ZEOLITE FILLED WITH CHITOSAN MEMBRANE FOR LIQUID PERMEATION SEPARATION OF ETHANOL AND WATER

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Title	Zeolite filled with chitosan membrane for liquid permeation separation of ethanol and water
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ABSTRACT

This research aims to improve the efficiency of ethanol/water separation of chitosan membrane by incorporating zeolite NaA as selective water absorbent. The chitosan membrane filled with zeolite NaA contents of 0, 20, 40 and 60% w/w were prepared by spin coating technique with a spinning speed of 250 rpm. The thickness of the membranes was controlled at 120±10 μm by the number of spinning layer. XRD pattern of the zeolite NaA in the chitosan membrane showed some positions which are not matched with the pure zeolite NaA. In addition, the morphology investigated by SEM exhibited that the zeolite NaA in the chitosan membrane cannot be clearly seen. This might be because the structures of zeolite NaA were destroyed by the acid, resulting in aluminosilicate aggregate. The zeolite NaA content in the membrane from TGA exhibited that the dried weight was less than the loaded wet zeolite NaA due to the water in the zeolite NaA structure and the coke deposit. The membranes were set up for liquid permeation with various ethanol concentrations. The permeates from the separation were analyzed by GC. Subsequently, the water and ethanol fluxes and separation factors were calculated. The results showed that the water, ethanol and total fluxes were decreased but the water separation factors were increased with an increasing ethanol concentration in the feed. This is because the membrane becomes more rigid, leading to a less diffusion. In the case of different zeolite NaA contents in the membrane, the water flux, total flux and water separation factor were increased but the ethanol flux was decreased when the zeolite NaA content was increased. This is because the aluminosilicate aggregate is selective for water. In addition, the interconnecting void is increased and leads to shorter diffusion pathway when the zeolite NaA content is increased.

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Chapter 1

Introduction

1.1 Introduction

The fluctuation in gasoline prices over the last couple of years tracks changes in the cost of crude oil. More expensive crude oil is driving up gasoline prices. But nowadays, the demand of gasoline still increasing therefore gasohol has been introduced as an alternative way to use as a fuel engines as gasoline. [1]

Gasohol is a fuel mixture ethanol and gasoline that can be used in the internal combustion engines of most modern automobiles and light-duty vehicles without need for any modifications on the engine or fuel system. [2] Ethanol can used as a gasoline additive due to its characteristics which is allowed to use in current engine and with high octane rating that tends to increase fuel efficiency. [3] Moreover, by using ethanol as gasoline additive also reduces harmful tailpipe emissions of carbon monoxide, particulate matter, oxides of nitrogen, and other ozone-forming pollutants. [4]

Normally, MTBE or methyl tert-buthyl ether is used as a gasoline additive but it is thought to be carcinogenic and when it leaks from an underground tank at a gas station, it can get into groundwater and contaminate wells so it has been singled out. [5] This is also the reason why gasohol is very popular. Ethanol is produced both as a petrochemical, through the hydration of ethylene, and biologically, by fermenting sugars with yeast. Which process is more economical depends on prevailing prices of petroleum and grain feed stocks. [4] The product of either ethylene hydration or fermentation is an ethanol-water mixture. [6] When this mixture is used as a gasoline additive, it causes to the phase-separation in a fuel tank and it cannot be efficiently shipped through modern pipelines, like gasoline, over long distances. [4, 7] Therefore, the ethanol must be purified before use.

The mixture of ethanol and water is an azeotropic mixture, and cannot be further purified by distillation. Liquid permeation is an important membrane process in chemical industries for separating azeotropic, close-boiling, isomeric and heat sensitive liquid mixtures. [8] Chitosan has a good film-forming, highly hydrophilic, and excellent chemical-resistant properties; so it has

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been intensively used in liquid permeation as dehydration membrane but the performance of a pure chitosan membrane is not satisfactory due to the larger free volume between the molecular chains. [9 - 10] With this, the liquid permeation performance can be improved by blending it with a high selective zeolite into a membrane matrix. [11]

This research work enhances the separation selectivity by choosing zeolite NaA and incorporated it into chitosan. The zeolite content with respect to chitosan is varied to improve the membrane performances. The characteristics changes in the resulting membranes are investigated and the resulting membranes are employed for the liquid permeation separation of ethanol-water. The separation selectivity is evaluated. The results are discussed in terms of liquid permeation separation efficiency of the membranes.

1.2 Objectives

1) To obtain high efficiency membranes for ethanol-water separation.
2) To understand the role of zeolite content in the characteristics of membranes and determine the appropriate content for good selectivity.
3) To obtain the ethanol-water separation by liquid permeation process.

1.3 Scope of work

1) Membranes preparation using 2% w/v of chitosan solution and filled with the different amounts of zeolite (20%, 40% and 60% w/w of chitosan).
2) Characterization of membranes with different amounts of zeolite by X-ray diffractometry, scanning electron microscope (SEM) and thermogravimetric analysis (TGA).
3) Investigate the effect of zeolite content in the characteristics of membranes.
4) Investigate the liquid permeation process of ethanol-water separation.
5) Determine the appropriate zeolite content in the membrane for a good selectivity.

1.4 Expectation

1) Prepare high efficiency membranes for ethanol-water separation.
2) Increase the purity of ethanol in order to develop industrial gasoline additive.

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Chapter 2

Theory and Literature Review

2.1 Gasohol [12]

There are several common ethanol fuel mixtures in use around the world. The use of ethanol in internal combustion engines (ICE) is only possible if the engine is designed or modified for that purpose. Ethanol can be blended with gasoline (petrol) in various ratios for use in unmodified gasoline engines, and with minor modifications can also be used with a higher content of ethanol.

Ethanol fuel mixtures have "E" numbers which describe the percentage of ethanol fuel in the mixture by volume, for example, E85 is 85% ethanol and 15% gasoline. Low ethanol blends, from E5 to E25, are also known as *gasohol*, though internationally the most common use of the term gasohol refers to the E10 blend.

2.1.1 Ethanol Production

Ethanol is a kind of alcohol produced from crop fermentation to convert starch into sugar and then convert sugar into alcohol. By distillation of alcohol to attain a pure alcohol of 95 percent which is called as Ethanol. Ethanol for blending with oil to fill in the car engine is a pure alcohol of 99.5 % by volume which is capable of using as fuel. [13]

The vast majority of ethanol for use as fuel is produced by fermentation. When certain species of yeast (e.g., Saccharomyces cerevisiae) metabolize sugar they produce ethanol and carbon dioxide as chemical equations below:

$$C_6H_{12}O_6 \rightarrow 2\ CH_3CH_2OH + 2\ CO_2$$

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 4\ CH_3CH_2OH + 4\ CO_2$$

The process of culturing yeast under conditions to produce alcohol is called fermentation. This process is carried out at around 35–40 °C. Toxicity of ethanol to yeast limits the ethanol concentration obtainable by brewing. Therefore, ethanol usually is obtained by fortification or distillation. The most ethanol-tolerant strains of yeast can survive up to approximately 15%

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ethanol by volume. [14] Then molecular sieve separation is needed to separate water from the ethanol. Pure ethanol of 95% by volume is moved through the zeolite-adsorption tower to separate water out. From that process, ethanol of 99.5% is obtained which is capable of using as fuel. [15]

2.2 Membrane Technology

A membrane is a selective barrier that permits the separation of certain species in a fluid by combination of sieving and sorption diffusion mechanism. Separation is achieved by selectively passing (permeating) one or more components of a stream through the membrane while retarding the passage of one or more other components. Membranes can selectively separate components over a wide range of particle sizes and molecular weights, from macromolecular materials such as starch and protein to monovalent ions. Membranes have gained an important place in chemical technology and are used in a broad range of applications.

Membrane processes are characterized by the fact that a feed stream is divided into 2 streams: retentate and permeate. The retentate is a part of the feed that does not pass through the membrane, while permeate is a part of the feed that does pass through the membrane. [16] The most general process can be depicted by the following Figure 2.1.

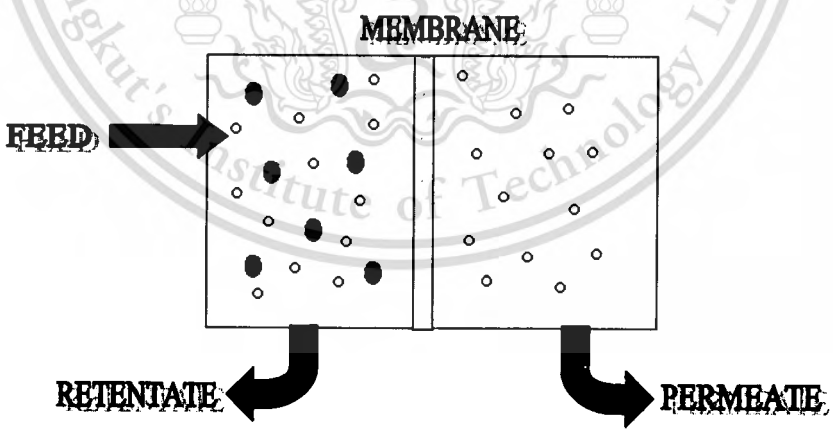

Figure 2.1 Membrane Separation Process.

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The key properties determining membrane performance are high selectivity and fluxes, good mechanical, chemical and thermal stability under operating conditions. Membrane characteristic should be low fouling tendencies and good compatibility with the operating environment, cost effective and defect-free production.

Although the major uses of membranes are in the production of potable water and separation of industrial gases, they can be used for many other important applications such as filtration of particulate matter from liquid suspensions, air or industrial flue gas and the dehydration of ethanol azeotropes. More specialized applications include ion separation in electrochemical processes, dialysis of blood and urine, artificial lungs, controlled release of therapeutic drugs, membrane-based sensors, etc.

2.2.1 Membrane Separation Processes

The following tables give an overview and a classification of membrane separation processes.

Table 2.1 Size of materials retained, driving force, and type of membrane. [17]

Process	Size of materials retained	Driving force	Type of membrane
Microfiltration	0.1 - 10 μm microparticles	Pressure difference(0.5 - 2 bar)	Porous
Ultrafiltration	1 - 100 nm macromolecules	Pressure difference(1 - 10 bar)	Microporous
Nanofiltration	0.5 - 5 nm molecules	Pressure difference (10 - 70 bar)	Microporous
Reverse Osmosis	< 1 nm molecules	Pressure difference (10 - 100 bar)	Nonporous
Dialysis	< 1 nm molecules	Concentration difference	Nonporous or microporous
Electrodialysis	< 1 nm molecules	Electrical potential difference	Nonporous or microporous
Pervaporation	< 1 nm molecules	Concentration difference	Nonporous
Gas Permeation	< 1 nm molecules	Partial pressure difference (1 - 100 bar)	Nonporous
Membrane Distillation	< 1 nm molecules	Partial pressure difference	Microporous

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Table 2.2 Examples of applications and alternative separation processes. [17]

Process	Applications	Alternative Processes
Microfiltration	Separation of bacteria and cells from solutions	Sedimentation, Centrifugation
Ultrafiltration	Separation of proteins and virus, concentration of oil-in-water emulsions	Centrifugation
Nanofiltration	Separation of dye and sugar, water softening	Distillation, Evaporation
Reverse Osmosis	Desalination of sea and brackish water, process water purification	Distillation, Evaporation, Dialysis
Dialysis	Purification of blood (artificial kidney)	Reverse osmosis
Electrodialysis	Separation of electrolytes from nonelectrolytes	Crystallization, Precipitation
Pervaporation	Dehydration of ethanol and organic solvents	Distillation
Gas Permeation	Hydrogen recovery from process gas streams, dehydration and separation of air	Absorption, Adsorption, Condensation
Membrane Distillation	Water purification and desalination	Distillation

Table 2.1 shows size of materials retained, driving force and type of membrane for various membrane separation processes. Porous membrane is used for microfiltration process and the size of materials retained is 0.1-10 μm. Microporous membrane is used for ultrafiltration and nanofiltration processes. However, nonporous membrane is used for many processes. Additionally, links to pages with more information on external Web site are provided. [17] Moreover, the examples of applications and separation processes which compete with the respective membrane separation process are shown in Table 2.2.

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2.2.2 Types of Membrane [18]

The principal types of membrane can be classified into 4 groups which are shown in Figure 2.2 to Figure 2.5

1) Porous membrane
2) Dense membrane
3) Electrically charged membrane
4) Liquid membrane

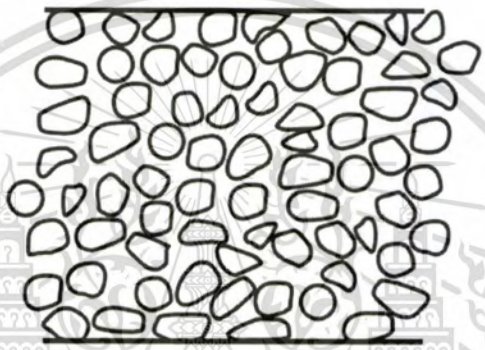

Figure 2.2 Porous membrane. [18]

Figure 2.3 Dense membrane. [18]

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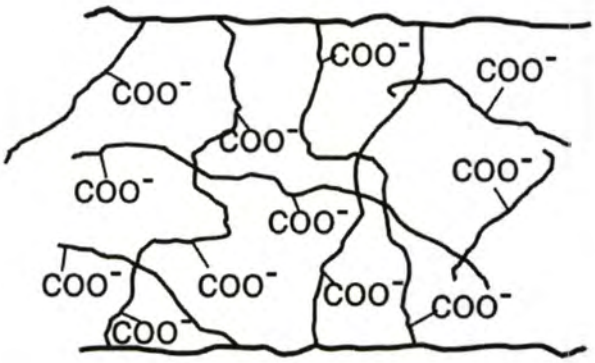

Figure 2.4 Electrically charged membrane. [18]

Figure 2.5 Liquid membrane. [18]

2.3 Liquid Phase Separation

2.3.1 Basic Explanations [19]

In liquid phase separation, a liquid mixture is passed across the surface of a membrane that is selectively permeable to one component or more than one component depending on the types of membrane and the feed mixtures. The membrane is enriched in this case the water molecules pass through the cell membrane from an area of high water concentration to one of low water concentration aiming to equalize the water concentrations on the two sides; this is called osmosis. Although osmosis does not require input of energy, it does use kinetic energy for separation phenomenon.

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2.3.2 Solution Diffusion Model

The solution-diffusion model has emerged over the past 20 years as the most widely accepted explanation of transport in dialysis, reverse osmosis, gas permeation, and pervaporation. The principle property of membranes used in separation applications is the ability to control the permeation of different species. Two models are used to describe this permeation process.

1) The solution diffusion model, in which permeants dissolve in the membrane material and then diffuse through the membrane by a concentration gradient. A separation is achieved between different permeants because of differences in the amount of material that dissolves in the membrane and the rate at which the material diffuses through the membrane.
2) The pore flow model, in which permeants are separated by pressure driven convective flow through tiny pores. A separation is achieved between different permeants because one of the permeants is excluded (filtered) from the pores in the membrane while other permeants can diffuse because of its small size.

Both models were proposed in the nineteenth century but the pore flow model was more popular until the mid 1940s.This is because it was closer to normal physical experience. However, during the 1940s, the solution diffusion model was used to explain transport of gases across polymeric films. This use of the solution diffusion model was relatively uncontroversial, but the transport mechanism in reverse osmosis membranes was a hotly debated issue in the 1960s and early 1970. By 1980, however, the proponents of solution diffusion had carried the day; currently only a few die hard pore flow modelers use this approach to rationalize reverse osmosis. [20]

When liquid mixtures pass through the membrane and then diffusion takes place according to the concentration gradient as following Fick's law. [21] Selectivity of the solubility-diffusion can be expressed by solubility selectivity. Diffusivity selectivity, solubility selectivity and selectivity from diffusion are shown by (2.1), (2.2), and (2.3), respectively. Typically, solution diffusion model of the osmosis gives a clear explanation.

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$$S_{i/j} = S^{S}_{i/j} S^{D}_{i/j} \quad (2.1)$$

$$S^{S}_{i/j} = \frac{C^{m}_{i}/C^{m}_{j}}{X_i/X_j} \quad (2.3)$$

$$S^{D}_{i/j} = \frac{D_i}{D_j} \quad (2.3)$$

C^{m}_{i} = Concentration of component i in membrane

C^{m}_{j} = Concentration of component j in membrane

D_i = Diffusion coefficient of component i

D_j = Diffusion coefficient of component j

X_i = Concentration of component i in feed

X_j = Concentration of component j in feed

$S_{i/j}$ = Selectivity of component i compared with j

$S^{S}_{i/j}$ = Selectivity from solution of component i compared with component j

$S^{0}_{i/j}$ = Diffusivity selectivity of component i compared with j

Flux and separation factor can be defined the efficiency of membrane.

a) Flux

Flux is the amount of a component permeated per unit area per unit time for a given membrane.

$$\text{Flux} = \frac{ml/hr}{m^2}$$

b) Separation factor

The performance of a given membrane for separation of mixtures can be expressed in terms of a parameter called selectivity.

$$\text{Separation factor} \quad \frac{Y_A/Y_B}{X_A/X_B}$$

Where Y_A = Mole fraction of A in permeate

Y_B = Mole fraction of B in permeate

X_A = Mole fraction of A in feed

X_B = Mole fraction of B in feed

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2.3.3 Plasticizing and Coupling effects

In order to explain mechanism of mass transfer in the membrane refers to the osmosis process where the mechanism is dissolution-diffusion, which is an important in liquid permeation.

Dissolution or absorption occurs from interaction between the substances and the membrane. Interaction may depend on these factors; Dipole moment between molecules of a feed substances and the membrane, ability of hydrogen bonding (H-bonds) occurrence, steric effect and activity value of substances. An ability of H-bonds between the membrane and substance will more likely dissolve in the hydrophilic membrane. In case of high polarity substances (H-F, H-O, H-N), the more interaction of dipole moment and / or hydrogen bonding occur and results in good dissolvation in hydrophilic membrane. Besides the structures of liquid substance also affect in dissolving in the membrane such as the more complexity structure, the less permeate pass through the membrane.

Diffusion depends on sizes and shapes of feed substances, therefore the substance with lower molecular weight and / or smaller size and shape will diffuse faster. The solution and diffusion of the substances in the membrane relate with the interaction between the liquid molecules and the membrane by either dipoles or H-bonding interaction which is resulting in change of physical properties of polymer. A good affinity between the liquid molecules and the membrane causes the swollen membrane which affects the properties of the membrane known as plasticizing effect. Normally, Plasticizing effect may accelerate high coefficient of diffusion of substances in the membrane resulted from (1) free movement of polymer encourages lower activation energy of diffusion (2) more free volume spaces leads to higher possibility of diffusion.

In the osmosis process, a mixture of two components: component i and component j in which an additional of component j may affect soluble and diffusible of component i. In solubility, component i will reduce it capability as component j is able to dissolve well in the membrane. Generally, potential of diffusion caused by 2 phenomena which are coupling effect and plasticizing effect. Coupling effect means an acting force existing between molecules of component i and j in polymer where it may affect a decrease in diffusion of component i. In the case of swollen membranes the gaps between the polymer chains if enhanced and hence, the diffusion of component i and coupling component will be increased. In plasticizing effect, the diffusion of component i may increase if the membrane can be swollen by component j.

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Ethanol/water separation using pure chitosan membrane, water is able to create plasticizing effect with the membrane which causes swollen membrane. This is because water has higher solubility than ethanol. It leads to an increase in ethanol flux when high water concentration is used as feed. According to coupling effect between ethanol and water by H-bonding, it is possible to increase diffusion of ethanol with high ethanol concentration in feed for separation of substances.

2.3.4 Factors affect the separation of substances

1. Feed concentration.

The high feed concentration leads to the higher permeation. The higher feed concentration can cause coupling and plasticizing effect. As the resulting from water/ethanol separation using hydrophilic membrane, the higher water concentration in feed, possesses the higher flux of water.

2. Size of substance.

The smaller size of substance has more chance to pass through the membrane compared to bigger size

3. Feed temperature.

Increasing in feed temperature, higher kinetic energy is obtained. This may enhance movement of substance pass through the membrane. Moreover, solubility in membrane is increased due to an ease movement of polymer chains. Therefore, flux is increased but separation factor is decreased. Flux can be enhanced depending on the temperature according to the Arrhernnius law as shown below:

$$J_i = A_i \exp(-\frac{Ea}{RT})$$

4. Pressure.

The higher pressure can act as the driving force to enhance diffusion of permeates through

the membrane.

5. Membrane.

Different types of membrane have different density. The high density membrane can result in slow diffusion because of an obstruction as compared to low density membrane.

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2.4 Chitin and Chitosan [22]

2.4.1 Introduction

Chitin is the second most ubiquitous natural polysaccharide after cellulose on earth and is composed of β (1-4)- linked 2-acetamido-2-deoxy-β-D-glucose (N-acetylglucosamine) (Figure 2.6). It is often considered as cellulose derivative, even though it does not occur in organisms producing cellulose. It is structurally identical to cellulose, but it has acetamide groups ($-NHCOCH_3$) at the C-2 positions. Similarly the principle derivative of chitin, chitosan is a linear polymer of α (1→4)-linked 2-amino-2-deoxy β—D-glucopyranose and is easily derived by N-deacetylation, to a varying extent that is characterized by the degree of deacetylation, and is consequently a copolymer of N-acetylglucosamine and glucosamine (Figure 2.7). Chitin is estimated to be produced annually almost as much as cellulose. It has become of great interest not only as an under-utilized resource but also as a new functional biomaterial of high potential in various fields and the recent progress in chitin chemistry is quite significant.

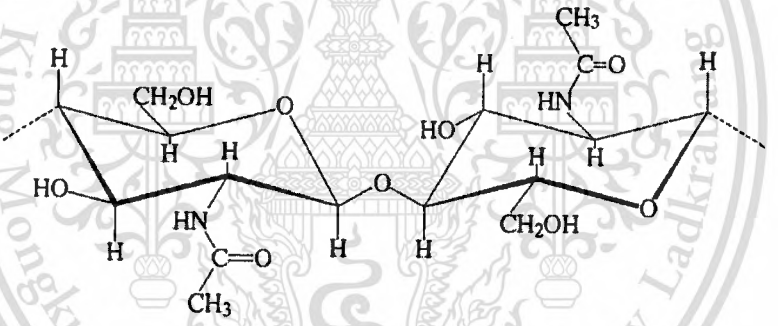

Figure 2.6 Structure of chitin. [22]

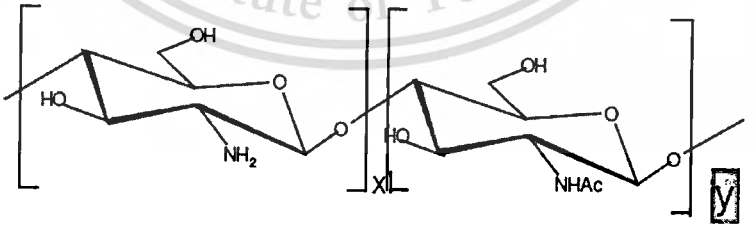

Figure 2.7 Partially deacetylated chitin. [22]

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Chitin is a white, hard, inelastic, nitrogenous polysaccharide found in the exoskeleton as well as in the internal structure of invertebrates. The waste of these natural polymers is a major source of surface pollution in coastal areas. The production of Chitosan from crustacean shells obtained as a food industry waste is economically feasible, especially if it includes the recovery of carotenoids. The shells contain considerable quantities of astaxanthin, a caroteniod that has so far not been synthesized, and which is marketed as a fish food additive in aquaculture, especially for salmon. The chitinous solid waste fraction of average Indian landing of shellfish was ranged from 60,000 to 80,000 t. The three parts of our motherland, India, are surrounded by ocean and its inner land is also very much rich with ponds, lakes, and lagons. The proper utilization of those water resources (aquaculture) in terms of research in chitin and chitosan can bring the economic and academic prosperity of the nation. Chitin and chitosan are now produced commercially in India, Poland, Japan, the US, Norway and Australia. A considerable amount of research is in progress on chitin/chitosan world over, including India, to tailor and impart the required functionalities to maximize its utility.

Chitin and chitosan the naturally abundant and renewable polymers have excellent properties such as, biodegradability, bio-compatibility, non-toxicity, and adsorption. The reaction of chitosan is considerably more versatile than cellulose due to the presence of NH_2 groups. Various efforts have been made to prepare functional derivatives of chitosan by chemical modifications; graft reactions, ionic interactions, and only few of them are found to dissolve in conventional organic solvents4. Chitosan is only soluble in aqueous solutions of some acids, and some selective N-alkylidinations3,5 and N-acylation4,6 have also been attempted. Although several water-soluble or highly swelling derivatives are obtained, it is difficult to develop the solubility in common organic solvents by these methods. Modification of the chemical structure of chitin and chitosan to improve the solubility in conventional organic solvents has been reviewed by many authors. On the other hand, only a few reviews have been reported on biomedical applications of chitin/chitosan, and no comprehensive review has yet been published covering the entire range of applications. The present review covers the literature from 1993 to 2003 dealing with properties, processing, and applications in various industrial and biomedical fields.

