CHAPTER V

PERFORMANCE OF SODIUM A ZEOLITE MEMBRANES SYNTHESIZED VIA MICROWAVE AND AUTOCLAVE TECHNIQUES FOR WATER–ETHANOL SEPARATION: RECYCLE-CONTINUOUS PERVAPORATION PROCESS

5.1 Abstract

The performance of sodium A (NaA) zeolite membranes with a surface area of 4.91 cm^2, synthesized on an alumina support via microwaving (MW) and autoclaving (AC, or conventional heating) using the recycle-continuous pervaporation of a water–ethanol mixture (10:90 vol.%), was studied. It was found that the process could produce ethanol having a concentration close to 100% (higher than 99.5%) after passing the mixture through the membrane for 120–140 h. The time-dependence separation factor and the total water flux were 3350–6050 and 0.4–1.0 $kg/m^2/h$, respectively. The time-dependence separation factor of this process was increased to higher than 10,000 when the percentage of ethanol at the retentate side was higher than 98%. The overall results showed good stability of the membranes for the water–ethanol separation.

5.2 Introduction

Sodium A (NaA) zeolite membranes are very well-known in the areas of organic-water separation and catalysis [1-4]. The most effective application of using the NaA zeolite membranes is water-ethanol separation, which shows very high selectivity [1,2]. The main parameters affecting the phase and performance of the zeolite are synthesis mixture, temperature, and time during synthesis [5]. NaA zeolite membranes can be synthesized in various forms, such as plates, tubes, etc. A well-known NaA zeolite membrane is synthesized on a tubular alumina (Al_2O_3) support, called "Tubular NaA zeolite membranes" [6]. The properties of the tubular NaA zeolite membranes are high thermal and organic chemical stability, high mechanical

strength, and uniform pore size distribution [1,7,8]. Generally, methods that can be used for producing the tubular NaA zeolite membranes are microwaving [9,10], electrophoretic, and autoclaving or conventional heating techniques [11].

Kita *et al.* [1] synthesized NaA zeolite on the cylindrical alumina support and showed a total water flux of 1.10-2.15 $kg/m^2/h$ and separation factor of higher than 10,000 at 323-348 K. Huang *et al.* [12] reported the preparation of NaA zeolite membrane using vacuum seeding in the conventional heating technique and produced a total water flux of 1.67 $kg/m^2/h$ and a separation factor higher than 10,000 for the water– ethanol separation. Li *et al.* [13] synthesized a NaA zeolite membrane on a tubular alumina support using the microwave synthesis technique without seeding, and studied the pervaporation of water–ethanol. They obtained a total water flux of around 0.51–0.64 $kg/m^2/h$ and a separation factor of higher than 10,000 at 338–343 K. In our previous work [14,15], the tubular NaA zeolite membranes synthesized by the microwave (MW) technique showed moderate performance in the separation of a water– ethanol mixture with a separation factor of 6532 at 343 K, while for those prepared by the autoclave (AC) technique, it showed a separation factor higher than 10,000. The total water flux of each technique was in the range of 0.5–1.5 $kg/m^2/h$.

Up to now, no reports have examined the performance of the NaA zeolite membrane synthesized on a tubular alumina support carried out using the recycle-continuous pervaporation method. In this work, we present the successful development of NaA zeolite membranes on a tubular alumina support synthesized by the MW and AC techniques. The synthesized membranes were tested with the recycle-continuous pervaporation of a water–ethanol mixture. The total water flux, time-dependence separation factor, percentage of ethanol produced, and time to achieve 99.5% ethanol from this process were determined for the stability of the synthesized NaA zeolite membranes.

5.3 Experimental

5.3.1 Materials

Fumed silicon dioxide (SiO_2, 390±40 m^2/g surface area, 0.007 μm average particle size) and aluminum hydroxide hydrate [$Al(OH)_3 \cdot xH_2O$, 51 m^2/g surface area] were purchased from Sigma-Aldrich, Inc., and were used as starting materials. Sodium hydroxide (NaOH), from 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, having 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 μm pore radius on average with 38% porosity coated with an α-alumina intermediate (0.06 μm pore size) on the top layer, was used in this work, and was obtained from the National (Thailand) Metal and Materials Technology Center (MTEC).

5.3.2 Equipment

The MW NaA zeolite membranes (MWMs) were synthesized using a microwave (MSP 1000, CEM Corporation with 220 V, 50 Hz input, 500 W, and 2450 MHz output), and the AC 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 gas chromatography 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 473 K, while the injector and detector temperatures were set at 473 K and 523 K, respectively.

5.3.3 NaA zeolite membrane synthesis

A tubular porous alumina support was cleaned by washing it twice in deionized water for 15 min to remove dirt from the surface [10,12], dried in a vacuum oven at 363 K for 24 h, and calcined in a furnace at 400 K for 3 h to burn off any impurities from 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 mm Hg (1.333 kPa), followed by drying at 333 K for 24 h before coating with NaA zeolite by MW and AC. 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. The NaA zeolite was synthesized using the $3Na_2O:Al_2O_3:SiO_2:410H_2O$ formula [3,10,13].

The coated tubular support was placed in a Teflon vessel containing the NaA zeolite solution prepared using the $50Na_2O:Al_2O_3:5SiO_2:1000\ H_2O$ formula and then this vessel was put in the MW or AC machine. (The synthesis conditions are summarized in Table 5.1.) The coated NaA zeolite membranes were washed with deionized water and dried at 343 K for 24 h before pervaporation testing.

