CHAPTER VI

OPTIMIZATION OF SYNTHESIS TIME FOR HIGH PERFORMANCE OF NAA ZEOLITE MEMBRANES SYNTHESIZED VIA AUTOCLAVE FOR WATER–ETHANOL SEPARATION

6.1 Abstract

NaA zeolite membrane is synthesized on a tubular alumina support by conventional heating or autoclave technique (ACMs). Effect of synthesis time on the performance of the membrane for water–ethanol separation via pervaporation at 343K is studied. It is found that the optimum synthesis time to produce high purity of ethanol (> 99.5% by volume) is 13 h with a total water flux and separation factor of 2.82 $kg/m^2/h$ and >10,000, respectively. The thickness of membrane obtained is around 7–9 μm. The overall results and the reproducibility of the membranes are discussed.

6.2 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]. Those 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, tubular NaA zeolite is the most favorable material synthesized on the surface of tubular alumina (Al_2O_3) support, and called "Tubular NaA zeolite membrane" [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 alcohol 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.

From the techno-economic point of view, the performance of NaA zeolite membrane used in the pervaporation system should be improved to reduce the cost of the operating system by improving the total water flux and/or the size of the membrane. In this study, we presented a successfully developed and reproducible NaA zeolite membrane with a shorter synthesis time to reduce the cost of the membranes. A remarkable performance of the NaA zeolite membranes, synthesized for a much shorter time to achieve higher than 99.5% by volume purity and a high production rate of ethanol, were illustrated by using a recycle-continuous pervaporation system. Moreover, two cycles of the pervaporation test were conducted to determine the stability of the membrane.

6.3 Experimental

6.3.1 Materials

Fumed silicon dioxide (SiO$_2$, 390±40m^2/g surface area, 0.007 μm average particle size, Sigma-Aldrich, Inc.) and aluminium hydroxide hydrate [Al(OH)$_3$.xH$_2$O, 51 m^2/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, or the distance of the zeolite membrane in the pervaporation reactor, of 4.3 cm), and a 0.3 μm pore radius on average with 38% porosity coated with an α-alumina intermediate (0.06 μm pore size) on the top layer. The support material was obtained from the National (Thailand) Metal and Materials Technology Center (MTEC).

6.3.2 NaA zeolite seed solution synthesis

The preparation of NaA zeolite seed was conducted using the molar composition of $50Na_2O:Al_2O_3:5SiO_2:1000H_2O$ [21]. The NaA seed crystal solution was prepared by dispersing 7 g of the seed, having a pore size of approximately 0.5 μm, in 1000 mL of water.

6.3.3 Support preparation

A tubular porous alumina support was cleaned by washing twice 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 60 K for 24 h to obtain the seed coated tubular alumina support.

6.3.4 NaA zeolite membrane synthesis

The seed-coated tubular alumina support was placed in a Teflon vessel containing NaA zeolite solution prepared using the $50Na_2O:Al_2O_3:5SiO_2:1000H_2O$ formula [3,18,22-23] before placing the vessel in the autoclave (AC) apparatus. The synthesis conditions are summarized in Table 6.1. The coated NaA zeolite membranes were washed with deionized water and dried at 343 K for 24 h prior to the pervaporation testing.

6.3.5 Pervaporation

The pervaporation system was set up, following our previous work [23]. The mixture used in this work was prepared using a 10:90 water:ethanol with the total amount of throughput of 570 mL. The experiments were carried out at 343 K with 10 mmHg at the permeate side with an optimum mixture flow rate by measuring

the amount of ethanol at 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.

6.3.6 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 6890N 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 and the oven temperature was set at 473K, while the injector and detector temperatures were set at 473 and 523K, respectively. The morphology of NaA zeolite membranes was analyzed using a field emission scanning electron microscope (FE-SEM, Hitachi/S-4800).