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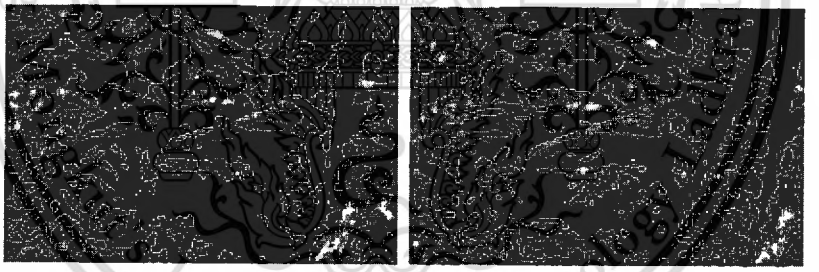
2.4.2 Chitin and Chitosan Processing

Chitin and chitosan are natural resources waiting for a market. They were waste products of the crabbing and shrimp canning industry. The US Department of Commerce reported in 1973 that they were over ,50,000 Mt of chitin produced as processing waste from shellfish, krill, clams, oysters, squid, and fungi. Commercially chitin and chitosan are of great importance owing to their relatively high percentage of nitrogen (6.89 per cent) compared to synthetically substituted cellulose. The crustacean shells mainly involve the removal of proteins and the dissolution of calcium carbonate that is present in crab shells in high concentrations. The resulting chitin is deacetylated in 40 per cent sodium hydroxide at 120 °X for 1-3 h. This treatment produces 70 per cent deacetylated chitosan.

The following four steps in chronological order of the process are needed to produce chitosan from crustacean shells: (i) Deproteinization, (ii) Deminera-lization (Unpublished data, one of the authors, Pradeep Kumar Dutta investigated a new method of demineralization of crustacean shells and claimed better property than the existing process), (iii) Decolouration, and (iv) Deacetylation. [22]



Crustacean shells →Size reduction →Protein separation →
(NaOH) →Washing Demineralization (HCl) →
Washing and dewatering →Decolouration →Chitin →
Deacetylation (NaOH) →Washing and Dewatering →Chitosan

2.4.3 Properties of Chitin and Chitosan

Most of the naturally occurring polysaccharides e.g., cellulose, dextrin, pectin, alginic acid, agar, agarose, and carragenas are natural and acidic in nature, whereas chitin and chitosan are examples of highly basic polysaccharides. Their properties include solubility in various media, solution, viscosity, polyelectrolyte behavior, polyoxysalt formation, ability to form films, metal chelations, optical, and structural characteristics

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Although the β (1-4) – anhydroglucosidic bond of chitin is also present in cellulose the characteristic properties of chitin/chitosan are not shared by cellulose18. Chitin is highly hydrophobic and is insoluble in water and most organic solvents. It is soluble in hexafluoroisopropanol, hexafluoroacetone, and chloroalcohols in conjunction with aqueous solutions of mineral acids and dimethylacetamide (DMAc) containing 5 per cent lithium chloride (LiCl). Recently the dissolution of chitosan in N-methyl morpholine-N-oxide (NMMO)/H_2O has been reported by Dutta et al. The hydrolysis of chitin with concentrated acids under drastic conditions produces relatively the pure amino sugar, D-glucosamine.

Depending on the extent of deacetylation, chitin contains 5 to 8 per cent (w/v) nitrogen, which is mostly in the form of primary aliphatic amino groups as found in chitosan. Chitosan undergoes the reactions typical of amines, of which N-acylation and Schiff reactions are the most important. Chitosan glucans are easily obtained under mild conditions but it is difficult to obtain cellulose glucans.

N-acylation with acid anhydrides or acyl halides introduces amin groups at the chitosan nitrogen. Acetic anhydride affords fully acetylated chitins. Linear aliphatic N-acyl groups higher than propionyl permit rapid acetylation of the hydroxyl groups in chitosan5, 6. Highly benzoylated chitin is soluble in benzyl alcohol, dimethyl sulphoxide (DMSO), formic acid, and dichloroacetic acid. The N-hexanoyl, N- decanoyl and N-dodecanoyl derivatives have been obtained in methanesulphonic acid.

Chitosan forms aldimines and ketimines with aldehydes and ketones, respectively, at room temperature. Reaction with ketoacids followed by reduction with sodium borohydride produces glucans carrying proteic and non-proteic amino acid groups. N-carboxy-methyl chitosan is obtained from glyoxylic acid. Examples of non-proteic amino acid glucans derived from chitosan are the N-carboxybenzyl chitosans obtained from o- and p-phthalaldehydic acids.

Chitosan and simple aldehydes produce N-alkyl chitosan upon hydrogenation. The presence of the more or less bulky substituent weakens the hydrogen bonds of chitosan; therefore, N-alkyl chitosans swell in water inspite of the hydrophobicity of alkyl chains. They retain the film forming property of chitosan. Chitosan is more versatile in comparision to chtin due to the presence of amino groups at the C-2 positions.

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1) Chemical Properties of Chitosan

The chemical properties of Chitosan as follows:

- Linear polymine.
- Reactive amino groups.
- Reaction hydroxyl group available.
- Chelates many transitional metal ions.

2) Biological Properties of Chitosan

Following are the biological properties of Chitosan:

- Biocompatible
  - Natural polymer,
  - Biodegradable to normal body constituents,
  - Safe and non-toxic
- Binds to mammalian and microbial cells aggressively,
- Regenerative effect on connective gum tissue,
- Acclerates the formation of osteoblast responsible for bone formation,
- Hemostatic,
- Fungistatic,
- Spermicidal,
- Antitumor,
- Anticholesteremic,
- Accelerates bone formation,
- Central nervous system depressant,
- Immunoadjuvant.

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2.4.4 Applications of Chitin and Chitosan

The interest in chitin originates from the study of the behaviour and chemical characteristics of lysozyme, an enzyme present in the human body fluids. It dissolves certain bacteria by cleaving the chitinous material of the cell walls. A wide variety of medical applications for chitin and chitin derivatives have been reported over the last three decades. It has been suggested that chitosan may be used to inhibit fibroplasia in wound healing and to promote tissue growth and differentiation in tissue culture.

The poor solubility of chitin is the major limiting factor in its utilization and investigation of its properties and structure. Despite these limitations, various applications of chitin and modified chitins have been reported in the literature, e.g., as raw material for man-made fibers. Fibers made of chitin and chitosan are useful as absorbable sutures and wound-dressing materials. This chitin sutures resist attack in bile, urine and pancreatic juice, which are difficult with other absorbable sutures. It has been claimed that wound dressings made of chitin and chitosan fibres44 accelerate the healing of wounds by about 75 per cent. Apart from their applications in the medical field, chitin and chitosan fibers have potential applications in wastewater treatment, where the removal of heavy metal ions by chitosan through chelation has received much attention. Their use in the apparel industry, with a much larger scope, could be a long-term possibility.

2.5 Zeolite [23]

Zeolite is crystalline aluminosilicate minerals. They have three-dimensional structures arise from a framework of $(SiO_4)^{4-}$ and $(AlO_4)^{5-}$ coordination polyhedral (Figure 2.8) linked by all their corners. The frameworks are generally very open and contain channels and cavities in which are located cations and water molecules (Figure2.9). The cations often have a high degree of mobility giving rise to facile ion exchange and the water molecules are readily lost and regained; this accounts for the well-known desiccant properties of zeolite.

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Figure 2.8 Representations of $(SiO_4)^{4-}$ or $(AlO_4)^{5-}$ tetrahedral. [23]

Many of the natural zeolite can be produced synthetically and several crystalline aluminosilicates with framework structures with no known natural counterpart have been made in the laboratory. The best known example of a synthetic zeolite is zeolite A, which can be related structurally to naturally occurring zeolite. It, like other synthetic zeolite, exhibits the definitive zeolitic properties of ion exchange and reversible water loss.

Another characteristic zeolite property arises from their molecular framework structures in that the combining of tetrahedral creating their porous structure happen to create regular arrays of apertures. These apertures are of such a size as to be able to selectively take up some molecules into their porous structure, whilst rejecting others on the basis of their larger effective molecular dimensions. This is the property of 'molecular sieving', which is largely unique to zeolite and responsible for their first commercial success.

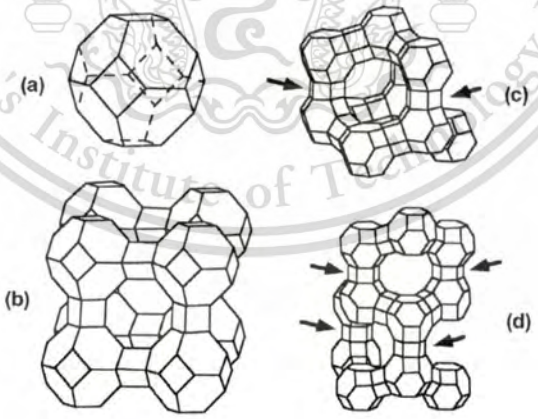

Figure 2.9 The framework structure of faujasite. Each line represents an oxygen atom and each junction represents a silicon or aluminium (Water molecules fill the space in the cages and cations float in the cages in this aqueous environment). [23]

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2.5.1 The structure of zeolite.

As stated earlier all zeolite have framework (three-dimensional) structures constructed by joining together $(SiO4)^{4-}$ and $(AlO4)^{5-}$ coordinated polyhedral. By definition these tetrahedral are assembled together such that the oxygen of each tetrahedral corner is shared with that in an identical tetrahedral (Si or Al), as shown in Figure 2.10. This corner (or vertex) sharing creates infinite lattices comprised of identical building blocks (unit cells) in a manner common to all crystalline materials.

Figure 2.10 Tetrahedral linked together to create a three-dimensional structure. [23]

These recurring units are called 'secondary building units' (sbus) and the simplest, classification described all known zeolite frameworks as arrangements linking eight sbus shown in Figure 2.11. These denote only the aluminosilicate skeleton (i.e. the Si, Al and O positions in space relative to each other) and exclude consideration of the cation and water moieties sited within the cavities and channels of the framework. The cation and water sites are complex and only fully defined in certain zeolite as will become apparent later.

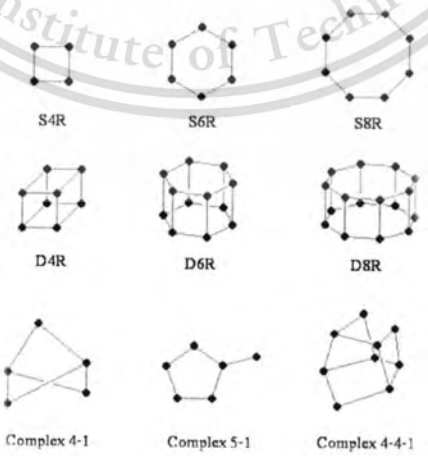

Figure 2.11 Secondary building units (SBUs) in zeolite. [23]

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For the present it should be noted that the number of cations present within a zeolite structure is determined by the number of $(AlO_4)^{5-}$ tetrahedral included in the framework. This arises from the isomorphous substitution of Al^{3+} for Si^{4+} into the component polyhedral, causing a residual negative charge on the oxygen framework. This negative charge is compensated by those cations present in the synthesis and held in the interstices of the structure on crystallization. The extent and location of water molecular incorporation depends upon (i) the overall architecture of the zeolite molecular structure, i.e. the size and shape of the cavities and channels present, and (ii) the number and nature of the cations in the structure.

The aluminosilicate skeleton can be represented in a number of ways, as for example in the traditional 'ball and stick' model (Figure 2.12). The most favored is the use of tetrahedral arrays; adopted by organic chemists, where the oxygen atoms are drawn as single 'bonds' joining together tetrahedral 'centers' depicting silicon and aluminium. This is the method used in Figure 2.12. Further perusal of Figure 2.11 shows that each sbu contains rings of tetrahedral which are equivalent to rings of oxygen atoms described as 'single six rings' etc. When the sbus are joined to create the infinite lattices they can proscribe larger rings containing 8, 10 or 12 linked tetrahedral (i.e. rings of 8, 10 or 12 oxygen atoms). These rings are obviously important structural features and are often called 'oxygen windows'.

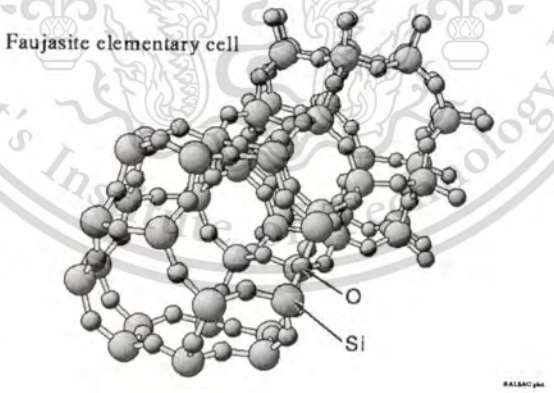

Figure 2.12 A ball and stick representation of the structure of the super cage unit with a framework diagram. [23]

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2.5.2 Zeolite application

Because of their unique porous properties, zeolites are used in a variety of applications with a global market of several million tons per annum. In the western world, major uses are in petrochemical cracking, ion-exchange (water softening and purification), and in the separation and removal of gases and solvents. Other applications are in agriculture, animal husbandry and construction. They are often also referred to as molecular sieves.

2.5.2.1 Catalysis

Zeolite has the ability to act as catalysts for chemical reactions which take place within the internal cavities. An important class of reactions is that catalysed by hydrogen-exchanged zeolite, whose framework-bound protons give rise to very high acidity. This is exploited in many organic reactions, including crude oil cracking, isomerisation and fuel synthesis. Zeolite can also serve as oxidation or reduction catalysts, often after metals have been introduced into the framework. Examples are the use of titanium ZSM-5 in the production of caprolactam, and copper zeolite in NOx decomposition.

Underpinning all these types of reaction is the unique microporous nature of zeolite, where the shape and size of a particular pore system exerts a steric influence on the reaction, controlling the access of reactants and products. Thus zeolite are often said to act as shape-selective catalysts. Increasingly, attention has focused on fine-tuning the properties of zeolite catalysts in order to carry out very specific syntheses of high-value chemicals e.g. pharmaceuticals and cosmetics.

2.5.3.2 Adsorption and separation

The shape-selective properties of zeolite are also the basis for their use in molecular adsorption. The ability preferentially to adsorb certain molecules, while excluding others, has opened up a wide range of molecular sieving applications. Sometimes it is simply a matter of the size and shape of pores controlling access into the zeolite. In other cases different types of molecule enter the zeolite, but some diffuse through the channels more quickly, leaving others stuck behind, as in the purification of para-xylene by silicalite.

Cation-containing zeolite are extensively used as desiccants due to their high affinity for water, and also find application in gas separation, where molecules are differentiated on the basis of their electrostatic interactions with the metal ions. Conversely, hydrophobic silica zeolite

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preferentially absorb organic solvents. Zeolite can thus separate molecules based on differences of size, shape and polarity.

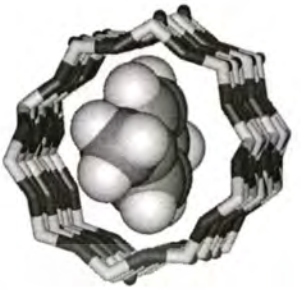

Figure 2.13 The shape of para-xylene means that it can diffuse freely in the channel of silicalite. [23]

2.5.2.3 Ion exchange

The loosely-bound nature of extra-framework metal ions (such as in zeolite NaA, right) means that they are often readily exchanged for other types of metal when in aqueous solution. This is exploited in a major way in water softening, where alkali metals such as sodium or potassium prefer to exchange out of the zeolite, being replaced by the "hard" calcium and magnesium ions from the water. Many commercial washing powders thus contain substantial amounts of zeolite. Commercial waste water containing heavy metals and nuclear effluents containing radioactive isotopes can also be cleaned up using such zeolite.

Figure 2.14 Sodium zeolite A used as a water softener in detergent powder. [23]

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2.5.2.4 Zeolite and the environment

Zeolite contribute to a cleaner, safer environment in a great number of ways. In fact nearly every application of zeolite has been driven by environmental concerns, or plays a significant role in reducing toxic waste and energy consumption.

In powder detergents, zeolite replaced harmful phosphate builders, now banned in many parts of the world because of water pollution risks. Catalysts, by definition, make a chemical process more efficient, thus saving energy and indirectly reducing pollution. Moreover, processes can be carried out in fewer steps, minimizing unnecessary waste and by-products. As solid acids, zeolite reduce the need for corrosive liquid acids, and as redox catalysts and sorbents, they can remove atmospheric pollutants, such as engine exhaust gases and ozone-depleting CFCs. Zeolite can also be used to separate harmful organics from water, and in removing heavy metal ions, including those produced by nuclear fission, from water.

2.6 Zeolite NaA

Chemical composition of zeolite NaA is $|Na_{12}(H_2O)_{27}|_8[Al_{12}Si_{12}O_{48}]_8$ and x-ray diffraction pattern is shown in figure 2.16. System structure is sodalite cage. Maximum diameter is 4.2 Å. Decompose at 700 °C. Silicon per aluminum equal to one so it is high polar and can be adsorbed high polar molecule such as water etc.

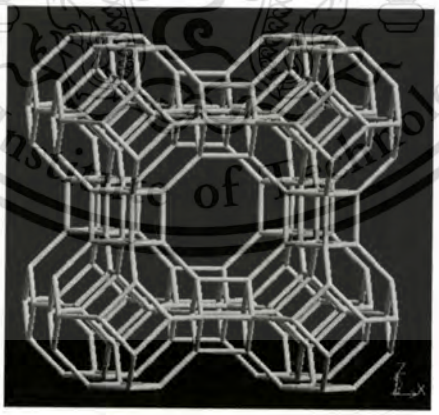

Figure 2.15 Zeolite NaA. [23]

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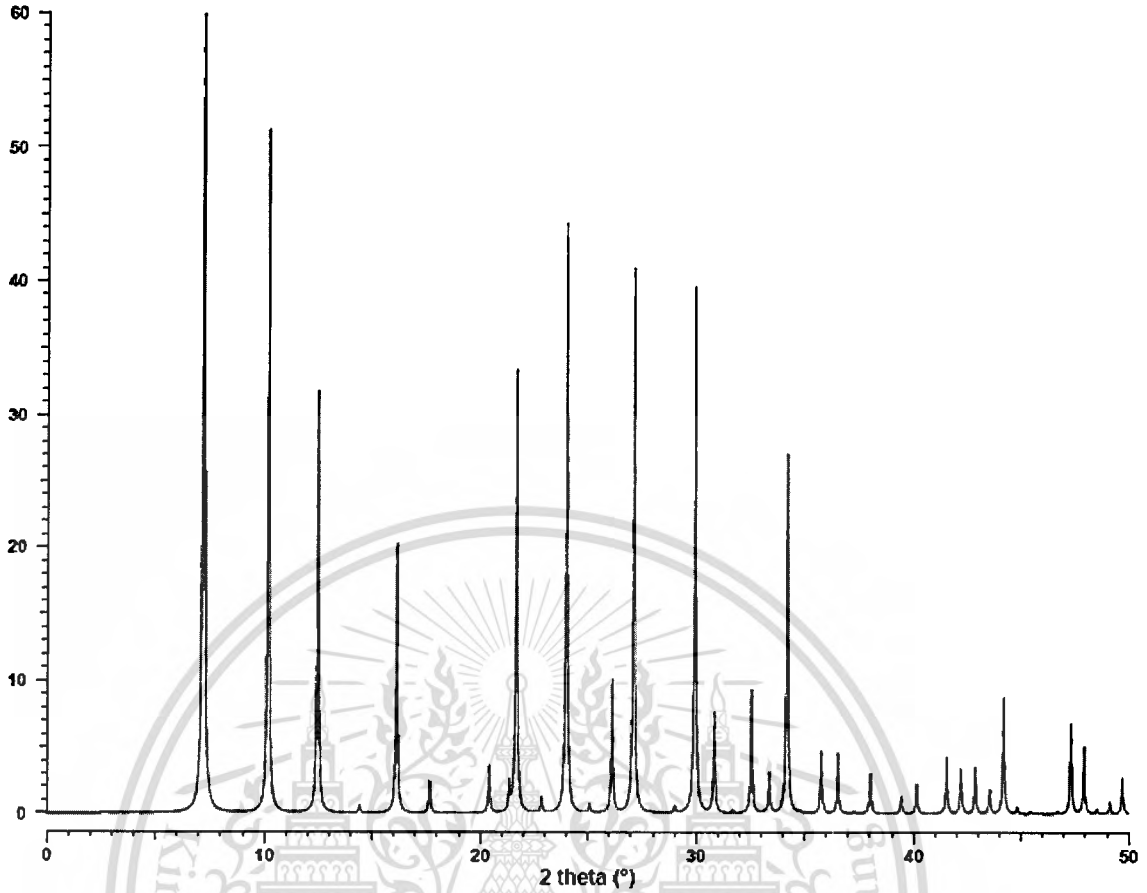

Figure 2.16 X-ray diffraction pattern of zeolite NaA. [23]

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2.7 Literature reviews

Zeolite filled Chitosan membranes for the separation of ethanol-water solutions has been investigated by many researchers. For example,

X. Chen et.al. [24] studied the preparation and characterization of HY zeolite-filled chitosan membranes using pervaporation separation (PV). It was found that the crystalline structure of chitosan was damaged with an increase in the zeolite content, indicating a strong interaction between the HYzeolite and chitosan. The separation factor of the ethanol–water mixture by PV was improved by addition of zeolite. When the HY zeolite content in the membrane was 20 wt %, the separation factor reached the maximum and remained constant during the PV process.

B.-B. Li et.al. [25] studied the chitosan-poly (vinyl alcohol)/ poly (acrylonitrile) (CS-PV/PAN) composite membranes for the separation of ethanol-water solutions using pervaporation. It was found that the separation factor (α) of CS-PVA/PAN composite membranes increased with an increase of PVA content from 0 to 40 wt%. The increase in the membrane thickness from 12 to 18 μm, the separation factor (α) of the CS-PVA/PAN composite membrane increased while permeation flux (J) decreased. With an increase of separation temperature, the separation factor (α) of CS membranes decreased but. On the other hand, PVA-PAN and CS-PVA/PAN composite membranes, the increase in separation factor but the decrease in permeation flux is observed.

N. Saim and H. Hassan [11] studied pervaporation separation of isopropanol/water mixtures using zeolite A filled chitosan membrane. It was found that both flux and selectivity increased with the addition of zeolite content in the membrane. This was explained on the basis of enhancement of hydrophilicity, selective adsorption and molecular sieving action by creation of pores in the membrane matrix.

H.-M. Guana et.al. [8] studied the poly (vinyl alcohol) multilayer mixed matrix membranes with zeolite A for the dehydration of ethanol-water mixture. It was found that the separation performance of the multilayer mixed matrix membranes (MMMM) is superior to that of multilayer homogenous membranes (MHM) without zeolite. The activation energy of the water permeation is significantly reduced from 16.22 to 10.12 kJ/mol after adding of zeolite A, indicating that water molecules require a much less energy to transport through the multilayer mixed matrix membranes because the presence of hydrophilic channels in the framework of

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zeolite. The excellent pervaporation performance of the MMMM is also resulted from the good contact between zeolite polymer matrix and cross-linked effect by fumaric acid.

P. Laomongkonnimit and K. Soontarapa [26] studied the chitosan-zeolite proton exchange membrane. They were expected for using as proton exchange membrane for substitution of import on widely used Nafion membrane. It was found that the zeolite contents less than 50% performed good separation factor as compared to Nafion membrane. In addition the tensile strength and ion exchange capacity of 4%crosslinked CS and 50% zeolite membrane were higher than those of Nafion membranes.

L. Aouinti and M. Belbachir [27] studied the maghnite-clay-H/polymer membrane for separation of ethanol-water azeotropes. The pervaporation and separation characteristics of azeotropic ethanol–water mixtures through these membranes were investigated using different weight percentages of Maghnite-H (0, 1, 2, 5, 7, 10 and 20 wt %). The best results were obtained for 7 wt. % of Maghnite-H, and an increase in the flux and separation factor was noticed.

J.-J. Shieh and R. Y.M. Huang [28] studied Chitosan/N-methylol nylon 6 blend membranes for the pervaporation separation of ethanol-water mixtures. Their pervaporation performances were investigated in terms of acid (H_2SO_4) post-treatment, feed concentration, blend ratios and temperature. The pervaporation performance of the blend membranes was significantly improved by ionizing with H_2SO_4. The blend ratio of chitosan and N-methylol nylon 6 played a different role at feed concentration. At a feed solution having low water content, an increase in chitosan content caused a decrease in permeability but an increase in separation factor. At a feed solution having high water content, the permeability increased with an increase in chitosan content, while the separation factor showed a maximum value around 60 wt% chitosan. It is proposed that extra permeation channels generated from the phase separation boundary between ionized chitosan and N-methylol nylon 6.

