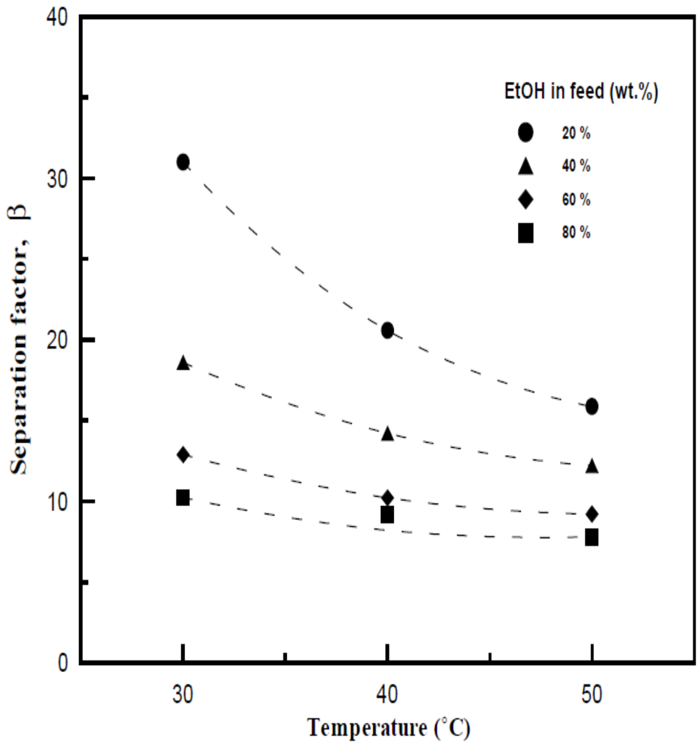


Fig. 8. The effect of temperature on the separation factor of ethanol–water solutions through C-membrane.

Increasing the temperature tends to increase the mobility of chain segments of the copolymer memvbrane and decreases the secondary interaction forces witin the membrane.

Reducing the degree of aggregation among these penetrating molecules within a membrane.

Composition of Feed

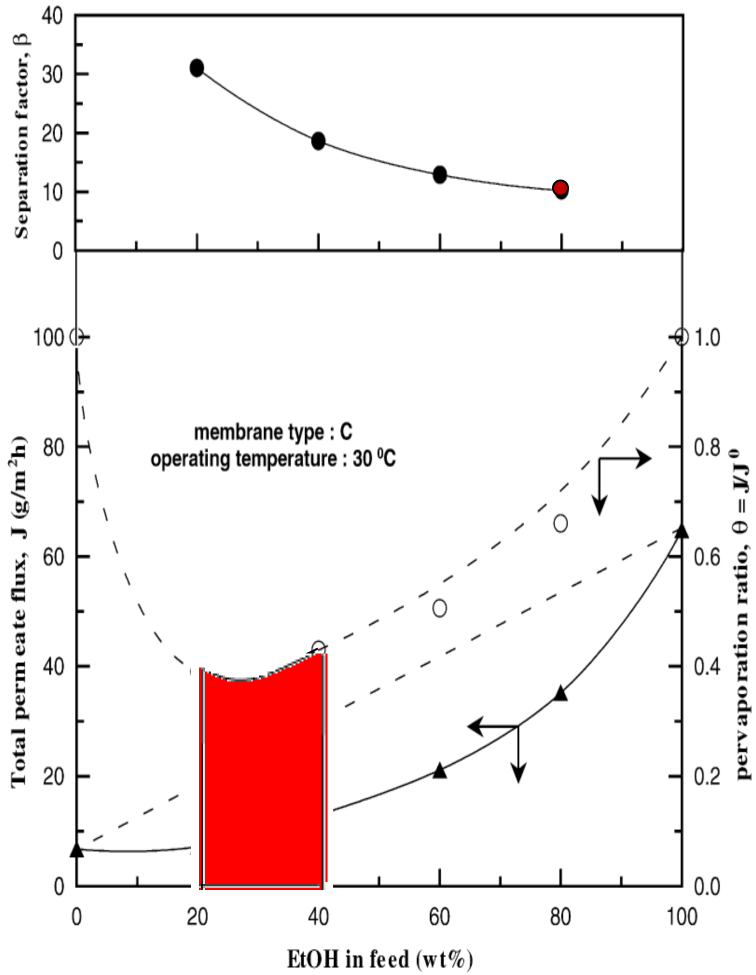


Fig. 3. Permeate flux and separation factor of ethanol aqueous solution through C-membrane at 30 °C.

The pervaporation ratios are minimal at a composition of approximately 20-40% ethanol, depending on the types of membrane and permeant.

The separation factor for the aqueous solution with high ethanol content was low

Because mainly effects of water clustering govern the rate and separation factor of pervaporation of solutions of less ethanol.
In contrast, the formation of water clusters in solutions of more ethanol is suppressed by competing interactions of ethanol and water with AA within the membrane

Composition of Feed

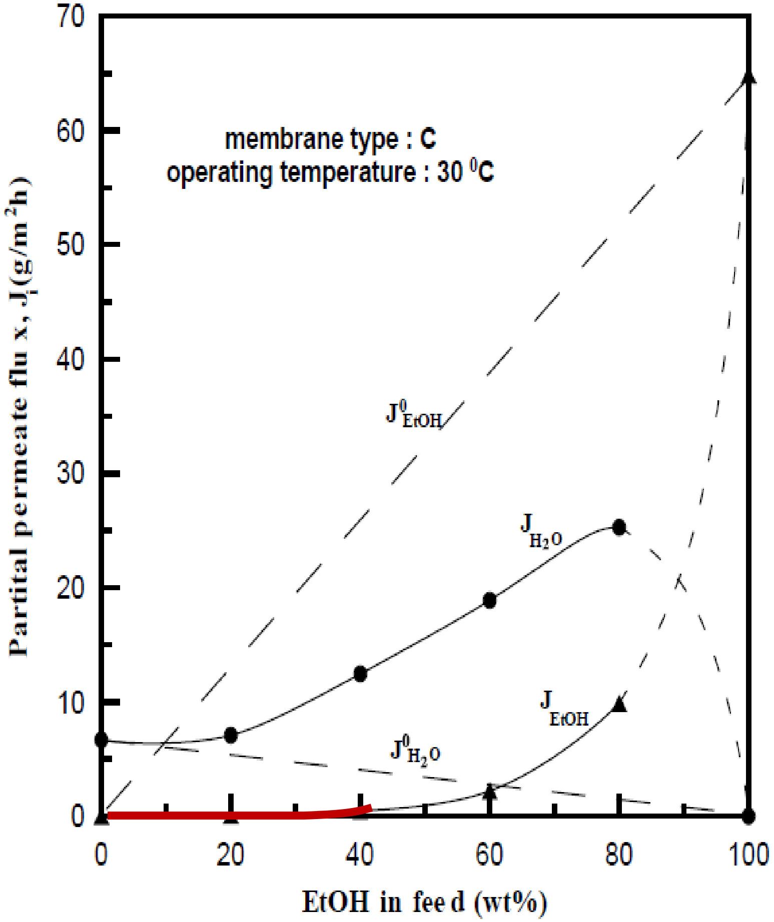


Fig. 4. The partial permeate flux of ethanol aqueous solutions through C-membrane at 30 °C.

The partial permeate flux drops drastically to near zero when the feed contains less than 40% ethanol.