

**SYNTHESIS, CHARACTERIZATION AND PERFORMANCE OF  
ZEOLITE A MEMBRANE FOR THE RECOVERY OF  
ALCOHOL FROM ALCOHOL-WATER MIXTURE USING  
PERVAPORATION PROCESS**

**by**

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## LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
BET	Brunaur-Emmett-Teller
BNRI	Bussan Nanotech Research Institute
BtOH	Butanol
CCD	Central composite design
DI	Deionized
DMB	Dimethylbutane
DMC	Dimethylcyclohexne
DOE	Design of experiments
ECN	Netherlands Energy Research Corporation
EDX	Energy dispersive X-ray
EPMA	Electron probe microanalysis
ETBE	Ethyl- <i>tert</i> -butylether
EtOH	Ethanol
FAU	Zeolite Faujasite
FIB	Focused ion beam
FTIR-ATR	Fourier transform infrared attenuated total reflectance method
Ge-ZSM-5	Germanium substituted Zeolite Socony Mobil 5
GIXRD	Grazing incidence X-ray diffraction
H-ZSM-5	Hydrogen substituted Zeolite Socony Mobil 5
IPA	Isopropanol
IZA	International Zeolite Association
LTA	Zeolite Linde Type A
MEK	Methylethylketone
MeOH	Methanol
MFI	Zeolite Mobil Five
MOR	Zeolite Mordenite
MP	Methylpentane
MTBE	Methyl- <i>tert</i> -butylether
NA	Not available
NaA	Zeolite sodium contained Linde Type A
NaX	Zeolite sodium contained Linde X

NaY	Zeolite sodium contained Linde Y
RD	Reactive distillation
Ref.	Reference
RHS	Right hand side
RSM	Response surface methodology
SEM	Scanning electron microscopy
Si/Al	Silica to alumina ratio
SS	Stainless steel
TEM	Transmission electron analysis
TGA	Thermal gravimetric analysis
TMAOH	Tetramethylammonium hydroxide
TPABr	Tetrapropylammonium bromide
TPAOH	Terapropylammonium hydroxide
XRD	X-ray diffraction
ZSM-5	Zeolite Socony Mobil Five

## LIST OF SYMBOLS

$A$	Factor code for temperature in DOE
$a_i$	Adsorption coefficient of component $i$ ( $\text{mol}/\text{m}^3 \cdot \text{Pa}$ )
$B$	Factor code for isopropanol feed concentration in DOE
$C$	Factor code for permeate pressure in DOE
$C_{IPA}$	Isopropanol feed concentration (wt/wt)
$D$	Factor code for feed flow rate in DOE
$D_i^s$	Maxwell-Stefan diffusivity of component $i$ ( $\text{m}^2/\text{s}$ )
$D_{ij}^s$	Maxwell-Stefan micropore counter-sorption diffusivity between component $i$ and component $j$ ( $\text{m}^2/\text{s}$ )
$D_{iv}^s$	Maxwell-Stefan surface diffusivity ( $\text{m}^2/\text{s}$ )
$D_{iM}'$	Maxwell-Stefan micropore diffusivity of component $i$ in the membrane ( $\text{m}^2/\text{s}$ )
$D_i^s(0)$	Maxwell-Stefan diffusivity at zero loading ( $\text{m}^2/\text{s}$ )
$E_J$	Activation energies ( $\text{kJ}/\text{mol}$ )
$e$	Error of the response $Y$ in statistical model
$J_i$	Flux of component $i$ ( $\text{kg}/\text{m}^2 \cdot \text{h}$ )
$J_o$	Pre-exponential factor
$l$	Thickness of the selective layer (m)
$l_{ZA}$	Thickness of zeolite layer (m)
$L_i$	Coefficient of proportionality of component $i$
$m$	Mass of permeate (kg)
$M$	Molecular weight ( $\text{kg}/\text{mol}$ )
$N_i$	Molar flux of component $i$ ( $\text{mol}/\text{m}^2 \cdot \text{s}$ )
$N_i^s$	Flux across the membrane ( $\text{kg}/\text{m}^2 \cdot \text{h}$ )
$n_i$	Mole fraction of component $i$ (mol/mol)
$P_i^G$	Membrane permeability of component $i$ (Barrer)
$P$	Pressure (kPa)
$p$	Partial pressure (Pa)
$p_i^*$	Partial equilibrium vapor pressure of component $i$ (Pa)
$q_i$	Molar loading of component $i$ (mol/kg)