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Chapter 3

Experimental

3.1 Materials

1)	Acetic acid (Commercial grade)	Carlo Erba Company
2)	Chitosan (Commercial grade)	TC Union Co., Ltd. Company
3)	Zeolite NaA (Commercial grade)	PQ chemical (Thailand) Co., Ltd. Company
4)	Sodium hydroxide (Analytical grade)	SD Fined-Chem Limited. Company
5)	Glutaraldyhyde (Analytical grade)	Fluka Chemical Company
6)	Ethanol (Analytical grade)	Carlo Erba Company
7)	Acetone (Analytical grade)	Carlo Erba Company
8)	Molecular sieve	Sigma-Aldrich Company
9)	Distilled water/ De-ionized water	

3.2 Apparatus

1) Beaker
2) Erlenmeyer flask
3) Graduate cylinder
4) Volumetric flask
5) Funnel
6) Spatula
7) Stirring rod
8) Glass plate with diameter 18 cm
9) Glove
10) Balance: SARTORIUS
11) Oven: MEMMERT
12) Hot plate and Magnetic stirrer: IKA - RCT BASIC
13) Universal indicator

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14) Peristaltic pump: WATSON – MARLOW 101 U/R

15) Ultrasonic bath/Sonicator: NEY PENTAL 14 H

16) Micrometer

17) Scanning Electron Microscopy (SEM): LEO – 1455 VP

18) Gas Chromatography Machine (GC): VARION 3800

19) Thermogravimetric analyzer (TGA): PERKIN ELMER- PYRIS 1 TGA

20) X-ray diffractometer (XRD): BRUKER – D8 ADVANCE

3.3 Experimental procedure

3.3.1 Membrane preparation

1) Preparation of 2% w/v Chitosan solution

Acetic acid solution was prepared in 100 ml flask by adding 2 ml of acetic acid in 96 ml of distilled water. 2 g of chitosan flake was weighed in 100 ml beaker and dissolved with an aqueous acetic acid. The mixture of chitosan flake and acetic acid solution was kept overnight or 12 hours. The chitosan solution was then stirred with the magnetic stirrer until clear solution is obtained or about 48 hours. Glutaraldehyde solution was prepared in 100 ml volumetric flask by pipette 0.1 ml of 50% glutaraldehyde into the flask and the distilled water was filled up to the mark of the flask. The membrane was enhanced crosslinked by added 1 ml of 0.1%v/v glutaraldehyde solution in 100 ml beaker of the chitosan solution and stirred for 1 hour. The bubbles in the solution were discharged by the sonicator for 30 minutes and left it over night in order to protect bubbles occurs in the membrane.

2) Preparation of 2% w/v Chitosan solution filled with Zeolite NaA

The amount of zeolite NaA 20% w/w of chitosan or 0.5 g was dispersed in 2 ml of distilled water by sonicator for 30 minutes. The zeolite NaA dispersed in distilled water was slowly added into the chitosan solution. The solution was stirred with the magnetic stirrer until good dispersion is obtained for 15 minutes. The experiment was repeated by increasing the amount of zeolite NaA to 40% and 60% w/w of chitosan or 1.33 g and 3 g, respectively.

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3) Preparation of the multi-layer membrane

Glass plate was placed in the middle of the spin coating machine. The spin coating machine was turn on in speed of 250 rpm. The 50 ml of chitosan solution was poured in the middle of the glass plate and spun until the solution cover the glass plate estimated about 5 seconds, then the machine is turned off. The glass plate with the solution was dried in an air oven at 50°C for 15 minutes, then the glass plate with solution was taken out from the air oven and the second layer was casted by poured another 50 ml of solution with the same spinning speed. The glass plate with the multi-layer was again dried in the air oven at 50°C for 24 hours.

10% v/v sodium hydroxide (NaOH) solution was prepared by weighing 10 g of sodium hydroxide and dissolved with 20 ml of distilled water in 100 ml beaker. The sodium hydroxide solution was added in 100 ml volumetric flask and distilled water was filled up to the mark of the flask. The dry membrane was neutralized by immersed in sodium hydroxide solution for 90 minutes. The membrane was washed with distilled water until pH equal to 7.5. The pH of the membrane was checked by universal indicator. The neutralized membrane was again dried in an air oven at 50°C for 2 hours. The membrane thickness is measured 3 times in different places by a micrometer. Average thickness of the membrane should be 120±10 micrometers. If the thickness of the membrane is less than specified, the experiment was repeated again with addition of the mixture solution until the thickness of the membrane approximately 120±10 micrometers. The dried membrane is stored in dust free container prior to use.

3.3.2 Characterization of the membrane

1) The membranes morphology can be determined by scanning electron microscopy (SEM).

The cross-section surface of the membrane was prepared and examined by Scanning Electron Microscopy (SEM). The sample was prepared by cutting the membrane into rectangular shape 0.5 x 2 cm^2. It was immersed in liquid nitrogen for 1 minute and broken into half. The prepared sample was placed on stub and coated with gold before analyzed.

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2) The zeolite structure in membranes can be determined by X-ray diffractometry (XRD).

The powder of zeolite NaA was pressed in the sample holder and the zeolite NaA structure in the membranes was prepared by cutting the membrane into square shape of 4 x 4 cm^2 and then was placed on the sample holder. Finally, the zeolite structure was analyzed with the conditions of CuK_α (40 kV, 40 mA), wavelength 1.5406 Å, angle 5-60° and step size 0.04%.

3) The zeolite content in the membranes can be determined by Thermogravimetric Analysis (TGA).

The samples were prepared by weighing 10-20 mg and then analyzed with the temperature range of 50 – 800 °C at a heating rate of 10°C/min under air zero atmospheres.

3.3.3 Liquid permeation process of ethanol/water separation

1) Assembly of the membrane and leaking test.

8 x 8 cm^2 base of the cell membrane was tight by using stainless steel rod and nuts at each corners as shown in Figure 3.1.

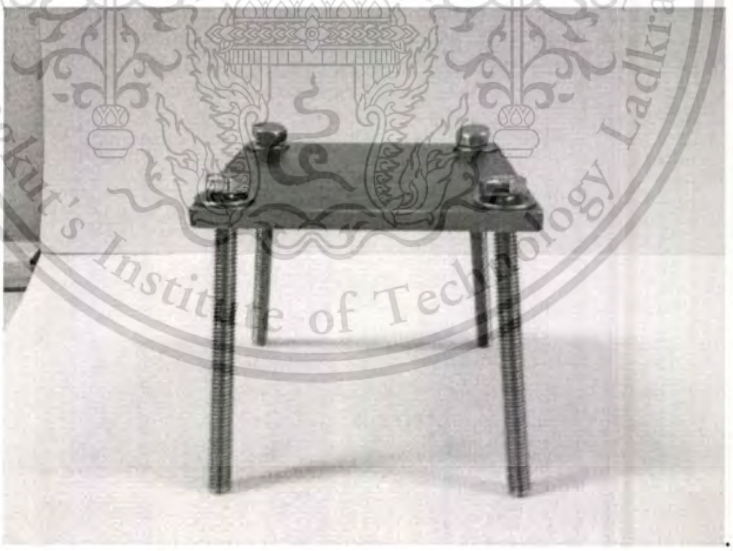

Figure 3.1 Base of the cell membrane (upside-down).

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The membrane cell was set up using through polypropylene frame as shown in Figure 3.2. The frames sizes are 8×8 cm^2 with the active membrane size 5×5 cm^2.

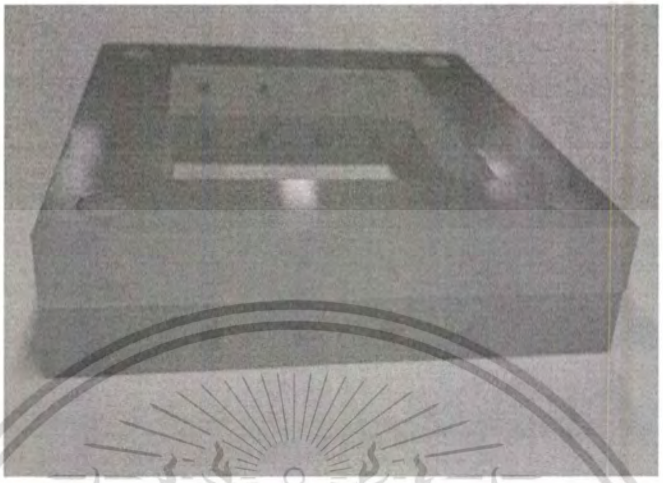

Figure 3.2 Polypropylene used as membrane cell.

The membrane size should be 9×9 cm^2 which is long enough for stretching on the lower membrane frame and then the upper frame was placed on the membrane. Finally, the membrane cell was tight by nuts in each corner for preventing the solution leak out as shown in Figure 3.3.

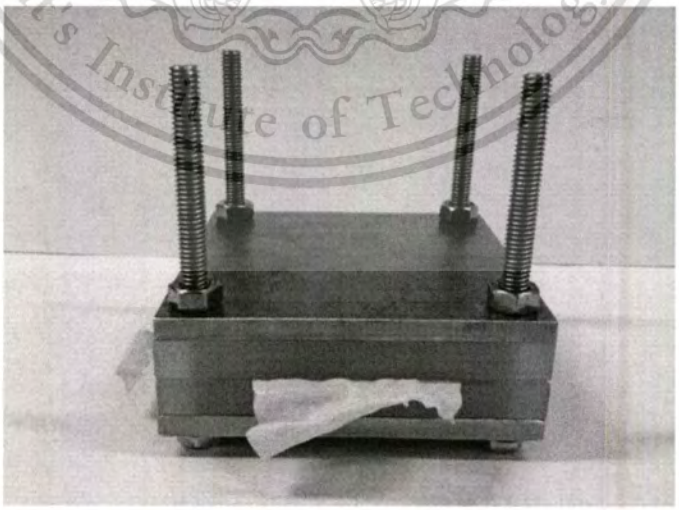

Figure 3.3 Cell membrane.

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The holes beside the cells were connected in by silicone tubes. The membrane leaking test was done by filling acetone solution into the membrane cell. The membrane cell was weighed and the data was recorded. The membrane cell was left for 1 or 2 hours before weighing again. If the weight is maintained indicating that the membrane cell is not leak, and then the acetone solution was poured out.

2) Study the efficiency of liquid permeation of the membrane.

Ethanol solutions with 50%, 75%, and 95% v/v were used as feed. The 50%, 75% and 95% v/v ethanol solutions were prepared in 100 ml volumetric flask by mixing 50 ml, 75 ml and 95 ml of ethanol and 50 ml, 25 ml and 5 ml of distilled water, respectively. The membrane cell was fed by 50% v/v ethanol solution in feed side while acetone solution was fed as carrier in the other side.

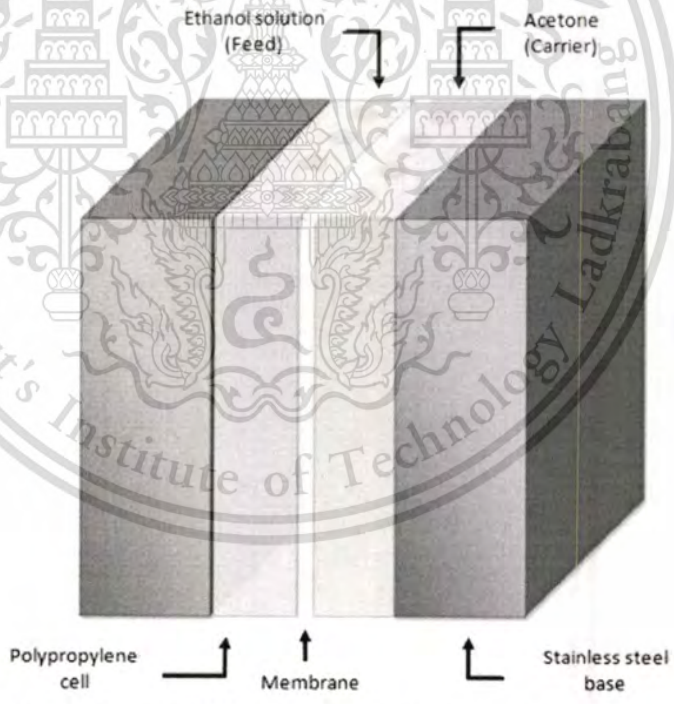

Figure 3.4 System of liquid permeation of membrane cell.

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The feed sample was collected before running separation process and the retentate solution also was collected separation until reaching equilibrium. While carrying on the separation process, the samples from permeate side were collected every 30 minutes until it reached the equilibrium. After the separation for 8 hours, the samples were analyzed by Gas Chromatography (GC) under the following conditions:

Type of Column	: Porapak Q
Column Oven Temperature	: 150 °C
Injector Temperature	: 200 °C
TCD Detector Temperature	: 160 °C
Filament Temperature	: 200 °C
Carrier gas	: Helium
Flow rate (ml/min)	: 40 ml/min
Pressure	: 5 psi
Sample size	: 0.5 μL

3.3.4 Point of interest

1) The efficiency of the membrane filled with the different amounts of zeolite NaA (20%, 40% and 60%) was studied.
2) The efficiency in liquid permeation of the membrane with different ethanol feed concentrations (50%, 75%, 95 % v/v) was studied.

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Chapter 4

Results and Discussion

4.1 Membrane preparation

Chitosan is pale yellow powder, dissolved with an acetic acid as shown in Figure 4.1. The solution prepared is pale clear yellow color with high viscosity as shown in Figure 4.2. The membranes were prepared by casting the solutions with spin coating machine as in Figure 4.3.

Figure 4.1 Chitosan powder in acetic acid solution.

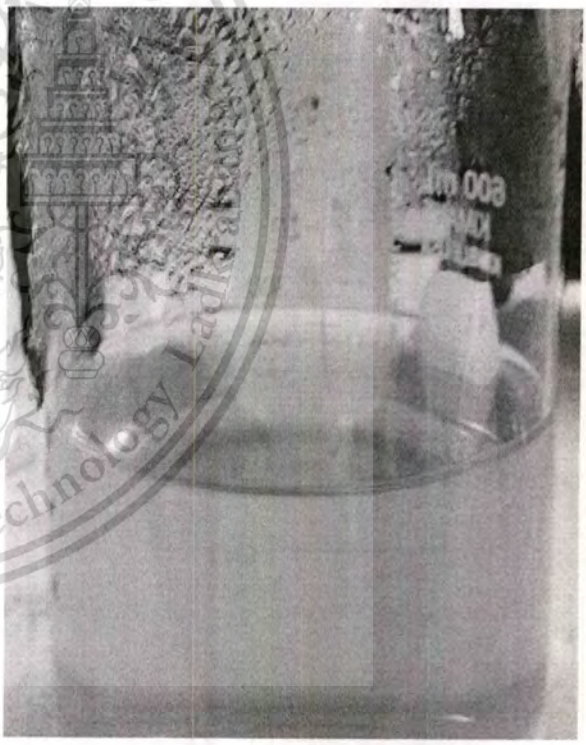

Figure 4.2 Chitosan solution.

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Figure 4.3 Spin coating machine and measuring tool.

The speed for spin coating machine was varied for adjusting thickness of the membranes. The thicknesses of the membranes are shown in Table 4.1.

Table 4.1 Thickness of multi-layer membranes with different spinning speeds using 100 ml of chitosan solution filled with 40% w/w zeolite NaA.

Conditions	Speed (rpm)	Thickness of the membrane (μm)	
		2 layers	3 layers
1	150	238±8.0	248±7.0
2	200	160±6.0	180±4.0
3	250	110±2.0	130±1.0
4	300	90±2.0	100±2.0

From the Table 4.1, the thicknesses of the membranes are varied with the speed of the spin coating machine by using 100 ml of chitosan solution filled with 40% w/w zeolite NaA. The value shows that with an increase in speed of the spin coating machine, the membrane thickness

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is decreased with a greater uniformity throughout the membrane. This is because the centrifugal force is increased with a speed of the machine. Therefore, the solution can be readily spread all over the glass support. The thickness of the membranes with spinning speed 250 and 300 rpm are similar but spinning speed 300 rpm was too fast to maintain the film at this viscosity. The solution was spread out off the plate. Hence, the spinning speed 250 rpm was more desirable.

The volume of the solution was adjusted to 50 ml in order to decrease the solution spreading out off the glass support and to reduce the interaction between the layers of the membrane. The thickness of chitosan membrane without and with 20%, 40%, and 60% w/w zeolite NaA of chitosan were prepared using 50 ml with spinning speed of 250 rpm as shown in Table 4.2. The membranes were now ready for liquid permeation process for ethanol/water separation.

Table 4.2 Thickness of multi-layer membranes using 50 ml of chitosan solution filled with different zeolite contents at 250 rpm.

Membrane	**%w/w Zeolite NaA**	**Thickness of the membrane (μm)**	
		2 layers	**3 layers**
Pure CS	-	60±1.0	110±1.0
Ze_20	20	50±1.0	100±1.0
Ze_40	40	70±0.5	133.3±0.2
Ze_60	60	130.0±0.4	-

The membranes with similar thicknesses (100-130 μm) were chosen to be tested for liquid permeation process for ethanol/water separation.

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4.2 Membrane Characterization

4.2.1 Zeolite structure in the membranes

The crystallinity of zeolite NaA and the chitosan membrane filled with 60% w/w zeolite NaA were investigated using X-ray Diffraction method (XRD) as shown in Figure 4.4.

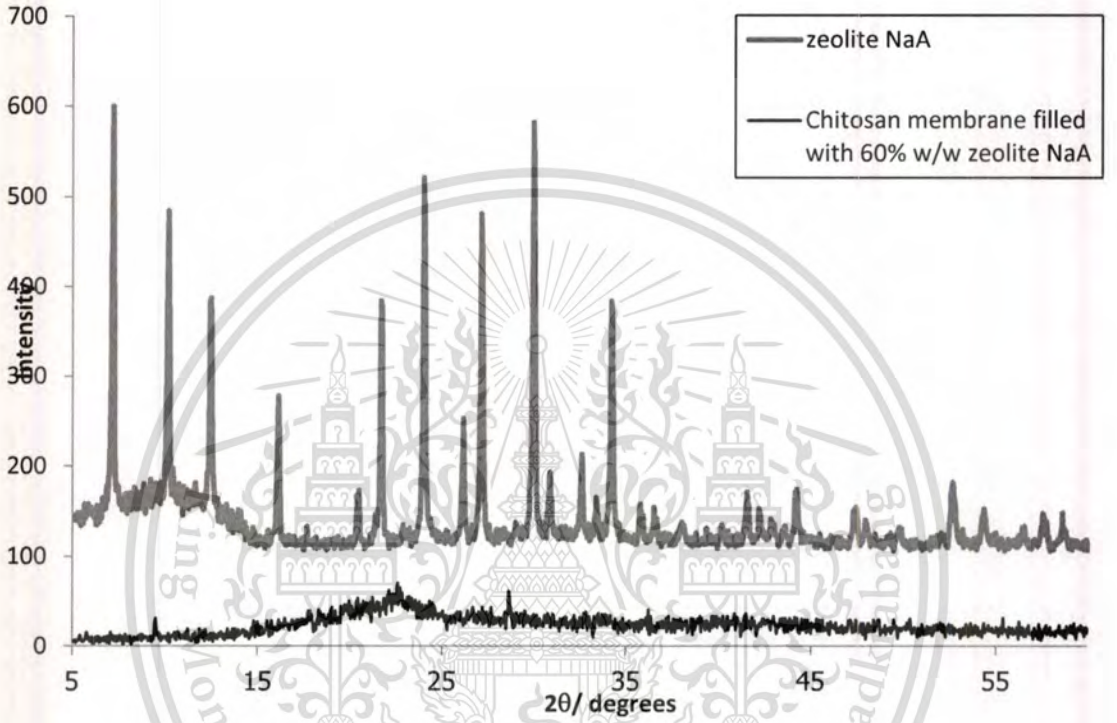

Figure 4.4 XRD patterns of zeolite NaA and chitosan membrane filled with 60% w/w zeolite NaA.

The XRD patterns of zeolite NaA in the chitosan membrane filled with 60% w/w zeolite NaA are not clearly observed because of overlapping with x-ray diffraction of chitosan. In addition, the structure of zeolite NaA might be destroyed in acidic solution (i.e. chitosan powder was dissolved in an aqueous acetic acid). This expected an existence of aluminosilicate aggregate.

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4.2.2 Membranes morphology

Morphology of the membrane was investigated using Scanning Electron Microscopy (SEM) in order to observe the dispersion of zeolite NaA in the chitosan membrane. The cross sections of the membrane are shown in Figures 4.5-4.8.

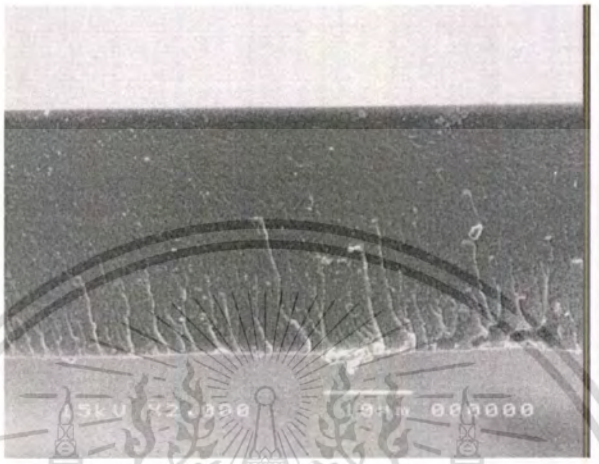

Figure 4.5 Cross section morphology of pure chitosan membrane.

Figure 4.6 Cross section morphology of membrane filled with 20% zeolite NaA.

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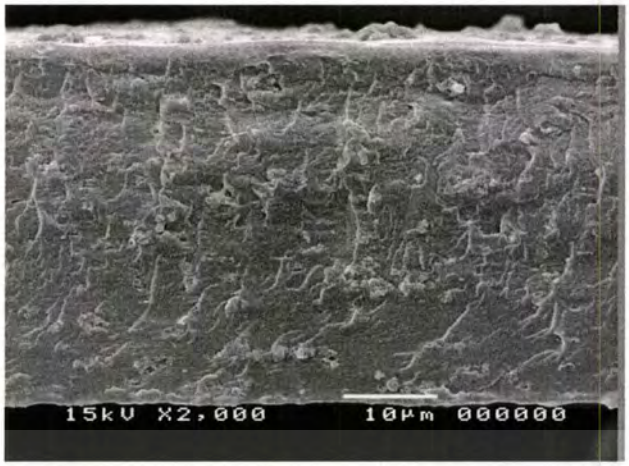

Figure 4.7 Cross section morphology of membrane filled with 40% zeolite NaA.

Figure 4.8 Cross section morphology of membrane filled with 60% zeolite NaA.

The zeolite NaA in the chitosan membrane cannot be clearly seen in Figures 4.6-4.8. It is suggested partial dissolution of the structure of zeolite NaA. Hence, the size of zeolite NaA is smaller than the original size (4 µm). Another possibility, it might be destroyed in acidic solution. Hence, the aluminosilicate aggregate was observed.

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The zeolite NaA content in the membranes (20%, 40% and 60% w/w) was investigated using Thermogravimetric analysis method (TGA) as shown in Table 4.3.

Table 4.3 Zeolite content in the membranes.

Membrane	%w/w loaded wet zeolite NaA	% w/w of remained residue	% w/w of dried zeolite NaA
Pure CS	-	6.14	-
Ze_20	20	20.09	15.18
Ze_40	40	28.24	24.56
Ze_60	60	52.18	49.72
Zeolite NaA	100	80.91	80.91

Note: The calculation is shown in Appendix A.

Table 4.3 showed that pure chitosan membrane has 6.14% remaining residue. This is because the remained chitosan was decomposed into coke. Therefore, the remaining weight observed is the weight of the coke deposit. From Table 4.3, the pure zeolite NaA contains 80 wt% of dried zeolite and the other 20 wt% is the percent of water in zeolite. This is because the zeolite NaA has a high affinity for water; therefore pure zeolite would contain a large amount of water inside. Hence, the dried zeolite contents of the membrane are lower than the %w/w wet zeolite NaA. From the same reason as zeolite and the coke deposit leads to the chitosan membranes filled with 20%, 40% and 60% w/w zeolite have the dried zeolite content of 15.18%, 24.56% and 49.72% w/w of zeolite, respectively.

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4.3 Liquid permeation test of water-ethanol separation

In this study, the chitosan membrane filled with 20%, 40% and 60% w/w zeolite were used for the water/ethanol separation using 50%, 75% and 95% v/v ethanol solution as feed. The samples from permeate side were analyzed by Gas Chromatograph (GC). Area from the chromatogram was used for calculation of water and ethanol fluxes (as shown in Appendix D). The relationship between flux of water and ethanol versus permeation time were plotted as Figures 4.9 – 4.12.

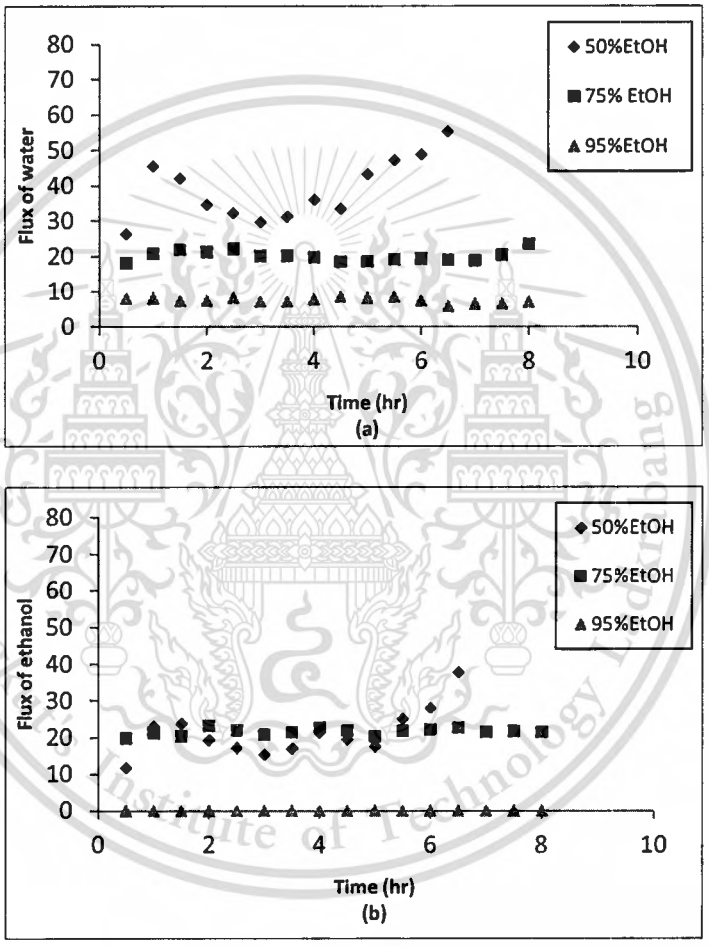

Figure 4.9 Water-ethanol separation of pure chitosan membrane with 50%, 75% and 95% v/v of ethanol solution (a) flux of water versus time (b) flux of ethanol versus time.

