# SEPARATION OF ETHANOL-WATER MIXTURE USING ZEOLITE 4A MEBRANE BY VAPOR PERMEATION PROCESS



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| **หัวข้อวิทยานิพนธ์** | การแยกของผสมน้ำและเอทานอล โดยใช้เยื่อเลือกผ่านซีโอไลต์ชนิด4เอ ในกระบวนการซึมผ่านของไอ |
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**บทคัดย่อ**

งานวิจัยนี้ได้ทำการเตรียมเมมเบรนซีโอไลต์เอโดยวิธีการสังเคราะห์แบบไฮโดรเทอร์มัล (Hydrothermal Synthesis) บนตัวรองรับ (Support) ซึ่งเป็นของผสมระหว่างซีโอไลต์เอ และดินขาว จากการศึกษาด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบกวาด พบว่าสามารถเตรียมเมมเบรนซีโอไลต์เอ ซึ่งมีขนาดผลึก 2.5-5.0 ไมครอนบนพื้นผิวของตัวรองรับได้ จากนั้นนำเมมเบรนซีโอไลต์เอที่เตรียมได้มาใช้ในการแยกของผสมระหว่างเอทานอล และน้ำ ด้วยเทคนิคการซึมผ่านของไอ โดยทำการทดลองที่อุณหภูมิ 85 องศาเซลเซียส ใช้เอทานอลในสารป้อนเข้มข้น 50-95% ปริมาตร ภายใต้ความดันบรรยากาศ ด้วยอัตราเร็วของก๊าซตัวพา 50-80 มิลลิลิตร/นาที จากการศึกษาผลของอัตราเร็วของก๊าซตัวพา เมื่อทำการเพิ่มอัตราเร็วของก๊าซตัวพา โดยที่ความเข้มข้นคงที่พบว่าที่ค่าการแพร่ผ่านของน้ำจะเพิ่มขึ้น (165-210 กรัม/ชั่วโมง/ตารางเมตร) และค่าการแยกเพิ่มขึ้นเมื่ออัตราเร็วของก๊าซตัวพาเพิ่มขึ้น (100 -250) การศึกษาผลของการเปลี่ยนแปลงความเข้มข้นของเอทานอลในสารป้อนและให้อัตราเร็วของก๊าซตัวพาคงที่ที่ 80 มิลลิลิตร/นาที พบว่า ค่าการแพร่ผ่านของน้ำลดลงเมื่อปริมาณความเข้มข้นของเอทานอลในสารป้อนเพิ่มขึ้น (1450 – 210 กรัม/ชั่วโมง/ตารางเมตร) และค่าการแยกเพิ่มขึ้น (130-250) จากนั้น ทำการศึกษาผลของความหนาของชั้นเมมเบรน โดยเปรียบเทียบเมมบรนที่ใช้เวลาสังคราะห์ 24 ชั่วโมง เมมเบรนที่ใช้เวลาสังเคราะห์ 48 ชั่วโมง และเมมเบรนที่นำเมมเบรนที่ใช้เวลาสังเคราะห์ 24 ชั่วโมง มาเคลือบชั้นเมมเบรนทับอีกชั้น พบว่ามีความหนาของชั้นเมมเบรนเพิ่มขึ้น 5 ไมครอน 6-7 ไมครอน และ 8-10 ไมครอนตามลำดับ จากนั้น นำมาทดสอบการแยกของผสมเอทานอลและน้ำที่ความเข้มข้นของเทานอลในสารป้อนเท่ากับ 95 % ปริมาตร อัตราเร็วของก๊าซตัวพา 80 มิลลิลิตรต่อนาที และอุณหภูมิ 85 องศาเซลเซียส พบว่า เมื่อ ความหนาของชั้นเมมเบรนเพิ่มขึ้นค่าการแพร่ผ่านของน้ำจะลดลง ( 210-150 กรัม/ชั่วโมง/ตารางเมตร) และค่าการแยกมีค่าเพิ่มขึ้น (150-500)

| | |
|---|---|
| **Thesis Title** | Separation of ethanol-water mixture using zeolite 4A membrane by vapor permeation process |
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## ABSTRACT

In this thesis, zeolite A membranes were prepared, using hydrothermal synthesis, on the surface of supports, which are the mixture of zeolite A and kaolin. XRD and SEM revealed that the surface of supports were covered with polycrystalline zeolite A film having grain size of 2.5-5.0 μm. The zeolite A membranes were used for the separation of ethanol/ water mixture in vapor phase. The experiment was carried out at 85$^{o}$ C, using 50-95% v/v ethanol as feed. The permeate was carried by Helium with flow rate 50-80 ml/min under atmospheric pressure and analyzed with on-line GC. It was found that the increase in carrier gas flow rate at the constant concentration leads to an increase in the permeation flux (165-210 g/hr m$^{2}$ ) and the separation factor (100 to 250). The effect of ethanol concentration in feed at the constant of carrier gas flow rate of 80 ml/min was found to decrease the permeation flux (1450 to 210 g/hr m$^{2}$) when the concentration of ethanol is increased ( 50-95% by volume) but increase the separation factor (130-250). The membrane layer of the zeolite A film prepared by i) 24 hour synthesis times, ii) 48 hour synthesis times, and iii) 24 hour synthesis time re-coating. Possessed thickness of 5, 6-7, and 8-10 micron, respectively. It was found that the permeation flux was decreased (210 to 150 g/hr m$^{2}$) with increase the zeolite film thickness (5-10 micron). However, the separation factor were increased with an increase in the membrane layer thickness(150 to 500).

# ACKNOWLEDGEMENT

The author would like to express my profound gratitude to my advisor, **Assoc. Prof. Dr. Tawan Sooknoi** for helpful suggestion and encouragements though out this thesis. I am also grateful to **Asst. Prof. Dr. Vanchat Chuenchom, Asst. Prof. Dr. Punnama Siriphannon and Dr. Sabaithip Tungkamanee** for serving as the chairperson and the committee, and their valuable comments.

The author would like to extend his sincere appreciation to all of my friends and my research group for their advice, support and encouragement.

Finally, the auther dedicated his work to above parents and my family for the constant love and encouragement.

**Attawit Aryuwat**

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## List of Abbreviations

| | |
|---|---|
| LTA | Line Type A |
| PEG | Poly(ethylene glycol) |
| PVA | Poly(vinyl alcohol) |
| AAS | Atomic Absorption Spectrophotometer |
| GC | Gas Chromatograph |
| SEM | Scanning Electron Microscopy |
| XRD | X-Ray Diffraction |
| SSA | Specific Surface Area |
| NaOH | Sodium Hydroxide |
| EtOH | Ethanol |

# CHAPTER 1

# INTRODUCTION

## 1.1 Motivation

The product from the fermentation of sugar contains ~ 10% ethanol in water. The traditional method for concentrating the ethanol is distillation. However, the ethanol-water system forms a low boiling point azeotope of ethanol content 96 % v/v or 95 % w/w. Which is not suitable for using ethanol in gasohol. In order to meet that objective, the ethanol must be concentrated up to more than 99.5 % v/v which is called "anhydrous or absolute ethanol". Therefore, it is interesting to the remove of water from the ethanol using processes other than distillation to obtain absolute ethanol which can be employed as the fuel. For solving this the membrane technology is very interesting particularly the zeolite membrane because 1) zeolite have uniform, molecular sized pores that provide significant differences in transport rate for some molecules and allow molecular sieving in some case, 2) most zeolite structures are chemically stable in strong solvents or low pH mixture, and 3) zeolite are stable at high temperature.

The chemistry of the zeolite can be modified to provide a suitable hydrophilic/hydrophobic surface, and the appropriate pore size and structure for certain application, including adsorption and separation. In particular, the zeolite A is regarded as a hydrophilic molecular sieve with high water adsorption capacity. Thus, the zeolite A is commonly grown on the surface of a support to improve the water selectivity of the membrane.

In this thesis, the zeolite A membranes were prepared on the surface of the supports, which were the mixture between zeolite A and clay. These membranes were used to separate ethanol-water mixture. Preparation and separation efficiency of membranes that could remove the water from the ethanol-water mixture was investigated.

## 1.2 Objectives

1. To obtain the zeolite A membrane with high water selectivity.
2. To separate water from the ethanol-water mixture by vapor permeation process using zeolite A membrane.
3. To obtain the suitable separation condition that give high water content in the permeat composition.

### 1.3 Scope of study

1. Prepare and characterize the support and the zeolite A membrane.
2. Investigate the effect of the feed composition on the separation performance of zeolite A membrane
3. Investigate the effect of carrier gas flow rate on the separation performance of the zeolite A membrane.
4. Investigate the effect of the thickness of membrane layer on the separation performance of the zeolite A membrane.

### 1.4 Expected results

The zeolite A membrane can be developed for using in the ethanol production industry. The result will provide the an appropriate membrane of choice and the optimum condition for separating water from ethanol solution giving, ethanol rich in the retentate and water rich in the permeate. The ethanol from the retentate would be applied as either fuels or fuel blending for automotive.

# CHAPTER 2

# THEORY AND LITERATURE REVIEW

## 2.1 Zeolite

Zeolites are crystalline, hydrated aluminosilicates of Group I and II elements. Structurally zeolites comprise a framework based on an infinitely extending three-dimensional network of $SiO_4$ and $[AlO_4]^{-1}$ tetrahedral linked through oxygen atoms. The framework structure encloses cavities occupied by ions and water molecules, both of which have considerable freedom of movement, permitting ion exchange and reversible dehydration. The isomorphic substitution of silicon by aluminum gives rise to a net negative charge compensated by cations. Zeolites can be represented by formula:

$$M_{2/n}O.Al_2O_3.xSiO_2.yH_2O \qquad (2.1)$$

Where M is the charge balancing cations with the valance n, x is $\geq 2$, and y is in a range of 10-10,000.

Different zeolites may have different Si/Al ratios and the tetrahedral $SiO_4$, $[AlO_4]^{-1}$ can also be isostructurally substituted by other elements such as Ga, Ge, Mn, Ti, and P, generating a molecular sieve. In an extreme case, zeolite molecular sieves may have a Si/Al ratio of infinity. Zeolite molecular sieves, such as silicalite, do not have a net negative framework charge, exhibit high degree of hydrophobicity, and have no ion exchange capacity.

Zeolite particles have been used in adsorption and separation processes and in shape selectivity catalytic processes. They are commercially used for adsorption and separation in two different ways. In one way, zeolites are in the form of granules. These exhibit high porosity with a pore size between 3-12 angstrom, depending on types of zeolites. The adsorption and separation process on molecular sieves are usually operated in non-continuous batch processes, involving alternate adsorption and desorption, and has low economic feasibility.

A second commercial use for adsorption and separation is the ceramic membranes. These exhibit high thermal, chemical, and mechanical stability, and can be used in continuous separation processes [4,6].

### 2.1.1 Zeolite A

Zeolite A exhibits the LTA (Line Type A) structure. It has a 3-dimemsional pore structure with pore running perpendicular to each other in the x, y, and z planes. The structure of zeolite A consider the arrangement of 24 primary building blocks, namely, $SiO_4$ and$AlO_4$ tetrahedral, to form the tetradecahedron cluster shown in Figure. 2.1. This secondary building block is called sodalite cage; its geometry is easy to visualize when the oxygen ions are represented as line and the Si and Al ions as points of intersection (Figure. 2.1).

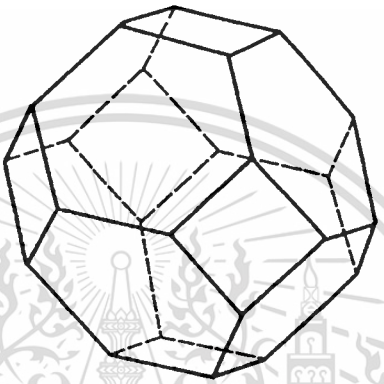
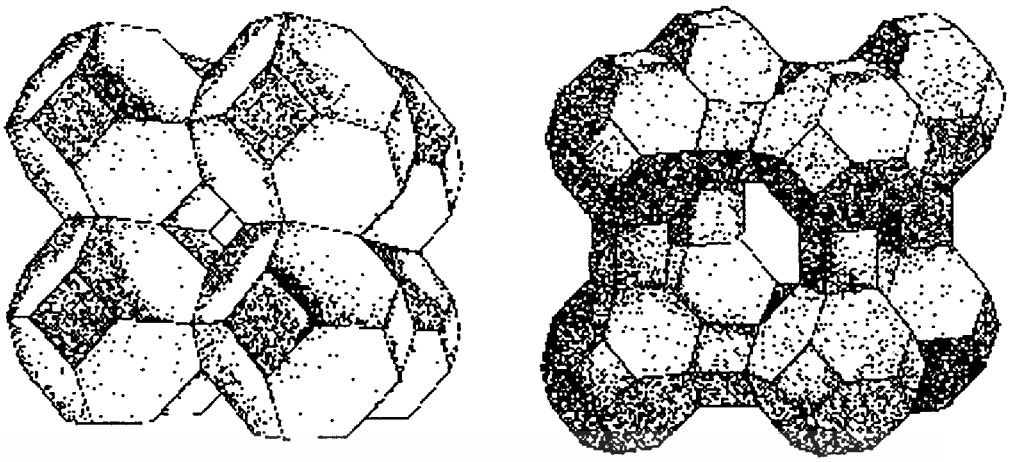


**Figure 2.1** A tetradecahedron formed 24 $SiO_4$ and $AlO_4$ tetrahedra [5].

When the sodalite cages are arranged in a regular array so that each square face of a truncated octahedron (i.e., each ring consisting of four oxygen ions) is shared by two sodalite cages, the structure of the mineral sodalite, shown in Figure. 2.2. The figure shows that the largest aperture into any enclosed volume is a six-membered oxygen ring that open into a sodalite cage. The ring is described primarily by the oxygen ions; a space-filling model shows that oxygen ions are larger than the cations, which almost seem to be buried between them. These rings have a diameter of 0.26 nanometers. Therefore, the cages can accommodate small molecules such as $H_2$ and $H_2O$, but access of larger molecule is geometrically excluded. Sodalite is therefore of virtually no interest as a catalyst [5].



(a) (b)

**Figure 2.2** (a) The sodalite structure, composed of truncated octahedra with shared square face. (b) Structure of zeolite A. The sodalite cages are connected by bridging oxygen ions between the four-membered rings [5].

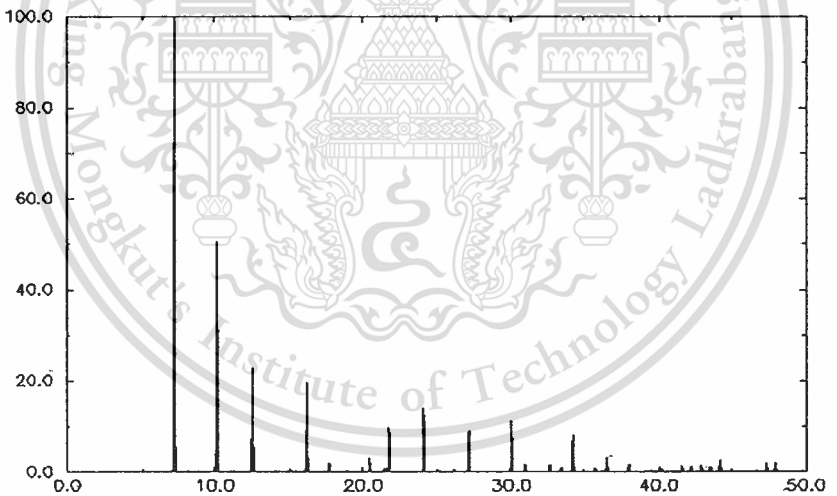



**Figure 2.3** The X-Ray Diffraction pattern of zeolite A [4].

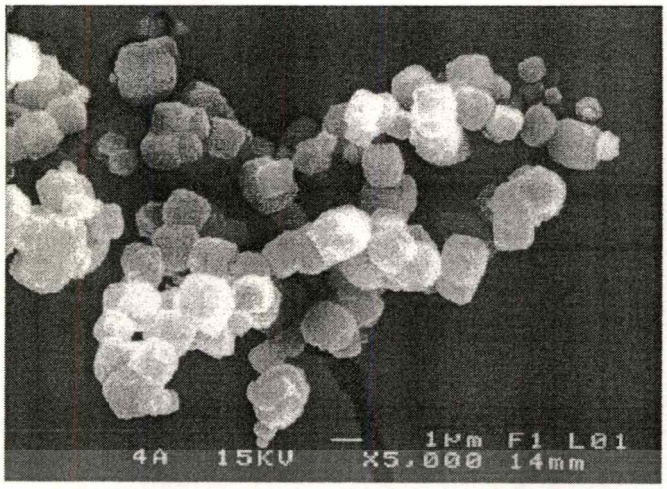



**Figure 2.4** The Scanning Electron Micrograph of zeolite A

It is possible, however, to obtain a catalytically interesting structure, called zeolite A, by stacking the sodalite cages in a more widely space manner, as shown in Figure 2.2(b). Now, the sodalite cages are connected by bridging oxygen ions between the four–membered oxygen rings. This structure has larger apertures than sodalite namely eight-membrered oxygen rings, each having a diameter of 0.42 nanometers and opening into a cavity, called an α-Cage, is surrounded by eight sodalite cages: this cavity is large enough to contain a sphere with a diameter of 1.14 nanometers. α-Cage is charateristic of zeolite A, among other; silicalite does not have alphacages. Zeolite A has a void volume fraction of 0.47, with Si/Al ratio of 1.0. It thermally decomposes at 700 $^{\circ}$C [5,8,9].

### 2.1.2 Synthesis of zeolite A

Zeolite A, like other zeolites, is synthesized in a gelling process. Sources of alumina (usually sodium aluminate) and silica (usually sodium silicate) are mixed in basic aqueous solution to give a gel. The alkali agent can be NaOH or solutions of quaternary ammonium salts, amines, or other polar organics. The gel is then heated to 70-300 $^{0}$C to crystallize the zeolite. The zeolite is normally synthesized in the Na+ form [6].

### 2.1.3 Application of zeolite A

Zeolite A is of much interest because its cage structure is useful in specific catalysis. The inner cavity is large enough for structure changing reactions to take place, but the small pore means only a specific structure can get into the cavity for the reaction, typically n-paraffins and olefins.

One use is in paraffin cracking. The small entry pore is selective towards linear paraffins, and cracking can occur on sites within the α-cage to produce smaller chain alkanes. Zeolite A is also widely used in ion exchange and separation [7,8].

## 2.2 Clay

The main elements in igneous rock are silica and alumina, which are the two essential elements in clay. The erosion and decomposition of the earth's surface is a continual process. Igneous rock is gradually eroded over hundreds of years to form fine grains. Cracked and broken by ice-cold water which seeps into the rock and turn to ice, constantly eroded by rain fall, washed away and ground down to tiny particles by action of running water in streams and river: eventually the seemingly indestructible rocks become the minute 'seeds' of clay.

Clay is the one of the cheapest and most abundant of all raw materials found throughout the world. The differences it exhibits in texture, quality and color, depend on how it was deposited and what other minerals it has collected for its formation.

### 2.2.1 Kaolin

Kaolin or china clay is found in rock formations and not in easily dug beds. It is mined by washing it out of the ground with high-pressure hosepipes and is then left to settle in large settling tanks. It may be presented chemically as $Al_2O_3{:}2SiO_2{:}2H_2O$. It is one of the most versatile of the industrial minerals and is used extensively for many applications. It is a unique industrial minerals because it

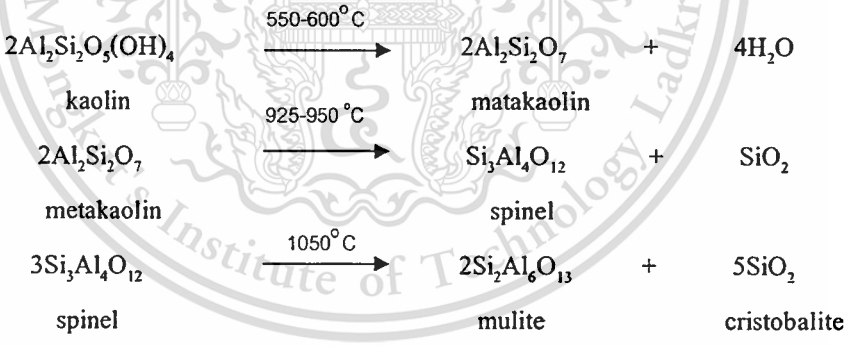
1) is chemically inert over a relatively wide pH range (except for catalytic activity in some organic systems);
2) is white or near white;
3) has good covering or hiding power when used as a pigment or extender in coating and filling;
4) is soft and nonabrasive;
5) has low conductivity of both heat and electricity; and
6) is lower in cost than most materials with which it competes.

Some uses of kaolin require rigid specification, including particle size, brightness, color, and viscosity. On the other hand, some uses have no critical specification, e.g., cement, where the only concern is light color and chemical composition. Ceramic specifications are variable in that

individual users may have different requirements as to strength, plasticity, fire color, and shrinkage. The major industries in which kaolin finds substantial use are paper, paint, ceramics, rubber, plastics, ink, catalyst, and fiberglass [12-14].