5.3.4 Pervaporation

NaA zeolite membrane was vertically packed in the reactor and sealed both sides of the tube with rubber rings and closed with stainless steel, as shown in Fig. 5.1. The mixture used in this work was prepared using 10:90 water:ethanol with the total amount of throughput of 570 ml. The experiments were carried out at 343 K with 10 mm Hg 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. For each membrane, the recycle-continuous pervaporation process was applied for 2 to 3 cycles for the determination of the membrane stability.

In this work, to evaluate membrane performance, there are four significant parameters considered:

1. Total water flux (J) is expressed as:

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

where W is the water permeate (kg), A is the membrane area (m^2), and t is time (h). In this work, the total water flux is determined when the time is varied in the recycle-continuous pervaporation testing. A high total water flux means that more water molecules pass through the membranes to the permeate side, indicating good performance of the membranes.

2. Time-dependence separation factor (T-α) is defined for recycle-continuous pervaporation as:

$$T\text{-}\alpha = [X_{H2O}/X_{EtOH}]_{perm} / [X_{H2O}/X_{EtOH}]_{reten} \qquad (2)$$

where X_{EtOH} and X_{H2O} are the molar fractions of ethanol and water, respectively. The subscripts of "perm" and "reten" represent permeate and retentate sides, respectively. A high T-α indicates good separation of water from the water-ethanol mixture, implying that a very small amount or none of the ethanol passed through the membrane to the permeate side.

3. Percentage of ethanol at the retentate side (%ethanol) is obtained by gas chromatography. The value should be increased with time, and close to 99.5% ethanol.

4. Time to achieve 99.5% ethanol is determined by measuring the time at which the %ethanol is chromatographically close to 99.5%. The time to achieve 99.5% ethanol should be as low as possible, meaning that the membranes can produce a high purity of ethanol within a short time.

5. Kilogram of 99.5% ethanol per square meter per hour (kg of 99.5% $EtOH/m^2/h$) is determined by calculating the total amount of ethanol produced using microwave membrane (MWM) and autocape (ACM).

In this work, the optimum feed flow rate for the pervaporation process was evaluated using an MWM for 10 h under specific operating conditions: a temperature of 343 K, a permeate side pressure of 10 mmHg, and an ethanol-to-water ratio of 90:10.

5.4 Results and Discussion

In addition to the four significant parameters used for describing the performances of MWMs and ACMs, the feed flow rate is also considered to be an important factor indirectly affecting the separation of water from the water-ethanol mixture, and is thus relevant to membrane performance.

5.4.1 Effect of feed flow rate

By varying the feed flow rate from 300 to 1200 ml/min, it is clear that it indeed affects the total water flux and time-dependence separation factor (Table 5.2). The total water flux and the time-dependence separation factor increased with increasing feed flow rate [16]. Sato and coworkers [17] showed a higher permeation flux of the water-ethanol system in the dehydration process at a higher feed flow rate. Moreover, the Reynolds number, representing flow conditions (a high feed flow rate provides a high Reynolds number) on the membrane surface, is enhanced by an increase in the feed flow rate thus increasing the permeation flux [16,17]. Jiraratananon and coworkers [18] showed that the total water flux increased with the feed flow rate. The concentration of water on the membrane surface also increased with the feed flow rate. However, when the feed flow rate was too high, it made the total water flux and the time-dependence separation factor decrease, as also found in our case in which water and ethanol concentrations on the membrane surface were increased with the feeding flow rate, enhancing the ethanol sorption in the membrane and as a result, reducing the separation factor. Furthermore, for the lower feed flow rate, the ethanol can accumulate on the membrane surface to form gel, causing less

permeated water to pass through the membrane, resulting in reducing the total water flux of pervaporation system [19].

The optimum feeding flow rate in this present work was found at 900 ml/min, giving the highest total water flux of 1.39 kg/m²/h and the time-dependence separation factor higher than 10,000.

5.4.2 Total water flux

In the recycle-continuous pervaporation process of the MWM, the average of the total water flux was found to be around 0.5–1.0 kg/ m²/h and it decreased slowly with increasing time [19]. This is due to the decrease of the amount of water in the retentate side while the pervaporation process continues, resulting in a decrease of the total water flux of the system [8,11,14]. When using the same membrane for the second test, the same trend as the first step of the total water flux was found (Fig. 5.2), indicating that the membrane is stable and can be reused for the separation of water from the water-ethanol mixture in the pervaporation process.

Similar to the ACM, it showed the same performance as the MWM, but the total water flux of this membrane was found to be lower, around 0.400-0.500 kg/m²/h (Fig. 5.3). The second test also resulted in the same trend as the first one, also indicating the stability of this membrane.

5.4.3 Separation factor: Time-dependence separation factor

The separation factor used in this work was the "time-dependence separation factor". As described previously, for this type of pervaporation process, the time-dependence separation factor was close to 5000, in agreement with Li and coworkers' study [20], and increased to higher than 10,000 when the amount of the water in the retentate side was very low, as shown in Fig. 5.4. As mentioned in the

study by Kita and coworkers [1], the separation factor was increased when the % water in the retentate side decreased.

The ACM showed the same performance as the MWM, giving a time-dependence separation factor close to 10,000 when the amount of water in the retentate was very low or when taking around 80 to 100 h, as shown in Fig. 5.5. As a conclusion, the membrane synthesized by either MW or AC could be used for producing a high concentration of ethanol.