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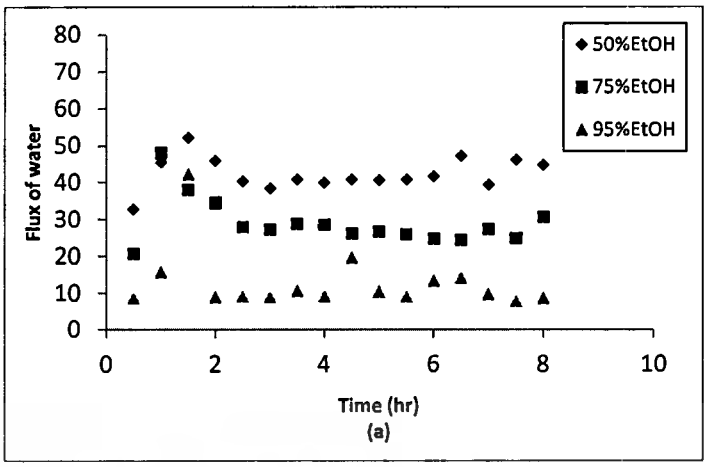

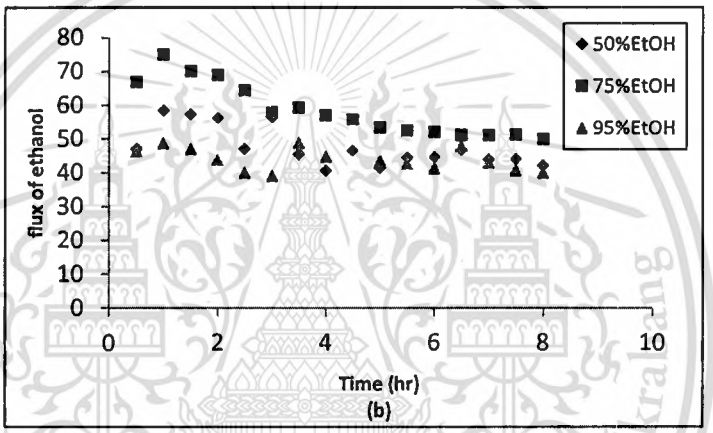

Figure 4.10 Water-ethanol separation of chitosan membrane filled with 20% zeolite NaA using 50%, 75% and 95% v/v of ethanol solution as feed (a) flux of water versus time (b) flux of ethanol versus time.

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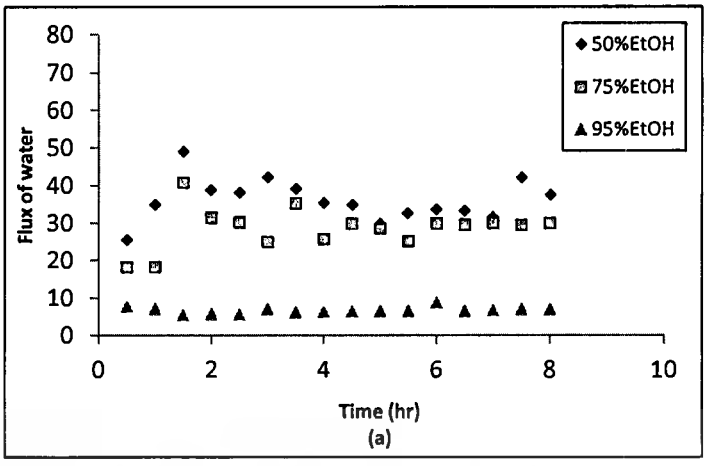

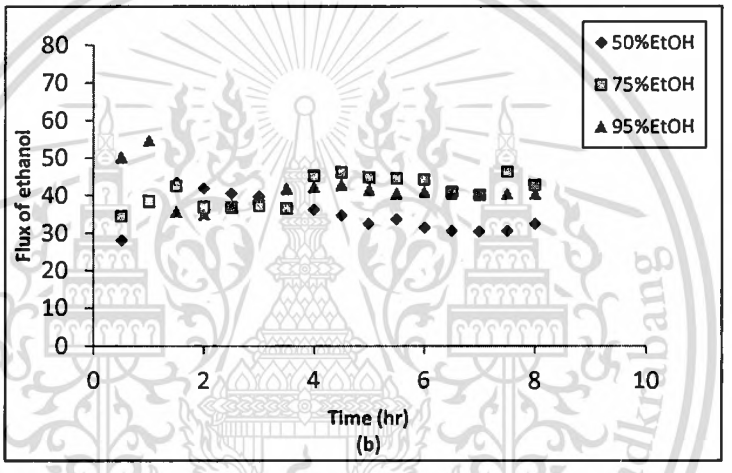

Figure 4.11 Water-ethanol separation of chitosan membrane filled with 40% w/w zeolite NaA using 50%, 75% and 95% v/v of ethanol solution as feed (a) flux of water versus time (b) flux of ethanol versus time.

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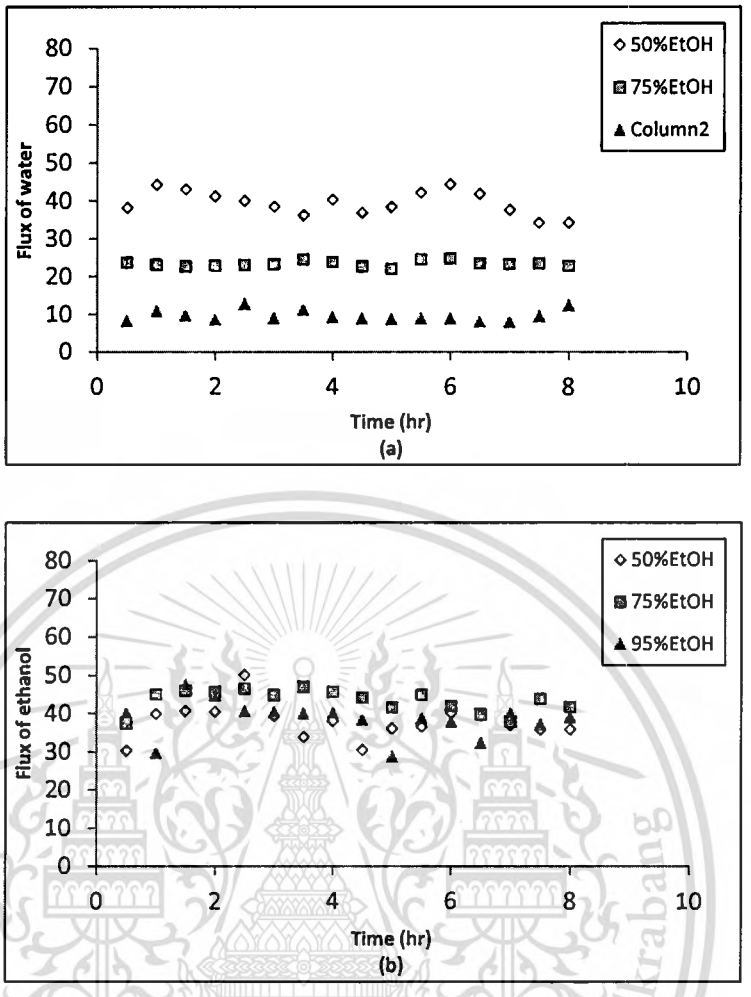

Figure 4.12 Water-ethanol separation of chitosan membrane filled with 60% w/w zeolite NaA using 50%, 75% and 95% v/v of ethanol solution as feed (a) flux of water versus time (b) flux of ethanol versus time.

Figures 4.9-4.12 showed that the water flux is decreased with an increase in the ethanol concentration for all membranes. In addition, water flux is increased with increasing the amount of zeolite in the membrane. The results including the water flux, ethanol flux, total flux and separation factor of the chitosan membrane without and with different zeolite NaA contents and with different feed concentrations were summarized in Table 4.3.

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Table 4.4 Flux and separation factor of membranes.

Membrane	% w/w Zeolite	Membrane Thickness (μm)	% v/v Ethanol	Flux Water ($g/hr.m^2$)	Flux Ethanol ($g/hr.m^2$)	Total flux ($g/hr.m^2$)	Separation factor
Pure CS	-	110	50%	48.73	39.30	88.03	4.05
			75%	19.35	30.95	50.29	1.53
			95%	6.49	-	6.49	α
Ze_20	20	100	50%	40.73	30.40	71.13	0.62
			75%	25.92	52.42	78.34	1.40
			95%	7.80	40.84	48.64	1.81
Ze_40	40	133.3	50%	40.80	31.37	72.17	1.16
			75%	29.96	49.28	79.24	1.98
			95%	8.61	40.35	48.96	2.44
Ze_60	60	130	50%	42.08	36.56	78.64	1.22
			75%	34.61	44.98	79.59	1.90
			95%	9.31	40.07	49.38	3.56

The case of the different feed concentrations, the water fluxes are decreased with an increase in the ethanol concentration in the feed for all membranes. The water diffusion describes the spread of water from regions of higher water concentration to the regions of lower water concentration. The concept of diffusion is the mass transfer driven by a concentration gradient. The water molecules diffuse through the membrane down a concentration gradient are shown as Figure 4.13.

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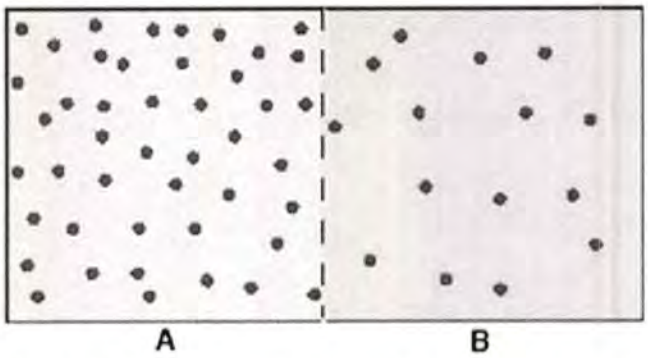

Figure 4.13 The diffusion of water from regions of higher water concentration (A) to regions of lower water concentration (B).

According to the above explanation, the more the water concentration in the feed, the more the driving force for diffusion. Therefore, high water flux diffuses through the membrane with 50% ethanol feed. In contrast, the lower the water concentration in the feed, the lower the driving force for diffusion as seen by 95% ethanol feed.

The ethanol flux of the membrane filled with 20%, 40% and 60% w/w zeolite NaA with different ethanol feed concentrations is approximately 40±10 g/ hr·m^2. This showed that the ethanol feed concentration does not strongly effect to the ethanol flux of these membranes. However, in the case of pure chitosan membrane at the lower ethanol concentration in the feed (50% and 75% v/v), the ethanol fluxes are decreased with increasing the ethanol concentration in the feed. This is because the feed with a low ethanol concentration containing high amount of water can swell the membrane. The swollen membrane becomes softer, hence more ethanol can pass through the membrane. This causes the high ethanol flux even at the lower ethanol concentration in the feed. On the other hand, at higher ethanol concentration in the feed (95% v/v), the feed contains low water content. The membrane is less swell as compared to that with low ethanol concentration in the feed and becomes more rigid. Accordingly, the ethanol cannot readily diffuse through the membrane and no ethanol flux can be observed at 95% v/v ethanol concentration in the feed.

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The total fluxes remain similar for the feed with the lower ethanol concentration (50% and 75% v/v). When the ethanol concentration in the feed is increased to the 95% v/v; however, the total flux is markly decreased. This is because the lower the water concentration in the feed, the less the swelling of the membrane. The rigid membrane provides slower permeation, hence the total flux is significantly decreased.

In the case of different zeolite NaA contents in the membrane, the water fluxes at higher ethanol concentration in the feed (75% and 95% v/v) are increased with increasing zeolite NaA content. This is because aluminosilicate is a hydrophilic mineral having good interaction with water. Therefore, more water can pass through the membrane; i.e. the water fluxes are increased. Moreover, when the aluminosilicate aggregate content is increased, the distances between each aluminosilicate aggregate in the dense membrane also decreased and this distance is called "Diffusion pathway". The gap between the aluminosilicate aggregate and chitosan known as "Interconnecting void" are also increased by increasing the zeolite NaA content. The diffusion pathway in the membrane with different zeolite NaA contents are demonstrated in Figure 4.14.

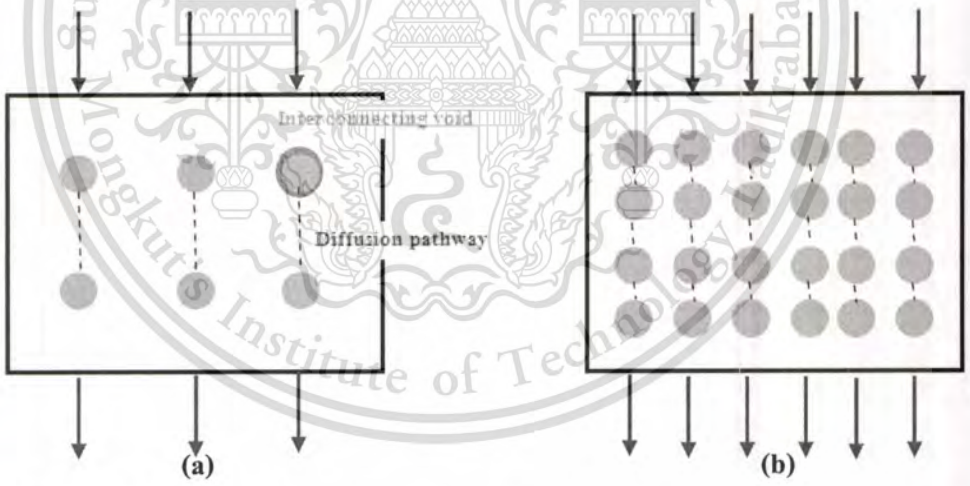

Figure 4.14 Diffusion pathway (a) low zeolite NaA content (b) high zeolite NaA content.

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It can be seen that water must diffuse through the dense membrane before reaching the zeolite particles. The membrane with lower amount of zeolite NaA, and hence aluminosilicate aaggregate as in Figure 4.14 (a) shows the longer diffusion pathway and lower interconnecting void. This inhibits molecular diffusion and hence the water flux is low. On the other hand, the membrane with higher amount of zeolite NaA added as in Figure 4.14 (b) shows the shorter diffusion pathway and higher interconnecting void. This would facilitate diffusion through the membrane leading to higher water flux.

However, at lower ethanol concentration in the feed (50%v/v), the water fluxes for the membrane filled with the zeolite NaA are in turn lower than the pure chitosan membrane. This is because at 50% v/v ethanol, the feed contains high amount of water that can swell the membrane. Swelling readily increased membrane flexibility that facilitates diffusion in the membrane. As the amount of zeolite NaA in the membrane is increased, i.e. more aluminosilicate aggregate, the membrane becomes harder. Hence, swelling of the membrane with the aluminosilicate aggregate would be relatively less, as compared to the pure chitosan membrane. Therefore, the water flux of the membrane with zeolite NaA is lower than that for pure chitosan membrane.

The ethanol flux for the pure chitosan is lower than that filled with zeolite NaA. This is because the chitosan membrane filled with zeolite NaA has interconnecting void. Therefore, when the water passes through the membrane, the ethanol also comes along with the water. This leads to an increase in ethanol flux when zeolite NaA is incorporated. However, when the zeolite NaA content in the membrane is increased, the ethanol flux is slightly decreased because aluminosilicate aggregate is selective for water. On the other hand, at lower ethanol concentration in the feed (50%v/v), the ethanol flux is in turn increased. This is because there is more interconnecting void between zeolite particles and chitosan, hence, the ethanol passes through the membrane. In addition, ethanol flux of the pure chitosan membrane is higher than that filled with zeolite NaA because of the effect of swelling as mentioned earlier.

As more interconnecting void is obtained, the total fluxes should be increased with increasing the zeolite NaA content as shown by the total fluxes of the higher ethanol concentration in the feed (75% and 95%). However, when comparing the chitosan membrane without and with zeolite NaA at lower ethanol concentration in the feed (50% v/v), the total flux of the membrane without zeolite NaA is higher than the total fluxes of the chitosan membrane filled with zeolite NaA. This is also because the effect of swelling as discussed earlier.

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The water separation factor is increased with an increase in ethanol concentration in the feed. However, at 50% v/v ethanol concentration, the feed contains the same volume fraction of water and ethanol. The water molecules interact with the ethanol molecules by strong H-bonding which is known as "Coupling effect". When the water passes through the membrane, the ethanol comes along with the water. Hence, the water separation factor of the lower ethanol concentration in the feed is relatively low. At higher ethanol concentration, the ethanol molecule cannot readily diffuse through the membrane filled with zeolite NaA as the aluminosilicate aggregate is selective for water. The water molecules strongly absorb and diffuse through the membrane. Hence, the water separation factor is high.

The water separation factor for the pure chitosan membrane used for 95% v/v ethanol solution showed the highest value in this study. This is because the membrane is less swollen by water as 95% ethanol concentration in the feed. The higher ethanol concentration in the feed, the membrane becomes harder. This is inhibiting ethanol diffusion through the membrane. No flux of ethanol can be obtained, thus the separation factor is extremely high.

For the case of the chitosan membrane filled with zeolite NaA, the separation factors are increased with increasing the zeolite NaA content. This is due to the high affinity for water of the aluminosilicate aggregate. Therefore, the separation factors are increased with increasing the zeolite NaA content.

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Chapter 5

Conclusion and Suggestion

This research aims to improve the efficiency of ethanol/water separation of chitosan membrane by incorporating zeolite NaA (20%, 40% and 60% w/w zeolite NaA). The XRD pattern of zeolite NaA in the chitosan membrane filled with 60% w/w zeolite NaA showed some positions which are not matched with pure zeolite NaA. Furthermore, the morphology of the zeolite NaA in the chitosan membranes filled with 20%, 40% and 60% w/w zeolite NaA cannot be clearly observed. This expected that the zeolite NaA might be destroyed in acidic solution and led to an existence of aluminosilicate aggregate. The %w/w of dried zeolite NaA of the membrane filled with 20%, 40% and 60% w/w zeolite NaA are 15.18, 24.56 and 49.72, respectively. These are lower than the %w/w loaded wet zeolite NaA because of the coke deposit and the water in zeolite NaA structure.

For the case of an increasing in the ethanol concentration in the feed, water flux is decreased due to the lower water concentration in the feed, the lower driving force for diffusion. The different ethanol concentrations in the feed do not strongly effect to the ethanol fluxes of the membrane. The total flux remains similar while the water separation factor is slightly increased. However, the pure chitosan membrane at lower ethanol concentration in the feed (50%v/v), the ethanol flux is decreased with increasing the ethanol concentration in the feed. This is because less swollen of the membrane and hence, this inhibits the ethanol diffusion through the membrane. On the other hand, no ethanol flux in the pure chitosan membrane can be observed at the high ethanol concentration in the feed (95% v/v). This is because the ethanol molecules cannot readily diffuse through the membrane while the water molecules strongly absorb and diffuse through the membrane. Therefore, the water separation factor is extremely high.

In the case of different zeolite NaA contents in the membrane, the water and total fluxes are increased with increasing zeolite NaA content. This is because the shorter diffusion pathway and the interconnecting void are increased. However, at lower ethanol concentration in the feed (50% v/v), the water and total fluxes for the membrane filled the zeolite NaA are lower than that of the pure chitosan membrane. This is because the membranes filled zeolite NaA are less swollen. The ethanol fluxes of the membrane are decreased with an increasing of zeolite NaA

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content because the aluminosilicate aggregate is selective for water. However, the ethanol flux at lower ethanol concentration in the feed (50% v/v) is in turn increased with increasing zeolite NaA content because of the increase of interconnecting void. The water separation factors are increased with increasing aluminosilicate aggregate. This is because it has a high affinity for water which allows water to pass through it. However, at 95% v/v ethanol solution; the water separation factor for the pure chitosan membrane showed the highest value. This is because the membrane becomes more rigid and leads to inhibit of the ethanol diffusion. Thus the separation factor is extremely high.

Suggestion

1. The pH of chitosan solution should be adjusted before the zeolite NaA is incorporated.
2. The zeolite content could be increased to enhance the efficiency of the membrane for water/ethanol separation due to the hydrophilicity, selective adsorption and molecular sieving of the zeolite.
3. The membrane can be used in other processes for water/ethanol separation, i.e. pervaporation and gas permeation.
4. The life time of the membrane should be studied by testing the separation for many times in order to observe the efficiency of the membrane.

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Appendix A

Thermogram

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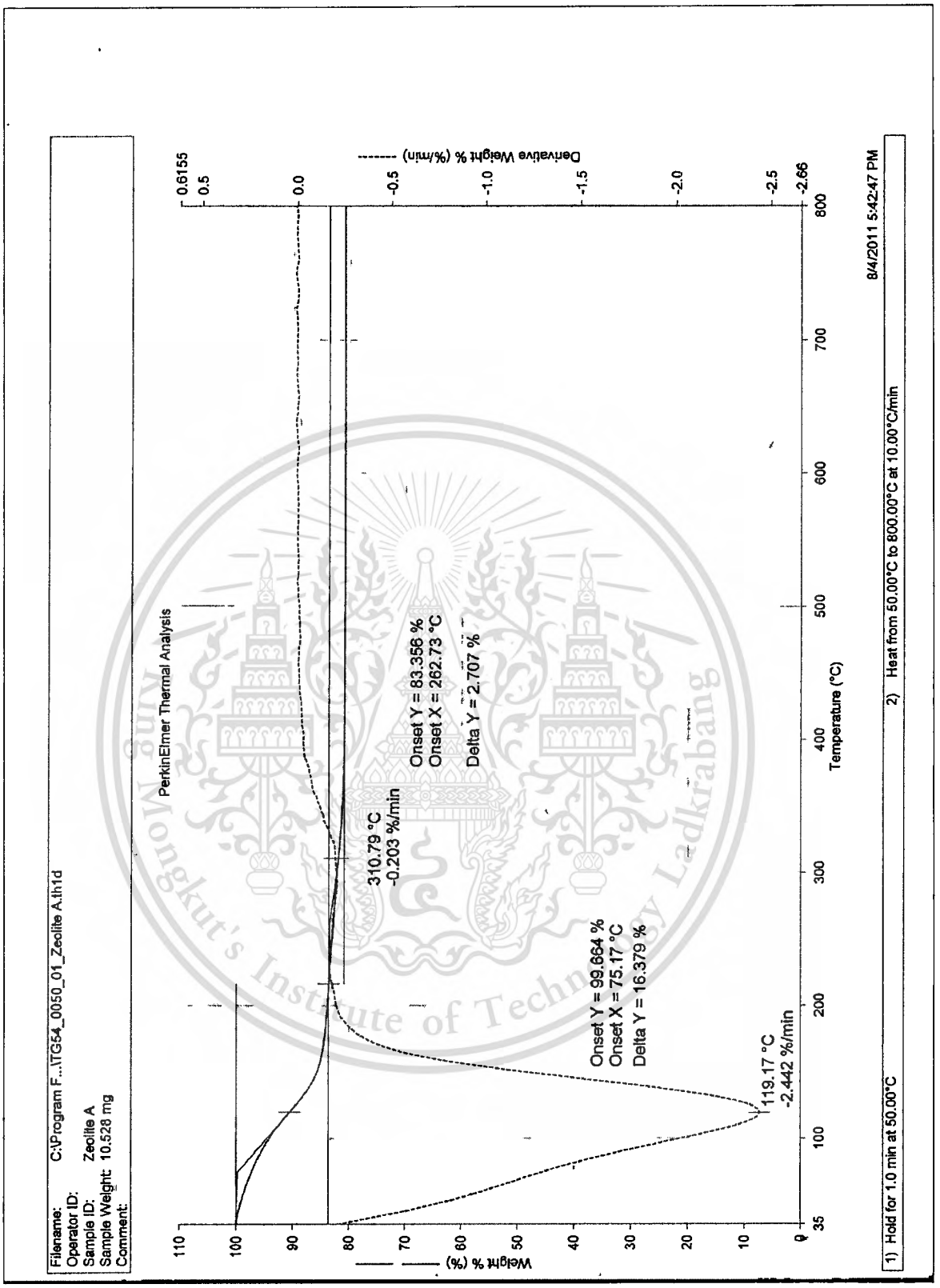

Figure A.1 Thermogram of zeolite NaA.

