กระบวนการแยกด้วยแผ่นเยื่อบาง สำหรับการแยกน้ำออกจากเอทานอล เพื่อผลิตเอทานอลที่มีความบริสุทธิ์สูง 99.5% โดยปริมาตร

4. จากการทดสอบประสิทธิภาพของแผ่นเยื่อบางซีโอไลท์ชนิดโซเดียม-เอ ด้วยกระบวนการแยกด้วยแผ่นเยื่อบางขนาดระดับห้องปฏิบัติการพบว่า แผ่นเยื่อบางซีโอไลท์ชนิดโซเดียม-เอที่สังเคราะห์ขึ้นมาได้นั้น มีความเสถียรต่อการใช้งานเป็นแผ่นเยื่อบางในกระบวนการแยกด้วยแผ่นเยื่อบางได้เป็นอย่างดี และยังสามารถใช้งานได้เป็นระยะเวลายาวนานอีกด้วย ซึ่งเหมาะสมกับการนำมาพัฒนาและปรับปรุง เพื่อผลิตขึ้นใช้ในขนาดระดับอุตสาหกรรมต่อไป
5. แผ่นเยื่อบางซีโอไลท์ชนิดโซเดียม-เอ ขนาดใหญ่นั้น สามารถสังเคราะห์ได้ด้วยกระบวนการการให้ความร้อน (autoclave technique)
6. ด้านประสิทธิภาพของแผ่นเยื่อบางซีโอไลท์ชนิดโซเดียม-เอขนาดใหญ่นั้น แผ่นเยื่อบางแสดงประสิทธิภาพปานกลาง ในการใช้เป็นแผ่นเยื่อบางในระบบการแยกด้วยแผ่นเยื่อบางเพื่อแยกน้ำออกจากเอทานอล โดยที่มีค่าการแยกที่ประมาณ 6,000 สำหรับระบบการแยกด้วยแผ่นเยื่อบาง
7. ทางด้านเทคโนเศรษฐกิจ (techno-economics) การผลิตเอทานอลที่มีความบริสุทธิ์สูง 99.5% โดยปริมาตรนั้น มีต้นทุนทางด้านพลังงานในการผลิตต่ำที่สุด เมื่อเทียบกับกระบวนการกลั่นแบบอะซีโอโทรป

***ข้อเสนอแนะ***

1. ควรมีการศึกษาถึงการสังเคราะห์แผ่นเยื่อบางชนิดโซเดียม-เอ ขนาดใหญ่ (ความยาว 30 เซนติเมตร) ต่อไป เพื่อศึกษาหาสภาวะที่เหมาะสม ในการใช้ในการสังเคราะห์แผ่นเยื่อบางขนาดใหญ่
2. การศึกษาถึงประสิทธิภาพของแผ่นเยื่อบางขนาดใหญ่ด้วยการใช้กระบวนการแยกนั้น ควรมีการปรับปรุง เพื่อให้การทดสอบเป็นไปอย่างมีประสิทธิภาพต่อไป
3. ในด้านการเตรียมตัวรองรับสำหรับใช้เป็นตัวรองรับ (support) ในการสังเคราะห์แผ่นเยื่อบางนั้น ควรมีการปรับปรุงพัฒนาประสิทธิภาพของตัวรองรับที่ได้ ตลอดจนพัฒนาสมบัติทางด้วยกายภาพ และความแข็งแรงของตัวรองรับที่สังเคราะห์ได้
4. อุปกรณ์สำหรับกระบวนการแยกด้วยแผ่นเยื่อบางขนาดใหญ่นั้น อุปกรณ์บางชิ้นควรมีการปรับปรุงให้สามารถใช้งานได้ดีขึ้น ตลอดจนอุปกรณ์บางชิ้นควรปรับปรุง เพื่อไม่ให้ส่งผลต่อประสิทธิภาพของแผ่นเยื่อบาง และไม่ทำความเสียหายต่อแผ่นเยื่อบางอีกด้วย
5. ควรมีการออกแบบอุปกรณ์เพื่อทดสอบแผ่นเยื่อบางขนาดใหญ่ทีละแท่ง เพื่อสามารถช่วยในการคัดเลือกแผ่นเยื่อบางชนิดโซเดียม-เอ ขนาดใหญ่ และเพื่อเพิ่มประสิทธิภาพของระบบการแยกด้วยแผ่นเยื่อบาง

**<u>บรรณานุกรม</u>**

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**คำชี้แจงอื่นๆ**

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**ภาคผนวก**

การตีลงพิมพ์ในวารสารนานาชาติบจากโครงการวิจัยนี้ คือ

1. หนึ่งในบทความวิจัยของโครงการนี้ ได้รับการตีพิมพ์ลงในวารสารนานาชาติ ("Performance of sodium A zeolite membranes synthesized via microwave and autoclave techniques for water–ethanol separation: Recycle-continuous pervaporation process", Desalination, 269 (2011), 78-83)

2. หนึ่งในบทความวิจัยของโครงการนี้ ได้รับการตีพิมพ์ลงในวารสารนานาชาติ ("Optimization of synthesis time for high performance of NaA zeolite membranes synthesized via autoclave for water-ethanol separation", Desalination, In press

3. หนึ่งในบทความวิจัยของโครงการนี้ ได้รับการตอบรับให้ไปเสนอผลงานวิจัยที่การประชุมนานาชาติ ("Technoeconomics-Simulation Comparison Between Pervaporation-Commercial Distillation for Ethanol Production", POLYCHAR 19 – World Forum on Advanced Materials, March 20-24, 2011, Kathmandu, Nepal) และอยู่ระหว่างการพิจารณาของคณะกรรมการเพื่อนำไปตีพิมพ์ในวารสาร Journal of Polymer Science and Technology.

4. หนึ่งในบทความวิจัยของโครงการนี้ ได้รับการตอบรับให้ไปเสนอผลงานวิจัยที่การประชุมนานาชาติ ("High Performance of Polybenzoxazine Membranes for Ethanol-Water Separation via Pervaporation Technique", POLYCHAR 19 – World Forum on Advanced Materials, March 20-24, 2011, Kathmandu, Nepal) และอยู่ระหว่างการพิจารณาของคณะกรรมการเพื่อนำไปตีพิมพ์ในวารสาร Journal of Polymer Science and Technology

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# Performance of sodium A zeolite membranes synthesized via microwave and autoclave techniques for water–ethanol separation: Recycle continuous pervaporation process

Dacho Kunnakorn [a,b], Thirasak Rirksomboon [a,b], Pavadee Aungkavattana [c], Neeranut Kuanchertchoo [d], Duangduen Atong [c], Santi Kulprathipanja [e], Sujitra Wongkasemjit [a,b,*]

[a] The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand
[b] Center for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, Bangkok, Thailand
[c] National Metal and Materials Technology Center (MTEC), Thailand Science Park, Patumthani, Thailand
[d] Faculty of Science, Ramkhamhaeng University, Bangkok, Thailand
[e] UOP, A Honeywell Company, Des Plaines, Illinois, USA

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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.

## 1. 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], electrophoresis, 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.

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[*] Corresponding author. The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand. Tel.: +66 2 2184133; fax: +66 22154459.
*E-mail address:* dsujitra@chula.ac.th (S. Wongkasemjit).

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## 2. Experimental

### 2.1. 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).

### 2.2. 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.

### 2.3. 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 on 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 1.) The coated NaA zeolite membranes were washed with deionized water and dried at 343 K for 24 h before pervaporation testing.

### 2.4. 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. 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:

$$J = W/(A^{*}t) \tag{1}$$

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:

$$T{-}\alpha = (X_{H2O}/X_{EtOH})_{perm}/(X_{H2O}/X_{EtOH})_{reten} \tag{2}$$

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 autoclave (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.

## 3. 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.

### 3.1. 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 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

**Table 1**
Synthesis conditions for MWMs and ACMs.

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

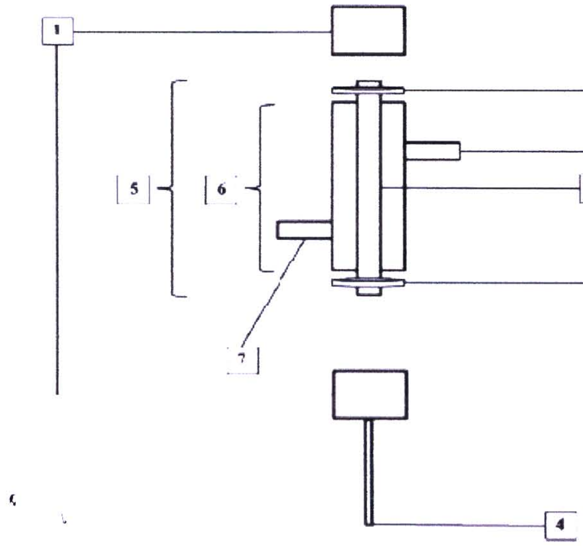

**Fig. 1.** Schematic of the reactor design composing of 1) stainless steel plug, 2) NaA zeolite membrane on alumina tube, 3) rubber rings, 4) permeate outlet, 5) length of zeolite membrane, 6) effective length of zeolite membrane, 7) feed inlet, and 8) feed outlet.

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/m$^2$/h and the time-dependence separation factor higher than 10,000.

### 3.2. 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/m$^2$/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. 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/m$^2$/h (Fig. 3). The second test also resulted in the same trend as the first one, also indicating the stability of this membrane.

**Table 2**
Effect of the feed flow rate on the pervaporation process.

| Feed flow rate (ml/min) | Average total water flux (kg/m$^2$/h) | Average time-dependence separation factor |
|---|---|---|
| 300 | 0.3439 | 6,440 |
| 600 | 0.6347 | >10,000 |
| 900 | 1.3839 | >10,000 |
| 1200 | 0.7557 | >10,000 |

### 3.3. 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. 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

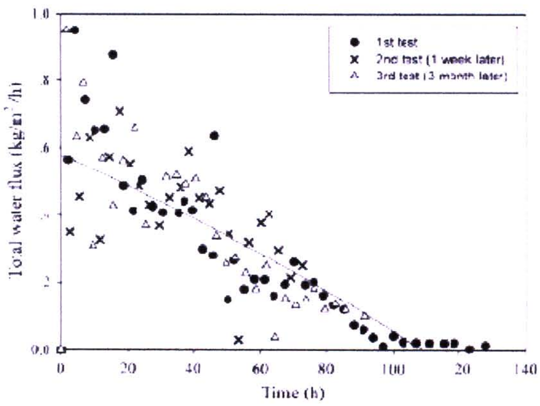

**Fig. 2.** Total water flux of the recycle-continuous pervaporation process using the MWM versus time.

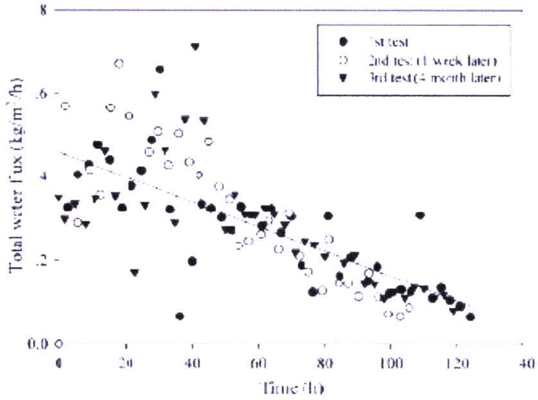

**Fig. 3.** Total water flux of the recycle-continuous pervaporation process using the ACM versus time.

of water in the retentate was very low or when taking around 80 to 100 h, as shown in Fig. 5. As a conclusion, the membrane synthesized by either MW or AC could be used for producing a high concentration of ethanol.

### 3.4. %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 and 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. 8 and 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).

### 3.5. 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. 6, due to a slight decrease of the separation factor, as confirmed by the data shown in Fig. 4.

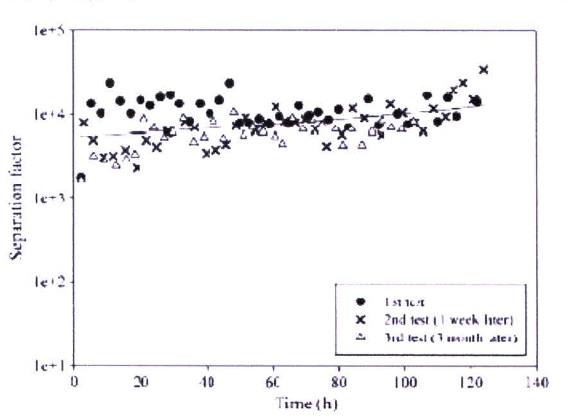

**Fig. 5.** Separation factor of the recycle-continuous pervaporation process using the ACM versus time.

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.