6.4 Results and discussion

6.4.1 NaA zeolite membranes

NaA zeolite membranes synthesized by AC technique for various synthesis times are summarized in Table 6.1. 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 Figure 6.1. The thickness of the synthesized NaA zeolite membranes was increased with the synthesis time from ACMs-3 to ACMs-1, consistent with our previous work [19] and that of Nikolakis *et al* [24], indicating that the synthesis time indeed has a significant effect on the thickness of membranes. However, in our case, the time required for the synthesis of a uniform homogeneous coating and distribution of NaA zeolite was shorter than those reported elsewhere [19, 24].

6.4.2 Performance of NaA zeolite membranes

The performance of the synthesized NaA zeolite membranes was determined in terms of total water flux ($kg/m^2/h$) and separation factor. The total water flux (J, $kg/m^2/h$) of the system can be calculated by using eq. 1;

$$J = W/[A*t] \qquad (1)$$

where W is the water permeate (kg), A is the membrane area (m^2), and t is the permeation time (h). The total water flux is used to determine the amount of water molecules that passed through the membranes to the permeate side. A high total water flux is generally an indicative of a good membrane.

Separation factor (α, dimensionless) can be calculated by using eq. 2;

$$\alpha = \frac{\left[X_{EtOH}/X_{H_2O}\right]_{perm}}{\left[X_{EtOH}/X_{H_2O}\right]_{reten}} \qquad (2)$$

where X_{EtOH} and X_{H2O} are the molar fractions of ethanol and water, respectively. The subscripts of perm and reten represent the permeate and the retentate sides in a period of time, respectively. The separation factor is an indicator that determines how efficient a membrane is in separating water from an ethanol–water mixture.

In this work, as summarized in Table 6.2, the results indicate that the total water flux increased as the membrane thickness decreased. The highest total water flux was undoubtedly obtained from the lowest membrane thickness of ACMs-3 synthesized for 13 h, with the separation factor remaining higher than 10,000 throughout the reaction, as shown in Figures 6.2 and 6.3 [23, 25]. Compared to our previous work [23], the separation factor maintained a very high level, higher than 10,000, throughout the reaction testing time and is much better. Nevertheless, unlike our study using a 10:90 water:ethanol mixture, Kittur et al. [25] showed that the separation factor could be increased to higher than 10,000 if the amount of water in the feed mixture was lower than 2%. Among ACMs synthesized, the time to produce 99.5 % ethanol (or higher) by using ACMs-3 was around 28 h, which is lower than those using ACMs-1 (33 h) and ACMs-2 (31 h), as shown in Figure 6.3a, owing to

the lower membrane thickness. Moreover, the resulting performance (the total water flux, separation factor and time to produce 99.5% ethanol, see Figures 6.2-6.4, respectively) of the ACMs-3 was still maintained for both the first and the second runs, indicating that those membranes have good performance and good stability for the water-ethanol separation in the pervaporation system.

As a result, the optimum synthesis time to provide the highest performance (the highest total water flux and the high separation factor) of the synthesized NaA zeolite membranes to separate water from the water-ethanol mixture in the pervaporation system was 13 h (ACMs-3).

6.4.3 Productivity of NaA zeolite membrane for producing 99.5% of ethanol

In this work, ACMs-3 (13 h synthesis time) could produce approximately 510 mL of 99.5% of ethanol in 28 h from the 10:90 water:ethanol feed with the total throughput of 570 mL, 0.019 L/h (10.13 kg of 99.5%ethanol/m^2/h), and approximately 4% of mass loss. As compared to our previous work [23], this work showed a production rate of ethanol that was approximately 35.54% higher, due to the much thinner synthesized membrane, which provided a much higher total water flux and thus reduced the total time for purifying ethanol to 99.5%.

