THE PREPARATION

OF ZEOLITE A COMPOSITE MEMBRANE

FOR ETHANOL/ETHYLENE/WATER SEPARATION

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หัวข้อวิทยานิพนธ์	การเตรียมเมมเบรนคอมโพสิตซีโอไลต์เอเพื่อใช้ในการแยกของผสมเอทานอล เอทิลีนและน้ำ
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บทคัดย่อ

งานวิจัยนี้ได้ทำการศึกษาการเตรียมเมมเบรนคอมโพสิตซีโอไลต์เอโดยวิธีการสังเคราะห์แบบไฮโดรเทอร์มัล (Hydrothermal Synthesis) บนตัวรองรับ (Support) ซึ่งเป็นของผสมระหว่างซีโอไลต์เอ และดินขาว จากการศึกษาด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบกวาด พบว่าสามารถเตรียมเมมเบรนซีโอไลต์เอซึ่งมีขนาดผลึก 2.5-5.0 ไมครอนบนพื้นผิวของตัวรองรับได้ จากนั้นนำเมมเบรนคอมโพสิตซีโอไลต์เอที่เตรียมได้มาใช้ในการแยกก๊าซผสมระหว่างเอทานอล เอทิลีนและน้ำด้วยเทคนิคการซึมผ่านของก๊าซ โดยทำการทดลองที่อุณหภูมิ 80-120 องศาเซลเซียล ใช้เอทานอลในสารป้อนเข้มข้น 60-95%โมล ภายใต้ความดันบรรยากาศ ด้วยอัตราเร็วของก๊าซตัวพา 30-50 มิลลิลิตร/นาที จากการศึกษาพบว่าเมมเบรนที่ได้จากการสังเคราะห์ 24 ชั่วโมง มีพื้นที่ผิวและความสามารถในการแยกสูงกว่า - รวมทั้งให้ปริมาณสารที่สามารถซึมผ่านมากกว่าเมมเบรนที่ได้จากการสังเคราะห์ 16 ชั่วโมง นอกจากนี้ยังพบว่าพื้นที่ผิวของเมมเบรน (416-452 ตารางเมตร/กรัม) ความสามารถในการแยก (44.1-232.1) และปริมาณสารที่สามารถซึมผ่าน (26.2-78.9 กรัม/ชั่วโมง/ตารางเมตร) มีค่าเพิ่มขึ้นเมื่อปริมาณซีโอไลต์เอในตัวรองรับเพิ่มขึ้น อย่างไรก็ตามการเพิ่มขึ้นของอุณหภูมิที่ใช้ในการแยก ยังส่งผลให้ความสามารถในการแยกลดลง แต่ทำให้ปริมาณสารที่สามารถซึมผ่านเพิ่มขึ้น ในทางตรงกันข้ามการเพิ่มขึ้นของอัตราเร็วของก๊าซตัวพา (30-50 มิลลิลิตร/นาที) และความเข้มข้นของเอทานอลในสารป้อนทำให้ความสามารถในการแยกเพิ่มขึ้น (68.9-204.2) แต่ปริมาณสารที่สามารถซึมผ่านลดลง (106.2-58.7 กรัม/ชั่วโมง/ตารางเมตร) ในการแยกน้ำจากของผสมเอทานอล เอทิลีน และน้ำ พบว่าความสามารถในการแยกของน้ำมีค่าน้อยกว่าเมื่อเทียบกับการแยกน้ำจากของผสมเอทานอลและน้ำ ขณะที่ปริมาณสารที่สามารถซึมผ่านมีค่าสูงกว่า นอกจากนั้นยังพบว่าปริมาณสารที่สามารถซึมผ่าน (115.6-105.2 กรัม/ชั่วโมง/ตารางเมตร) และความสามารถในการแยก (126.9-52.4) ลดลงเมื่ออุณหภูมิที่ใช้ในการแยกเพิ่มขึ้น

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ABSTRACT

In this thesis, zeolite A composite membranes were prepared, using hydrothermal synthesis, on the surface of supports, which are the mixture of zeolite A and kaolin. The Scanning Electron Microscope 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 experiment was carried out at 80-120^{O} C, using 60-95% mol ethanol in feed, under atmospheric pressure, and 30-50 ml/min carrier gas flow rate. It was found that the membrane with 24 hours synthesis time gave higher surface area, separation factor and permeation flux than that with 16 hours synthesis time. Moreover, it was shown that the membrane surface area (416 to 452 m^2/g), separation factor (44.1 to 232.1) and permeation flux (26.2 to 78.9 g/hr m^2) 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 (68.9 to 204.2) but reduced the permeation flux (106.2 to 58.7 g/hr m^2). 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 (115.6 to 105.2 g/hr m^2) and the separation factor of water (126.9 to 52.4) were decreased with an increase in the separation temperature.

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Finally, the author dedicated her work to her beloved parents and her family for their constant love and encouragement.

Suree Tanyapanyachon

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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

In the dehydration of ethanol for ethylene production, water is an undesirable product, which has influence on the ethylene concentration in the product. The ethylene yield and ethylene concentration of the product can be increased when the water is removed from the product mixture because the chemical equilibrium of the reaction can be shifted forward. Therefore, this thesis is interested in the removal of water from the dehydration of ethanol for the production of dry ethylene, which can be employed to make liquid fuels and aromatics [1,2].

The chemistry of the zeolite can be modified to provide a suitable hydrophilic/hydrophobic surfaces, and the appropriate pore size and structure for certain applications, 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 porous support to improve the water selectivity of the membrane [3-5].

In this thesis, the zeolite A composite membranes will be prepared on the surface of the supports, which are the mixture of zeolite A and kaolin. These membranes will be used to separate ethanol/ethylene/water mixture, which is the product mixture from the dehydration of ethanol. The ethylene can be used as feed for production of liquid fuels and aromatics, via oligomerization and aromatization reactions. Accordingly, preparation and separation efficiency of the membranes for water removal from the ethanol/ethylene/water mixture are investigated.

1.2 Objectives

1. To obtain the zeolite A composite membrane with high water selectivity.
2. To obtain the preferable methodology for the synthesis of zeolite A composite membrane.
3. To obtain suitable separation conditions which give high water content in the permeate composition.
4. To separate water from ethanol/ethylene/water mixture by gas permeation using zeolite A composite membrane.

1.3 Scope of study

1. Prepare and characterize the support and the zeolite A composite membrane.
2. Investigate the effect of the synthesis time of zeolite A composite membrane and zeolite A content in the support.
3. Investigate the effect of the synthesis time of the zeolite A composite membrane, zeolite A content in the support, separation temperature, carrier gas flow rate and feed composition on the separation performance.
4. Investigate the separation of ethanol/ethylene/water mixture using zeolite A composite membrane.

1.4 Expected results

1. The zeolite A composite membrane with high water selectivity can be obtained.
2. The preferable methodology for synthesis of the zeolite A composite membrane can be obtained.
3. The appropriate condition for ethanol/water separation can be obtained.
4. The zeolite A composite membrane can be used to remove the water from ethanol/ethylene/water mixture by gas permeation.

CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 Zeolites

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 ≥ 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 andAlO_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).

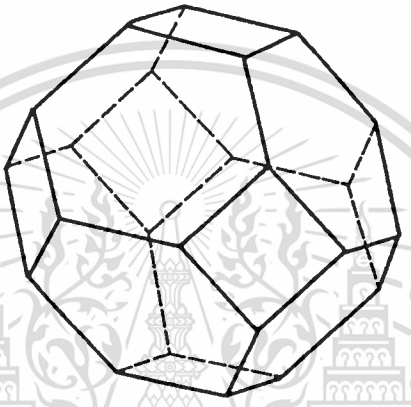
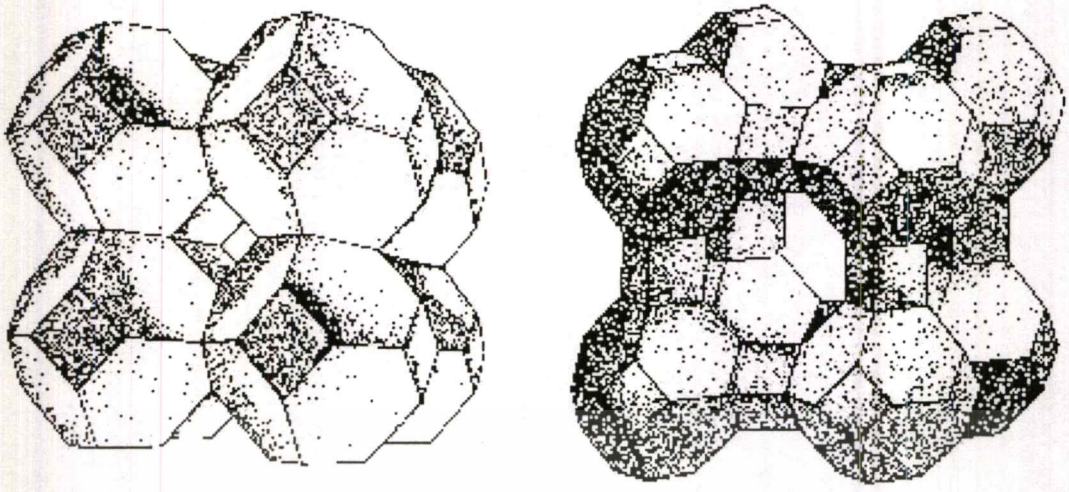


Figure 2.1 A tetradecahedron formed 24 SiO_4 and AlO_4 tetrahedra [5].

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].

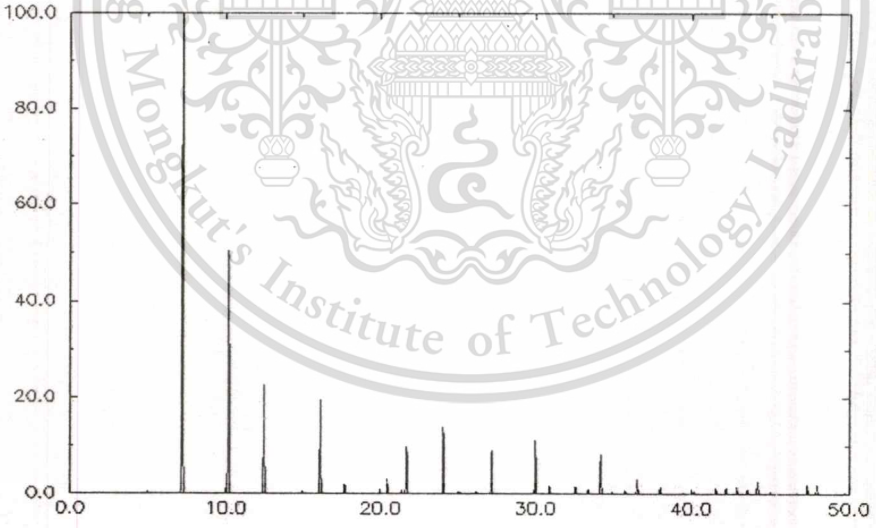


Figure 2.3 The X-Ray Diffraction pattern of zeolite A [4].

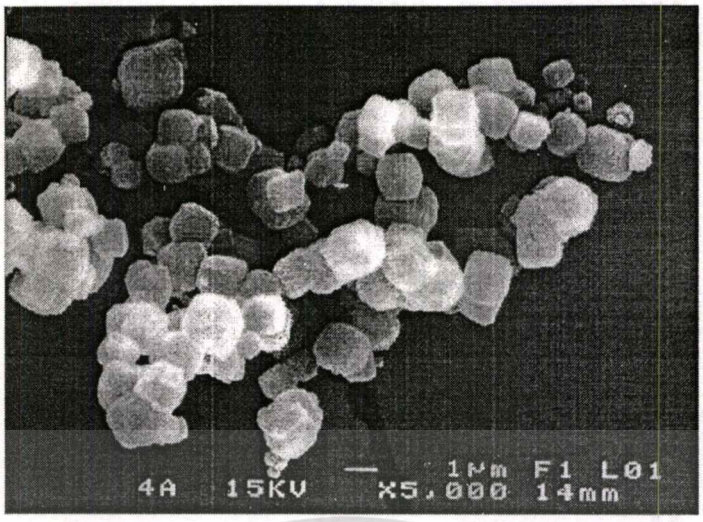


Figure 2.4 The Scanning Electron Micrograph of zeolite A

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.,

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.

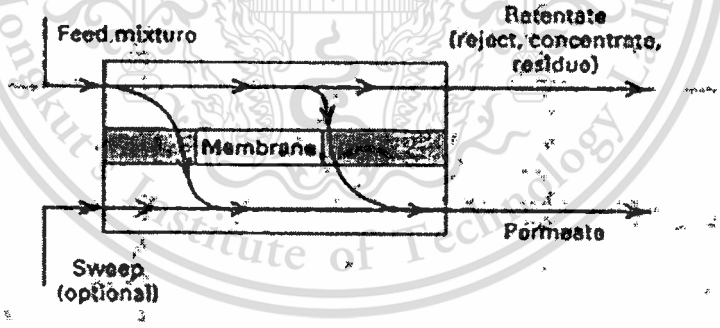


Figure 2.5 General membrane process [18]

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].

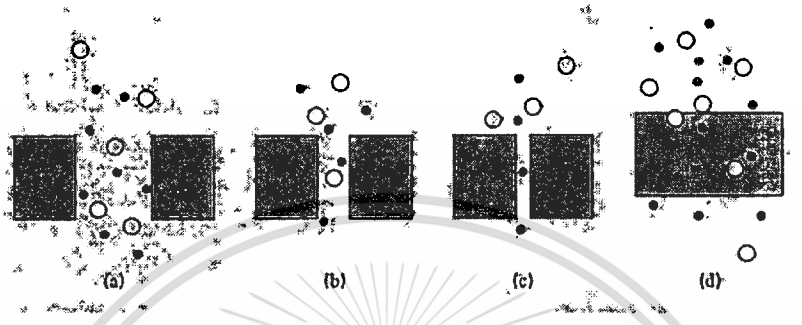


Figure 2.6 Mechanism of transport in membranes. (Flow is downward.) (a) bulk flow through pores; (b) diffusion through pores; (c) restricted diffusion through pores; (d) solution-diffusion through dense membrane [18]

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.

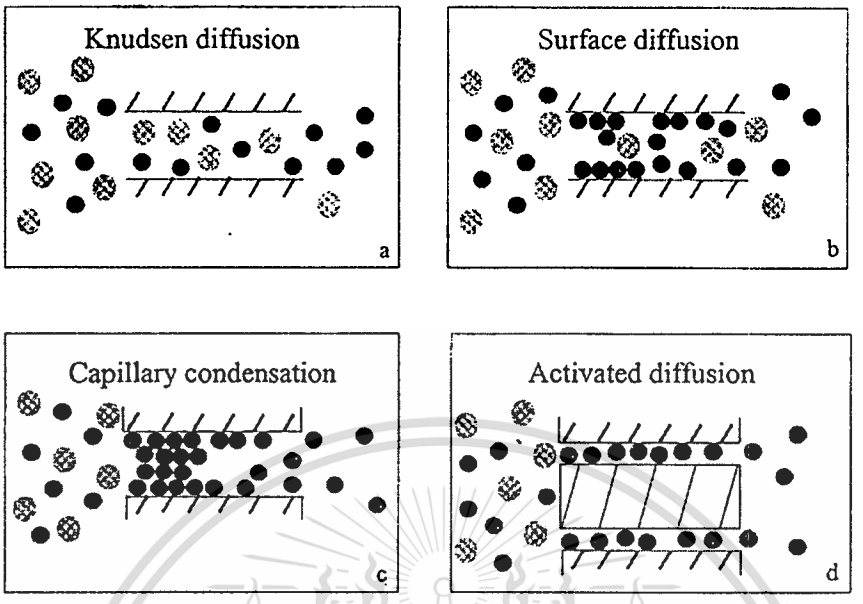


Figure 2.7 Micropore diffusion mechanism [3]

2.3.2 Pervaporation

Pervaporation is a relatively new membrane separation process that has elements common with reverse osmosis and membrane gas separation. In pervaporation, the liquid mixture to be separated (feed) is placed contact with one side of a membrane and the permeated product (permeated) is removed as a low-pressure vapor from the other side. The permeated vapor can be condensed and collect or release as desired. The feed to the membrane module is a liquid mixture (e.g., an alcohol-water mixture) at pressure, P_1, that usually ambient or elevated high enough to maintain a liquid phase as the feed depleted of species A and B to produce the product retentate. A membrane is selective for species A, but species B usually has some finite permeability. The retentate is enriched in species B. Generally a sweep fluid is not used on the other side of membrane, but pressure, P_2 is maintained at or below the dew point of the permeate, making it vaporized. Vaporization may occur near the downstream face of the membrane, such that the membrane can be considered to operate with two zones, a liquid phase zone and vapor phase zone, as show in Figure 2.8. Alternatively, the vapor phase may only exist on the permeate site of the membrane. The vapor permeate is enriched in species A. Overall permeabilities of species A and B depend on their solubilities and diffusion rates though the membrane. The chemical

potential gradient across the membrane is the driving force for the mass transport. The driving force can be created by applying either a vacuum pump or an inert purge (normally air or stream) on the permeate side to maintain the permeate vapor pressure lower than the partial pressure of the liquid [17-22].

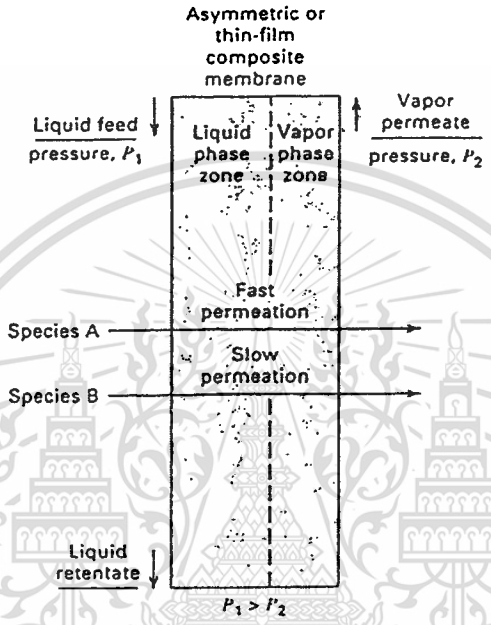


Figure 2.8 Pervaporation process [17]

The applications of the prevaporation can be classified into three categories: dehydration of organic solvents, removal of organic compounds from aqueous solutions and separation of anhydrous organic mixtures. Currently, pervaporation has been commercialized for two applications: one is the dehydration of alcohol and other solvents, and other is the removal of small amounts of organic compounds from contaminate waters. In latter applications, pollution control and solvent recovery are effected simultaneously. There are also some other promising applications such as aroma recovery and beer dealcoholization in the food industries and product recovery from fermentation broths for enhanced bioconversion.

Pervaporation can be applied successfully to mixtures that are difficult to separate by the conventional techniques such as the case for azeotropic mixtures or mixtures of liquid with very small differences in vapor pressure. Pervaporation may also be used for dehydrating chemicals that might be heat sensitive.

2.3.3 Requirements for Membrane

Pervaporation is a rate-controlled separation process, In developing pervaporation membranes, three issues must be addressed: membrane productivity, membrane selectivity, and membrane stability.

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.

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

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

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

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 α 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].

2.3.4 Gas permeation

In gas permeation, the feed gas, at high pressure P_1, contains some low-molecular-weight species (MW < 50) to be separated from small amounts of higher-molecular-weight species. Usually a sweep gas is not used, but the other side of the membrane is maintained at a much lower pressure, P_2, often near ambient pressure. The membrane, often dense but sometimes microporous, is permselective for certain of the lower-molecular-weight species in the gas feed, shown in Figure 2.9 as the A species. If the membrane is dense, these species are adsorbed at the surface and then transported through the membrane by one or more mechanisms. Thus permselectivity depends on both membrane adsorption and the membrane transport rate. Usually all mechanisms are formulated in term of a partial pressure or fugacity driving force. The product is a permeate that is enriched in the A species and a retentate that is enriched in B. A near-perfect separation is generally not achievable. If the membrane is microporous, pore size is extremely important because it is usually necessary to block the message of species B. Otherwise, unless molecular weight of A and B differ appreciably, only a very modest separation is achievable, as was discussed in connection with Knudsen diffusion [17-21].

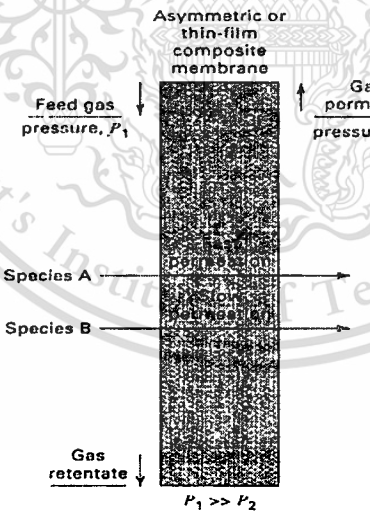


Figure 2.9 The gas permeation [18]

Since the early 1980s, applications of gas permeation with dense polymeric membranes have increased dramatically. Applications include (1) separation of hydrogen from methane; (2) adjustment of H_2-to-CO ratio in synthesis gas; (3) O_2 enrichment of air; (4) N_2 enrichment of air;

(5) removal of CO_2; (6) drying of natural gas and air; (7) removal of helium; and (8) removal of organic solvents from air.

Gas permeation must compete with distillation at cryogenic conditions, adsorption, and pressure-swing adsorption. Some of the advantages of gas permeation are low capital investment, ease of installation, ease of operation, absence of rotating parts, high process flexibility, low weight and space requirements, and low environmental impact. In addition, if the feed gas already at so high pressure that a gas compressor is not needed, no utilities are required.

Since 1986s, the most rapidly developing application for gas permeation has been air separation, for which available membrane have separation factors for O_2 with respect to N_2 of 3 to 7. However, product purity is economically limited to the retentate of 95-99% N_2 and the permeate of 30-45% O_2. Thus, the largest application of gas permeation is the product of nitrogen rather than oxygen.

Early applications of gas permeation used dense (nonporous) membranes of cellulose acetates and polysulfone, which are still predominate, although polyimides, polyamides, polycarbonates, polyetherimides, sulfonated polysulfones, teflon, polystyrene, and silicone rubber are also finding applications for temperatures to at least 70 °C. Although plate and flame and tubular modules can be used for gas permeation, almost all large-scaled applications used spiral-wound or hollow–fiber modules because of their higher packing density. When the feed contains condensable gases, it may be necessary to preheat the gas prior to entry into the membrane system to prevent condensation on the membrane as the retentate become richer in the high-molecular-weight species. For high temperature applications where polymer cannot be used, membranes of glass, carbon, and inorganic oxide are available, but are limited in their selectivity [18,23,24].

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].

2.5 Overview of the Thesis

In this thesis the separation of ethanol/ethylene/water mixtures using zeolite A composite membrane have been studied. The zeolite A composite membranes can be prepared by coating the polycrystalline zeolite A, using the hydrothermal synthesis on the surface of disk supports, which are the mixture between zeolite A and kaolin [35]. The synthesis of zeolite A composite membrane and design of the separation cell will be discussed in section 3.5 and 3.6. The characterization of supports and zeolite A composite membranes using conventional techniques, such as X-ray diffraction, scanning electron microscope, gas adsorption analyzer, etc. are demonstrated in section 4.1 and 4.2.

The zeolite A composite membrane was used for separation ethanol/water mixture and ethanol/ethylene/water mixture. In the ethanol/water separation, the effect of synthesis time and zeolite A content in the support on the separation performance are studied in section 4.3.1 and 4.3.2, respectively. It was suggested [29,30] that the separation temperature, feed composition and carrier gas flow rate would also strongly effect on the separation factor and permeation flux. Accordingly, the effect of the separation temperature from 80 to 120^{o}C was investigated in section 4.3.3. Also the gas mixture with different feed composition from 60 to 95% mol was tested and the results were discussed in section 4.3.4. Carrier gas flow rate was employed from 30 to 50 ml/min, and its effect on separation factor and permeation flux were discussed in section 4.3.5 in order to obtain the appropriate separation condition.

Moreover, the separation of ethanol/ethylene/water mixtures, which are the products mixture of the ethanol dehydration is studied in section 4.4. The effect of the separation temperature was particularly investigated for this feeding mixture in order to elevate a possibility of the membrane for an application in membrane reactor.

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Reagents

1. Carbon dioxide (CO_2), (High purity 99.99%, TIG Co., LTD.)
2. Deionized water
3. Ethanol (C_2H_5OH), (Absolute, Fluka)
4. Ethylene (C_2H_4), (High purity 99.99%, TIG Co., LTD.)
5. Kaolin (Fluka)
6. Ludox (colloid silica, 40% SiO_2,Aldrich)
7. Poly(ethylene glycol) (PEG)(Fluka)
8. Poly(vinyl alcohol) (PVA)(Fluka)
9. Sodium aluminate ($Na_2Al_2O_4$)(Riedel de Haën)
10. Sodium Hydroxide (NaOH) (Carlo Erba Reagenti)
11. Sodium metasilicate (Na_2SiO_3)(Fluka)
12. Triethanolamine $(HOCH_2CH_2)_3N$ (Fluka)
13. Zeolite A (PQ Chemicals Thailand LTD.)

