

## Design and Optimization of Pervaporation Systems using Zeolite Membranes

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Zeolite NaA membrane displayed excellent water-permselective performance in pervaporation (PV) for water/organic liquid mixtures. The efficiency of double tube-type module, which is composed of a NaA membrane inserted in the steel tube, increases with an increase in the feed flow rate and exhibited 100% at Reynolds number > 1000. For dehydration plant of EtOH/H<sub>2</sub>O binary solution 30kg/h from 90 wt% to more than 99.8wt% at 120°C, the value for PV based on piston flow model approximately agreed with temperature and concentration measured at the module outlet. The improved module, which is the configuration that the necessary heat for evaporation of the permeate components can be directly supplied in the module by installing NaA membranes inside the tubes of a heat exchanger, was constructed. In comparison with the ordinary PV plant, the required membrane area of the module decreases about 15%. In addition, intermediate heat exchangers and the piping became unnecessary.

Key words: Zeolite NaA membrane, Pervaporation, Dehydration, Ethanol aqueous solution, Double tube-type module

### 1. INTRODUCTION

Pervaporation (PV) is an attractive means as an effective and energy-efficient technique for dehydration of water/organic mixtures [1]. Zeolite membranes offered significant potential for PV agent with high chemical and thermal stability. In order to purify isopropanol (IPA) from cleaning process in industries such as precision machinery and electronics, and to dehydrate ethanol (EtOH) used in food industry, PV plants using zeolite membranes (NaA or T-type) have been used practically [2,3]. In these PV plants, multi-stage systems with equal membrane area/stage using external heat exchangers have been adopted. Because of the relative high permeation flux in the higher water feed concentration range, the abrupt temperature drop of the feed liquid phase can be observed. Since the permeation flux decreases with decreasing temperature, it is advantageous to provide intermediate heating against the feed before entering the next stage. Maintaining maximum operation temperature throughout the whole system becomes an important prerequisite for an optimum performance and an effective reduction of the required membrane area. The stage means the number of heating for supplying the loss attributed to the PV process.

Recently, a dehydration plant of EtOH/H<sub>2</sub>O binary solution 30kg/h from 90wt% to more than 99.8wt% at 120°C using an iso-thermal module with zeolite NaA membranes was built and the PV plant has been working now. In this paper, the efficiency of double tube-type module using zeolite NaA membrane was measured with EtOH/H<sub>2</sub>O binary solution. In order to build the PV plant, multi-stage systems were discussed. As the results, the improved module, which is the configuration that the necessary heat for evaporation of the permeate can be directly supplied in the module by installing NaA membranes inside the tubes of a heat exchanger, was

used in the PV plant.

### 2. EXPERIMENTAL

#### 2.1 Zeolite NaA membrane and double tube-type module

Zeolite NaA membranes were grown hydrothermally on the surface of porous cylindrical mullite tubes (12mm outer diameter, 1.5mm thickness, 800mm length, 1.0 μm average pore size, 40 porosity). The details of preparation have been discussed elsewhere [4].

The molar composition of the starting gel was Al<sub>2</sub>O<sub>3</sub>:SiO<sub>2</sub>:Na<sub>2</sub>O:H<sub>2</sub>O=1:2:2:120. Hydrothermal synthesis was made at 373 K for 3.5 hours. Figure 1 shows the SEM microphotograph of the membrane. The surface of the mullite support is completely covered with NaA zeolite crystals. These crystals tend to be very closely bound together with little space between them. The membrane thickness was about 10 μm and the crystals are arranged randomly.

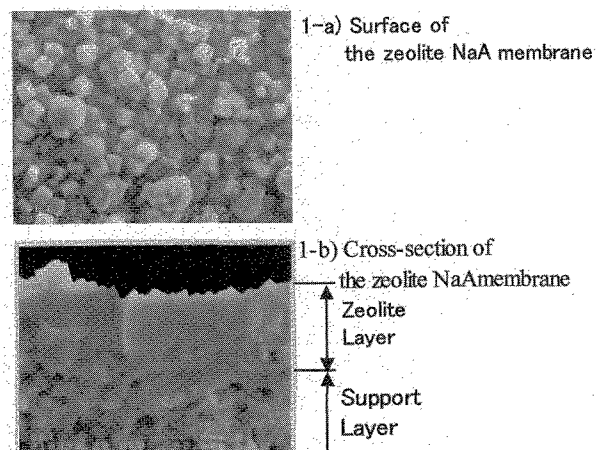


Figure 1 SEM Images of zeolite NaA membrane

The effect of the feed flow rate on a module performance was tested in PV unit containing a NaA membrane in a double tube-type module. The details of measuring device and a double tube-type module have been described elsewhere [5,6]. The double tube-type module is composed of a NaA membrane inserted in the steel tube (14.3mm inner diameter). The permeate is compressed to ambient pressure by mechanical booster pump with vacuum pump allowing the condensation at temperatures above the freezing point of the mixture. The permeate pressure was maintained at 0.133kPa. Experiments were carried out using a feed mixture composed of 10wt% water in EtOH at 120°C.