6.4.4 Reproducibility of NaA zeolite membranes (ACMs)

Reproducibility of the synthesized NaA zeolite membrane is mainly a criterion for industrial and economic views. In this work, all NaA zeolite membranes were synthesized using the same conditions, excepting only the difference in the synthesis times (13, 15, and 20 h). For each synthesis time, two NaA zeolite membranes were synthesized to investigate their reproducibility (see Figure 6.5). Those zeolite membranes clearly showed a good reproducibility for the water–ethanol separation in the pervaporation system with a high total water flux and a separation factor maintaining in a level higher than 10,000 throughout the reaction time. In fact, the higher total water flux achieved from these membranes was better than our previous works [19, 20, 23] and Sato and Nakane' study [26]. A high total

water flux with a good separation factor higher than 10,000 maintained throughout the reaction is definitely a good characteristic of the membrane for highly pure ethanol production, making it economically feasible for industries.

6.5 Conclusions

NaA zeolite membranes were successfully synthesized by conventional heating or autoclave technique. The optimum synthesis time, providing the best performance for water–ethanol separation in the pervaporation system, was 13 h. The best performance of the membrane found was 2.82 $kg/m^2/h$ total water flux and higher than 10,000 separation factor. A good reproducibility and a good stability obtained in this work are suitable for industrial use to produce high purity of ethanol.

6.6 Acknowledgements

6.7 References

1. D. Shah, K. Kissick, A. Ghorpade, R. Hannah, D. Bhattacharyya, Pervaporation of alcohol-water and dimethylformamide–water mixtures using hydrophilic zeolite NaA membranes: mechanisms and experimental results, *J. Membr. Sci.* 179 (2000) 185–205.

2. H.M. van Veen, Y.C. van Delft, C.W.R. Engelen, P.P.A.C. Pex, Dewatering of organics by pervaporation with silica membranes, *Sep. Purif. Technol.* 22–23 (2001) 361–366.

3. H. Kita, K. Horii, Y. Ohtoshi, K. Tanaka, K.I. Okamoto, Synthesis of a zeolite NaA membrane for pervaporation of water/organic liquid mixtures, *J. Membr. Sci.* 14 (1995) 206–208.

4. D. Van Baelen, B. Van der Bruggen, K. Van den Duggen, J. Degreve, C. Vandecasteele, Pervaporation of water–alcohol mixtures and acetic acid–water mixtures, *Chem. Eng. Sci.* 60 (2005) 1583–1590.

5. S. Nair, M. Tsapatsis, Synthesis and properties of zeolite membranes, in: S. Auerbach, K. Carrado, P. Dutta (Eds.), *Handbook of Zeolite Science and Technology*, Marcel Dekker, New York, 2003, pp. 867–919.

6. A. Huang, Y.S. Lin, W. Yang, Synthesis and properties of A-type zeolite membranes by secondary growth method with vacuum seeding, *J. Membr. Sci.* 245 (2004) 41–51.

7. M. Nomura, T. Yamaguchi, S.I. Nakao, Ethanol/water transport through silicalite membranes, *J. Membr. Sci.* 144 (1998) 161–171.

8. T. Bein, Synthesis and applications of molecular sieve layers and membranes, *Chem. Mater.* 8 (1996) 1636-1653.

9. J. Caro, M. Noack, P. Kolsch, and R. Schafer, Zeolite membranes – state of their development and perspective, *Micropor. Mesopor. Mater.* 38 [1] (2000) 3-24.

10. H. Ahn, H. Lee, S.B. Lee, Y. Lee, Pervaporation of an aqueous ethanol solution through hydrophilic zeolite membranes, *Desalination* 193 (2006) 244–251.

11. X. Xu, Y. Bao, C. Song, W. Yang, J. Liu, L. Lin, Microwave-assisted hydrothermal synthesis of hydroxyl-sodalite zeolite membrane, *Microporous Mesoporous Mater.* 75 (2004) 173–181.

12. Y. Li, J. Liu, W. Yang, Formation mechanism of microwave synthesized LTA zeolite membranes, *J. Membr. Sci.* 281 (2006) 646–657.