3.2 Apparatus

1. Atomic Absorption Spectrophotometer (AA-680, Shimadzu)- Graphite Furnace Atomizer (GFA-4B, Shimadzu)
2. Autoclave (276AC2, Parr Instrument Company)
3. Cooling
4. Droppers
5. Electrical balance (TC-254, Denver Instrument Company)
6. Furnace (Vecstar Furnaces)
7. Gas Adsorption Analyzer (Autosorb-1C, 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 beaker
15. Scanning Electron Microscope (Scanning Microscope 6400, Joel)
16. Separation cell
17. Thermometer
18. Volumetric cylinder
19. X-Ray Diffractrometer (D8 Advance, Bruker)

3.3 Process of the study

A process of the study of the gas separation 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 Preparation of zeolite A composite membrane

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 (Autosorb-1C)

3.3.2.4 Determine the Silicon /Aluminium ratio of the support by Atomic Absorption Spectroscopy

3.3.3 Separation testing

3.3.3.1 Effect of synthesis time of the zeolite A composite membrane

3.3.3.2 Effect of zeolite A content in the support

3.3.3.3 Effect of the separation temperature

3.3.3.4 Effect of the carrier gas flow rate

3.3.3.5 Effect of the feed composition

3.3.3.6 Ethanol/ethylene/water separation

3.4 Preparation of the support and zeolite A composite membrane

3.4.1 Preparation of support [32]

Preparation of the support which has 50.0% weight of zeolite A can be provided by mixing 10 grams of zeolite A powder and 10 grams of kaolin. Then, the mixture of 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 grams of sodium metasilicate (Na_2SiO_4) have already been dissolved. The suspension was homoginized by stirring and heating at 80 °C to evaporate water for 2 hours. Then, the sample was crushed into powder and dry at 80 °C for 4 hours.

The support disk having a diameter of 13 mm, was prepared by pressing 0.25 grams of the powder mixture with 5 tons pressure loading. Finally, the support disk was calcined at 650 °C for 1 hour [32]. Using the same procedure, the supports having 62.5 and 75.0 % weight of zeolite A content could be prepared from this method.

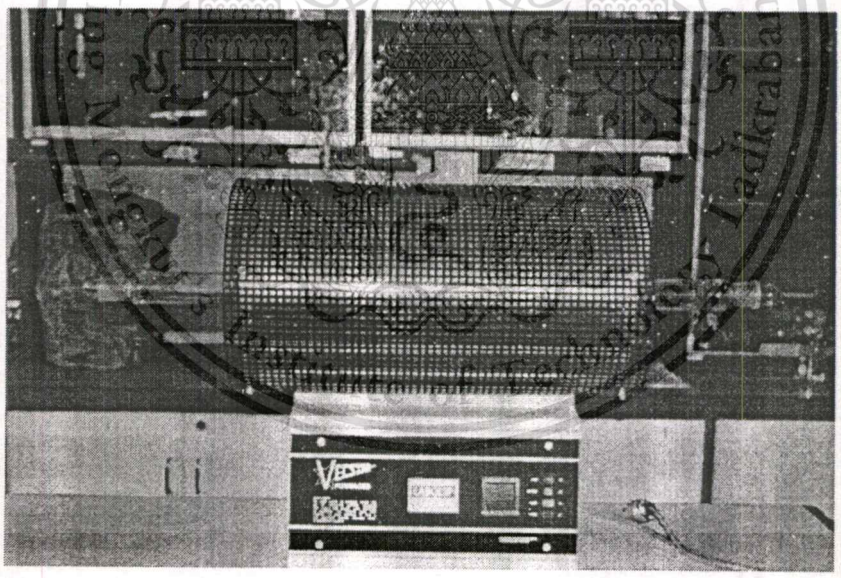


Figure 3.1 Calcination of the support in a tube furnace

3.4.2 Treatment of support [12]

The support disk was placed vertically in a liquid consisting 0.35 grams of sodium hydroxide (NaOH) and 12.65 grams of water, as shown in Figure 3.2. After 16 hours at room

temperature, a support disk and liquid were heated at 85 °C for 8 hours. After this step, the support disk was washed and stored in water [12].

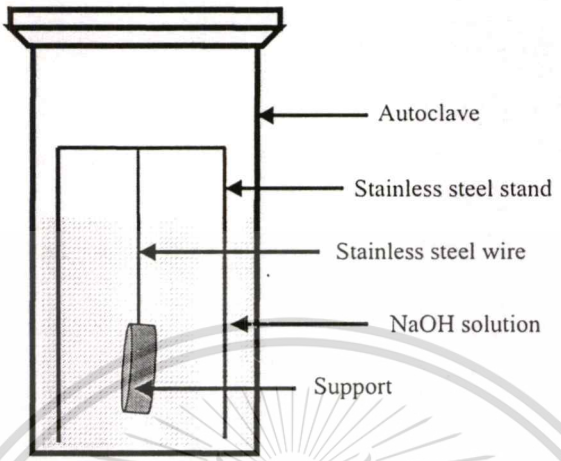


Figure 3.2 The support disk was placed in the sodium hydroxide solution

3.4.3 Zeolite A composite membrane preparation [32]

The wet support disk was placed in the aluminosilicate gel with the composition of Al_2O_3:0.72 SiO_2:1.72 Na_2O:165.95 H_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 added 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 were heated at 85 °C for 24 hours. After that, the membrane disk was thoroughly washed and heated at 300 °C for 2 hours in the high temperature oven. The heating rate is 6 °C / hr. Finally, the membrane disk was slowly cooled down in the high temperature oven.

The zeolite A composite membrane at synthesis time of 16 hours can be prepared in the same procedure. Whereby the wet support disk and gel were heated at 85 °C for 16 hours.

3.5 Characterization of support and zeolite A composite membrane

3.5.1 X-Ray Diffraction (XRD)

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

3.5.2 Scanning Electron Microscopy (SEM)

The crystal morphology and the crystal size were determined by scanning electron microscope (Jeol 6400 Scanning Microscope, Chulalongkorn University Instruments Service Center). The sample was prepared by placing 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 were taken at the magnification of 5,000 times.

3.5.3 Gas Adsorption Analyzer (Autosorb-1C)

Gas adsorption analyzer (Autosorb-1, Quantachrome) was used for the investigation of the specific surface area (SSA) of the support and the zeolite A composite 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 gasing station. Heating mantle was installed and the temperature was raised to 350 $^{\circ}$C. The sample was out-gassed for 24 hours. The sample cell was then removed from the out gasing station after the nitrogen or carbon dioxide was filled and attached to the analysis station. The analysis parameter was shown in Table A.1 (Appendix A).

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

3.5.4 Determination of Si / Al ratio

The silicon/aluminium ratio was determined by graphite furnace atomic absorption spectrophotometer (AAS, AA-680 Shimadsu). For this purpose, the sample was prepared by heating the disk support sample at 650 ^{o}C for 3 hours and 50 milligrams of treated disk support sample was weighed in a Ni-crucible. Then, 5 ml of 30 percent weight sodium hydroxide solution (30% NaOH) was transferred into the crucible and evaporated by heating. After that, the crucible was heated with swirling by gas burner for approximately 10 minutes. The crucible was cooled and washed by boiling water and the solution was transferred to a 100 ml beaker. Then, 5 ml of 1+1 hydrochloric acid solution was added to the beaker and stirred. Finally, the solution was diluted to 250 ml in a graduated flask.

For the determination of silicon, 1.0 ml of the stock solution was diluted to 50 ml in a volumetric flask. Absorption wavelength was set to 251.6 nm. The 10 µl of sample was injected to the graphite furnace atomic absorption spectrophotometer by micropipette. The sample in graphite furnace was dried at 150 ^{o}C for 30 seconds. Then the temperature was raised to 900 ^{o}C for 20 seconds for ashing. Finally, the ash was atomized at 2700 ^{o}C for 5 seconds. Argon was used as carrier gas at a flow rate at 1.5 l/min during drying and ashing.

For the determination of aluminium, 0.5 ml of stock solution was diluted to 50 ml in a volumetric flask. Absorption wavelength was set to 309.3 nm for determining aluminium. 10 µl of sample was injected to the graphite furnace atomic absorption spectrometry by micropipette.

The sample of aluminium in graphite furnace was dried at 150 ^{o}C for 30 seconds. Then the temperature was raised to 800 ^{o}C for 20 seconds for ashing. Finally, the ash was atomized at 2600 ^{o}C for 3 seconds. Argon was used as carrier gas at a flow rate at 1.5 l/min. The temperature program for the determination of silicon and aluminium was shown in Table 3.1.

Table 3.1 The temperature program for determination of silicon and aluminium

Element	Wavelength (nm.)	Dried	Ashing	Atomized
Silicon	251.6	150 ^{o}C, 30 sec Ar	900 ^{o}C, 20 sec Ar	2700 ^{o}C, 5 sec
Aluminium	309.3	150 ^{o}C, 30 sec Ar	800 ^{o}C, 20 sec Ar	2600 ^{o}C, 3 sec

The concentration of each metal was calculated using a calibration curve of standard sample. The standard of the silicon was prepared by diluted 1000 ppm of standard silicon solution to 1, 2, 4, 6, 8 and 10 ppm in a 50 ml graduated flask. While the standard of the aluminium was prepared by diluted 1000 ppm of standard aluminium solution to 0.5, 1, 2, 4, and 5 ppm in a 50 ml graduated flask. The standard absorbance was determined by graphite furnace atomic absorption spectrophotometry at the same condition for determining the sample. The calibration curves were plotted and the concentration of the samples can be calculated by comparing with the standard calibration curves [Appendix D].

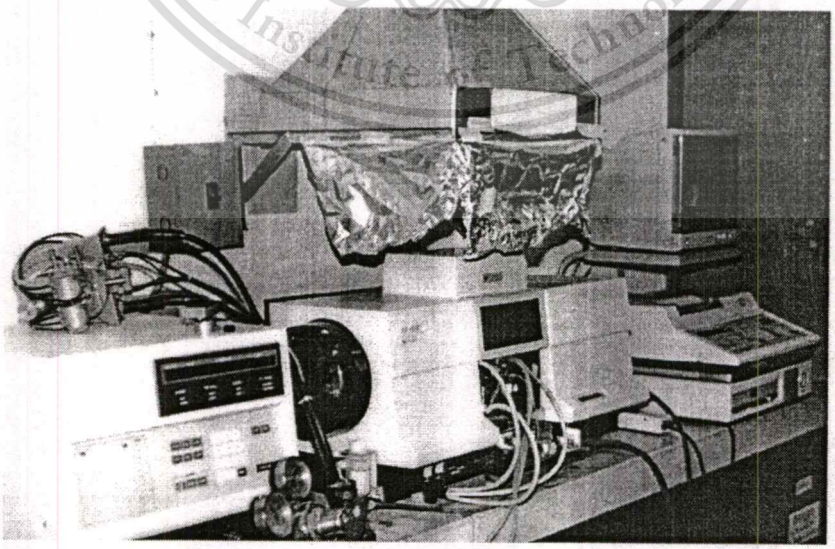


Figure 3.4 Atomic absorption spectrophotometer (AAS), AA-680 Shimadz

3.6 Separation testing

The zeolite A composite membrane synthesized according to 3.4.3, has been fixed between two metal rings with a inside diameter of 10 mm using cyanoacrylate adhesive. The component is called a membrane cell, as shown in Figure 3.5.

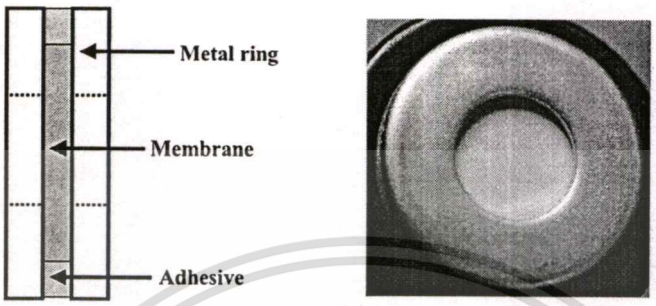


Figure 3.5 Membrane cell: the zeolite A composite membrane was fixed with the metal rings

Then the membrane cell was jointed with 4-ways Pyrex glass tube. The component is called the separation cell, as shown in Figures 3.6 and 3.7.

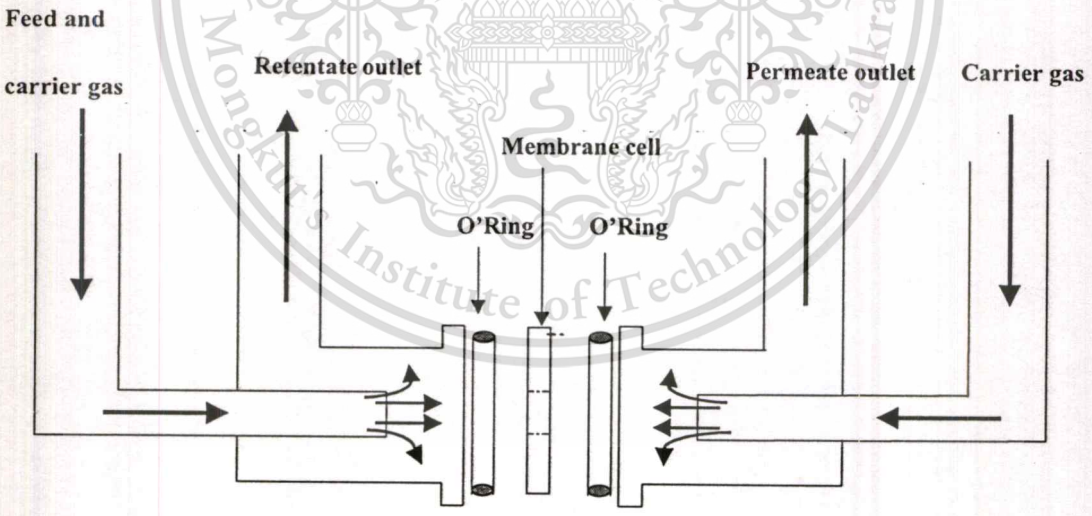


Figure 3.6 The diagram of the separation cell

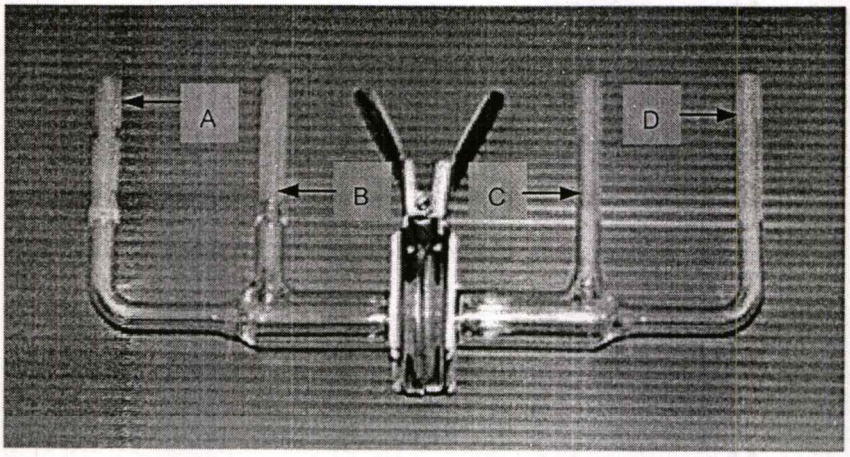


Figure 3.7 The separation cell : A is feed inlet, B is feed outlet, C is permeate outlet, and D is carrier gas inlet

The separation cell was connected with the feed gas and the carrier gas lines. The feed gas and carrier gas was primarily purged through the separation cell for leak detection. Then, the separation cell was placed into a sand bath and heated by electronic heater, as shown in Figure 3.8.

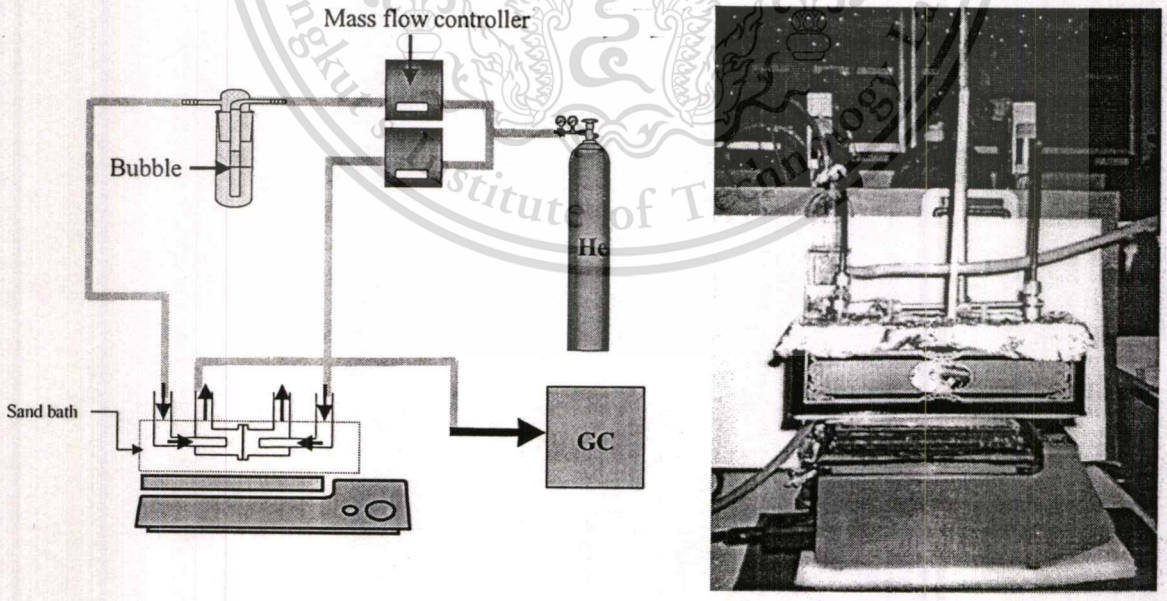


Figure 3.8 The separation unit

The separation testing was performed by feeding ethanol and water vapor using gas bubbling with helium through a liquid mixture at 10 ^{O}C. The helium gas carried the vaporized feed mixture to the membrane. The carrier gas flow rate of the feeding side was set to be the same as the permeate side for all runs. The flow rate of carrier gas for both side were controlled by mass flow controller (MASS TRAK, Sierra Instrument, INC). The separation testing was carried out at atmospheric pressure. Before separation, the zeolite A composite membrane was treated by heating the membrane at 80 ^{O}C, under flow of the carrier gas overnight. The feed gas mixture was firstly collected as liquid by trapping with liquid nitrogen for determination of the feed loading. Then, the feed line was connected to the sampling valve of Gas Chromatograph. After 2 hours, the gas feed mixture was analyzed every 20 minutes for at least 4 times in order to determine the feed composition at steady state. Then the feed line was connected to the feed inlet of the separation cell and the retentate outlet was connected to the sampling valve. The gas feed mixture was flowed through the membrane for another 2 hours until the system approach the steady state. After that, the ratentate mixture was injected every 20 minutes for determining the retentate composition (~1 hour). Then the sampling line was connected to the permeate outlet for determining the permeate composition in a similar manner as carried out for feed and retentate. The calculations of the permeation flux and separation factor were shown in Appendix F.

The feed, retentate, and permeate composition were analyzed by gas chromatography using 3800 Gas Chromatograph, Varian, with Gas Chrom 254 packed column (1/8 in. diameter and 1.8 m. length). The gas samples flowed through the sampling loop (1ml) of a 6-port valve, which were then injected to the injection port (200 ^{O}C) and the packed column (120^{O}C for 5 minutes) was connected with a TCD detector (200^{O}C). Helium was used as carrier gas at a flow rate of 30 ml/min. For the gas sample of ethanol/ethylene/water mixture, the sample was analyzed by gas chromatography using 3800 Gas Chromatograph, Varian, with Gas Chrom 254 packed column (1/8 in. diameter and 1.8 m. length). The injection port temperature was set at 200^{O}C and the separation temperature was started at 50^{O}C for 2 minutes. Then the temperature was raised to 120^{O}C with a heating rate 20^{O}C/min and hold at that temperature for 5 minutes and 50 seconds. Helium was used as carrier gas at a flow rate of 30 ml/min.

3.6.1 Effect of synthesis time

The zeolite A composite membranes, prepared with the synthesis time of 16 and 24 hours on the support having 75.0 weight percentage of zeolite A, were used for investigation the effect

of the synthesis time. The experiment was carried out at 80 ^{O}C, using 80% mol of ethanol in feed mixture [28], and 50 ml/min of the carrier gas flow rate.

3.6.2 Effect of zeolite A content in the support

In the effect of the zeolite A content in the support, the zeolite A composite membranes were prepared on the supports having 75.0%, 62.5%, and 50.0% weight of the zeolite A content. The separation experiment was carried out at 80 ^{O}C, 80% mol of ethanol in the feed mixture, and 50 ml/min of the carrier gas flow rate.

3.6.3 Effect of the separation temperature

The effect of the separation temperature was evaluated using the zeolite A composite membrane having a good separation performance in section 3.6.2. The separation experiment was carried out using 80% mol of ethanol in the feed mixture [28], 50 ml/min of the carrier gas flow rate, at temperatures of 80, 100, and 120 ^{O}C.

3.6.4 Effect of the carrier gas flow rate

The zeolite A composite membrane from section 3.6.3 was used for the investigation on the effect of the carrier gas flow rate. The separation experiment was carried out at the optimum temperature from section 3.6.3, using 80% mol of ethanol in feed mixture, with the carrier gas flow rate of 30, 40, and 50 ml/min.

3.6.5 Effect of the feed composition

The effect of the feed composition was determined using the appropriate condition obtained from sections 3.6.3 and 3.6.4. The various the feed compositions of 40, 60, 80, and 95% mol of ethanol in the feed mixture were used.

3.6.6 Ethanol/ethylene/water separation

The ethylene gas with the flow rate of 0.79 ml/min (3.2×10^{-5} mol/min) was mixed with the vapor mixture having 80% mole of ethanol. The gas mixture was carried to the membrane using the 50 ml/min of carrier gas flow rate. The separation was carried out at of 80, 100, and 120 ^{O}C.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization of zeolite A composite membrane on the different supports

The zeolite A composite membrane was prepared on the surface of disk supports, which are the mixture of zeolite A and kaolin. Whereby, the supports were calcined for one hour at 650 ^{o}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.

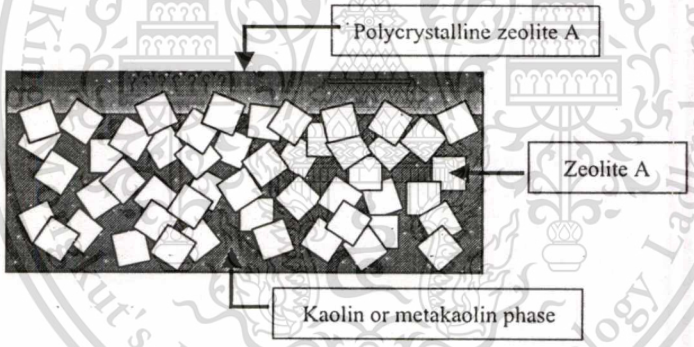


Figure 4.1 Illustration of zeolite A composite membrane

4.1.1 The structure determination

The XRD patterns of the supports having 50.0%, 62.5% and 75.0% weight of zeolite A were shown in Figures 4.2(a)-4.4(a).

The XRD patterns of these supports show that the intensity of the peak at 2θ = 9.1, which refers to the kaolin phase (Figures 4.5) decreased respectively. Whilst, the intensity of the peaks at 2θ = 7.2, 10.2, 12.5, 30.0, and 34.3, which refer to the zeolite A phase (Figure 4.6) increased respectively when the zeolite A content in the support increased.

After treatment with sodium hydroxide solution, the peak intensity at 2θ = 9.1 of the supports having 50.0% and 62.5% weight of the zeolite A content decreased. This is due to the

fact that some of metakaolin can be converted to zeolite A, as shown in Figures 4.2(b)-4.3(b). Moreover, the peak at 2θ = 9.1 of the support having 75.0% weight of zeolite A could not be observed presumably because the metakaolin was completely converted to the zeolite A, as shown in Figure 4.4(b). However, the intensity of the peaks at 2θ = 7.2, 10.2, 12.5, 30.0, and 34.3 of all supports increased significantly due to an increase in the zeolite A phase.

After growth of zeolite A membrane on the support surface, the intensity of the peaks at 2θ = 7.2, 10.2, 12.5, 30.0, and 34.3 of all supports increased markedly, while the peak at 2θ = 9.1 of the all supports could not be observed, as shown in Figures 4.2(c)-4.4(c). The XRD patterns of zeolite A membrane on all of supports were coincided with XRD pattern of zeolite A powder as shown in Figure 4.6. These results showed that the zeolite A membrane could be well prepared on all of the treated supports.

4.1.2 The surface morphology determination

The surface morphologies of the untreated supports, treated supports, and zeolite A composite membranes were investigated by Scanning Electron Microscope (SEM). The surface morphologies of the untreated supports, treated supports, and zeolite A composite membranes were shown in Figures 4.7, 4.8, and 4.9. The SEM images of the supports show that the surface of the support having 50.0% weight of zeolite A was more closely packed, as compared to those having 62.5% and 75.0% weight of zeolite A. After treatment with sodium hydroxide solution, the loss of continuous phase on the surfaces of all supports were observed. This is because some of the metakaolin was dissolved in the sodium hydroxide solution and converted to zeolite A. After growth, the surfaces of all treated supports were completely covered by zeolite A with a crystallite size of 2.5-5.0 μm. The crystals tend to intergrowth on one another forming a polycrystalline surface of zeolite A membrane. The zeolite A crystals on the support having 75.0% weight of zeolite A content are fairly uniformed, as compared to those on other supports.