$q_M$	Saturation molar loading, (mol/kg)
$q^T$	Total molar loading (mol/kg)
$Q_i^*$	Dimensionless flux for component $i$
$Q$	Membrane permeance ( $\text{g/m}^2 \cdot \text{h} \cdot \text{kPa}$ )
$R$	Ideal gas constant ( $8.314 \text{ J/mol} \cdot \text{K}$ )
$S$	Membrane surface area ( $\text{m}^2$ )
$s$	Sum of counts
$t$	Permeation time (h)
$T$	Temperature (K)
$u_i$	Velocity of the diffusing component $i$ (m/s)
$V$	Feed flow rate ( $\text{dm}^3/\text{h}$ )
$v_i$	Molar volume of component $i$
$x_i$	Mass fraction of component $i$ in the feed (kg/kg)
$x'_i$	Mole fraction of component $i$ in the feed (mol/mol)
$y_i$	Mass fraction of component $i$ in the permeate (kg/kg)
$y'_i$	Mole fraction of component $i$ in the permeate (mol/mol)
$X$	Independent variable
$Y$	Response
$z$	Distance of diffusion

### *Greek Letters*

$\mu_i$	Chemical potential of component $i$ (J/mol)
$\eta$	Dimensionless membrane thickness
$\theta_i$	Fractional surface occupancy of component $i$
$\theta_{n+1}$	Fraction of unoccupied site
$\alpha_i$	Selectivity for the component $i$ with respect to component $j$ .
$\beta$	Constant in statistical model
$\gamma_i$	Activity coefficient
$\varepsilon$	Porosity
$\rho_s$	Density of zeolite NaA ( $1900 \text{ kg/m}^3$ )

*Subscripts*

<i>a</i>	Alcohol
<i>f</i>	Feed
<i>i</i>	Component <i>i</i>
<i>j</i>	Component <i>j</i>
<i>M</i>	Membrane
<i>p</i>	Permeate
<i>x</i>	Sample
<i>r</i>	Reference
<i>W</i>	Water

**SINTESIS, PENCIRIAN DAN PRESTASI MEMBRAN ZEOLITE A UNTUK  
PEROLEHAN SEMULA ALKOHOL DARIPADA CAMPURAN ALKOHOL-  
AIR DENGAN MENGGUNAKAN PROSES PERVAPORASI**

**ABSTRAK**

Prestasi pemisahan membran seramik komersial dan membran zeolite A yang disintesis telah dikaji dalam perolehan semula alkohol daripada campuran alkohol-air dengan menggunakan kaedah pervaporasi. Membran zeolite A disintesis atas sokongan  $\alpha$ -alumina berbentuk tuib dan cakera dengan menggunakan kaedah sintesis gelombang mikro. Pengaruh pembijian terhadap sintesis membran telah dikaji. Membran zeolite yang disintesis telah dicirikan dengan XRD (struktur), SEM (ketebalan membran) dan TGA (kestabilan terma). Eksperimen pervaporasi pada keadaan kendalian yang berbeza telah dijalankan untuk menilai prestasi pemisahan membran. Keputusan tersebut menunjukkan bahawa prestasi bagi membran yang disintesis dengan pembijian adalah lebih baik berbanding dengan membrane yang disintesis tanpa pembijian.

