

CHAPTER III EXPERIMENTAL

3.1 Materials

Fumed silicon dioxide (SiO_2 , $390\pm 40\text{m}^2/\text{g}$ surface area, $0.007\ \mu\text{m}$ average particle size, Sigma-Aldrich, Inc.) and aluminium hydroxide hydrate [$\text{Al}(\text{OH})_3 \cdot x\text{H}_2\text{O}$, $51\ \text{m}^2/\text{g}$ surface area, Sigma-Aldrich, Inc.] were used as starting materials. Sodium hydroxide (NaOH, Lab-Scan Analytical Sciences) was used as a base catalyst. Ethyl alcohol (ethanol, UN 1170, 99.5%) was purchased from J.T. Baker Solusorb. The tubular porous α -alumina support used in this work had an 11 mm O.D., a 9 mm I.D., a 6 cm length (with effective length, the distance of zeolite membrane in the pervaporation reactor, is 4.3 cm), and a $0.3\ \mu\text{m}$ pore radius on average with 38% porosity coated with an α -alumina intermediate ($0.06\ \mu\text{m}$ pore size) on the top layer and was obtained from the National (Thailand) Metal and Materials Technology Center (MTEC).

For simulating pervaporation system and azeotropic distillation system, Pro II with PROVISION version 8.0 was used to obtain the total amount of energy required for purification of ethanol to reach 99.5%wt, total ethanol production rate, total stage of each distillation column, and total amount of membrane surface area for the pervaporation system.

3.2 Materials Characterization

Powder X-ray diffraction (XRD) patterns were carried out using a Rigaku X-ray diffractometer with CuK_α as a source in a range from 5° to 50° with a step of $2^\circ/\text{min}$. The morphology of NaA zeolite membranes was carried out by a field emission scanning electron microscope (FE-SEM, Hitachi/S-4800). Hydrothermal crystallization by microwave heating technique was carried out using Milestone's Ethos Microwave Solvent Extraction Lab-station. The frequency of the microwave radiation was 2.45 GHz. Hydrothermal crystallization by autoclave heating technique

was carried out using a SANYO-Gallenkamp vacuum oven. An EDWARDS LS63P vacuum pump was used in the pervaporation unit. The separated water-ethanol products were analyzed using an Agilent Technologies 6890N gas chromatography (GC) equipped with an HP-Plot/Q capillary column and a TCD detector. About 0.5 μL of the samples was injected under the following conditions: the helium used as the carrier gas was set at 55 kPa, the oven temperature was set at 473K, while the injector and detector temperatures were set at 473 K and 523 K, respectively.

The performance of NaA zeolite membrane was evaluated in term of total water flux ($\text{kg}/\text{m}^2/\text{h}$) and separation factor (dimension less).

Total water flux (J) is expressed as:

$$J = W / [A \cdot t] \quad (\text{I})$$

Separation factor (α) is expressed as:

$$\alpha = [X_{\text{H}_2\text{O}}/X_{\text{EtOH}}]_{\text{perm}} / [X_{\text{H}_2\text{O}}/X_{\text{EtOH}}]_{\text{reten}} \quad (\text{II})$$

3.3 Precursor Preparation

In this study, NaA zeolite powder was synthesized using alumatrane and silatrane precursors synthesized, following Wongkasemjit *et al.* (Opornsawad *et al.*, 2001; Piboonchaisit *et al.*, 1999).

3.3.1 Alumatrane Synthesis (Opornsawad *et al.*, 2001)

The preparation of alumatrane or tris(alumatranxyloxy-*i*-propyl)amine, was carried out by mixing aluminium hydroxide 0.1 mole, TIS 0.125 mole and ethylene glycol (EG, 100 mL) in a 250 mL two-necked round bottom flask. The mixture was homogeneously stirred at room temperature before being heated to 200 °C under nitrogen in an oil bath for 10 h. Excess EG was removed under vacuum at 110 °C in order to obtain the crude product. The crude solid was washed with acetonitrile, dried under vacuum at room temperature, and characterized using TGA and FTIR.

3.3.2 Silatrane Synthesis (Piboonchaisit *et al.*, 1999)

0.1 Mole fumed silica, 0.125 mole triethanolamine were mixed in a 250 mL two-necked round bottom flask containing 100 mL EG. The mixture was heated at 200 °C under nitrogen for 10 h in oil bath. The rest of EG was removed under vacuum at 110 °C. The brownish white solid was washed with acetonitrile in order to obtain the white powder and dried under vacuum at room temperature before characterization using TGA and FTIR.

3.3.3 NaA Zeolite Seed Solution Synthesis (Kuanchertchoo *et al.*, 2007)

The preparation of NaA zeolite powder was conducted using the molar composition $50\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:5\text{SiO}_2:1000\text{H}_2\text{O}$. The NaA seed crystal solution was prepared by dispersing about 7 g of NaA zeolite (0.5 μm pore size an average) in 1000 mL of water.

3.4 NaA Zeolite Membrane Preparation

The preparation of NaA zeolite membranes started with the seeding technique by coating NaA seed crystal on the surface of the tubular alumina support using vacuum seeding at 10 mmHg (1.333 kPa) for 2 min, followed by drying at 333 K for 24 h.

The seed coated tubular alumina support was placed in a Teflon vessel containing the NaA zeolite solution prepared using the $50\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:5\text{SiO}_2:1000\text{H}_2\text{O}$ formula (Li *et al.*, 2006; Li *et al.*, 2006; Veen *et al.*, 2001) before placing the vessel in the autoclave, microwave, or electrophoretic apparatus. The synthesis conditions are summarized in Table 1. The coated NaA zeolite membranes were washed with deionized water and dried at 343 K for 24 h before pervaporation testing.

Table 3.1 Synthesis conditions for microwave membranes (MWMs), autoclave membranes (ACMs), and electrophoretic membranes (EPMs).

Condition for synthesis	MWMs	ACMs	EPMs
Temperature (K)	363	333	333
Time (hour)			
First time	0.333	10	10
Second time	0.167	10	10

3.5 Pervaporation System for Water-Ethanol Separation

The pervaporation system was kept constant at 343 K. A circulation pump (Masterflex) was used to pump the water-ethanol ratio of 10:90 with the 510 mL total amount of throughput from the heat tank to the pervaporation unit. The permeate was collected in the vessel, cooled by using the liquid nitrogen, to calculate the total water flux ($\text{kg/m}^2/\text{h}$) and the separation factor (dimensionless). An EDWARDS LS63P vacuum pump equipped with the pervaporation unit was used at the permeate side and kept pressure constant at 10 mmHg.

The total water flux and the separation factor were used to determine the performance of the synthesized NaA zeolite membrane in pervaporation units, calculated by using eq. I and II.

3.6 Techno-economics Simulation

The techno-economics comparison between the azeotropic distillation system and the hybrid system was studied by using PRO II simulation program; we assumed that 1000 kg/h of water-ethanol mixture (50%wt of ethanol and 50%wt of water) was used as a feedstock to produce 99.5% ethanol. The temperature and the pressure of the initial feedstock were set at 298 K, 1 atm for the azeotropic distillation system and 343K, 1 atm for the pervaporation unit in the hybrid system. For the practical azeotropic distillation system, distillation column followed by azeotropic distillation

was used to produce 99.5% ethanol. For the hybrid system, the distillation column followed by the pervaporation system, using NaA zeolite membrane, was used to produce 99.5% ethanol.