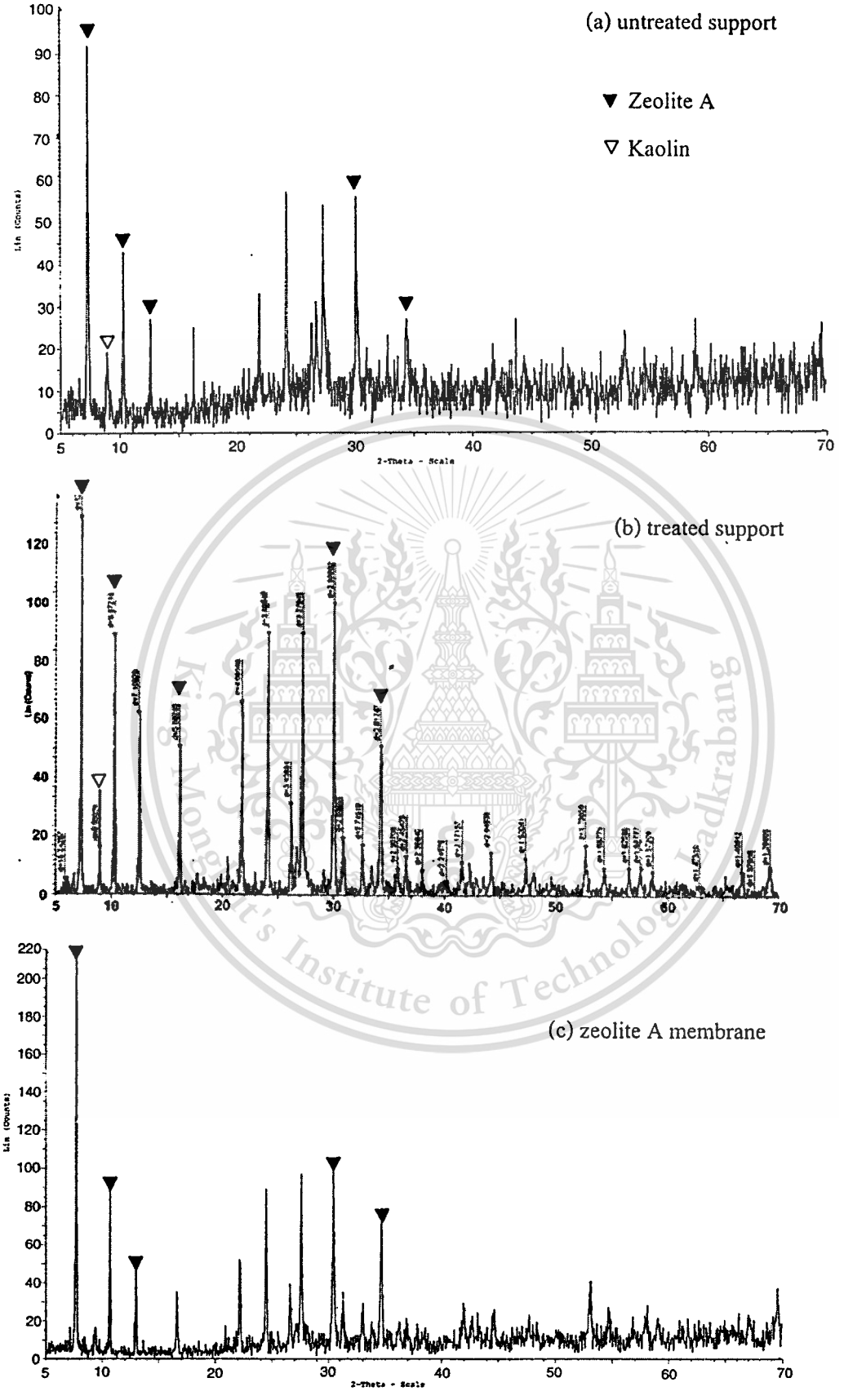


Figure 4.2 The XRD pattern of support composed of kaolin and zeolite A (50.0:50.0)

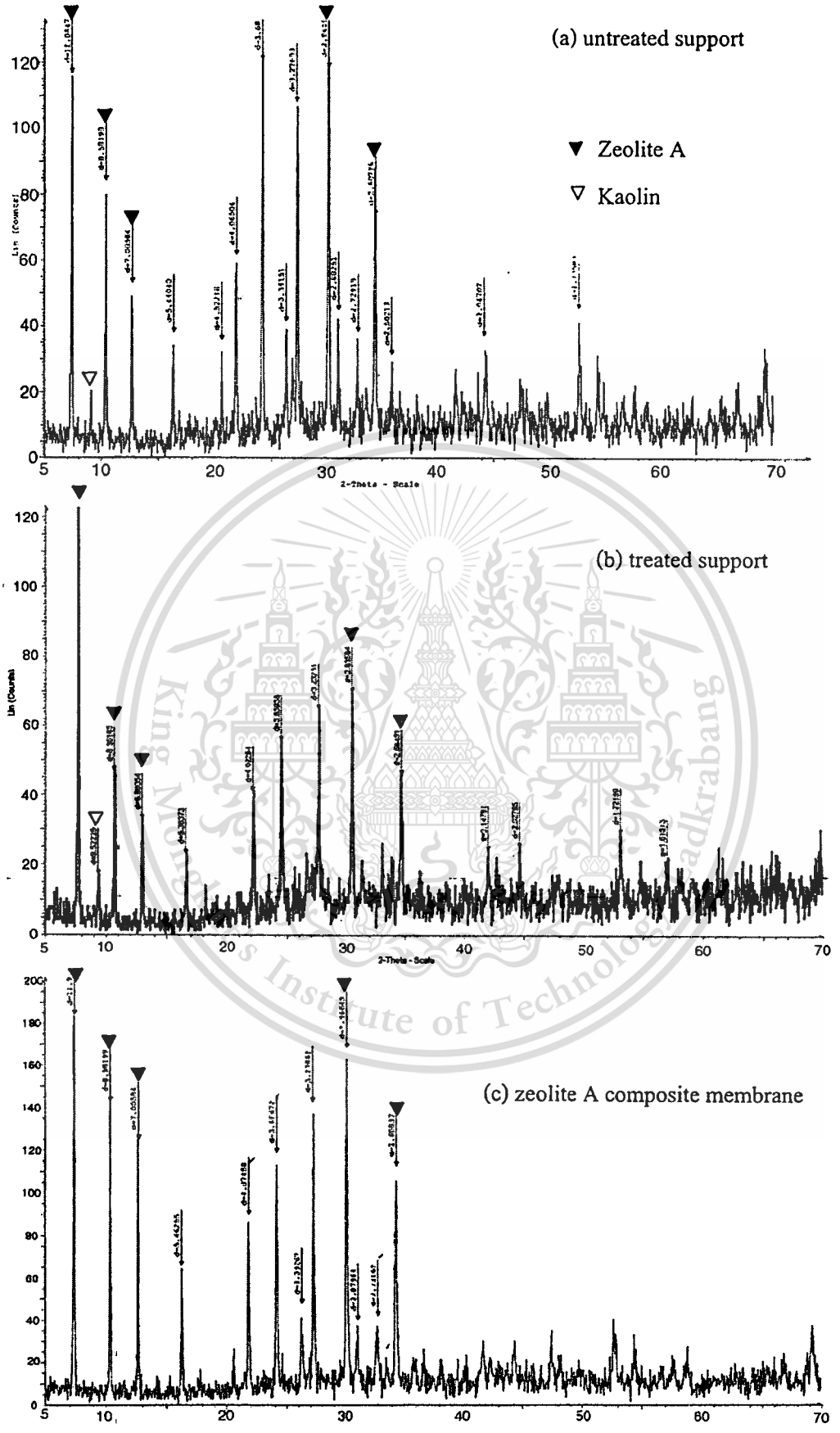


Figure 4.3 The XRD pattern of support composed of kaolin and zeolite A (62.5:37.5)

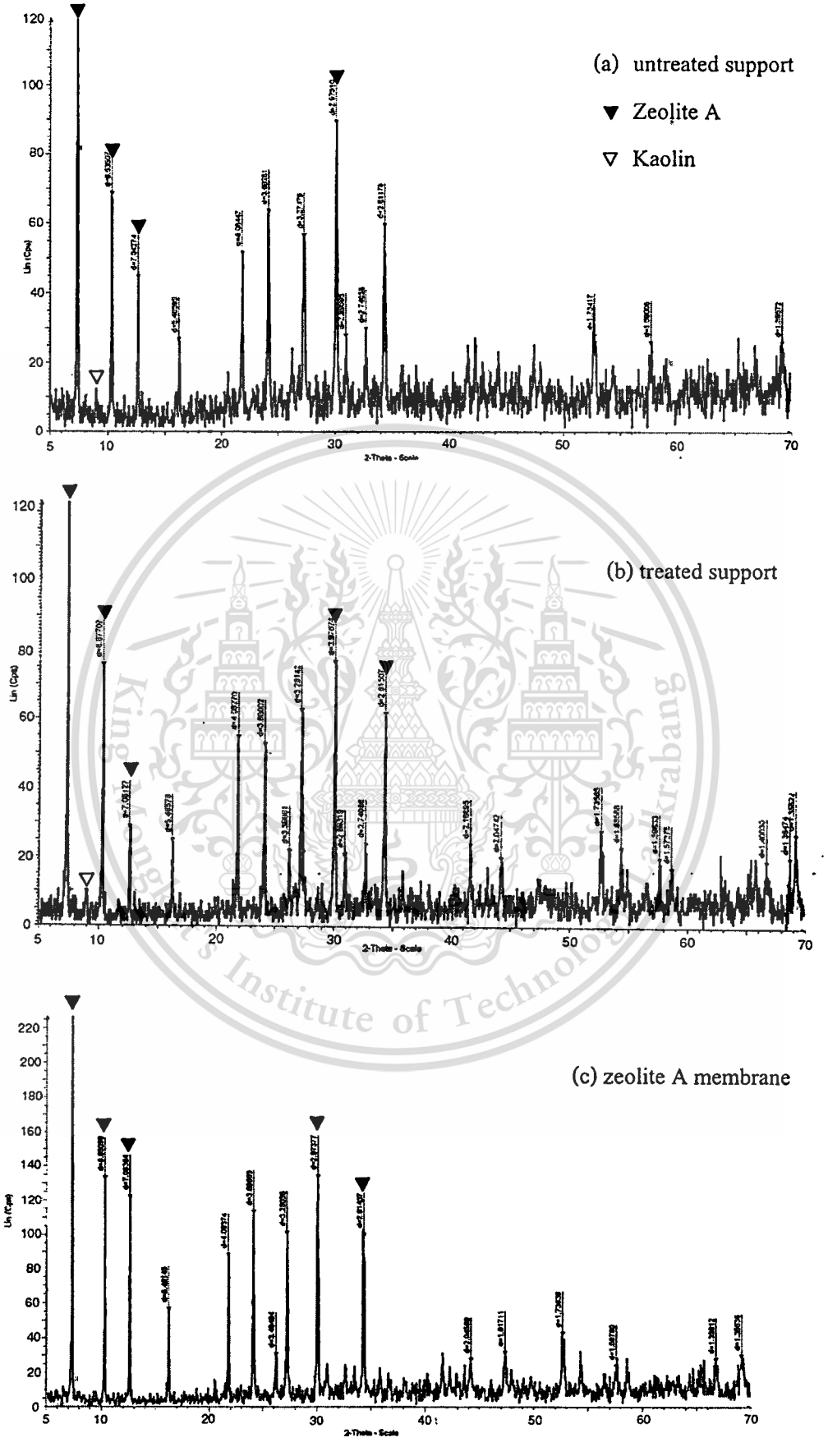


Figure 4.4 The XRD pattern of support composed of kaolin and zeolite A (75.0:25.0)

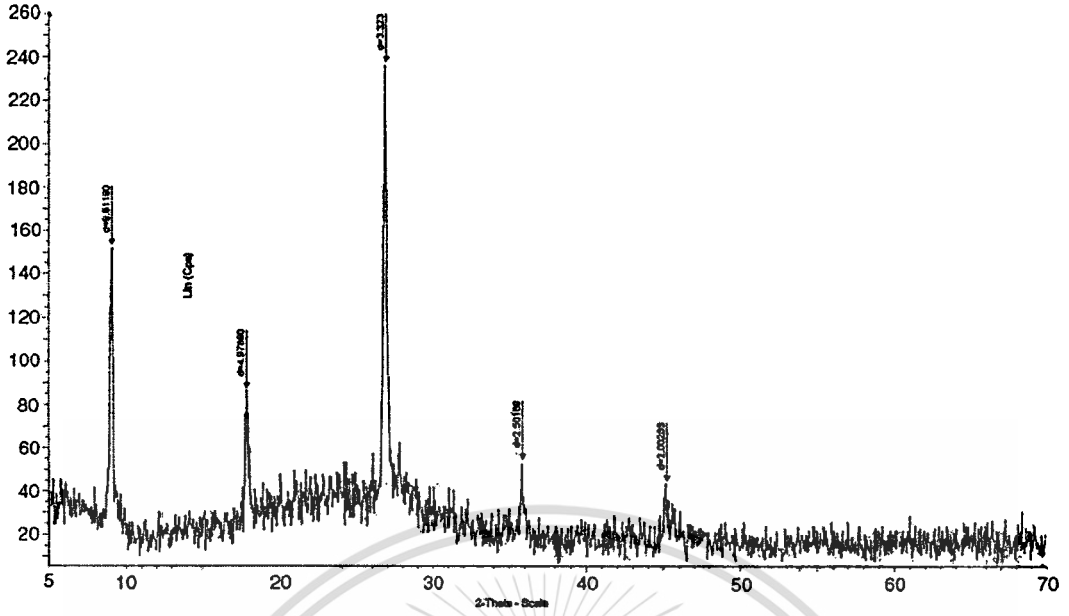


Figure 4.5 The XRD pattern of kaolin

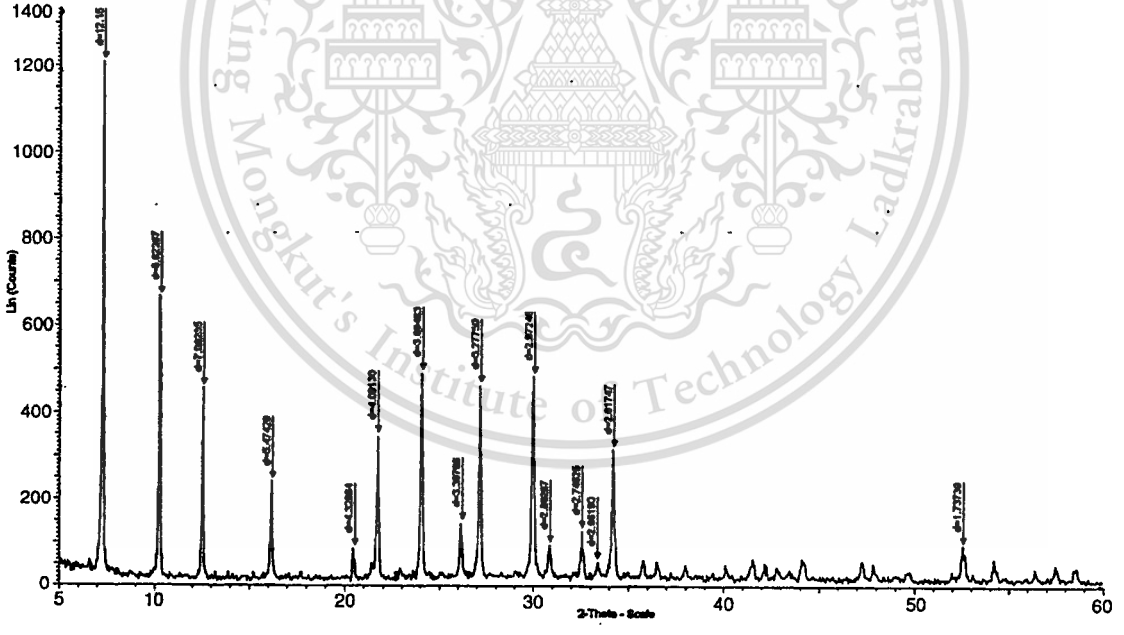
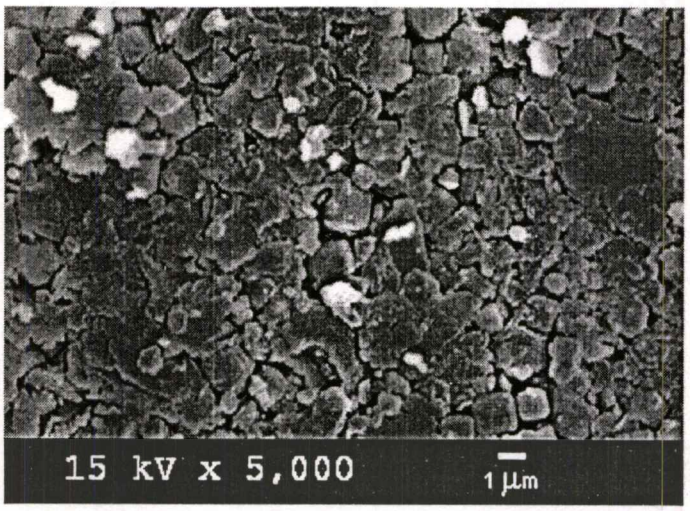
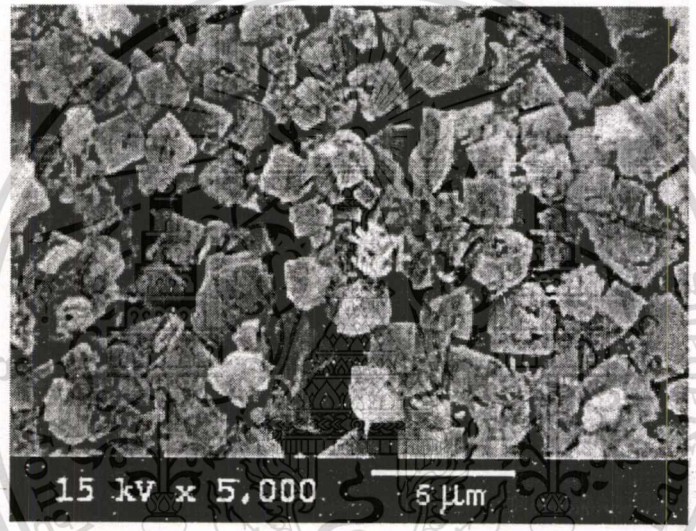


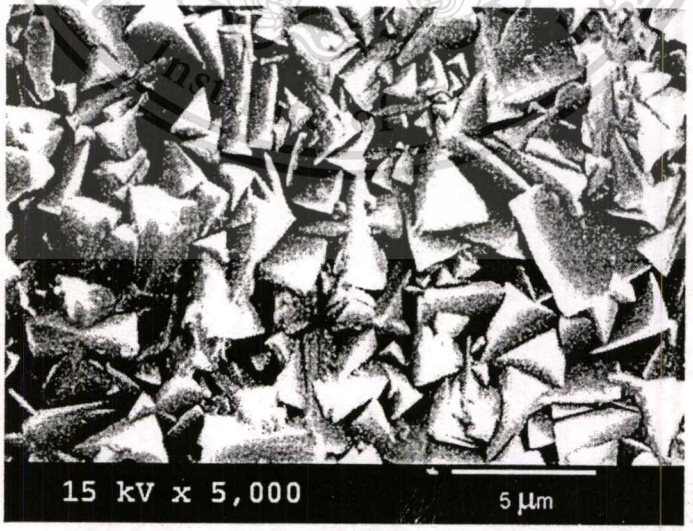
Figure 4.6 The XRD pattern of zeolite A powder



(a) untreated support

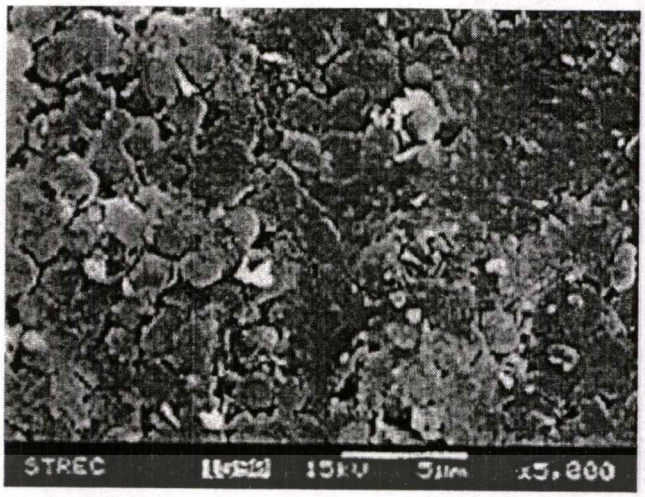


(b) treated support

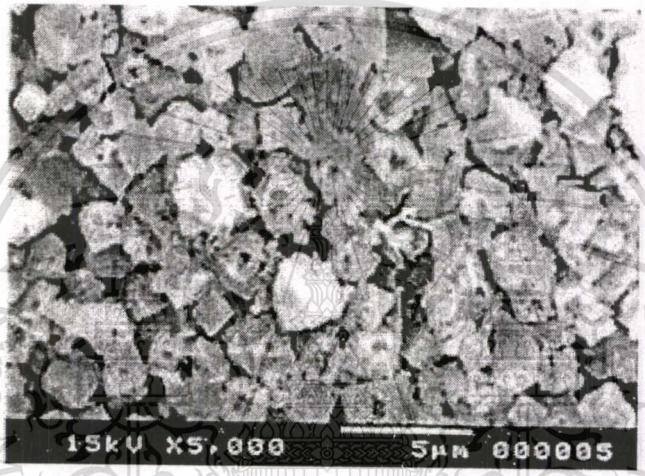


(c) zeolite A membrane

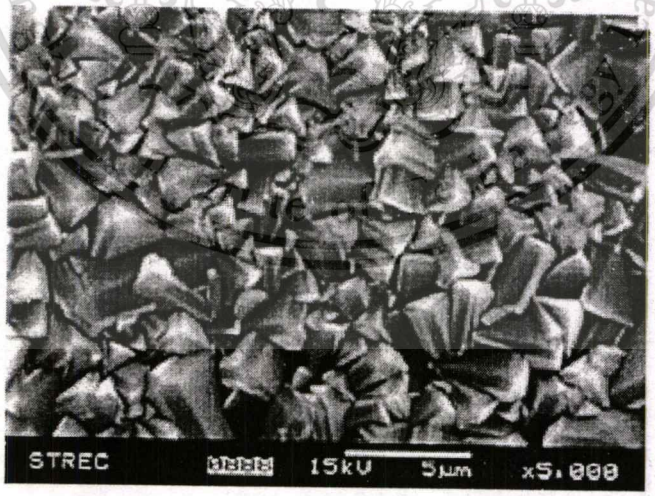
Figure 4.7 The SEM image of the support (50.0:50.0)



(a) untreated support

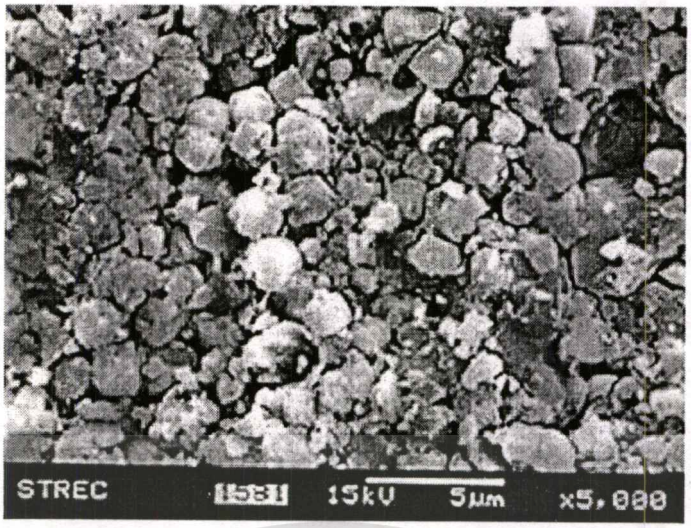


(b) treated support

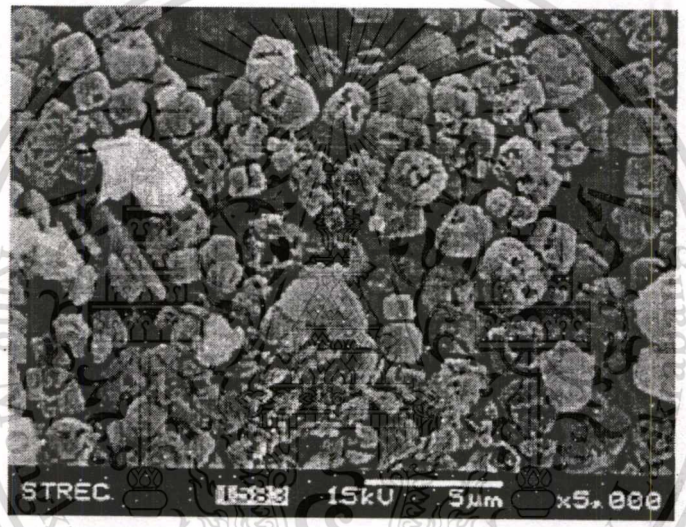


(c) zeolite A membrane

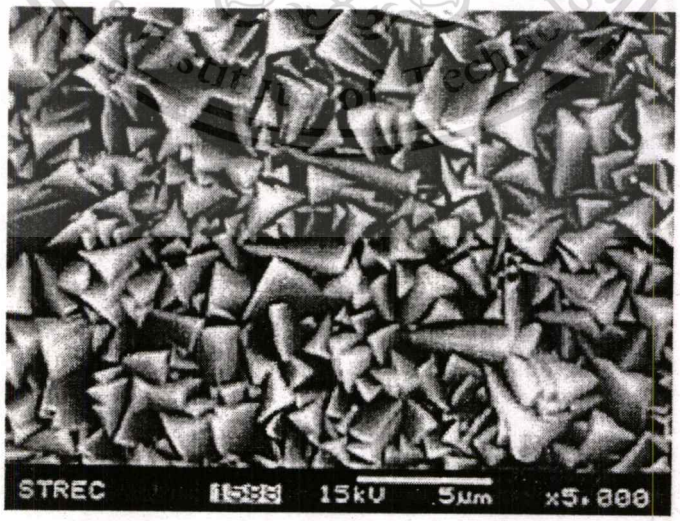
Figure 4.8 The SEM image of the support (62.5:37.5)



(a) untreated support



(b) treated support



(c) zeolite A membrane

Figure 4.9 The SEM image of the support (75.0:25.0)

4.1.3 Specific surface area determination

The specific surface area (SSA) of the supports and zeolite A membranes were investigated by the gas adsorption technique at –196 ^{o}C, using nitrogen adsorbate and at 0^{o}C using CO_2 adsorbate. It was found that the specific surface area of the support is increased when the % weight of zeolite A is increased. 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. Accordingly, the results from the carbon dioxide adsorption were used to determine the specific surface area. It was shown that the increase in specific surface area of the support is predominately arisen from the increase of % weight of zeolite A content.