Membran seramik komersial yang didapati daripada Pervatech BV telah digunakan dalam kajian proses pervaporasi terhadap larutan berair isopropanol dan etanol. Pengaruh suhu suapan, komposisi suapan, tekanan penelapan dan kadar aliran terhadap prestasi membran telah dikaji dengan menggunakan rekabentuk eksperimen (DOE) yang digabungkan dengan metodologi permukaan sambutan (RSM). Rekabentuk komposit tengah (CCD) telah digunakan untuk mendapatkan keadaan proses yang optimum. Keputusan kajian menunjukkan bahawa untuk mendapatkan

fluks penelapan boleh diterima sebanyak  $2.41 \text{ kg/m}^2\cdot\text{h}$  dan optimum kememilihan sebanyak 1131, suhu suapan, komposisi suapan isopropanol, tekanan penelapan dan kadar aliran adalah  $75^\circ\text{C}$ , 94 wt%, 1 kPa and  $84 \text{ dm}^3/\text{h}$  secara berasingan. Fluks penelapan optimum sebanyak  $9.16 \text{ kg/m}^2\cdot\text{h}$  boleh didapati pada suhu suapan  $90^\circ\text{C}$ , komposisi suapan isopropanol 81 wt%, tekanan penelapan 1 kPa dan kadar aliran  $100 \text{ dm}^3/\text{h}$ . Kememilihan optimum sebanyak 1415 pula boleh didapati pada suhu suapan  $69^\circ\text{C}$ , komposisi suapan isopropanol 96 wt%, tekanan resapan 1 kPa dan kadar aliran  $41.05 \text{ dm}^3/\text{h}$ .

Model pervaporasi yang asas telah digunakan untuk menentukan parameter pemisahan bagi proses pervaporasi dengan menggunakan data-data eksperimen. Fluks air telah diramalkan daripada model tersebut dengan menggunakan parameter pemisahan yang ditentukan. Data fluks simulasi tersebut didapati sepadan dengan data fluks eksperimen dengan pembezaan ralat sebanyak  $\pm 10\%$ . Tenaga pengaktifan bagi fluks penelapan air dan isopropanol yang ditentukan dari persamaan Arrhenius adalah sebanyak 44.1-47.2 kJ/mol dan 66.5-84.0 kJ/mol.

**SYNTHESIS, CHARACTERIZATION AND PERFORMANCE OF ZEOLITE  
A MEMBRANE FOR THE RECOVERY OF ALCOHOL FROM ALCOHOL-  
WATER MIXTURE USING PERVAPORATION PROCESS**

**ABSTRACT**

The separation performance of the commercial ceramic membrane and self-synthesized zeolite A membrane was studied for the recovery of alcohol from alcohol-water mixture using pervaporation method. Zeolite A membrane was synthesized on  $\alpha$ -alumina tubular and disc-shaped supports using the microwave synthesis method. The seeding effect on the membrane synthesis was investigated. The synthesized zeolite membranes were characterized by XRD (structure), SEM (membrane thickness) and TGA (thermal stability). Pervaporation experiments at different operating conditions were conducted to evaluate the membrane separation performance. The results showed that the performance for the membrane synthesized with seeding was much better than those synthesized without seeding.

Commercial ceramic membrane supplied by Pervatech BV was used in the pervaporation process studies on isopropanol and ethanol aqueous solutions. The effects of feed temperature, feed concentration, permeate pressure and feed flow rate on the membrane separation performance were studied using design of experiments (DOE) coupled with response surface methodology (RSM). The center composite design (CCD) was used to obtain optimum process condition. The results showed that in order to obtain an acceptable permeation flux of  $2.41 \text{ kg/m}^2\cdot\text{h}$  and optimum selectivity of 1131, the temperature, isopropanol feed concentration, permeate

pressure and feed flow rate were 75°C, 94 wt%, 1 kPa and 84 dm<sup>3</sup>/h respectively. The optimum permeation flux of 9.16 kg/m<sup>2</sup>.h was obtained at temperature of 90°C, isopropanol feed concentration of 81 wt%, permeate pressure of 1 kPa and feed flow rate of 100 dm<sup>3</sup>/h respectively. The optimum selectivity of 1415 was obtained at the temperature of 69°C, isopropanol feed concentration of 96 wt%, permeate pressure of 1 kPa and feed flow rate of 41.05 dm<sup>3</sup>/h respectively.