5.4.4 %Ethanol in the retentate side

The %ethanol in the retentate side for the recycle-continuous pervaporation process was determined using gas chromatography, as described previously. It was found that a high percentage of ethanol was achieved when using either MWM or ACM, close to 100% (99.92 and 99.8%), as shown in Figs. 5.6 and 5.7, respectively. However, it took longer for the ACM to reach 99.8% ethanol since the membrane synthesized by AC was thicker than that synthesized by MW, as shown in Figs. 5.8 and 5.9, respectively. The thicker membrane also affected the total water flux. The same membrane was used for the second test; it also showed the same trend, as compared to the first test, implying that this membrane has high stability and can be used to produce high purity ethanol (higher than 99.5% ethanol).

5.4.5 Time to achieve 99.5%ethanol

In this work, the time for obtaining 99.5% of ethanol in the retentate side of the recycle-continuous pervaporation process was determined to describe the performance of the membrane. Comparing between the MWM and the ACM, the time taken to achieve 99.5% ethanol for the MWM was lower because the thickness of the MWM was less, making it take a shorter time to achieve the 99.5%ethanol. For both the MWM and the ACM, the time taken to achieve the 99.5% ethanol was around 100 to 130 h, suggesting that the high purity (99.5%) can be produced using these membranes. However, for the third run of MWM, time to achieve

99.5%ethanol was slightly higher than the first and second runs, as can be seen in Fig. 5.6, due to a slight decrease of the separation factor, as confirmed by the data shown in Fig. 5.4.

The membrane surface area is another parameter affecting the time taken to obtain the 99.5%ethanol, as described by Van Veen and coworkers [3], who showed an increase in the ethanol production as the surface area was increased. In this work, the membrane surface area was fixed at 4.91 cm^2 (0.0004910 m^2), calculated from the inner and the outer diameters of the membrane used of 0.800-0.900 and 1.100-1.200 cm, respectively, with 4.3 cm effective length. This was used to produce 500 ml of 99.5%ethanol in 115 h (0.10 L/day). The error in mass balance of this system is approximately 6% due to loss of ethanol while sampling the solution to check the %ethanol in the retentate.

5.4.6 Kilogram of 99.5%ethanol per square meter per hour (kg of 99.5%EtOH/m^2/h)

For the membrane having surface area of 0.0004910 m^2, the MW technique could produce 500 ml of ethanol in 107.5 h (average) or 7.474 kg of 99.5%EtOH/m^2/h whereas the AC technique produced 500 ml of ethanol in 125 h (average) or 6.428 kg of 99.5%EtOH/m^2/h.

5.4.7 Structure of NaA zeolite membrane

It is well-known that the performance of separation is also affected by the zeolite membrane [9]. From SEM images shown in Figs. 5.8 and 5.9, it is clearly seen that smaller zeolite crystals formed by the MW technique is well inter-grown (Fig. 5.8a) while the AC technique gave big crystals and gaps (Fig. 5.9a). This is a reason why MWM showed a better performance for the separation [9].

5.4.8 Stability of the NaA zeolite membrane

Comparing between MWMs and ACMs, the total water flux $(kg/m^2/h)$ of the MWMs was higher, and the time needed for obtaining high purity ethanol was shorter although the separation factor was almost the same. Thus, only MWMs were used for further study.

The stability of the NaA zeolite membrane synthesized by the MW technique was determined using the recycle-continuous pervapora-tion process for the third run after the first run had been carried out for three months (after each run, the MWM was washed with distilled water and kept in the reactor at room temperature and atmospheric pressure). The resulting performance was still maintained, comparing to the first two runs (see the total water flux in Fig. 5.2, the %ethanol produced in the retentate side in Fig. 5.6, and the total time taken to produce higher than 99.5%ethanol concentration). According to these results, we can conclude that the NaA zeolite membrane synthesized by the MW technique appeared to have good stability [17] for use in the pervaporation process of water–ethanol separation.

Similarly, the ACMs also showed the same performance of the third run as the first and second runs. However, in this case, the third run was performed four months later (after the first run and kept the membranes in the reactor at room temperature and atmospheric pressure), indicating that the ACMs also have a good stability for use in the pervaporation process for the water–ethanol separation (Figs. 5.3, and 5.7).

5.5 Conclusions

Sodium A (NaA) zeolite membranes were successfully synthesized by microwave (MW) and autoclave (AC) techniques, and can be used in the pervaporation process for the separation of water from an water–ethanol mixture. A high purity of ethanol (99.5%) can easily be obtained using either the MW or AC

membrane under recycle-continuous mode of water–ethanol separation. The total water flux $(kg/m^2/h)$ of MW and AC membranes for the recycle-continuous pervaporation process for water–ethanol separation was found to be around 0.50 to 1.00 $kg/m^2/h$ and decreased with time due to a lower amount of water in the retentate side. The time-dependence separation factor of the MW and AC membranes for the recycle-continuous pervaporation process for water–ethanol separation was around 5000 and increased to higher than 10,000 when the amount of the water in the retentate side was very low with increasing separation time. The MW and AC membranes showed good performance for use in the pervaporation process of the water– ethanol separation, and appeared to have good selectivity and stability.

5.6 Acknowledgments

5.7 References

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

2. D. Shah, K. Kissick, A. Ghorpade, R. Hannah and 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.

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

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

5. S. Nair and M. Tsapatsis, Synthesis and properties of zeolite membranes: In 'Handbook of Zeolite Science and Technology' (Marcel Dekker, New York, **1993**) 875.

6. A. Huang, Y.S. Lin and 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 and S.I. Nakao, Ethanol/water transport through silicalite membranes, J. Membr. Sci., 144 (**1998**) 161-171.