### 3.5. 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

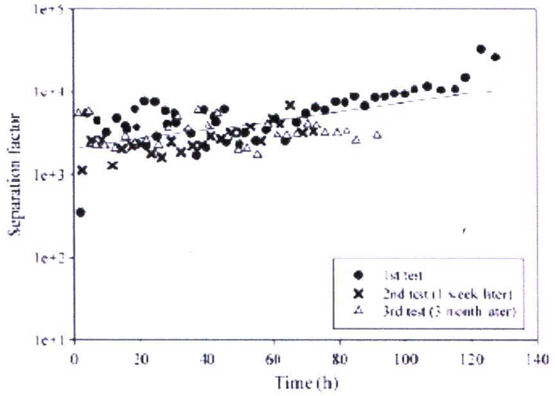

**Fig. 4.** Separation factor of the recycle-continuous pervaporation process using the MWM versus time.

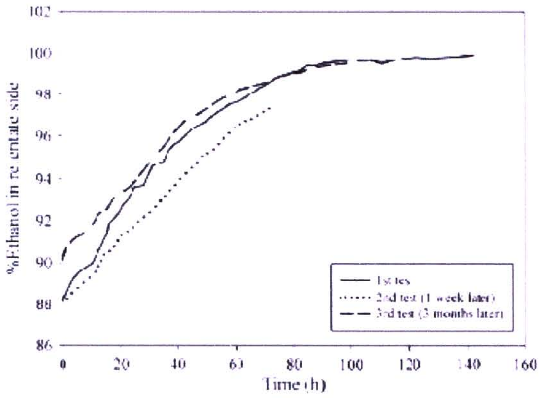

**Fig. 6.** %Ethanol in the retentate side of the recycle-continuous pervaporation process using the MWM versus time.

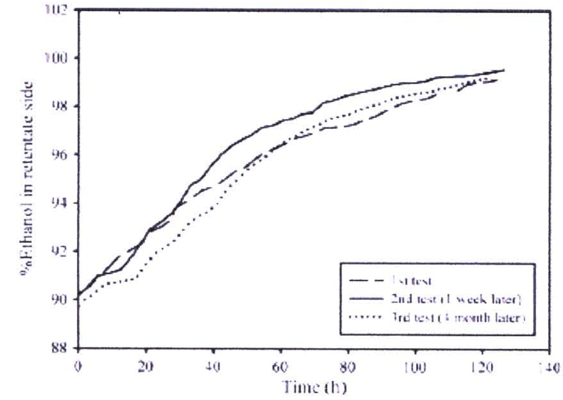

**Fig. 7.** %Ethanol in the retentate side of the recycle-continuous pervaporation process using the ACM versus time.

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.

### 3.7. 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. 8 and 9, it is clearly seen that smaller zeolite crystals formed by the MW technique is well inter-grown (Fig. 8a) while the AC technique gave big crystals and gaps (Fig. 9a). This is a reason why MWM showed a better performance for the separation [9].

### 3.8. 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.

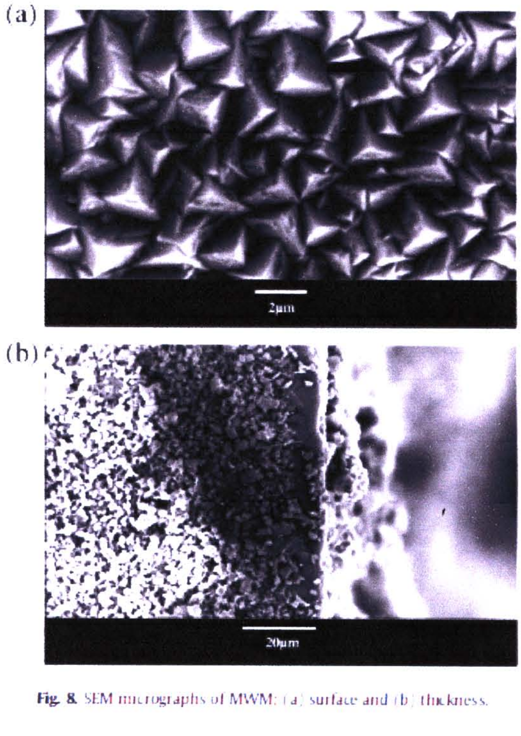

**Fig. 8.** SEM micrographs of MWM: (a) surface and (b) thickness.

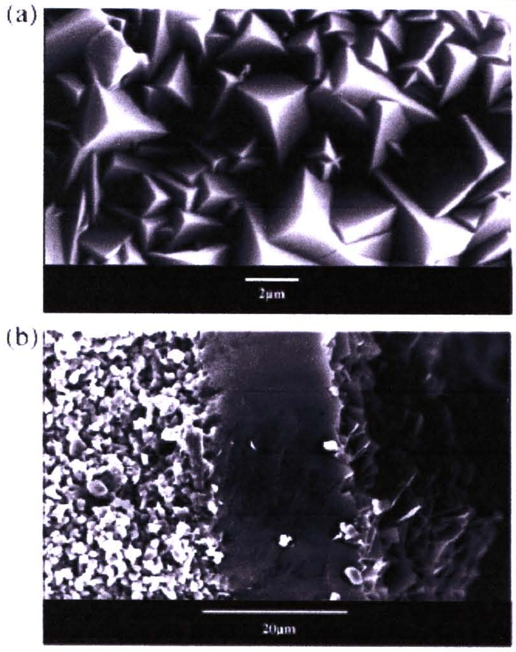

**Fig. 9.** SEM micrographs of ACM: (a) surface and (b) thickness.

The stability of the NaA zeolite membrane synthesized by the MW technique was determined using the recycle-continuous pervaporation 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. 2, the %ethanol produced in the retentate side in Fig. 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. 3, and 7).

## 4. 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.

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

Dacho Kunnakorn [a,1], Thirasak Rirksomboon [a,1], Pavadee Aungkavattana [b], Neeranut Kuanchertchoo [c], Duangdao Atong [b], Khantima Hemra [b], Santi Kulprathipanja [d], Sujitra Wongkasemjit [a,*,1]

[a] *The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand*
[b] *National Metal and Materials Technology Center (MTEC), Thailand Science Park, Patumthani, Thailand*
[c] *Faculty of science, Ramkhamhaeng University, Bangkok, Thailand*
[d] *UOP, A Honeywell Company, Des Plaines, Illinois, USA*

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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$^2$/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.

## 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 ($Al_2O_3$) 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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[*] Corresponding author. Tel.: +66 2 2184133; fax: +66 202154459.
*E-mail address:* dsujitra@chula.ac.th (S. Wongkasemjit).
[1] Center for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, Bangkok, Thailand.

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## 2. Experimental

### 2.1. Materials

Fumed silicon dioxide ($SiO_2$, 390 ± 40 $m^2/g$ surface area, 0.007 µm average particle size, Sigma-Aldrich, Inc.) and aluminium hydroxide hydrate [$Al(OH)_3.xH_2O$, 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).

### 2.2. NaA zeolite seed solution synthesis

The preparation of NaA zeolite seed was conducted using the molar composition of $50Na_2O.Al_2O_3.5SiO_2.1000H_2O$ [24]. The NaA seed crystal solution was prepared by dispersing 7 g of the seed, having a particle size of approximately 0.5 µm, 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 $50Na_2O$:$Al_2O_3$:$5SiO_2$:$1000H_2O$ formula [3,13,25,26] 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 µL 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.

**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 |

## 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 Navajas et 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 ($kg/m^2/h$) and separation

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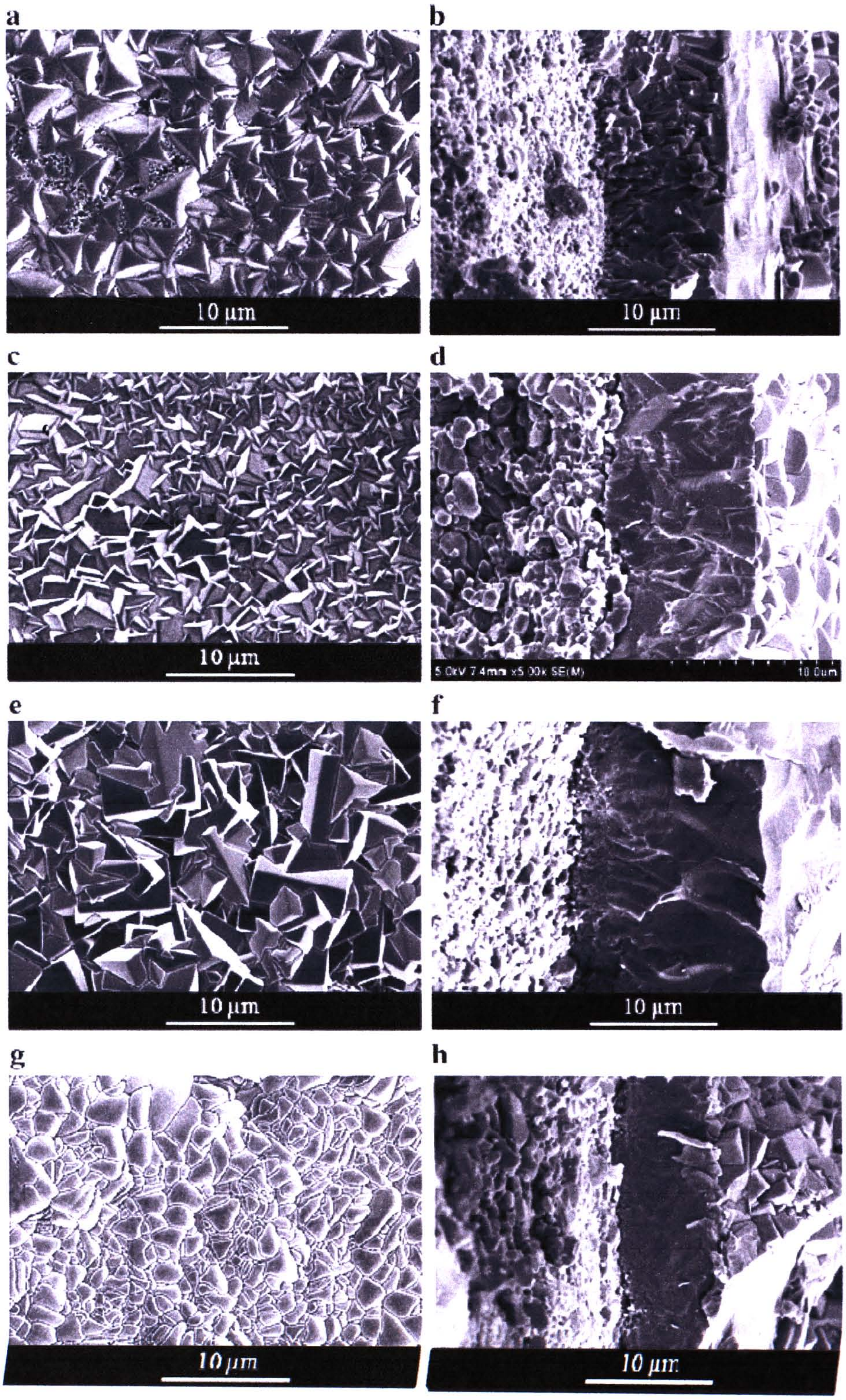

**Fig. 1.** SEM micrographs of ACMs: a, b) ACMs-3 (10 + 3 h), c, d) ACMs-2 (10 + 5 h), e, f) ACMs-1 (10 + 10 h) and g, h) ACMs-4 (8 + 3 h).

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factor. The total water flux (J, kg/m²/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 (m²), 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 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 $X_{H_2O}$ 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.

All ACMs membranes were studied for performance, stability, and reproducibility using a recycle-continuous pervaporation system and two cycles of the pervaporation test, respectively. The total water flux of the pervaporation system (see Fig. 2) decreased with an increase in the separation time for all of the ACMs. This is due to a decrease in the amount of water on the retentate side, as the pervaporation process continued [26]. Ahn et al. [10] also found that the water flux of the pervaporation system decreased with an increase in ethanol concentration in the feed mixture. This result strongly agrees with our case, as clearly seen in Fig. 3 when compared to Fig. 2. The ethanol concentration increased with the separation time, meaning less water molecules present in the feed. When the amount of water in the feed mixture was low, the vapor pressure of the water in the feed was decreased, leading to a reduction of the driving force for water to pass through the membrane. As a result, the total water flux of the system decreased. Up to this point, it can be concluded that not only the membrane thickness, but also the ethanol concentration (or water concentration) in the feed affect the total water flux of the pervaporation system [27].

In this study, it is obvious that the total water flux increased from 1.36 to 2.82 kg/m²/h when the membrane thickness decreased from 16–13 to 7–9 μm, as summarized in Table 2. Kalyani et al. [23] studied the effect of zeolite thickness on the water flux of the pervaporation system and found that the water flux decreased from 0.1 kg/m²/h to 0.016 kg/m²/h with an increase in the zeolite thickness from 20 μm to 120 μm. Moreover, Malekpour et al. [22] also found that the water flux of the pervaporation system for water–ethanol decreased with an increase in membrane thickness. It can be concluded that the increased membrane thickness increases the distance between the permeate and the retentate sides, slowing the diffusion of the water molecules from the retentate side to the permeate side, and that is why the total water flux decreased with an increase in the membrane thickness. Negishi et al [21] also showed that the total water flux decreased rapidly from 2 to lower than 0.5 kg/m²/h with an increase in the reaction time (or the membrane thickness) from 20 to 80 h. However, in their case, the separation factors obtained from those membranes were lower than 10,000, whereas our membranes still provided higher than 10,000 separation factor.