13. X. Zhang, W. Zhu, H. Liu, T. Wang, Novel tubular composite carbon-zeolite membranes, *Mater. Lett.* 58 (2004) 2223–2226.

14. B. Oonkhanond and M.E. Mullins, The preparation and analysis of zeolite ZSM-5 membranes on porous alumina supports, *J. Membr. Sci.* 194 [1] (2001) 3-13.

15. J. Zah, H. M. Krieg, and J.C. Breytenbach, Layer development and growth history of polycrystalline zeolite A membranes synthesized from a clear solution, *Micropor. Mesopor. Mater.* 93 [1-3] (2006) 141-150.

16. A. Huang, W. Yang, J. Liu, Synthesis and pervaporation properties of NaA zeolite membrane prepared with vacuum-assisted method, *Sep. Purif. Technol.* 56 (2007) 158-167.

17. Y. Li, H. Chen, J. Liu, W. Yang, Microwave synthesis of LTA zeolite membranes without seeding, *J. Membr. Sci.* 277 (2006) 230-239.

18. N. Kuanchertchoo, R. Suwanpreedee, S. Kulprathipanja, P. Aungkavattana, D. Atong, K. Hemra, T. Rirksomboon, S. Wongkasemjit, Effects of synthesis parameters on zeolite membrane formation and performance by microwave technique, *Appl. Organomet. Chem.* 21 (2007) 841-848.

19. N. Kuanchertchoo, S. Kulprathipanja, P. Aungkavattana, D. Atong, K. Hemra, T. Rirksomboon, S. Wongkasemjit, Preparation of uniform and nano-sized NaA zeolite using silatrane and alumatrane precursors, *Appl. Organomet. Chem.* 20 (2006) 775-783.

20. M. Kondo, M. Komori, H. Kita, K.I. Okamoto, Tubular-type pervaporation module with zeolite NaA membrane, *J. Membr. Sci.* 133 (1997) 133-141.

21. X Xu., Y. Bao, C. Song, W. Yang, J. Liu, and L. Lin, Synthesis, characterization and single gas permeation properties of NaA zeolite membrane, *J. Membr. Sci.* 249 [1-2] (2005) 51-64.

22. A. Tavolaro and P. Tavolaro, LTA zeolite composite membrane preparation, characterization and application in a zeolitic membrane reactor, *Catal. Commun.* 8 [5] (2007) 789-794.

23. D. Kunnakorn, T. Rirksomboon, P. Aungkavattana, N. Kuanchertchoo, D. Atong, S. Kulprathipanja and S. Wongkasemjit, Performance of sodium A zeolite membranes synthesized via microwave and autoclave techniques for water-ethanol separation : Recycle-continuous pervaporation process, *Desalination* (2010) Article in press.

24. V. Nikolakis, G. Xomeritakis, A. Abibi, M. Dickson, M. Tsapatsis and D.G. Vlachos, Growth of a faujasite-type zeolite membrane and its application in the

separation of saturated/unsaturated hydrocarbon mixtures, *J. Membr. Sci.* 184 (2001) 209-219.

25. A.A. Kittur, S.S. Kulkarni, M.I. Aralaguppi and M.Y. Kariduraganavar, Preparation and characterization of novel pervaporation membranes for the separation of water-isopropanol mixtures using chitosan and NaY zeolite, *J. Membr. Sci.* 247 (2005) 75-86.