Table 4.1 The specific surface area of the supports having different % weight of zeolite A

Support (zeolite A : kaolin)	Secific surface area[1] (m^2/g) (N_2)	Specific surface area[2] (m^2/g) (CO_2)
0:100	30	-
50:50	12	285
62.5:37.5	10	341
75:25	9	408
100:0	-	560

The disk samples were calcined at 650 ^{o}C for one hour; Specific surface area[1]: nitrogen as an adsorbate gas; specific surface area[2]: carbon dioxide as an adsorbate gas

After the supports were treated with sodium hydroxide solution, the specific surface areas of all supports increased, as compared to the untreated supports. This is because some of metakaolin was converted to the zeolite A, which is corresponded to the XRD and SEM results. The specific surface areas of the treated supports were shown in Table 4.2.

Table 4.2 The specific surface area of the untreated supports, treated supports, and zeolite A composite membranes

Supports (zeolite A : kaolin)	Specific surface area of untreated support (m^2/g)	Specific surface area of treated support (m^2/g)	Specific surface area of zeolite A membrane (m^2/g)
50:50	285	346	416
62.5:37.5	341	412	454
75:25	408	416	452

Table 4.2 also shows the specific surface areas of the zeolite A membranes on the different supports. It was found that the zeolite A membrane, which was synthesized on the support containing 62.5%-75.0 % weight of zeolite A has a high specific surface area. Since an increase the % weight of zeolite A in the support not only increases the membrane specific surface area but also facilitates the formation of zeolite A membrane on the support. Because the hydrophilicity of the support increased when the % weight of zeolite A in the support is increased, the additional formation of zeolite A which is hydrophilic can be induced. Therefore, the large number of polycrystalline zeolite A membrane was obtained on the support having high % weight of zeolite A.

4.1.3 Elemental analysis

The silicon and aluminium contents of the supports were determined by graphite furnace atomic absorption spectrophotometer. The Si/Al ratios of the supports with different zeolite A contents were shown in Table 4.3. As the % weight of zeolite A in support is increased, the Si/Al ratio of the support is decreased, due to the fact that the zeolite A is an aluminium rich material. Therefore, the aluminium content of the supports would be increased by increasing the zeolite A content in the support.

Table 4.3 The Si/Al ratios of the supports with different zeolite A content

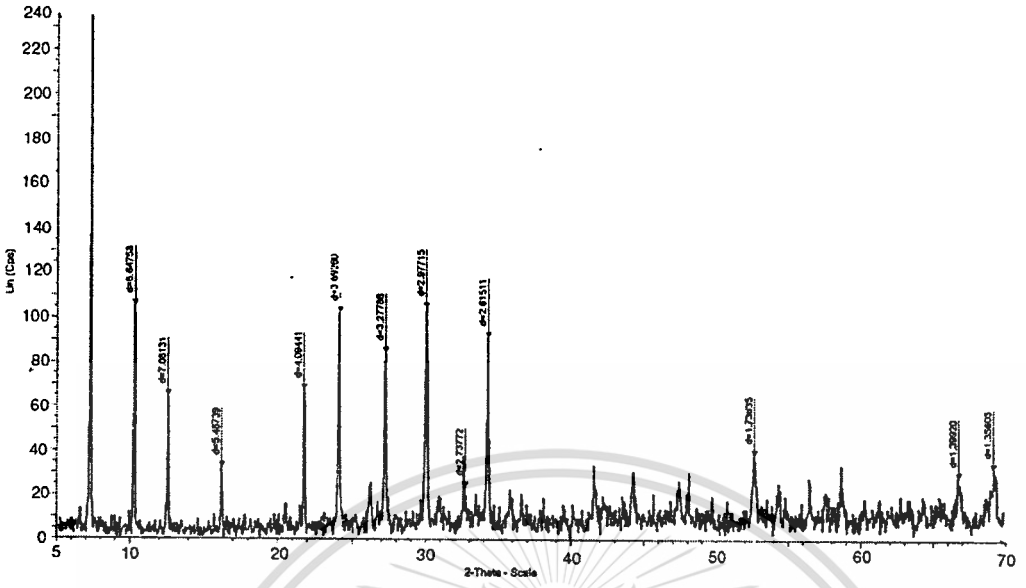
Supports (zeolite A:kaolin)	Si/Al
0:100 (Kaolin)	2.04
50.0:50.0	1.54
62.5:37.5	1.42
75.0:25.0	1.21
100:0	1.06

4.2 Characterization of zeolite A composite membrane on the different synthesis times

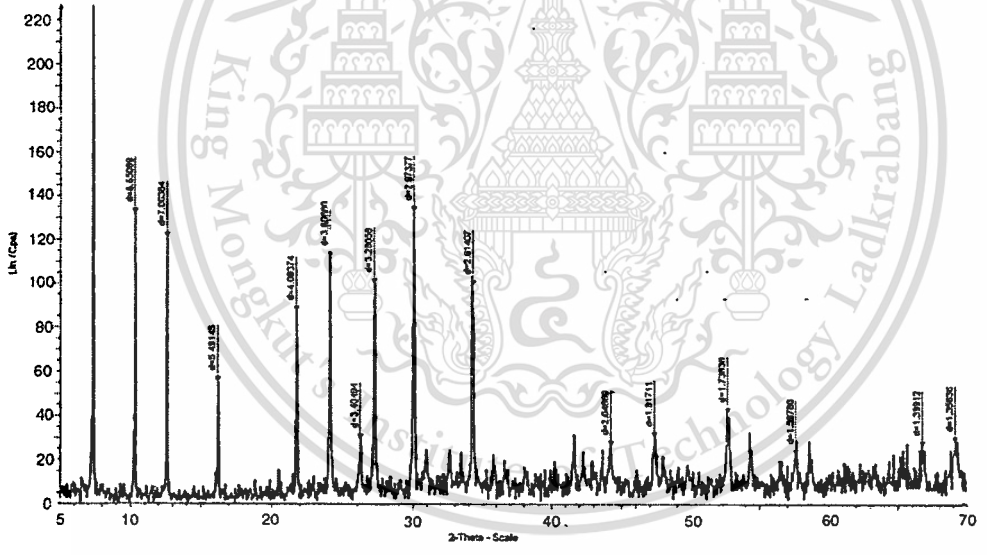
The zeolite A membranes, which are synthesized on support having 75.0% weight of zeolite A for 16 hours and 24 hours, were used to investigate the effect of the synthesis time on the membrane thickness and specific surface area.

The XRD patterns of the zeolite A composite membranes at synthesis time of 16 and 24 hours were shown in Figure 4.10. The typical peaks at 2θ = 7.2, 10.2, 12.5, 30.0, and 34.3 coincide with the crystalline peaks of the zeolite A powder (cf. Figure 4.6).

It was found by the cross sectional observation using SEM that the thickness of the membranes synthesized for 16 hours and 24 hours, were approximately 20 μm and 25 μm respectively, as shown in Figures 4.11(a) and 4.11(b). Moreover, the Table 4.4 shows that the specific surface area of the zeolite A composite membrane was slightly increased with an increase the thickness of polycrystalline zeolite A layer on the support. It is also obvious that the synthesis time effect not only on the membrane thickness but also the crystal size distribution. The distribution of the crystal size synthesized for 24 hours is better than that of crystal synthesized for 16 hours, as shown in Figures 4.12(a) and 4.12(b). This is because the water content and Na_2O/SiO_2 ratio of the gel composition is so high (~2.39), but the synthesis temperature is quite low (~85°C). Thus, the crystal growth rate presumably is slower than the nucleation rate, resulting in the broad crystal size distribution for the shorter synthesis time [36]. In contrast, the longer synthesis time is provided the perfect crystallization, resulting in the well-distributed polycrystalline.

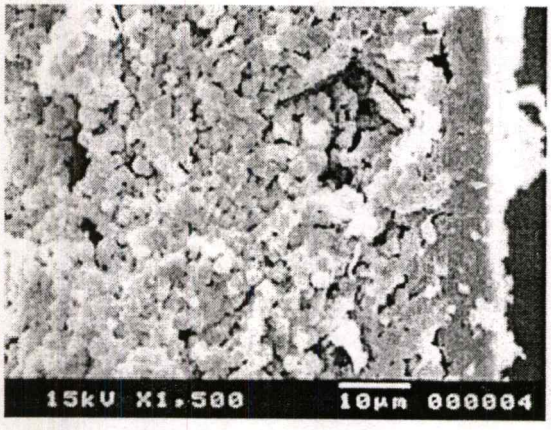


(a) zeolite A membrane for 16 hours synthesis time

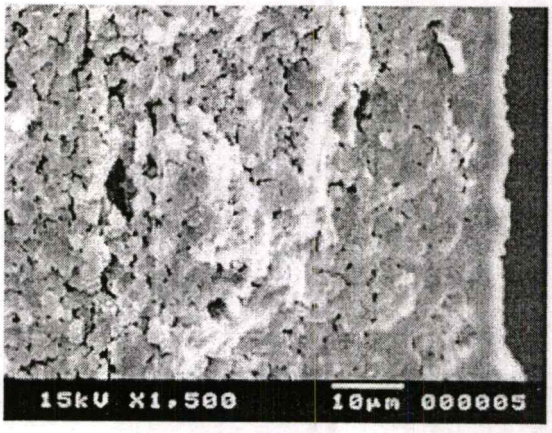


(b) zeolite A membrane for 24 hours synthesis time

Figure 4.10 The XRD patterns of zeolite A composite membranes

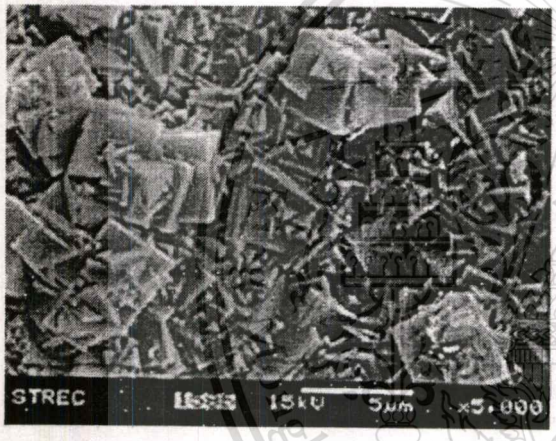


(a) 16 hours

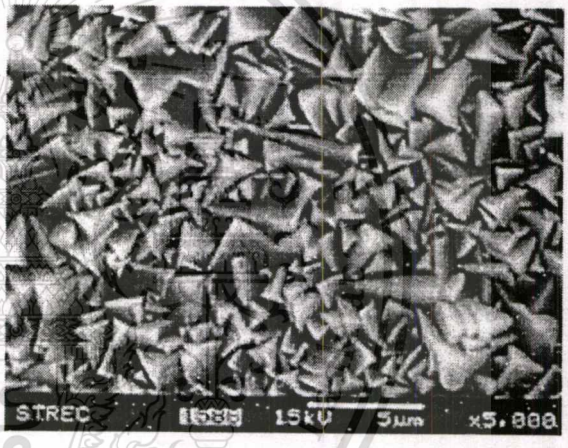


(b) 24 hours

Figure 4.11 The cross sectional SEM images of the zeolite A membrane at different synthesis time



(a) 16 hours



(b) 24 hours

Figure 4.12 The SEM images of the zeolite A membrane at different synthesis time

Table 4.4 The specific surface area of the zeolite A membranes at the different synthesis time

Synthesis time (hours)	Specific surface area[2] (m^2/g)
16	446
24	452

4.3 Separation process

4.3.1 Effect of the synthesis time

The effect of the synthesis time on the separation performance is shown in Table 4.5. It was found that the separation factor markedly increased when the synthesis time was increased, as a result of an elevated thickness of polycrystalline zeolite A. Since the hydrophilicity and specific surface area of the membrane increase, as shown in Table 4.4. A strong interaction of the water molecule which is a high polar molecule, with the membrane is obtained. Hence, the ethanol adsorption is decreased by an increase in the water adsorption. The water concentration in the permeate side increase accordingly due to an increase water diffusion through the membrane. This resulted in an increase in the separation factor when a membrane with longer synthesis time was used. Beside, an increase in the specific surface area of the zeolite A composite membrane cause an increase in the permeation flux.

Table 4.5 The effect of synthesis time on the separation performance.

Synthesis time(hrs.)	Feed (%mol)		Retentate (%mol)		Permeate (%mol)		Separation Factor(α)	Flux (g/hr m^2)
	Ethanol	Water	Ethanol	Water	Ethanol	Water		
16	79.2	20.8	80.6	19.4	9.5	90.5	36.2	68.8
24	78.4	21.6	79.1	20.9	1.5	98.5	232.1	78.9

Feed composition 80%mol ethanol, separation temperature=80°C, atmospheric pressure, and carrier gas flow =50ml/min (n=2)

Consequently, the synthesis time at 24 hours was used for the investigation on the effect of the zeolite A content in the support.

4.3.2 Effect of the zeolite A content in the support

In order to investigate the effect of the zeolite A content in the support, the zeolite A membranes were prepared on the supports having 50.0%, 62.5%, and 75.0% weight of zeolite A. The gas separation experiments were carried out at 80 °C using a H_2O/EtOH mixture with EtOH concentration of 80%mol and 50 ml/min of carrier gas flow rate. Gas permeation performance of zeolite A membrane on the support with different zeolite A content is shown in Table 4.6.

Table 4.6 The effect of the zeolite A content in the support on the separation performance

% weight zeolite A in support	Feed (%mol)		Retentate (%mol)		Permeate (%mol)		Separation Factor (α)	Flux (g/hr m^2)
	Ethanol	Water	Ethanol	Water	Ethanol	Water		
50	81.6	18.4	81.6	18.4	9.2	90.8	44.1	26.2
62.5	77.6	22.4	79.5	20.5	1.7	98.3	204.2	58.7
75	78.4	21.6	79.1	20.9	1.5	98.5	232.1	78.9

Feed composition 80%mol ethanol, separation temperature=80°C, atmospheric pressure, and carrier gas flow =50ml/min (n=2)

It was found that the separation factor and the permeation flux were increased when the zeolite A content in the support increased. This is because the hydrophilicity of the supports increases with the increase in aluminium content of the supports (Table 4.3), which enhances the affinity of the supports to polar molecules. Moreover, the increase in the specific surface area of the zeolite A composite membrane (Table 4.2) would facilitate the adsorption and diffusion of water molecule. On the other hand, the adsorption of ethanol molecule is reduced by competitive adsorption of water molecule in the gas mixture resulting in an increase in the separation factor. Moreover, the higher zeolite A content in the support would facilitate larger mass transport through the hydrophilic membrane. This leads to an increase in the permeation flux when the zeolite content in support was increased. Therefore, the zeolite A membrane that prepared on the 75.0% weight of zeolite A content support give a higher separation factor and permeation flux, as compared to those prepared on 62.5% and 50.0%, respectively. In accordance, this membrane was selected for an investigation on the effect of separation temperature.

4.3.3 Effect of the separation temperature

A study on the effect of the separation temperature was carried out at 80, 100, and 120 ^{o}C using 80%mol of ethanol as feed and 50 ml/min of carrier gas flow rate. As the temperature increases from 80 ^{o}C to 120 ^{o}C, the separation factor dramatically decreases from 232.1 to 20.7 as shown in Table 4.7.

Table 4.7 The separation performance of the zeolite A membrane that synthesized on 75.0% weight zeolite A in support

Separation Temp. (^{O}C)	Feed (%mol)		Retentate (%mol)		Permeate (%mol)		Separation Factor(α)	Flux (g/hr m^2)
	Ethanol	Water	Ethanol	Water	Ethanol	Water		
80	78.4	21.6	79.1	20.9	1.5	98.5	232.1	78.9
100	80.5	19.5	79.7	20.3	10.1	89.9	36.8	69.8
120	79.1	20.9	79.9	20.1	15.5	84.5	20.7	64.6

Feed composition 80%mol ethanol, atmospheric pressure, and carrier gas flow =50ml/min (n=2)

This was later found that the membrane was cracked at higher temperature, as shown in Figure 4.13, causing a leak through the membrane. Hence, no separation selectivity can be obtained. The crack of the membrane might be caused by high zeolite A content in the support. Since the zeolite A is a single crystal material and it does not have an adhesion force between crystallite. This leads to the decrease in the adhesion force between the zeolite and kaolin when zeolite A content is increased, resulting in the reduced mechanical strength of the membrane. The other possibility can arise from the adhesive, cyanoacrylate used for fix the membrane with the metal rings, as shown in Figure 3.5 (section 3.6). The shrinkage of the cyanoacrylate adhesive can occur from deep curing at high temperature [37]. This was observed from the color change from white to pale yellow after exposure at high temperature for more than ten hours.

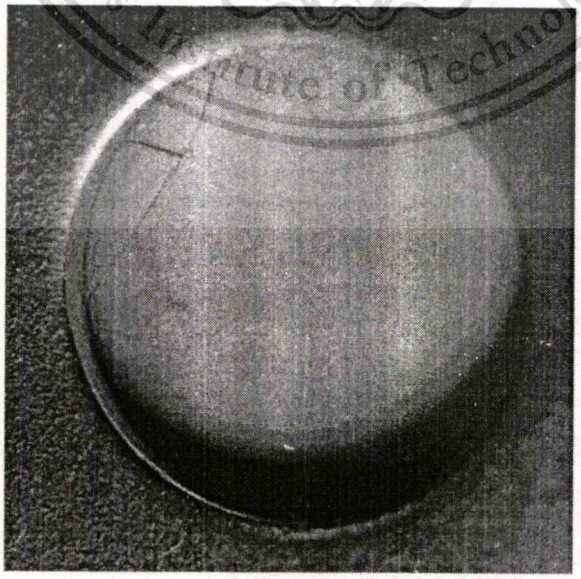


Figure 4.13 The cracked membrane after heating

Because of the strength limitation of zeolite A membrane on the support containing 75.0% weight of zeolite A, the zeolite A membrane on the support containing 62.5% weight of zeolite A was used to investigate the effect of the separation temperature, as shown in Table 4.8. It can be seen that the permeation flux is increased with the increase in separation temperature while the separation factor is decreased.

Table 4.8 The effect of temperature on the separation performance

Separation	Feed (%mol)		Retentate (%mol)		Permeate (%mol)		Separation	Flux
Temp.(^{o}C)	Ethanol	Water	Ethanol	Water	Ethanol	Water	Factor(α)	(g/hr m^2)
80	77.6	22.4	79.5	20.5	1.7	98.3	204.2	58.7
100	79.6	20.4	81.2	18.8	3.1	96.9	122.8	97.9
120	79.4	20.6	79.6	20.4	5.8	94.2	62.4	97.4

Feed composition 80%mol ethanol, atmospheric pressure, and carrier gas flow =50ml/min (n=2)

As the temperature increases from 80 ^{o}C to 100 ^{o}C, the permeation flux of the gas mixture increases from 58.7 to 97.9. The increase of the separation temperature causes further increase of the permeation flux of the gas mixture, as a result of the high diffusion rate of the gas mixture at high temperature. Accordingly, these molecules can diffuse more quickly through the membrane and a higher flux is obtained. However, the concentration of ethanol in gas mixture within the pore would be increased while the concentration of water would be reduced at a certain period of the time. This leads to a decrease in the interaction between diffusing water molecules in the pore, and also a decrease in the capillary condensation of water, which usually takes place at low temperature. Therefore, the separation factor is reduced at higher temperature.

At higher temperature (120 ^{o}C) the permeation flux is however similar to that at 100 ^{o}C. This is because the separation using zeolite membrane are always based significantly on the interactions between membrane surface and the diffusing molecules as discussed previously in section 2.3.1.2. Therefore, the separation can be occurred by the first adsorption of the gaseous mixture molecules on the feed side of the membrane surface and followed by the diffusion of those molecules through the membrane to the permeate side, as shown in Figure 4.14.

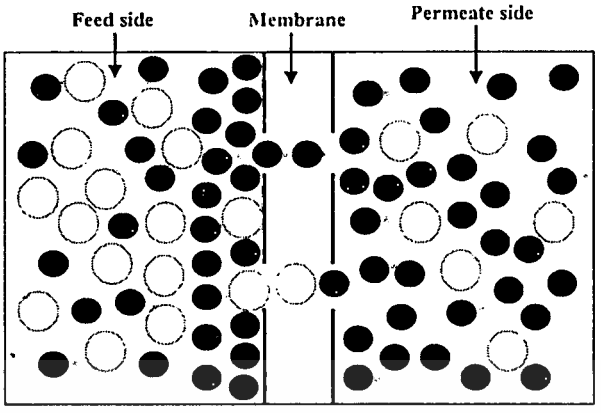


Figure 4.14 The separation mechanism via surface diffusion

At higher separation temperature (120 ^{o}C), the adsorption capacity of the gas mixture molecules on the membrane surface is limited because the diffusion rate becomes more important than the adsorption step at higher temperature [38]. Owing to the continuous flow of the gas mixture, some partial of the gas mixture, which did not adsorb on the membrane surface could flow out at the retentate outlet, as shown in Figure 4.15. It was obvious that the amount of the gas mixture in the permeate side did not change when the separation temperature was risen to 120 ^{o}C, as shown in Table 4.9. Therefore, there seem to be a limitation of the permeation flux of the membrane particularly at higher temperature, as shown in Table 4.8.

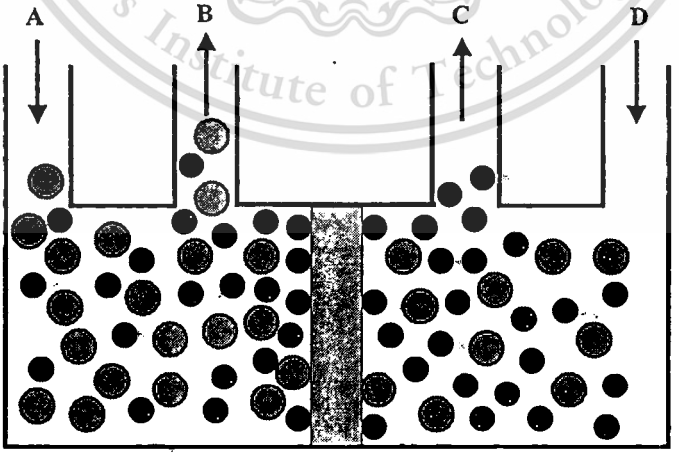


Figure 4.15 The continuous separation process; A: feed inlet, B: retentate outlet, C: permeate outlet, and D: carrier gas inlet.

Table 4.9 The amount of the gas mixture in the feed, retentate, and permeate

Separation Temperature (^{o}C)	Feed (g/hr)	Retentate (g/hr)	Permeate (g/hr)	% Permeate
80	0.1740	0.1653	0.0046	2.65
100	0.1852	0.1754	0.0077	4.15
120	0.1849	0.1771	0.0076	4.14

However, the adsorption of the gas mixture decreases when the diffusion rate increases. The adsorption selectivity of water was reduced with an increase of temperature, leading to a decrease of the separation factor. It is caused by the fact that the adsorption of water molecules that adsorb on the membrane surface decrease, while diffusion through the membrane increase at higher temperature. Hereupon, the capillary condensation of the water molecule would decrease, leading to an enhancement in the adsorption and diffusion of the ethanol molecules (weakly adsorbing molecule). This would reduce the separation factor at high separation temperature.

