



## Optimization of synthesis time for high performance of NaA zeolite membranes synthesized via autoclave for water–ethanol separation

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### ABSTRACT

Membrane separation process using NaA zeolite membrane is a good alternative process for ethanol production in terms of both energy consumption and environmental friendliness. However, the highest cost for the membrane separation process is from the membrane production step. The reduction of the membrane production cost by optimization of the synthesis time is, thus, necessary to the cost-effective production of ethanol production. The main focus of this work is to obtain NaA zeolite membranes synthesized on a tubular alumina support using a conventional heating or autoclave technique. Effect of the synthesis time on the performance of the membrane for water–ethanol separation via pervaporation at 343 K is studied. It is found that the optimum synthesis time to produce a high purity of ethanol (>99.5% by volume) is only 13 h with a total water flux and separation factor of 2.82 kg/m<sup>2</sup>/h and >10,000, respectively. The thickness of the membrane obtained is around 7–9 μm. The overall results and the reproducibility of the membranes are discussed.

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### 1. Introduction

Pervaporation is a method that is used to separate liquid mixture by partial vaporization through either non-porous or porous membranes. Non-porous membranes, such as organic polymer membranes, provide several disadvantages, such as swelling, low separation factor, and a low resistance to solvent and high temperature [1,2]. These drawbacks can be overcome by using ceramic membranes, such as NaA zeolite membranes. Sodium A zeolite (NaA) is very well known in organic–water separation and catalysis [1–4]. Especially in the separation area, a tubular NaA zeolite called “Tubular NaA zeolite membrane” is the most favorable material synthesized on the surface of tubular alumina (Al<sub>2</sub>O<sub>3</sub>) support [5]. The properties of the tubular NaA zeolite membranes include a high thermal and chemical stability, high mechanical strength, and uniform pore size distribution [1,6–9]. NaA zeolite membrane can be synthesized by various methods, such as hydrothermal [10–15], microwave [16–18], or electrophoretic technique [19,20]. Its pore size is around 0.4 nm, which is suitable for separating water from ethanol mixture because the kinetic diameters of water and ethanol are around 0.3 and 0.42 nm,

respectively. Thus, water molecules can easily penetrate through the pores of the membrane and be separated out of the mixture.

Navajas et al. [15] found a decrease in the separation factor as synthesis time was decreased. Negishi et al. [21] described the effect of the synthesis time by prolonging the synthesis time from 20 to 80 h and found that the membrane thickness increased to around 20 μm. Similar to the work done by Malekpour et al. [22], they investigated not only the effect of synthesis time on the zeolite membrane thickness, but also the effect of zeolite thickness on the performance of zeolite membrane. They found that the water flux of a pervaporation system decreased with an increase in the membrane thickness. Furthermore, Kalyaniet et al. [23] also showed the membrane performance increased with a decrease in the membrane thickness. In terms of techno-economics for industrial usage, a higher permeate flux of the membrane for the ethanol production is more preferable for its shorter production time and lower energy consumption. In this study, a successfully developed and reproducible NaA zeolite membrane – with a shorter synthesis time to achieve higher than 99.5% by volume purity and a higher production rate of ethanol, considerably lowering a membrane production cost – was illustrated using a recycle-continuous pervaporation system. A better understanding of the effect of synthesis time on the performance of NaA zeolite membrane was also discussed. Moreover, two cycles of the pervaporation test were conducted to determine not only the stability of the membrane, but also the reproducibility of our home-made NaA zeolite membrane.

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## 2. Experimental

### 2.1. Materials

Fumed silicon dioxide ( $\text{SiO}_2$ ,  $390 \pm 40 \text{ m}^2/\text{g}$  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  $\alpha$ -alumina support used in this work had an 11 mm O.D., a 9 mm I.D., a 6 cm length (with effective length, or the distance of the zeolite membrane in the pervaporation reactor, of 4.3 cm), and a  $0.3 \mu\text{m}$  pore radius on average with 38% porosity coated with an  $\alpha$ -alumina intermediate ( $0.06 \mu\text{m}$  pore size) on the top layer. The support material was obtained from the National (Thailand) Metal and Materials Technology Center (MTEC).

### 2.2. NaA zeolite seed solution synthesis

The preparation of NaA zeolite seed was conducted using the molar composition of  $50\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:5\text{SiO}_2:1000\text{H}_2\text{O}$  [24]. The NaA seed crystal solution was prepared by dispersing 7 g of the seed, having a particle size of approximately  $0.5 \mu\text{m}$ , in 1000 mL of water.