### 2.2.2. Kaolin transitions

When heated, kaolin-type clays undergo several transitions in air. The first of these take place at about 550°C and produces the disordered matakaolin phase by an endothermic dehydroxylation reaction. Although considerable controversy has been concerned with the nature of the metakaolin phase, it is now generally concluded that matakaolin is not a simple mixture of amorphous silica and alumina but retains some order which is associated with the hexagonal layers. Metakaolin is believed to be a defect phase in which the tetrahedral silica layers of the original clay structure are largely retained; adjacent are the $AlO_4$ tetrahedral units derived from the original octahedral layer. It is known to be more reactive. Either acids or alkalis more easily leach it. The metakaolin is then stable to about 925°C where it rearranges to give a defect alumina-silica spinel, which is also referred to as a gamma-alumina type structure. The so-called $\gamma$-$Al_2O_3$ phase converts to mullite, $3Al_2O_3{:}2SiO_2$, and /or silimanite at about 1050°C. The phase transition of kaolin can be demonstrated as below;




It is apparent from the stoichiometry that to form zeolite A only the alkali sodium is needed. After forming the initial matakaolin slurry, a low temperature, aging treatment improves the conversion of the clay to zeolite.

In order to form zeolites which have $SiO_2/Al_2O_3$ ratio greater than 2, additional $SiO_2$ must be added to metakaolin. For example, to produce zeolite X, a typical reaction mixture have a composition of $4Na_2O{:}Al_2O_3{:}4SiO_2{:}160H_2O$. The additional silica may be added in the form of sodium silicate or other sources such as colloidal silica [15,16].

**2.3 Membrane Separation**

Membrane separation technology is a rapidly expanding field. Organic and inorganic materials have been used as membranes in variety separation process such as microfiltration, ultrafiltration, dialysis, electrodialysis, reverse osmosis, and gas permeation. Most membranes have been made from organic polymer and also from inorganic materials such as ceramic, metal, clay, and glasses.

In the membrane separation process, a feed consisting of a mixture of two or more components is partially separated by means of a semipermeable barrier (the membrane) through which one or more species move faster than another or other species. The most general membrane process is shown in Figure 2.5 where the feed mixture is separated into a retentate (that part of the feed that dose not pass through the membrane, i.e., is retained) and a permeate (that part of the feed that pass through the membrane). Although the feed, retentate, and permeate are usually liquid or gas, they may also be solid.

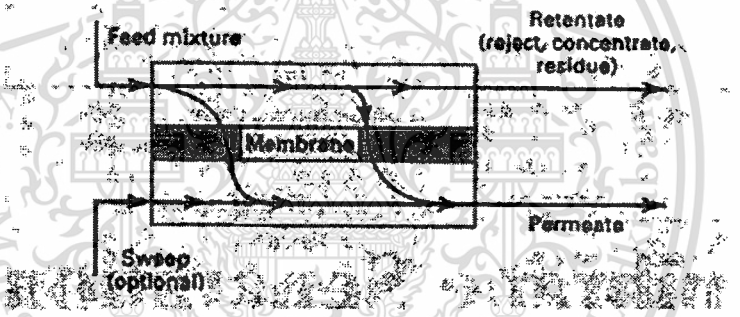



**Figure 2.5** General membrane process [18]

In membrane separation: 1) the two products are miscible, 2) the separating agent is a semipermeable membrane, and 3) a sharp separation is often difficult to achieve. Thus, membrane separation differ in two or three of these respects from the more common separation operations of absorption, stripping, distillation, and liquid-liquid extraction.

**Table 2.1** Industrial Applications of Membrane Separation Processes

**1. Reverse osmosis:**

Desalinization of brackish water

Treatment of wastewater to remove a wide variety of impurity

Treatment of surface and ground water

Concentration of foodstuffs

Removal of alcohol from beer and wine

**2. Dialysis:**

Separation of nickel sulfate from sulfuric acid

Hemodialysis (removal of waste metalbolites, excess body water, and restoration of electrolyte balance in blood

**3. Eletrodialysis:**

Production table salt from seawater

Treatment of wastewater from electroplating

Demineralization of cheese whey

Production of ultra pure water for the semiconductor industry

**4. Microfiltration:**

Sterilization of drug

Purification of antibiotic

Separation of mammalian cell from liquid

**5. Ultrafiltration:**

Preconcentration of milk before making cheese

Recovery of vaccine and antibiotic from fermentation broth

Color removal from Kraft black in paper making

**6. Pervaporation:**

Dehydration of ethanol-water azeotrope

Removal of water from organic solvent

Removal of organic from water

**Table 2.1** (continues)

| |
|---|
| **7. Gas permeation:** |
| Separation of $CO_2$ of $H_2$ from methane and other hydrocabons |
| Adjustment of the $H_2$/CO ratio in synthesis gas |
| Recovery of helium |
| Recovery methane from biogas |
| **8. Liquid membrane:** |
| Recovery of zinc from wastewater in the viscose fiber industry |
| Recovery of nickel from electroplating solution |

### 2.3.1 Transport in membranes

Membrane can be macroporous, microporous, or dense (nonporous). Only microporous or dense membranes are permselective. However, macroporous membrane are widely used to support thin microporous and dense membrane when significant pressure difference across the membrane are necessary to achieve a reasonable throughput. The theoretical basis transport through microporous membranes is more highly developed than that for dense membranes, so porous membrane will be discussed first.

#### 2.3.1.1 Porous membrane

Mechanisms for the transport of liquid and gas molecules through a porous membrane are depicted in Figure 2.6. If the pore diameter is large compared to the molecular diameter, and a pressure difference exists across the membrane, bulk or convective flow through the pores occurs, as shown in Figure 2.6(a). Such a flow is generally undesirable because it is not permselective and, therefore, no separation between components of the feed occurs. If fugacity, activity, chemical potential, concentration, or partial pressure differences exist across the membrane for the various components, but the pressure is the same on the both sides of the membrane, permselective diffusion of the components through the pore will take place, effecting a separation as shown in Figure 2.6(b). If the pores are of the order of molecular size for at least some of the components in the feed mixture, the diffusion of those components will be restricted (hindered) as shown in Figure 2.6(c), resulting in an enhanced separation. Molecules of size larger than the pores will be prevented altogether from diffusing through the pores. This special case is highly desirable and is referred to as sieving. Another special case exists for gas diffusion where the pore size and /

or pressure (typically a vacuum) is such that the mean free path of the molecules is greater than the pore diameter, resulting in so called Knudsen diffusion, which is dependent on molecular weight [17,19-21].

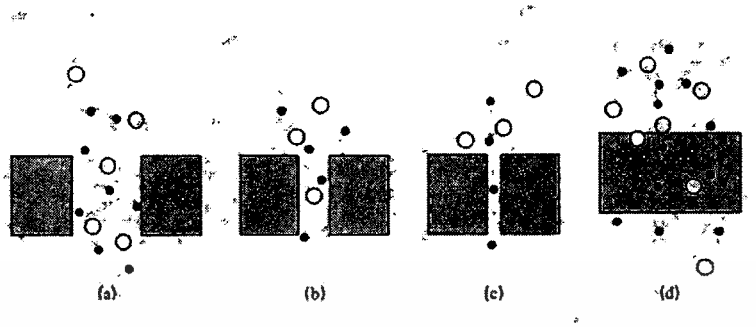



**Figure 2.6** Mechanism of transport in membranes. (Flow is downward.) (a) bulk flow through pores; (b) diffusion through pores; (c) restricted diffusion through pores; (d) solution-diffusion through dense membrane [18]

#### 2.3.1.2 Diffusion through zeolite membranes

Molecules diffuse through the pores via various diffusion mechanisms as shown in Figure 2.7. Zeolite can be size and shape selective allowing more easily straight-chain than branched hydrocarbons to pass through, for example. When used for catalytic reactions, they can be intermediate or product shape selective as well. However, separation using zeolite membranes are not always based simply on size or shape of the diffusing species. When interactions between the surface and the diffusing molecules are important, adsorption occurs and surface diffusion and / or capillary condensation can dominate the transport. In these cases, separations where the larger molecules preferentially pass through the membrane can occur. Additionally, "non-zeolite" pores – pathways through the membrane such as those crystals or any pathway other than the well-defined zeolite pores can exist in the membrane. Transport of molecules through these non-zeolite pores can be in series with or in parallel to zeolite pore diffusion. Thus, various models are being developed to describe transport of gases and liquid through zeolites. Molecules diffuse through the pores via various diffusion mechanisms were shown in Figure 2.7.

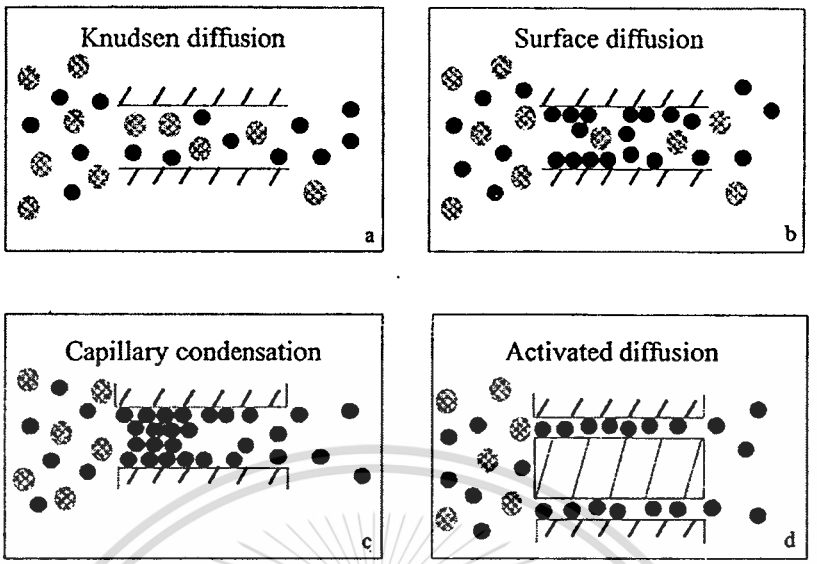



**Figure 2.7** Micropore diffusion mechanism [3]

### 2.3.2 Requirements for Membrane

Membrane productivity is a measure of the quantity of a component that permeates through a specific area of membrane in a given unit of time. Membrane productivity is frequently charaterized by permeation flux which relates to the product rate to the membrane area required to achieve the separation.

$$\text{Flux} = \frac{\text{(volume flow rate g/hr )}}{\text{(membrane area,m}^2\text{)}} \qquad (2.2)$$

When describing the selectivity of a membrane for the separation of a mixture composed of components A and B, the separation factor is defined as

$$\alpha = \frac{(P_A/P_B)}{(F_A/F_B)} \qquad (2.3)$$

where $P_A$ and $P_B$ respectively represent average concentrations, defined in %mol, of A and B in liquid permeate

$F_A$ and $F_B$ respectively represent average concentrations, defined in %mol, of A and B in liquid feed

Note that the numerical value of $\alpha$ is independent of the concentration units used, as being the ratio of ratios. When the separation factor is unity no separation occurs; when it approaches infinity, the membrane becomes perfectly 'semipermeable'. It is the membrane selectivity that forms the basis for separating a mixture.

Membrane stability is the ability of a membrane to maintain both the permeability and selectivity under specific system conditions for an extended period of time. Membrane stability is affected by the chemical, mechanical, and thermal properties of the membrane [22].

### 2.3.3 Vapor Permeation

A variant of the pervaporation process was commercialized quite recently for ethanol-water separation. The ethanol feed solution is vaporized before delivery to the membrane unit ; a vacuum is provide to remove the permeate ( this thesis the carrier used to carrier the permeate). This process thus has as much in common with gas separation as it does pervaporation. In contrast with pervaporation, however, uniformly high temperatures can be maintained throughout the membrane unit without interstage reheating because enthalpy of vaporization need not be supplied adiabatically from the feed stream. Since permeation flux varies directly with temperature, operation under essentially isothermal conditions results in a higher overall water removal rate. Consequently, fewer stages are needed to reach a given ethanol purity. Figure 2.8 shows the process flow diagram of a large vapor permeation plant in operation, with a capacity of dehydrating 30,000 liters/day of 94% ethanol to 99.9%.

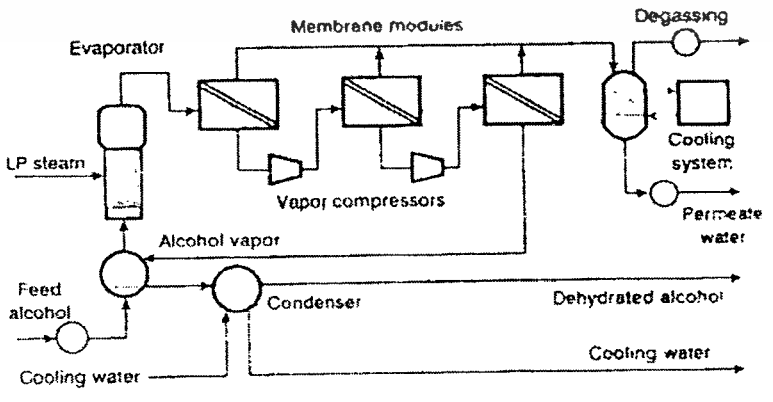



**Figure 2.8** Medium-scale (30,000 liters/day) ethanol dehydration system by vapor permeation (Lurgi GmbH )

From the mentioned aboved, vapor permeation is a varian of pervaporation[21]. In pervaporation, volatile organic components are removed from a liquid feed mixture through a semipermeable membrane into a gas phase as show in figure 2.9 . The separation components from liquid mixture is determined not only by differences in their vapor pressures but also by their permeation rate through the membrane. The driving force for permeation is the chemical potential difference of the components between the two phases separated by the membrane, however, the chemical potential gradient is usually induced by applying a vacuum on the permeated side of a membrane, by using a sweeping gas to remove the permeating components, or by applying a temperature difference between the liquid feed mixture and the permeate gas phase.

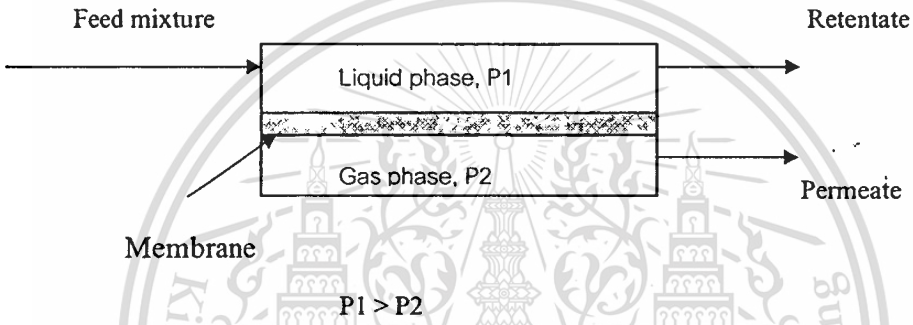



**Figure 2.9** Operation principle of pervaporation.

## 2.4 Literature Review

The polymer membranes are widely employed for the separation of liquid or gas mixture using pervaporation and gas permeation techniques [22,25-27]. This separation process can be applied successfully to mixtures, which are difficult to separate by conventional techniques, such as the azeotropic mixture or mixtures of liquids with very small differences in vapor pressure. For example, the silicone rubber membrane and polyvinyl alcohol membrane are mainly used for separating ethanol-water mixture. These membrane, however, have not been used practically because of insufficient permeation rate and insufficient thermal, mechanical and chemical stability [22,26,27].

Under these circumstances particular attentions have been paid to the utilization of a synthetic inorganic material as a separation membrane, since it has significantly high thermal,

mechanical, and chemical stability, compared with the polymer membrane. However, the inorganic or composite membranes have limited because of insufficient selectivity [6,22,25].

As fore-mentioned shortcoming of the polymeric membrane and inorganic or composite membranes, the zeolite composite membranes, which have significantly permeation selectivity and high thermal, mechanical, and chemical stability, have been realized by forming a membrane of zeolite on the porous support such as alumina, stainless steel, and clay. The common types of zeolites, which are coated on the porous support, are silicalite, X, Y and A type zeolite. These membranes are suitable for separation ethanol-water mixture [26,28-30].

The zeolite A composite membrane, which has a high water selectivity, has been widely used to separate ethanol-water mixture by pervaporation [26,29,30]. The different type of supports, which has different Si/Al ratio such as mullite and alumina support effect to the separation factor of the membrane. The permeability of the membrane increases with an increase in the alumina content of the support and reaches a constant at 70% weight of alumina. In the way, the separation factor of the membrane having the mullite support is better than that of the membrane having the alumina support [26,29].

The separation factor and permeation flux of the membranes is studied in a broad feed composition and separation temperature. The separation factor and permeation flux have been found to be strongly dependent on the feed composition and separation temperature. The separation factor and permeation flux are increased with an increase in the separation temperature. On other hand, the separation factor and permeation flux are decreased with a rise in the percent weight of ethanol in the feed composition [29].

Moreover, the separation factor and permeation flux of the membranes are studied on the effect of feed velocity and carrier gas flow rate. Change of feed velocity and carrier gas flow have obviously influence on the permeation flux but seem to have no effect on the separation factor [30].

Furthermore, the zeolite membrane cannot only be used for separation but also be used in membrane reactor because of its unique molecular sieving effect and/or catalytic properties due to the well defined pore structure of zeolites. The zeolite membrane used in chemical reactor offers a possibility to develop more effective catalytic process for the equilibrium-restricted reactions. The membrane is rendered catalytically active and a feedstock is passed through the upstream face of the membrane under catalytic conditions. For cases where all or at least one of the reaction products have higher permeability than the reactant(s), they will emerge from the downstream side of the membrane. In equilibrium limited reactions, this will lead to a higher single-pass conversion of the

reactant(s) than that normally observed and allowed by thermodynamic equilibrium constraints. At least one or all of the reaction products are collected on the downstream side of the membrane. Other advantages can be realized, for example, when one or all of the products inhibit or poison the desired reaction, or when they would undergo undesired secondary reactions. There are many types of zeolite membranes that were used in the membrane reactor [31-34].

The zeolite A composite membrane has been used as a membrane reactor for dehydration of diethylene glycol which is an equilibrium-restricted, mildly endothermic reaction. The products of the reaction, mainly 1,4-dioxane and water, form an azeotropic mixture. This membrane can be enhanced the yield of the desired product since the water that is an undesired co-product, can be continuously removed from the reaction [30].

The hydrophobic membrane such as silicalite membrane was studies for separate ethanol-water mixture by pervaporation and vaporpermeation process[39]. This reseach was investigated the transport mechanism of ethanol-water mixtures by pervaporation and vaporpermeation process. It was found that ethanol permeance was independent of water concentration in feed. Water permeance, however, seriously decreased by the presence of ethanol in feed, and water permeation was restricted by ethanol. The adsorption-diffusion model was considered for transport mechanism through the silicalite membrane. Ethanol selective adsorbed to silicalite membrane from ethanol-water vapor. The diffusion coefficients of water and ethanol were calculated based on the adsorption-diffusion model, and the results showed almost tha same diffusivity between the single component and mixture feed case. Thus, high ethanol selective permeation through the silicalite membrane was explained by the ethanol selective adsorption to the slicalite membrane.

The recent reseach about zeoliteA membrane in separation process is separation of ethanol/ethylene/water [40]. Zeolite A composite membranes were prepared, using hydrothermal synthesis, on the surface of supports composed of zeolite A and kaolin. The SEM revealed that the surface of supports were covered with polycrystalline zeolite A having crystal size of 2.5-5.0 μm. The zeolite A composite membranes were used for the separation of ethanol/ethylene/water mixture in gas phase. The permeation measurement showed that the membrane surface area, separation factor and permeation flux were increased with the increase in the zeolite A content (50 to 75%wt). However, the increase in separation temperature resulted in a reduced separation factor but an improved permeation flux. On the other hand, the increase in carrier gas flow rate and ethanol concentration in the feed enhanced the separation factor but reduced the permeation flux. In the ethanol/ethylene/water mixture, the separation factor of water was lower than that in the

ethanol/water mixture whilst the higher permeation flux was obtained. The study on the temperature effect showed that the permeation flux and the separation factor of water were decreased with an increase in the separation temperature.

In this research the zeolite A membrane will be synthesis by the optimum condition from the mentioned aboved. That is the support have zeolite A powder 62.5% and kaoline 37.5%, synthesis time 24 hours. In the membrane layer thickness effect the synthesis time will be increased from 24 hours to 48 hours and the membrane that 24 hour synthesis time will be re-coating with the zeolite gel again, therefore the thickness of the layer would be increased. The separation of ethanol-water mixture is separated by vapor permeation technique through the zeolite A membrane. The effect of feed composition, carrier gas flow rate, and the effect of membrane layer thickness of zeolite A membrane on the separation factor and permeation flux of these membranes are studied in these research.

# CHAPTER 3

# EXPERIMENTAL DETAILS

## 3.1 Reagents

1. Deionized water
2. Ethanol ($C_2H_5OH$),(Absolute,Fluka)
3. Kaolin(Fluka)
4. Ludox(colloid silica,40% $SiO_2$ ,Aldrich)
5. Poly(ethaylene glycol) (PEG) (Fluka)
6. Poly(vinyl alcohol)(PVA)(Fluka)
7. Sodium aluminate($Na_2Al_2O_4$)(Riedel de Haen)
8. Sodium hydroxide(NaOH) (Carlo Erba Reagenti)
9. Sodium metasilicate($Na_2SiO_3$)(Fluka)
10. Triethanolamine $(HOCH_2CH_2)_3N$(Fluka)
11. Zeolite A (PQ Chemical Thailand LTD.)