4.3.4 Effect of the carrier gas flow rate

A study on the effect of carrier gas flow rate was carried out at 80^{o}C using 80 %mol EtOH as feed, with various gas flow rate of about 30, 40, and 50 ml/min. The separation performance is shown in Table 4.10.

Table 4.10 The separation performance on the various carrier gas flow rate

Carrier gas	Feed (%mol)		Retentate (%mol)		Permeate (%mol)		Separation	Flux
He (ml/min.)	Ethanol	Water	Ethanol	Water	Ethanol	Water	Factor(α)	(g/hr.m^{2})
30	76.6	23.4	79.6	20.4	4.6	95.4	68.9	88.9
40	76.6	23.4	78.2	21.8	4.3	95.7	73.0	86.7
50	77.6	22.4	79.5	20.5	1.7	98.3	204.2	58.7

Feed composition 80%mol ethanol, separation temperature=80^{o}C, and at atmospheric pressure (n=2)

When the carrier gas flow rate increases, it means that the feed loading or concentration of the gas mixture on the membrane surface will be increased at certain period of time. This

results in the multilayer adsorption due to the high amount of the adsorbing molecules. The thickness of the adsorbed layer increased while the space available in the pore decreased. Accordingly, the pore blocking by capillary condensation of a higher polar molecule (water), may well take place. This is because the water molecules possesses strong interaction with each other and it would become liquid (condensate), which can fill the pore, particularly at the temperature lower than its boiling point (separation temperature 80 ^{o}C) [38], as shown in Figure 4.16. Therefore, the permeation flux is decreased when the carrier gas flow rate is increased.

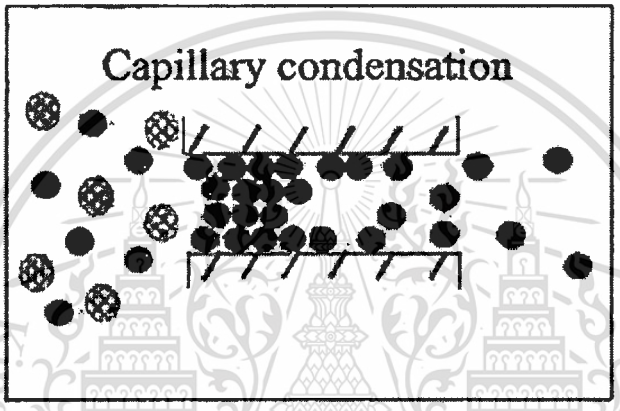


Figure 4.16 The illustration of the capillary condensation in the pore [3]

In the case of separation factor, it was found that the separation factor decrease with the decrease in carrier gas flow rate. At low carrier gas flow rate, the feed loading or the concentration of the gas mixture on the membrane surface is low while the contact time is high. Therefore, there is a high possibility for a less polar molecule (ethanol) could be adsorbed on the membrane surface and diffused through the membrane. Because the small number of water molecules would be adsorbed as monolayer and some of ethanol can diffuse through the monolayer water surface, as shown in Figure 4.17. This results in 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 concentration of the gas mixture on the membrane surface increase, 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 (strongly adsorbing molecule) in the pore, resulting in an increase of separation factor. The fact that water selectively adsorption and undergo capillary condensation may well arise from its higher polarity and lower vapor pressure as compared to those of ethanol.

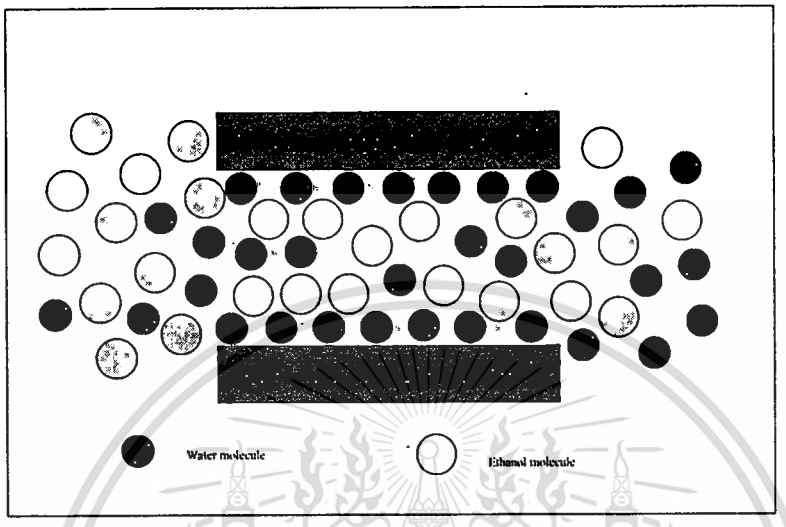


Figure 4.17 The illustration of the water monolayer adsorption

4.3.5 Effect of the feed composition

A study on the effect of feed composition was carried out at 80 ^{o}C using 50 ml/min of carrier gas and the various percent mole of the ethanol in the liquid feed, namely 40, 60, 80, and 95 %mol. Table 4.11 shows the effect of the feed composition on the separation performance.

However, the gas feed mixture at 40%mol of ethanol could not be achieved. The liquid feed mixture of 40%mol of ethanol can only give 60%mol of ethanol in the gas feed mixture. This is due to the low vapor pressure of water, as compared to ethanol. Therefore, the investigation could not be done at 40%mol of ethanol in vapor phase.

Table 4.11 The effect of feed composition on the separation performance

%mol	Feed (%mol)		Retentate (%mol)		Permeate (%mol)		Separation	Flux
Ethanol	Ethanol	Water	Ethanol	Water	Ethanol	Water	Factor(α)	(g/hr m^2)
60	60.4	39.6	61.9	38.1	1.3	98.7	113.3	106
65	65.3	34.7	67.7	32.3	1.6	98.4	115.5	98.0
80	77.6	22.4	79.5	20.5	1.7	98.3	204.2	58.7
95	93.3	6.7	93.7	6.3	13.4	86.6	90.3	72.9

Separation temperature=80°C, atmospheric pressure, and carrier gas flow =50ml/min (n=2)

As the mole fraction of ethanol in feed mixture is increased, the feed loading of gas mixture increased as shown in Table 4.12 because the vapor pressure of ethanol is higher than that of water. Since the separation is governed by the surface diffusion, the preferential sorption of the molecule having strong interaction with the membrane surface becomes more important. When the mole fraction of ethanol in the feed mixture is increased, the polarity of the gas mixture and the interaction between molecules and membrane surface would be decreased. This would also decrease the adsorption of the gas mixture on the membrane surface which can be seen in Table 4.12 that the amount of the gas mixture (g/hr.) in the permeate side was decreased. Therefore, the decrease in the permeation flux is obtained when the mole fraction of ethanol increased (60% to 80%), as shown in Table 4.11.

Table 4.12 The amount of the gas mixture in the feed, retentate, and permeate

%mol of ethanol	Feed loading (g/hr)	Retentate (g/hr)	Permeate (g/hr)
60	0.1402	0.1315	0.0083
65	0.1552	0.1464	0.0075
80	0.1740	0.1653	0.0046
95	0.2118	0.2059	0.0057

Table 4.13 The composition of the gas mixture (g/hr.) in feed and permeate side

%mol of ethanol	Feed (g/hr.)		Permeate (g/hr.)	
	Ethanol	Water	Ethanol	Water
60	0.1115	0.0287	0.0003	0.0080
65	0.1285	0.0267	0.0003	0.0072
80	0.1564	0.0176	0.0004	0.0044
95	0.2060	0.0058	0.0016	0.0041

A study of the feed composition was also shown that the zeolite A composite membrane is a water selective membrane for 60% to 80%mol of ethanol in the feed mixture. Since the water permselectivity of the membrane remains higher than 98%, as shown in Table 4.11. Moreover, the observed increase in the separation factor is due to the fact that the mole fraction of water in the feed mixture was decreased.

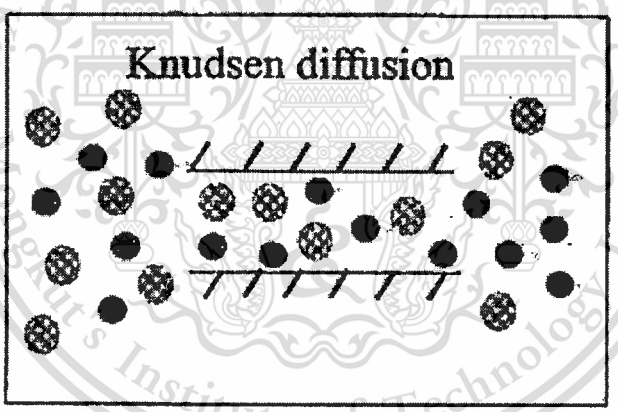


Figure 4.18 The illustration of the knudsen diffusion

At a higher mole fraction of ethanol (95%), there is so small amount of water in the feed mixture, which results in a decrease in the interaction between gas molecules and the membrane surface. This leads the transport mechanism of the gas mixture to be least in the transition region of surface diffusion to knudsen diffusion. For the knudsen diffusion, interaction between molecules are negligible and molecules of different species move entirely independent of each other under the action of their own concentration (or partial pressure) gradient [38]. The illustration of the knudsen diffusion is shown in Figure 4.18. Thus, ethanol, the higher partial

pressure component could increasingly diffuse through the membrane. Accordingly, it can be seen in Table 4.13 that the amount of ethanol (g/hr.) in the permeate side is relatively high. Hence, the permeation flux of 95 %mol of ethanol turn to be higher than that of 80%mol of ethanol, as shown in Table 4.11. In addition, as the characteristic of the transport through the membrane appeared to be influenced by knudsen diffusion of ethanol richen gas, the capillary condensation of water unlikely to take place. Consequently, the water permselectivity of the membrane is dramatically decreased causing the decrease in the separation factor, as also shown in Table 4.11. However, it is worth noting that selective of the membrane is still determine by adsorptivity of the gas molecules.

4.4 Ethanol/ethylene/water separation

A study on the separation of three component: ethanol, ethylene, and water was carried out at 80, 100, and 120 ^{O}C, using 50 ml/min of carrier gas (He). The ethylene gas with 0.79 ml/min ($3.2x10^{-5}$ mol/min) was mixed with the liquid mixture having 80%mol of ethanol. The separation performance of the ethanol/ethylene/water mixture was compared to the ethanol/water mixture, as shown in Table 4.14.

Table 4.14 The separation performance of water in the ethanol/ethylene/water mixture and ethanol/water mixture

Separation Temp. (^{O}C)	Permeation flux(g/hr m^2)		Separation factor of water (α)	
	$C_2H_5OH/C_2H_4/H_2O$	C_2H_5OH/H_2O	$C_2H_5OH/C_2H_4/H_2O$	C_2H_5OH/H_2O
80	115.6	58.7	126.9	204.2
100	113.3	97.9	92.2	122.8
120	105.2	97.4	52.4	62.4

It was found that the permeation flux of the ethanol/ethylene/water mixture is higher than that one of the ethanol/water mixture. When the ethylene molecules were added into the ethanol/water mixture, the interaction between ethanol and water molecule was decreased since the ethylene could dilute the concentration of water and ethanol in feed mixture. Then the polarity of the gas mixture and the interaction between gas molecules and the membrane surface became less. This again leads to the transport mechanism of the gas mixture to be least in the transition

region of the surface diffusion to the knudsen diffusion, but in a higher extent as compared to that observed with 95% ethanol. Therefore, the gas mixture containing molecules with molecular size smaller than the pore of the membrane can easily diffuse through the membrane.

However, the separation factor of water in the ethanol/water mixture is higher than that in the ethanol/ethylene/water mixture. This is because the transport mechanism of the ethanol/water mixtures is the surface diffusion. For surface diffusion, the interaction between molecule and the membrane surface is more important. The separation by the surface diffusion can be obtained by the preferential sorption of one species of the components of the gas mixture. This means that the bulk gas phase diffusion of a non sorbing molecule is decreased by adsorption of an sorbing molecule in the mixture resulting in an increase in the separation factor [38]. The illustration of the surface diffusion is shown in Figure 4.19.

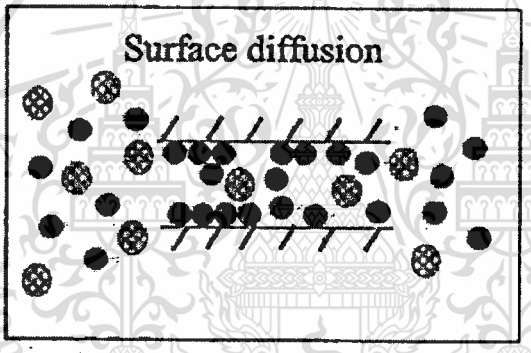


Figure 4.19 The illustration of the surface diffusion [3]

Therefore, in the ethanol/water mixture, the water molecule, a strongly adsorbing molecule, can better adsorb and diffuse through the membrane, as compared to the ethanol molecule (weakly adsorbing molecule). This leads to an increase in the separation factor of water. On the other hand, in the ethanol/ethylene/water mixture (approach knudsen diffusion), the interaction between molecule and the membrane surface is less important as discussed earlier in section 4.3.5. Therefore, the ethanol and ethylene molecules, the even less polar molecule could increasingly diffuse through the membrane. Thus, the separation factor of water is decreased when the ethylene was added into the ethanol/water mixture.

The separation temperature effect on the separation performance was shown in Tables 4.15 and 4.16.

Table 4.15 The composition of the gas mixture at different separation temperature

Temp.	Feed (%mol)			Retentate (%mol)			Permeate (%mol)		
(°C)	Ethylene	Water	Ethanol	Ethylene	Water	Ethanol	Ethylene	Water	Ethanol
80	27.8	15.9	56.3	28.4	14.4	57.2	1.1	96.0	2.9
100	27.9	15.2	57.0	27.9	14.1	58.0	2.2	94.3	3.5
120	28.0	15.3	56.6	28.4	14.0	57.6	4.7	90.5	4.8

Table 4.16 The effect of the separation temperature on the separation performance

Temp.	Separation factor	Separation factor	Separation factor	Flux
(°C)	Ethylene	Water	Ethanol	(g/hr m^2)
80	0.0299	126.9	0.0229	115.6
100	0.0588	92.2	0.0273	113.3
120	0.1268	52.4	0.0388	105.2

It was found that the permeation flux of the gas mixture decrease when the separation temperature increase. This is due to the fact that the permeation flux of the knudsen diffusion relate to the reciprocal of the square root of temperature when other parameters are constant, as shown in equation 4.1.

$$F = \frac{2\varepsilon r}{3\tau \cdot \theta_k \cdot L}\left(\frac{8}{\pi RTM}\right)^{1/2} \quad (4.1)$$

Where : F = Permeation (mol/m^2s Pa)

ε = Porosity

r = Pore radius (m)

τ = Tortuosity

θ_k = Reflection factor

L = Thickness (m)

T = Temperature (K)

M = Molecular weight

At higher temperature, the kinetic energy of the gas mixtures is increased causing in an increase in the intermolecular collision. Thus, the permeation flux of the gas mixture decreased when the separation temperature increased.

In case of the separation factor, an increase in the separation temperature decreased separation factor of the water, while the separation of ethanol and ethylene was increased. This

appears to be in same manner as observed in the ethanol/water system. Although, the characteristic of the gas mixture diffusion was governed by knudsen diffusion, the permselectivity was still determined by adsorption selectivity of the certain molecule. Therefore, the adsorption of the gas mixture on the membrane surface would decrease with rise of the temperature but the diffusion rate of the gas mixture would increase as discussed previously in section 4.3.3. The separation by the surface diffusion becomes less important at high temperature causing the decrease in the adsorption selectivity of water, a high polar molecule. Therefore, the separation factor of the water was decreased while more ethanol and ethylene molecules, which are weakly adsorbing molecules and weakly interaction with the membrane surface, could increasingly diffuse through the membrane, resulting in the increase of the separation factor of ethanol and ethylene. However, the zeolite A composite membrane can still regarded in water selective membrane for ethanol/ethylene/water system.

CHAPTER 5

CONCLUSION AND SUGGESTION

5.1 Conclusion

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

The study on effect of the synthesis time shows that the membrane prepared from 24 hours of synthesis time, give higher separation factor and permeation flux than that from 16 hours of the synthesis time. This is because the thickness of zeolite A membrane on the support surface increase when the synthesis time is increased, which can be observed by SEM and the measured surface area.

The study on the effect of the zeolite A content in the support shows that the increase in the hydrophilicity of the support, together with the surface area of the membrane can facilitate the adsorption and diffusion of water molecule. This leads to a higher separation factor and permeation flux. Moreover, an increase in the zeolite A content in the support also leads to the decrease in the membrane strength. It can be observed by the crack of the membrane at a high separation temperature (> 80 ^{o}C).

The study on the effect of separation temperature shows that the separation factor is decreased when the separation temperature is increased for all cases. This is because the transport system possesses the surface diffusion characteristic (ethanol/water mixture) where the separation by adsorption becomes less important than that by the diffusion at high temperature. Therefore, at high separation temperature, the separation selectivity of water on the membrane surface is reduced.

Moreover, the permeation flux for the surface diffusion is increased with rise of the separation temperature. This is because the diffusion rate increases at high temperature causing the decrease in the capillary condensation of water. In contrast, the permeation flux of the ethanol/ethylene/water mixture is decreased when the separation temperature is increased. This is because, in the system influenced by the knudsen diffusion, the permeation flux is related to the reciprocal of the square root of temperature.

The study on the effect of the carrier gas flow rate shows that an increase in the carrier gas flow rate, decrease the permeation flux but increase the separation factor. This is because, at

higher carrier gas flow rate, or higher feed loading, the pore blocking by capillary condensation of water takes place. This leads to the decrease in the adsorption and diffusion of the ethanol molecule through the membrane.

The study on the effect of feed composition shows that the water permselectivity of the membrane is higher than 98% for the feed mixture containing a less than 80% mole of ethanol. However, the permeation flux decreased with an increase in the percent mole of ethanol because the adsorption of the gas mixture on the membrane surface decreased. At higher mole fraction of ethanol (95%), it is found that the permeation flux was increased while the separation factor was reduced. This is because there is so small amount of water molecule in the feed mixture. Therefore, the transport mechanism of the gas mixture to be least in the transition region of the surface diffusion to the knudsen diffusion.

It is shown that the appropriate separation condition, which gave the optimum separation factor and higher permeation flux, is favored at 80 ^{o}C with 50 ml/min of carrier gas flow rate.

The study on the separation of ethanol/ethylene/water mixture shows that the permeation flux of the ethanol/ethylene/water mixture is higher than that of the ethanol/water mixture. However, the separation factor of water in the ethanol/ethylene/water mixture is lower than that in the ethanol/water mixture. This is because the transport mechanism of the ethanol/ethylene/water mixture appeared to be partially governed by the knudsen diffusion, in which the interaction between molecule and the membrane surface is less important for the transportation. Therefore, the ethanol and ethylene molecules can increasingly diffuse through the membrane leading to the decrease in the separation factor but the increase in the permeation flux.

5.2 Suggestion for Further Studies

5.2.1 For future study the effect of pressure should be investigated. The separation factor and permeation flux could be increased, if the different pressure across the membrane can be applied.

5.2.2 The synthesis of zeolite A membrane on the support with a relatively higher porousity, i.e: mulite, or γ-alumina should be investigated in order to improve the permeation flux.

5.2.3 The synthesis of zeolite A membrane on the tabular support should be investigated in order to improve the separation performance and permselectivity of the membrane. Additionally, this membrane could be developed to a membrane reactor, which can improve the catalytic performance of the reactions limited by chemical equilibrium, such as ethanol dehydration at low temperature.

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APPENDICES

Appendix A

Surface Area and BET Plot from Gas Adsorption Analyzer

Table A.1 The gas adsorption analysis parameter

Adsorbate gas	Temperature (K)	P_0 (mmHg)	Equilibrium time (min.)
N_2	77	760 (P_0 station)	3
CO_2	273	26142	3

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows® Version 1.19

Sample ID	support S50:50				
Description	BET 21 points				
Comments					
Sample Weight	0.0875 g				
Adsorbate	Carbon Dioxide	Outgas Temp	350.0 °C	Operator	Suree
Cross-Sec Area	21.0 Å²/molecule	Outgas Time	3.0 hrs	Analysis Time	229.3 min
NonIdeality	9.100E-06	P/Po Toler	3	End of Run	06/07/2001 14:32
Molecular Wt	44.0100 g/mol	Equil Time	3	File Name	DISK50_1.RAW
Station #	1	Bath Temp.	273.00		

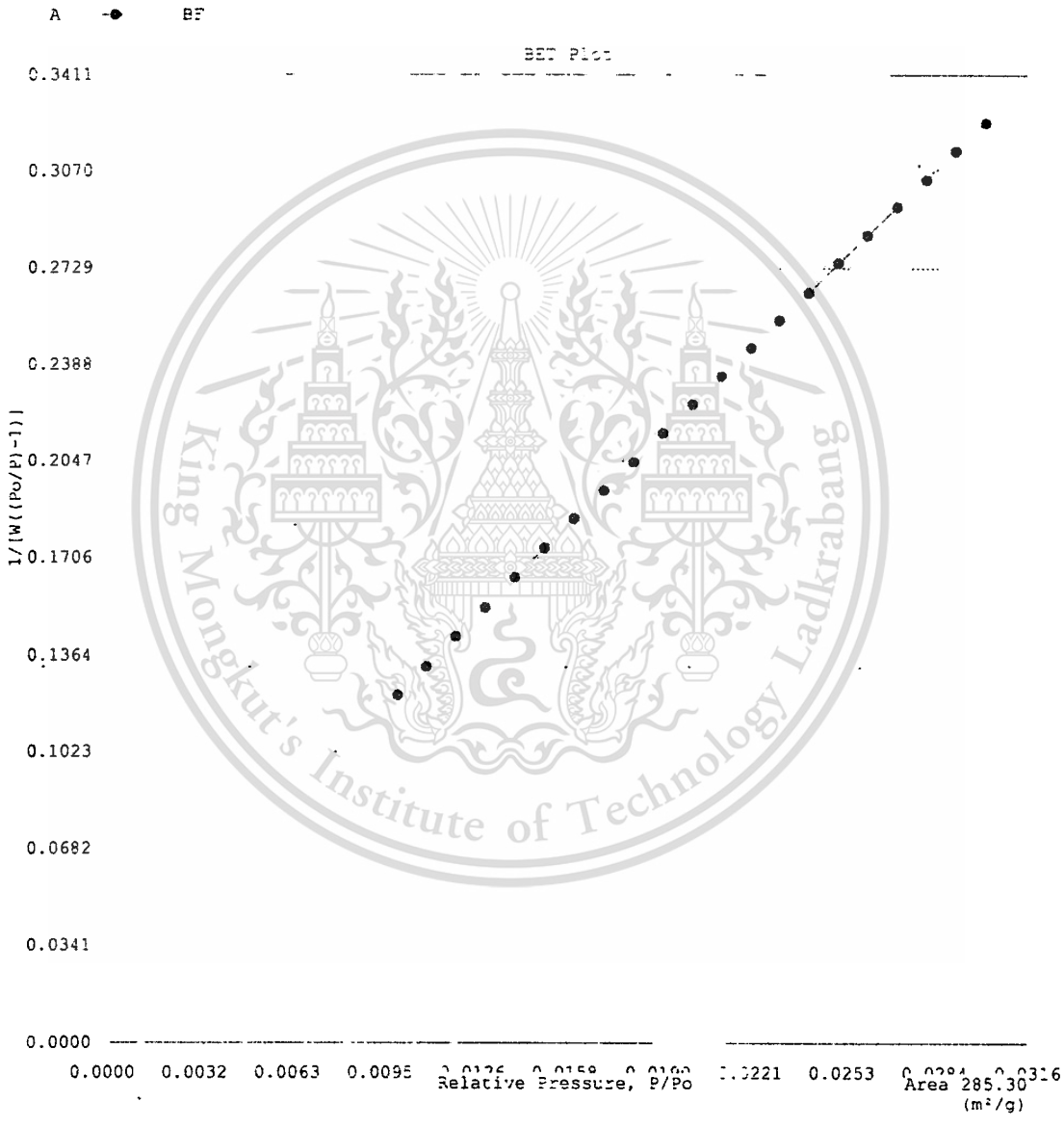

Figure A.1 The BET plot of the support having 50.0%wt of zeolite A

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows® Version 1.19

Sample ID	support S62.5:37.5				
Description	BET 21 points				
Comments					
Sample Weight	0.0325 g				
Adsorbate	Carbon Dioxide	Outgas Temp	350.0 °C	Operator	Suree
Cross-Sec Area	21.0 Å²/molecule	Outgas Time	3.0 hrs	Analysis Time	136.4 min
NonIdeality	9.100E-06	P/Po Toler	0	End of Run	06/01/2001 09:16
Molecular Wt	44.0100 g/mol	Equil Time	3	File Name	DISK62.RAW
Station #	1	Bath Temp.	273.00		