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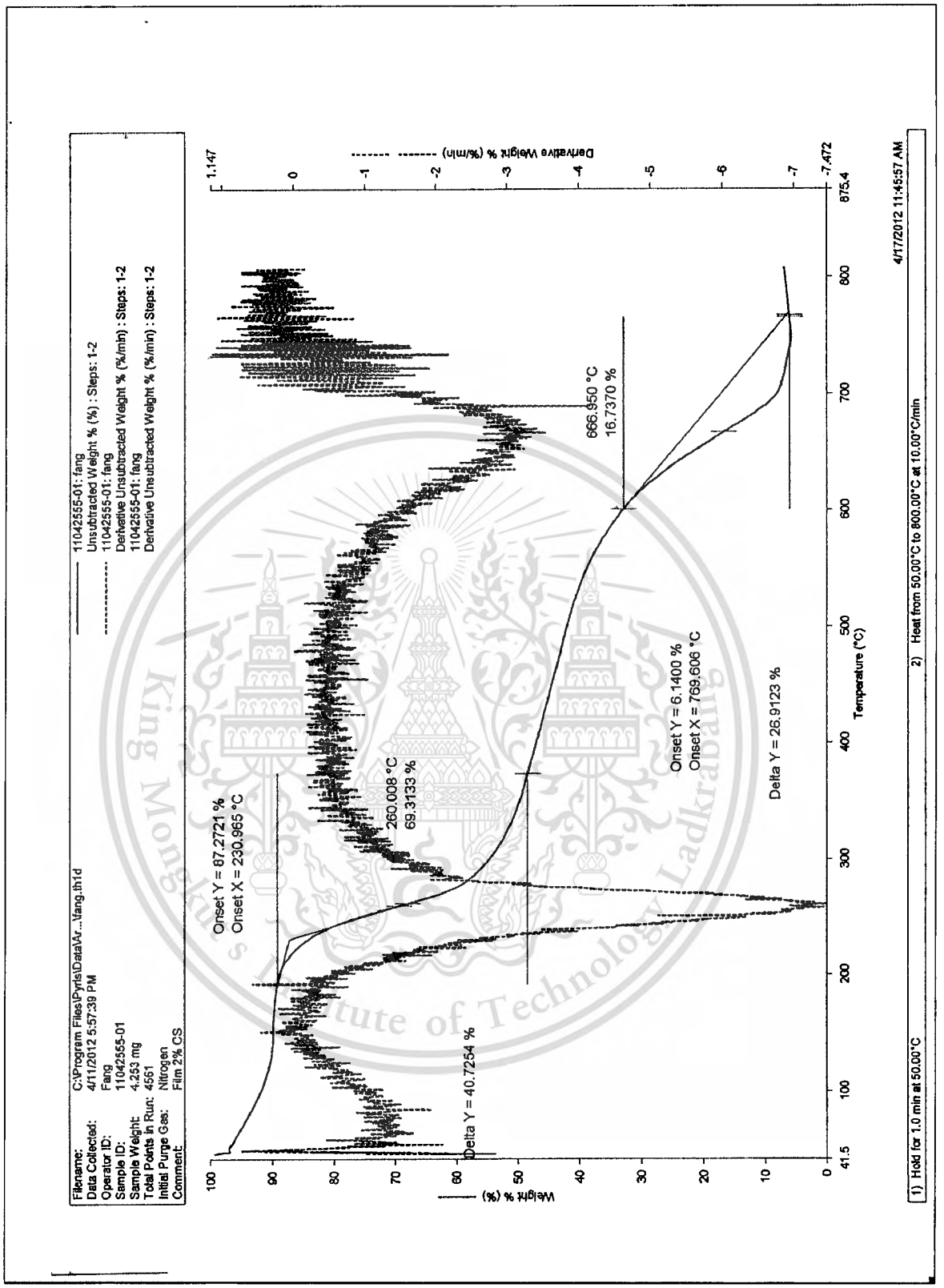

Figure A.2 Thermogram of the pure chitosan membrane.

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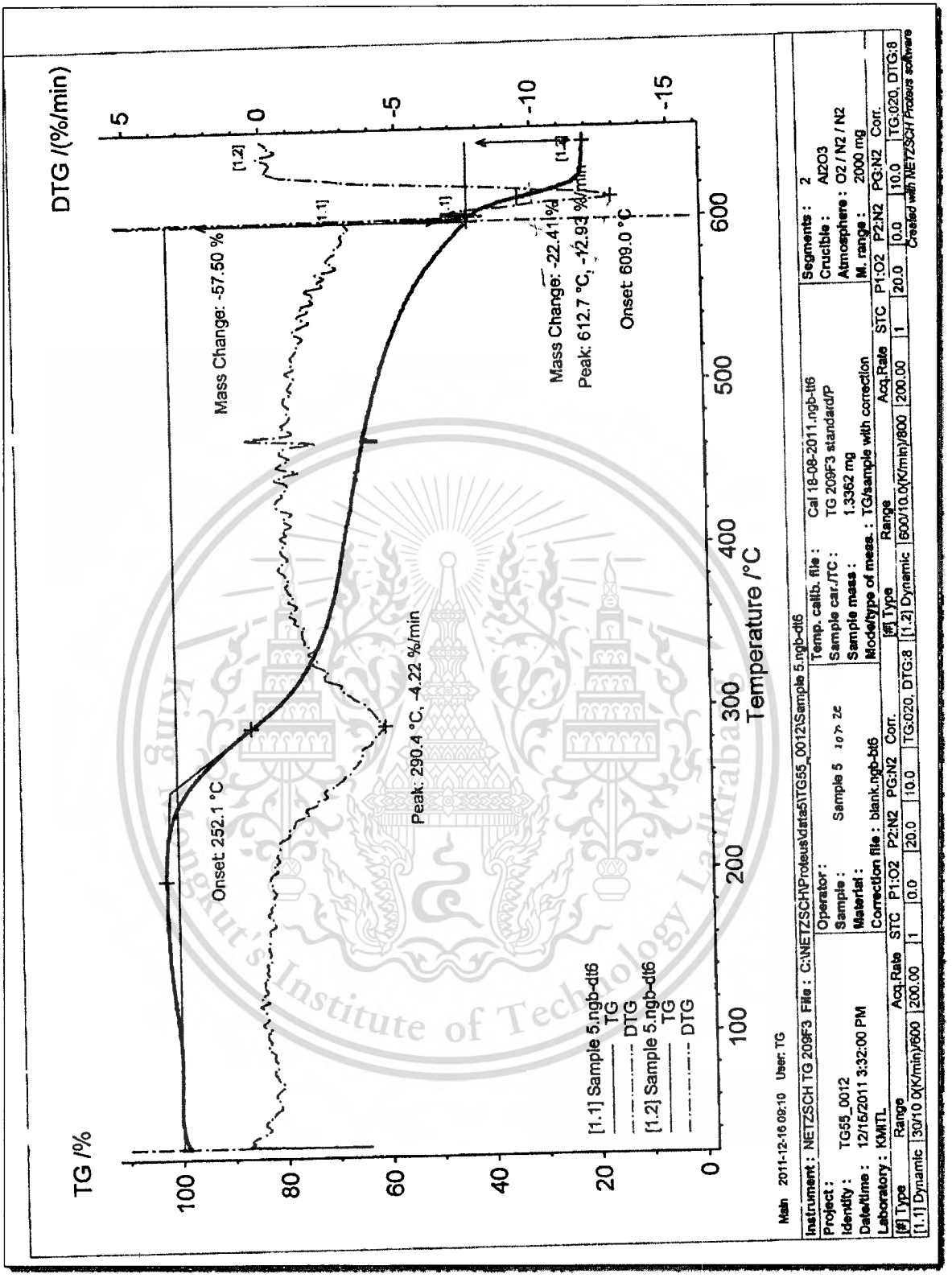

Figure A.3 Thermogram of the chitosan membrane filled with 20% w/w zeolite NaA.

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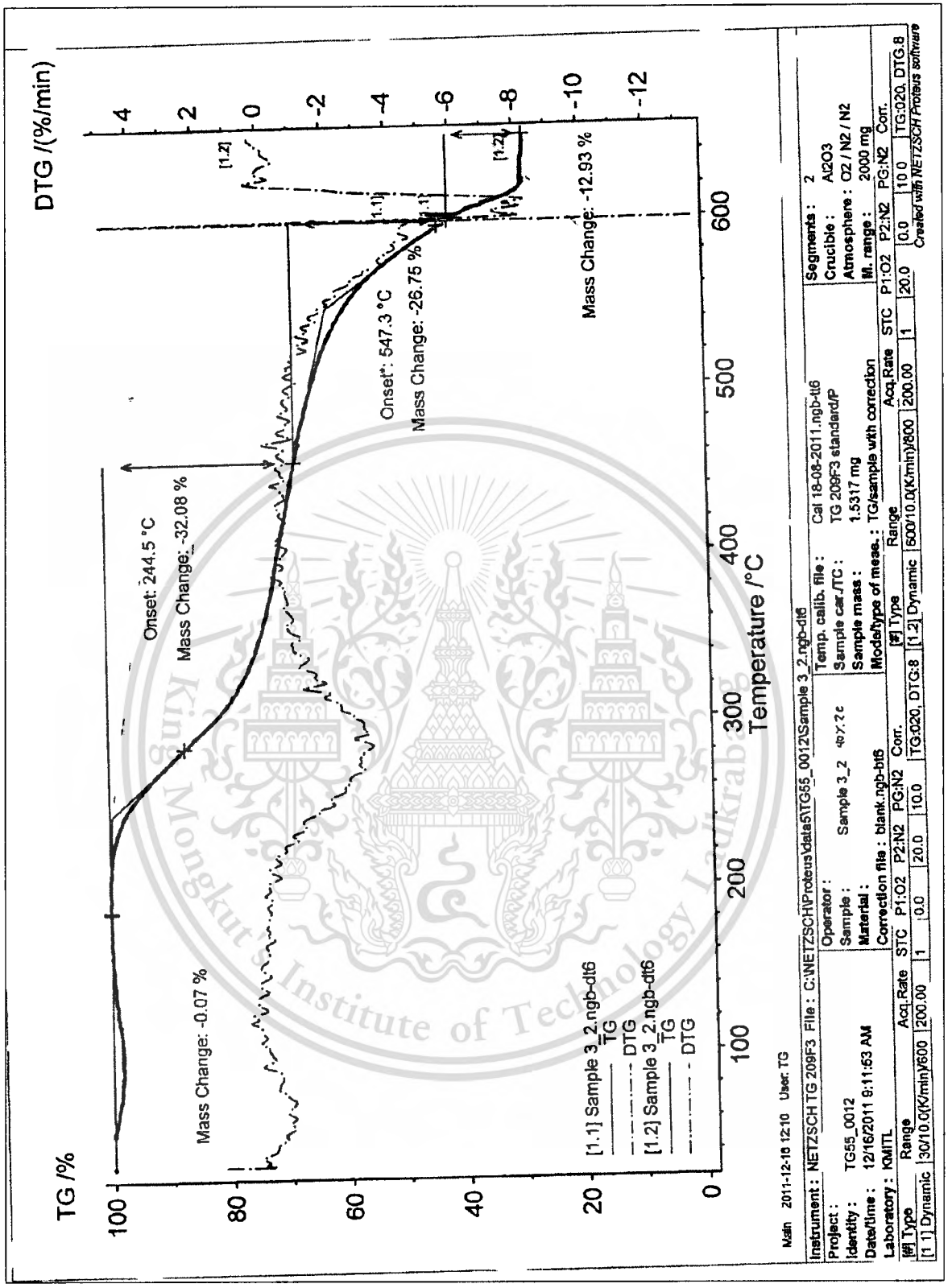

Figure A.4 Thermogram of chitosan membrane filled with 40% w/w zeolite NaA.

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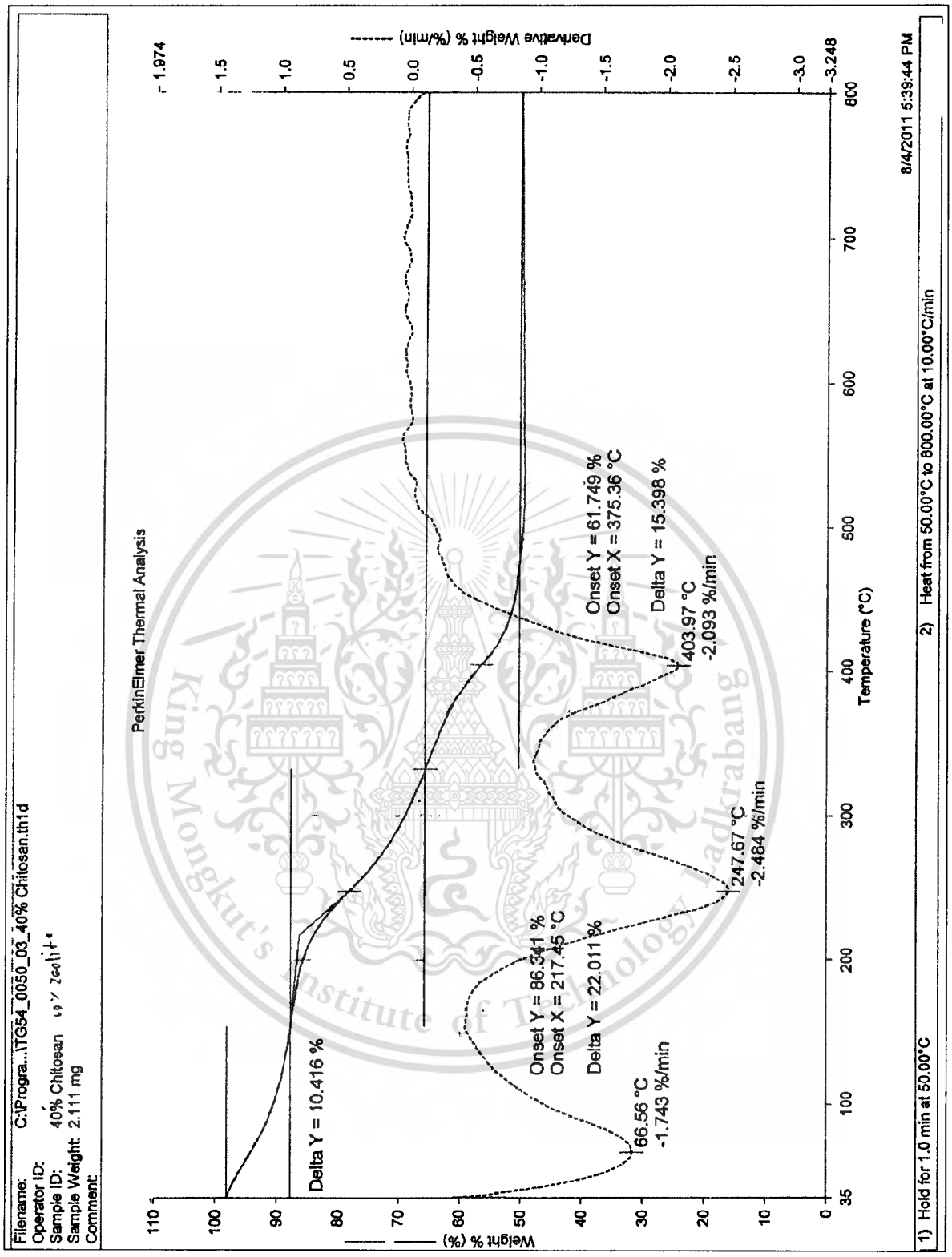

Figure A.5 Thermogram of chitosan membrane filled with 60% w/w zeolite NaA.

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Calculation

Example: The calculation for the chitosan membrane filled with 20% zeolite NaA

From Figures A.2 and A.3:

- % w/w of remained residue

Pure chitosan	100 g	Remained residue from chitosan	6.14 g	
Chitosan	80 g	Residue	=	$\frac{6.14 \times 80}{100}$
			=	4.912 g

- %w/w of dried zeolite NaA

%w/w of dried zeolite NaA = % w/w of Remained residue from membrane – Residue

= 20.09 – 4.912

= 15.178 %wt

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Appendix B

Chromatogram

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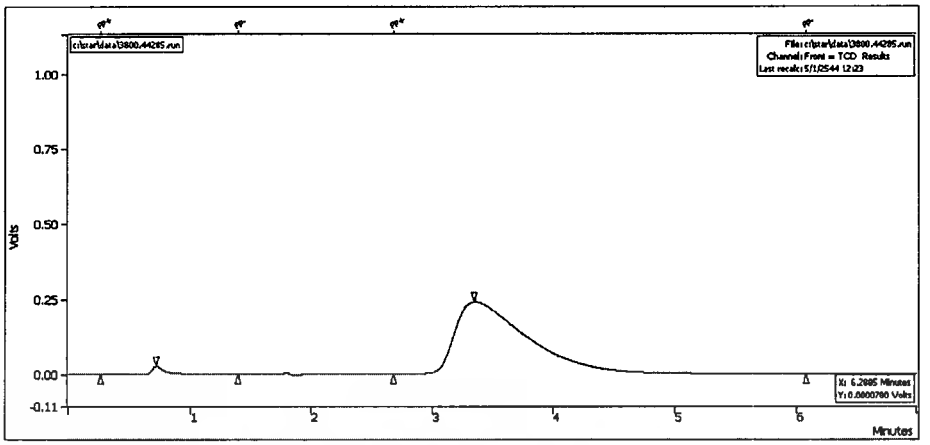

Figure B.1 Chromatogram of pure acetone.

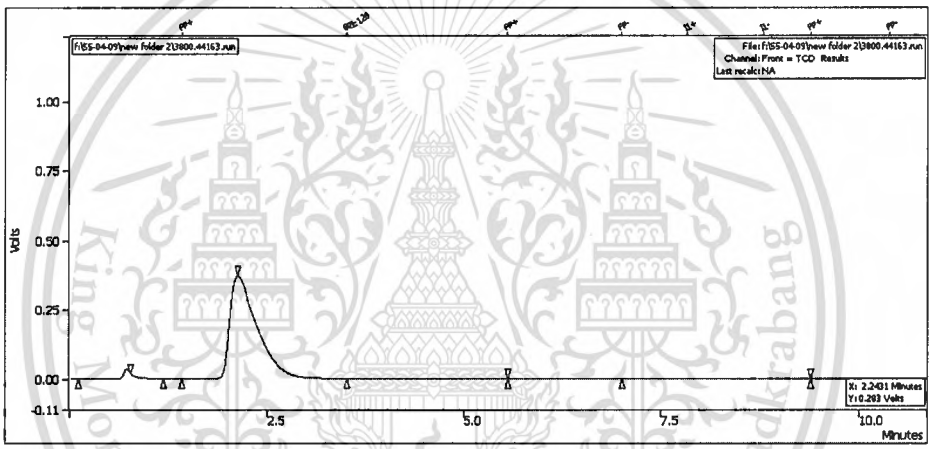

Figure B.2 Chromatogram of pure ethanol.

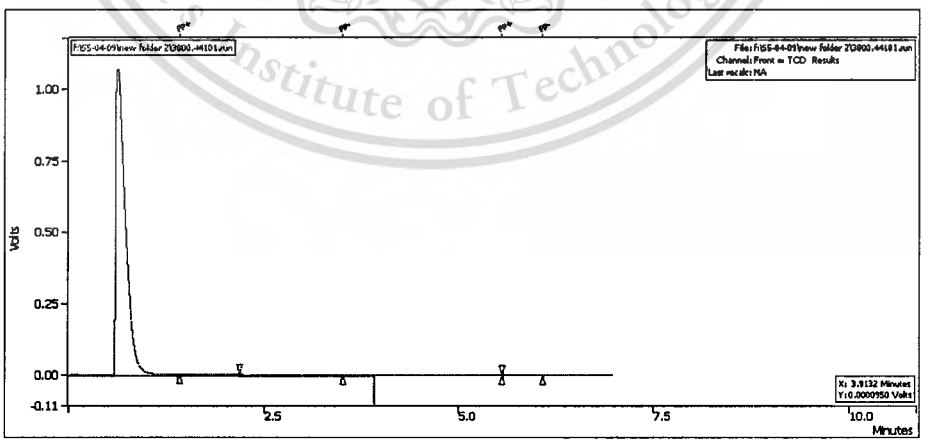

Figure B.3 Chromatogram of water.

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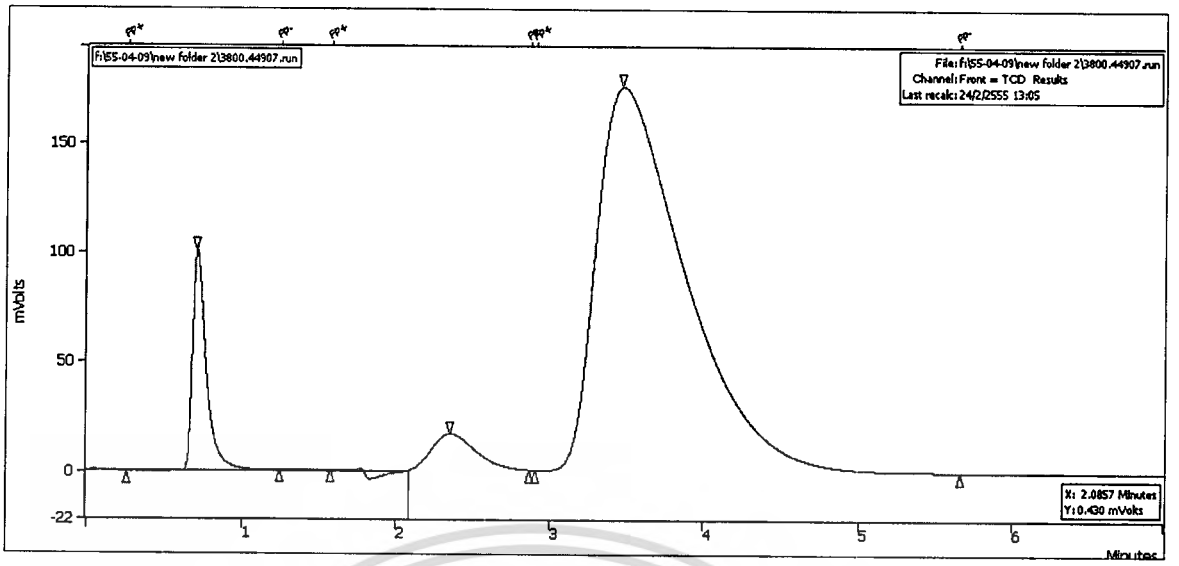

Figure B.4 Chromatogram of water/ethanol separation using pure chitosan membrane with 50% v/v ethanol feed solution at 4 hours.

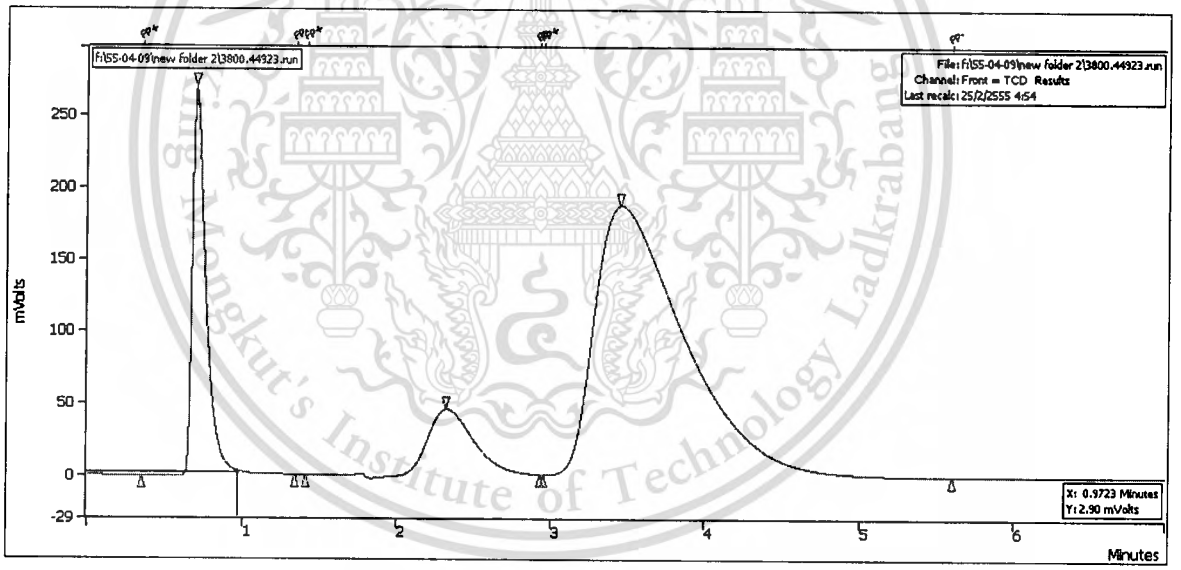

Figure B.5 Chromatogram of water/ethanol separation using pure chitosan membrane with 50% v/v ethanol feed solution at 8 hours.