The highest total water flux, 2.82 kg/m²/h, was undoubtedly obtained from the lowest membrane thickness of ACMs-3 synthesized for 13 h, with the separation factor still remaining higher than 10,000 throughout the separation, as shown in Figs. 2 and 4 [26,29]. Compared to those presented elsewhere [21,26,27] our zeolite membranes ACMs-1, ACMs-2, and ACMs-3, provided a very high level of separation factor, higher than 10,000 throughout the separation testing time, and a considerably high total water flux. Nevertheless, unlike our study using a 10:90 water:ethanol mixture, Kittur et al. [29] explained 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%.

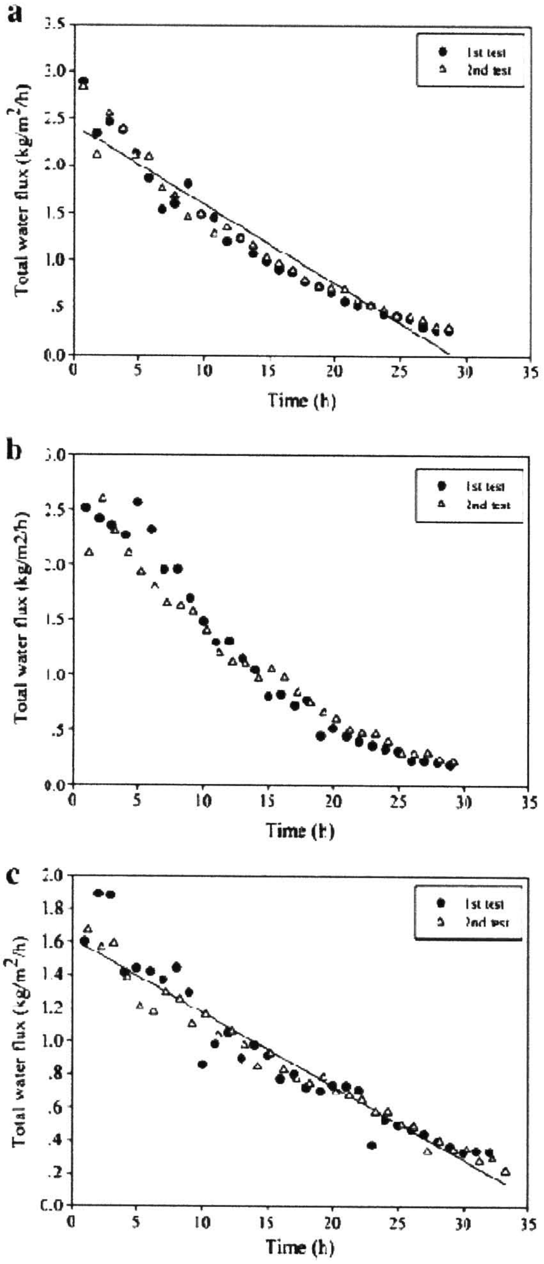

Fig. 2. Total water flux (kg/m²/h) versus time (h) of the ACMs synthesized for a) 13, b) 15, and c) 20 h.

As expected, among ACMs synthesized, the shortest time, 28 h, to produce 99.5% ethanol (or higher) was achieved by using ACMs-3 while ACMs-1 and ACMs-2 took 33 and 31 h, respectively, to reach 99.5% ethanol, as shown in Fig. 3, owing to the effect of the membrane thickness. Moreover, the resulting performance (the total water flux,

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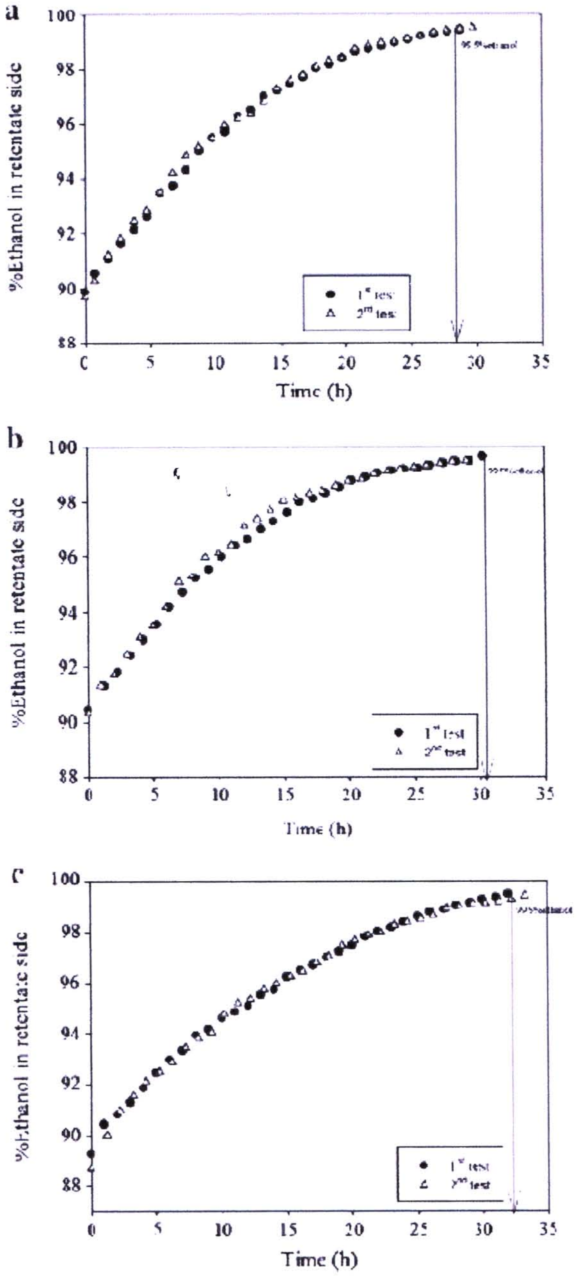

**Fig. 3** %Ethanol on the retentate site versus time (h) of the ACMs synthesized for a) 13, b) 15 and c) 20 h.

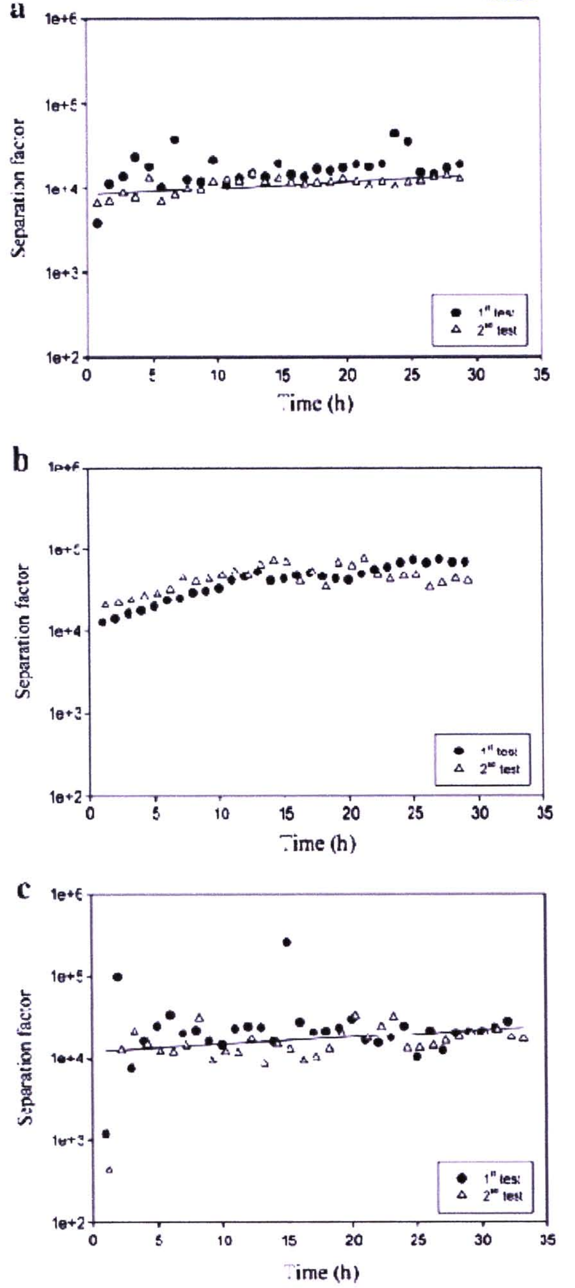

**Fig. 4** Separation factor versus time (h) of the ACMs synthesized for a) 13, b) 15, and c) 20 h.

**Table 2**
Thickness, total water flux, and separation factor of NaA zeolite membranes.

| Conditions | Membrane thickness (μm) | Total water flux (kg m$^{2}$ 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 |

the separation factor, and the time to produce 99.5% ethanol, see Figs. 2–4, respectively) of the ACMs-3 was still maintained for the first and the second runs, indicating that those membranes have good performance and good stability for 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

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**Table 3**
t-Test data for the total water flux of ACMs-1, ACMs-2 and ACMs-3.

| | α (level of significant) | p-value (probability) |
|---|---|---|
| ACMs-1 : ACMs-3 | 0.05 | 0.0025 |
| ACMs-1 : ACMs-2 | | 0.015 |
| ACMs-2 : ACMs-3 | | 0.010 |

system was 13 h using ACMs-3, which was thus chosen for further study.

### 3.3. *Statistical analysis*

In this work, *t*-test was used to determine the statistical difference between the pervaporation system using different membranes, as summarized in Tables 3 and 4. From Table 3, all data from the *t*-test provided a p-value higher than α (α = 0.05), indicating that all of our NaA zeolite membranes (ACMs-1, ACMs-2 and ACMs-3) showed a statistically significant difference in terms of total water flux (kg $m^{-2}$ h) between those membranes for water–ethanol separation in the pervaporation system. In other words, using different ACM membranes provided different values of total water flux for water–ethanol separation in the pervaporation system.

The *t*-test data in Table 4, comparing ACMs-3 and ACMs-2 to ACMs-1, gave p-values of ACMs-3:ACMs-1 and ACMs-2:ACMs-1 lower than α (α = 0.05). That means that a decrease of the synthesis time from 20 h to 15 h and from 20 h to 13 h has a statistically significant difference on the time to achieve 99.5%EtOH (or 99.5%EtOH that can be produced). However, in the case of the decrease of the synthesis time from 15 h to 13 h, the p-value was higher than 0.05, meaning an insignificant difference in the time to achieve 99.5%EtOH. Hence, from both Tables 3 and 4, the decreasing synthesis time has a significant effect on the total water flux (kg $m^{-2}$ h) and the time to achieve 99.5%EtOH for the water–ethanol separation in the pervaporation system.

### 3.4. *Productivity of NaA zeolite membrane for producing 99.5% of ethanol*

In this work, ACMs-3 could produce approximately 510 mL of 99.5% of ethanol in 28 h from the 10:90 water:ethanol feed with a 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 those reported elsewhere [21,22,26,27], this work showed a production rate of ethanol that was approximately 35.54% higher due to the much thinner membrane synthesized in our group, resulting in a much higher total water flux, and thus much less time for purifying ethanol to 99.5%.

### 3.5. *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 Fig. 5).

**Table 4**
t-Test data for the time to achieve 99.5%EtOH of ACMs-1, ACMs-2 and ACMs-3 using the pervaporation system.

| | α | p-value |
|---|---|---|
| ACMs-1 : ACMs-3 | 0.05 | 0.018 |
| ACMs-1 : ACMs-2 | | 0.005 |
| ACMs-2 : ACMs-3 | | 0.24 |

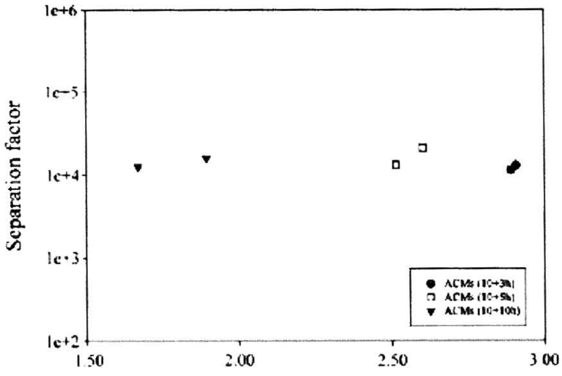

**Fig. 5.** Reproducibility of ACMs for 13, 15, and 20 h in synthesis time.

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 a level higher than 10,000 throughout the reaction time. In fact, the higher total water flux achieved from these membranes was better than previous works [19,20,26,30]. 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.

## 4. 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 only 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. The work obtained a good reproducibility and a good stability which would be suitable for industrial use in producing a high purity of ethanol.