A basic pervaporation transport model was employed to determine the separation parameters for the pervaporation process from the experimental data. The water flux was predicted from the model using the separation parameters. The simulated flux data were in agreement with the experimental flux data within an error of  $\pm 10\%$ . The activation energy for water and isopropanol permeation flux determined from Arrhenius type relation was 44.1-47.2 kJ/mol and 66.5-84.0 kJ/mol respectively.

# **CHAPTER ONE**

## **INTRODUCTION**

### **1.1 MEMBRANE SEPARATION TECHNOLOGY**

During the past few decades, membrane separation processes has become one of the emerging technology which underwent a rapid growth. It has drawn the attention of researchers in the separation technology field with its better performance compared to the conventional separation technology. Membrane separation process is advantageous in terms of energy savings, environmentally friendly, easy operation and has a greater flexibility in designing the systems (Nunes and Peinemann, 2006). Membrane separation involves partially separating a feed containing a mixture of two or more components by using a semipermeable barrier (membrane) through which one or more of the species moves faster than other species. A membrane is a thin sheet of natural or synthetic material that covers a surface and is permeable to certain component in the solution. Membranes can be classified according to their morphology as dense, porous and composite membranes. The main membrane separation technologies include microfiltration, ultrafiltration, reverse osmosis and nanofiltration, electrodialysis, gas-separation and pervaporation (Baker, 2004). The principle of membrane separation process, type of membrane used, driving forces and examples of the application of the established membrane separation technologies are presented in Table 1.1.

Table 1.1: Summary of the established membrane separation technologies (Baker, 2004)

<b>Process</b>	<b>Principle</b>	<b>Type of Membrane</b>	<b>Initial or Feed phase</b>	<b>Driving Force</b>	<b>Industrial Applications</b>
Microfiltration	Separation of organic and polymeric compounds with micro pore ranges of 0.1-10 $\mu\text{m}$ .	Finely microporous 0.1-10 $\mu\text{m}$	Liquid or gas	Pressure difference 35-350 kPa	Removal of suspended solids, bacteria in pharmaceutical, electronics industries.
Ultrafiltration	Separation of water and microsolute from macromolecules and colloids.	Finely microporous 1-100 nm	Liquid	Pressure difference 140-700 kPa	Removal of colloidal material from wastewater, food process streams.
Reverse Osmosis	Passage of solvents through a dense membrane that is permeable to solvents but not solutes.	Dense solution-diffusion	Liquid	Pressure difference 700-7000 kPa	Drinking water from sea, brackish or groundwater; production of ultra-pure water for electronics and pharmaceutical industries.
Electrodialysis	Ions are transported through a membrane from one solution to another under the influence of an electrical potential.	Electrically charged films	Liquid	Voltage difference 1-2 V	De-ionized water from conductive spacers, recovery of organic acids from salt, heavy metal recovery.
Gas separation	Component of mixture of gaseous is removed through a pressure gradient.	Dense solution-diffusion	Vapor or gas	Pressure difference 700-7000 kPa	Removal of nitrogen from air, hydrogen from petrochemical/refinery vents, carbon dioxide from natural gas, propylene and VOCs from petrochemical vents.
Pervaporation	Component of a mixture diffuses through, evaporates under a low pressure and is removed by a vacuum.	Dense solution-diffusion	Liquid	Vapor pressure 7-70 kPa	Dehydration of solvents, separation of azeotropic mixtures