### 2.3. Support preparation

A tubular porous alumina support was twice washed in deionized water for 15 min to remove dirt from the surface [12,16], dried in a vacuum oven at 363 K for 24 h, and calcined in a furnace at 400 K for 3 h to eliminate any impurities on its surface. The unsoiled tubular alumina support was placed in a vacuum seeding system containing the NaA seed crystal solution for 2 min at 10 mmHg (1.333 kPa), followed by drying at 333 K for 24 h to obtain the seed coated tubular alumina support.

### 2.4. NaA zeolite membrane synthesis

The seed-coated tubular alumina support was placed in a Teflon vessel containing 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 [3,18,25,26] before placing the vessel in the autoclave (AC) apparatus. The synthesis conditions are summarized in Table 1. To improve the formation of tubular NaA zeolite membranes on the alumina support, each membrane was synthesized twice (double-stage synthesis). The first synthesis time was to generate NaA zeolite crystals on the tubular alumina support, while the second synthesis time was to improve the NaA zeolite membrane on the support and to decrease any defects from the first incomplete synthesis. The coated NaA zeolite membranes were washed with deionized water and dried at 343 K for 24 h prior to the pervaporation testing.

### 2.5. Pervaporation

The pervaporation system was set up, following our previous work [26]. The mixture used in this work was prepared using a 10:90 water:ethanol mixture with a total amount of throughput of 570 mL. The experiments were carried out at 343 K with 10 mmHg on the

permeate side with an optimum mixture flow rate by measuring the amount of ethanol on the retentate side. The quantities of ethanol and water were determined using a gas chromatograph (GC). For each membrane, the recycle-continuous pervaporation process was applied for 2 to 3 cycles to determine the membrane stability.

### 2.6. Equipment

Autoclave NaA zeolite membranes (ACMs) were synthesized 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 6890 N GC equipped with an HP-Plot/Q capillary column and a TCD detector. About  $0.5 \mu\text{L}$  of the samples was injected under the following conditions: helium was used as the carrier gas with a carrier gas flow rate of 55 kPa, and the oven temperature was set at 473 K, while the injector and detector temperatures were set at 473 and 523 K, respectively. The morphology of the NaA zeolite membranes was analyzed using a field emission scanning electron microscope (FE-SEM, Hitachi/S-4800). The *t*-test function (TTEST) using Microsoft Excel program, version 2007, was used to determine the statistical data in terms of performance for ACMs for water-ethanol separation in the pervaporation system.

## 3. Results and discussion

### 3.1. NaA zeolite membranes

Various synthesis times, viz. 20, 15, 13, and 11 h, denoted as ACMs-1, ACMs-2, ACMs-3, and ACMs-4, respectively, were studied for synthesizing NaA zeolite membranes by AC technique, as summarized in Table 1. All synthesized NaA zeolite membranes, except ACMs-4 synthesized for 11 h, showed homogeneous coating and good distribution on the surface of the membranes, as shown in Fig. 1. ACMs-4 (Fig. 1g) did not provide good-intergrowths of NaA zeolite on the support surface like the others. The main reason is possibly that the synthesis time of 11 h was not sufficient to completely coat the NaA zeolite crystal on the support surface. As can be seen from Figs. 1b), 1d), and 1f), denser of NaA zeolite membranes were observed when the synthesis time was increased, consistent with Navajaset al. [15], who studied the effect of synthesis time on the separation factor and found the separation factor of the water-ethanol system decreased to less than 10,000 when synthesis time was decreased from 24 to 2 h. Yuan et al. [27] also studied the morphology of NaA zeolite affecting the performance of zeolite membrane for the water-ethanol separation and found that the performance of NaA zeolite membrane was very poor when the good-intergrowth of NaA zeolite was not observed. Similar to our case (Fig. 1g) for the zeolite synthesized for the shortest time period, the well-intergrowth of zeolite was hardly observed, causing this membrane to have a separation factor lower than 10,000.

The thickness of the synthesized NaA zeolite membranes increased with the synthesis time from ACMs-3 (13 h) to ACMs-1 (20 h), consistent with our previous work [19] and the works studied by Negishi et al. [21] and Nikolakis et al. [28], indicating that the increase of the synthesis time has a significant effect on the thickness of the membranes. However, in our case, the time required for the synthesis of uniform and homogeneous NaA zeolite coating on the alumina support was shorter with remarkable performance, as discussed in more detail in the next section, than those reported elsewhere [19,21,28].

### 3.2. Performance of NaA zeolite membranes

The performance of the synthesized NaA zeolite membranes was determined in terms of total water flux ( $\text{kg}/\text{m}^2/\text{h}$ ) and separation

**Table 1**  
Synthesis time for synthesis of autoclave membranes (ACMs) at 333 K.

Synthesis time (h)	ACMs-1	ACMs-2	ACMs-3	ACMs-4
First time	10	10	10	8
Second time	10	5	3	3

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