## 3.2 Apparatus

1. Atomic Absorption Spectrophotometer (AA-680,Shimadzu)-Graphite Furnace Atomizer(GFA-Shimadzu)
2. Autoclave (276AC2, Parr instrument Company)
3. Water cooling circulator
4. Heating mantle
5. Electrical balance (TC-254, Denver Instrument Company)
6. furnace (Vecstar Furnaces)
7. Gas Adsorption Analyzer (Autosorb-1 C,Quantachrome)
8. Gas chromatograph (3800 Gas Chromatograph,Varian)
9. Graphite Furnace Atomizer (GFA-4B,Shimadzu)
10. High temperature oven (Isotemp,Fisher Scientific)
11. Hot plate (Framo M21/1,Geratetechnik)

12. Magnetic stirrer
13. Plastic bottles
14. Plastic beakers
15. Scanning Electron Microscope(LEO 1455VP,LEO Electron Microscopy, Scientific Instrument Service Centre,KMITL)
16. Separation cell
17. Thermometer
18. Volumetric cylinder
19. X-Ray Powder Diffractrometer(D8 Advance,Bruker AG, Scientific Instrument Service Centre,KMITL)
20. X-ray Fluorescence Spectrometer(SRS 3400, Bruker AG, Scientific Instrument Service Centre,KMITL)
21. Peristaltic pump(WATSONMARLOW, 101U/R)

**3.3 Process of study**

A process of the study on the vapor permeation using zeolite A composite membrane comprises the following stages:

**3.3.1 Preparation of the support and zeolite A composite membrane**

3.3.1.1 Preparation of support

3.3.1.2 Treatment of support

3.3.1.3 Hydrothermal crystallization of zeolite A film on treated support

**3.3.2 Characterization of support and zeolite A composite membrane**

3.3.2.1 Investigate the structure of the support and zeolite A composite membrane by X-Ray Diffractometer

3.3.2.2 Investigate the morphology of the support and zeolite A composite membrane by Scanning Electron Microscopy

3.3.2.3 Determine the surface area of the support by Gas Adsorption Analyzer (Autosorp-1C)

3.3.2.4 Determine the Silicon/Aluminium ratio of the support by X-ray Fluorescence spectroscopy

**3.3.3 Separation testing**

3.3.3.1 Effect of the carrier gas flow rate

3.3.3.2 Effect of the feed composition

3.3.3.3 Effect of thickness of the zeolite A layer

**3.4 Experimental Details.**

**3.4.1 Preparation of the support and zeolite A membrane**

**3.4.1.1 Preparation of the support**

Ceramic support containing 62.5% weight of zeolite A and 37.5% kaolin can be prepared by mixing 12.5 grams of zeolite A powder and 7.5 grams of kaolin in the plastic beaker 250 ml. Then, the mixture of the zeolite A powder and kaolin was added to 23 grams of water in which 0.19 grams of polyvinyl alcohol (PVA), 0.75 grams of polyethylene glycol (PEG) and 0.75 gram of sodium metasilicate ($Na_2SiO_4$) have already been dissolved. The suspension was homogenized by stirring and heating at 80 $^{\circ}$C to evaporate water for 2 hours. Then, the sample was grinded into powder and dry at 80 $^{\circ}$C for 4 hours.

The support disk having a diameter of 13 mm, can be prepared by pressing 0.25 grams of the powder mixture with 5 tons pressure loading. Finally, the support disk was calcined at 650 $^{\circ}$C for 1 hour.

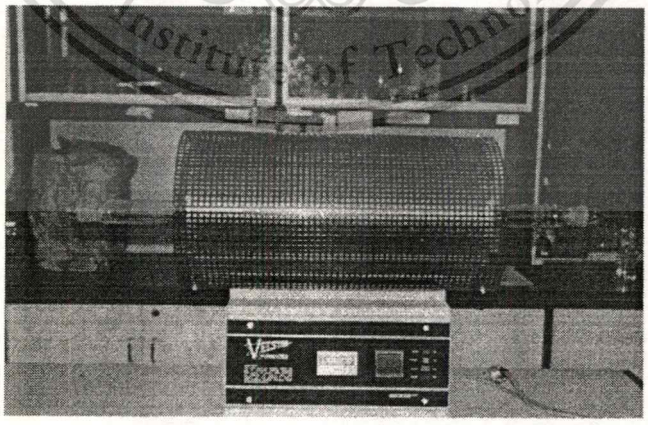


**Figure 3.1**Calcinations of support in a tube furnace.

### 3.4.1.2 Treatment of support

The support disk was placed vertically in a solution consisting of 0.35 grams of sodium hydroxide (NaOH) and 12.65 grams of water, as shown in Figure 3.2. After that, keep the autoclave at room temperature for 16 hours and then a support disk and solution was heated at 85 $^{o}$C for 8 hours. After this step, the support disk was washed and stored in water.

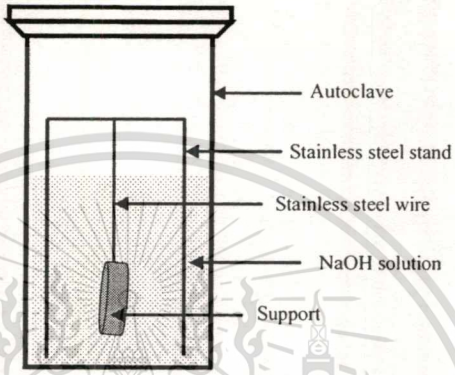



**Figure 3.2** Treatment of support in the sodium hydroxide solution

### 3.4.1.3 Zeolite A membrane preparation

The wet support disk was placed in the aluminosilicate gel with the composition of $Al_2O_3$ : $0.72SiO_2$ : $1.72Na_2O$ : $165.95H_2O$ : $2.70(HOCH_2CH_2)_3N$. The aluminosilicate gel can be prepared by mixing 1.03 grams of sodium aluminate ($Na_2Al_2O_4$) and 0.65 grams of colloidal silica (ludox 40%). Then, the mixture of sodium aluminate and colloidal silica was add to 17.54 grams of water in which 0.31 grams of sodium hydroxide (NaOH) and 2.53 grams of triethanolamine $[(HOCH_2CH_2)_3N]$ have already been dissolved. The gel was stirred for 20 minutes. The wet support disk was placed vertically in the gel, as shown in Figure 3.2 . The wet support disk and gel was heated at 85$^{o}$C for 24 hours. After that, the membrane disk was thoroughly washed and heated at 300 $^{o}$C for 2 hours in the furnace. The heating rate is 1 $^{o}$C/min. Finally, The membrane disk was slowly cooled down in the furnace.

**3.4.2 Support and zeolite A membrane characterization**

**3.4.2.1 The structure determination of support and zeolite A membrane by X-ray diffractrometer(XRD).**

The structure of supports and zeolite A membrane were determined by X-ray diffractrometer (D8 Advance, Bruker, Scientific Instruments Service Center,KMITL). The sample was prepared by fixing the disk onto sample holder. CuK$\alpha$ X-ray beam were used for analysis at 40 kV and 30 mA. The sample was scanned from 2$\theta$ angle 5° to 60° with 1 second/step time and 0.04 2$\theta$/step increment. X-ray diffraction patterns of the sample was compared with the X-ray diffraction pattern of standard zeolite A powder for the structure determination.

**3.4.2.2 Determination of the Si/Al ratio of support and zeolite A membrane by X-ray fluorescence Spectrophotometer (XRF).**

The silicon/aluminium ratio of the membrane can be determined by X-ray fluorescence spectrometer (SRS 3400, Bruker AG, Scientific Instruments Service Center, KMITL). The sample was prepared by mixing 4.5 gram of boric acid and 0.5 gram of membrane. The sample is packed onto sample holder and compressed at 150 KN. The sample was then placed in the sample chamber of X-ray fluorescence spectroscopy. Rhodium is used as source for analysis at 50 kV, 60 mA.

**3.4.2.3 Determination of the surface area of the support and zeolite A membrane by Gas Adsorption Analyzer (Autosorp-1 C, Quantachrome).**

Gas adsorption analyzer (Autosorb-1C, Quantachrome) was used for the investigation of the specific surface area (SSA) of the support and the zeolite A membrane. The sample was prepared by weighing 70-100 milligrams of sample fragment into a cleaned and dried sample cell. The sample cell was attached to the out-gassing station. Heating mantle was installed and the temperature was raised to 350 °C. The sample was out-gassed for 24 hours. The cell was removed from the out gassing station after the nitrogen or carbon dioxide was filled and then attached to the analysis station.

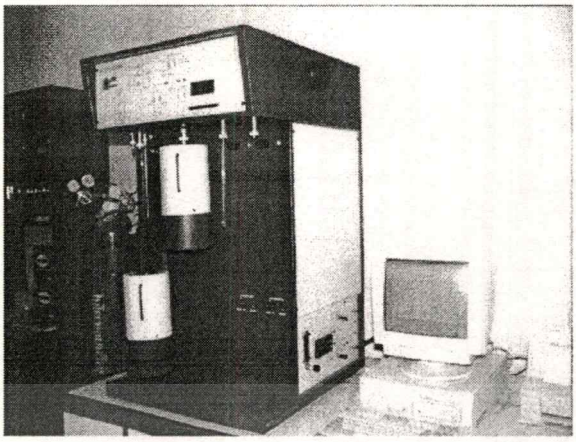


**Figure 3.3** Gas adsorption analyzer (Autosorb-1C, Quantachrome)

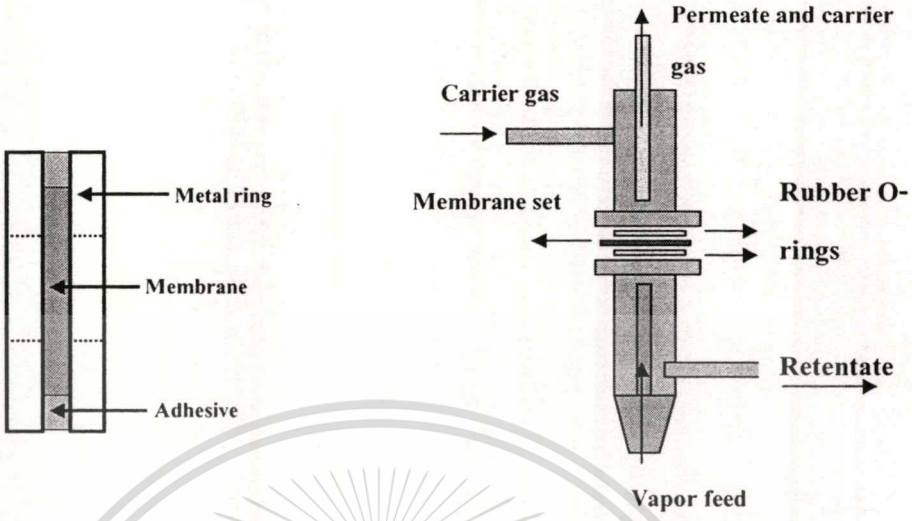
**3.4.2.4 Determination of the surface morphology of the support and zeolite A membrane by Scanning Electron Microscope (SEM).**

The crystal morphology and the crystal size was determined by scanning electron microscope (LEO 1455VP, LEO Electron Microscopy, Scientific Instruments Service Center, KMITL). The sample was prepared by placing on the disk sample onto the sample holder. It was then coated with gold by ion sputtering. The sample was placed in the sample chamber of the scanning electron microscope and evacuated from ambient pressure to $10^{-4}$ torr. The scanning electron micrographs was taken at the magnification of 1,000-5,000 times.

**3.4.3 Investigation on the separation performance of zeolite A membrane using vapor permeation process**

**3.4.3.1 Separation testing**

The zeolite A membrane synthesized according to 3.4.1.3 , was fixed between two metal rings with an inside diameter of 10 mm using cyanoacrylate adhesive. The component is called a membrane set, as shown in Figure 3.4A. The diameter of the membrane after assembly with metal ring is about 10 mm from original diameter 13 mm therefore the membrane surface is about $7.85 \times 10^{-5}$ $m^2$.

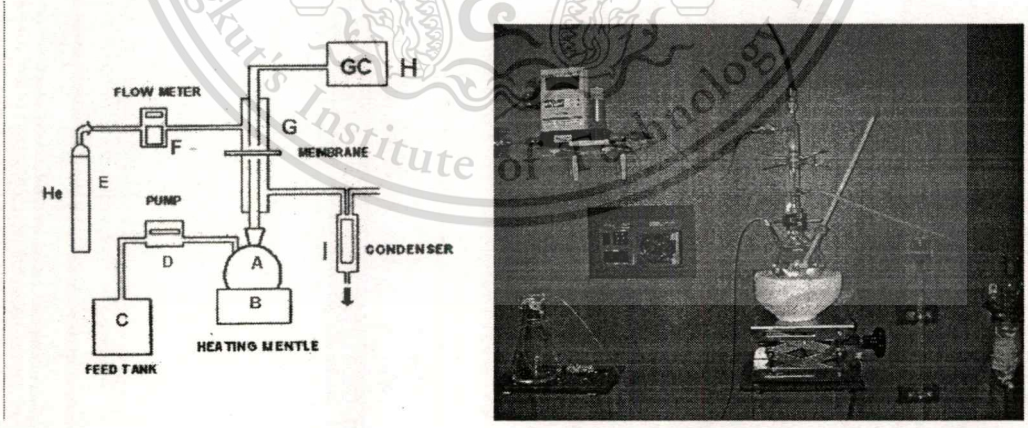



(A) (B)

**Figure 3.4 (A)** Membrane set : the zeolite A membrane was fixed with the metal rings.

**(B)** Membrane cell : the membrane set will be placed into the membrane cell.

Then the membrane set was placed into separation cell made by 4-ways Pyrex glass tube shown in Figure 3.4B.




(A) (B)

**Figure 3.5A** Separation diagrame: (A) feed chamber; (B) hot plate; (C) feed reservoir; (D) peristaltic pump; (E) carrier gas helium; (F) flow meter; (G) membrane cell; and H) Gas chormatograph

**Figure 3.5B** Separation unit

The separation cell was connected with the liquid feed chamber (A) and the carrier gas lines as shown in figure 3.5A. Then, the carrier gas helium was primary purged though cell for leak detection. The liquid feed in the chamber was heated by hot plate.

The separation testing can be performed by feeding the vapor of ethanol-water mixture into the chamber by peristatic pump. The liquid feed can be vaporized by heating at the temperature 85 $^{o}$C. The feed vapor were reach the membrane. The permeate, helium will carry permeate to Gas chromatograph as vapor at the flow rate of 50-80 ml/min, which were sampled every 10 minutes for determining the permeate composition. The flow rate of carrier gas was controlled by mass flow controller (MASS TRAK, Sierra Instrument, INC). The retentate side was connected with cooling trape. The liquid from retentate was condensed and collected. The separation testing was carried out at the atmospheric pressure for 2-3 hours.

Feed composition = mole ratio of ethanol/water in retentate + mole ratio of ethanol /water in permeate

Due to the small among of permeate diffusing though membrane, the concentration of retentate was represent as feed concentration in calculation separation factor.

The permeate and retentate were analyzed by Gas chromatography using 3800 Gas chromatograph, Varian, with PorapackQ pack column (1/8 in. diameter and 1.8 m length). It was flowed through the sampling loop (1 ml) of 6-port valve, which was then injected to injection port (200$^{o}$C). The separation temperature was started at 50 $^{o}$C . Then, the temperature was raised to 140 $^{o}$C with heating rate 20 $^{o}$C/min and hold at this temperature for 113 minute. Helium was used as carrier gas at flow rate of 30 mi/min. The liquid that collected from retentate can be analyzed by Gas chromatography at the same condition of the permeate but also the liquid was injected to the injection port by syring and hold in the oven at the temperature 140$^{o}$C for 30 minute.

**3.4.3.2 Effect of carrier gas flow rate.**

The effect of the carrier gas flow rate can be investigate by changing carrier gas flow rate 50, 60, 70 and 80 ml/min with a fixed feed composition of 95 percent by volume of ethanol in the feed mixture at temperature at 85$^{o}$C.

**3.4.3.3 Effect of feed composition**

The effect of the feed composition were investigated at optimum carrier gas flow rate providing high separation flux from section 3.4.3.1 . The various the feed composition of 95, 90, 80, 70, 60 and 50 percent by volume of ethanol in the feed mixture were used.

**3.4.3.4 Effect of membrane layer thickness**

The membrane layer thickness can be varied by two method 1) increase synthesis time from 24 hours to 48 hours and 2) the secondary growth of the membrane for another 24 hours synthesis time. The membrane layer thickness can be determined by scanning electron microscope (LEO 1455VP, LEO Electron Microscopy, Scientific Instruments Service Center, KMITL). After that, The separation efficiency of the membranes was compared using the carrier gas flow rate that provide a high separation factor from section 3.4.3.1 and feed composition is fixed at 95% by volume and the temperature was fixed at 85 $^{\circ}$C.

# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.1 Characterization of zeolite A membrane on the kaolin support.

The zeolite A composite membrane was prepared on the surface of disk support, which are the mixture of zeolite A and kaolin. Whereby, the supports were calcined for one hour at 650 °C for transformation of kaolin to metakaolin, some of which was subsequently converted into zeolite A by treatment with sodium hydroxide solution (3% weight NaOH). Then, the zeolite A membrane was prepared on the surface of the treated supports using the hydrothermal synthesis. The zeolite A composite membrane can be visualized as a wafer of polycrystalline zeolite A on the mixture of zeolite A granules and kaolin as illustrated in Figure 4.1[40].

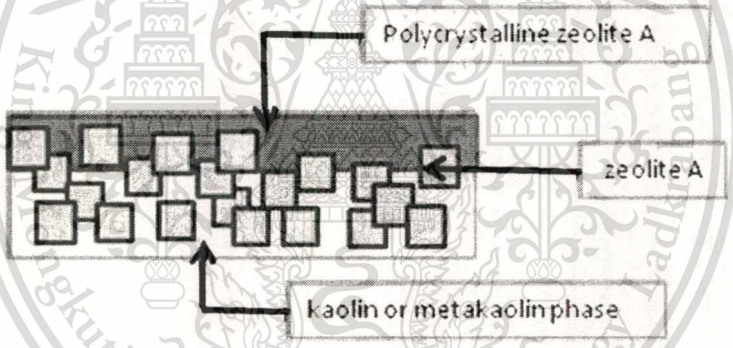



Figure 4.1 Illustration of zeolite A composite membrane[40]

### 4.1.1 The structure and the surface morphology determination

The XRD patterns of the calcined support, treated support, and zeolite A membrane were shown in Figure 4.2.

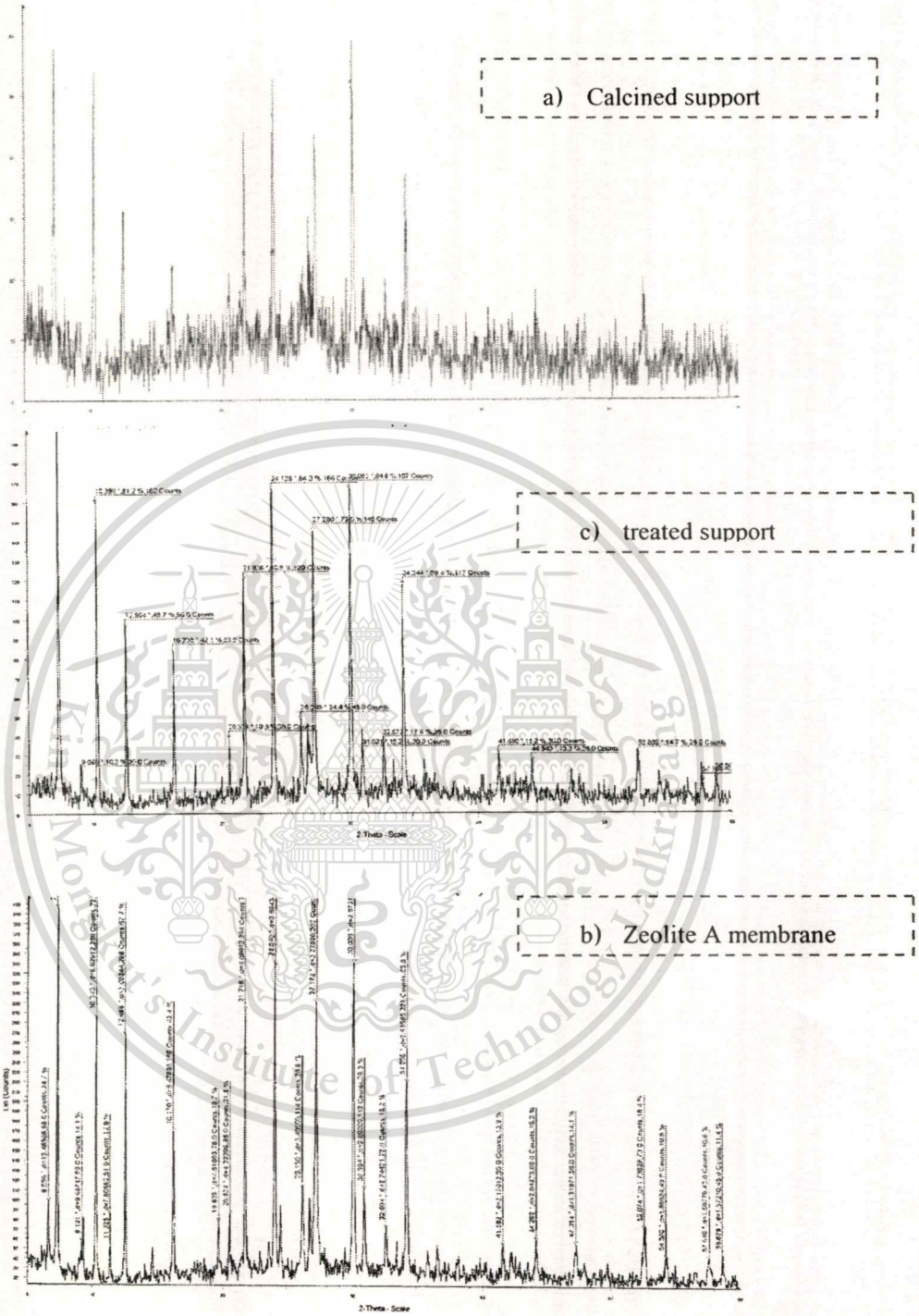



**Figure 4.2** The XRD pattern of (a) calcined support, (b) treated support and (c) zeolite A membrane.

The XRD pattern of these supports show the intensity of the peaks at $2\theta$ = 7.2, 10.2, 12.5, 30.0, and 34.3 (Figure 4.2), which refer to the zeolite A phase (Figure 4.2(c)). However, the intensity of

the peak at $2\theta$ = 26.8, which refer to the kaolin phase (Figure 4.3(a)) is also observed. It was belived that calcination at 650 $^{\circ}$C transforms kaolin to metakaolin (Figure 4.3(b)) [15,16].