## 1.2 PERVAPORATION

Most of the membrane separation technologies are well-developed and established. Among these technologies, pervaporation is still a rapidly developing membrane separation technology. Pervaporation is a process that has elements in common with reverse osmosis and membrane gas separation. It also has many similarities with vapor permeation, which uses gaseous components on the feed side of the membrane. However, the vapor permeation flux strongly depend on feed pressure whereas the pervaporation flux are independent of the feed pressures (Bowen et al., 2004a). Pervaporation is used for the separation of water from organic liquids by partial vaporization through a porous membrane. The membrane acts as a selective barrier between the two phases, the liquid phase feed and the vapor phase permeate. It allows the desired components of the liquid feed to transfer through it by vaporization (McCabe et al., 2005). Separation by pervaporation is almost independent of the vapor liquid equilibrium, because the transport resistance depends on the sorption equilibrium and mobility of the permeate components in the membrane. A vacuum is kept on the permeate side of the membrane while the feed side of the membrane is kept at atmospheric or elevated pressure so that a pressure difference is created over the membrane in order to maintain the driving force for the pervaporation process. Figure 1.1 shows the overview of the pervaporation process. The desired component in the feed which is in the liquid form permeates through the membrane and evaporates while passing through the membrane because the partial pressure of the permeating component is kept lower than the equilibrium vapor pressure.

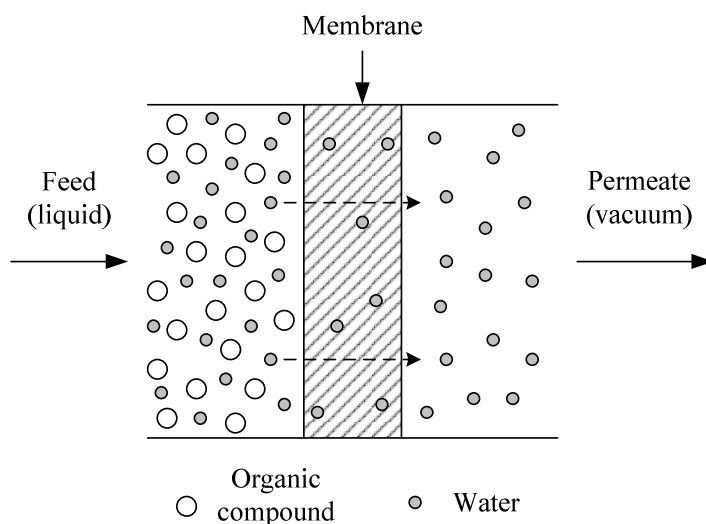


Figure 1.1: Overview of the pervaporation process for aqueous organic mixtures.

Pervaporation is a mild process, therefore it is very effective for separation of those mixtures which cannot be subjected to the harsh conditions of distillation. Pervaporation has advantages in terms of low energy consumption. No entrainer is required in pervaporation, thus there is no contamination of the original mixtures (Xiao et al., 2006). It can be used for breaking azeotropes, dehydration of solvents and other volatile organics, organic/organic separations such as xylene isomers separations, acid separations and wastewater purification (Pera-Titus et al., 2006a). Recently pervaporation has gained increasing interest on the part of the chemical industry as an effective and energy-efficient technology to carry out separations which were difficult to achieve by conventional means (Sekulic et al., 2005). This technology has better separation capacity and energy efficiency which could lead to 40-60% energy reductions (de Bruijn et al., 2003).

Different types of membranes are being used for pervaporation: polymeric membranes, ceramic membranes, and composite membranes. Over the last decades considerable efforts have been put in the development of ceramic membranes for pervaporation as these membranes show better resistance towards harsher chemical, pressure and thermal conditions (Li et al., 2007c). An example of the ceramic membranes is the zeolite membranes that have the unique properties of zeolite in a film-like configuration. Zeolite membranes have been widely used for pervaporation in both laboratory studies and application in process in the industry (Huang et al., 2007a; Kyotani et al., 2007; Pera-Titus et al., 2008a).