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

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

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

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

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

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

14. N. Kuanchertchoo, R. Suwanpreedee, S. Kulprathipanja, P. Aungkavattana, D. Atong, K. Hemra, T. Rirksomboon and S. Wongkasemjit, Effects of synthesis

parameters on zeolite membrane formation and performance by microwave technique, Appl. Organomet. Chem., 21 (**2007**) 841-848.

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

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

17. K. Sato, K. Aoki, K. Sugimoto, K. Izumi, S. Inoue, J. Saito, S. Ikeda and T. Nakane, Dehydrating performance of commercial LTA zeollite membranes and application to fuel grade bio-ethanol production by hybrid distillation/vapor permeation process, Microporous Mesoporous Mater., 115 (**2008**) 184-188.

18. R. Jiraratananon, A. Chanachai, R. Y.M. Huang and D. Uttapap, Pervaporation dehydration of ethanol-water mixtures with chitosan/hydroxyethylcellulose (CS/HEC) composite membranes: I. Effect of operating conditions, J. Membr. Sci., 195 (**2002**) 143-151.

19. S. Bhattacharya and S.T. Hwang, Concentration polarization, separation factor, and Peclet number in membrane processes, J. Membr. Sci., 132 (**1997**) 73-90.

20. Y. Li, H. Zhou, G. Zhu, J. Liu and W. Yang, Hydrothermal stability of LTA zeolite membranes in pervaporation, J. Membr. Sci., 297 (**2007**) 10-15.