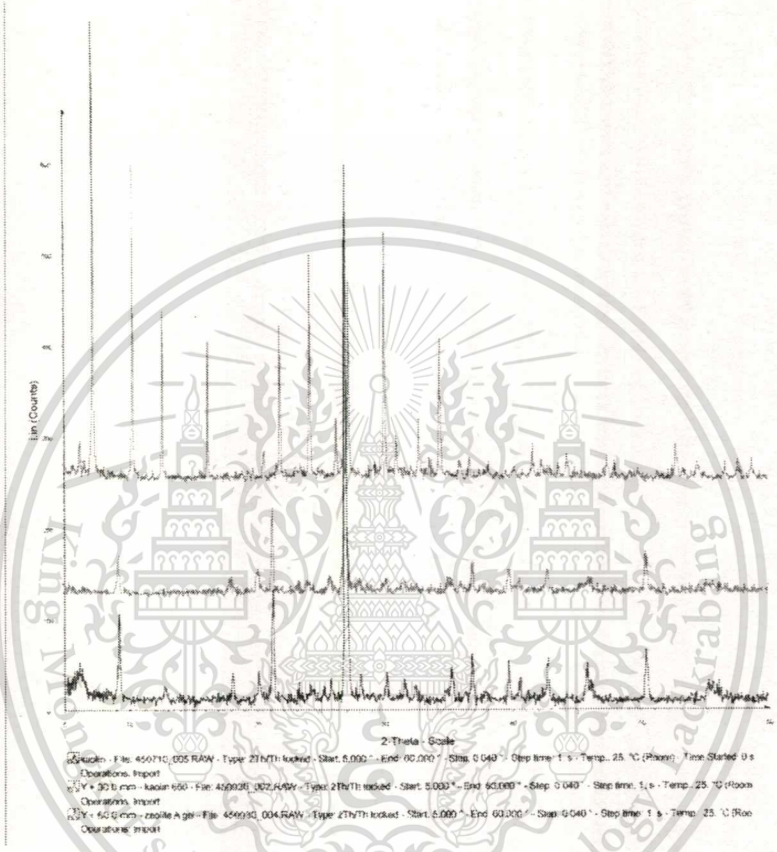
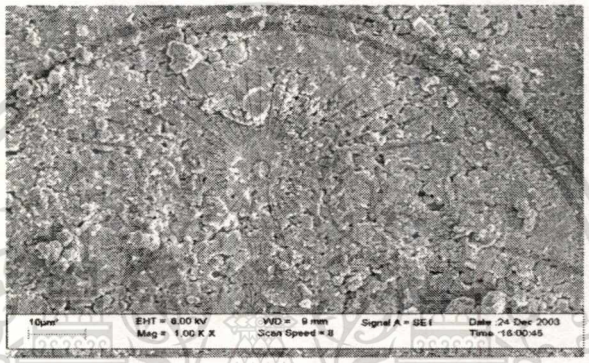



**Figure 4.3** The XRD pattern of (a) kaolin, (b) metakaolin, and (c) zeolite A powder

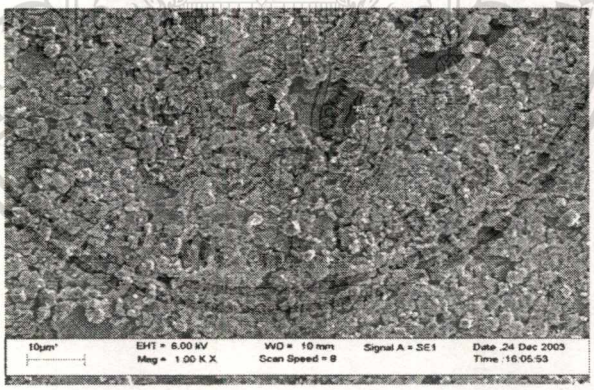
After treatment with sodium hydroxide solution the metakaolin phase can be converted to zeolite A as the peak intensity at $2\theta$ = 26.8 was decreased and the intensity of the peaks at $2\theta$ = 7.2, 10.2, 12.5, 30.0, and 34.3 increased significantly. This is due to an increase in the zeolite A phase (Figure 4.2(b) ).

After growth of zeolite A membrane on the support surface, The intensity of the peaks at $2\theta$ = 7.2, 10.2, 12.5, 30.0, and 34.3 of the support increased markedly, as shown in Figure 4.2(c) . This suggests the formation of zeolite A on the support surface ( Figure 4.4(c) ).

The surface morphologies of the calcined support, treated support, and zeolite A membrane were investigated by Scanning Electron Microscope(SEM), as shown in Figure 4.4(a) – 4.4(c). It is indicated that the calcined support have the metakaolin phase as observed by plate crystal structure of metakaolin (Figure 4.4(a)) compared with metakaolin morphology shown in Figure 4.5. After treatment with sodium hydroxide solution the metakaolin phase can be converted to zeolite A. The SEM shows a cubic crystal of zeolite ( Figure 4.4(b)). After growth with zeolite A the support was covered by polycrystalline layer of zeolite A as shown by SEM in Figure 4.4(c).

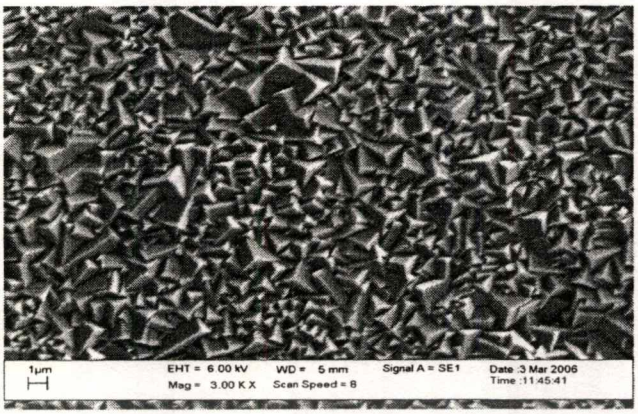



(a)




(b)

**Figure 4.4** The SEM image of (a) support calcined, (b) treated support, and (c) zeolite A membrane




(c)

**Figure 4.4** (continues)The SEM image of (a) support calcined, (b) treated support, and (c) zeolite Amembrane

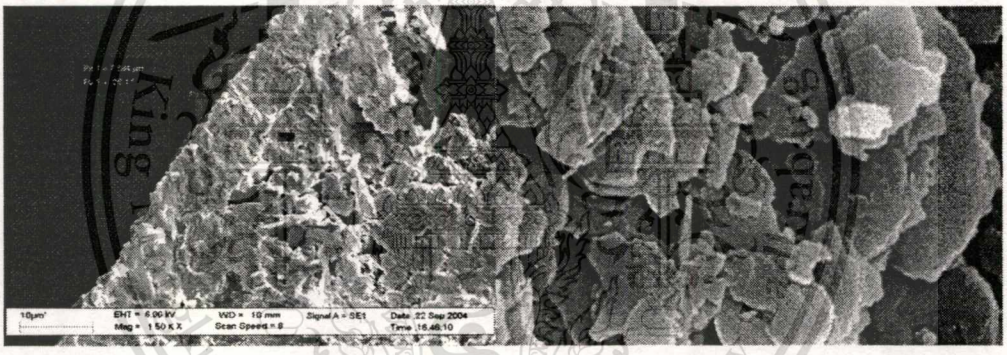
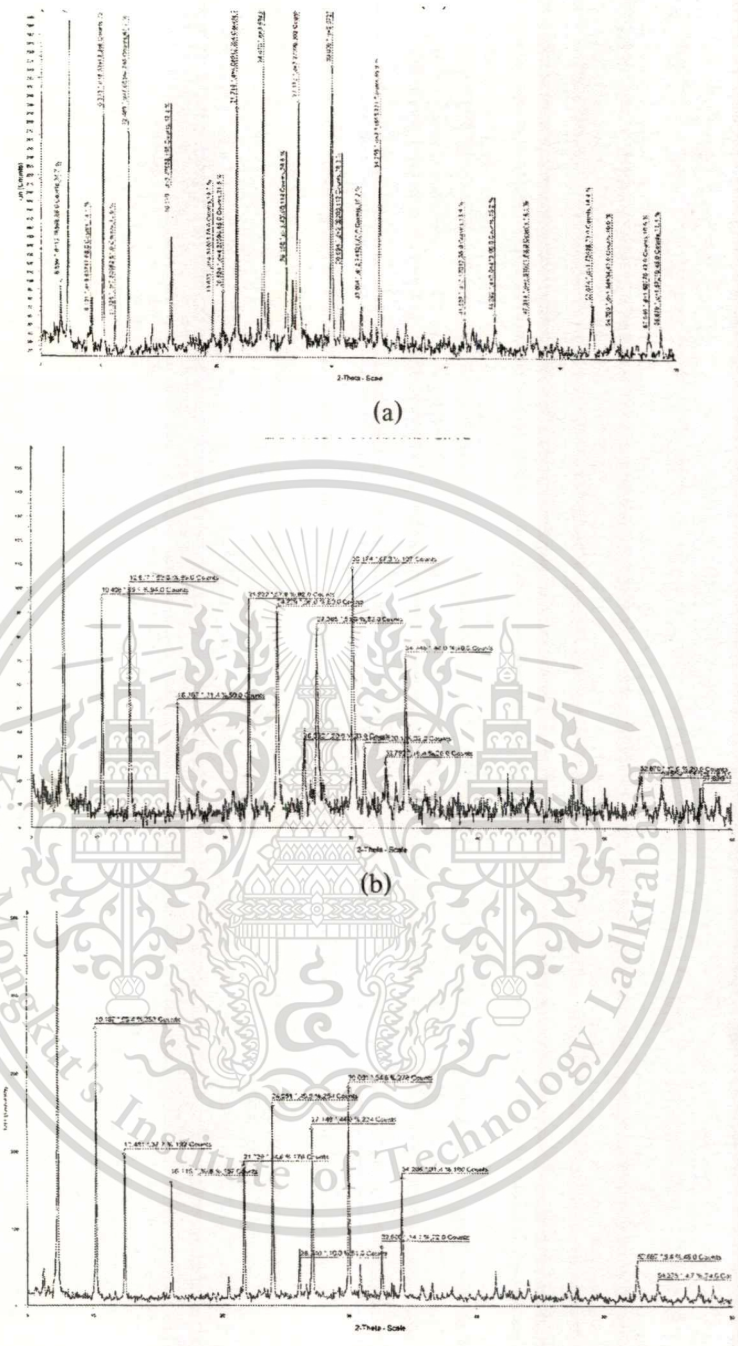


**Figure 4.5** Morphology of metakaolin[14]

The zeolite A membrane prepared using 24 and 48 hour synthesis times show the same XRD pattern but the intensity of the zeolite A membrane prepared at 48 hour is slightly higher than that of 24 hour, as shown in Figure4.6(a) and 4.6(b) . This is because the crystallization time was increased.



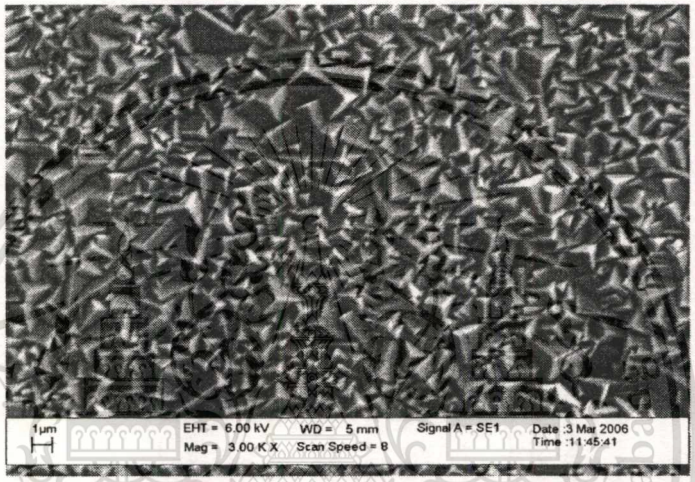
(a)

(b)

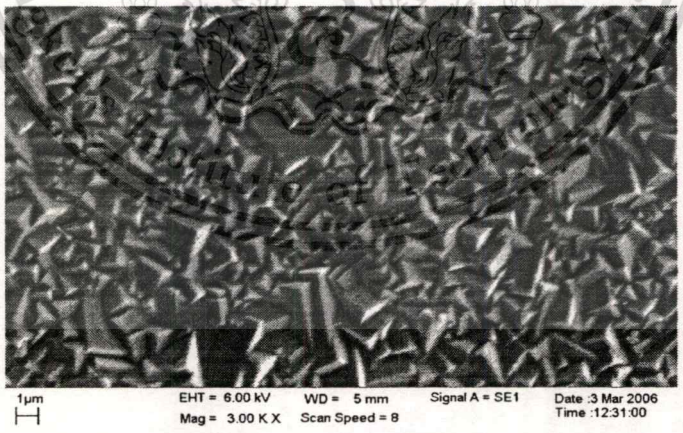
(c)

**Figure 4.6** The XRD pattern of membrane from synthesis time(a) 24 hour, (b) 48 hour and (c) secondary growth of 24 hour zeolite A membrane.

However, it can be seen that membrane surface with 48 hour synthesis time show a slightly larger crystal size than that with 24 hour synthesis time. In addition a small increase in thickness of membrane layer is obtained for membrane 48 hour synthesis time, as shown in Figure 4.7(a) - 4.7(b) and 4.8(a) – 4.8(b). Although, synthesis time was increased for 2 times, the thickness increase only ~30 % (5-7 μm). This is because the concentration of gel is limited. Increasing in synthesis time shall not markedly effect the crystallinity, crystal size, and thickness if the gel are used up.

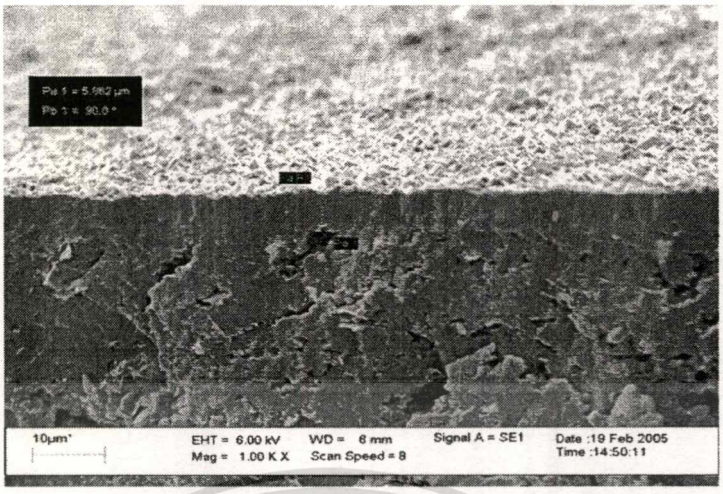



(a) 24 hour synthesis time

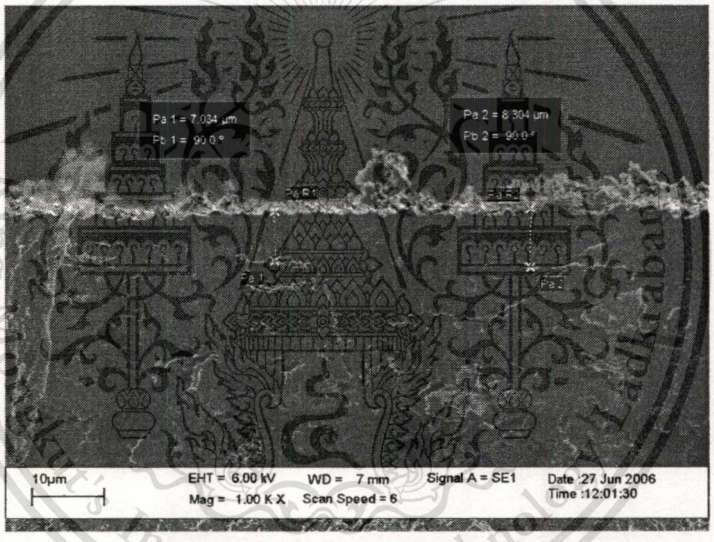



(b) 48 hour synthesis time

**Figure 4.7** The SEM image of zeolite A membrane surface (a) 24 hour synthesis time (b) 48 hour synthesis time




(a) 24 hour synthesis time

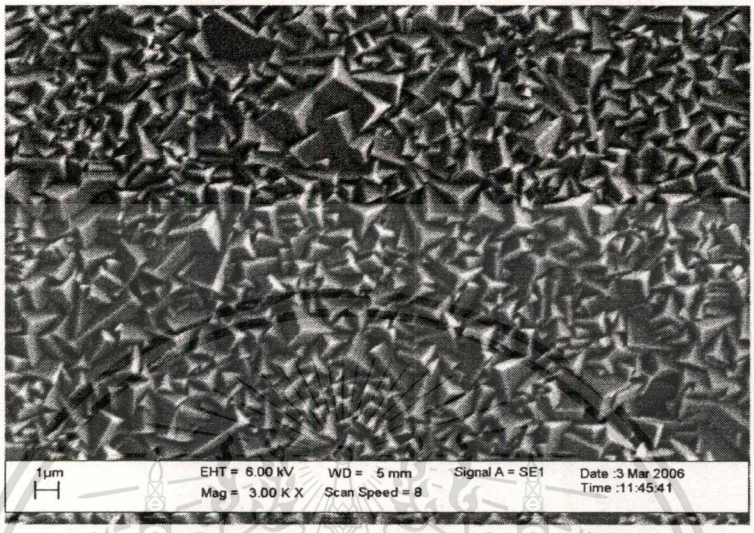



**(b)**

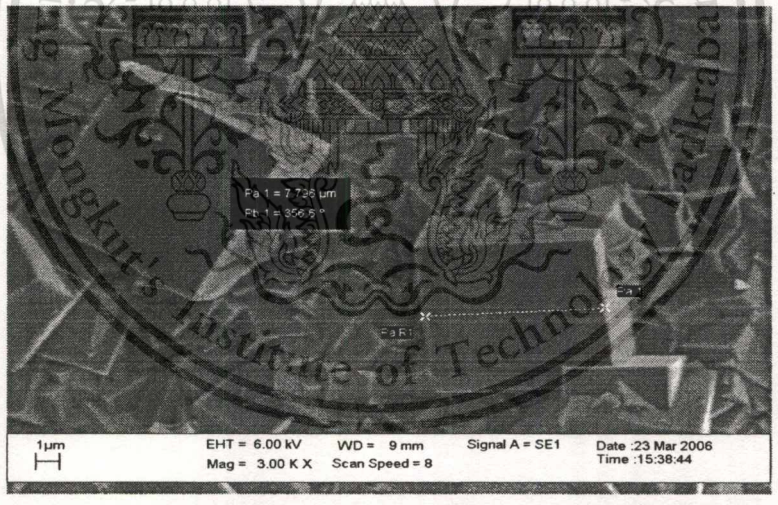
**Figure 4.8** The SEM image of zeolite A membrane cross section (a) 24 hour synthesis time (b) 48 hour synthesis time

Secondary growth of the zeolite A membrane on the membrane prepared using 24 hour synthesis time show an increased crystallinity of the membrane layer, as compared to parent membrane as shown by XRD at Figure 4.6. This is because there is another zeolite A layer growth on the previous layer. Since additional crystallization was taken place on the zeolite A membrane layer, the membrane with the secondary coating possesses a higher thickness, as confirmed by SEM. The thickness of the membrane layer were measured and listed in the Table 4.1. In addition, large crystal of zeolite A can be

found on the membrane with secondary growth. This indicates a secondary nucleation on the primary zeolite A layer when secondary growth is applied.