### **1.3 ZEOLITE MEMBRANE**

Zeolites are aluminosilicates with a broad range of aluminium to silicon ratio. They form crystalline structure with well-defined pores in the range of several nanometers (nm). Zeolite membranes have been widely studied in pervaporation due to their unique characteristics such as pore structure, adsorption properties and their mechanical, chemical and biological stability (Kyotani et al., 2007; Van Hoof et al., 2006). Several zeolite structures such as ZSM-5 (Navajas et al., 2006), zeolite A (Li et al., 2007a), mordenite (Sato et al., 2008), zeolite Y (Chen et al., 2007a), are reported as membranes used for pervaporation. The characteristics of these zeolite structures are summarized in Table 1.2. Zeolite membranes offer several advantages over polymeric membranes. One of the advantages is that zeolite membranes do not swell. Zeolites have uniform and molecular-sized pores that cause significant differences in transport rate for some molecules, and allow molecular sieving in some cases. Besides, most of the zeolite membranes are more chemically and thermally stable than polymeric membranes, thus allowing the separation of strong

solvents or low pH mixtures at high temperature (Bowen et al., 2004a). At high aluminium to silicon ratio, the crystal and especially the inner lumen of the pore is hydrophilic with a preferential sorption of water inside the pores (Huang and Yang, 2008). In particular, NaA-type zeolites also known as zeolite A are extremely hydrophilic and the pores of crystals are accessible for water molecules only, hence NaA-type zeolite membranes are widely studied as pervaporative membranes for the dehydration of alcohol or other solvents (Namboodiri and Vane, 2007; Zah et al., 2006a).

Table 1.2: Characteristics of the zeolites used in membrane and its application in pervaporation (Okumus et al., 2003).

	<b>Zeolite</b>			
	<b>A</b>	<b>Y</b>	<b>ZSM-5</b>	<b>Mordenite</b>
<b>Structure type</b>	LTA	FAU	MFI	MOR
<b>Si/Al ratio</b>	1	2.3	8 - $\infty$	4
<b>Cations</b>	Na	Na, Ca	Na	Na
<b>Pore size</b>				
<b>[100]</b>	0.41×0.41 nm		0.51×0.55 nm;	0.65×0.70 nm;
<b>[010]</b>			0.53×0.56 nm	0.34×0.48 nm;
<b>[001]</b>				0.26×0.57 nm
<b>[111]</b>		0.74×0.74 nm		
<b>Channel Network</b>	Three-dimensional	Three-dimensional	Three-dimensional	One-dimensional
<b>Application</b>	Dehydration of organic mixtures.	Separation of MeOH/MTBE mixtures.	Separation of xylene isomers.	Separation of benzene/ <i>p</i> -xylene mixtures.

## 1.4 PROBLEM STATEMENT

Removal of water from alcohol-water solutions in the industry is frequently sought but faces difficulties in the separation especially when an azeotrope is involved. The concentration and purification of alcohol is necessary for many chemical processes. For example isopropanol with a purity of 99.5% is required as an important solvent in pharmaceutical and electronics industries while absolute or anhydrous ethanol is used as fuel alcohol and solvent for laboratory and industrial applications, where water will react with other chemicals. Conventional methods such as extractive distillation, azeotropic distillation, and liquid-liquid extraction are costly and exhibit some drawbacks. In view of this, new approaches have been adapted to separate azeotropic solutions. A good example would be pervaporation which is an effective and energy-efficient technique. Currently, pervaporation still remains as a competitive technology with only a handful of companies which are offering industrial pervaporation systems. The reasons for the insignificant spread of commercial applications might be due to two plausible reasons: (1) economical feasibility and (2) incomplete development of process technology for the membrane manufacturing which includes poor reproducibility (Ju et al., 2006).

Zeolite membrane such as zeolite A membrane which has high solvent-resistant properties is being widely used for the pervaporation of alcohol-water mixtures. The reproducibility in the membrane fabrication is crucial in industrial mass production. However, the difficulties in reproducing the different variables with each seeding and synthesis processes explain the low reproducibility resulted for the zeolite membrane (Xu et al., 2001). This low reproducibility is a commonly

encountered problem due to the large number of factors that are involved in the zeolite membrane formation.