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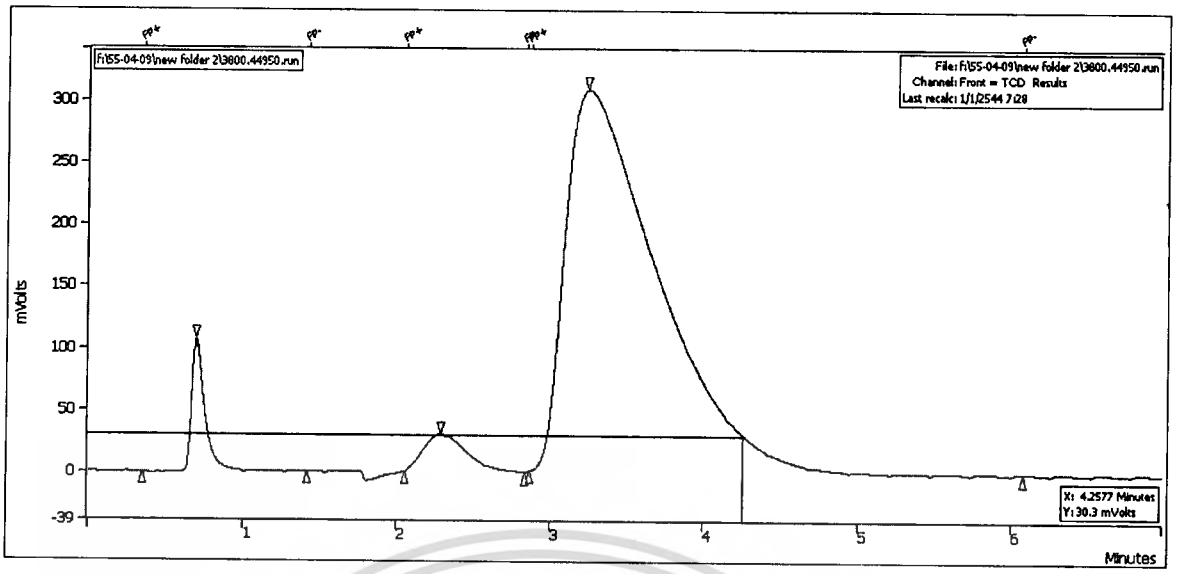

Figure B.6 Chromatogram of water/ethanol separation using pure chitosan membrane with 75% v/v ethanol feed solution at 4 hours.

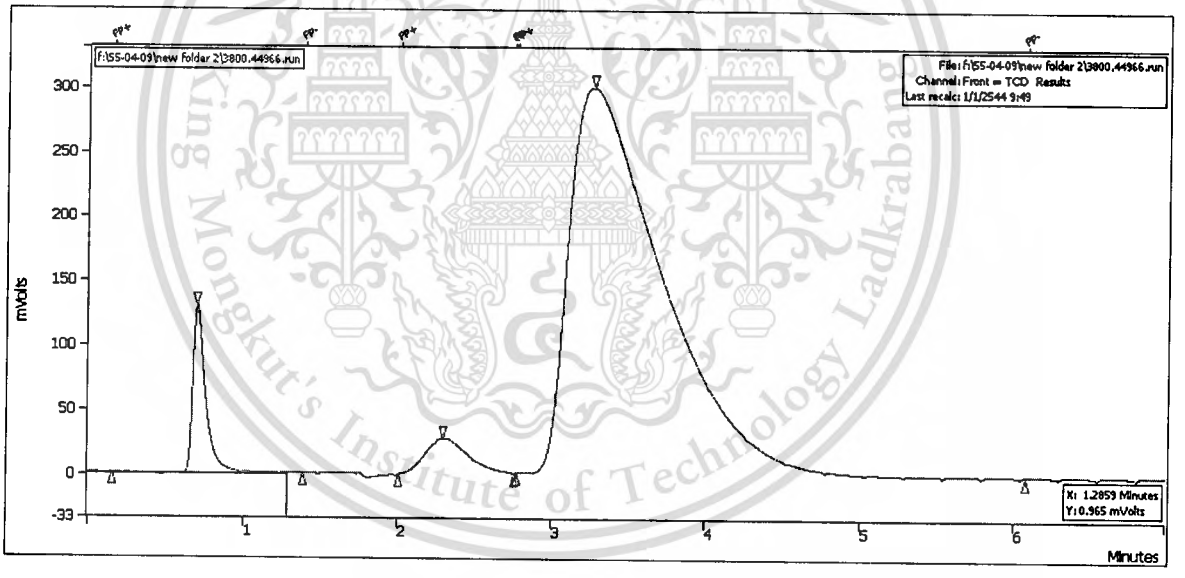

Figure B.7 Chromatogram of water/ethanol separation using pure chitosan membrane with 75% v/v ethanol feed solution at 8 hours.

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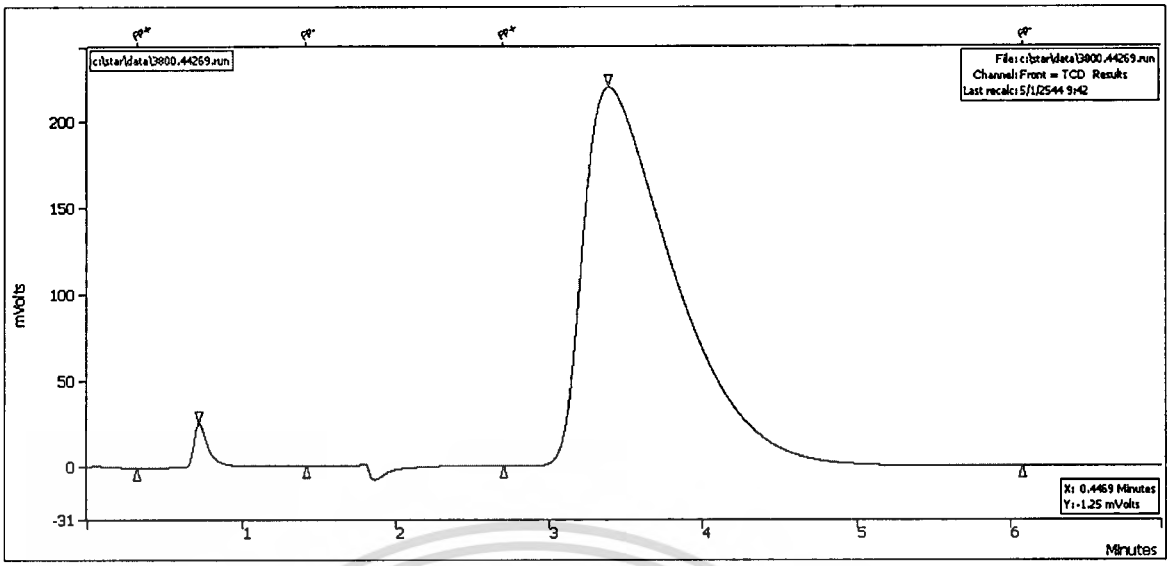

Figure B.8 Chromatogram of water/ethanol separation using pure chitosan membrane with 95% v/v ethanol feed solution at 4 hours.

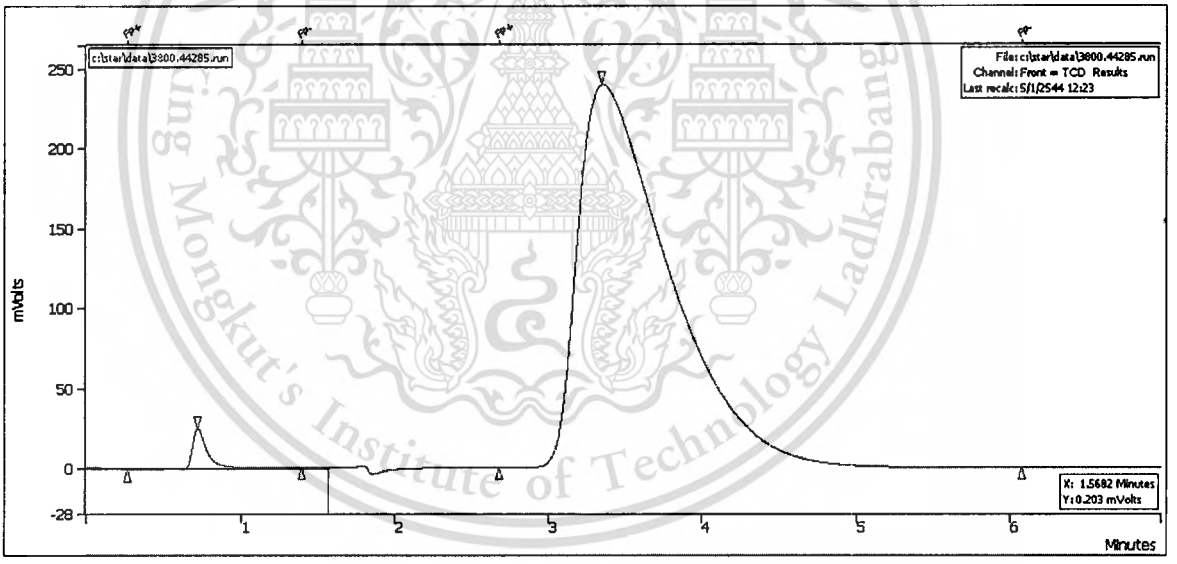

Figure B.9 Chromatogram of water/ethanol separation using pure chitosan membrane with 95% v/v ethanol feed solution at 8 hours.

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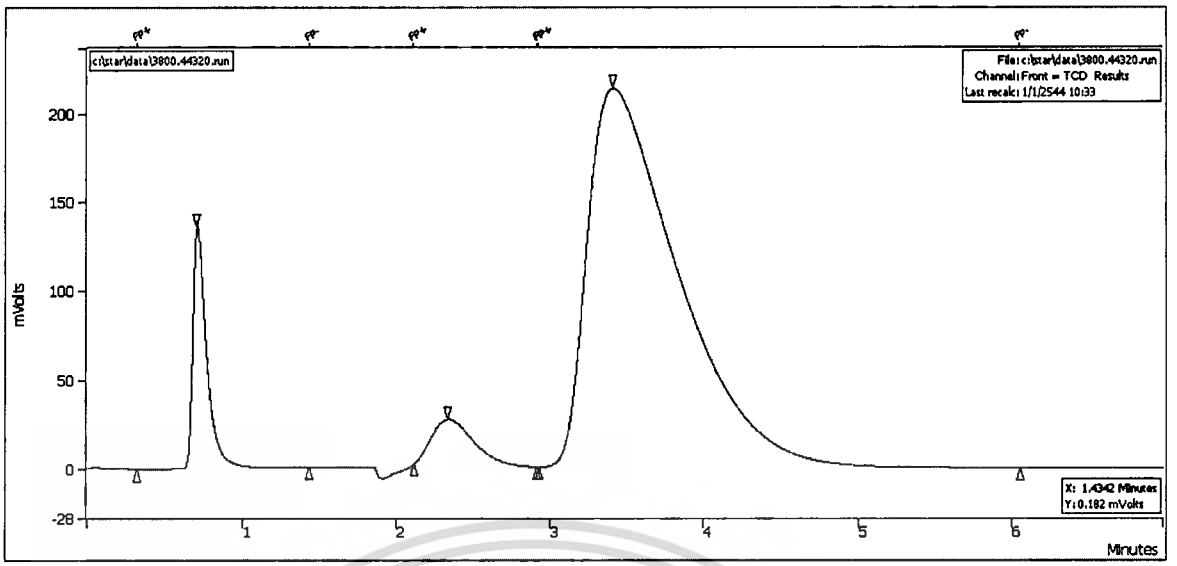

Figure B.10 Chromatogram of water/ethanol separation using chitosan membrane filled with 20% w/w zeolite and 50% v/v ethanol feed solution at 4 hours.

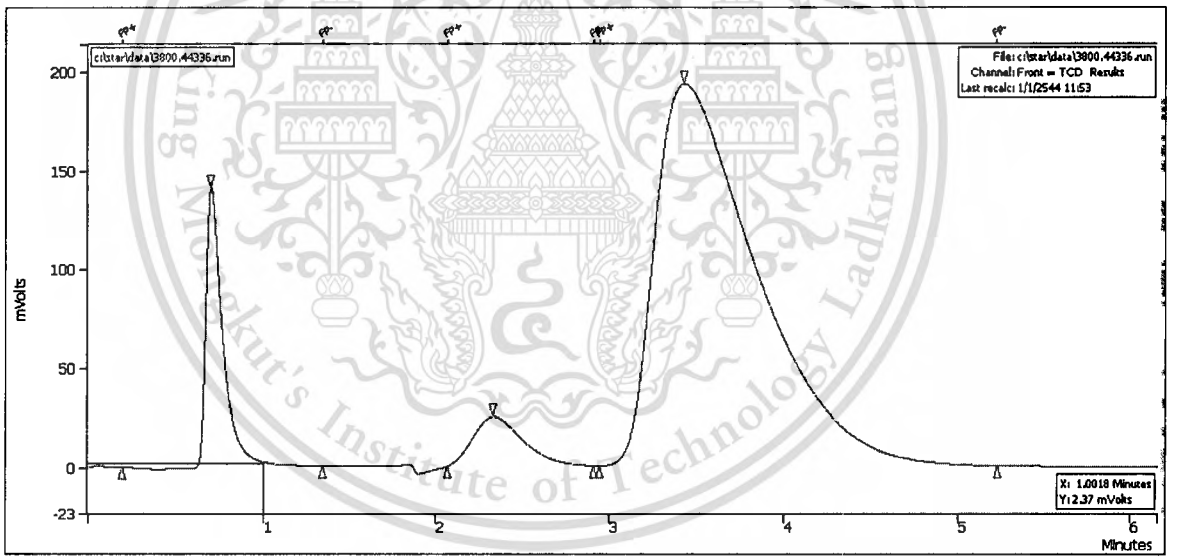

Figure B.11 Chromatogram of water/ethanol separation using chitosan membrane filled with 20% w/w zeolite and 50% v/v ethanol feed solution at 8 hours.

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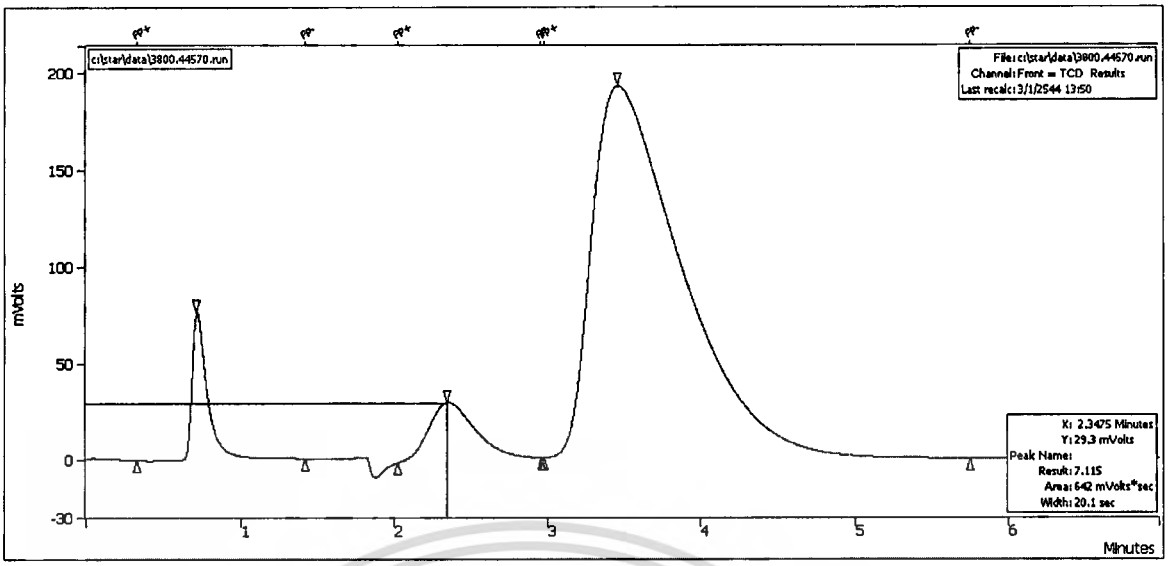

Figure B.12 Chromatogram of water/ethanol separation using chitosan membrane filled with 20% w/w zeolite and 75% v/v ethanol feed solution at 4 hours.

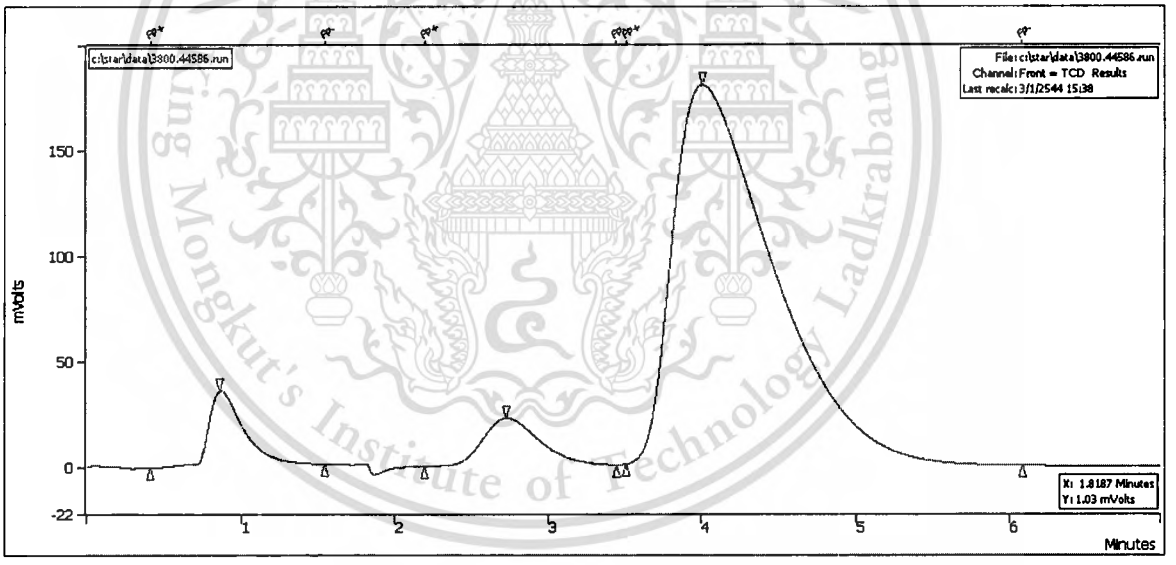

Figure B.13 Chromatogram of water/ethanol separation using chitosan membrane filled with 20% w/w zeolite and 75% v/v ethanol feed solution at 8 hours.

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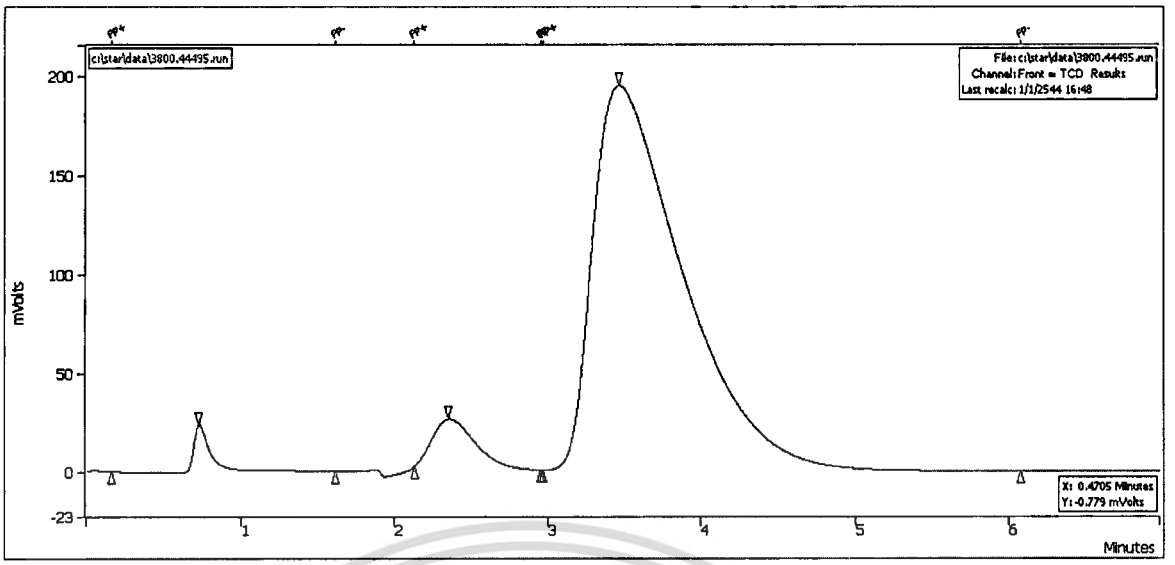

Figure B.14 Chromatogram of water/ethanol separation using chitosan membrane filled with 20% w/w zeolite and 95% v/v ethanol feed solution at 4 hours.

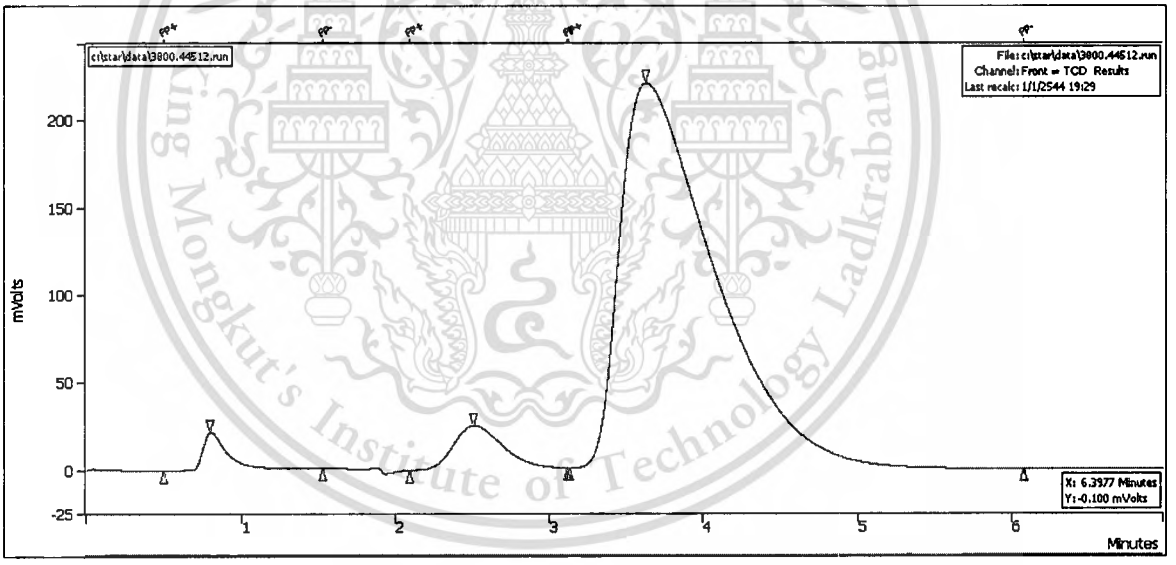

Figure B.15 Chromatogram of water/ethanol separation using chitosan membrane filled with 20% w/w zeolite and 95% v/v ethanol feed solution at 8 hours.

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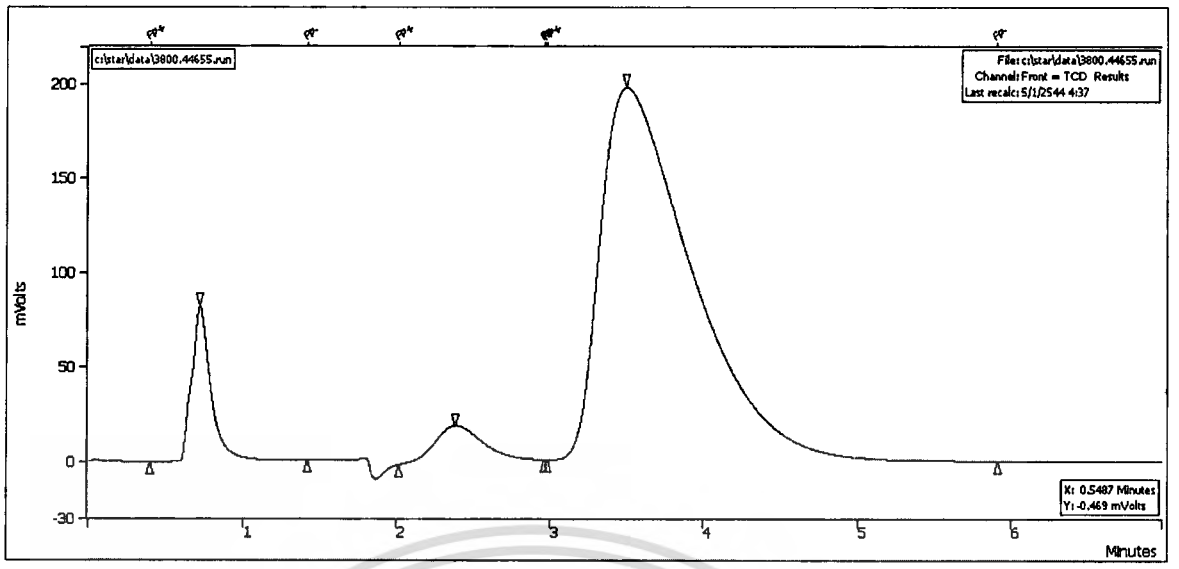

Figure B.16 Chromatogram of water/ethanol separation using chitosan membrane filled with 40% w/w zeolite and 50% v/v ethanol feed solution at 4 hours.