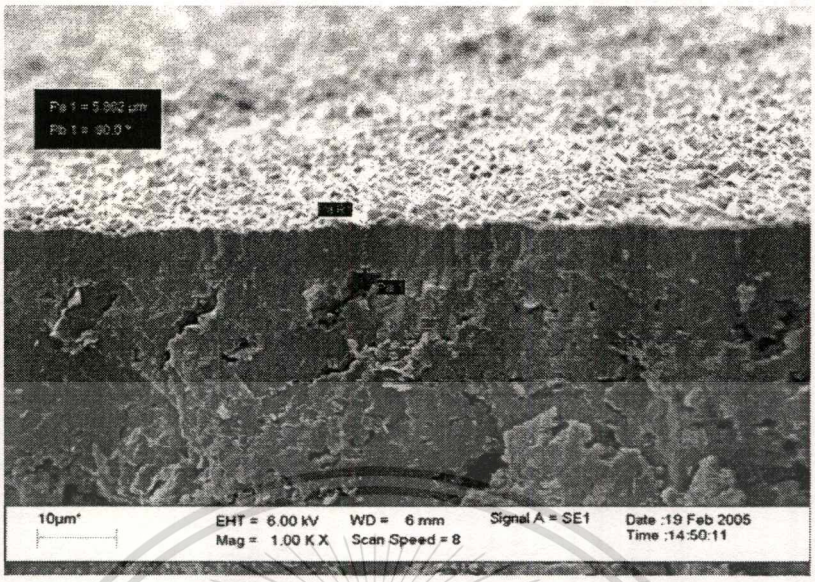



(a) 24 hour synthesis time

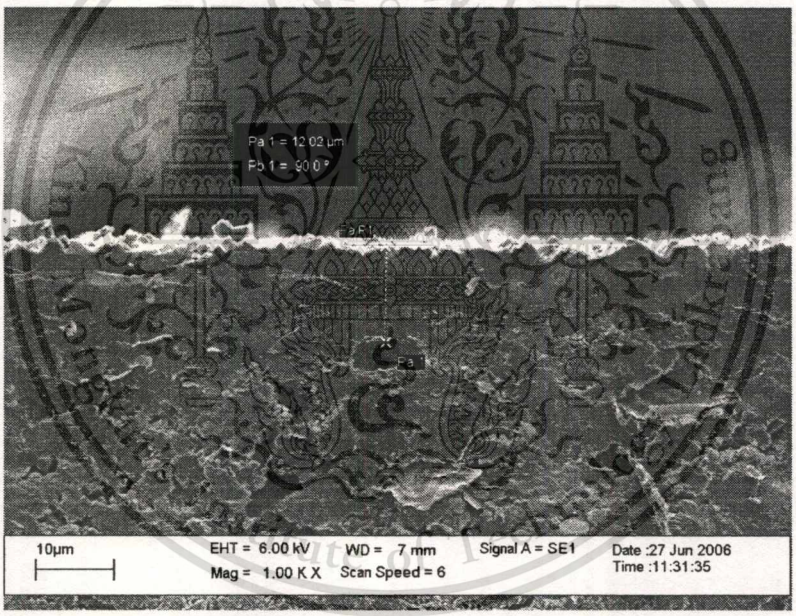



(b) secondary coat of membrane 24 hour synthesis time

**Figure 4.9** The SEM image of zeolite A membrane surface (a) 24 hour synthesis time, and (b) secondary coat of membrane 24 hour synthesis time




(a)




(b)

**Figure 4.10** The SEM image of cross section (a) membrane 24 hour synthesis time, and (b) secondary growth of membrane 24 hour synthesis time.

**Table 4.1** The thickness of membrane layer on the difference of the synthesis method

| Membrane type | Thickness of membrane layer (μm) |
|---|---|
| 24 hour synthesis times | 5 |
| 48 hour synthesis times | 6-7 |
| 24 hour synthesis time re-coating | 8-10 |

### 4.1.2 Specific surface area determination

Specific surface areas (SSA) of the calcined support, treated support and zeolite A membranes were investigated by the gas adsorption technique at 0 $^{\circ}C$ , using $CO_2$ as adsorbate. The specific surface area of zeolite A cannot be determined using $N_2$ as adsorbated gas because the nitrogen cannot be adsorbed in the micropore of zeolite A at relatively low pressure ($P/P_0 = 10^{-6}$ torr). Eventhough , the nitrogen's diameter is smaller than the zeolite A pore. This is owing to the poor interaction between hydrophilic surface of the zeolite A and the non-polar nitrogen gas[40]. Accordingly, the results from the carbon dioxide adsorption were used to determine the specific surface area. The Table 4.2 shows specific surface area of the calcined support, treated support, membrane with 24 hour synthesis time, membrane with 48 hour synthesis time and membrane with secondary growth of membrane 24 hour synthesis time. It was found that after the calcined support was treated with sodium hydroxide solution 3% w/w, the specific surface area of the treated support was increased. This is because the metakaolin phase changed into zeolite A when it was treated by sodium hydroxide solution. This result was confirmed by XRD (Figure 4.2) and SEM (Figure 4.4). After the treated support was growth by zeolite A gel for 24 hour synthesis time it was found that the specific surface area of the zeolite A membranes with 24 hour synthesis time was slightly higher than the calcined support and treated support. This is because the zeolite A crystal was growth as polycrystalline cover the support surface. This result was also confirmed by XRD (Figure 4.2)and SEM (Figure 4.4).

When compared the specific surface area of membrane with 24 hour synthesis time, 48 hour synthesis time and secondary growth of membrane with 24 hour synthesis time, it was found that the specific surface area of the membrane with secondary growth is higher than that with 24 hour synthesis time and that with 48 hour synthesis time. This is because the first layer of the zeolite A polycrystalline was covered by the new layer. This layer may secondarily cover the defect or the impurity of the first

layer. However, the membrane with 24 hour synthesis time have slighly higher specific surface area than the membrane with 48 hour synthesis time. This is because when the synthesis time was too long the zeolite gel composition can be changed. Hence, some of the impurity may be formed or the crystal may be dissolved into the solution(Figure 4.11). These phenomenon can reduce purity and hence the specific surface of the membrane.

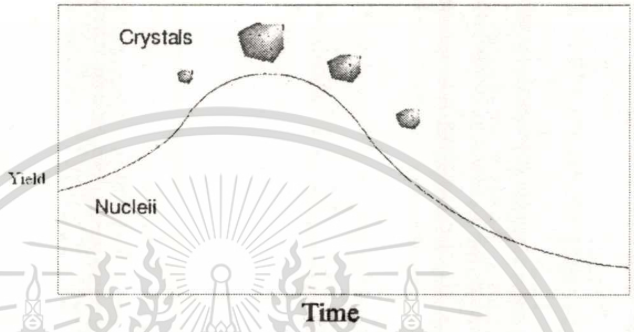



**Fig 4.11** Illustration between crystallization time and yield [36].

**Table 4.2** The specific surface area of the support and all types zeolite A membrane

| Sample | Specific surface area[1] ($m^2/g$) ($CO_2$) |
|---|---|
| support calcined | 377 |
| Support treated | 415 |
| Zeolite A membrane 24 hours synthesis times | 483 |
| Zeolite A membrane 48 hours synthesis times | 449 |
| Zeolite A membrane 24 hours syntesis time re-coating | 572 |

*Specific surface area[1] : carbondioxide as an adsorbate gas*

### 4.1.3 Elemental analysis

The silicon and aluminium contents of the support and zeolite A membranes were determined by X-ray fluorescence spectrometer to confirmation that the product will not change to the other

material (metakaoline and zeolite have Si/Al ratio ~ 1[40]). It was found that, similar Si/Al ratio is obtained for support and all membranes. This is because the sample containing mostly zeolite A and kaolin which possess the same Si/Al ratio. Therefore no significant change in Si/Al ratio can be observed when support was treated with sodium hydroxide solution and growth with zeolite A .

**Table 4.3** The Si/Al ratios of the support and all types of zeolite A membrane

| Sample | Si/Al |
|---|---|
| calcined support | 0.93 |
| Treated support | 0.97 |
| Zeolite A membrane 24 hours synthesis time | 0.95 |
| Zeolite A membrane 48 hour synthesis time | 0.99 |
| Secondary coating of membrane 24 hour synthesis time | 1.06 |

### 4.2 Separation process

In this study, it was shown that separation ethanol/water mixture using zeolite A membrane in vapor permeation process has an advantage of increased permeation flux, as compared to the gas permeation process. Thus, vapor permeation process employs the difference in concentration of gas between feed side and permeated side as the driving force. The driving force for vapor permeation is usually higher than that for gas permeation process because the concentration of feed side is higher than the permeate side under atmospheric pressure. It can be seen from the Table 4.4 that the permeation flux and separation factor of vapor permeation process is higher than those of gas permeation process[40]. This is because the permeation fluxes depend strongly on feed concentration. Therefore higher concentration is typically preferred. In the case of separation factor, vapor feed have high possibility to adsorb on the membrane surface than the gas feed. This is because random movement pattern of gas leads to a reduced possibility for a molecule to adsorb on the membrane surface, as compared to the high concentration vapor. Therefore, water which is high polar molecule, can easily adsorb and condensed on the membrane surface. This leads to an inhibition of less polar

molecule, ethanol, to compete in adsorption. Consequently, separation factor for vapor permeation is higher than the gas permeation process.

**Table 4.4 Comparison between vapor permeation process and gas permeation process.**

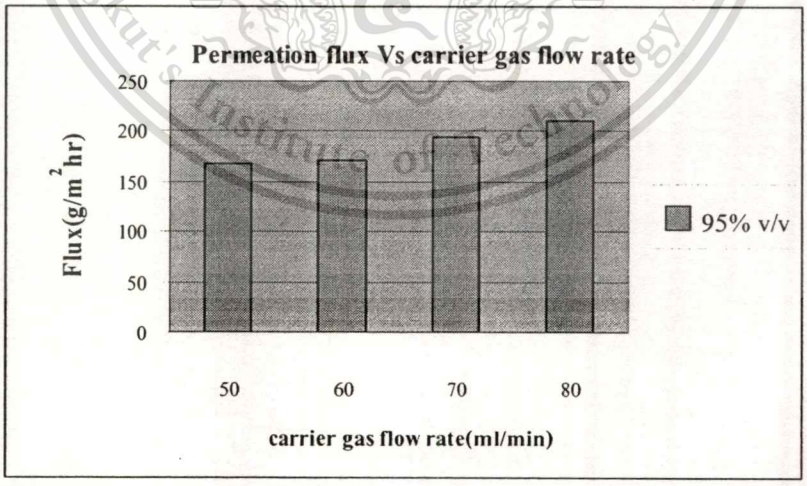
| Process | Flux($g/m^2hr$) | Separation factor |
|---|---|---|
| Vapor permeation | 167.00 | 96.73 |
| Gas permeation | 72.90 | 90.30 |

*Feed composition 95% v/v of ethanol, atmostpheric pressure, and carrier gas flow rate = 50 ml/min*

### 4.2.1 Effect of carrier gas flow rate in the permeation side.

Since azeotropic ethanol is boiled at 78 $^{o}$C but in this thesis all component must be in vapor phase. Therefore, the temperature were set at 85 $^{o}$C. Since higher temperature lead to a lower permselectivity as shown in previous study[40].

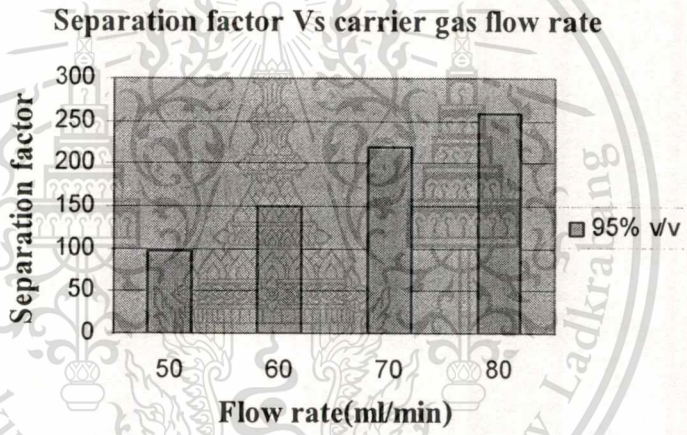
The study on the effect of carrier gas flow rate in the permeation side was carried out at that temperature with feed concentration of feed at 95% by volume of ethanol (azeotropic composition). Separation were tested with various carrier gas flow rate (50, 60, 70, and 80 ml/min) in the permeation side. The separation performance are shown in Figure 4.12 and Figure 4.13.




*Feed composition 95% volume of ethanol, atmospheric pressure, and varies carrier gas flow rate*

**Figure 4.12** The permeation flux on the effect of the carrier gas flow rate in the permeation side.

When the carrier gas flow rate was increased, rate of desorption of permeate on the membrane surface at permeate side was increased. This results in high permeation flux when a high carrier gas flow rate is employed. At a low carrier gas flow rate, the rate of permeate desorption is low. This also leads to low diffusivity of the molecule in the membrane, providing a high possibility a less polar molecule (ethanol) to adsorb on the membrane surface. Since the molecular size of ethanol is larger than that of water, it would have a relatively lower diffusion rate[22,25]. Therefore, the diffusion of water molecule was inhibited by some ethanol molecule adsorbed on the membrane surface. Accordingly , the permeation flux is reduced when the carrier gas flow rate is decreased.




*Feed composition 95% volume of ethanol, atmospheric pressure, and varies carrier gas flow rate*

**Figure 4.13** The separation factor on the effect of the carrier gas flow rate

Enhanced adsorption of ethanol at low carrier gas flow rate has not only decreased the permeation flux, but also reduced the separation factor. At low carrier gas flow rate, the permeate on the membrane surface at the permeate side is low because the desorption rate of the permeate is low. Therefore, there is a high possibility for the less polar molecule (ethanol) to adsorb on the membrane surface and diffuse through the membrane. Since the total diffusion is reduced, water molecules would be retained in the zeolite pore, as monolayer. In this case, some of ethanol can diffuse through the monolayer water surface, as shown in Figure 4.14. This results is a reduced separation factor because the selectivity arising from diffusivity difference between water and ethanol becomes more important

than the competitive adsorption of water over that of ethanol (weakly adsorbing molecule). On the other hand, at the high carrier gas flow rate, the permeate on the membrane surface at the permeate side is high. This is because the permeate was flushed away by high flow rate of carrier gas, leading to a rapid desorption of the permeate molecule. Therefore, the pore blocking by capillary condensation of a higher polar molecule (water), may well take place. This is because the water molecule possesses strong interaction with each other and it would become liquid (condensation in the internal surface of zeolite pore), particularly at the temperature not higher than its boiling point (separation temperature is 85 $^{o}$C ), as shown in Figure 4.15.

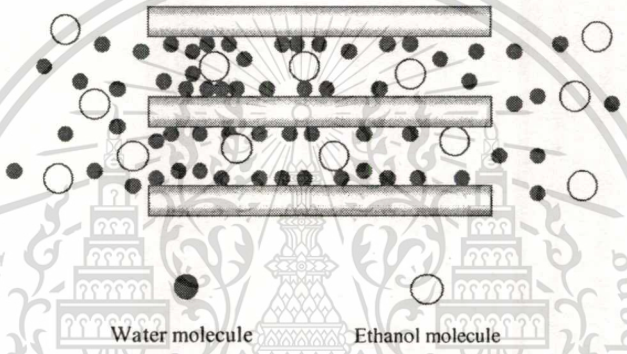



**Figure 4.14** The illustration of the water monolayer adsorption

The competitive adsorption of water over that of ethanol become more important than the diffusivity difference between water and ethanol. Thus, the adsorption and diffusion of ethanol (weakly adsorbing molecule) is decreased by the capillary condensation of water (strong adsorbing molecule) in the pore, resulting in an increase in separation factor.

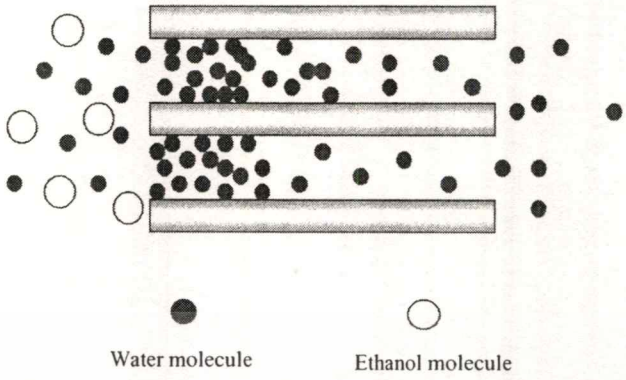


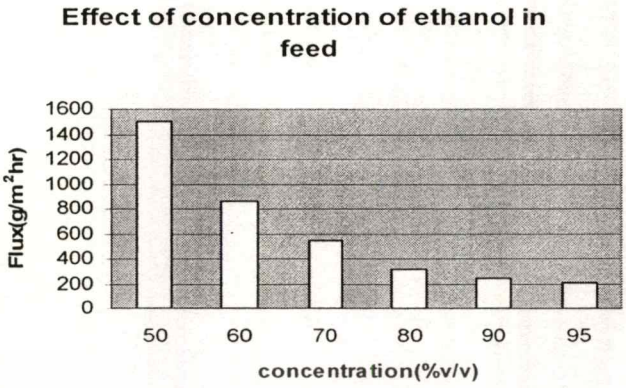

**Figure 4.15** The illustration of the capillary condensation in the pore[40].

### 4.2.2 Effect of the feed composition

A study on the effect of feed composition was carried out at 85 $^{o}$C using 80 ml/min of carrier gas and various concentration of the ethanol in the liquid feed (50, 60,70, 80, 90, and 95 %volume). Figure 4.16 and Figure 4.17 shows the effect of the feed composition on the permeation flux and separation factor respectively.

When the feed mixture contains higher water, the permeation flux is increased. This is because such the feed mixture are highly hydrophilic. Zeolite A membrane which is also hydrophilic [9,22,36], can strongly interact with the feed mixture that possess hydrophilic character. Adsorption and diffusion of the high water content feed can be facilitated. Therefore, permeation flux is high as shown in Figure 4.16.

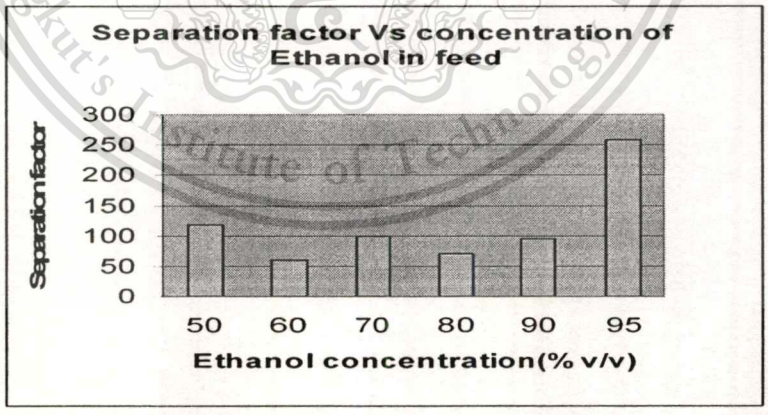
In contrast, increasing ethanol in feed can readily reduce their hydrophilic character. Hence, the interaction between the feed and membrane surface is poor, leading to a gradually decrease in permeation flux as ethanol content in the feed mixture is increased.




*Feed composition 50-95% volume ethanol, atmospheric pressure, and carrier gas flow =80ml/min*

**Figure 4.16** The relationship between effect of ethanol concentration in feed and permeation flux.

In the case of separation factor (Figure 4.17), it can be seen that the separation factor was slightly increase when the feed have low water content( Figure 4.18). This is because at the high ethanol concentration, the feed have hydrophobic character but the membrane have high hydrophilic by nature. In particular, at 95% ethanol, low flux is obtained. Only water can adsorp and diffuse thought the membrane layer provide high separation factor.




*Feed composition 50-95% volume ethanol, atmospheric pressure, and carrier gas flow =80ml/min*

**Figure 4.17** The relationship between effect of ethanol concentration in feed and separation factor

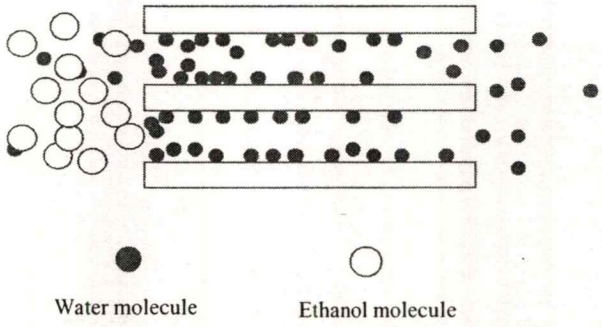
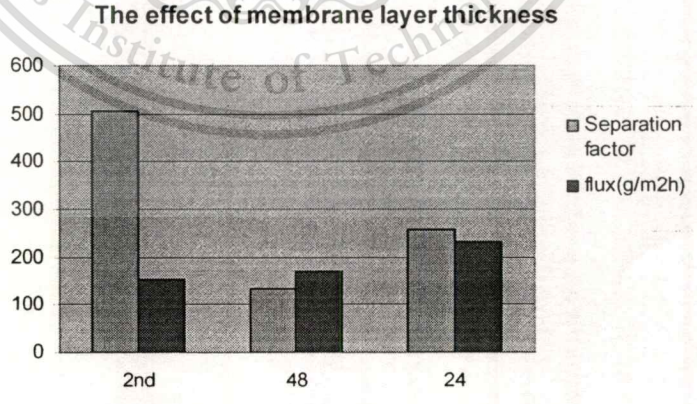



**Figure 4.18** Illustrate the water molecule diffused through the ethanol in zeolite pore

### 4.2.3 Effect of the membrane layer thickness

The high permselectivity for water through a zeolite A membrane is ascribed to two factors: high adsorption selectivity and higher diffusivity for water. In general, zeolite membranes may contain certain defects that generated non-selective interstitial pores. Consequently, the separation performance of zeolite membranes significantly depends on the membrane quality. This is because such defects can reduce selectivity dramatically. The most common method of suppressing these defects in zeolite A membrane is to grow a thicker zeolite layer, where each new layer of crystals cover the defects in the previous layer. In this thesis increase in layer thickness of zeolite A membranes can be accomblished by 2 methods i) extend the synthesis time from 24 hour to 48 hour and ii) secondary coating of the zeolite A membrane 24 hour synthesis time. The thickness of membrane prepared by above methods is shown in table 4.1, and the separation performance is shown in 4.19.