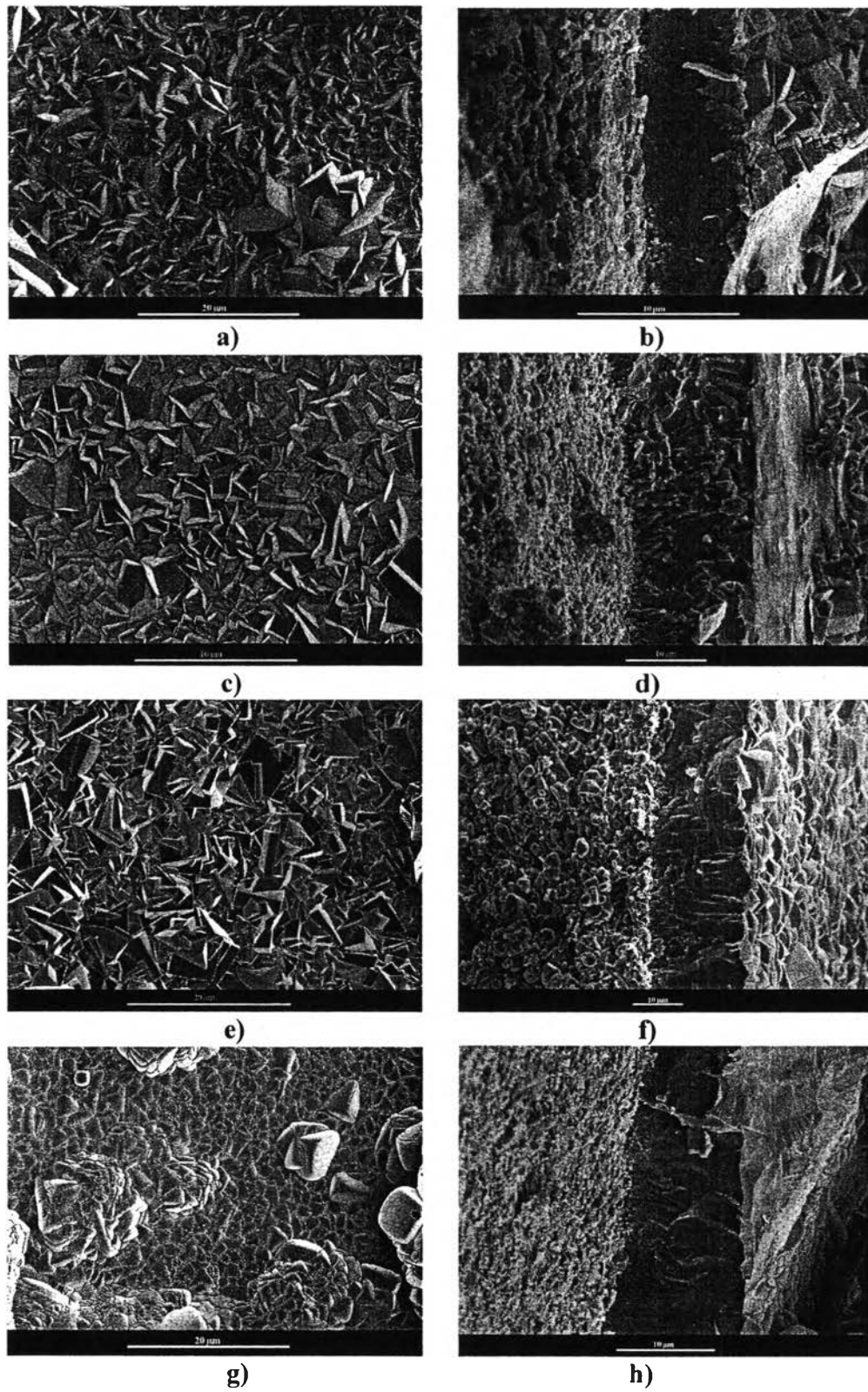26. K. Sato and T. Nakane, A high reprocucible fabrication method for induxtrial production of high flux NaA zeolite membrane, *J. Membr. Sci.* 301 (2007) 151-161.