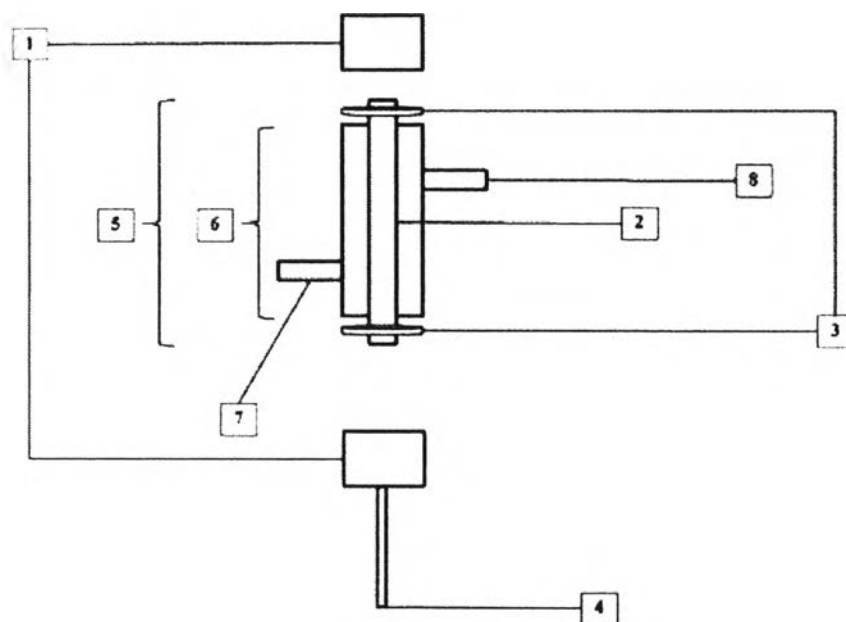
Figure 5.1 Schematic of the reactor design composing of 1) stainless steel plug, 2) NaA zeolite membrane on alumina tube, 3) rubber rings, 4) permeate outlet, 5) length of zeolite membrane, 6) effective length of zeolite membrane, 7) feed inlet, and 8) feed outlet.
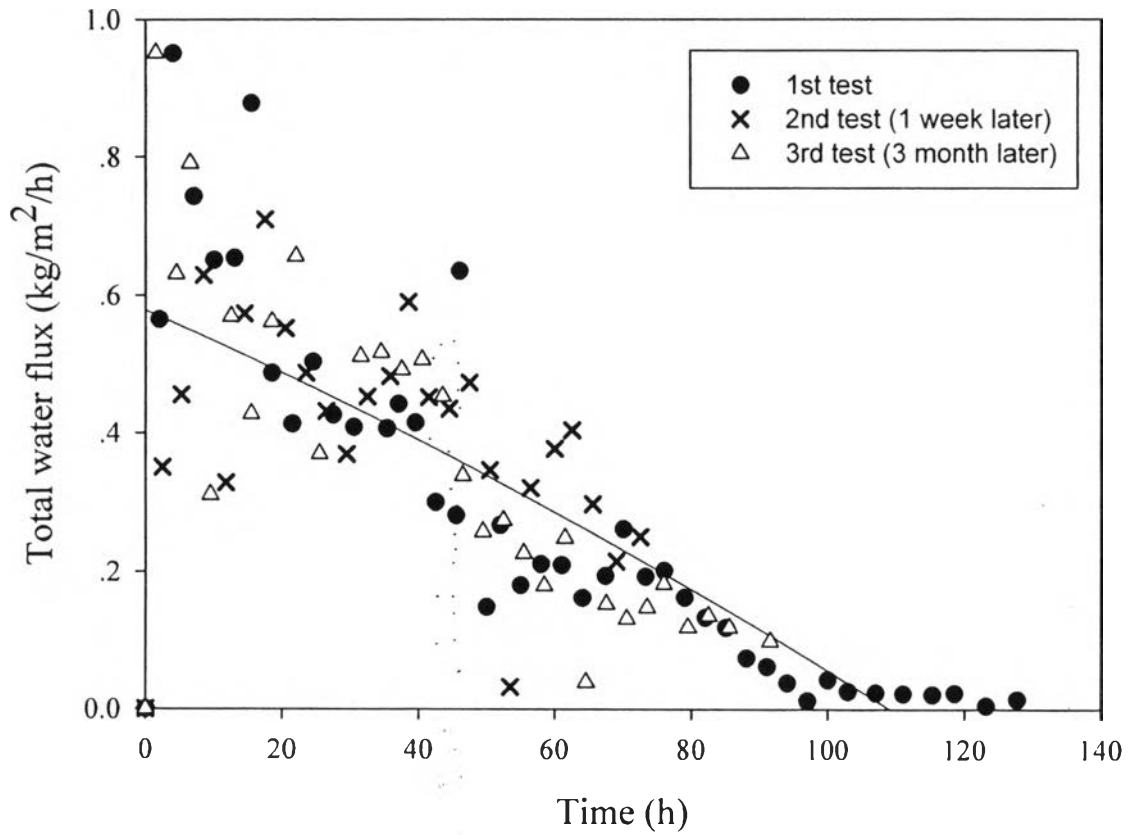
Figure 5.2 Total water flux of the recycle-continuous pervaporation process using the MWM versus time.
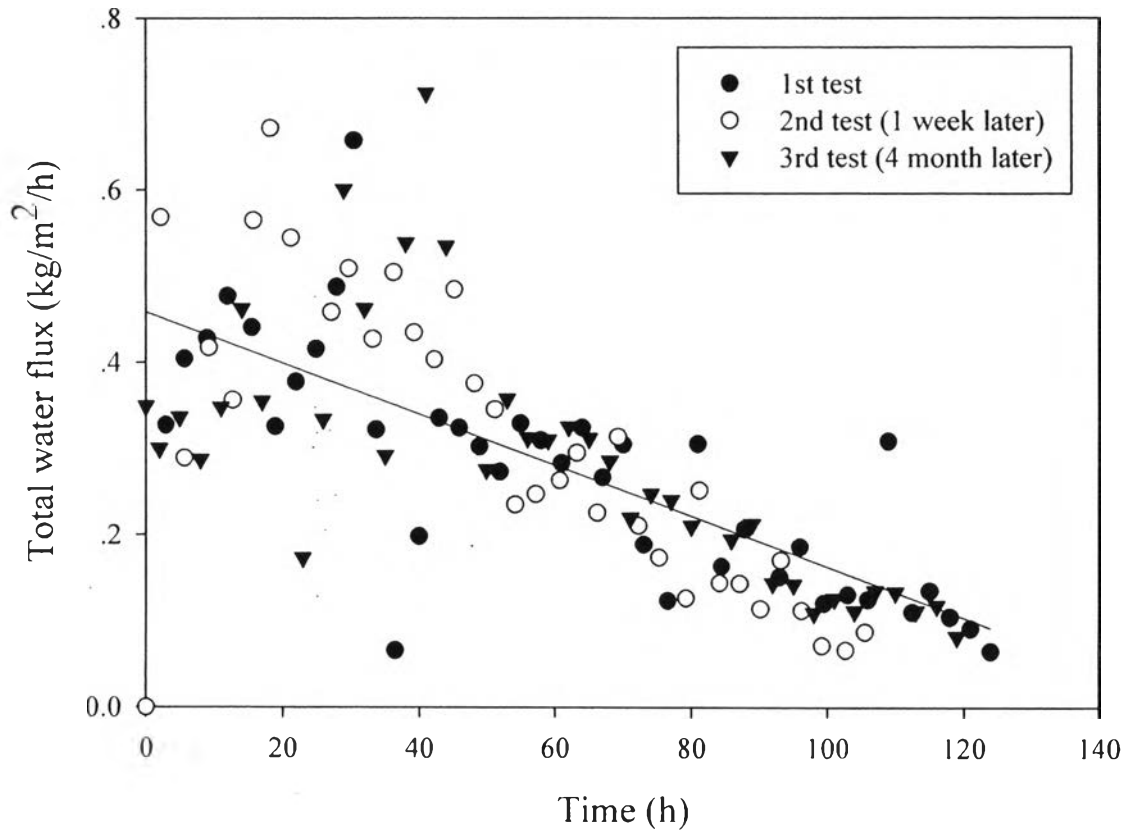
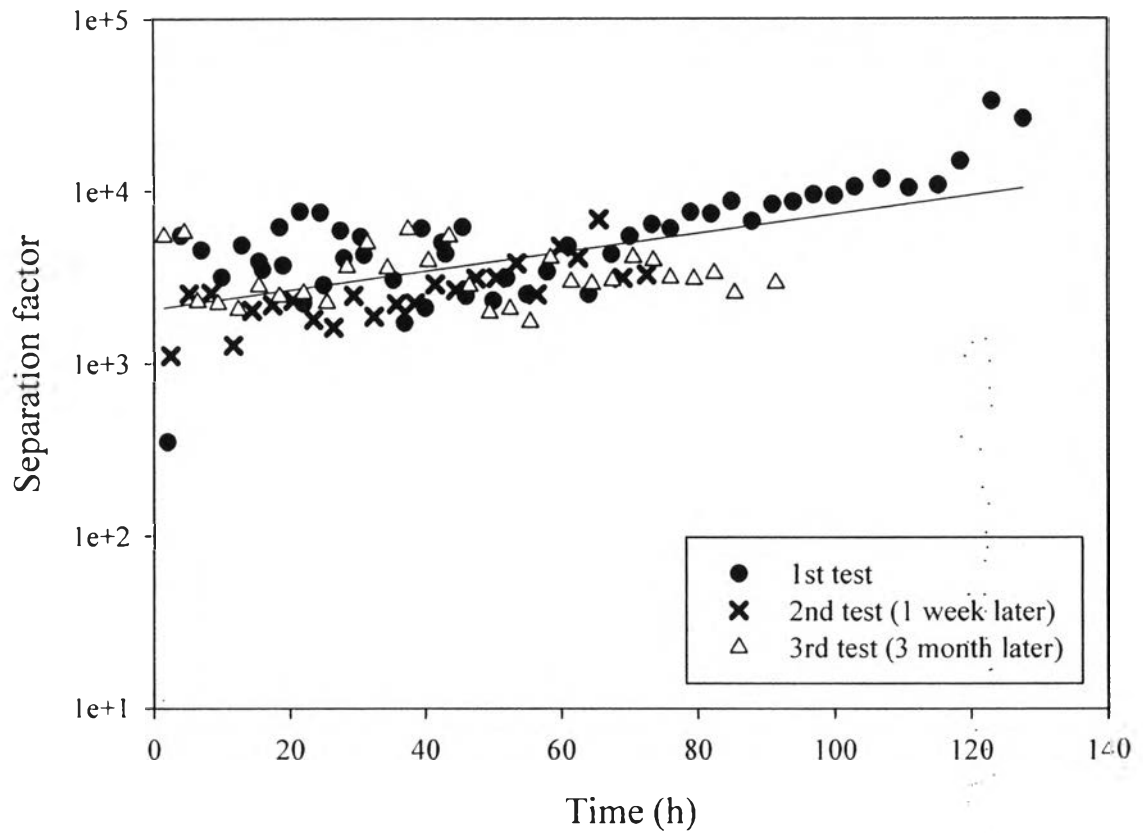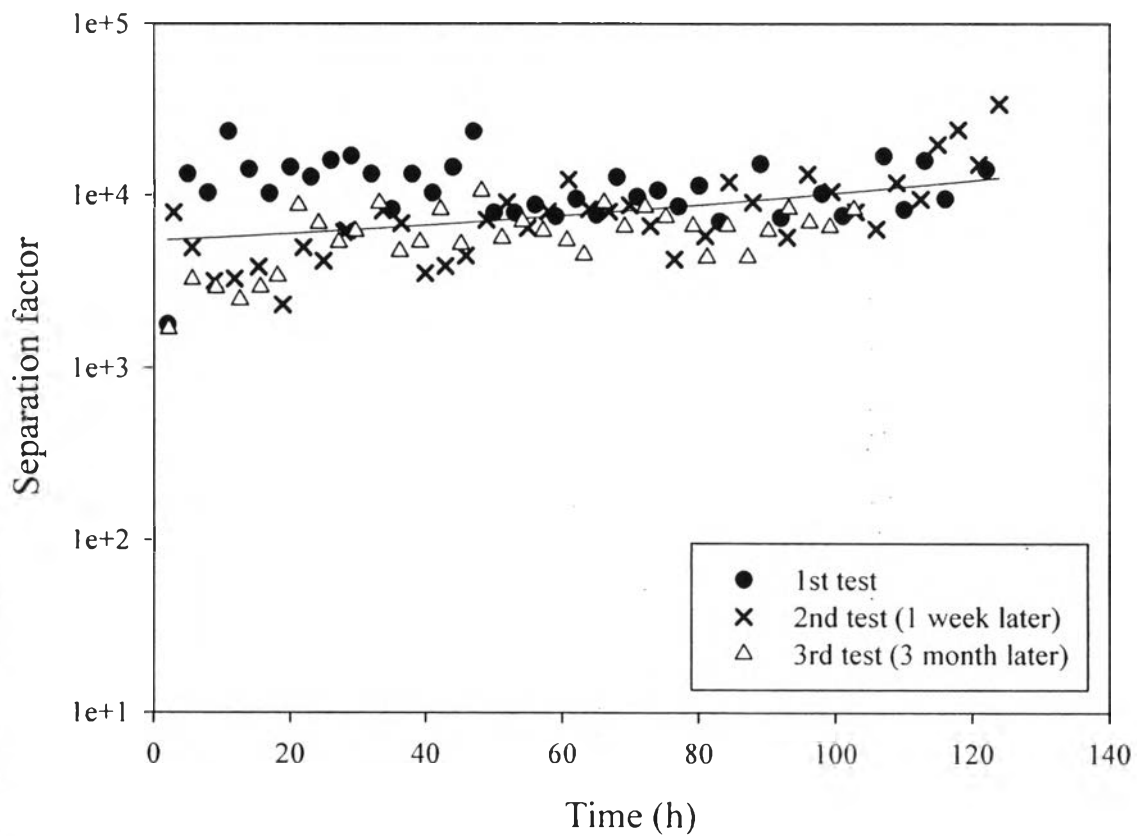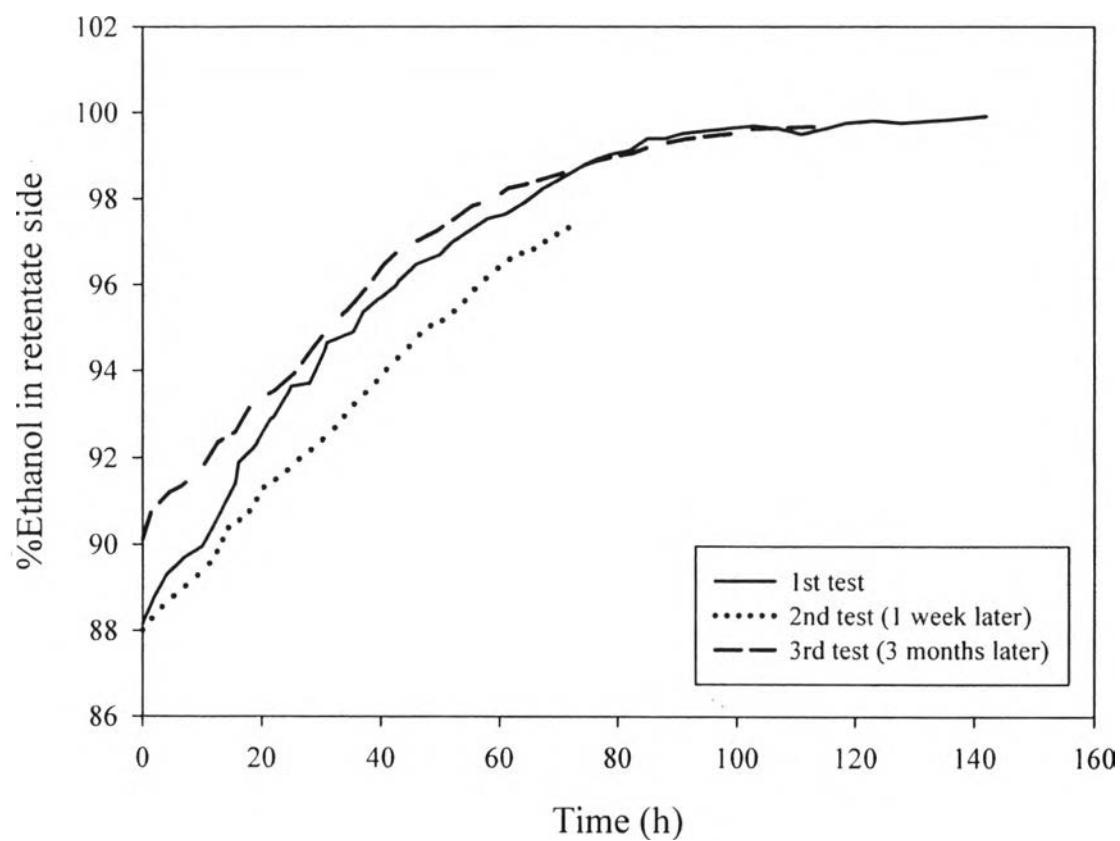**Figure 5.3** Total water flux of the recycle-continuous pervaporation process using the ACM versus time.