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# Techno-economic comparison of energy usage between azeotropic distillation and hybrid system for water–ethanol separation

**D. Kunnakorn[1], T. Rirksomboon[1], K. Siemanond[1], P. Aungkavattana[2], N. Kuanchertchoo[3], D. Atong[2], K. Hemra[2], S. Kulprathipanja[4], R.B. James[4] and S. Wongkasemjit[1,*]**

[1]The Petroleum and Petrochemical College and the Center for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, Bangkok, Thailand

[2]National Metal and Materials Technology Center (MTEC), Thailand Science Park, Patumthani, Thailand

[3]Faculty of science, Ramkhamhaeng University, Bangkok, Thailand

[4]UOP, A Honeywell Company, Des Plaines, Illinois, USA

[*]Correspondence to: Tel: 66-2-2184133, Fax: 66-202154459, Email: dsujitra@chula.ac.th

## Abstract

Conventional azeotropic distillation, consuming very high energy, is mostly used to produce high purity ethanol for renewable energy usage. In this study, the techno-economic comparison between azeotropic distillation (distillation followed by practical azeotropic distillation) and hybrid system (distillation followed by pervaporation system) for producing high purity of ethanol is demonstrated using the Pro II by Provision version 8.0. In the hybrid system, NaA zeolite membrane is used to separate the water from ethanol-water mixture. It is found that the hybrid system is the most effective technique for producing more than 99.4 %wt of ethanol with an energy consumption of 52.4% less than the azeotropic distillation.

**Keywords**: Techno-economic analysis; azeotropic distillation; NaA zeolite membrane; pervaporation

## Introduction

Although the most widely used technique to produce ethanol is the distillation process, it can only produce ethanol with a purity close to 95 %wt owing to the formation of the azeotropic phase between water and ethanol [1-2]. The azeotropic distillation, involving the additional component called "entrainer" to separate water from ethanol by distillation [3], was thus introduced to solve this problem. However, azeotropic distillation is not only an energy-consuming process, but is also environmentally unfriendly, due to the toxicity of the entrainer used [4-5]. Pervaporation technique is the technique used to solve these problems because it consumes less energy and is more environmentally friendly [5-6]. The separation of this technique depends on the diffusion coefficient and relative affinity of each component in a membrane [2, 7]. By applying vacuum at the permeate side, it creates a driving force across the membrane to separate one component from the mixture. This technique can overcome the azeotropic composition problem found in the distillation process.

Membranes used in the pervaporation system are polymeric, inorganic or ceramic, and mixed-matrix membranes, depending on particular applications [8-11]. Sodium A zeolite membrane is a good candidate for water-ethanol separation using the pervaporation system [10, 12] since water can more easily pass through the membrane and go to the permeate side due to the hydrophilicity of the membrane, resulting in higher purity of ethanol in the retentate side.

Although a hybrid system — the distillation process followed by the pervaporation technique — has proven to be a better way to produce high purity ethanol (higher than 99.5%wt), the techno-economic analysis of this system has not yet been studied. In this article, the techno-economic analysis of the azeotropic distillation using benzene or cyclohexane as an entrainer was explored, comparing it to the hybrid system using the software called PRO II by Provision version 8.0 as a simulation program. Lab-scale pervaporation system of water-ethanol separation using our home-made NaA zeolite membrane was introduced to collect data and simulate the hybrid system.

## Experimental

### *Materials*

Fumed silicon dioxide ($SiO_2$, 390±40$m^2/g$ surface area, 0.007 μm average particle size) and aluminum hydroxide hydrate [$Al(OH)_3.xH_2O$, 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 obtained from the National (Thailand) Metal and Materials Technology Center (MTEC), having an 11 mm O.D., a 9 mm I.D., a 6 cm length, and a 0.3 μm pore radius on average with 38% porosity, and coated with an α-alumina intermediate (0.06 μm pore size) on the top layer, was used in this work.

### *NaA zeolite membrane synthesis*

The synthesis followed those reported elsewhere [12-14]. A tubular porous alumina support was cleaned by washing twice in deionized water for 15 min to remove dirt from the surface, 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 mmHg (1.333 kPa), followed by drying at 60 K for 24 h before coating with NaA zeolite autoclave technique. 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 seed was synthesized using the formula composition as follows: $3Na_2O$: $Al_2O_3$: $SiO_2$: $410H_2O$ [7,13,15].

The coated tubular support was placed in a teflon vessel containing the NaA zeolite solution prepared using the $50Na_2O$: $Al_2O_3$: $5SiO_2$: $1000H_2O$ formula. The vessel was then equipped in the autoclave machine and placed in the vacuum oven at 333k for 20 h to obtain the NaA zeolite membrane. The membranes were washed with deionized water and dried at 343 K for 24 h before pervaporation testing.

***Pervaporation experiment***

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 ($kg/m^2/h$) 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;

$$\text{Total water flux } (J) = W/[A*t] \qquad (I)$$

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 was determined when the time was varied in the recycle-continuous pervaporation testing.

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

where $X_{EtOH}$ and $X_{H_2O}$ are the molar fractions of ethanol and water, respectively. The subscripts of perm and reten represent the permeate and the retentate sides, respectively.

***Sample Analysis***

The separated water–ethanol products were analyzed using an Agilent Technologies 6890N gas chromatograph 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 473K and 523K, respectively.

***Simulation programs***

To compare the processes between the azeotropic distillation system and the hybrid system, 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. The first distillation column for both systems was the same, thus, a comparison between the pervaporation and the practical azeotropic distillation systems was studied for comparison in term of techno-economics for 99.5%wt of ethanol production.

For simulating both systems, 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 of ethanol, total ethanol production rate, total stage of each distillation column, and total amount of membrane surface area for the pervaporation system. Moreover, in the azeotropic distillation system, since benzene and cyclohexane were used as an entrainer to purify ethanol from 94 to 99.5 %wt, a comparison between benzene and cyclohexane was also studied in term of energy and production points of view.

## Results and discussion

### *Pervaporation testing results*

As can be seen in Fig. 1 and Table 1, to reach 99.5%wt of ethanol, the lab-scale pervaporation system for water-ethanol separation using our home-made NaA zeolite membrane showed an impressive performance with the total water flux as high as 2.12 kg/m$^2$/h and the separation factor higher than 10,000 for all membranes tested and all water-ethanol mixtures in the ranges from 90–95% (below the azeotropic point) and 95–99.5% (above the azeotropic point).

### *Simulation program*

For simulating the azeotropic distillation (distillation column followed by practical azeotropic distillation column) and the hybrid (distillation column followed by pervaporation unit) systems using the PRO II program, the feed flow rate was assumed as 1,000 kg/h with 50:50 ethanol:water at atmospheric pressure. 298 K was employed as the initial feed temperature before moving to the distillation column of both systems to reduce the energy consumption of the distillation process. The temperature of the practical azeotropic distillation column of the azeotropic distillation system was set at 351 K, while that of the pervaporation unit of the hybrid system was set at 343 K, which is the same as the one set in the lab scale pervaporation testing.

1. Distillation column

Ethanol-water mixture with the %wt ratio of 50:50 was first purified in the distillation column to obtain a higher purity of ethanol. Total distillation column stages of 20 at the stage number 18 and the reflux ratio (R) of 20 was acquired from the simulation program, as shown in Fig. 2. The feed rate of the ethanol mixture produced from this process was 531.84 kg/h with 94 %wt with 6 %wt of water which is close to the azeotropic composition of water and ethanol (around 95:5 %wt of ethanol:water) [3, 16]. That means that other techniques are needed to combine with the distillation column to increase the purity of ethanol.

2. Azeotropic distillation

A result of the azeotropic distillation from the PRO II simulation program, requiring 25 stages of practical azeotropic distillation column with the reflux ratio of 20, is shown in Fig. 3. The 531.84 kg/h of the product feed rate with a composition close to azeotropic point of ethanol obtained from the distillation column was moved to the practical azeotropic distillation column, using benzene (or cyclohexane) as an entrainer fed from the top of the column. The azeotropic mixture stream was fed from the bottom at stage 23. The entrainer can break the azeotropic mixture (water-ethanol azeotrope), resulting in a very high purity of ethanol (as high as 99 %wt of ethanol with the feed flow rate of 504.97 kg/h). However, the final specification of the required ethanol for industry is at least 99.5%wt of ethanol; thus, the addition of the second practical azeotropic distillation column, using the same conditions as the first one, was introduced in the system, as can be seen in Table 2. The purity of the ethanol produced was increased, but still contained less than 99.5%wt of ethanol. The addition of the third practical azeotropic distillation column was thus conducted, causing higher investment, operation, and energy costs, as stated in *Hoof et al.* [2] who also found that total cost increased with a rise in the capacity and the amount of azeotropic distillation column.

In addition, changing the type of the entrainer from benzene to cyclohexane, as shown in Fig. 4, indicated that 3 kg/h of cyclohexane, higher than benzene, was required to produce 99 %wt of ethanol, as shown in the figure, implying that benzene was more effective than cyclohexane for purifying the ethanol in this simulation program.

3. Hybrid system (distillation followed by pervaporation system)

The hybrid system studied in this work is shown in Fig. 5. The first distillation column was the same as that used in the azeotropic distillation process, meaning that the starting feed stream for the pervaporation system was 531.84 kg/h, having the composition of 94 %wt of ethanol and 6 %wt of water. From the simulation program, it was found that 15 $m^2$ surface area of the NaA zeolite membrane was required to produce 99.5%wt of ethanol with the ethanol amount of 502.44 kg/h.

### *Techno economic calculations*

In this work, we consider the total energy required to produce 99.5 %wt of ethanol, examining not only both the azeotropic distillation and the hybrid systems, but also the type of entrainer, benzene and cyclohexane. To compare the cost of the operation for both systems, the energy required for the practical azeotropic distillation was compared to that required for the pervaporation system, as summarized in Table 3. The pervaporation system consumed less energy to produce 99.5%wt of ethanol; hence the whole mixture was not needed to distill, as compared to the azeotropic distillation system, which requires the addition of the second and the third azeotropic columns. In the pervaporation system, only the permeating component, which is pure water, required a heat of evaporation, as mentioned by *Hoof et al.* [2], who also found that the energy required for water evaporation in the pervaporation system was lower than that in the azeotropic distillation system. Furthermore, even though the energy required ($Q_R$) for producing ethanol by using cyclohexane was slightly lower than benzene, the amount of cyclohexane required for purifying ethanol to 99 %wt was higher, as can be seen in Table 4. From this point, we may infer that benzene was a more effective entrainer than cyclohexane for using as an entrainer in the practical azeotropic distillation.

Commercially, the energy required to produce 99.5%wt ethanol was expressed in terms of condenser energy required ($Q_C$) and reboiler energy required ($Q_R$) in the distillation and the practical azeotropic distillation columns. Thus, considering the cost of each system in the purification of ethanol, it was assumed that both of $Q_C$ and $Q_R$ were come from electric energy needed and used to calculate the total cost of the operation of each system. However, the important value in the process was the supplied heat ($Q_R$) to produce ethanol. Rejecting the heat to environment is not expensive, as long as it can reject at ambient temperature. Thus, the total energy required and calculated comes from the energy required ($Q_R$) for producing ethanol and the total energy ($Q_R$+$Q_C$) for producing ethanol.

The electricity cost used in the calculation using the techno-economics analysis was 35€/MW.h, as used in the study of *Hoof et al.* [2]; thus, the cost of the total energy required and the cost of the total energy of each system were determined, as shown in Tables 5 and 6. The azeotropic distillation system (distillation followed by practical azeotropic distillation) consumed 54% more energy than the pervaporation system, resulting in a very high energy cost, consistent with the results found by *Hoof et al.* [2]. Furthermore, although the azeotropic distillation system, consisting of the second and the third practical azeotropic distillation columns, could produce high purity of the ethanol, the operating cost was remarkably high. In other words, the addition of the practical azeotropic distillation column in the distillation system was not good in terms of a techno-economics view.

As a result, the hybrid system of distillation column followed by a pervaporation system using our home-made NaA zeolite membrane was the best system for producing ethanol at very high purity (higher than 99.5%wt) at much lower cost.

## Conclusions

Using a techno-economics analysis, the hybrid process system using NaA zeolite membrane was more economically attractive than the azeotropic distillation process system. It not only saved significant energy required for producing 99.5 %wt of ethanol, but was also an environmentally friendly process. For the azeotropic distillation system, benzene was a better entrainer than cyclohexane in term of investment cost. Moreover, using the data obtained from the laboratory scale for the pervaporation system carried out using NaA zeolite membrane, the results from a simulation provided a good performance for the water-ethanol separation. We may conclude that the combination of this system and a distillation was suitable and efficient in term of techno-economic analysis for the ethanol production.