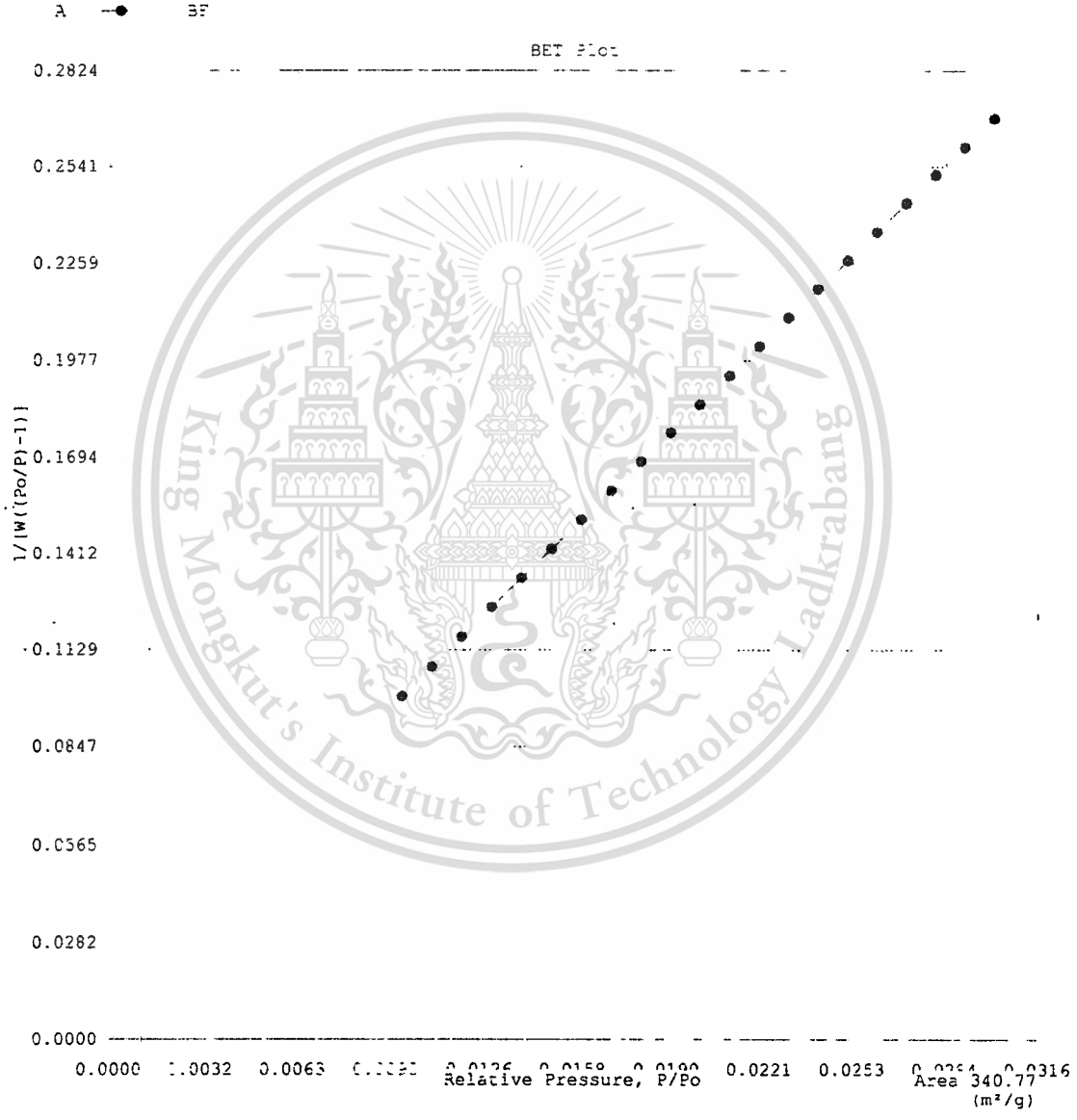

Figure A.2 The BET plot of the support having 62.5%wt of zeolite A

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows® Version 1.19

Sample ID	support S75:25				
Description	BET 21 points				
Comments					
Sample Weight	0.0901 g				
Adsorbate	Carbon Dioxide	Outgas Temp	350.0 °C	Operator	Suree
Cross-Sec Area	21.0 Å²/molecule	Outgas Time	3.0 hrs	Analysis Time	228.3 min
NonIdeality	9.100E-06	P/Po Toler	[illegible]	End of Run	06/08/2001 09:45
Molecular Wt	44.0100 g/mol	Equil Time	[illegible]	File Name	DISK75.RAW
Station #	[illegible]	Bath Temp.	273.00		

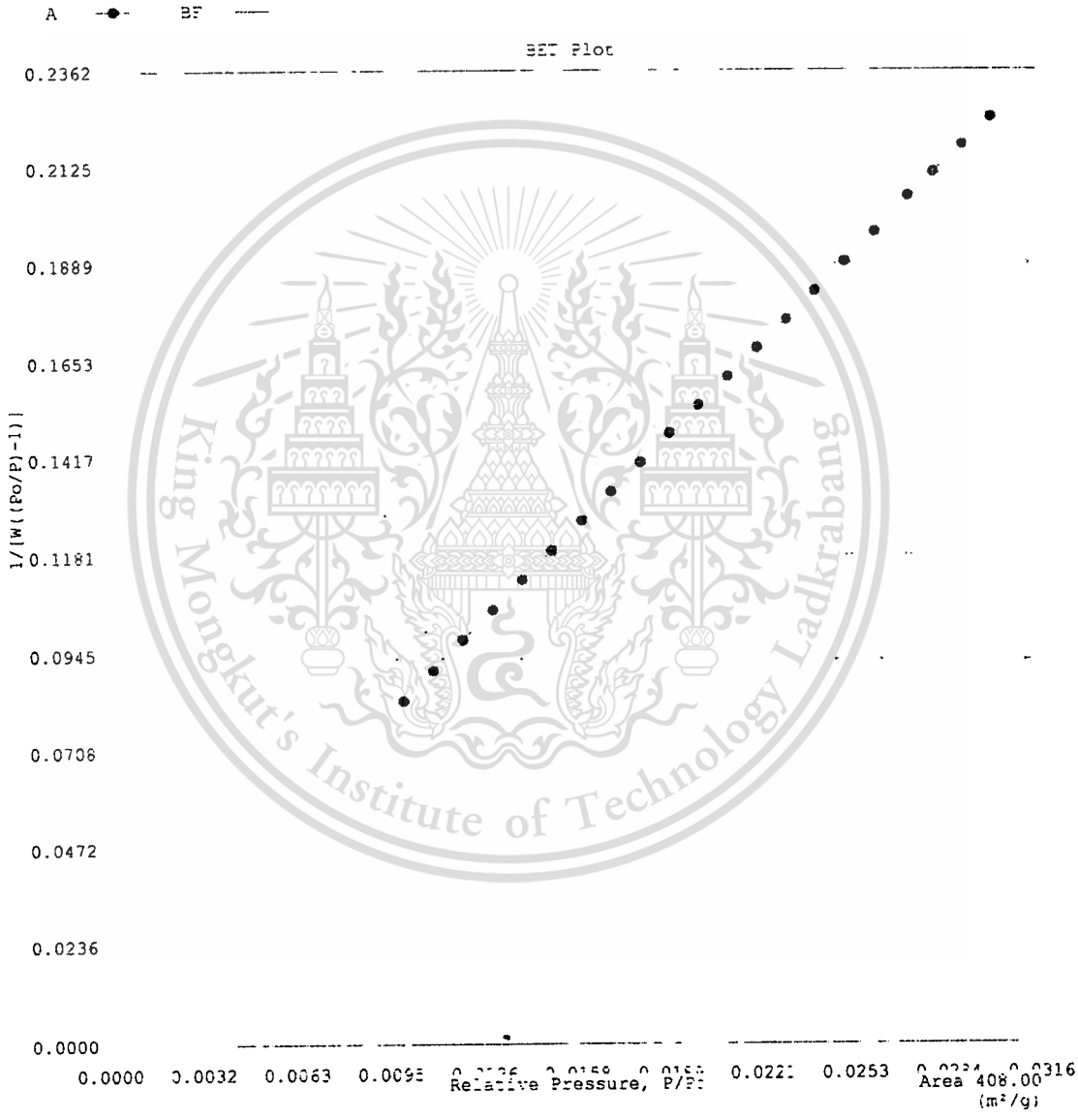

Figure A.3 The BET plot of the support having 75.0%wt of zeolite A

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows® Version 1.19

Sample ID	support S50:50 Treated				
Description	BET 21 points				
Comments					
Sample Weight	0.0876 g				
Adsorbate	Carbon Dioxide	Outgas Temp	350.0 °C	Operator	Suree
Cross-Sec Area	21.0 Å²/molecule	Outgas Time	3.0 hrs	Analysis Time	305.5 min
NonIdeality	9.100E-06	P/Po Toler	0	End of Run	07/24/2001 16:36
Molecular Wt	44.0100 g/mol	Equil Time	3	File Name	440724_1.RAW
Station #	1	Bath Temp.	273.00		

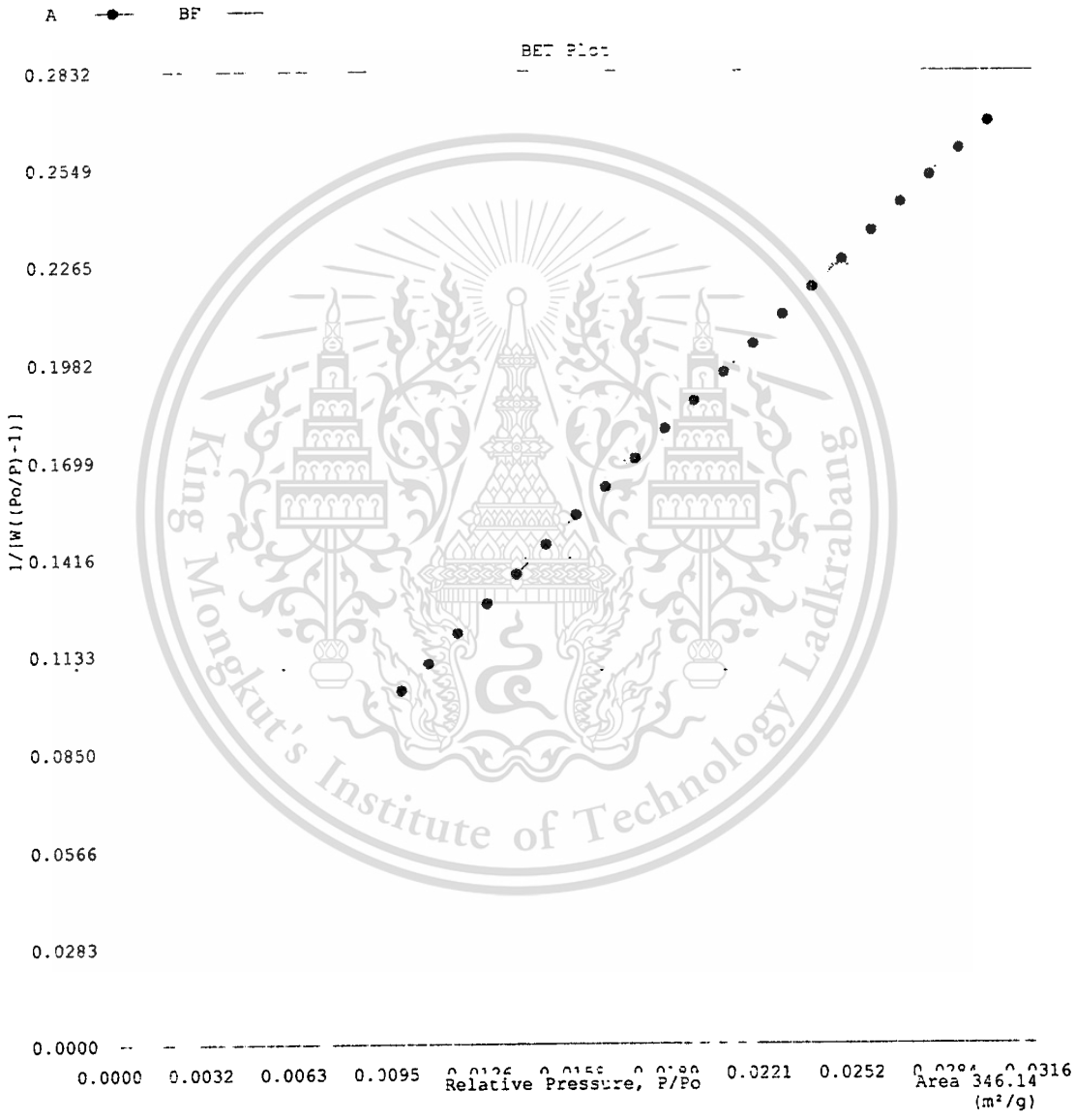

Figure A.4 The BET plot of the treated support having 50.0%wt of zeolite A

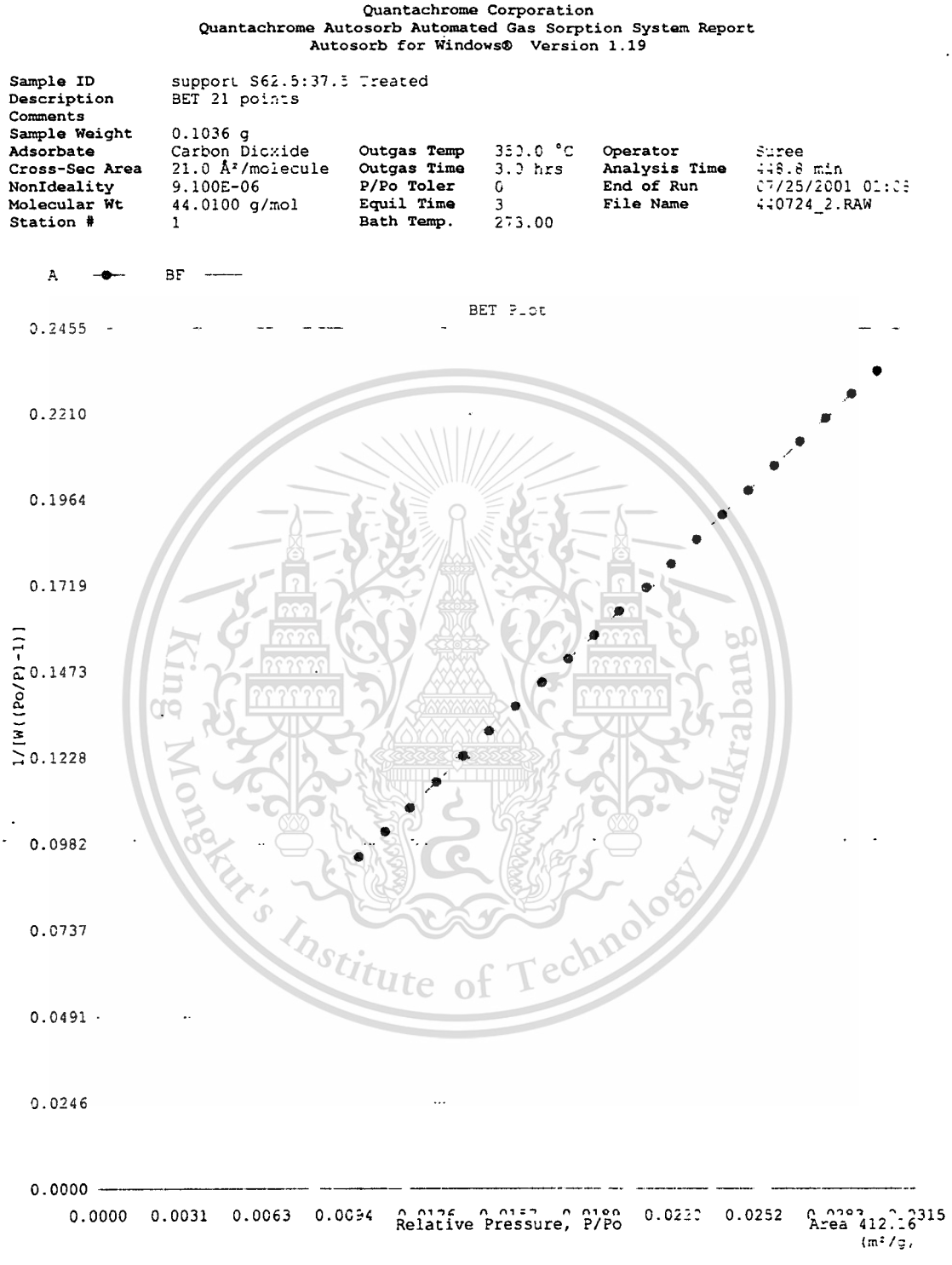

Figure A.5 The BET plot of the treated support having 62.5%wt of zeolite A

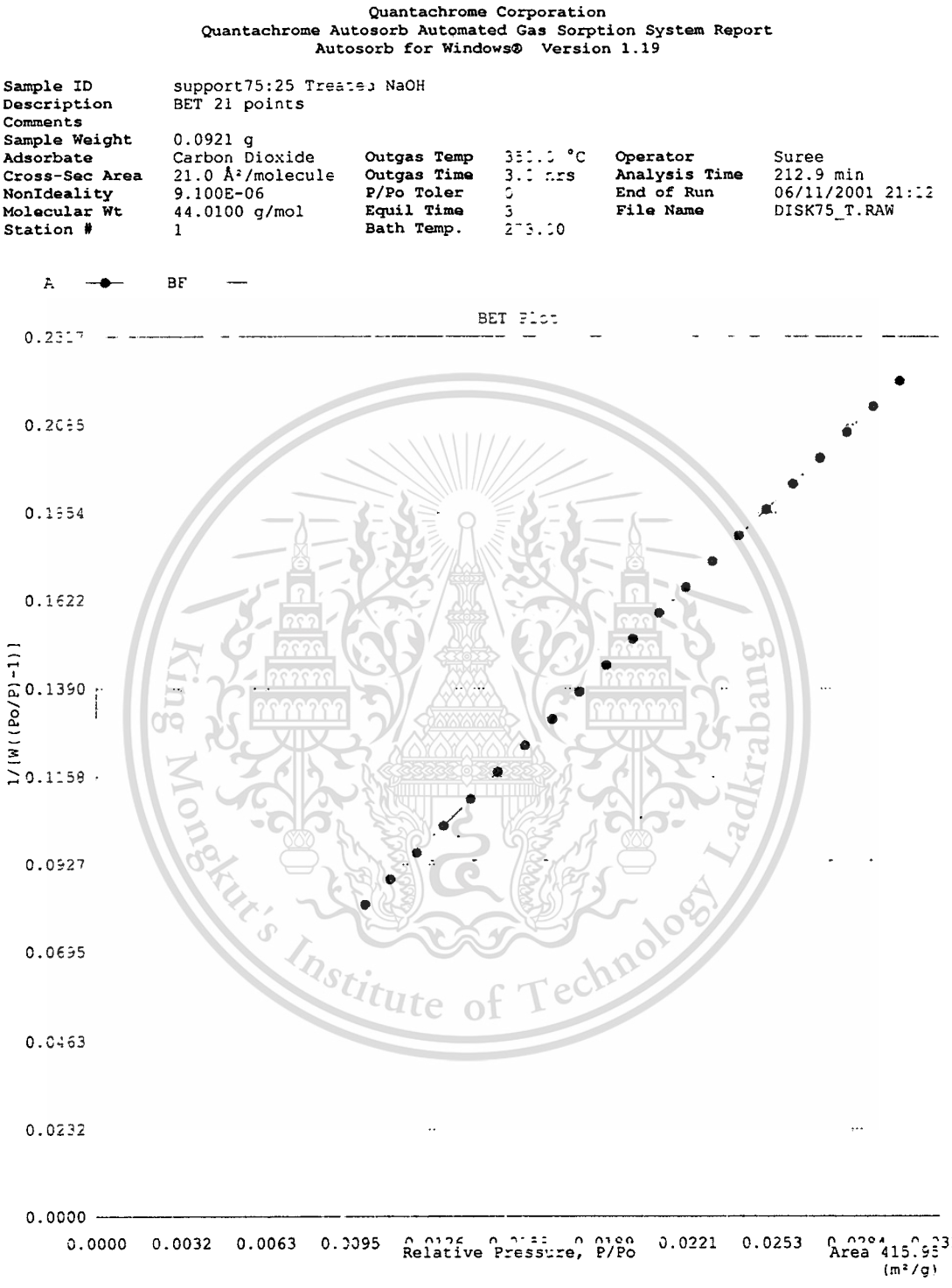

Figure A.6 The BET plot of the treated support having 75.0%wt of zeolite A

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows® Version 1.19

Sample ID	Membrane 4A S50_24				
Description	BET 21 points				
Comments					
Sample Weight	0.0870 g				
Adsorbate	Carbon Dioxide	Outgas Temp	350.0 °C	Operator	Suree
Cross-Sec Area	21.0 Å²/molecule	Outgas Time	3.0 hrs	Analysis Time	457.5 min
NonIdeality	9.100E-06	P/Po Toler	1	End of Run	06/13/2001 21:50
Molecular Wt	44.0100 g/mol	Equil Time	3	File Name	MS50_24.RAW
Station #	1	Bath Temp.	273.00		

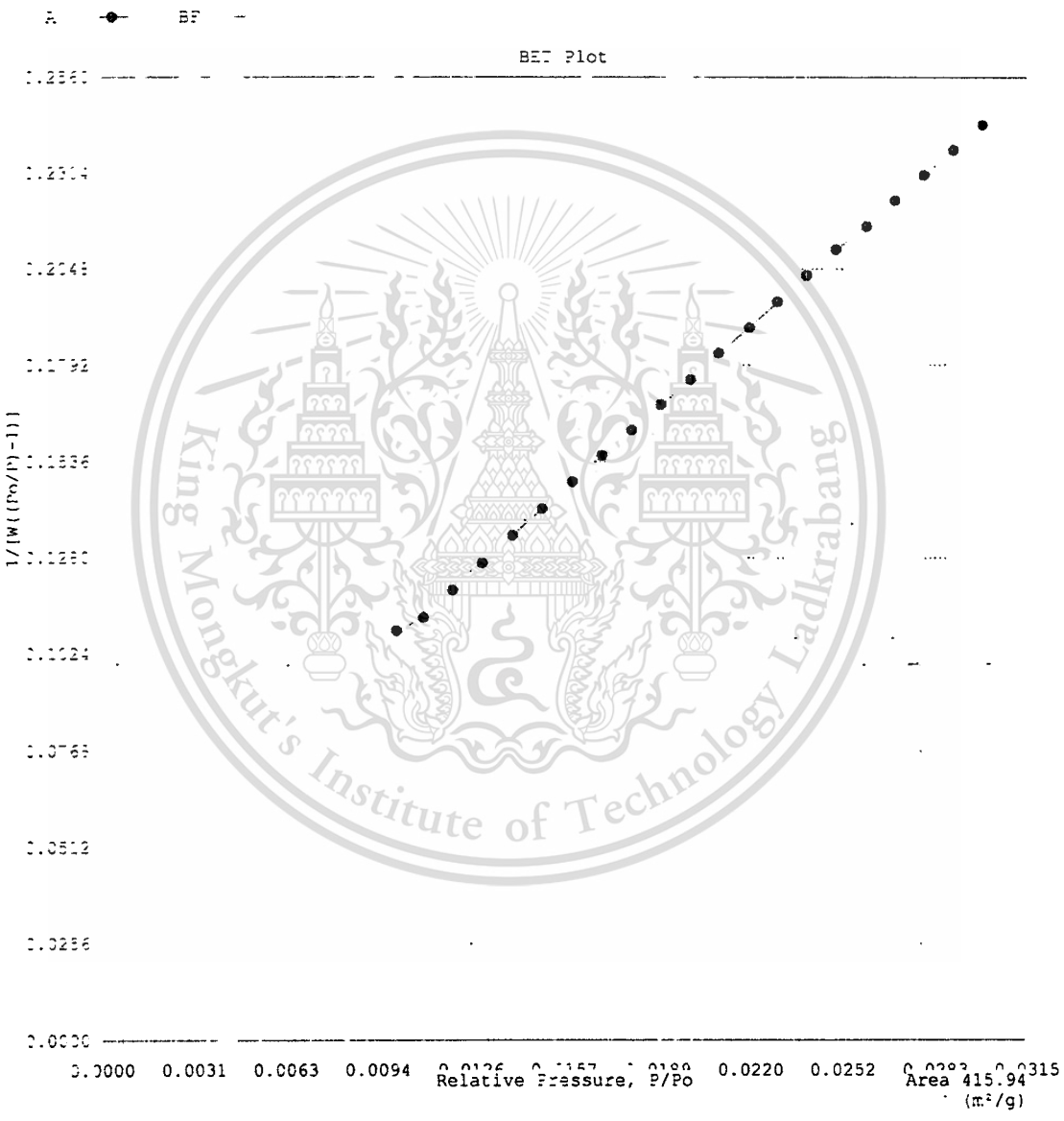

Figure A.7 The BET plot of the zeolite A membrane on support having 50.0%wt of zeolite A

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows® Version 1.19

Sample ID	Membrane 4A S62_24				
Description	BET 21 points				
Comments					
Sample Weight	0.0868 g				
Adsorbate	Carbon Dioxide	Outgas Temp	350.0 °C	Operator	Suree
Cross-Sec Area	21.0 Å²/molecule	Outgas Time	3.0 hrs	Analysis Time	394.0 min
NonIdeality	9.100E-06	P/Po Toler	0	End of Run	06/12/2001 21:34
Molecular Wt	44.0100 g/mol	Equil Time	3	File Name	MS62_24.RAW
Station #	1	Bath Temp.	273.00		