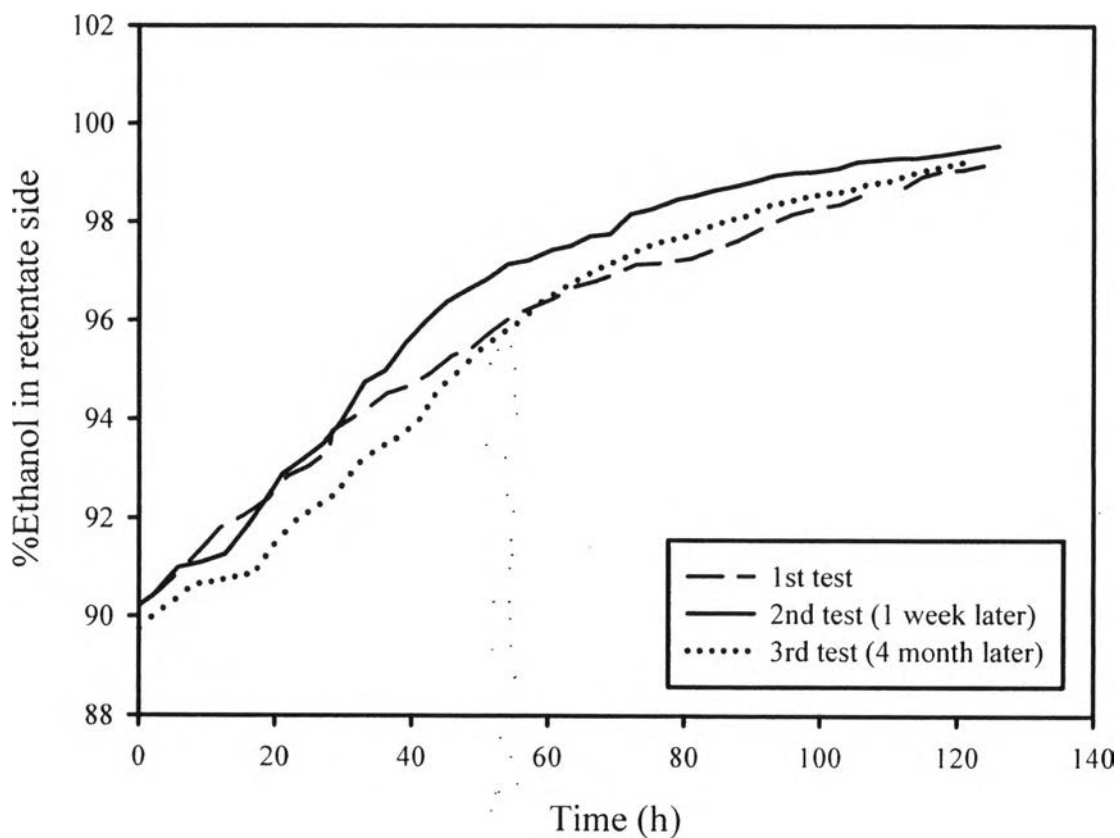**Figure 5.4** Separation factor of the recycle-continuous pervaporation process using the MWM versus time.