*Feed composition 95% volume ethanol, atmospheric pressure, and carrier gas flow =80ml/min*

**Figure 4.19** The effect of membrane layer thickness separation factor and separation factor

In the case of permeation flux, it was found that the permeation flux decreases with an increase in the thickness. That is because, from Darcy's law[17], flux is reverse-proportional to the membrane thickness. It can be seen that the permeation flux is in the order of : membrane with 24 hour synthesis time > 48 hour synthesis time > secondary growth of membrane 24 hour synthesis time.

Darcy's law : $J = k(p_o - p_l)/l$

$J$ = permeation flux

$k$ = Darcy's law coefficient

$p_o$, $p_l$ = pressure in the fluids at the feed and permeate interfaces

$l$ = the membrane thickness

However, it can be seen that the separation factor of membrane with 48 hour synthesis time is relatively low despite it possesses a slightly higher thickness, as compared to the membrane with 24 hour synthesis time. This is presumably because the membrane with 48 hour synthesis time have a possibility to contain number of defects since the synthesis time is so high that dissolution of zeolite A polycrystalline layer may well take place in some parts. This leads to a formation of other non-zeolitic species. The formation of non-zeolitic species is consistant with the XRD result as discussed earlier (section 4.1.1). This can give rise in defects of the membrane. Accordingly, ethanol can be adsorbed and diffused through such defects, leading to lower separation factor, as compared to the membrane with 24 hour synthesis time.

In the other words, we can discuss the difference in synthesis time (24 hour synthesis time and 48 hour synthesis time) as shown in Figure 4.11. This diagram illustrate the relationship between synthesis time and yield of crystallization. At the beginning, nucleation slowly leads to precursors for a particular unit cell or part of unit cell. After that the nuclei will be growth rapidly to form a crystal. At this point crystal will be stable and optimum time for perfect zeolite crystal can be reached. If crystallization time is longer. The zeolite crystal may be dissolved in to solution and the other species will forms. This can give rise in defects of the crystal and non-zeolitic species. The defect and non-zeolitic species can reduce specific surface area (section 4.1.2) and separation performance of the membrane as observed previously[36].

For secondary growth of membrane with 24 hour synthesis time, it was found that the separation factor markedly increased when the thickness of the polycrystalline zeolite A layer is increased (Figure 4.8 and 4.10). Since the hydrophilic and specific surface area of membrane increases

(Table 4.2), a strong interaction between the water molecule, which is a high polar molecule and the membrane is obtained. In addition, the defect from the primary growth was diminished by the secondary growth of polycrystalline zeolite A layer. Accordingly, the ethanol adsorption is decreased while an increase in the water adsorption is expected. This resulted in an increase in selective diffusion of water through the membrane and hence higher the separation factor when a membrane layer thickness was increased.

# CHAPTER 5

# CONCLUSION AND SUGGESTION

## 5.1 Conclusion

From the results of the ethanol/water separation using zeolite A membrane, it can be concluded that:

The study on effect of the carrier gas flow rate of 95% v/v ethanol in feed mixture shows that the permeation flux and separation factor was increased when the carrier gas flow rate was increased. This is because at the high carrier gas flow rate the competitive adsorption of water over ethanol become significant as the membrane is highly selective for water. The pore blocking by capillary condensation of water take place. Ethanol molecule can not readily diffuse through the membrane at this condition.

The study on the effect of feed composition shows that, when the concentration of ethanol in feed is increased, the permeation flux was slightly decreased. However the separation factor was increased. This is because, the feed show higher hydrophobic character when the ethanol content in feed was increased. It was suggested that the hydrophobic properties of the feed have the effect for selective adsorption and the zeolite A membrane exhibits a higher selectivity for water adsorption.

The study on the effect on membrane layer thickness shows that the high separation factor was obtained when thickness of the membrane layer was increased, hence, the permeation flux as shown by Darcy's law was reduced because the permeation flux is impropotional to the membrane thickness. The permeation flux is in order of : membrane 24 hour synthesis time > 48 hour synthesis time > secondary growth of membrane 24 hour synthesis time. The separation factor increase with membrane layer thickness. This is because the hydrophilic and specific surface area of membrane was increased. However, separation factor of membrane 48 hour synthesis time is relatively low despite that it posses a high thickness, as compared with membrane 24 hour synthesis time. This is presumably because the membrane 48 hour synthesis time have a possibility to contain number of defects since the synthesis time is high. Dissolution of zeolite A polycrystalline layer may take place in some parts leading to formation of other non-zeolitic species as shown by XRD.

## 5.2 Suggestion for Future studies

5.2.1 For future study application of zeolite A membrane has kaolin as support should be using in other membrane application or separation other water-organic mixture.

5.2.2 The effect of membrane layer thickness give higher separation factor but reduced permeation flux. The study on the thickness of membrane due to the defect from synthesis method in one procedure the defect may be take place. Should be reduce the thickness of membrane and looking for alternative way to modify method that reduced defect on the membrane surface.

5.2.3 The zeolite A membrane have the kaolin as the support can be developed to the membrane reactor in the process that concerning water or polar molecule as the product or side reaction. In this case the membrane reactor can be change the chemical equilibrium for higher production in industrial chemical process.

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# APPENDIX A

# CALCULATION

## A 1 Calculation of chemical composition in supports and membranes

The Si/Al ratio of supports and membrane are determined by X-ray fluorescence spectroscopy (XRF). The data from XRF of the supports and membrane as shown in Table A1.

**Table A1** Data from XRF, calculations of Si/Al ratio of the supports and zeolite A membrane

| Sample | $Al_2O_3$(%wt) | $SiO_2$(%wt) | $Na_2O$(%wt) | Si/Al |
|---|---|---|---|---|
| Calcined support | 38.2 | 41.6 | 19.7 | 0.93 |
| Support treated | 37.0 | 42.2 | 20.7 | 0.97 |
| Zeolite A membrane 24 hour synthesis time | 34.9 | 40.0 | 24.7 | 0.95 |
| Zeolite A membrane 48 hour synthesis time | 33.9 | 39.8 | 25.3 | 0.99 |
| Secondary coat of membrane 24 hour synthesis time | 32.5 | 41.0 | 25.8 | 1.06 |

**A1.1 calculation of Si/Al ratio** of zeolite A 24 hour synthesis time : ( molecular weight of $SiO_2$ = 60.09, molecular weight of $Al_2O_3$ = 101.96)

Mole of $SiO_2$ = [40.0/60.09]

= 0.67

Mole of $Al_2O_3$ = [34.9/101.96]

= 0.34

From the above result, the silicon/aluminium ratio is calculated as follows:

1 mole of Si equivalent with 2 mole of Al

0.67 mole of Si = 2 (0.34) mole of Al

Thus; Si/Al = 0.67/(0.34 x2)

= 0.98

## A 2 Calculation of Response factor (Rf)

### A 2.1 Calculation of Response factor (Rf) of ethanol

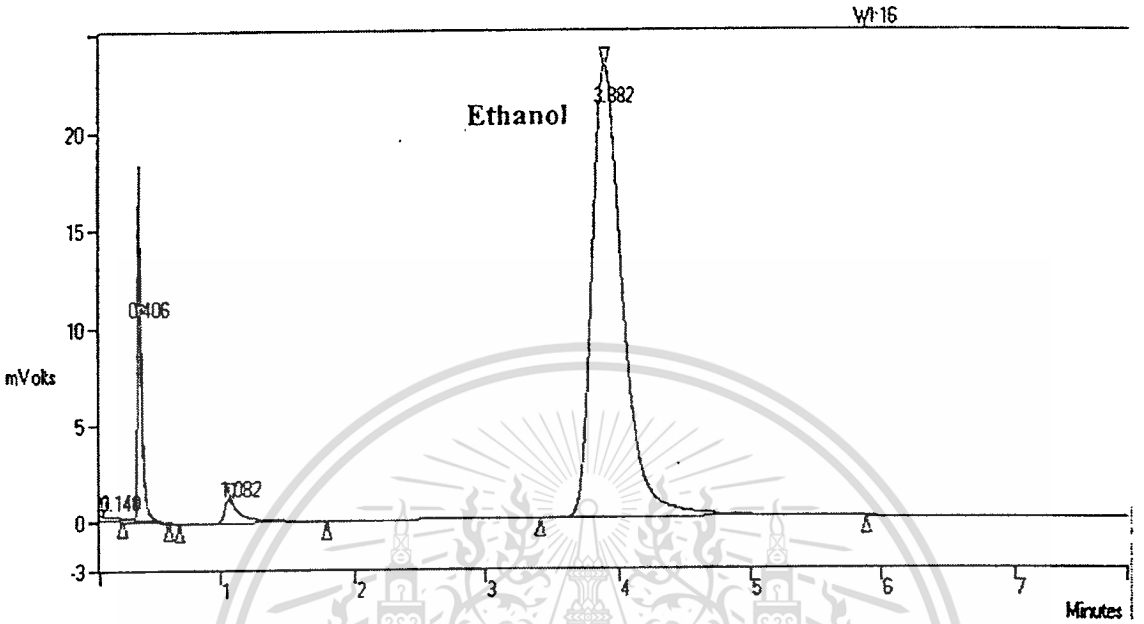


**Figure A2.1** Chromatogram of ethanol.

**Table A 2.1** Data for calculation and experimental condition.

| Data | Value |
|---|---|
| Peak Area | 363633 Counts |
| Vapor pressure | 5.8 kPa |
| Atmospheric pressure | 104.3739 kPa |
| Temperature | 20 °C |

Response factor = Cs/As ..... (1)

Cs = (Pi/Patm) x 100 ..... (2)

Rf = Response factor

Cs = Percent mole of standard

As = Peak area of standard

Pi = vapor pressure of standard

Patm = atmospheric pressure

From Equation (2) Cs = (5.8/104.3739) x 100

= 5.557 % mol

As = 363633

Rf = 5.557/363633

$Rf_{ethanol}$ = $1.528 \times 10^{-5}$

**A 2.2 Calculation of Response factor (Rf) of water**

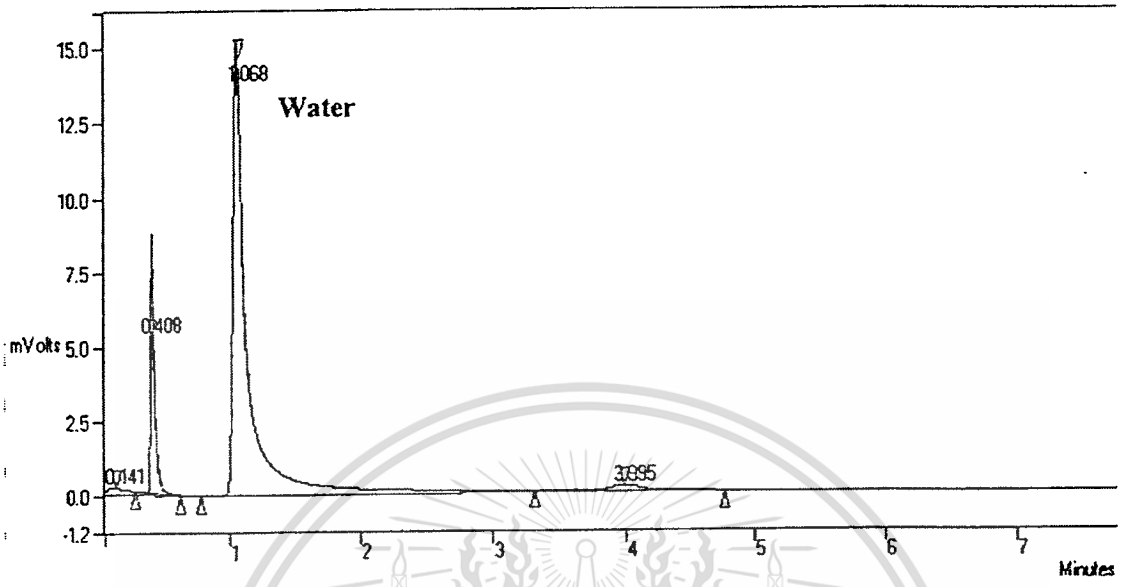


**Figure A2.2** Chromatogram of water.

**Table A 2.2** Data for calculation and experimental condition.

| Data | Value |
|---|---|
| Peak Area | 106748 Counts |
| Vapor pressure | 2.3 kPa |
| Atmospheric pressure | 104.3739 kPa |
| Temperature | 20 $^{o}$C |

Response factor = Cs/As ..... ..... (1)

Cs = (Pi/Patm) x 100 ..... (2)

Rf = Response factor

Cs = Percent mole of standard

As = Peak area of standard

Pi = vapor pressure of standard

Patm = atmospheric pressure

From Equation (2) Cs = (2.3388/104.3739) x 100

= 2.241 % mol

As = 106748.8

Rf = 2.241/106748.8

$Rf_{water} = 2.099 \times 10^{-5}$

## A 2.3 Determine the Flux and separation factor

### A 2.3.1 Determine the Flux

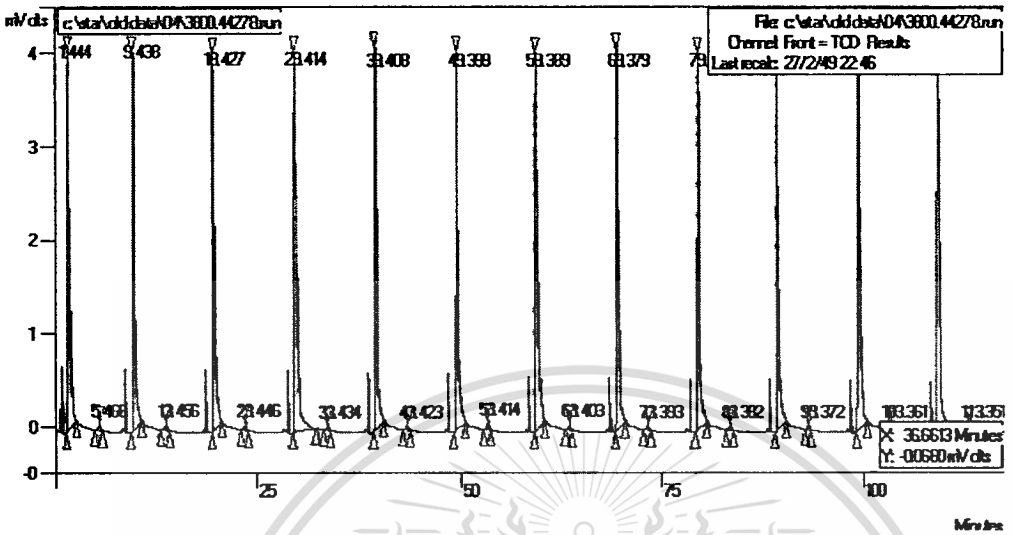


**Figure A 2.3** Chromatogram of the permeate on the effect of concentration of ethanol 50% v/v in feed , 80 ml/min of He, temperature 85 $^{o}$C.

**Table A 2.3** Data for calculation and experimental condition

| Data | Value |
|---|---|
| Peak area of water | 115103 Counts |
| Peak area of ethanol | 440 Counts |
| Carrier gas flow rate, He | 79.47 ml/min |
| Atmospheric pressure | 1.0303 atm |
| Temperature | 300 K |
| Surface area of the membrane | $7.85 \times 10^{-5}$ $m^2$ |

A 2.3.1 Determine The Flux

$$Rf = Cs/As \quad \text{.....(1)}$$

$$Cs = Rf \times As \quad \text{.....(2)}$$

Rf = Response factor

C = Percent mole of substant

A = Peak area

**Water**

From equation (2) $C_{water} = A_{water} \times Rf_{water}$

$= 115103 \times 2.099 \times 10^{-5}$

Percent mole of water in permeate = 24.16012 % mol

**Ethanol**

From equation (2) $C_{ethanol} = A_{ethanol} \times Rf_{ethanolr}$

$= 440 \times 1.528 \times 10^{-5}$

Percent mole of ethanol in permeate = 0.06688 % mol

**Determines the concentration of He ( $C_{He}$)**

from the carrier gas flow rate at the flow meter 79.47 ml/min , the carrier gas flow rate at the vent 84.5 mi/min

$C_{He} = (79.47/84.5)\times 100$

concentration of He = 94.05 % mol

The He concentration 94.05 % mol have the flow rate = 84.5 ml/min

The water concentration 24.16012 % mol have the flow rate = (84.5 x 24.160120)/ 94.05

Therefore, the water flow rate = 21.71 ml/min

Therefore, the ethanol concentration 0.06688 % mol will be have the flow rate

= (84.5 x 0.06688)/ 94.05

= 0.0600 ml/min

From the ideal gas $PV = nRT$ .....( 3 )

$n = PV/RT$ .....( 4 )

P = Pressure

V = Volumetric

n = mole

R = Gas constant

T = Absolute temperature(K)

**Water** ; from equation (4) $n = PV/RT$

$= (1.0303 \times 21.71)/(0.082*300*1000)$

$= 9.09 \times 10^{-4}$ mol/min

Mass flow rate of water = 0.923438844 g/hr .....( 5 )

**Ethanol** ; from equation (4) $n = PV/RT$

$= (1.0303 \times 0.0600)/(0.082*300*1000)$

$= 2.51 \times 10^{-6}$ mol/min

Mass flow rate of ethanol = 0.006533 g/hr .....( 6 )

Determine the Flux ;

Flux = Flow rate / Surface area of membrane.....(7)

Surface area of membrane = $7.85 \times 10^{-5}$ $m^2$

Water flux ; from (5) $Flux_{water} = 0.923438844 / (7.85 \times 10^{-5})$

$= 1176.355215$ g/ $m^2$hr

Ethanol flux ; from (6) $Flux_{water} = 0.006533 / (7.85 \times 10^{-5})$

$= 8.321871$ g/ $m^2$hr

**A 2.3.2 Determine the separation factor**

Separation factor ($\alpha$) = $[Y_{water}/Y_{ethanol}]_{permeate}/[X_{water}/X_{ethanol}]_{feed}$ .....(1)

$Y_{wate}$ = Mole fraction of water in permeat

$Y_{ethanol}$ = Mole fraction of ethanol in permeat

$X_{water}$ = Mole fraction of water in feed

$X_{ethano}$ = Mole fraction of ethanol in feed

The feed have the concentration of ethanol 50% v/v or 23.63% mol.

Therefore, the water in feed = 100- 23.63

= 76.37 % mol

From equation (1) Separation factor ($\alpha$) = [ 24.16012 /0.06688 ] / [76.37/23.63]

= 111.7748

# APPENDIX B

## GAS CHROMATOGRAM

### B.1 Effect of the feed composition

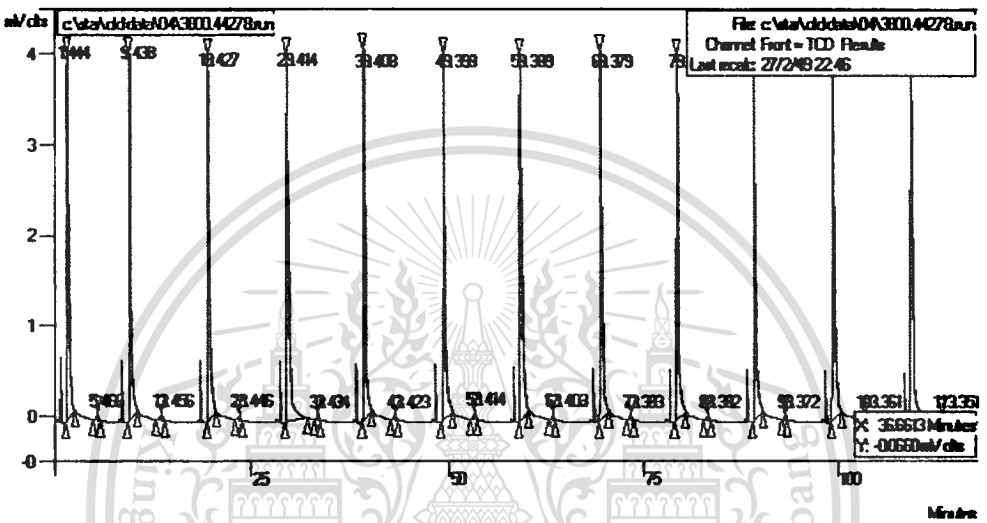

**Figure B 1.1** Gas chromatogram of the permeate on the effect of concentration of ethanol 50% v/v in feed, 80 ml/min of He, temperature 85 °C.