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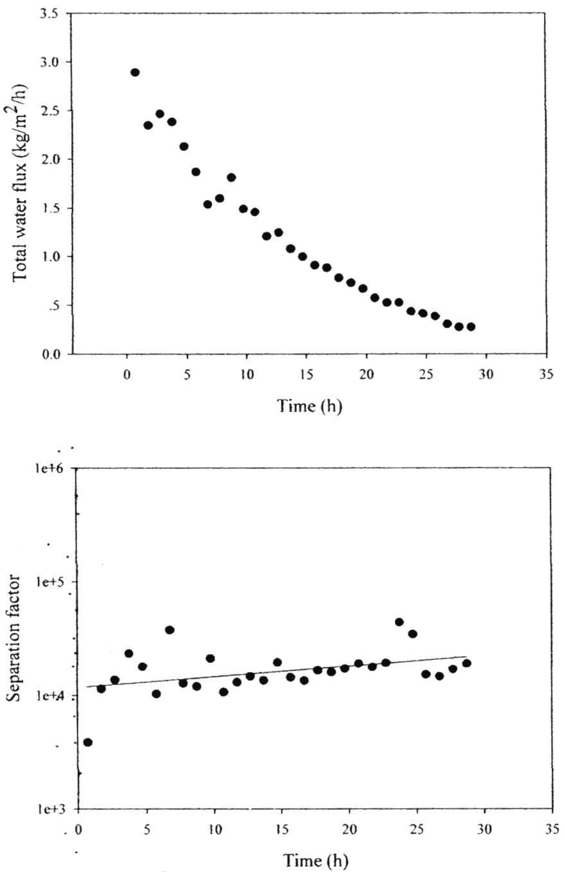

**Figure 1** Total water flux ($kg/m^2/h$) and separation factor of the pervaporation system using NaA zeolite membrane.

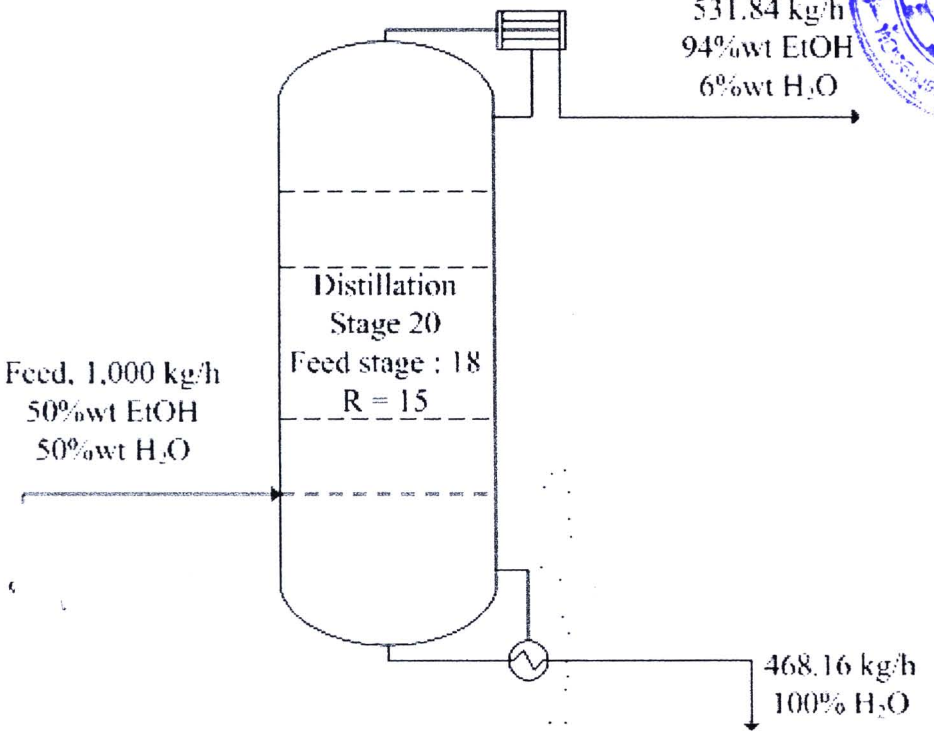

**Figure 2** Ethanol purification in the distillation column using PRO II simulation program.

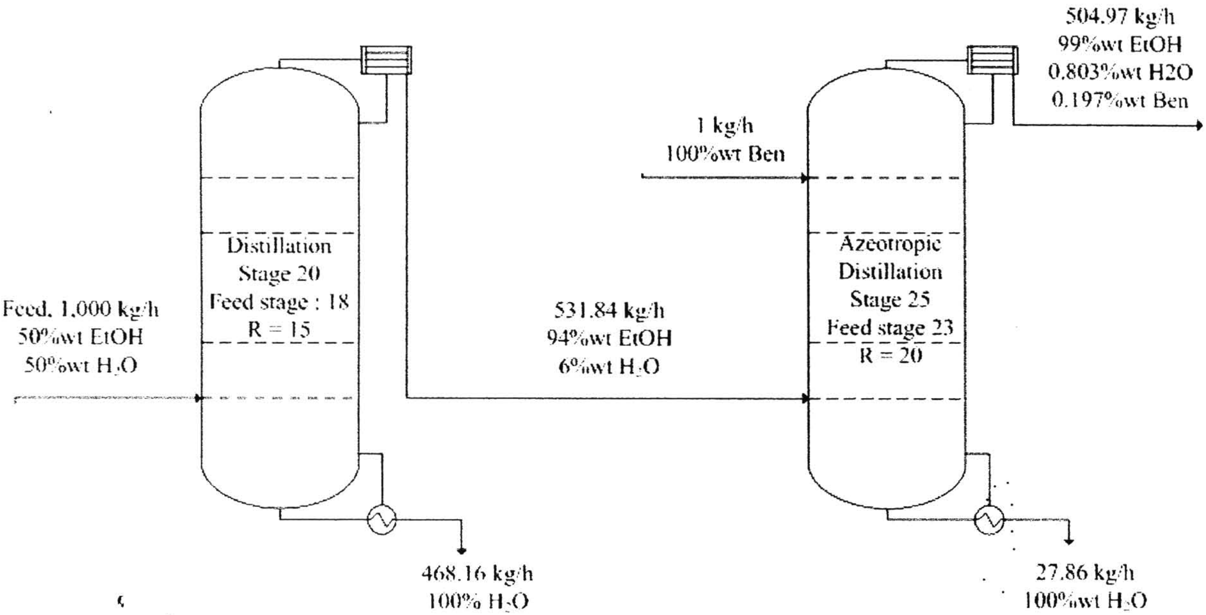

**Figure 3** Azeotropic distillation system (distillation column followed by practical azeotropic distillation column) using benzene (Ben) as an entrainer.

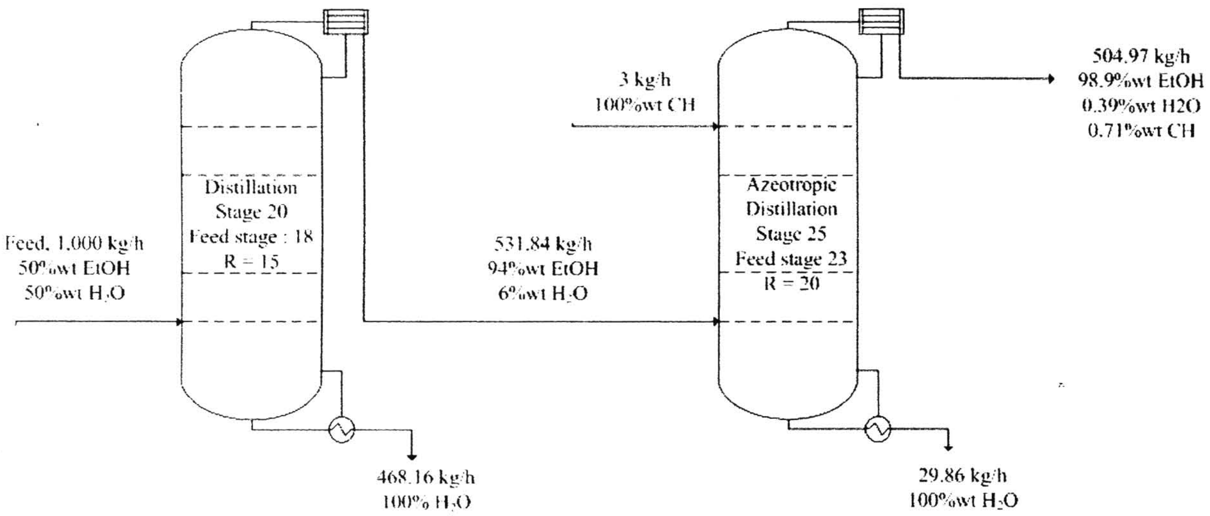

**Figure 4** Azeotropic distillation system (distillation column followed by practical azeotropic distillation column) using cyclohexane (CH) as an entrainer.

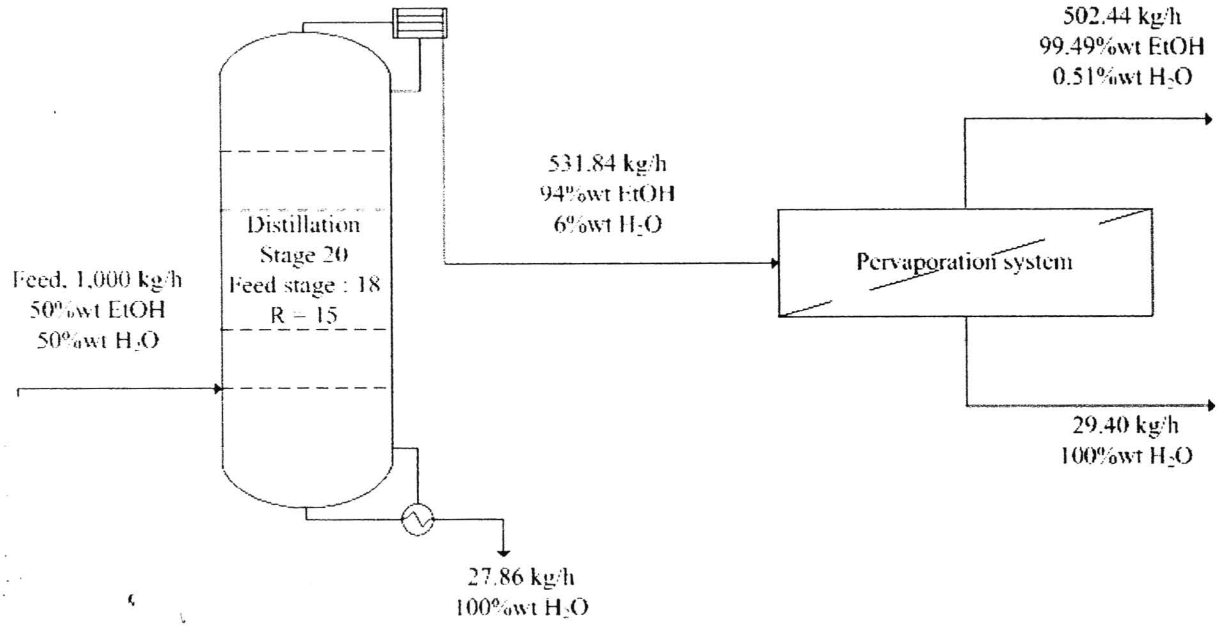

**Figure 5** Schematic diagram of the hybrid system, composing of distillation column and pervaporation system.

**Table 1** Performances of synthesized NaA zeolite membrane in lab scale pervaporation system for water-ethanol separation.

| % Ethanol feedstock | Final % ethanol | Average total water flux ($kg/m^2/h$) | Average separation factor | Time (h) |
|---|---|---|---|---|
| 90 | 95 | 2.12 | > 10,000 | 8.75 |
| 95 | 99.5 | 0.76 | > 10,000 | 20 |

**Table 2** Data obtained from simulation program of distillation column followed by azeotropic distillation column to produce 99.5 %wt ethanol.

| Column | Inlet feed flow rate (kg/h) | Inlet feed composition (%EtOH:%$H_2O$: %Entrainer) | Product stream flow rate (kg/h) | Product composition (%EtOH:%$H_2O$: % Entrainer) |
|---|---|---|---|---|
| Distillation | 1,000 | 50:50 | 531.84 | 94:6 |
| 1st Azeotropic distillation | 531.84 | 94:6 | 504.97 | 99:0.803:0.197(Bz) |
| 2nd Azeotropic distillation | 504.97 | 99:0.803:0.197 (Bz) | 503.60 | 99.26:0.39:0.35(Bz) |
| 3rd Azeotropic distillation | 503.60 | 99.26:0.39:0.35 (Bz) | 502.89 | 99.33:0.156:0.514(Bz) |

**Table 3** Total energy required for each process to produce high purity of ethanol.

| Technique | Energy required: (MJ/kg ethanol) | | | | | | | | | %Ethanol product (%wt) |
|---|---|---|---|---|---|---|---|---|---|---|
| | Distillaiton column | | 1st Practical azeotropic | | 2nd Practical azeotropic | | 3rd Practical azeotropic | | Pervaporation system | |
| | $Q_C$* | $Q_R$** | $Q_C$ | $Q_R$ | $Q_C$ | $Q_R$ | $Q_C$ | $Q_R$ | | |
| Distillation | 7.96 | 8.18 | - | | - | - | - | - | - | 94 |
| Azeotropic distillation[a] | 7.96 | 8.18 | 10.14 | 10.02 | - | - | - | - | - | 99 |
| Azeotropic distillation[b] | 7.96 | 8.18 | 10.14 | 10.02 | 10.31 | 9.79 | - | - | - | 99.26 |
| Azeotropic distillation[c] | 7.96 | 8.18 | 10.14 | 10.02 | 10.31 | 9.79 | 10.25 | 9.74 | - | 99.33 |
| Hybrid system | 7.96 | 8.18 | - | | - | - | - | - | 1.134 | 99.50 |

*$Q_C$ = Condenser energy required, **$Q_R$ = Reboiler energy required

[a] distillation column followed one practical azeotropic distillation, [b] distillation column followed two practical azeotropic distillation, [c] distillation column followed three practical azeotropic distillation.