The compositions of the feed and permeate were determined by gas or liquid chromatography. Separation factor was defined by

$$\alpha = (y_{H_2O}/y_{EtOH}) / (X_{H_2O}/X_{EtOH})$$

where  $y_{H_2O}/y_{EtOH}$  is the weight ratio of water to ethanol in the permeate and  $X_{H_2O}/X_{EtOH}$  is that of water to ethanol in the feed.

## 2.2. PV plant

Figure 2 shows a flow scheme of the ordinary multi-stage PV system for dehydration of EtOH solution 30kg/h from 90wt% to more than 99.8wt% at 120°C.

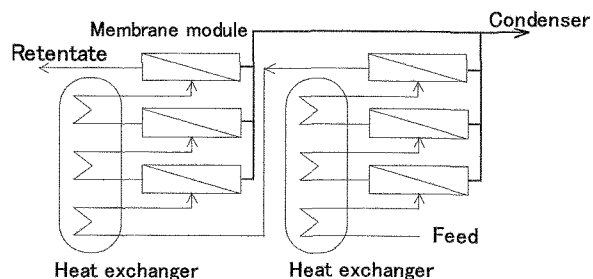


Figure 2 Flow diagram of the ordinary multi-stage PV system

For the purpose of an effective reduction of the required membrane area, 4 systems (adiabatic process, 2 multi-stage, iso-thermal process) were examined. The adiabatic process means the operation without intermediate heating. In multi-stage system using external heat exchangers, there are 2 configurations which are the equal membrane area/stage (multi-stage type 1) and the almost same temperature drop/stage (multi-stage type 2). The iso-thermal process uses the improved module, which installs NaA membranes inside the tubes of a heat exchanger, as shown in figure 3.

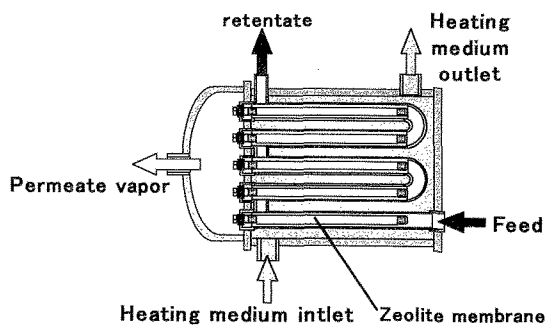


Figure 3 iso-thermal PV module

A minimum membrane area in a double tube-type module is 0.03m<sup>2</sup> (a NaA membrane). By connecting several modules, it is possible to make multi-stage type 1, or multi-stage type 2.

Temperature and concentration of the each module outlet for the plant operation were measured.

## 3. RESULT AND DISCUSSION

### 3.1. Double tube-type module performance

PV performance of the NaA membranes for water/organic mixtures is summarized in Table 1.

Table 1. PV performance of the NaA zeolite membrane for water / organic mixtures

Feed solution (A/B, wt% of A)	Temperature (°C)	Flux (kg·m <sup>-2</sup> ·h <sup>-1</sup> )	Separation Factor
Water / methanol (10)	50	0.57	1,800
	105	3.50	2,700
Water / ethanol (5)	75	1.10	3,300
Water / ethanol (10)	75	2.15	5,700
	105	4.68	7,200
Water / 2-propanol (10)	75	2.85	10,000

In the entire feed range of water/alcohol mixtures, the total permeation flux was substantially equal to the water flux, and alcohol flux was 10<sup>-3</sup> times less than water flux. With an increase in the water content, the total permeation flux increased initially linearly and then sublinearly and finally saturated. The water concentration in permeate was held very close to 100% for the whole range of the feed water concentration.

With increasing temperature, the water flux increased significantly, whereas alcohol flux hardly changed, and as the result separation factor increased. Thus the PV performance was much better at a higher temperature. The NaA membranes were highly water-permeable for these mixtures and displayed extremely high permeation fluxes and separation factors [7-10]. Table 2 shows PV properties of the membrane for water/ethanol mixture.

Figure 4 shows the dependence of the water flux  $Q_{H_2O}$  through the NaA membrane on the partial vapor pressure  $p_{H_2O}$  for water/organic mixtures [3].