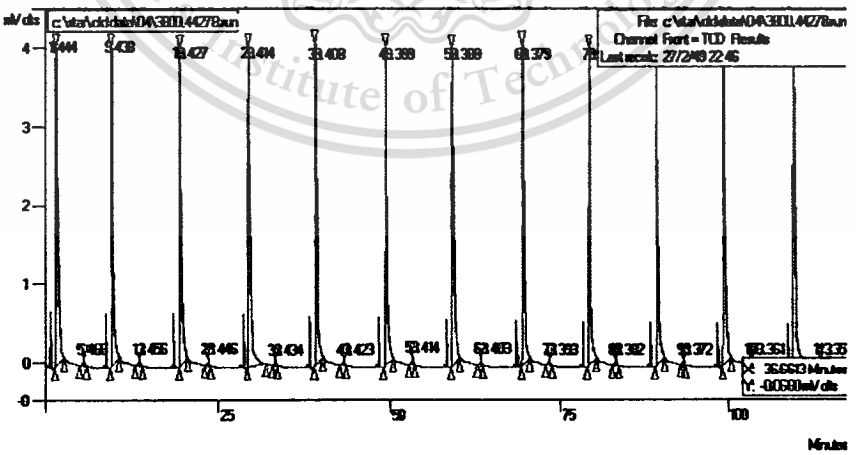

**Figure B1.2** Gas chromatogram of the permeate on the effect of concentration of ethanol 60% v/v in feed , 80 ml/min of He, temperature 85 °C.

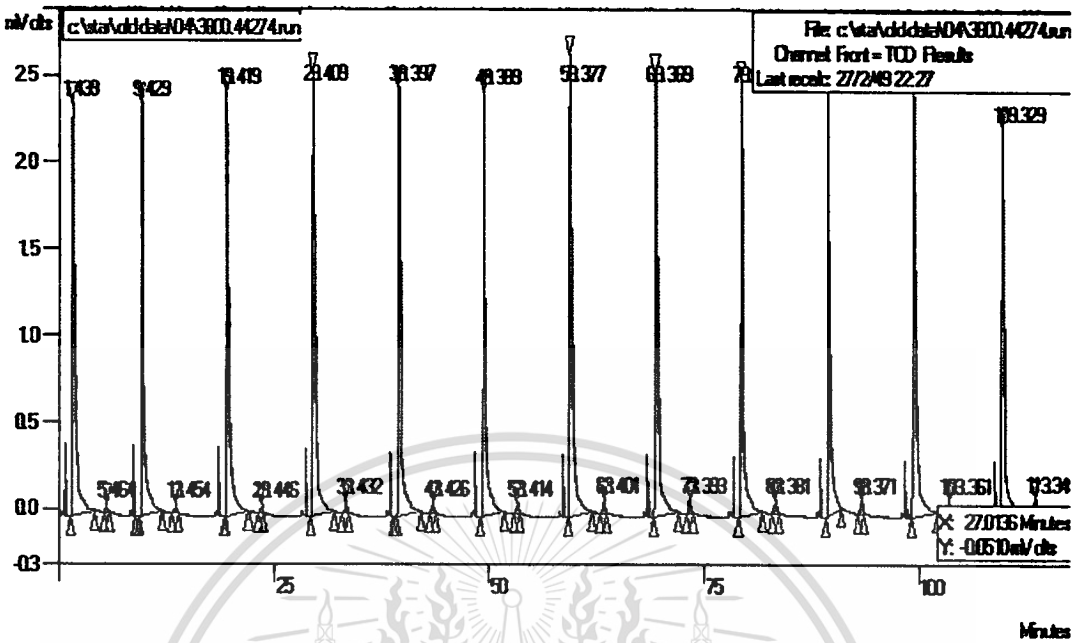


**Figure B1.3** Gas chromatogram of the permeate on the effect of concentration of ethanol 70% v/v in feed , 80 ml/min of He, temperature 85 °C.

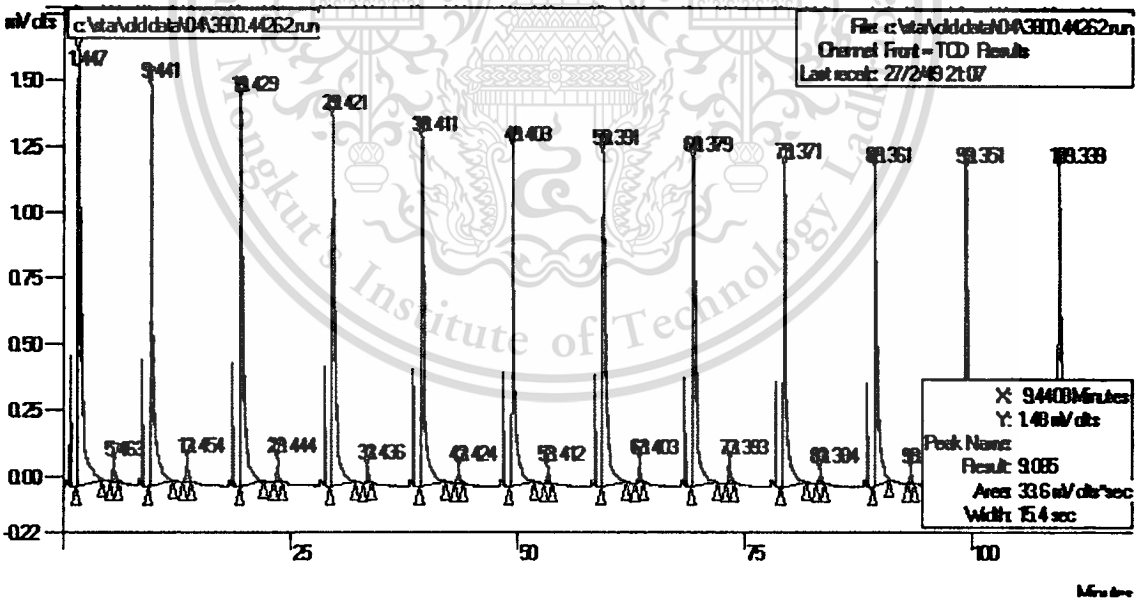


**Figure B1.4** Gas chromatogram of the permeate on the effect of concentration of ethanol 80% v/v in feed , 80 ml/min of He, temperature 85 °C.

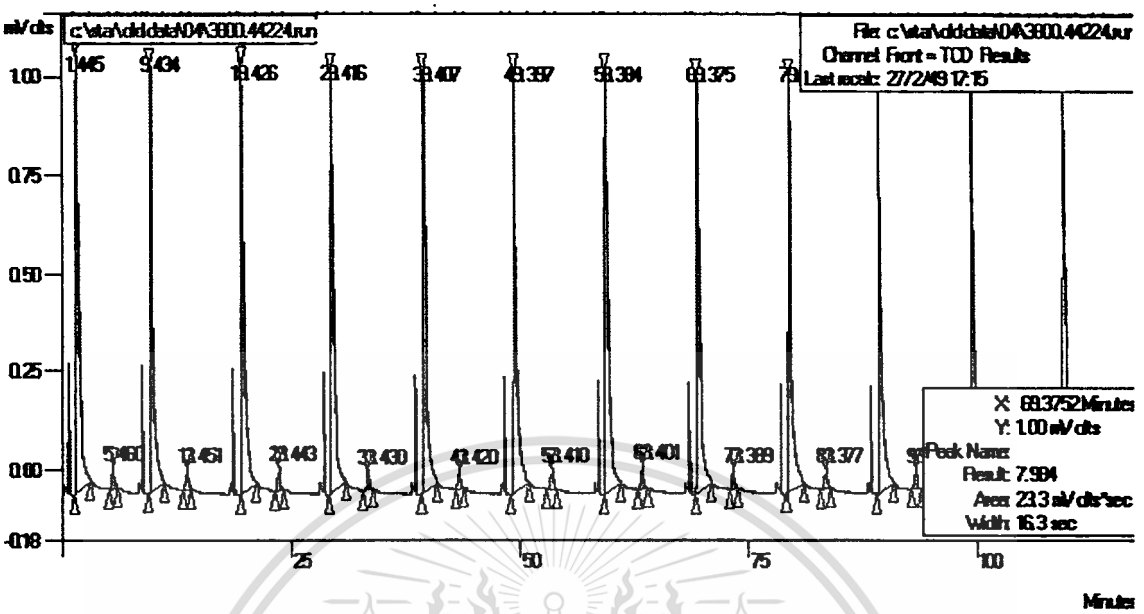


**Figure B1.5** Gas chromatogram of the permeate on the effect of concentration of ethanol 90% v/v in feed , 80 ml/min of He, temperature 85 °C.

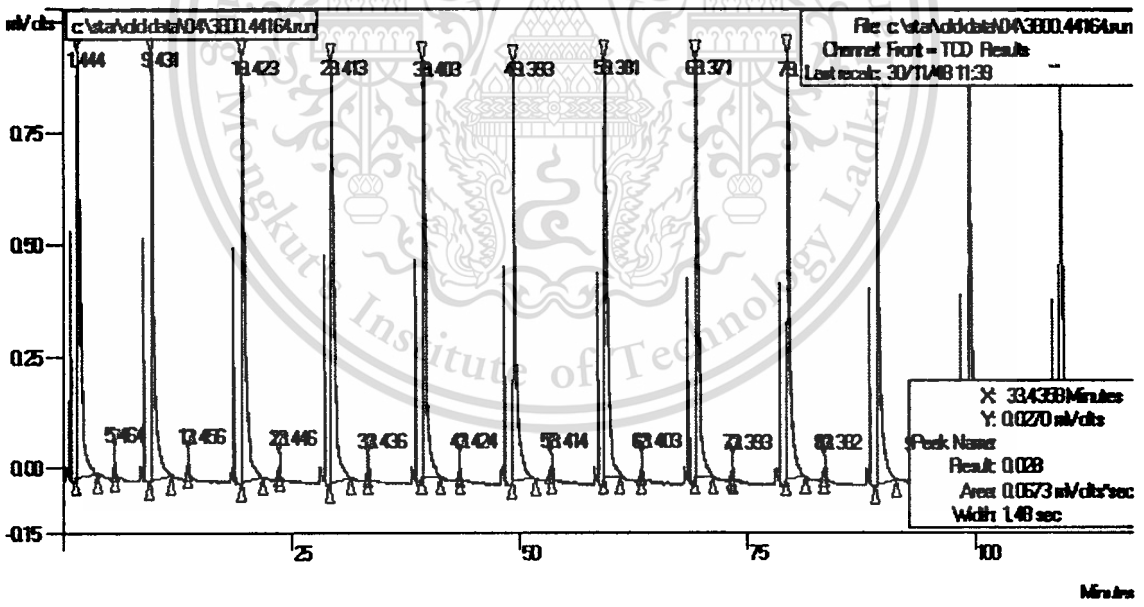


**Figure B1.6** Gas chromatogram of the permeate on the effect of concentration of ethanol 95% v/v in feed , 80 ml/min of He, temperature 85 °C.

**B.2 Effect of the carrier gas flow rate**

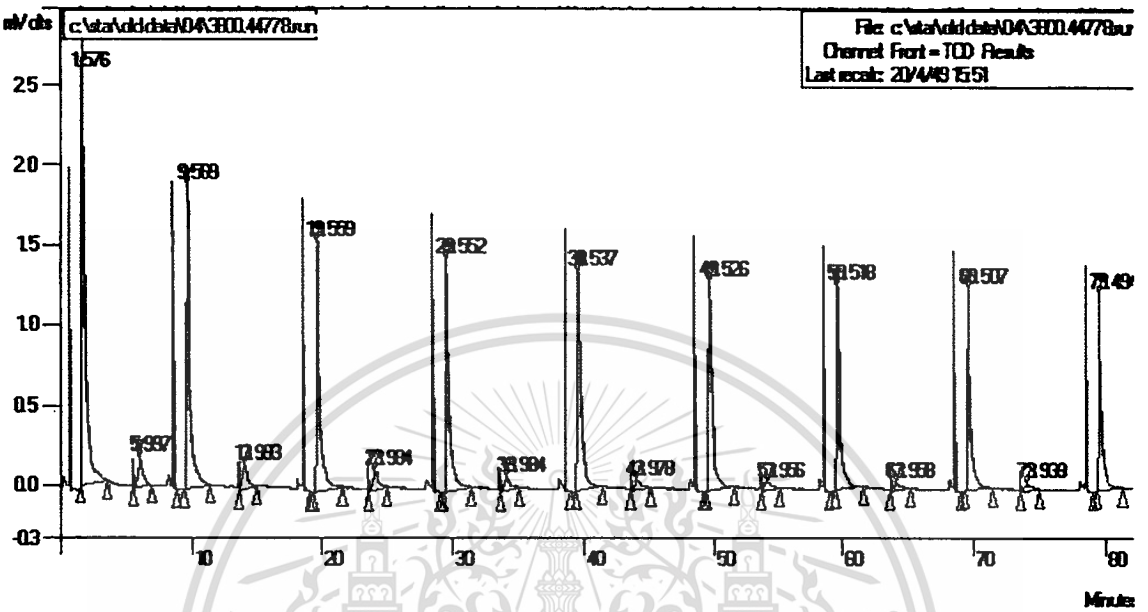


**Figure B2.1** Gas chromatogram of the permeate on the effect of carrier gas flow rate 50 ml/min of He, temperature 85 °C, and feed composition 95% v/v of ethanol

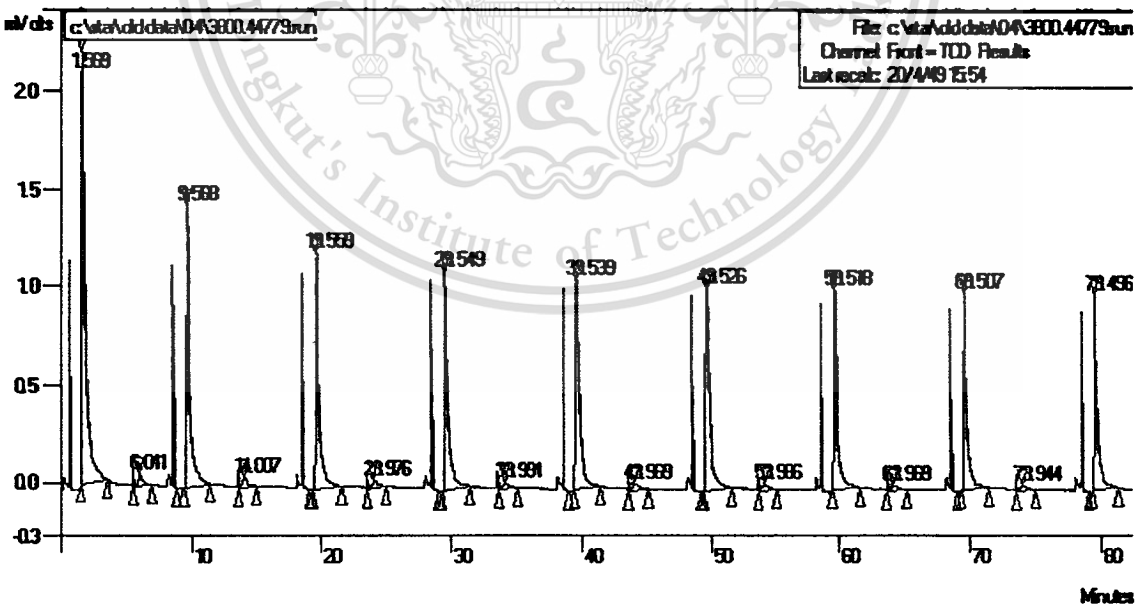


**Figure B2.2** Gas chromatogram of the permeate on the effect of carrier gas flow rate 60 ml/min of He, temperature 85 °C, and feed composition 95% v/v of ethanol.

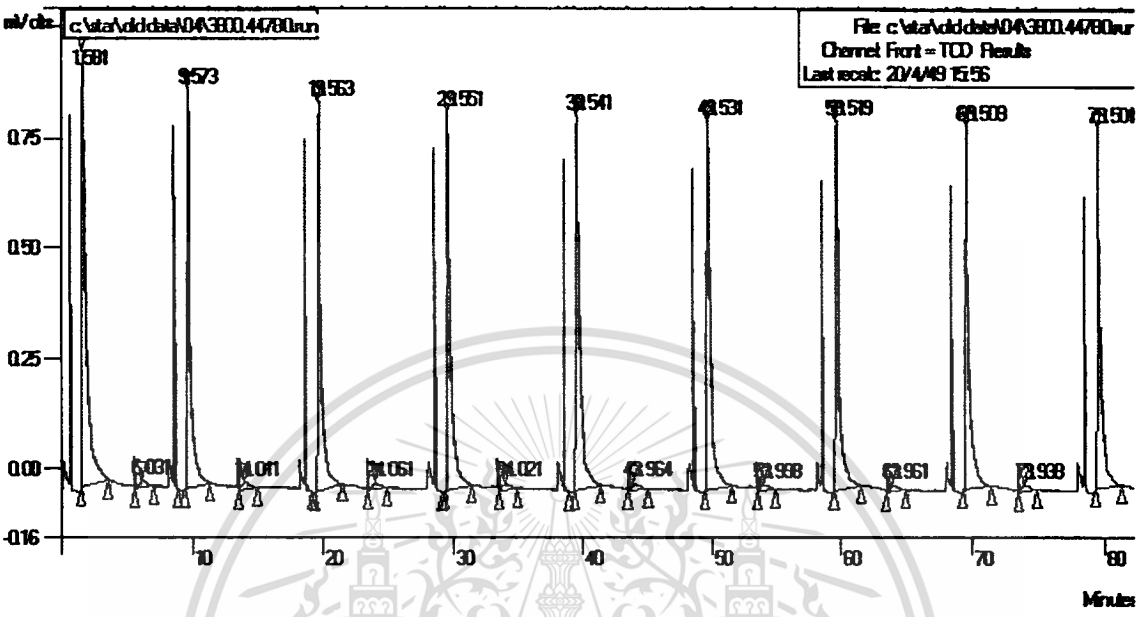


**Figure B2.3** Gas chromatogram of the permeate on the effect of carrier gas flow rate 70 ml/min of He, temperature 85 °C, and feed composition 95% v/v of ethanol.

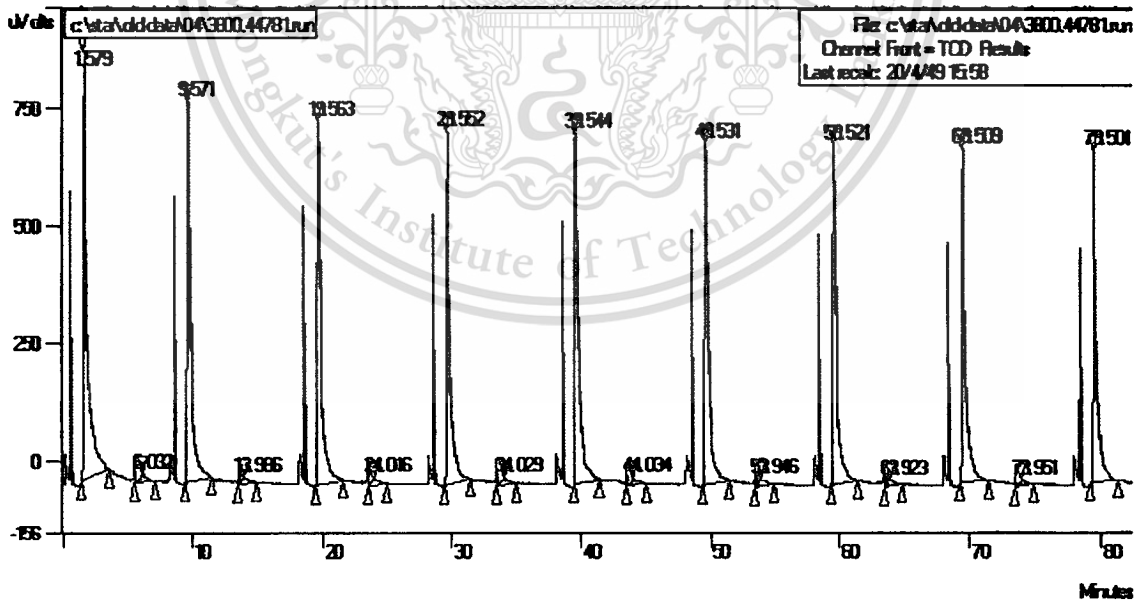


**Figure B2.1** Gas chromatogram of the permeate on the effect of carrier gas flow rate 80 ml/min of He, temperature 85 °C, and feed composition 95% v/v of ethanol.