**Table 4** Practical azeotropic distillation using different types of entrainer.

| **Entrainer** | **Total amount required (kg/h)** | **Final %wt ethanol produced** | **Total amount of ethanol produced (kg/h)** | **Energy required (MJ/kg)** | |
|---|---|---|---|---|---|
| | | | | **$Q_C$** | **$Q_R$** |
| Benzene (Ben) | 1 | 99.00 | 504.98 | 10.14 | 10.02 |
| Cyclohexane (CH) | 3 | 98.90 | 504.97 | 10.076 | 9.958 |

**Table 5** Cost of operating energy required ($Q_R$) for each system.

| Technique | Total energy required : $Q_R$ (MJ/kg ethanol) | | | | | Total energy required (MJ/kg) | Total cost of operation system (€/kg) |
|---|---|---|---|---|---|---|---|
| | **Distillation column** | **1st Practical azeotropic** | **2nd Practical azeotropic** | **3rd Practical azeotropic** | **Pervaporation system** | | |
| Distillation | 8.18 | - | - | - | - | 8.18 | 0.0794 |
| Azeotropic distillation[a] | 8.18 | 10.02 | - | - | - | 18.20 | 0.1771 |
| Azeotropic distillation[b] | 8.18 | 10.02 | 9.79 | - | - | 27.99 | 0.2723 |
| Azeotropic distillation[c] | 8.18 | 10.02 | 9.79 | 9.74 | - | 37.73 | 0.3675 |
| Hybrid system | 8.18 | - | - | - | 1.134 | 9.314 | 0.0906 |

**Table 6** Cost of total operating energy ($Q_R + Q_C$) for each system.

| Technique | Total energy for Producing Ethanol : $Q_C+Q_R$ (MJ/kg ethanol) | | | | | Total energy required (MJ/kg) | Total cost of operation system (€/kg) |
|---|---|---|---|---|---|---|---|
| | Distillation column | 1st Practical azeotropic | 2nd Practical azeotropic | 3rd Practical azeotropic | Pervaporation system | | |
| Distillation | 16.14 | - | - | - | - | 16.14 | 0.1568 |
| Azeotropic distillation[a] | 16.14 | 20.16 | - | - | - | 36.30 | 0.350 |
| Azeotropic distillation[b] | 16.14 | 20.16 | 20.10 | - | - | 56.40 | 0.5495 |
| Azeotropic distillation[c] | 16.14 | 20.16 | 20.10 | 19.99 | - | 76.39 | 0.742 |
| Hybrid system | 16.14 | - | - | - | 1.134 | 17.274 | 0.168 |

# High Performance of Polybenzoxazine Membranes for Ethanol-Water Separation via Pervaporation Technique

Kansiri Pakkethati, Nutshinun Tungsattabutrat, Thanyalak Chaisuwan*
Sujitra Wongkasemjit*

The Petroleum and Petrochemical College and the National Center of Excellence for
Petroleum, Petrochemicals and Advanced Materials, Chulalongkorn University,
Bangkok 10330 Thailand
*Address author correspondence:
Tel. 66-2-218-4133; Fax. 66-2-215-4459; e-mail address: dsujitra@chula.ac.th
Tel. 66-2-218-4143; Fax. 66-2-215-4459; e-mail address: thanyalak.c@hotmail.com

## Abstract

Pervaporation process is used to separate ethanol-water mixture by partial vaporization through a non-porous selectively permeable polybenzoxazine membrane synthesized by using bisphenol-A, formaldehyde, and two different types of diamine, 1,6-hexanediamine (hda) and ethylenediamine (eda), denoted as poly(BA-hda) and poly(BA-eda), respectively. It is found that both membranes with a thickness of 200 μm are suitable for the ethanol–water separation via pervaporation process at a feed temperature of 70 °C. However, poly(BA-eda) membrane provides higher permeation flux and separation factor with increasing ethanol concentration.

**Keywords:** Pervaporation, Polybenzoxazine, Permeation flux, Separation factor

## 1. Introduction

Pervaporation process using membranes has become of great interest in the past decade since it not only saves both energy and cost in separation of azeotropic mixtures or similar boiling-point mixtures but can also be used in many applications, such as the removal of polluting compounds and volatile organic compounds from the feed solution, dehydration of organic solvents [1], recovery of ethanol from fermentation broths [2,3], etc. In the pervaporation process, permeate is passed through a non-porous or porous membrane via partial vaporization. When a liquid mixture is in contact with a membrane, one of the components is preferentially eliminated from the mixture because of its higher attraction to, and/or faster diffusivity in, the membrane. Many polymeric membranes, such as poly(dimethylsioxane) (PDMS) [4], polyimide [5] and polyurethane [6], have been widely used for separation of the water and ethanol mixture via pervaporation because the selectivity and permeability of the membranes can be tailored to effectively separate all kinds of chemicals [7].

Recently, we have developed polybenzoxazine (PBZ) membrane for ethanol-water separation using pervaporation technique [8]. PBZ is a phenolic resin type that offers a number of outstanding properties, including a high glass-transition temperature ($T_g$), high thermal stability, good mechanical properties, low shrinkage upon polymerization, and excellent molecular design flexibility [9].

In this study, the new PBZ membrane, called poly(BA-eda) membrane, was successfully synthesized and studied with regard to its efficiency in separating water from ethanol when compared with a poly(BA-hda) membrane. The effects of aliphatic chain length, feed temperature, feed concentration, and membrane thickness on the pervaporation performance were also investigated.

## 2. Experimental

### *2.1 Materials*

1,4-Dioxane (analytical grade, Labscan, Ireland), bisphenol-A (BPA, 97% purity, Aldrich, Germany), hda (98% purity, Aldrich, Germany), ethanol (99.9% purity, J.T. Baker; White Group, Malaysia), formaldehyde (analytical grade, 37%wt. in water, Merck, Germany), and eda (99% purity, Fluka, Switzerland) were all used as received.

### *2.2 Methodology*

#### 2.2.1 Synthesis of Polybenzoxazine Precursors

Polybenzoxazine precursors were prepared using BPA, formaldehyde, and eda or hda with a mole ratio of 1:1:4, respectively [8, 10-11]. BPA (6.84 g, 30 mmol) was first dissolved in 15 mL of 1,4-dioxane in a 50 mL glass bottle and stirred until clear solution was obtained, followed by adding formaldehyde solution (9.73 g, 324 mmol). The temperature was kept at 10 °C, using an ice bath. Diamine (eda or hda) was then added dropwise into the mixture while continuously stirring for approximately 1 h until transparent viscous liquid was obtained. A heat treatment at 100 °C was required to accelerate the reaction to obtain the PBZ precursors, abbreviated as poly(BA-eda) and poly(BA-hda), for PBZ membrane preparation. The PBZ precursors were purified by washing with 200 mL of 0.1 M $NaHCO_3$ solution before solvent removal by evaporation and drying under vacuum. The characterization was analysized by proton nuclear magnetic resonance spectroscopy ($^1H$-NMR, Varian Mercury 300) using deuterated chloroform ($CDCl_3$) as a solvent.

#### 2.2.2 Preparation of Polybenzoxazine Membranes

PBZ precursors were cast on a glass plate at room temperature using Elcometer 3580 casting knife film applicator (from elcometer/inspection equipment). The membranes were dried at room temperature in air for one day and further dried at 80 °C in an air-circulating oven for one day to remove excess solvent, yielding the yellow transparent membranes. The PBZ membranes were prepared with thicknesses of 100, 200, and 300 μm to study the effect of the thickness. An attenuated total reflectance infrared spectrometer (ATR-IR, Thermo Nicolet Nexus 670) was used to analyze the chemical structure of PBZ membranes, using ZnSe 45° (flat plate) with a scanning resolution of 4 $cm^{-1}$. The membrane morphology was also investigated on a scanning electron microscope (SEM, hitachi/s-4800).

***2.3 Pervaporation Study***

A pervaporation experiment schematic drawing is shown in Fig. 1. The membranes with various thicknesses (100, 200, and 300 μm), were placed in a stainless steel reactor. A flow rate of 900 mL/min was used to circulate the ethanol-water mixture in which the concentration was varied (5, 10, 15, and 20% ethanol) from the feed reservoir to a permeation unit. The temperature of the feeding mixture was also varied at 40°, 50°, 60°, and 70 °C. The performances of the membranes were determined by measuring % ethanol and water in the permeate side to calculate the permeate flux ($kg/m^2h$) and the separation factor. The quantities of the ethanol and the water were determined using gas chromatography (GC, Agilent GC-6890). Samples of 0.5 μL were injected under the following conditions: helium as carrier gas, thermal conductivity detector (TCD) with pressure setting at 55 kPa, oven temperature set at 200 °C, injector and detector temperatures set at 200 ° and 250 °C, respectively. The separation factor and the permeate flux ($kg/m^2h$) were determined by using the following equations:

$$\text{Permeation flux (J, kg/m}^2\text{h)} = \frac{M}{At} \qquad (1)$$

where M = permeate weight (kg),

A = effective membrane surface area ($m^2$), and

t = pervaporation time (h).

$$\text{Separation Factor } (\alpha_{\text{water/ethanol}}) = \frac{Y_{water}/Y_{ethanol}}{X_{water}/X_{ethanol}} \qquad (2)$$

where $Y_{water}$ = mole fraction of water in the permeate,

$Y_{ethanol}$ = mole fraction of ethanol in the permeate,

$X_{water}$ = mole fraction of water in the the feed, and

$X_{ethanol}$ = mole fraction of ethanol in the feed.

## 3. Results and discussion

### *3.1 Characterization of PBZ Precursors* and membranes

Unlike the traditional solvent method, in which more solvent, more heat, and longer reaction time are required [12], both poly(BA-eda) and poly(BA-hda) were synthesized via quasi-solventless within one hour at low temperature. The resulting Poly(BA-eda) and poly(BA-hda) were confirmed by $^1$H-NMR measurement. $^1$H-NMR spectra (Fig. 2) show that the characteristic peaks assigned to the methylene protons of O–$CH_2$–N were found around 4.80 to 4.82 ppm. The methylene protons of Ar–$CH_2$–N of the ring-closed benzoxazine were observed around 3.90 to 3.94 ppm. The peaks at approximately 2.85 to 2.92 represent the methylene protons of the ring-opened benzoxazine. Moreover, the characteristic peaks of the methyl protons of BPA were observed around 1.55 to 1.57 ppm. These results agree with those reported by Takeichi *et al.* [12] and Ning *et al.* [13].

The chemical structure of poly(BA-eda) and poly(BA-hda) were also confirmed using ATR-IR (not shown). The out-of-plane bending vibration of C–H was observed at 932 cm$^{-1}$. The band assigned to asymmetric stretching of C–O–C and C–N–C were found at 1233 and 1128 cm$^{-1}$, respectively. Furthermore, the $CH_2$ wagging of oxazine ring was observed at 1378 cm$^{-1}$. In addition, the band at 1502 cm$^{-1}$ represents the stretching of trisubstituted benzene ring. These results are in agreement with the study of Ning and Ishida [13].

The SEM micrographs (Fig. 3) show that the resulting PBZ membranes are dense membranes. From Fig. 3c, the cross-section of poly(BA-eda) shows a few marks due to sample preparation process, but no flaw was observed in this case.

### *3.2 Pervaporation Analysis*

#### 3.2.1 Effect of feed temperature

In this study, the effect of the feed temperature, from 40° to70 °C at 10 °C intervals, was studied using 200 μm of thickness of poly(BA-eda) and poly(BA-hda) membranes and 10:90 ethanol:water. The results show that at low temperatures of 40° and 50 °C of feed mixtures, poly(BA-eda) had high permeation flux but rather low separation factor, as presented in Fig. 4 and Table 1, respectively.

Huang and Yeom [14] also investigated the effect of pervaporation temperature and suggested that the apparent activation energy was a function of permeate concentrations, due to the plasticizing effect of permeates and the interaction between permeates and the polymer. The Arrhenius-type equation was used to explain the relationship between temperature and permeation flux similar to the explanation of Qunhui *et al.* [15]

$$J = J_o \exp\left(\frac{-Ep}{RT}\right) \qquad (3)$$

where $J_0$ is permeation rate constant, R is gas constant, T is temperature in terms of Kelvin, and Ep is the activation energy for permeation, which can be obtained from the slope of the curve plotted between ln J and 1/T. The activation energy shows the amount of energy in excess of the average energy level required to permeate through the membrane.