Figure 6.1 SEM micrographs of ACMs; a,b) ACMs-3 (10+3h), c,d) ACMs-2 (10+5h),e,f) ACMs-1 (10+10h) and g,h) ACMs-4 (8+3h)
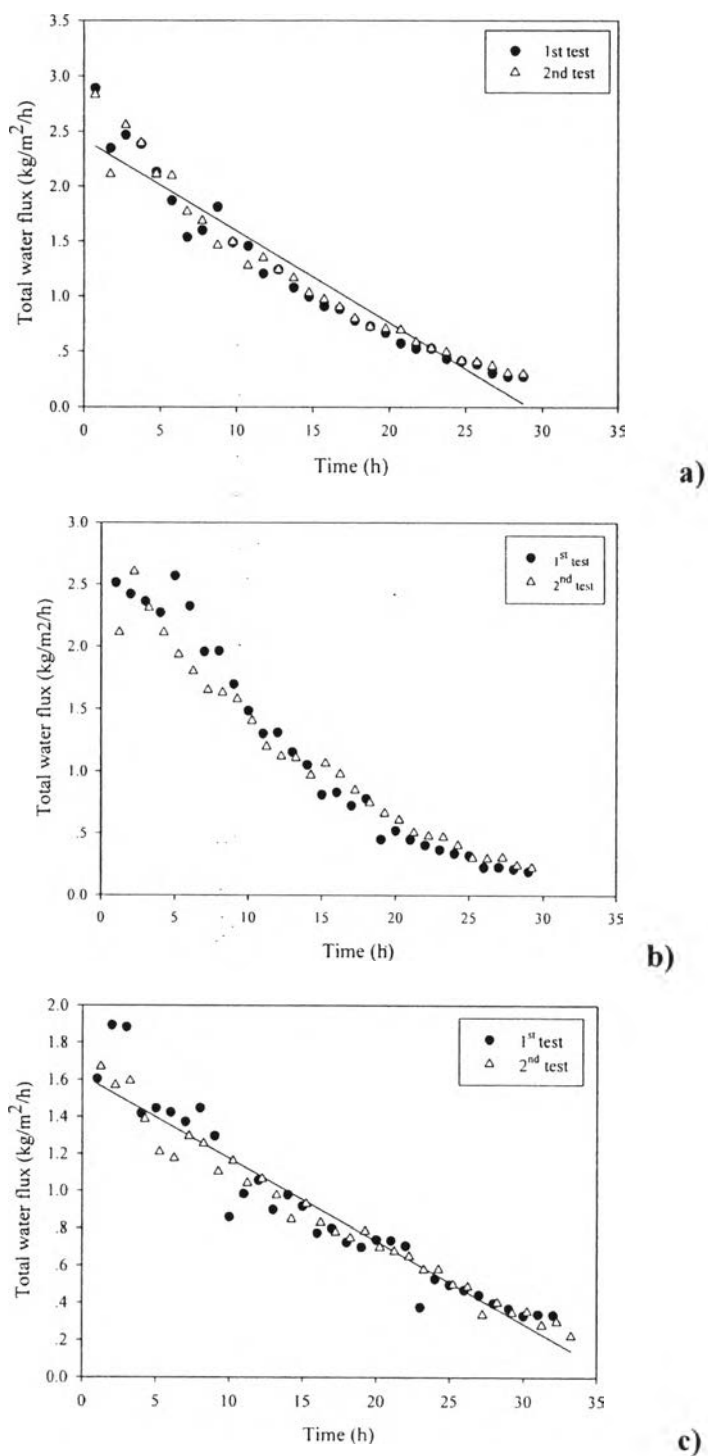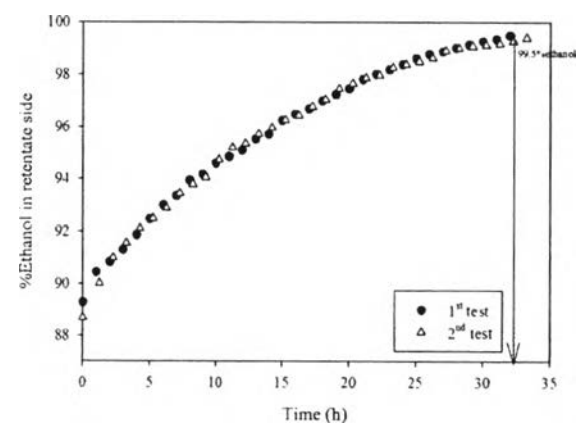
Figure 6.2 Total water flux (kg/m²/h) versus synthesis time (h) of the ACMs