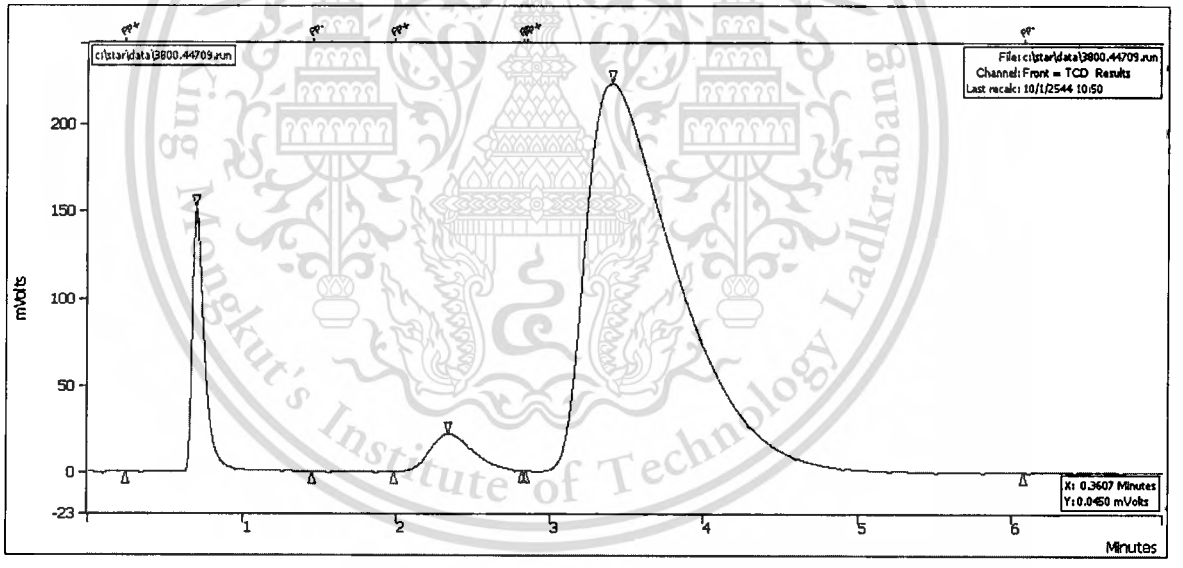

Figure B.17 Chromatogram of water/ethanol separation using chitosan membrane filled with 40% w/w zeolite and 50% v/v ethanol feed solution at 8 hours.

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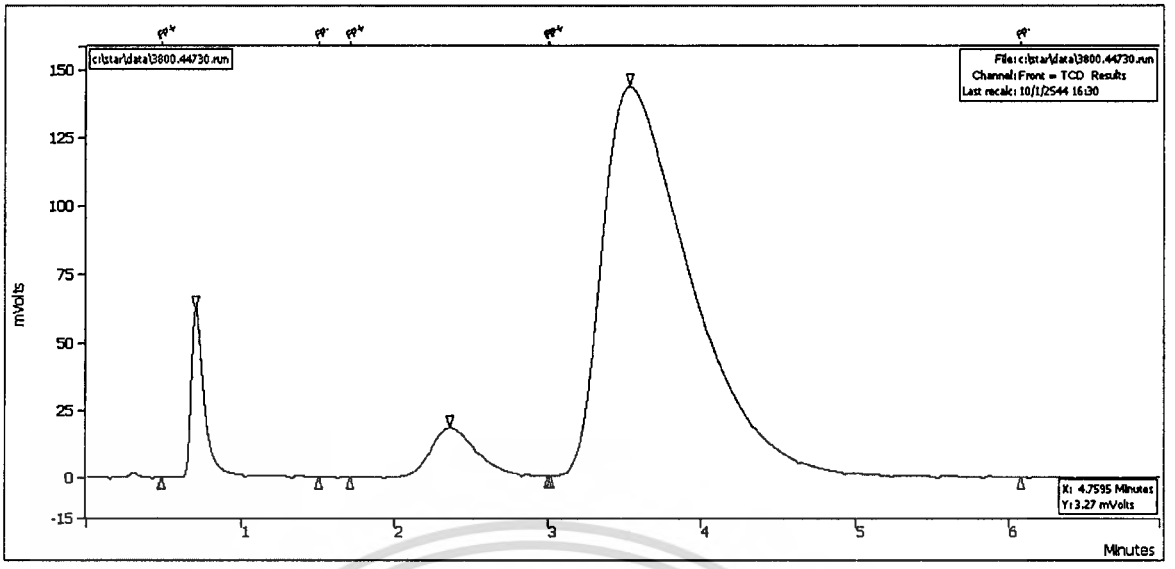

Figure B.18 Chromatogram of water/ethanol separation using chitosan membrane filled with 40% w/w zeolite and 75% v/v ethanol feed solution at 4 hours.

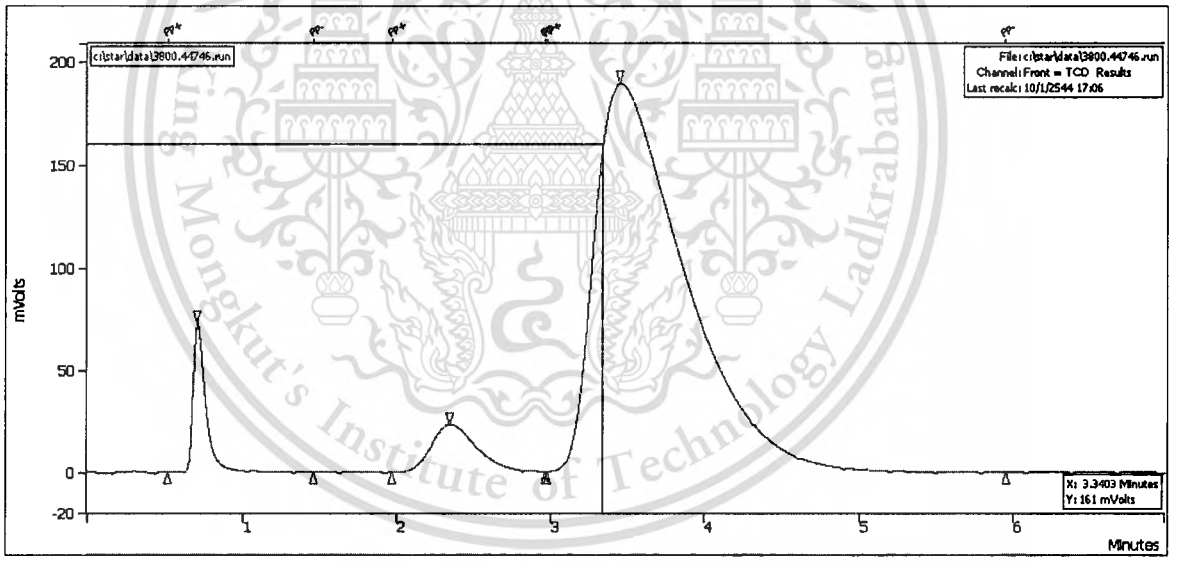

Figure B.19 Chromatogram of water/ethanol separation using chitosan membrane filled with 40% w/w zeolite and 75% v/v ethanol feed solution at 8 hours.

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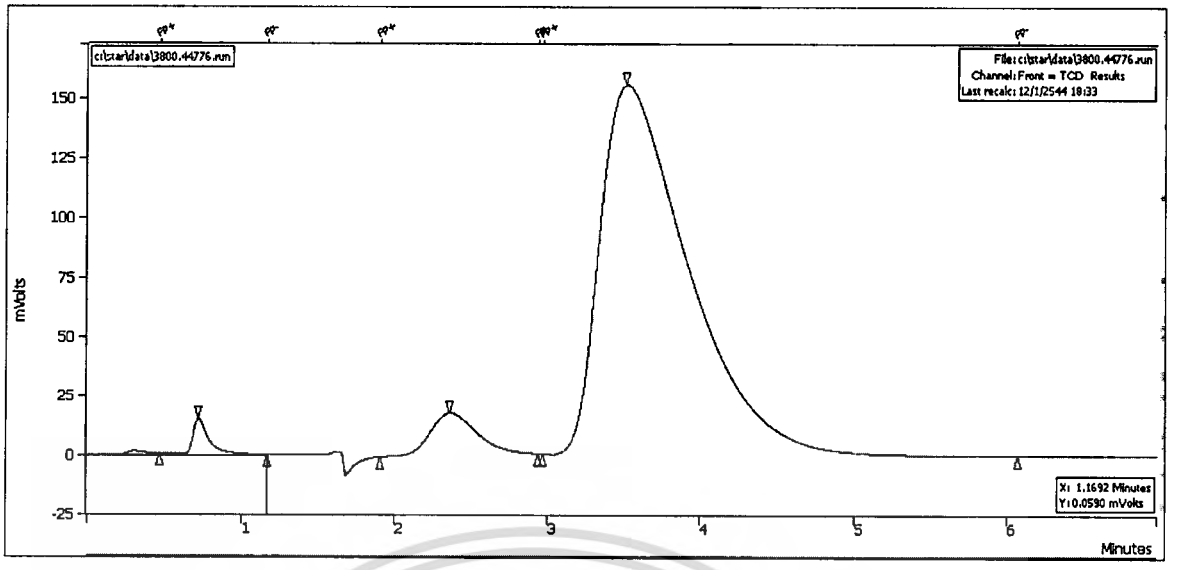

Figure B.20 Chromatogram of water/ethanol separation using chitosan membrane filled with 40% w/w zeolite and 95% v/v ethanol feed solution at 4 hours.

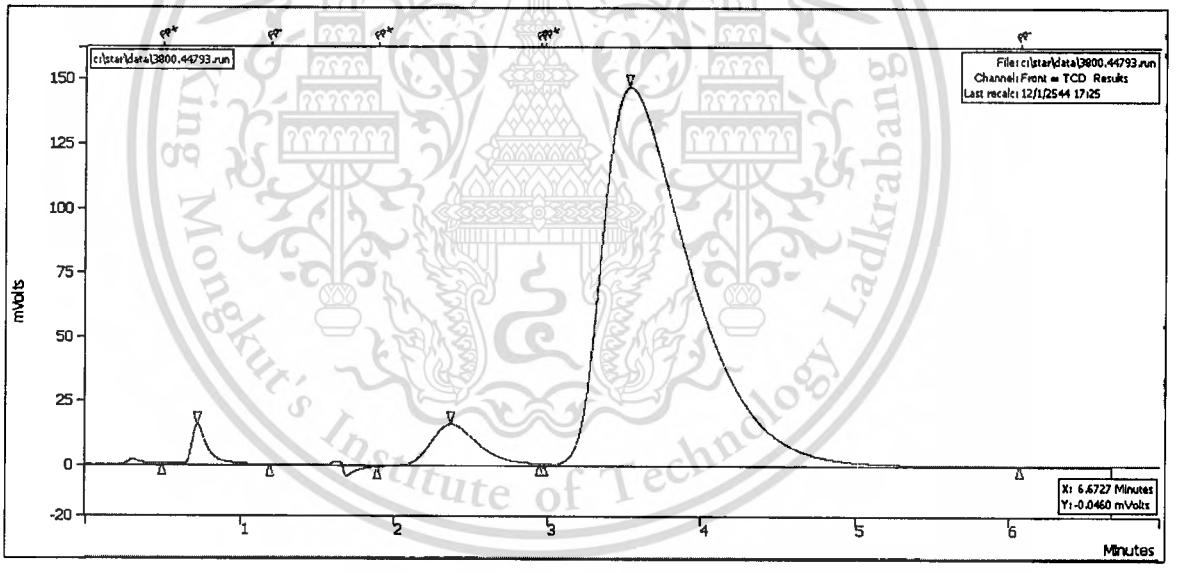

Figure B.21 Chromatogram of water/ethanol separation using chitosan membrane filled with 40% w/w zeolite and 95% v/v ethanol feed solution at 8 hours.

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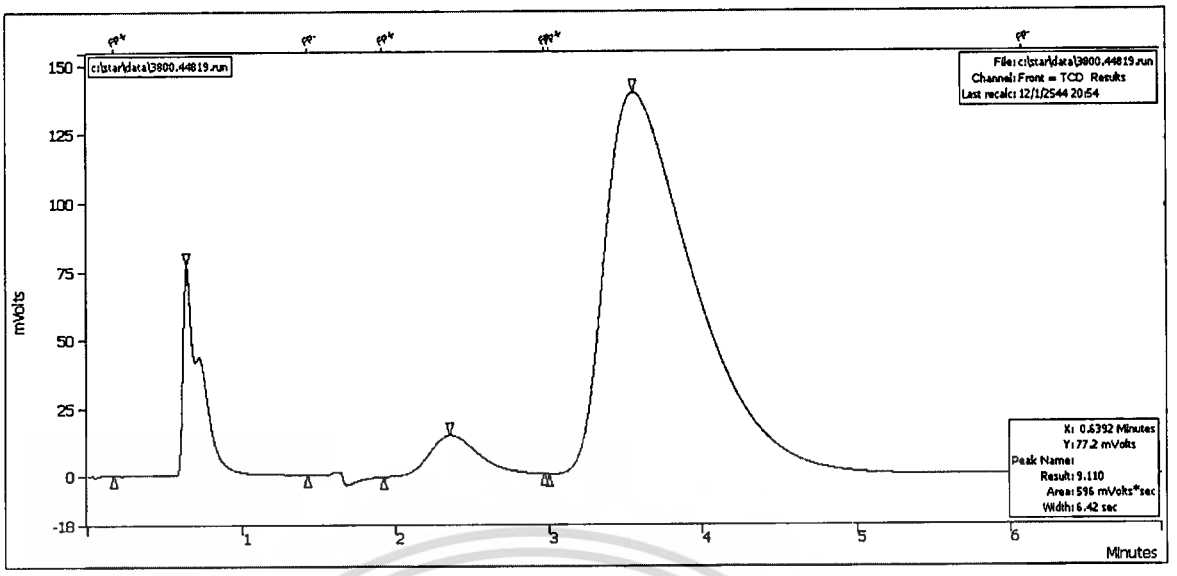

Figure B.22 Chromatogram of water/ethanol separation using chitosan membrane filled with 60% w/w zeolite and 50% v/v ethanol feed solution at 4 hours.

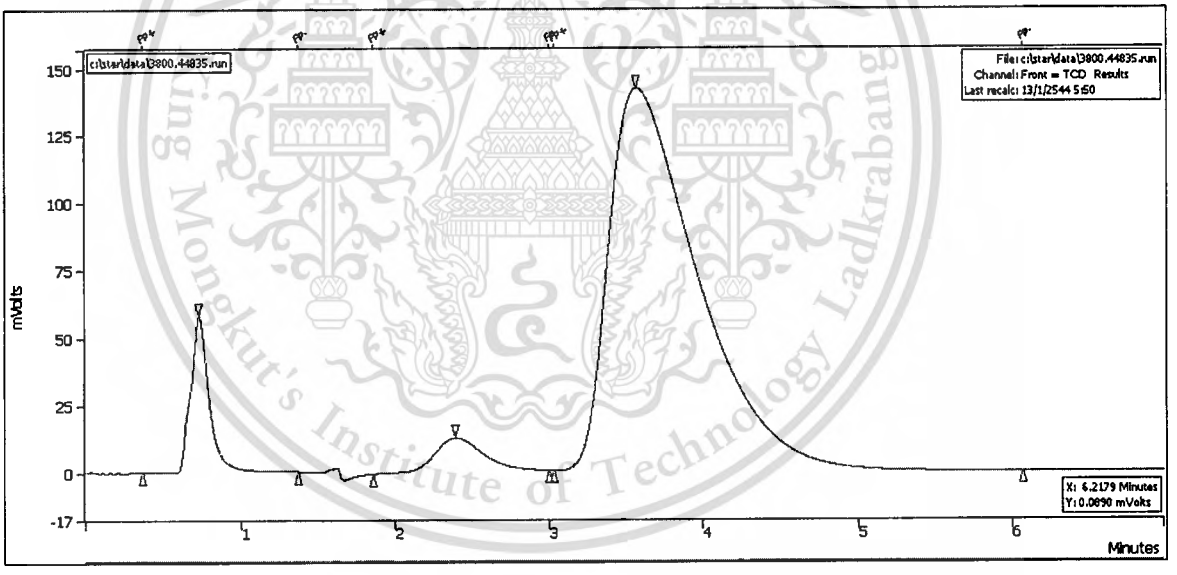

Figure B.23 Chromatogram of water/ethanol separation using chitosan membrane filled with 60% w/w zeolite and 50% v/v ethanol feed solution at 8 hours.

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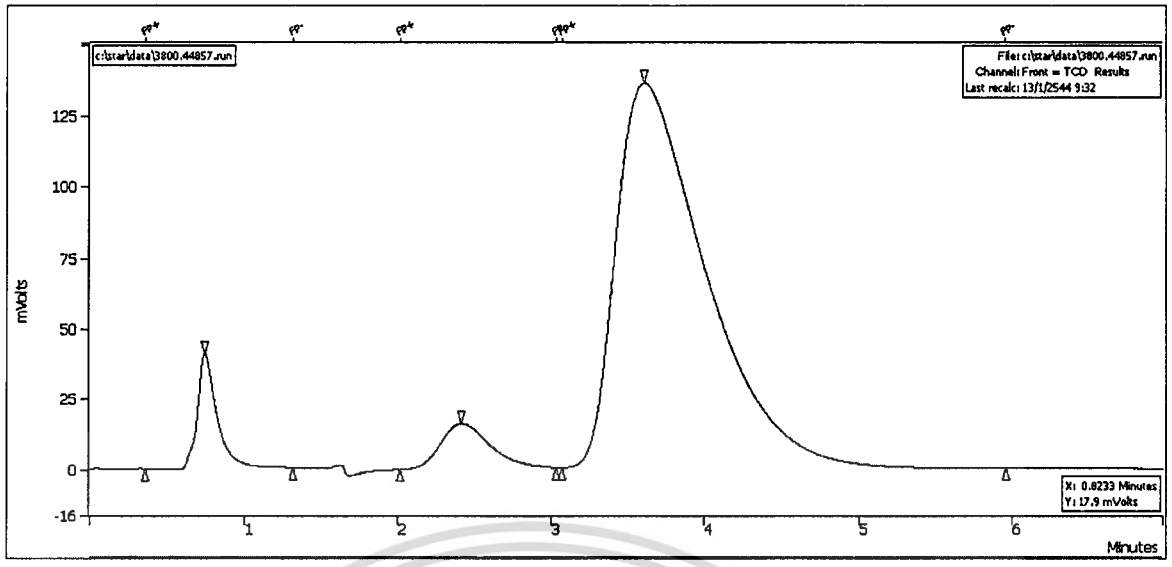

Figure B.24 Chromatogram of water/ethanol separation using chitosan membrane filled with 60% w/w zeolite and 75% v/v ethanol feed solution at 4 hours.

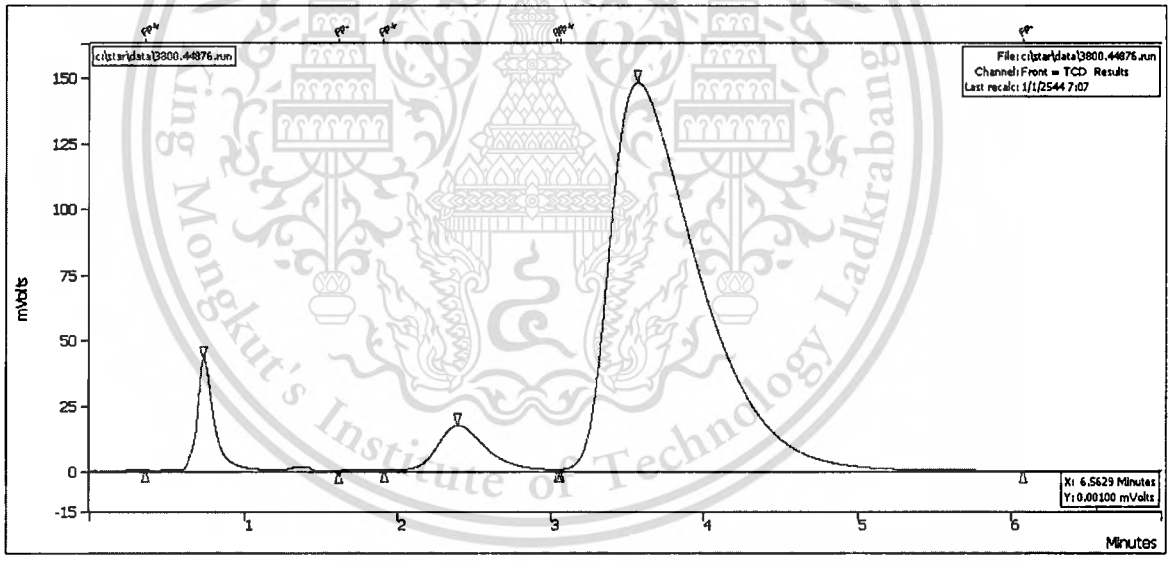

Figure B.25 Chromatogram of water/ethanol separation using chitosan membrane filled with 60% w/w zeolite and 75% v/v ethanol feed solution at 8 hours.

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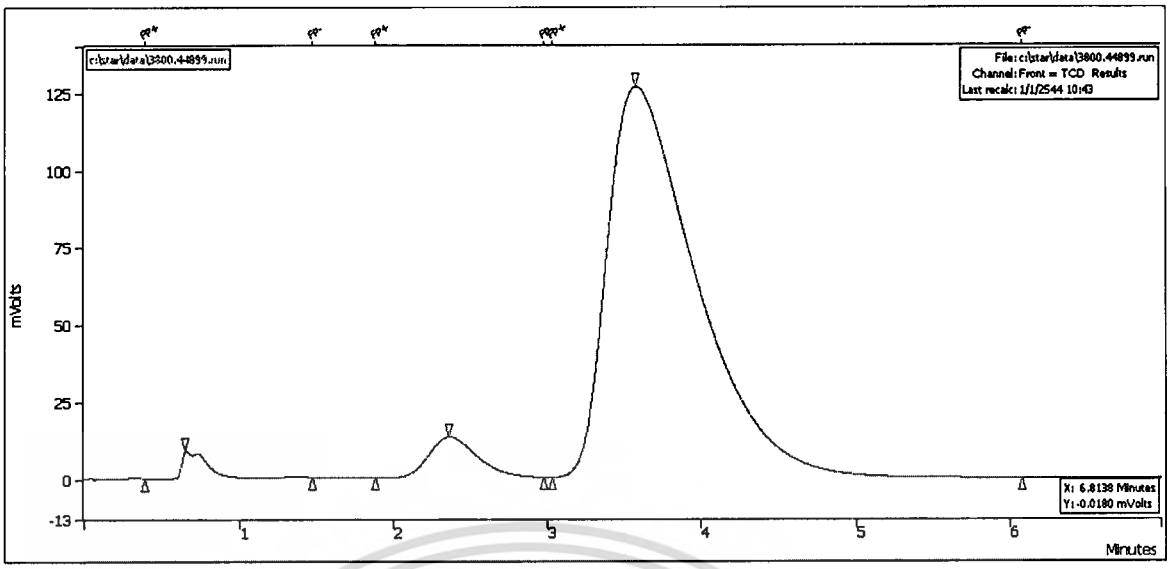

Figure B.26 Chromatogram of water/ethanol separation using chitosan membrane filled with 60% w/w zeolite and 95% v/v ethanol feed solution at 4 hours.

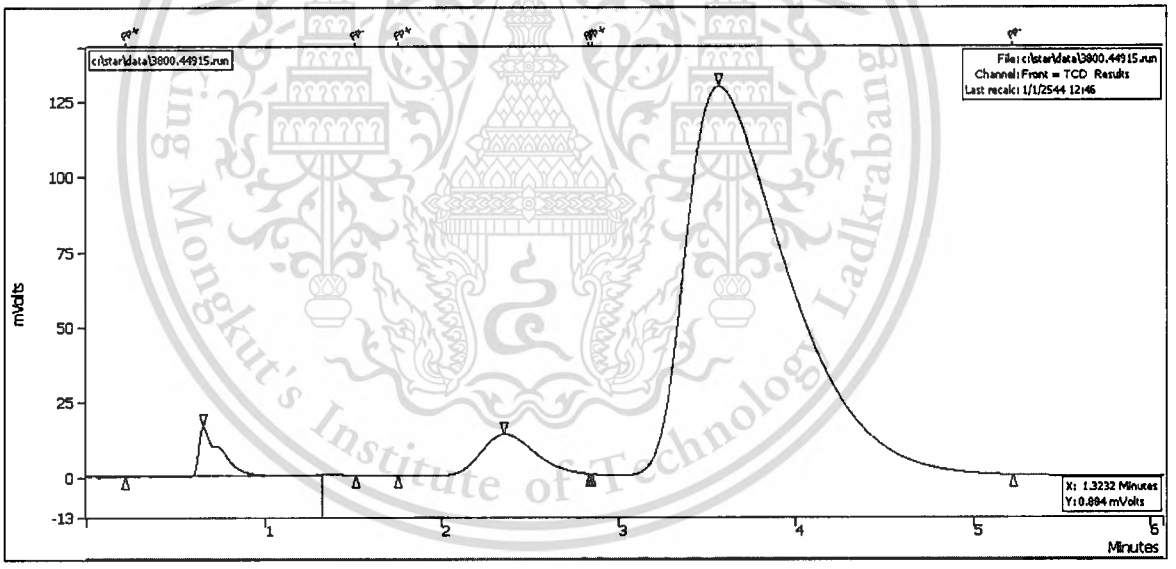

Figure B.27 Chromatogram of water/ethanol separation using chitosan membrane filled with 60% w/w zeolite and 95% v/v ethanol feed solution at 8 hours.