From the principle of pervaporation, the permeate component undergoes a liquid-vapour phase change when it passes through a dense polymeric membrane, and finally only the vapour phase passes through the permeate side. Therefore, the separation performance and the activation energy are generally determined from the vapour phase of the permeated side. In the case of poly(BA-hda) membrane, we found that the average activation energy calculated from all testing temperatures was 3.74 kJ/mol. However, in the case of poly(BA-eda) membrane, the vapour phase appeared at only high testing temperatures (60° and 70 °C) while at low temperatures (40° and 50 °C) there was some liquid in the permeate side that cannot be used to calculate the activation energy. Therefore, the energy activation of both poly(BA-hda) and poly(BA-eda) membranes could be compared at only high testing temperature. The activation energy of poly(BA-hda) was 3.18 kJ/mol, while that of poly(BA-eda) membrane was 9.40 kJ/mol, meaning that at high temperature poly(BA-eda) membrane needed higher energy for water molecules to permeate through membrane more than poly(BA-hda) membrane. Thus, poly (BA-eda) membrane showed higher permeation flux than poly (BA-hda) membrane. Moreover, at high temperature, both membranes showed high permeation fluxes and high separation factors, consistent with the explanation of Quihui *et al.* [15] that at high temperature the interactions of the permeates, such as those between water–water, water–ethanol and ethanol–ethanol, became weaker, but the interaction between permeates and membrane was restored, resulting in more water passing through the membrane. In addition, the solubility parameter, which is the ratio of molar attraction and molar volume constants, can also be used to support the affinity of membranes toward ethanol. The solubility of water, ethanol, poly(BA-hda), and poly(BA-eda) membranes is presented in Table 2. It can be seen that the solubility of both poly(BA-hda) and poly(BA-eda) membranes has better affinity toward ethanol than water, allowing more water to pass through.

As discussed earlier, the temperature strongly affects the separating performance. At low temperature, however, the poly (BA-eda) membrane showed a high permeation flux and low separation factor because polymer molecules contain a shorter aliphatic chain length [–$(CH_2)_2$–], leading to less ethanol absorption, thus causing both ethanol and water to pass through and finally condense into a liquid phase which is a mixture of ethanol and water. Moreover, Quihui *et al.* [15] suggested that at low temperature the interactions between permeate molecules became stronger and the interaction between permeates and membrane became weaker, making both water and ethanol pass through the membrane. However, poly (BA-hda) membrane, in which polymer molecules have a longer aliphatic chain length [–$(CH_2)_6$–], could absorb more ethanol and allow only water molecules to pass through, resulting in low permeation flux with high separation factor.

### 3.2.2 Effect of feed concentration

The feed concentration studied was varied from 5 to 20% ethanol using poly(BA-eda) and poly(BA-hda) membranes with a thickness of 200 μm via pervaporation at 70 °C feed temperature, as shown in Fig. 5. The mixture concentration slightly affected the permeation flux. The permeation flux increased with an increase in ethanol concentration. This is probably due to an increase in membrane-free volume when ethanol concentration increased, resulting in an increase in side-chain mobility.

As a result, small-size water cluster can easily pass through the membrane-free volume. The results are in agreement with the work of Mohammadi [4], who studied pervaporation of dilute alcoholic mixtures using PDMS membrane. Huang *et al.* [16] also studied the effect of ethanol concentration on the separation of polyphosphazene with three different pendant groups and concluded that an increase of ethanol content enhanced ethanol sorption into the membrane, and, as a result, the membrane swelled more. These results were similar to those from our study in which both membranes showed high permeation flux when ethanol concentration was increased, especially in the case of poly(BA-hda) membrane containing a longer aliphatic chain length [$-(CH_2)_6-$], the permeation flux increased with an increase in ethanol concentration due to higher ethanol absorption, resulting in a greater swelling ability that allowed more water molecules to pass through. However, poly(BA-eda) membrane containing a shorter aliphatic chain length [$-(CH_2)_2-$] showed a slight increase in the permeation flux due to a lower ethanol absorption capacity. However, the separation factor of both membranes with all feed concentrations showed more than 10000. Thus, changing the feed concentration did not have a significant effect on the separation performance.

### 3.2.3 Effect of membrane thickness

Using the appropriate temperature of 70 °C, which provided the highest permeation flux and high separation factor, and 10:90 ethanol:water, the effect of membrane thickness (100, 200, and 300 μm) was investigated. When compared at the same thickness, the permeation flux was higher when poly(BA-eda) membrane was used, as shown in Fig. 6 and Table 3. As discussed earlier, poly(BA-eda) membrane, containing a shorter aliphatic chain length [$-(CH_2)_2-$], provided less ethanol sorption, allowing more water to pass through the membrane to the permeate side. Undoubtedly, the tendency of the permeation fluxes of both membranes decreased with an increase in the thickness of the membranes, consistent with Villaluenga *et al.* [17] Qunhui *et al.* [15] also studied the effect of various thicknesses of multi-layered membrane on the permeation flux and found that the swelling profile in the membrane was a function of the thickness. In our study, at the lowest thickness (100 μm), poly (BA-hda) membrane presented a very large amount of the total permeation flux due to a high degree of membrane swelling. Meanwhile, some ethanol molecules were also adsorbed in the membrane, resulting in some ethanol molecules present in the permeate. Nevertheless, the permeation flux of the thinnest poly(BA-eda) membrane (100 μm) could not be obtained since this membrane was more rigid, causing the membrane to be brittle and more easily damaged after swelling.

## 4. Conclusions

Polybenzoxazine membranes, including poly(BA-eda) and poly(BA-hda), were successfully prepared using quasi-solventless technique and employed to separate ethanol-water mixture in pervaporation process. The membrane thickness, the feed temperature and the feed concentration affected the separation performance. The permeation flux increased with an increase in the feed temperature and with a decrease in the membrane thickness. The suitable temperature of the feed solution and the thickness of the poly(BA-eda) and poly(BA-hda) membranes for 10:90 ethanol:water separation via the pervaporation process were 70 °C and 200 μm, respectively. Additionally, poly(BA-eda) membrane can be used for 20:80 ethanol:water separation.

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# CAPTIONS OF TABLES AND FIGURES

**Table 1** Separation factor of ethanol-water using poly(BA-eda) and poly(BA-hda) membranes as a function of the feed temperature

| Polybenzoxazine membrane | Separation factor (α) | | | |
|---|---|---|---|---|
| | 40 °C | 50 °C | 60 °C | 70 °C |
| poly(BA-eda) | 1.25 | 20.55 | >10,000 | >10,000 |
| poly(BA-hda) | >10,000 | >10,000 | >10,000 | >10,000 |

**Table 2** Solubility of water, ethanol, poly(BA-hda), and poly(BA-eda)

| Materials | Solubility $(cal)^{0.5}/(cm)^{1.5}$ |
|---|---|
| water | 18.63 |
| ethanol | 8.33 |
| poly(BA-hda) | 11.11 |
| poly(BA-eda) | 12.65 |

**Table 3** Separation factor of poly(BA-eda) and poly(BA-hda) membranes as a function of membrane thickness

| Polybenzoxazine membrane | Separation factor (α) | | |
|---|---|---|---|
| | 100 μm | 200 μm | 300 μm |
| poly(BA-eda) | - | >10,000 | >10,000 |
| poly(BA-hda) | 76.59 | >10,000 | >10,000 |