**B.3 Effect of the membrane layer thickness.**

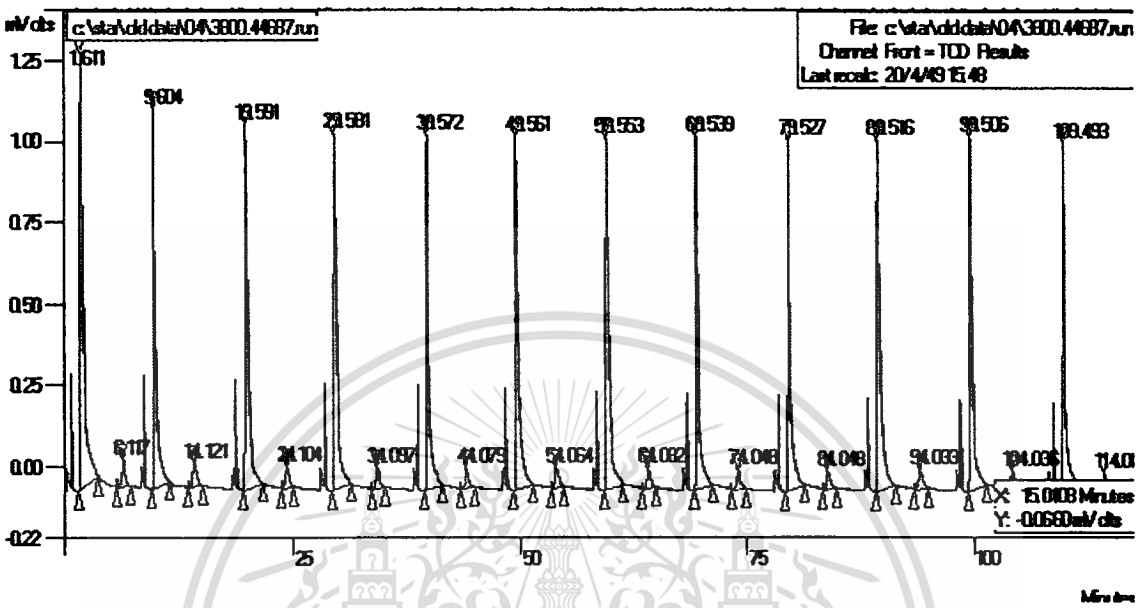


**Figure B3.1** Gas chromatogram of the membrane layer thickness, membrane 24 hour synthesis time 80 ml/min of He, temperature 85 $^{\circ}$C, and feed composition 95% v/v of ethanol.

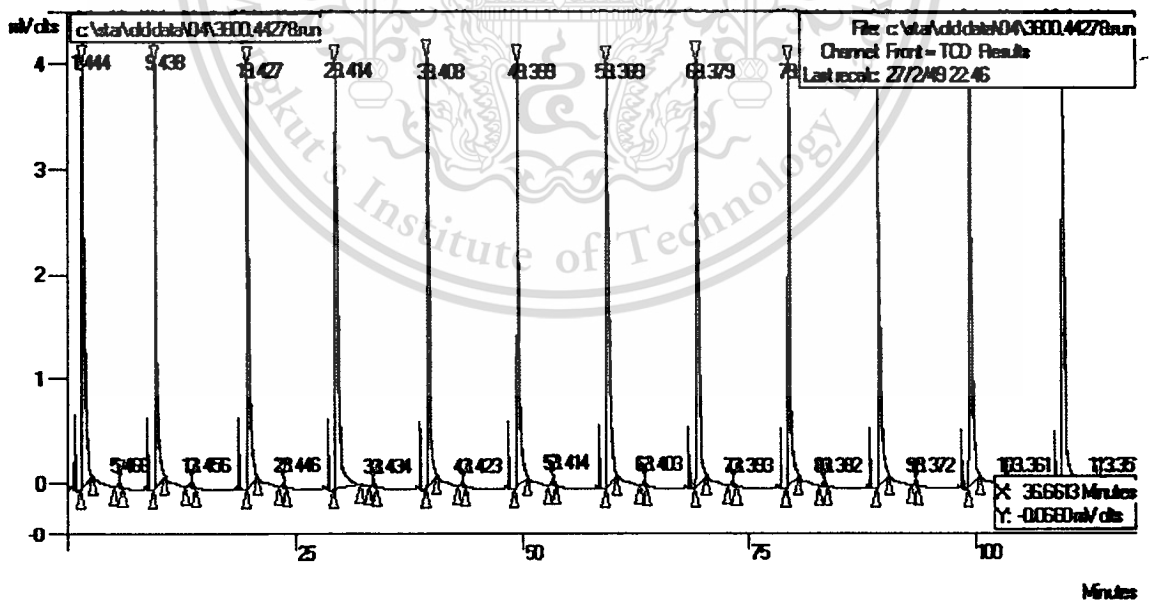


**Figure B3.2** Gas chromatogram of the membrane layer thickness, membrane 48 hour synthesis time, 80 ml/min of He, temperature 85 $^{\circ}$C, and feed composition 95% v/v of ethanol.

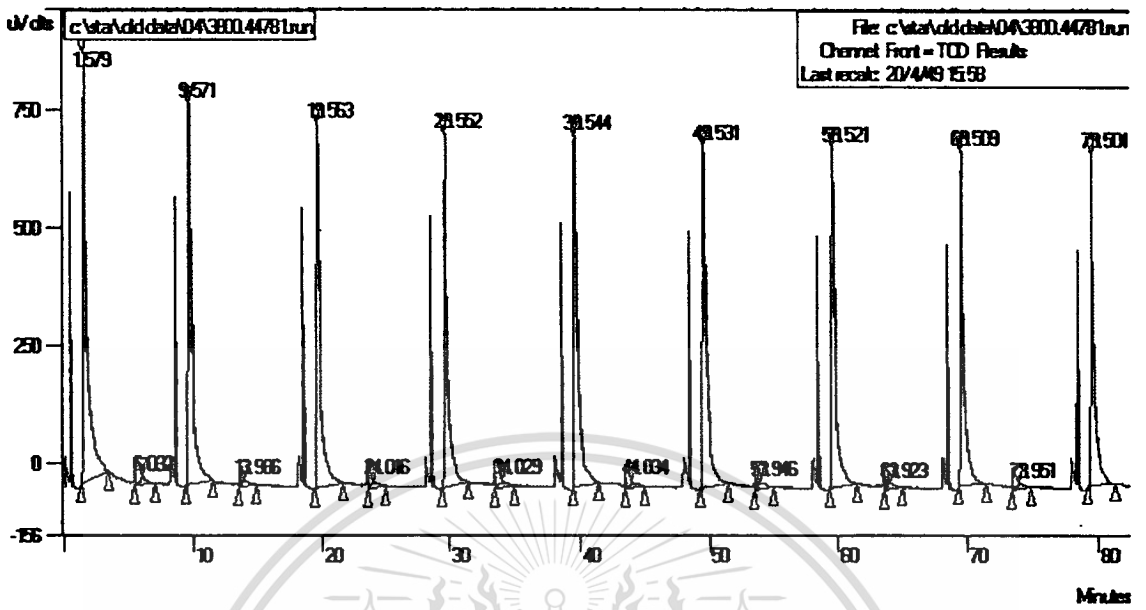


**Figure B3.3** Gas chromatogram of the membrane layer thickness, secondary coat of membrane 24 hour synthesis time, 80 ml/min of He, temperature 85 °C, and feed composition 95% v/v of ethanol.

# APPENDIX C

## DATA

**Table C.1** The results from the study on effect of feed composition using zeolite A membrane 24 hour synthesis time.

| % Ethanol in feed | Area(counts) | | $\alpha_{water/ethaol}$ | Flux(g/m$^2$hr) | | |
|---|---|---|---|---|---|---|
| | water | ethanol | | water | ethanol | total |
| 50 | 115178 | 419 | 117.4533185 | 1177.122 | 7.924691 | 1185.046 |
| | 115103 | 440 | 111.7747606 | 1176.355 | 8.321871 | 1184.677 |
| | 117858 | 492 | 102.353747 | 1204.511 | 9.305365 | 1213.817 |
| | 118131 | 422 | 119.6082706 | 1207.301 | 7.981431 | 1215.283 |
| | 126035 | 302 | 178.3175155 | 1288.08 | 5.71183 | 1293.792 |
| | 115204 | 428 | 115.0094618 | 1177.387 | 8.094911 | 1185.482 |
| 60 | 70043 | 969 | 46.32851409 | 715.841 | 18.32703 | 734.168 |
| | 70832 | 996 | 45.58034157 | 723.9046 | 18.83769 | 742.7423 |
| | 77875 | 855 | 58.37667489 | 795.8842 | 16.17091 | 812.0551 |
| | 71945 | 883 | 52.22125714 | 735.2795 | 16.70048 | 751.98 |
| | 72658 | 853 | 54.59361053 | 742.5664 | 16.13308 | 758.6995 |
| | 71584 | 818 | 56.0880147 | 731.5901 | 15.47112 | 747.0612 |
| 70 | 48548 | 545 | 89.66356649 | 496.1616 | 10.30777 | 506.4694 |
| | 48428 | 723 | 67.42165439 | 494.9352 | 13.67435 | 508.6096 |
| | 49035 | 718 | 68.74211721 | 501.1388 | 13.57978 | 514.7186 |
| | 50879 | 725 | 70.63854235 | 519.9845 | 13.71217 | 533.6967 |
| | 49509 | 343 | 145.2884876 | 505.9831 | 6.487277 | 512.4704 |
| | 49349 | 402 | 123.5644306 | 504.3479 | 7.603164 | 511.951 |

**Table C.1** (continues)The results from the study on effect of feed composition using zeolite A membrane 24 hour synthesis time.

| | | | | | | |
|---|---|---|---|---|---|---|
| 90 | 24172 | 955 | 96.81179012 | 247.0384 | 18.06224 | 265.1006 |
| | 23130 | 944 | 93.71792732 | 236.3891 | 17.8542 | 254.2433 |
| | 23016 | 894 | 98.47168438 | 235.224 | 16.90853 | 252.1326 |
| | 23205 | 879 | 100.9745053 | 237.1556 | 16.62483 | 253.7804 |
| | 23427 | 943 | 95.02196813 | 239.4245 | 17.83528 | 257.2597 |
| | 23293 | 975 | 91.37762111 | 238.055 | 18.44051 | 256.4955 |
| 95 | 20842 | 637 | 267.3419291 | 213.0057 | 12.0478 | 225.0535 |
| | 16201 | 562 | 235.5443139 | 165.5746 | 10.6293 | 176.2039 |
| | 15742 | 472 | 272.5116214 | 160.8836 | 8.927098 | 169.8107 |
| | 14924 | 511 | 238.6335261 | 152.5236 | 9.664719 | 162.1883 |
| | 15193 | 462 | 268.7006274 | 155.2728 | 8.737965 | 164.0108 |
| | 14548 | 535 | 222.1859684 | 148.6809 | 10.11864 | 158.7995 |

*Separation condition: temperature 85 $^{o}$C, 80 ml/min of He, and atmospheric pressure*

| | | | | | | |
|---|---|---|---|---|---|---|
| | 24172 | 955 | 96.81179012 | 247.0384 | 18.06224 | 265.1006 |
| | 23130 | 944 | 93.71792732 | 236.3891 | 17.8542 | 254.2433 |
| 90 | 23016 | 894 | 98.47168438 | 235.224 | 16.90853 | 252.1326 |
| | 23205 | 879 | 100.9745053 | 237.1556 | 16.62483 | 253.7804 |
| | 23427 | 943 | 95.02196813 | 239.4245 | 17.83528 | 257.2597 |
| | 23293 | 975 | 91.37762111 | 238.055 | 18.44051 | 256.4955 |
| | 20842 | 637 | 267.3419291 | 213.0057 | 12.0478 | 225.0535 |
| | 16201 | 562 | 235.5443139 | 165.5746 | 10.6293 | 176.2039 |
| 95 | 15742 | 472 | 272.5116214 | 160.8836 | 8.927098 | 169.8107 |
| | 14924 | 511 | 238.6335261 | 152.5236 | 9.664719 | 162.1883 |
| | 15193 | 462 | 268.7006274 | 155.2728 | 8.737965 | 164.0108 |
| | 14548 | 535 | 222.1859684 | 148.6809 | 10.11864 | 158.7995 |

*Separation condition: temperature 85 $^{o}$C, 80 ml/min of He, and atmospheric pressure*

**Table C.2** The results from the study on effect of carrier gas flow rate using zeolite A membrane 24 hour synthesis time.

| Carrier gas flow rate(ml/min) | Area(counts) | | $\alpha_{water/ethaol}$ | Flux(g/m$^2$hr) | | |
|---|---|---|---|---|---|---|
| | water | ethanol | | water | ethanol | total |
| 50 | 50656 | 5312 | 77.91838548 | 317.4239 | 61.60036 | 379.0243 |
| | 35454 | 4482 | 64.6339215 | 222.1641 | 51.97531 | 274.1394 |
| | 29998 | 3782 | 64.80938414 | 187.9754 | 43.85779 | 231.8332 |
| | 27392 | 2748 | 81.44682008 | 171.6455 | 31.86705 | 203.5126 |
| | 24896 | 2252 | 90.32922984 | 156.0049 | 26.11521 | 182.1201 |
| | 24384 | 1944 | 102.4886582 | 152.7966 | 22.54351 | 175.3401 |
| 60 | 41541 | 1941 | 174.8712965 | 320.6483 | 27.72643 | 348.3747 |
| | 26863 | 1751 | 125.3532171 | 207.3511 | 25.01235 | 232.3635 |
| | 22988 | 1503 | 124.9710234 | 177.4406 | 21.46977 | 198.9104 |
| | 21424 | 1192 | 146.8559079 | 165.3684 | 17.02726 | 182.3956 |
| | 20350 | 1041 | 159.7279075 | 157.0784 | 14.87028 | 171.9486 |
| | 19722 | 1014 | 158.9205713 | 152.2309 | 14.4846 | 166.7155 |
| 70 | 21200 | 761 | 227.6241423 | 198.4852 | 13.1854 | 211.6706 |
| | 17461 | 688 | 207.3708904 | 163.4788 | 11.92057 | 175.3993 |
| | 17265 | 707 | 199.5327955 | 161.6437 | 12.24977 | 173.8935 |
| | 17023 | 597 | 232.9854963 | 159.378 | 10.34387 | 169.7218 |
| | 16446 | 569 | 236.164784 | 153.9758 | 9.858729 | 163.8345 |
| | 16574 | 541 | 250.3209438 | 155.1742 | 9.37359 | 164.5478 |
| 80 | 20842 | 637 | 267.3419291 | 213.0057 | 12.0478 | 225.0535 |
| | 20563 | 562 | 298.9628867 | 210.1543 | 10.6293 | 220.7836 |
| | 21563 | 472 | 373.2796399 | 220.3743 | 8.927098 | 229.3014 |
| | 21363 | 511 | 341.5926037 | 218.3303 | 9.664719 | 227.9951 |
| | 20846 | 462 | 368.6785546 | 213.0466 | 8.737965 | 221.7845 |
| | 20965 | 535 | 320.1903235 | 214.2628 | 10.11864 | 224.3814 |

*Separation condition: temperature 85 $^{o}$C, ethanol in feed 95 % v/v , and atmospheric pressure*

**Table C.3** The results from the study on effect of membrane layer thickness

| Membrane type | Area(counts) | | $\alpha_{water/ethaol}$ | Flux(g/m$_2$hr) | | |
|---|---|---|---|---|---|---|
| | water | ethanol | | water | ethanol | total |
| 24 hour synthesis time | 20842 | 637 | 267.3419 | 213.0057 | 12.0478 | 225.0535 |
| | 20563 | 562 | 298.9629 | 210.1543 | 10.6293 | 220.7836 |
| | 21563 | 472 | 373.2796 | 220.3743 | 8.927098 | 229.3014 |
| | 21363 | 511 | 341.5926 | 218.3303 | 9.664719 | 227.9951 |
| | 20846 | 462 | 368.6786 | 213.0466 | 8.737965 | 221.7845 |
| | 20965 | 535 | 320.1903 | 214.2628 | 10.11864 | 224.3814 |
| 48 hour synthesis time | 26863 | 1751 | 125.3532 | 165.3684 | 21.46977 | 186.8382 |
| | 22988 | 1503 | 124.971 | 157.0784 | 17.02726 | 174.1056 |
| | 21424 | 1192 | 146.8559 | 152.2309 | 14.87028 | 167.1012 |
| | 20350 | 1041 | 159.7279 | 148.1477 | 14.4846 | 162.6323 |
| | 19722 | 1014 | 158.9206 | 143.3157 | 13.17041 | 156.4861 |
| | 19193 | 922 | 170.0901 | 143.9795 | 14.45603 | 158.4355 |
| secondary coating of membrane 24 hour synthesis time | 21596 | 506 | 557.3299 | 202.1927 | 6.965218 | 209.1579 |
| | 21658 | 503 | 550.8922 | 202.7732 | 8.715186 | 211.4884 |
| | 21730 | 435 | 481.2908 | 203.4473 | 7.53699 | 210.9843 |
| | 21972 | 447 | 516.3294 | 205.713 | 7.744907 | 213.4579 |
| | 21823 | 423 | 560.9559 | 204.318 | 7.329073 | 211.6471 |
| | 22483 | 453 | 474.8186 | 210.4973 | 7.848865 | 218.3461 |

*Separation condition: temperature 85 $^{o}$C, ethanol in feed 95 % v/v , and atmospheric pressure*

# APPENDIX D

# SURFACE AREA

**Table D.1** Surface area of the calcined support

| $P/P_0$ | Volume(cc/g) | BET |
|---|---|---|
| 1.0056E-02 | 25.2580 | 2.052E-01 |
| 1.2057E-02 | 27.5524 | 2.256E-01 |
| 2.4064E-02 | 29.9284 | 2.426E-01 |
| 2.6060E-02 | 32.0410 | 2.595E-01 |
| 2.8060E-02 | 34.4727 | 2.717E-01 |
| 2.0059E-02 | 35.7004 | 2.840E-01 |
| 2.2062E-02 | 36.3211 | 2.960E-01 |
| 2.5026E-02 | 37.4213 | 3.106E-01 |
| 2.9102E-02 | 38.3156 | 3.212E-01 |
| 3.0145E-02 | 39.1524 | 3.310E-01 |
| | | |

**Surface area = 377.60 $m^2/g$**

**Table D.2** Surface area of the treated support.

| $P/P_o$ | Volume(cc/g) | BET |
|---|---|---|
| 9.8398E-03 | 37.3206 | 1.356E-01 |
| 1.0055E-02 | 38.9902 | 1.327E-01 |
| 1.2041E-02 | 41.4801 | 1.496E-01 |
| 1.4043E-02 | 43.9911 | 1.649E-01 |
| 1.6044E-02 | 46.3043 | 1.793E-01 |
| 1.8047E-02 | 48.7219 | 1.921E-01 |
| 2.0053E-02 | 50.9069 | 2.047E-01 |
| 2.2131E-02 | 51.9399 | 2.219E-01 |
| 2.4092E-02 | 53.7543 | 2.339E-01 |
| 2.6074E-02 | 56.3527 | 2.420E-01 |
| 2.7864E-02 | 58.9563 | 2.511E-01 |

**Surface area = 414.70 $m^2/g$**

**Table D.3** Surface area of the zeolite A membrane with 24 hour synthesis time.

| $P/P_0$ | Volume(cc/g) | BET |
|---|---|---|
| 9.9789E-03 | 55.3580 | 9.273E-02 |
| 1.2032E-02 | 58.8429 | 1.054E-01 |
| 1.4044E-02 | 61.7041 | 1.176E-01 |
| 1.6061E-02 | 63.6517 | 1.306E-01 |
| 1.8061E-02 | 65.7120 | 1.426E-01 |
| 2.0059E-02 | 67.9101 | 1.535E-01 |
| 2.2068E-02 | 69.7136 | 1.649E-01 |
| 2.4072E-02 | 71.2199 | 1.764E-01 |
| 2.6073E-02 | 72.7484 | 1.874E-01 |
| 2.8076E-02 | 74.1191 | 1.985E-01 |
| 3.0156E-02 | 76.2064 | 2.014E-01 |

**Surface area = 489.3 $m^2/g$**

**Table D.4** Surface area of zeolite A membrane with 48 hour synthesis time.

| $P/P_0$ | Volume(cc/g) | BET |
|---|---|---|
| 1.0003E-02 | 57.5784 | 8.937E-02 |
| 1.1059E-02 | 59.3834 | 9.590E-02 |
| 1.1981E-02 | 60.5506 | 1.020E-01 |
| 1.2992E-02 | 61.6004 | 1.088E-01 |
| 1.3997E-02 | 62.5954 | 1.155E-01 |
| 1.5012E-02 | 63.4664 | 1.223E-01 |
| 1.6014E-02 | 64.3089 | 1.289E-01 |
| 1.7022E-02 | 65.0876 | 1.355E-01 |
| 1.8024E-02 | 65.8300 | 1.420E-01 |
| 1.9028E-02 | 66.5258 | 1.485E-01 |
| 2.0030E-02 | 67.8576 | 1.549E-01 |

**Surface area = 448.40 $m^2/g$**

**Table D.5** Surface area of the secondary growth of zeolite A membrane with 24 hour synthesis time.

| $P/P_0$ | Volume(cc/g) | BET |
|---|---|---|
| 1.0001E-02 | 62.7736 | 9.196E-02 |
| 1.1047E-02 | 64.6655 | 8.798E-02 |
| 1.2053E-02 | 66.5531 | 9.336E-02 |
| 1.3053E-02 | 68.4264 | 9.844E-02 |
| 1.3988E-02 | 69.7475 | 1.036E-01 |
| 1.5044E-02 | 71.6893 | 1.085E-01 |
| 1.6012E-02 | 72.7065 | 1.140E-01 |
| 1.6988E-02 | 74.0273 | 1.189E-01 |
| 1.7994E-02 | 75.2034 | 1.241E-01 |
| 1.8998E-02 | 76.3472 | 1.292E-01 |
| 2.0046E-02 | 78.2110 | 1.332E-01 |

**Surface area = 575.90 $m^2/g$**

# AUTHOR BIOGRAPHY

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