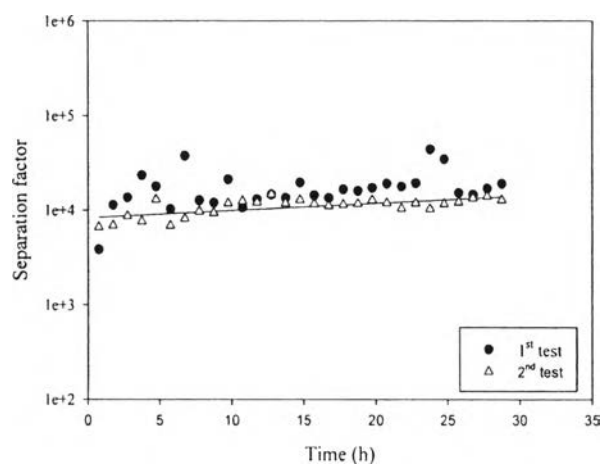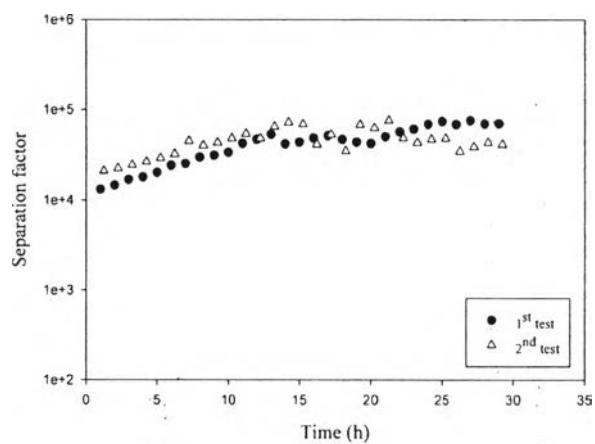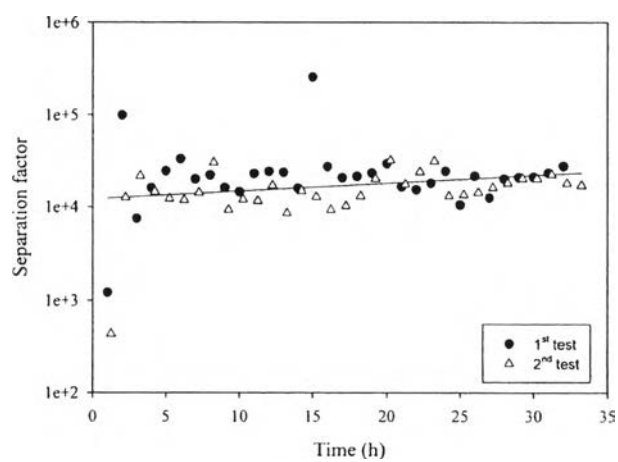synthesized for a) 13, b) 15, and c) 20 h
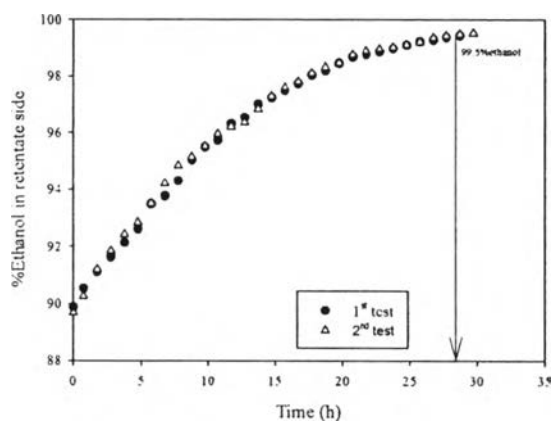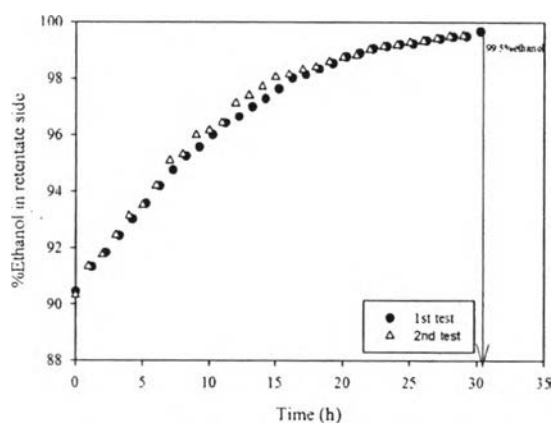
Figure 6.3 %Ethanol in the retentate site versus synthesis time (h) of the ACMs synthesized for a) 13, b) 15, and c) 20 h