Table 2. PV properties of the membrane for water/ethanol mixture

T [°C]	X <sub>BtOH</sub> [wt%]	Q <sub>H2O</sub> [kg/hm2]	α [-]
120	90	10.1	8.98*
	99	1.53	1.36*
110	90	6.89	6.50*
	99	0.997	0.978*
100	90	4.71	4.57*
	99	0.73	0.691*

\* Calculation using equations 1 and 2.

For water component in water/organic mixtures, the water flux  $Q_{H_2O}$  varied in proportion to partial pressure, as shown in equation 1. The partial vapor pressure  $p_{H_2O}$  in equilibrium with the feed solution and the partial vapor pressure  $p_{H_2O}$  of the permeate side are calculated

by Wilson's equation and Antoine's equation.

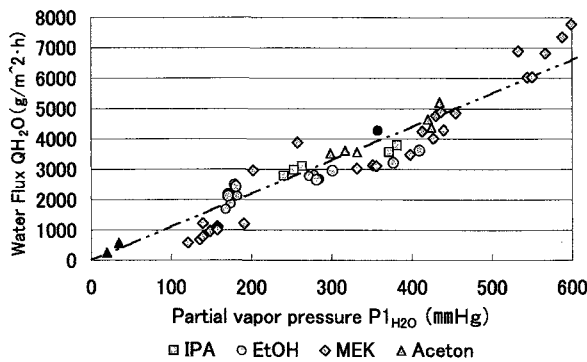


Figure 4. Dependence of the water flux  $Q_{H_2O}$

The partial vapor pressure  $p_{1H_2O}$  in equilibrium with the feed solution and the partial vapor pressure  $p_{2H_2O}$  of the permeate side are calculated by Wilson's equation and Antoine's equation. The ethanol flux  $Q_{EtOH}$  was correlated with water concentration  $X_{H_2O}$  and temperature  $T$  of the feed, using equation 2.

$$Q_{H_2O} = C_{H_2O} \cdot 13 \cdot (p_{1H_2O} - p_{2H_2O}) \approx C_{H_2O} \cdot 13 \cdot p_{1H_2O} \quad (1)$$

$p_{1H_2O} \gg p_{2H_2O}$

$$Q_{EtOH} = C_{EtOH} \cdot (-0.092 \cdot X_{H_2O}^2 - 0.023 \cdot X_{H_2O} + 3.34) \exp(-4100/(T+273.15) - 1/323.15) \quad (2)$$

Where  $C$  is module efficiency, and subscripts  $H_2O$  and  $EtOH$  denote water and ethanol, respectively.

The effect of feed solution flow velocity on the module efficiency is shown in figure 5. The module efficiency increased in proportion to the feed flow rate and exhibited 100% at Reynolds number (defined by  $(D-d) \cdot u / \nu$ ,  $D$  is inner diameter of the steel tube,  $d$  outer diameter of the membrane,  $u$  feed velocity and  $\nu$  kinetic viscosity of feed solution)  $> 1000$ .  $Re$  for the PV plant is about 1200, and the flow pattern on hydrodynamics is laminar flow.

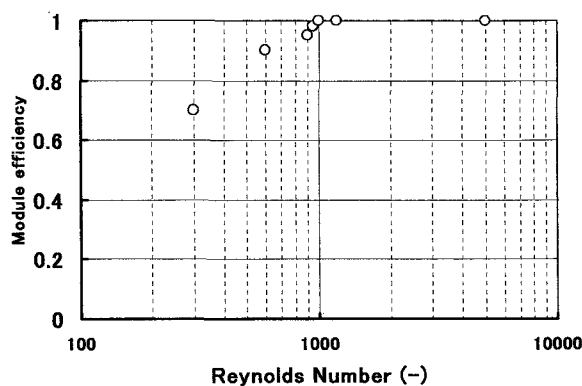


Figure 5 Effect of feed flow rate on module efficiency (evaluation: PV with 90wt% EtOH aqueous solution at 120°C)

These results suggest that in spite of laminar flow, diffusivities in the feed components is more sensitive than the permeation properties of the membrane at 120°C. As the result, concentration polarization and temperature polarization on PV plants might hardly have effect upon the membrane performance ( $C_{H_2O} = C_{EtOH} = 1$ ).

### 3.2. PV Plant

On the ordinary PV plants, the intermediate heating are provided for reduction of the required membrane areas before entering the next stage. With the view to reducing required membrane areas effectively, the experimental results were discussed using the piston flow model [11].

$$dM = (Q_{H_2O} + Q_{EtOH}) \cdot dS \quad (3)$$

$$d[T \cdot M \cdot (C_{pH_2O} X_{H_2O} + C_{pEtOH} X_{EtOH})] = (\lambda_{H_2O} \cdot Q_{H_2O} + \lambda_{EtOH} \cdot Q_{EtOH}) \cdot dS \quad (4)$$

Where  $C_p$  is specific heat,  $M$  feed mass flow rate,  $S$  membrane area, and  $\lambda$  latent heat.