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Appendix C

Results

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Table C.1 Flux of water and ethanol from permeate side that pass through the pure chitosan membrane with 110 μm at various times by using 50% v/v ethanol solution.

Time (hr)	Flux of H_2O ($ml/m^2 \cdot hr$)	Flux of Ethanol ($ml/m^2 \cdot hr$)
0.5	26.2648	16.2800
1	45.5704	32.2104
1.5	42.1392	33.1928
2	34.6800	26.8064
2.5	32.2008	24.0696
3	29.7352	21.2624
3.5	31.2400	23.8592
4	36.0096	29.6136
4.5	33.5480	27.0872
5	43.2176	24.5608
5.5	47.0656	35.0872
6	48.7344	39.2976
6.5	55.2360	52.7712
7	71.0512	67.0168
7.5	88.1480	84.2104
8	89.1216	81.6136

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Table C.2 Flux of water and ethanol from permeate side that pass through the pure chitosan membrane with 110 μm at various times by using 75% v/v ethanol solution.

Time (hr)	Flux of H_2O ($ml/m^2 \cdot hr$)	Flux of Ethanol ($ml/m^2 \cdot hr$)
0.5	18.1224	27.7192
1	20.8160	29.6840
1.5	21.9176	28.4912
2	21.3464	32.4208
2.5	22.1224	30.7368
3	20.1632	28.9824
3.5	20.2040	29.9648
4	19.7952	31.7192
4.5	18.5304	30.5960
5	18.6120	28.3504
5.5	19.2240	30.4560
6	19.3464	30.9472
6.5	19.0200	31.7192
7	18.8160	29.9648
7.5	20.408	30.3152
8	23.5096	29.8944

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Table C.3 Flux of water and ethanol from permeate side that pass through the pure chitosan membrane with 110 μm at various times by using 95% v/v ethanol solution.

Time (hr)	Flux of H_2O ($ml/m^2 \cdot hr$)	Flux of Ethanol ($ml/m^2 \cdot hr$)
0.5	8.0816	-
1	8.2040	-
1.5	7.5096	-
2	7.5096	-
2.5	8.3264	-
3	7.3056	-
3.5	7.2648	-
4	7.9176	-
4.5	8.5712	-
5	8.2040	-
5.5	8.5712	-
6	7.4688	-
6.5	5.9584	-
7	6.4896	-
7.5	6.5304	-
8	6.9792	-

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Table C.4 Flux of water and ethanol from permeate side that pass through the chitosan membrane filled with 20% zeolite and 100 μm at various times by using 50% v/v ethanol solution.

Time (hr)	Flux of H_2O ($ml/m^2 \cdot hr$)	Flux of Ethanol ($ml/m^2 \cdot hr$)
0.5	32.8568	47.1576
1	45.5096	58.2456
1.5	52.1224	57.4032
2	45.9176	56.2800
2.5	40.2448	46.9472
3	38.3672	56.4912
3.5	40.8976	45.4032
4	39.9176	40.6312
4.5	40.8568	46.4560
5	40.7344	41.4032
5.5	40.7344	44.4208
6	41.7136	44.6312
6.5	47.2240	46.7368
7	39.4280	44.0000
7.5	46.2448	44.0696
8	44.6120	42.0344

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Table C.5 Flux of water and ethanol from permeate side that pass through the chitosan membrane filled with 20% zeolite and 100 μm at various times by using 75% v/v ethanol solution.

Time (hr)	Flux of H_2O ($ml/m^2 \cdot hr$)	Flux of Ethanol ($ml/m^2 \cdot hr$)
0.5	20.7344	66.8768
1	48.0816	74.9472
1.5	37.9584	70.1752
2	34.4896	68.9120
2.5	27.9584	64.3504
3	27.3056	57.8944
3.5	28.7752	59.2976
4	28.6120	57.0520
4.5	26.0408	55.7192
5	26.6936	53.4032
5.5	25.9176	52.4208
6	24.8160	52.0000
6.5	24.4080	51.1576
7	27.3056	50.9472
7.5	24.8568	51.1576
8	30.6120	49.8944

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Table C.6 Flux of water and ethanol from permeate side that pass through the chitosan membrane filled with 20% zeolite and 100 μm at various times by using 95% v/v ethanol solution.

Time (hr)	Flux of H_2O ($ml/m^2 \cdot hr$)	Flux of Ethanol ($ml/m^2 \cdot hr$)
0.5	8.5304	46.3152
1	15.7544	48.7016
1.5	42.2856	47.0872
2	8.8408	43.8592
2.5	9.0344	40.0000
3	8.8976	39.0872
3.5	10.6528	48.8416
4	9.0608	44.7016
4.5	19.7136	84.0696
5	10.4080	43.5080
5.5	9.0200	42.5960
6	13.2648	41.4032
6.5	14.1632	47.7368
7	9.5912	42.9472
7.5	7.7984	40.8416
8	8.7344	40.0000

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Table C.7 Flux of water and ethanol from permeate side that pass through the chitosan membrane filled with 40% zeolite and 133.3 μm at various times by using 50% v/v ethanol solution.

Time (hr)	Flux of H_2O ($ml/m^2 \cdot hr$)	Flux of Ethanol ($ml/m^2 \cdot hr$)
0.5	25.5096	28.2800
1	34.9384	38.3152
1.5	49.1016	43.4384
2	38.8976	41.8240
2.5	38.0816	40.4912
3	42.2856	39.7192
3.5	39.1424	36.5608
4	35.4688	36.2104
4.5	34.9384	34.8064
5	29.7952	32.5608
5.5	32.6120	33.6136
6	33.7952	31.3680
6.5	33.5096	30.6664
7	31.6728	30.3856
7.5	42.0816	30.6664
8	37.5912	32.4208

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Table C.8 Flux of water and ethanol from permeate side that pass through the chitosan membrane filled with 40% zeolite and 133.3 μm at various times by using 75% v/v ethanol solution.

Time (hr)	Flux of H_2O ($ml/m^2 \cdot hr$)	Flux of Ethanol ($ml/m^2 \cdot hr$)
0.5	18.2448	34.5960
1	18.2448	38.5256
1.5	40.8160	42.5960
2	31.5504	36.9824
2.5	30.2856	36.9120
3	24.9792	37.3328
3.5	35.3056	36.6312
4	25.7136	45.2624
4.5	29.9584	46.2464
5	28.6528	44.8416
5.5	25.1832	44.5608
6	29.9584	44.2800
6.5	29.6320	40.8416
7	30.0408	40.1400
7.5	29.5504	46.3856
8	30.0816	42.8064

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Table C.9 Flux of water and ethanol from permeate side that pass through the chitosan membrane filled with 40% zeolite and 133.3 μm at various times by using 95% v/v ethanol solution.

Time (hr)	Flux of H_2O ($ml/m^2 \cdot hr$)	Flux of Ethanol ($ml/m^2 \cdot hr$)
0.5	7.7136	50.3152
1	7.1424	54.7368
1.5	5.4688	35.7880
2	5.7136	35.0168
2.5	5.6728	37.1928
3	7.1016	39.7192
3.5	6.2448	41.7536
4	6.4080	42.1752
4.5	6.4896	42.8064
5	6.4896	41.4736
5.5	6.6120	40.5608
6	8.7344	40.9120
6.5	6.6120	40.3504
7	6.7344	40.2800
7.5	7.0200	40.3504
8	6.9792	40.3504

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Table C.10 Flux of water and ethanol from permeate side that pass through the chitosan membrane filled with 60% zeolite and 130 μm at various times by using 50% v/v ethanol solution.

Time (hr)	Flux of H_2O ($ml/m^2 \cdot hr$)	Flux of Ethanol ($ml/m^2 \cdot hr$)
0.5	38.1632	30.2456
1	44.3264	39.9296
1.5	43.0608	40.7016
2	41.2240	40.4208
2.5	40.1224	50.1048
3	38.5304	39.368
3.5	36.2856	33.8944
4	40.4080	37.9648
4.5	36.9792	30.5256
5	38.4488	36.0696
5.5	42.0816	36.5608
6	44.4080	40.1400
6.5	41.8360	39.4384
7	37.6320	36.9120
7.5	34.2448	35.8592
8	34.2448	35.8592

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Table C.11 Flux of water and ethanol from permeate side that pass through the chitosan membrane filled with 60% zeolite and 130 μm at various times by using 75% v/v ethanol solution.

Time (hr)	Flux of H_2O ($ml/m^2 \cdot hr$)	Flux of Ethanol ($ml/m^2 \cdot hr$)
0.5	23.7136	37.4032
1	23.1832	45.0520
1.5	22.7344	46.0344
2	22.9384	45.7536
2.5	23.1016	46.5256
3	23.3056	44.8416
3.5	24.5304	47.0168
4	23.8768	45.7536
4.5	22.7344	44.2104
5	22.0816	41.6136
5.5	24.6120	44.9824
6	24.8160	42.0344
6.5	23.5504	39.7888
7	23.3872	37.8944
7.5	23.5096	43.8592
8	22.8568	41.7536

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Table C.12 Flux of water and ethanol from permeate side that pass through the chitosan membrane filled with 60% zeolite and 130 μm at various times by using 95% v/v ethanol solution.

Time (hr)	Flux of H_2O ($ml/m^2 \cdot hr$)	Flux of Ethanol ($ml/m^2 \cdot hr$)
0.5	8.1632	40.0696
1	10.7752	29.7536
1.5	9.7136	47.4384
2	8.612	44.7016
2.5	12.7344	40.6312
3	9.0608	40.4208
3.5	11.1832	40.0000
4	9.3056	40.0696
4.5	8.9792	38.3856
5	8.8160	28.7714
5.5	8.9384	38.7368
6	8.8976	37.8240
6.5	8.1224	32.3504
7	7.8768	40.0000
7.5	9.4688	37.1928
8	12.4488	39.0168

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Appendix D

Calculation

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Table D.1 Information from chromatogram of liquid permeation test for water-ethanol separation with the chitosan membrane filled with 60% zeolite and 130 μm at various times.

Time (hr)	Area			Area water/Acetone	Average	Area Ethanol/Acetone	Average
	Water	Ethanol	Acetone				
Feed	561774	5101431	5262634	0.1067	0.1014	0.9693	0.9074
	632759	5556675	6571877	0.0962		0.8455	
0.5	96970	280435	4925876	0.0196	0.02	0.0569	0.0571
	111627	311732	5424257	0.0205		0.0574	
1	112639	291445	5029580	0.0223	0.0264	0.0264	0.0424
	168850	323021	5520717	0.0305		0.0574	
1.5	160616	416595	6121667	0.0262	0.0238	0.068	0.0676
	119296	374726	5562295	0.0214		0.0673	
2	129682	373706	5864186	0.0221	0.0211	0.0637	0.0637
	141885	447198	7010390	0.0202		0.0637	
2.5	111267	312745	5492041	0.0202	0.0312	0.0569	0.0579
	228623	319158	5411550	0.0422		0.0589	
3	103981	316967	5535164	0.0187	0.0222	0.0572	0.057
	135347	305535	5252644	0.0257		0.0581	
3.5	132066	344209	6117179	0.0215	0.0274	0.0562	0.057
	207520	360019	6222522	0.0333		0.0578	
4	105075	288062	5080585	0.0206	0.0228	0.0566	0.0571
	161019	370336	6423935	0.025		0.0576	
4.5	125266	308058	5571840	0.0224	0.022	0.0552	0.0547
	113153	281789	5198371	0.0217		0.0542	
5	94027	268599	4711994	0.0199	0.0216	0.057	0.0574
	125704	309650	5353802	0.0234		0.0578	
5.5	132188	323716	5849923	0.0225	0.0219	0.0553	0.0552
	110522	285154	5160816	0.0214		0.0552	

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Time (hr)	Area			Area water/Acetone	Average	Area Ethanol/Acetone	Average
	Water	Water	Water				
6	143894	348247	6416358	0.0224	0.0218	0.0542	0.0539
	117160	294259	5479943	0.0213		0.0536	
6.5	109449	258845	5591197	0.0195	0.0199	0.0462	0.0461
	93822	211669	4600002	0.0203		0.046	
7	90779	278576	4904705	0.0185	0.0193	0.0567	0.057
	107544	304422	5305498	0.0202		0.0573	
7.5	127773	308695	5694917	0.0224	0.0232	0.0542	0.053
	129582	277913	5363166	0.0241		0.0518	
8	161299	282112	5168218	0.0312	0.0305	0.0545	0.0556
	415830	788872	13865944	0.0299		0.0568	

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1. Calculation of % v/v H_2O

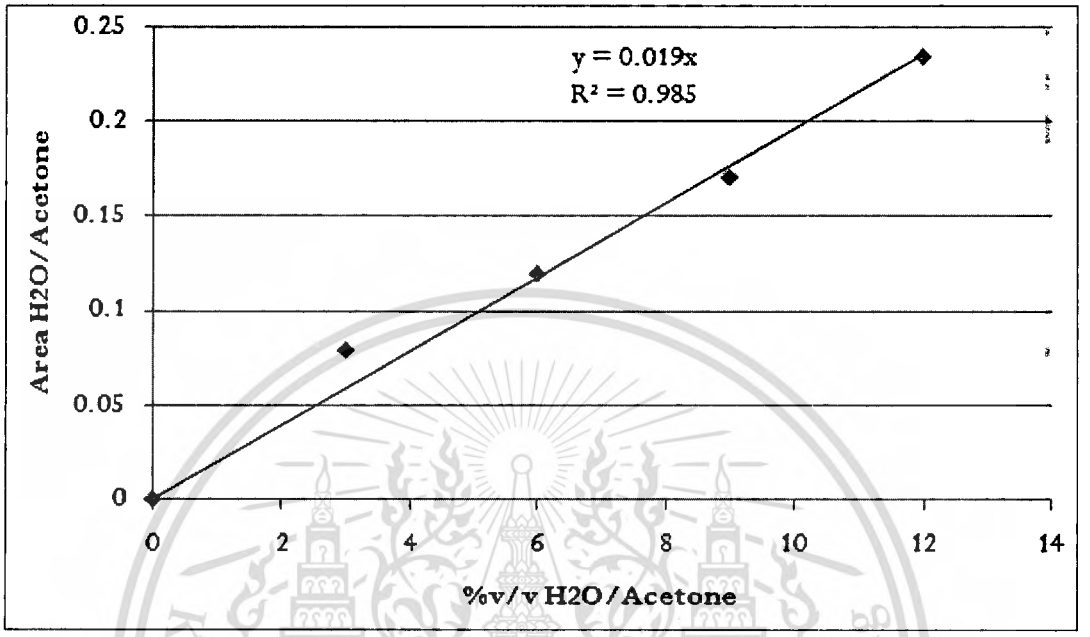

Figure D.1 calibration curve of %v/v H_2O/Acetone versus Area H_2O/Acetone.

Example:

From Figure C.3:

Y	=	0.0196x
Area H2O/Acetone	=	0.0196(% v/v H2O/Acetone)
0.0228	=	0.0196(% v/v H_2O/Acetone)
% v/v H_2O/Acetone	=	0.0228/0.0196
% v/v H_2O/Acetone	=	1.1632 %v

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2. Calculation of %v/v Ethanol

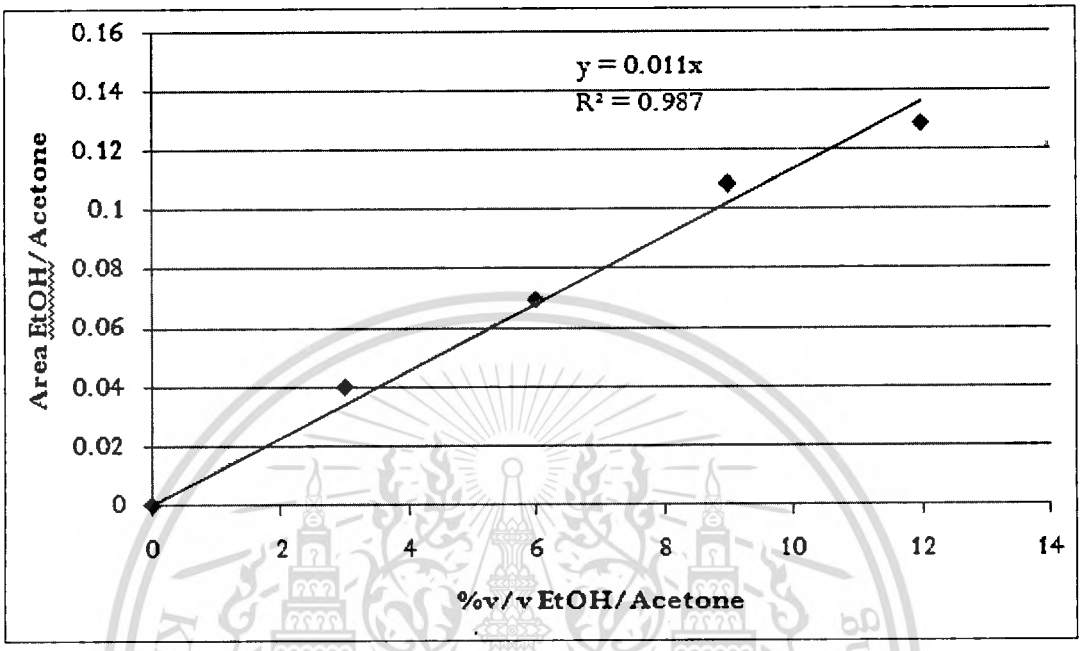

Figure D.2 Calibration curve of %v/v Ethanol/Acetone versus Area ethanol/Acetone.

Example:

From Figure C.4:

Y	=	0.0114x
Area Ethanol/Acetone	=	0.0114(%v/v Ethanol/Acetone)
0.0571	=	0.0114(%v/v Ethanol/Acetone)
%v/v Ethanol/Acetone	=	0.0571/0.0114
%v/v Ethanol/Acetone	=	5.0087 %v

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3. Calculation of flow rate of substance in permeate side

- At %v/v H_2O/Acetone = 1.1632 %v

Permeate	100 ml/hr		H_2O	1.1632 ml/hr
If permeate	2 ml/hr	H_2O	=	$\frac{1.1632 \times 2}{100}$
			=	0.0232ml

- At %v/v Ethanol/Acetone = 5.0087 %v

Permeate	100 ml	Ethanol		5.0087 ml/hr
If permeate	2 ml/hr	Ethanol =		$\frac{5.0087 \times 2}{100}$
			=	0.1 ml

4. Calculation of flux of substance

$$\text{Flux} = \frac{flow\ rate}{area}$$

Total flux = Flux of H_2O + Flux of Ethanol

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4.1 Calculation of flux of water

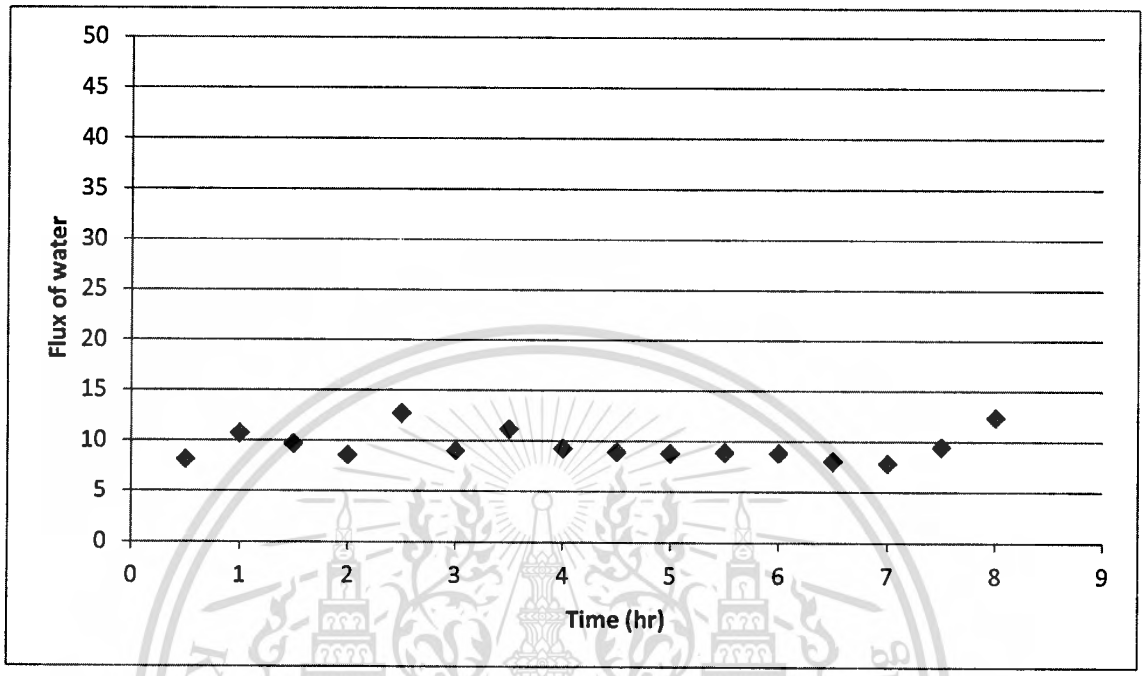

Figure D.3 Graph between flux of water versus time (hr) of the chitosan membrane filled with 60% zeolite and 95% ethanol solution used as feed.

From Figure D.5:

- Flux H_2O

$$\text{Flux} = \frac{ml/hr}{m^2}$$

$$\text{Flux of water} = \frac{0.0232}{0.0025}$$

$$= 9.28 \text{ ml/hr.m}^2$$

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4.2 Calculation of flux of ethanol

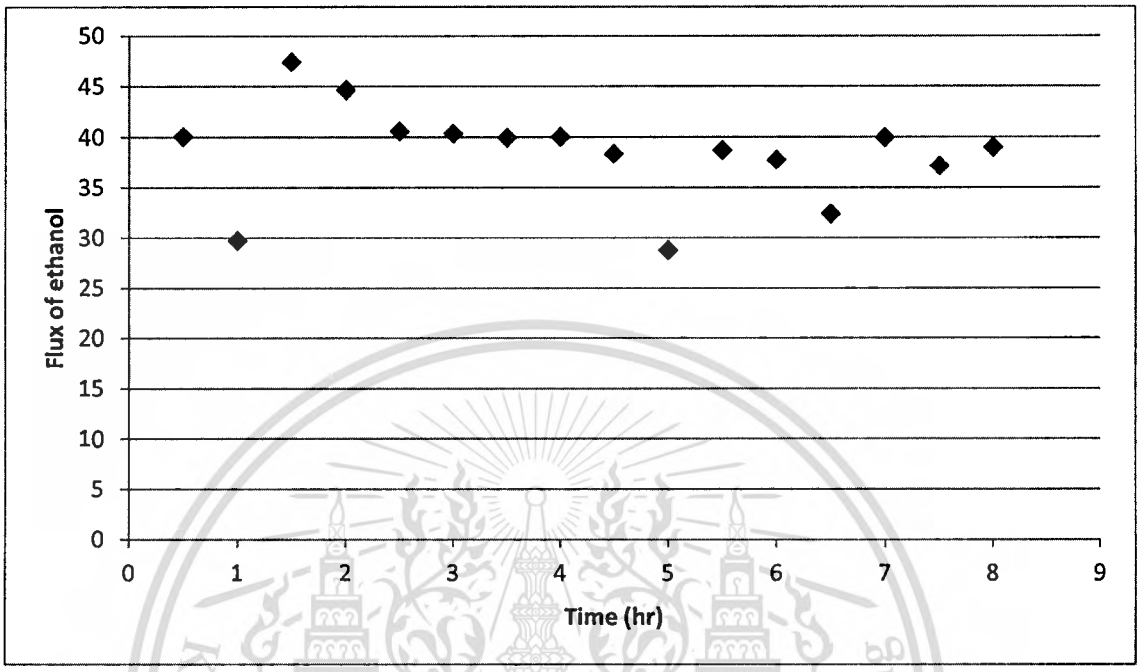

Figure D.4 Graph between flux of ethanol versus time (hr) of the chitosan membrane filled with 60% zeolite and 95% ethanol solution used as feed.

From Figure D.5:

- Flux ethanol

$$\text{Flux of ethanol} = \frac{0.100}{0.0025}$$

$$= 40 \text{ ml/hr.m}^2$$

$\therefore$ Total flux = 9.28 + 40 = 49.28 ml/hr.m^2

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5. Calculation of separation factor

$$\text{Separation factor} = \frac{Y_A/Y_B}{X_A/X_B}$$

- Mole of water in permeate side $= \dfrac{ml \times density}{molecular\ weight}$

$$= \frac{0.0116 \times 1}{18} = 6.44 \times 10^{-4} \text{ mole}$$

- Mole of Ethanol in permeate side $= \dfrac{ml \times density}{molecular\ weight}$

$$= \frac{0.05 \times 0.789}{46} = 8.591 \times 10^{-4} \text{ mole}$$

$Y_A = 6.44 \times 10^{-4} / (6.44 \times 10^{-4} + 8.591 \times 10^{-4}) = 0.4292$

$Y_B = 8.591 \times 10^{-4} / (6.44 \times 10^{-4} + 8.591 \times 10^{-4}) = 0.5707$

$X_A = 0.0028 / (0.0028 + 0.0136) = 0.1739$

$X_B = 0.0136 / (0.0028 + 0.0.0136) = 0.8242$

$\therefore$ Separation factor $= \dfrac{0.4292/0.5707}{0.1739/0.8242}$

$= 3.5643$

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