Figure 6.4 Separation factor versus time (h) of the ACMs synthesized for a) 13, b) 15, and c) 20 h.
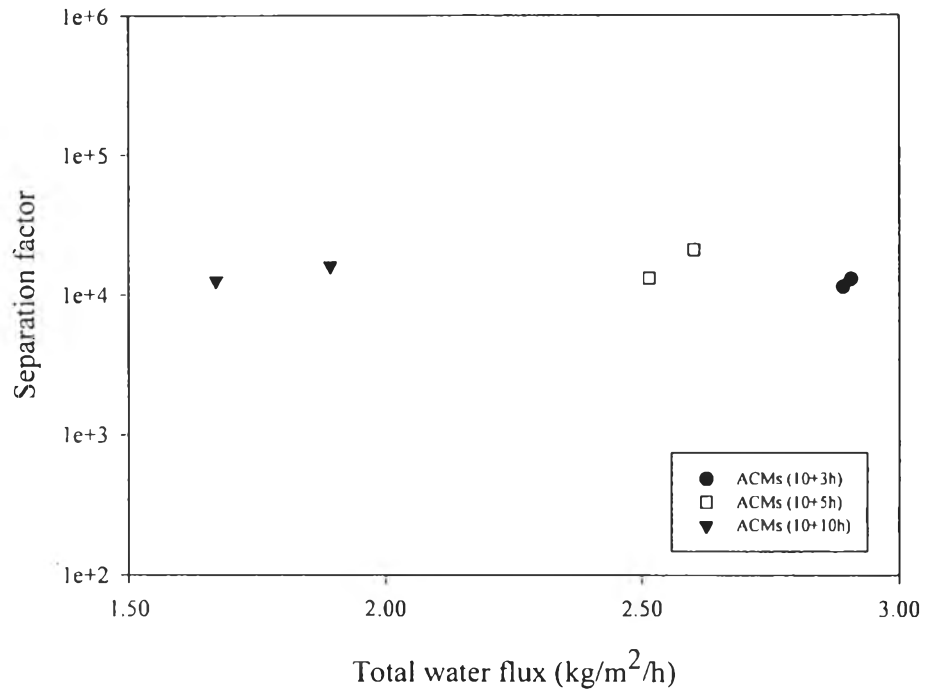
Figure 6.5 Reproducibility of ACMs for 13, 15 and 20h in synthesis time

Table 6.1 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

Table 6.2 Thickness, total water flux, and separation factor of NaA zeolite membranes.

Conditions	Membrane thickness (µm)	Total water flux (kg/m²/h)	Separation factor
ACMs-1	16-18	~ 1.86	> 10,000
ACMs-2	~ 13-14	~ 2.51	> 10,000
ACMs-3	~ 7-9	~ 2.82	> 10,000
ACMs-4	~ 6-9	-	< 10,000