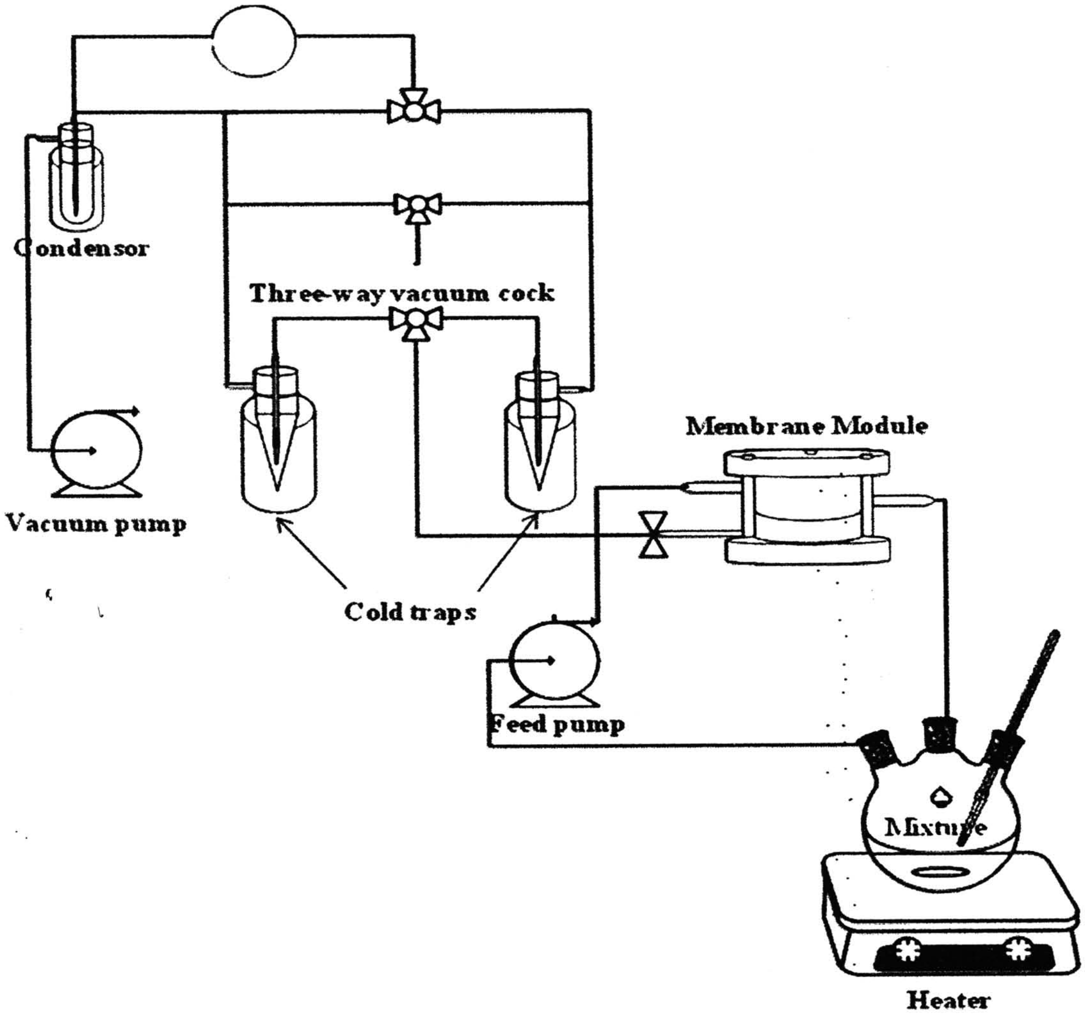

**Figure 1** Experimental set up for the pervaporation apparatus.

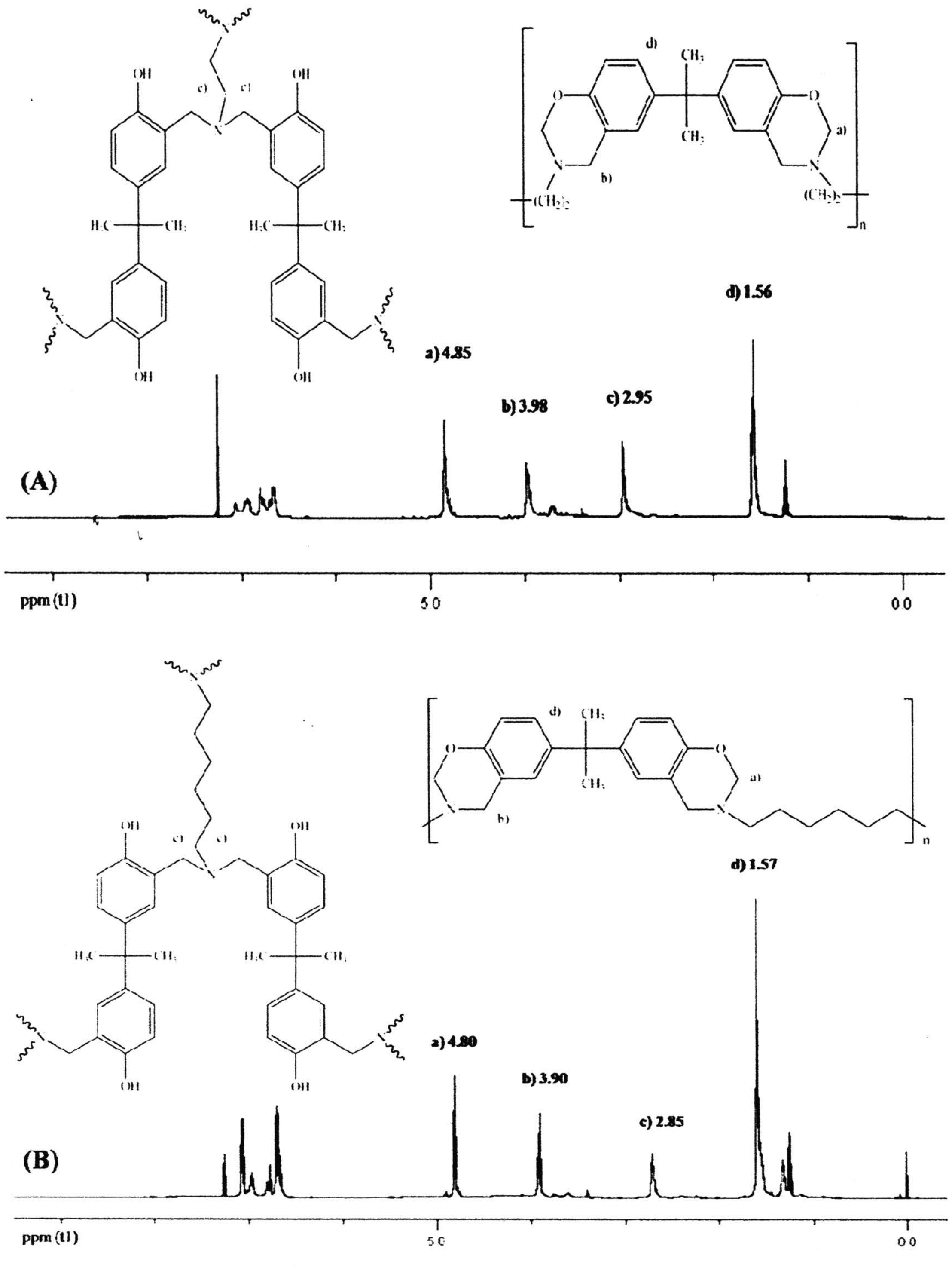

**Figure 2** $^1$H-NMR spectra of polybenzoxazine precursors: poly(BA-eda) (A) and poly(BA-hda) (B).

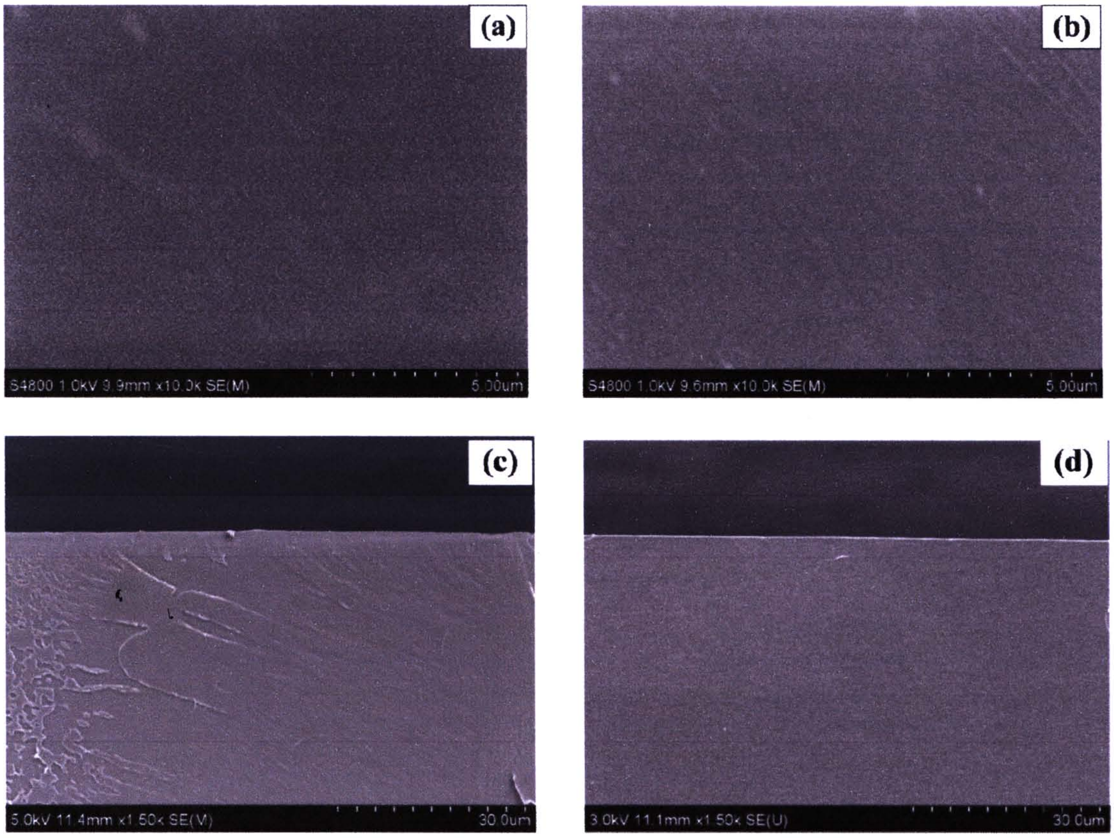

**Figure 3** SEM micrographs of surface and cross-section of poly(BA-eda) (a)(c) and poly(BA-hda) (b)(d), respectively.

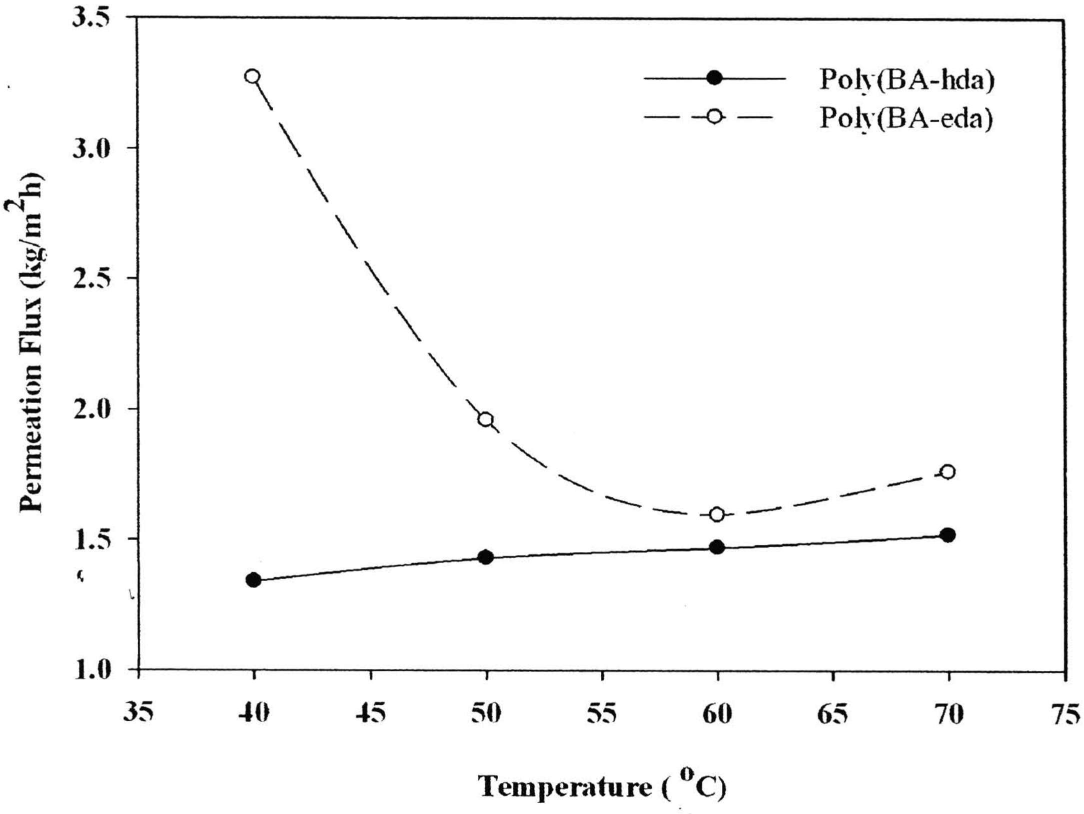

**Figure 4** Total permeation fluxes of poly(BA-eda) and poly(BA-hda) membranes as a function of the feed temperature.

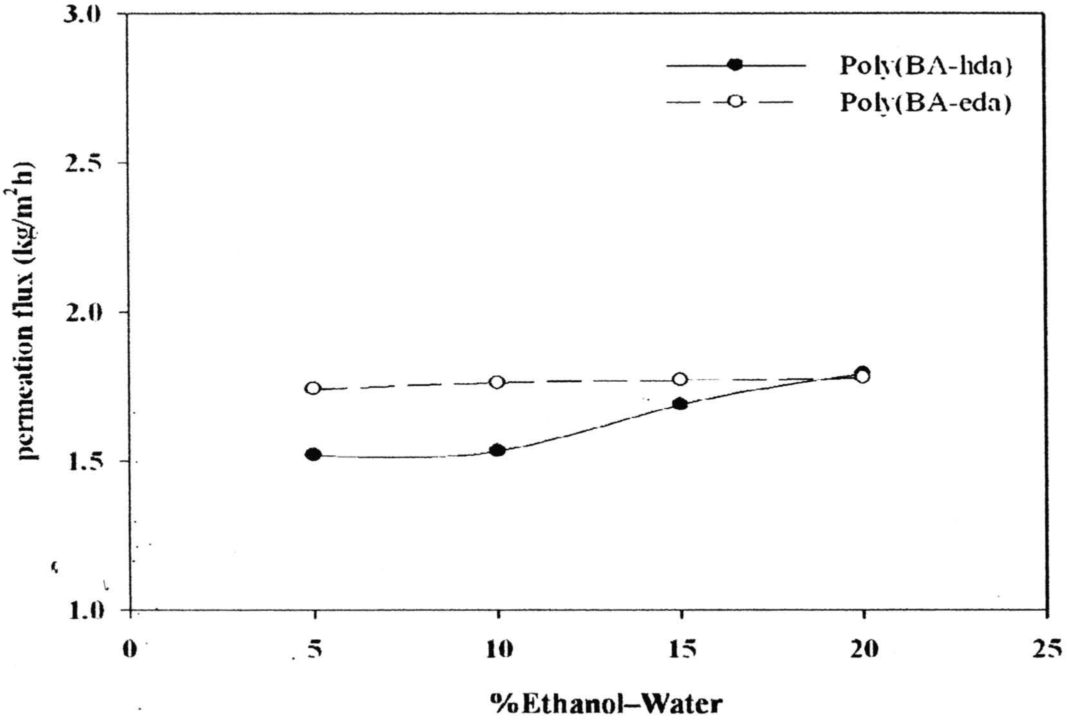

**Figure 5** Total permeation fluxes of poly(BA-eda) and poly(BA-hda) membranes as a function of the feed concentration.

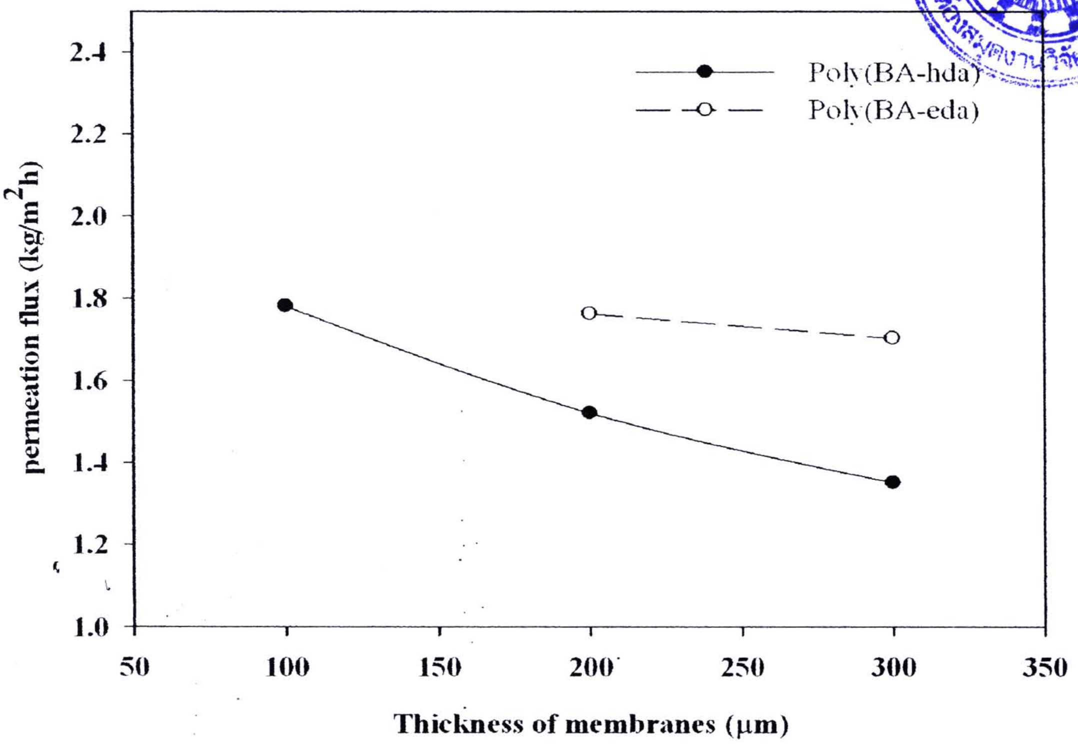

**Figure 6** Total permeation fluxes of poly(BA-eda) and poly(BA-hda) membranes as a function of the membrane thickness.

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(รองศาสตราจารย์ ดร. สุจิตรา วงศ์เกษมจิตต์)
หัวหน้าโครงการฯ
กันยายน พ.ศ.๒๕๕๔