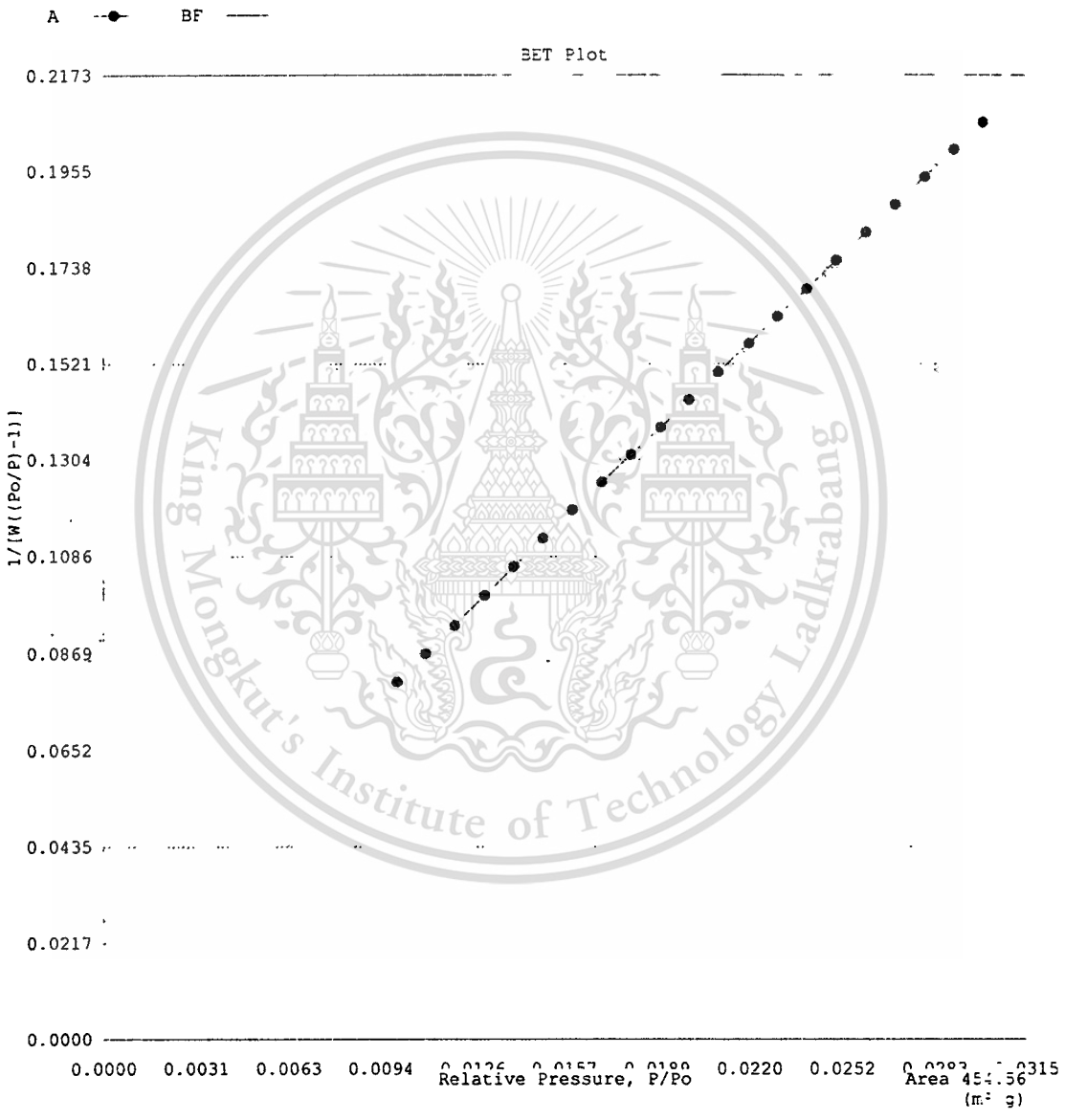

Figure A.8 The BET plot of zeolite A membrane on support having 62.5%wt of zeolite A

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows® Version 1.19

Sample ID	4A membrane S75_24				
Description	BET 21 points				
Comments					
Sample Weight	0.0911 g				
Adsorbate	Carbon Dioxide	Outgas Temp	350.0 °C	Operator	Suree
Cross-Sec Area	21.0 Å²/molecule	Outgas Time	3.0 hrs	Analysis Time	245.1 min
NonIdeality	9.100E-06	P/Po Toler	0	End of Run	06/09/2001 10:48
Molecular Wt	44.0100 g/mol	Equil Time	3	File Name	MS75_24.RAW
Station #	1	Bath Temp.	273.00		

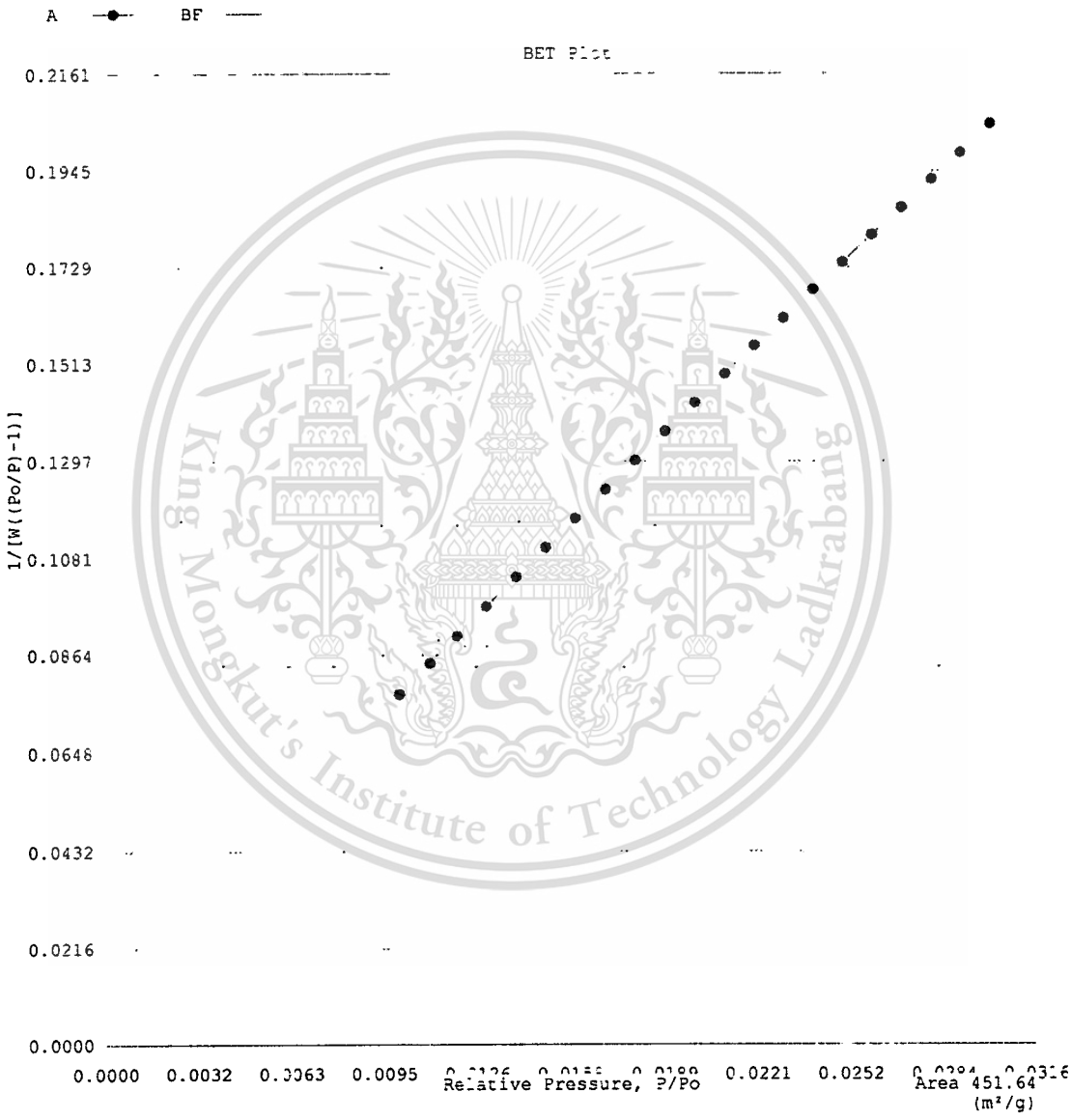

Figure A.9 The BET plot of zeolite A membrane on support having 75.0%wt of zeolite A

Appendix B

Gas Chromatogram

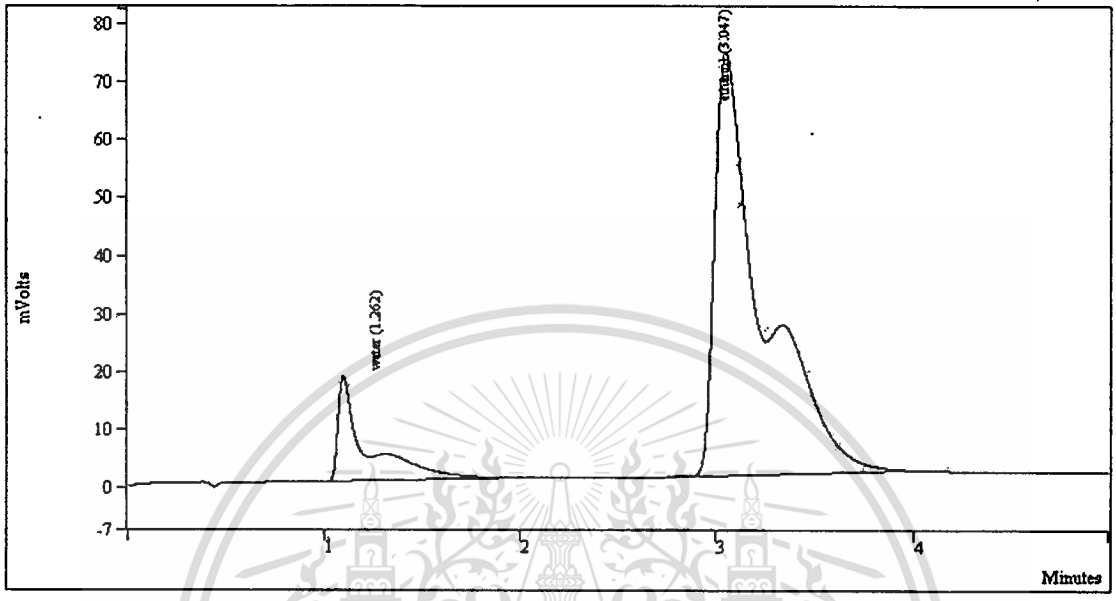

Figure B.1 Gas chromatogram of the feed in the ethanol/water separation at 80°C, 40 ml/min of He, 80 % mole of ethanol in feed mixture

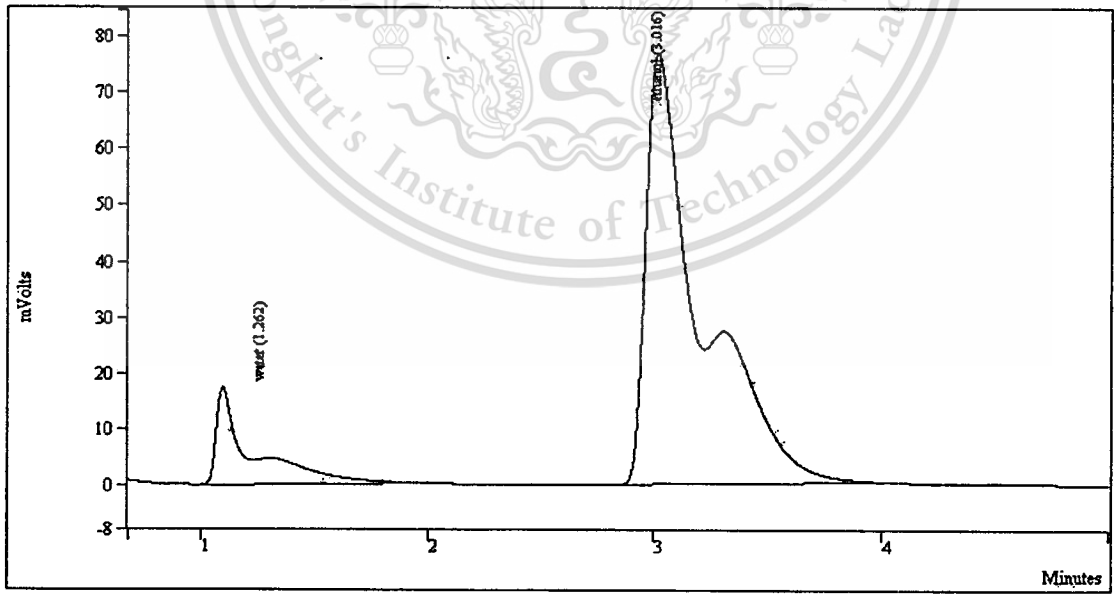

Figure B.2 Gas chromatogram of the retentate from the ethanol/water separation at 80°C, 40 ml/min of He, 80 % mole of ethanol in feed mixture

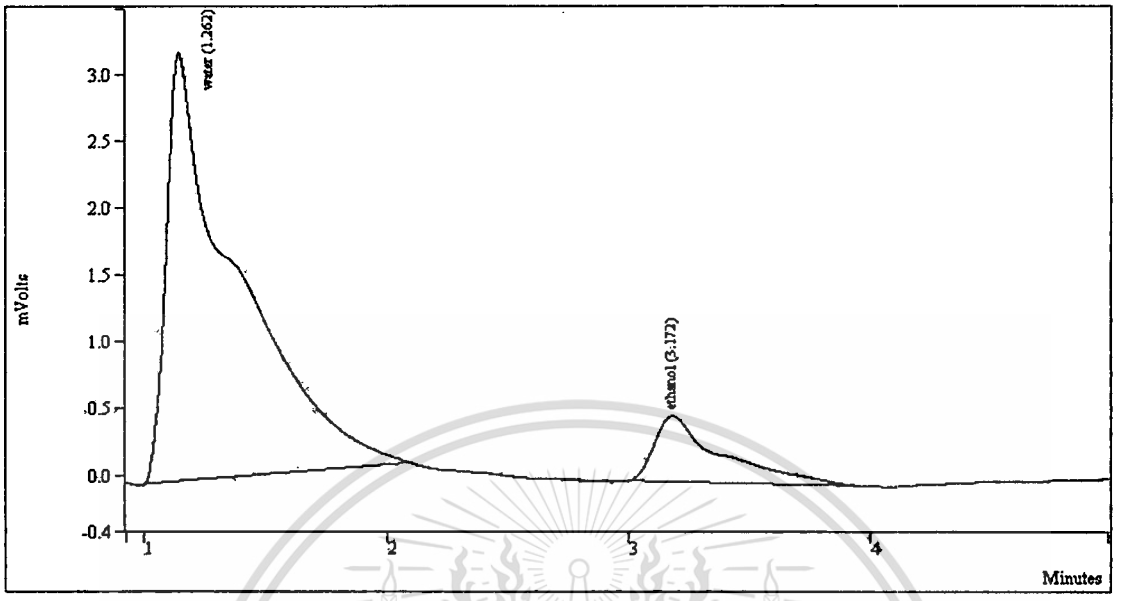

Figure B.3 Gas chromatogram of the permeate from the ethanol/water separation at 80°C, 40 ml/min of He, 80 % mole of ethanol in feed mixture

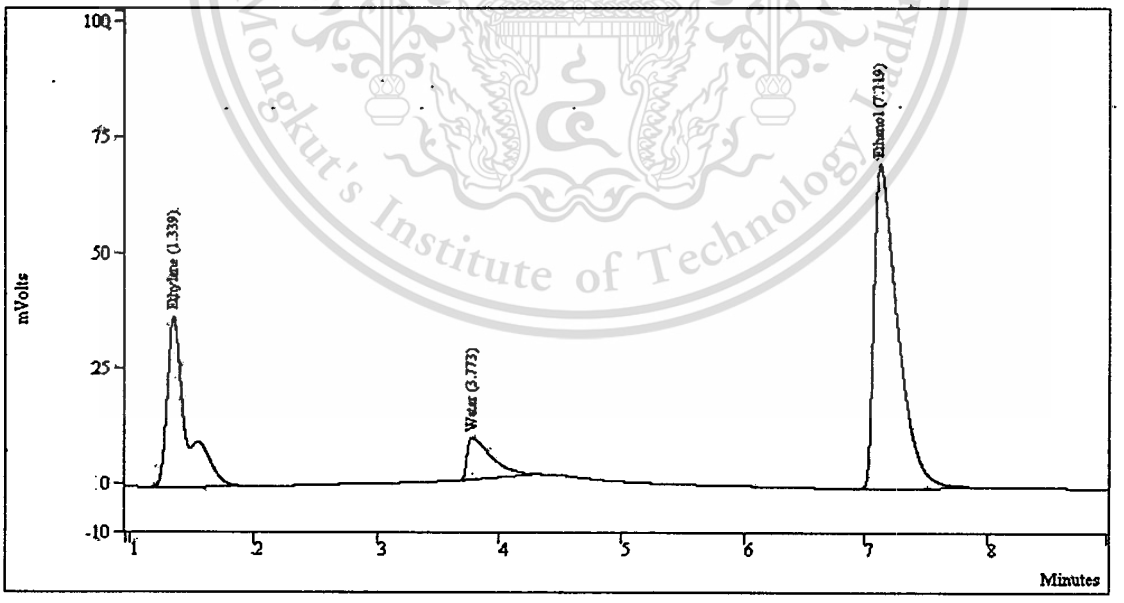

Figure B.4 Gas chromatogram of the feed in the ethanol/ethylene/water separation at 80°C, 40 ml/min of He

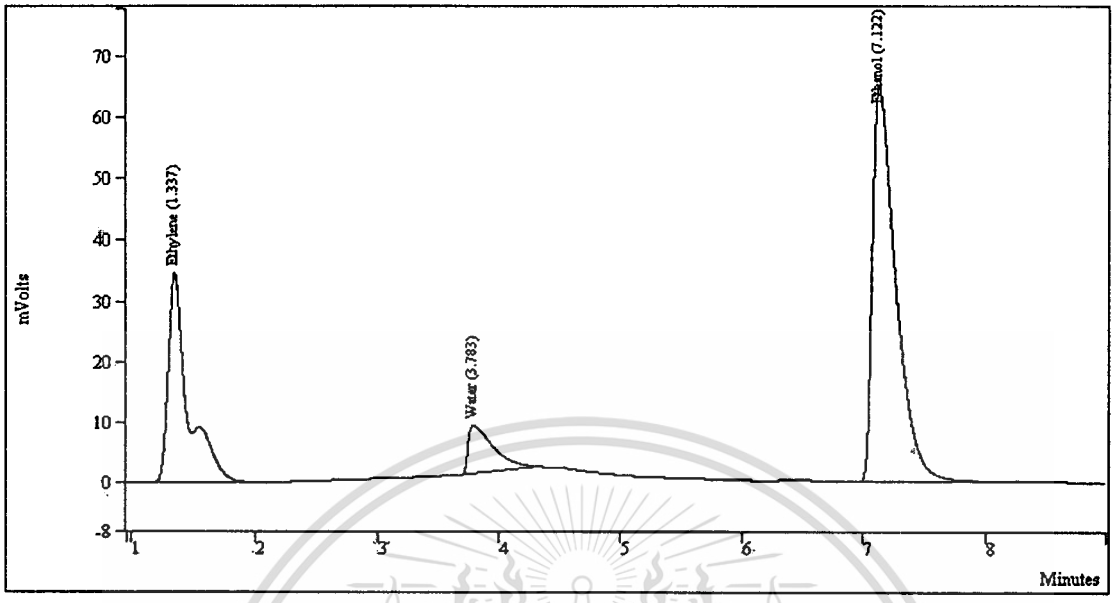

Figure B.5 Gas chromatogram of the retentate from the ethanol/ethylene/water separation at 80°C, 50 ml/min of He

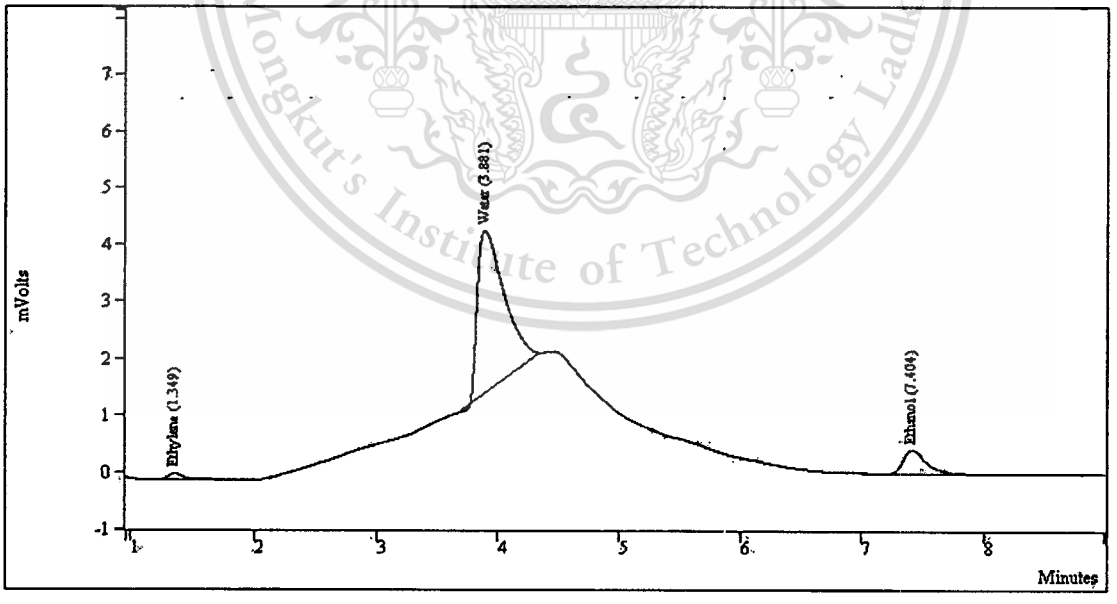

Figure B.6 Gas chromatogram of the permeate from the ethanol/ethylene/water separation at 80°C, 50 ml/min of He

Appendix C

Result from Gas Chromatography

Table C.1 The results from the study on effect of synthesis time

Synthesis	Feed (g/hr)		Retentate (g/hr)		Permeate (g/hr)		Separation	Flux	Feed	Retentate	Permeate	%	(%) Mass
time	Ethanol	Water	Ethanol	Water	Ethanol	Water	factor	(g/hr m^2)	(g/hr)	(g/hr)	(g/hr)	Permeate	Balance
16	0.1503	0.0154	0.1435	0.0134	0.0011	0.0043	36.2	68.8	0.1657	0.1569	0.0054	3.26	98.0
24	0.1440	0.0155	0.1371	0.0142	0.0002	0.0060	232.1	78.9	0.1595	0.1513	0.0062	3.89	98.8

Zeolite A membrane on support having 75.0% weight zeolite A

Separation condition: Temperature 80°C, Feed composition 80% mole ethanol, atmospheric pressure, and 50 ml/min of He

Table C.2 The results from the study on effect of zeolite A content in the support

%Zeolite A	Feed (g/hr)		Retentate (g/hr)		Permeate (g/hr)		Separation	Flux	Feed	Retentate	Permeate	%	(%) Mass
content	Ethanol	Water	Ethanol	Water	Ethanol	Water	factor	(g/hr m^2)	(g/hr)	(g/hr)	(g/hr)	Permeate	Balance
50.0	0.1136	0.0100	0.1118	0.0099	0.0004	0.0017	44.1	26.2	0.1236	0.1217	0.0021	1.67	100.0
62.5	0.1563	0.0177	0.1501	0.0152	0.0002	0.0044	204.2	58.7	0.1740	0.1653	0.0046	2.65	97.7
75.0	0.1440	0.0155	0.1371	0.0142	0.0002	0.0060	232.1	78.9	0.1595	0.1513	0.0062	3.89	98.8

Separation condition: Temperature 80°C, Feed composition 80% mole ethanol, atmospheric pressure, and 50 ml/min of He

Table C.3 The results from the study on effect of separation temperature using zeolite A membrane on the support having 75.0%wt.of zeolite A

Temperature	Feed (g/hr)		Retentate (g/hr)		Permeate (g/hr)		Separation	Flux	Feed	Retentate	Permeate	%	(%) Mass
(^{o}C)	Ethanol	Water	Ethanol	Water	Ethanol	Water	factor	(g/hr m^{2})	(g/hr)	(g/hr)	(g/hr)	Permeate	Balance
80	0.1440	0.0155	0.1371	0.0142	0.0002	0.0060	232.1	78.9	0.1595	0.1513	0.0062	3.89	98.8
100	0.1612	0.0153	0.1537	0.0153	0.0012	0.0043	36.8	69.8	0.1765	0.1690	0.0055	3.10	98.9
120	0.1493	0.0154	0.1434	0.0141	0.0016	0.0035	20.7	64.6	0.1647	0.1575	0.0051	3.08	98.7