Figure 5.5 Separation factor of the recycle-continuous pervaporation process using the ACM versus time.

Figure 5.6 %Ethanol in the retentate side of the recycle-continuous pervaporation process using the MWM versus time.
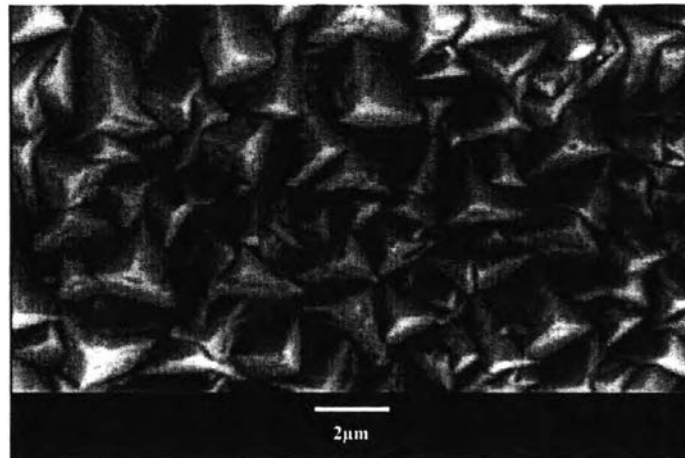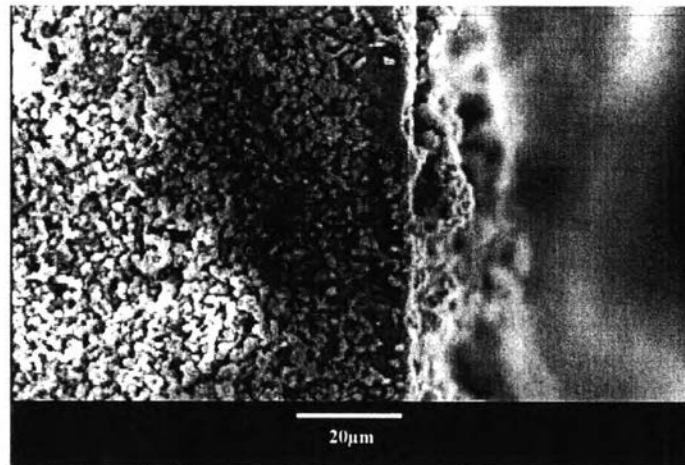
Figure 5.7 %Ethanol in the retentate side of the recycle-continuous pervaporation process using the ACM versus time.
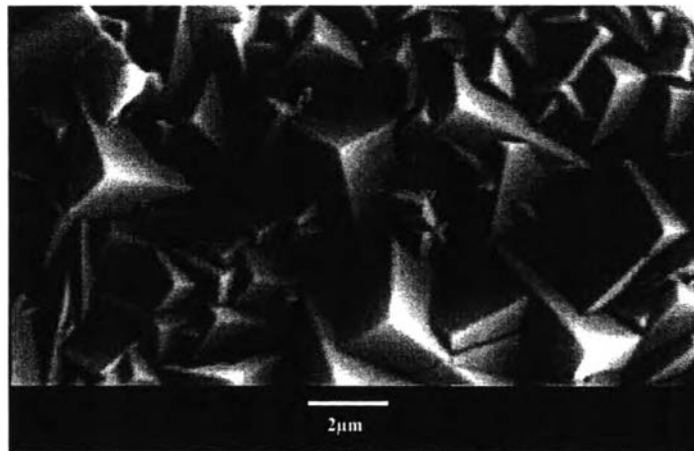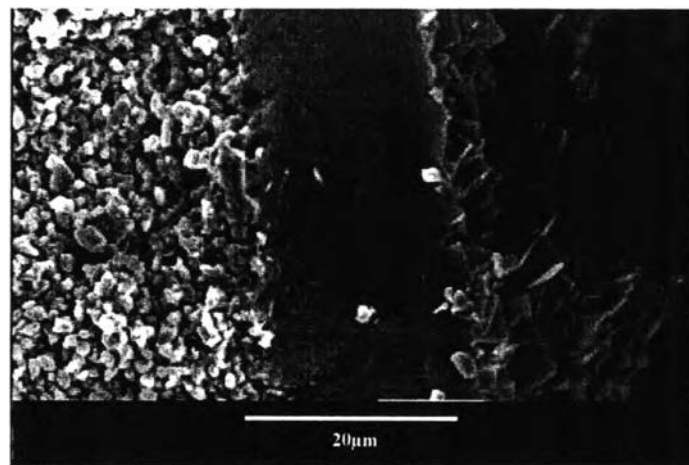
(a)

(b)

Figure 5.8 SEM micrographs of MWM; (a) surface and (b) thickness

(a)

(b)

Figure 5.9 SEM micrographs of ACM; (a) surface and (b) thickness

Table 5.1 Synthesis conditions for MWMs and ACMs.

Condition for synthesized	MWM	ACM
Temperature (K)	363	333
Time for synthesized (hours)		
First time	0.333	10
Second time	0.167	10

Table 5.2 Effect of the feed flow rate on the pervaporation process.

Feed flow rate (ml/min)	Average total water flux (kg/m²/hr)	Average time-dependence separation factor
300	0.3439	6,440
600	0.6347	> 10,000
900	1.3839	> 10,000
1,200	0.7557	> 10,000