Temperature and EtOH concentration profiles on the feed, which were calculated by simultaneous equations (1)~(4), are plotted against the membrane area in figure 6. Table 3 shows comparison of the calculated values with the experimental results on temperature and concentration of the final stage retentate for 4 systems. These results suggest that the piston flow model [11] could make an approximate estimate for temperature and concentration of the module outlet.

For multi-stage type 1, the relatively high permeation flux in the higher water feed concentration range, which is born in the early stage, produces the lower water concentration in the retentate. At the same time, the retentate liquid temperature decreases sharply in proportion to the PV heat of permeate components.

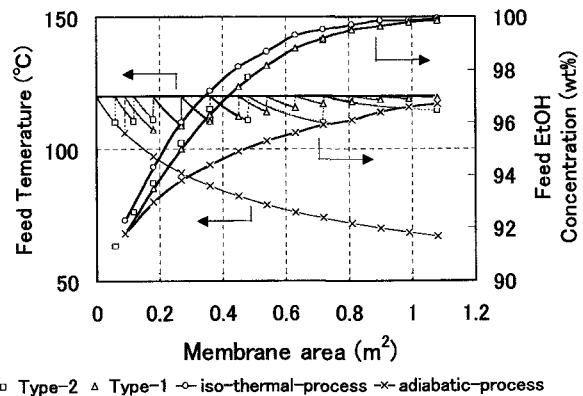


Figure 6. Multi-stage pervaporation system intermediate heating

Table 3. Stage number and membrane area required to dehydrate under 0.2wt%.

System	Final retentate		Stage		Membrane area (m <sup>2</sup> )	
	Temp (°C)	EtOH Conc (wt%)	No.			
adiabatic process	67.0*	66.8	97.3*	96.70	1	1.08
multi-stage Type 1	119.5*	119.5	99.86*	99.85	12	1.08
multi-stage Type 2	114.3*	114.7	99.84*	99.82	7	1.05
Iso-thermal process	120.0*	120.0	99.84*	99.82	1	0.93

\* Experimental value

The decreasing temperature of the retentate liquid brings on an increase in the required membrane area. On the other hand, the relatively low permeation flux in the lower water feed concentration range, which is born in the final stage, is low in dehydration compared with the

permeation flux of the early stage. At the same time, the retentate liquid temperature decreases little. In spite that the required membrane area for the lower water feed concentration range is almost the same as the one for the isothermal condition, intermediate heating is provided excessively. To dehydrate under 0.2wt%, the type 1 was composed of 12 stages and the total membrane area was 1.08m<sup>2</sup> (36 NaA membranes).

For multi-stage type 2 with the approximately same temperature drop (ca. 10 °C) per stage, required membrane area per stage should be increased with the lower water feed concentration range. To dehydrate under 0.2wt%, the type 2 was composed of 6 stages and the total membrane area of 1.05m<sup>2</sup> was required (35 NaA membranes).

For adiabatic process, temperature of the final retentate liquid lowered to 67 °C and the final water concentration reached only 3wt%.

For iso-thermal process using the improved module, the total membrane areas to dehydrate under 0.2 wt% were 0.93m<sup>2</sup> (31 NaA membranes). In comparison with the ordinary PV plant (multi-stage type 1), the required membrane area of the module decreases about 15% in order that the necessary heat for evaporation of the permeate components during PV process could be directly supplied by heating medium. In addition, intermediate heat exchanger and the piping became unnecessary. The PV plant with the improved module has been working now.

#### 4. CONCLUSION

(1) The efficiency of double tube-type module with 0.03 m<sup>2</sup> (a NaA membrane) increases with an increase in the feed flow rate and exhibited 100% at Reynolds number > 1000.

(2) For dehydration plant of EtOH/H<sub>2</sub>O binary solution 30kg/h from 90 wt% to more than 99.8wt% at 120 °C, the piston flow model could make an approximate estimate for temperature and concentration of the module outlet.

The total membrane areas of the dehydration plant were 1.08 m<sup>2</sup> for multi-stage type1, 1.05m<sup>2</sup> for multi-stage type 2, and 0.93 m<sup>2</sup> for iso-thermal process.

(3) The improved module, which is the configuration that the necessary heat for evaporation of the permeate components can be directly supplied in the module by installing the membranes inside the tubes of a heat exchanger, was constructed. In comparison with the ordinary PV plant, the required membrane area of the module decreases about 15%. In addition, intermediate heat exchangers and the piping became unnecessary.

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