Separation condition:Feed composition 80% mole ethanol, atmospheric pressure, and 50 ml/min of He

Table C.4 The results from the study on effect of separation temperature using zeolite A membrane on the support having 62.5%wt.of zeolite A

Temperature	Feed (g/hr)		Retentate (g/hr)		Permeate (g/hr)		Separation	Flux	Feed	Retentate	Permeate	%	(%) Mass
(^{o}C)	Ethanol	Water	Ethanol	Water	Ethanol	Water	factor	(g/hr m^{2})	(g/hr)	(g/hr)	(g/hr)	Permeate	Balance
80	0.1563	0.0177	0.1501	0.0152	0.0002	0.0044	204.2	58.7	0.1740	0.1653	0.0046	2.65	97.7
100	0.1683	0.0169	0.1608	0.0146	0.0006	0.0071	122.8	97.9	0.1852	0.1754	0.0077	4.15	98.8
120	0.1679	0.0170	0.1610	0.0161	0.0010	0.0066	62.4	97.4	0.1849	0.1771	0.0076	4.14	99.9

Separation condition: Feed composition 80% mole ethanol, atmospheric pressure, and 50 ml/min of He

Table C.5 The results from the study on effect of carrier gas flow rate using zeolite A membrane on the support having 62.5%wt.of zeolite A

He	Feed (g/hr)		Retentate (g/hr)		Permeate (g/hr)		Separation	Flux	Feed	Retentate	Permeate	%	(%) Mass
(ml/min)	Ethanol	Water	Ethanol	Water	Ethanol	Water	factor	(g/hr m^2)	(g/hr)	(g/hr)	(g/hr)	Permeate	Balance
30	0.1024	0.0122	0.0978	0.0098	0.0008	0.0062	68.9	88.9	0.1146	0.1076	0.007	6.09	100.0
40	0.1228	0.0147	0.1141	0.0124	0.0007	0.0061	73.2	86.7	0.1375	0.1265	0.0068	4.95	97.0
50	0.1563	0.0177	0.1501	0.0152	0.0002	0.0044	204.2	58.7	0.1740	0.1653	0.0046	2.65	97.7

Separation condition: Temperature 80°C, Feed composition 80% mole ethanol, and atmospheric pressure

Table C.6 The results from the study on effect of feed composition using zeolite A membrane on the support having 62.5%wt.of zeolite A

%Ethanol	Feed (g/hr)		Retentate (g/hr)		Permeate (g/hr)		Separation	Flux	Feed	Retentate	Permeate	%	(%) Mass
in liquid	Ethanol	Water	Ethanol	Water	Ethanol	Water	factor	(g/hr m^2)	(g/hr)	(g/hr)	(g/hr)	Permeate	Balance
40	0.1116	0.0286	0.1060	0.0255	0.0003	0.0072	113.3	106.2	0.1402	0.1315	0.0083	5.95	99.7
60	0.1285	0.0267	0.1234	0.0230	0.0003	0.0072	115.5	98.0	0.1552	0.1464	0.0075	4.86	99.2
80	0.1563	0.0177	0.1501	0.0152	0.0002	0.0044	204.2	58.7	0.1740	0.1653	0.0046	2.65	97.7
95	0.2060	0.0058	0.2006	0.0053	0.0016	0.0041	90.3	72.9	0.2118	0.2059	0.0057	2.70	99.9

Separation condition: Temperature 80°C, 50 ml/min of He, and atmospheric pressure

Table C.7 The feed composition of ethanol/ethylene/water separation using zeolite A membrane on the support having 62.5%wt.of zeolite A

Temperature	Feed (g/hr)			Retentate (g/hr)			Permeate (g/hr)		
(^{o}C)	Ethylene	Water	Ethanol	Ethylene	Water	Ethanol	Ethylene	Water	Ethanol
80	0.0570	0.0209	0.1896	0.0555	0.0181	0.1836	0.0002	0.0083	0.0006
100	0.0561	0.0197	0.1888	0.0537	0.0174	0.1833	0.0003	0.0079	0.0007
120	0.0547	0.0192	0.1818	0.0533	0.0169	0.1777	0.0006	0.0068	0.0009

Separation condition: Feed composition 0.79 ml/min ($3.2x10^{-5}$ mol/min) with 80% mol vapor of ethanol,

50 ml/min of He, and atmospheric pressure

Table C.8 The results from the study on ethanol/ethylene/water separation using zeolite A membrane on the support having 62.5%wt.of zeolite A

Separation factor of ethylene	Separationt factor of water	Separation factor of ethanol	Flux (g/hr m^2)	Feed (g/hr)	Retentate (g/hr)	Permeate (g/hr)	%Permeate	Mass Balance (%)
0.03	126.9	0.02	115.6	0.2675	0.2572	0.0091	3.39	99.6
0.06	92.2	0.03	113.3	0.2646	0.2544	0.0089	3.36	99.5
0.13	52.4	0.04	105.2	0.2558	0.248	0.0083	3.23	100.0

Separation condition: Feed composition 0.79 ml/min ($3.2x10^{-5}$ mol/min) with 80% mole vapor of ethanol,

50 ml/min of He, and atmospheric pressure

Appendix D

Elemental Analysis from Graphite Furnace Atomic Absorption Spectrophotometer (AAS)

Standard Curve Preparation for Elemental Analysis

The calibration curve for silicon and aluminium was prepared by plotting standard concentration of each element with the absorbance obtained from graphite furnace atomic absorption spectrophotometer.

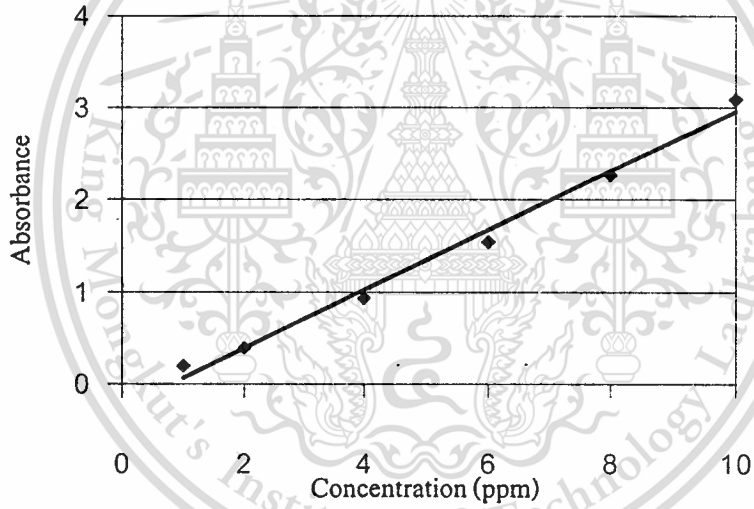

Figure D.1 Relation of concentration and absorbance data for silicon determination

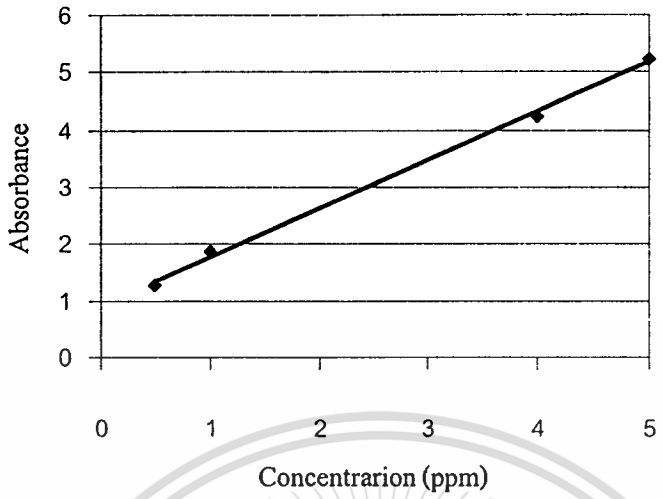

Figure D.2 Relation of concentration and absorbance data for aluminium determination

Calculation for Elemental Analysis

The elemental analysis of supports was followed by comparison the absorbance of sample with the standard calibration curve. Practically, the equation fitted to the calibration curve was employed to calculate the sample concentration.

Equation fitted for the calibration curve of silicon:

$$A = 0.3200C - 0.2512$$

- C is the concentration of silicon in sample (ppm)
- A is the absorbance of the sample

Equation fitted for the calibration curve of aluminium

$$A = 0.8492C + 0.9269$$

- C is the concentration of silicon in sample (ppm)
- A is the absorbance of the sample

Appendix E

Standard Curve for Gas Chromatography Analysis

Standard Curve Preparation

The standard curve for correcting the area percentage from gas chromatography analysis to the molar concentration of sample was prepared by analysis of the standard solution containing ethanol and water by gas chromatography. Standard concentration (mole of sample) was plotted with the area of the sample.

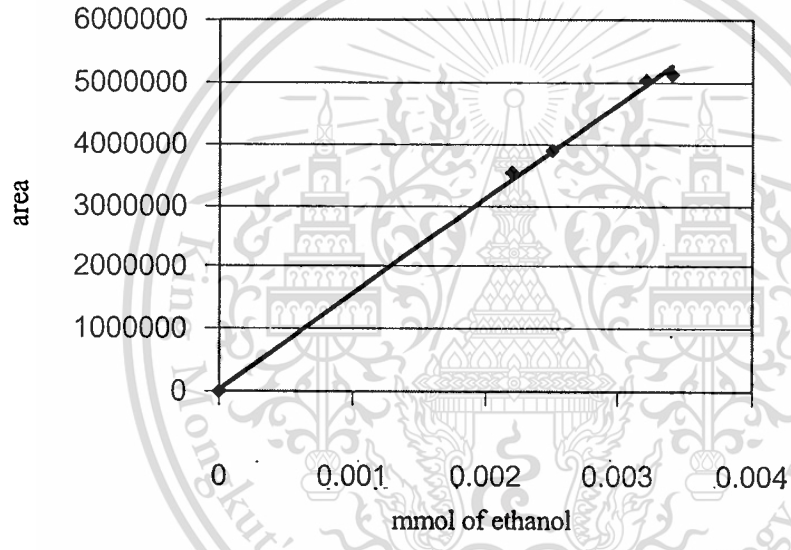

Figure E.1 The standard curve of ethanol (the mmol of ethanol was plotted with the area)

The equation fitted the standard curve of ethanol is shown below;

$$Y = (2x10^{9})X + 39269$$

- Y is the concentration of ethanol (mmol) in the standard solution
- X is the area of the ethanol from GC analysis

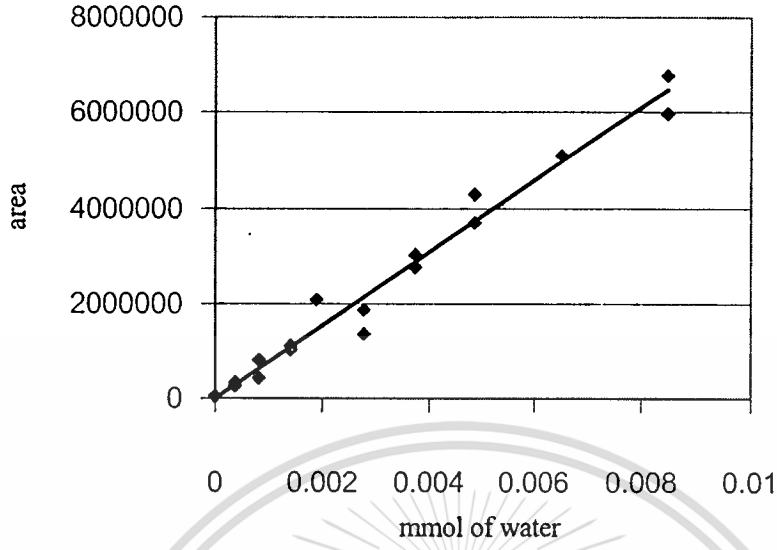

Figure E.2 The standard curve of water (the mmol of water was plotted with the area)

The equation fitted the standard curve of water is shown below;

$$Y = (8x10^{8})X + 8400$$

- Y is the concentration of water (mmol) in the standard solution
- X is the area of the ethanol from GC analysis

These standard curves were converted to the curve that the area percentage was plotted with the mole percentage of the sample by this equation.

$$A = RC$$

$$\%A = \frac{A_1}{A_1 + A_2} = \frac{C_1R_1}{C_1R_1 + C_2R_2}$$

Where A_1 and A_2 are the area of ethanol and water from GC

R_1 and R_2 are the response factor of ethanol and water

C_1 and C_2 are the concentration of ethanol and water

The standard curves for ethanol and water determinations that the area percentage was plotted with the concentration (%mol) are shown in Figures E.3 and E.4.

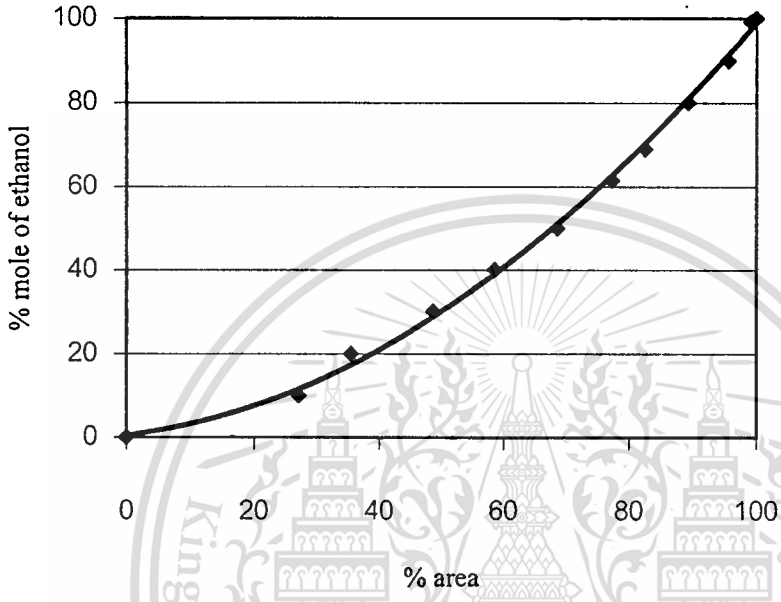

Figure E.3 The standard curve of ethanol for determine the ethanol concentration

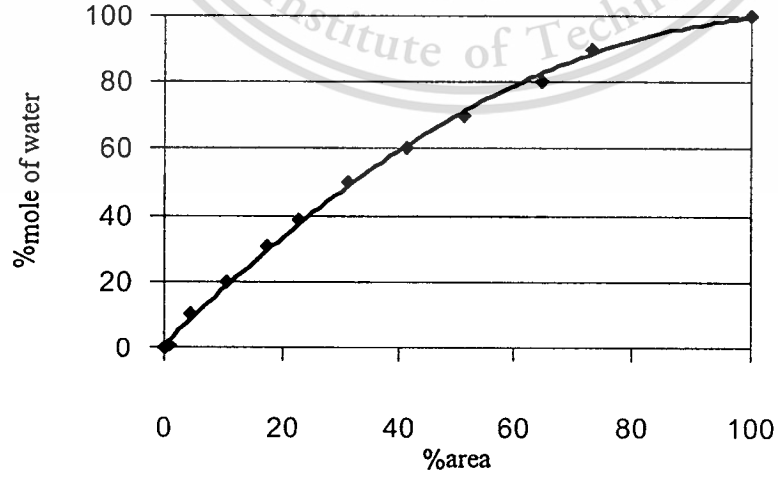

Figure E.4 The standard curve of water for determine the water concentration

Equation fitted the standard curve of ethanol is shown below;

$$y = 0.0079x^2+0.196x-0.517$$

- x is the average area percentage of ethanol in sample
- y is the molar percentage of ethanol

Equation fitted the standard curve of water is shown below;

$$y = -0.0079x^2+1.7748x+0.9433$$

- x is the average area percentage of water in sample
- y is the molar percentage of water

Equation of one point standard for ethylene is shown below;

$$y = 1.01A$$

- A is the average area percentage of ethylene in sample
- y is the relative molar concentration of ethylene

Appendix F

Calculation of the Composition, Separation Factor, and Permeation Flux

Calculation the Composition of Feed, Retentate, and Permeate in Ethanol/Water Separation

The feed, retentate, and permeate composition were calculate from GC result. For example, the area percentage of the feed from the ethanol/water separation at 80°C, using 80% mol of ethanol in feed mixture, 40 ml/min of carrier gas, and using zeolite A membrane on the support having 62.5%wt of zeolite A is shown in Figure F.1.

Peak No	Ret. Time (min)	Peak Name	Result ()	Area (counts)
1	1.262	water	13.452	204944
2	3.016	ethanol	86.548	1318589
		Totals	100.000	1523533

Peak No	Ret. Time (min)	Peak Name	Result ()	Area (counts)
1	1.262	water	13.504	197459
2	3.011	ethanol	86.496	1264725
		Totals	100.000	1462184

Figure F.1 Area percent of the feed composition from gas chromatography

- **The percent mole of ethanol**

The percent mole of ethanol can be calculated from equation fitted the standard curve

$$y = 0.0079x^2+0.196x+0.517$$

- x is the average area percentage of ethanol in sample (2)
- y is the molar percentage of ethanol

$$\% \text{ mol of ethanol} = 0.0079(86.53)^2+0.196(86.53)+0.517$$

$$= 76.63$$

- **The percent mole of water**

The percent mole of ethanol can be calculated from equation fitted the standard curve

$$y = -0.0079x^2+1.775x+0.9433$$

- x is the average area percentage of water in sample (2)
- y is the molar percentage of water

$$\% \text{ mol of water} = -0.0079(13.47)^2+1.7748(13.47)+0.9433$$
$$= 23.42$$

- **Normalization**

Total mole percentage of all component = 76.63+23.42

= 100.05

Normal to 100 percent

% mol of water = (76.63 x 100)/100.5

= 76.59

% mol of water = (23.42 x 100)/100.5

= 23.41

The retentate and permeate composition can be calculated in the same manner as carried out for the feed composition. The composition of feed, retentate, and permeate was shown in Table F.1.

Table F.1 The composition of feed, retentate, and permeate of ethanol/water separation

Feed (%mol)		Retentate (%mol)		Permeate (%mol)	
ethanol	water	ethanol	water	ethanol	water
76.59	23.41	78.24	21.76	4.29	95.71

Calculation of Separation Factor for Ethanol/Water Separation

The separation factor can be calculated from the mole ratio of water to ethanol in permeate divided with the mole ratio of water to ethanol in feed. It can be expressed as following.

$$separation\ factor(\alpha) = \frac{[Y_{water} / Y_{ethanol}]}{[X_{water} / X_{ethanol}]}$$

- Y is the mole percentage of component in the permeate
- X is the mole percentage of component in the feed

For example;

$$\text{Separation factor} = \frac{(95.71/4.29)}{(23.41/76.59)}$$

$$= 72.99$$

Calculation the Composition of Feed, Retentate, and Permeate in Ethanol/Ethylene/Water Separation

The feed, retentate, and permeate composition were calculate from GC result. For example, the area percentage of the feed from the ethanol/ethylene/water separation at 80°C, 40 ml/min of carrier gas, and using zeolite A membrane on support having 62.5%wt of zeolite A is shown in Figure F.2.

Peak No	Ret. Time (min)	Peak Name	Result ()	Area (counts)
1	1.339	Ethylene	27.038	399856
2	3.773	Water	8.740	129252
3	7.119	Ethanol	64.222	949759
		Totals	**100.000**	**1478867**

Peak No	Ret. Time (min)	Peak Name	Result ()	Area (counts)
1	1.337	Ethylene	27.785	408470
2	3.776	Water	8.645	127088
3	7.121	Ethanol	63.570	934546
		Totals	**100.000**	**1470104**

Figure F.2 Area percent of the feed composition from gas chromatography

- **The percent mole of ethylene**

The percent mole of ethylene can be calculated from the equation shown below;

$$y = 1.01A$$

- A is the average area percentage of ethylene in sample (2)
- y is the relative molar concentration of ethylene

For example;

% mol of ethylene = (1.01) x 27.42

= 27.77

- **Normalization**

Total area percentage of ethanol and water = 63.90+8.70

= 72.60

Normal to 100 percent

% mol of ethanol = (63.90 x 100)/72.60

= 88.02

% mol of water = (8.70 x 100)/72.60

= 11.98

- **The percent mole of ethanol in ethanol/water mixture**

% mol of ethanol = $0.0079(88.02)^2+0.196(88.02)+0.517$

= 78.97

- **The percent mole of water in ethanol/water mixture**

% mol of water = $-0.0079(11.98)^2+1.7748(11.98)+0.9433$

= 21.07

- **Normalization**

Total mole percentage of ethanol and water in ethanol/water mixture

= 78.97+21.07

= 100.4

Normalize to 100 percent

% mol of ethanol in ethanol/water mixture = (78.97 x 100)/100.4

= 78.94

% mol of water in ethanol/water mixture = (21.07 x 100)/72.60

= 21.06

Total mole percentage of ethanol ethylene and water = 100

Mole percentage of ethanol and water = 100-27.77

= 72.23

Normalize mole percent of ethanol and water to 100 percent

% mol of ethanol = (78.94 x 72.23)/100

= 57.02

% mol of water = (21.06 x 72.23)/100

= 15.21

The retentate and permeate composition can be calculated in the same manner as carried out for the feed composition. The composition of feed, retentate, and permeate was shown in Table F.2.

Table F.2 The composition of feed, retentate, and permeate of ethanol/ethylene/water separation

Feed (%mol)			Retentate (%mol)			Permeate (%mol)		
Ethylene	ethanol	water	Ethylene	ethanol	water	Ethylene	ethanol	water
27.77	57.02	15.21	27.92	57.97	14.11	2.21	3.50	94.29

Calculation of Separation Factor for Ethanol/Ethylene/Water Separation

The separation of water, ethanol, and ethylene can be calculated in a same manner as calculated for ethanol/water separation. It can be expressed as following.

$$separation\ factor\ of\ water = \frac{\left[Y_{water}/(Y_{ethanol}+Y_{ethylene})\right]}{\left[X_{water}/(X_{ethanol}+X_{ethylene})\right]}$$

- Y is the mole percentage of component in the permeate
- X is the mole percentage of component in the feed

For example;

$$\text{Separation factor of water} = \frac{(94.29)/(3.50+2.21)}{(15.21)/(57.02+27.77)}$$

$$= 92.21$$

$$separation\ factor\ of\ ethanol = \frac{\left[Y_{ethanol}/(Y_{water}+Y_{ethylene})\right]}{\left[X_{ethanol}/(X_{water}+X_{ethylene})\right]}$$

- Y is the mole percentage of component in the permeate
- X is the mole percentage of component in the feed

For example;

$$\text{Separation factor of ethanol} = \frac{(3.50)/(94.29+2.21)}{(57.02)/(15.21+27.77)}$$

$$= 0.0273$$

$$separation\ factor\ of\ ethylene = \frac{\left[Y_{ethylene}/(Y_{water}+Y_{ethanol})\right]}{\left[X_{ethylene}/(X_{water}+X_{ethanol})\right]}$$

- Y is the mole percentage of component in the permeate
- X is the mole percentage of component in the feed

For example;

$$\text{Separation factor of ethylene} = \frac{(2.21)/(94.29+3.50)}{(27.77)/(15.21+57.02)}$$

$$= 0.0588$$

Calculation of the Permeation Flux

- Feed

At steady state, feeding inject is presumably constant during the experiment. Accordingly, as the sample was loaded in fixed loop sample valve, the average total area of feed is equal to the feed loading for each injection.

The average total area of feed (A_F) = Feed loading (a, g/hr)

For example;

1492859 = 0.1375 g/hr

- Retentate

$$\text{Retentate} = \frac{\text{The average total area of retentate } (A_R) \times \text{Feed loading (a)}}{\text{The average total area of feed } (A_F)}$$

For example;

$$\text{Retentate} = \frac{1373561 \times 0.1375}{1492859}$$

$$= 0.1265 \text{ g/hr}$$

- Permeate

$$\text{Permeate} = \frac{\text{The average total area of permeate } (A_P) \times \text{Feed loading (a)}}{\text{The average total area of feed } (A_F)}$$

For example;

$$\text{Permeate} = \frac{73872 \times 0.1375}{1492859}$$

$$= 0.0068 \text{ g/hr}$$

- Permeation flux

$$\text{Permeation flux (g/hr m}^2\text{)} = \frac{\text{Permeate (g/hr)}}{\text{Area of membrane (m}^2\text{)}}$$

For example;

$$\text{Permeation flux (g/hr m}^2\text{)} = \frac{0.0068}{3.14 \times 0.005^2}$$

$$= 88.68 \text{ g/hr m}^2$$

- Percent permeate

$$\text{Percent permeate} = \text{(Permeate / Feed loading) x 100}$$

For example;

$$\text{Percent permeate} = (0.0068 / 0.1375) \times 100$$

$$= 4.95$$

For the ethanol/ethylene/water separation, the permeation flux can be calculated in the same manner as the ethanol/water separation.

AUTHOR BIOGRAPHY

Ms. Suree Tanyapanyachon was born on September 9, 1976 in Bangkok. She received a Bachelor Degree in Industrial Chemistry from the Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang in 1998. She has been a graduated student of the Program of Petrochemical and Hydrocarbon Chemistry, Graduate School, King Mongkut's Institute of Technology Ladkrabang, since 1999.