Despite these issues, pervaporation with zeolite membrane still holds a bright future. Therefore it is envisaged that with further improvement in the synthesis of zeolite membrane, these will find their respective areas of applications in the industry. The development of a more convenient and effective synthesis methods that are capable to make the process variable more stable and suitable for large-scale manufacture with high reproducibility remain a challenge for researchers.

## **1.5 OBJECTIVES**

The present research has the following objectives:

- i. To synthesize and characterize zeolite A supported membrane useful for pervaporation process.
- ii. To test the pervaporation rig for the recovery of alcohol from alcohol-water mixtures using commercial tubular ceramic membrane and optimize the operating parameters of the pervaporation unit using Design of Experiments (DOE) coupled with Response Surface Methodology (RSM).
- iii. To test the synthesized zeolite A membrane performance for the separation of isopropanol-water and ethanol-water systems using the optimum operating condition determined from process optimization studies.
- iv. To obtain the separation parameters from the experimental data using the basic pervaporation transport equation for the prediction of the membrane performance.

## 1.6 SCOPE OF STUDY

The first part of the present study was to synthesize a defect-free, high flux, high selectivity zeolite A membrane using the microwave synthesis method. The effect of seeding on the membrane performance was investigated. Tubular and disc-shaped  $\alpha$ -alumina will be used as the supports for the all the membranes synthesized. Membrane characterization will be carried out using SEM, XRD and TGA. For evaluation of the membrane performance, separation of alcohol from alcohol-water mixtures using pervaporation was conducted. The separation performance of each synthesized membrane using different synthesis approach was compared at various operating conditions.

The second part of the present study focused on the investigation of the effect of operating parameters such as feed temperature, feed concentration, feed flow rate and permeate pressure on the performance of the membrane for the dehydration of isopropanol aqueous mixtures using pervaporation. The performance of the membrane was studied in terms of permeation flux and selectivity. The effects of feed temperature (60-90 °C), feed concentration (80-96 wt% IPA), feed flow rate (40-100 dm<sup>3</sup>/h) and permeate pressure (1-5 kPa) on permeation flux and selectivity were studied using Design of experiments (DOE) coupled with Response Surface Methodology (RSM). The ranges of these parameters were decided based on literature search and practical viability of the experimental rig.

The last part of the present study was to obtain the separation parameters from the basic pervaporation transport equation. The experimental data were used to estimate the transport parameters of the model. The membrane performance in terms

of permeation flux was predicted using the membrane separation transport parameters. The simulated permeation flux was compared with experimental permeation flux data. Besides that, the activation energy for permeation fluxes was also determined from the Arrhenius-type relation.

## **1.7 ORGANIZATION OF THE THESIS**

This thesis contains five chapters. In the first chapter, a brief introduction about the different types of membrane separation technologies established is presented. The theory, general characteristic of pervaporation and recent application of zeolite membrane in pervaporation are also briefly discussed. A problem statement lists out some of the problems unsolved in the recovery of alcohol from alcohol-water mixtures using pervaporation and in the synthesis of zeolite membrane, thus giving a direction to the present research work.

Chapter two presents a literature review on the different type of membrane used in pervaporation studies and the different type of synthesis approach used to produce zeolite membrane that were developed for the past few decades. This is followed by the methods used for membrane characterization. Besides that, the application of pervaporation in alcohol dehydration and organic-organic separation are also reviewed. The industrial application of pervaporation is reviewed as well. At the end of the chapter, the pervaporation modeling from the transport mechanism and design of experiments is presented.



In chapter three, a detailed description of the experimental works is elaborated. The materials and chemicals used in the present study are presented. The procedures applied for the zeolite A membrane synthesis such as the preparation of the  $\alpha$ -alumina membrane support and the microwave synthesis method of the membrane with and without seeding are elaborated. Various characterization methods used in the present study are also presented. At the end of the chapter, the designs of the tubular membrane cell are presented. The details for the pervaporation test rig setup and the operating procedure for the rig are given. The process evaluation and data analysis are also given.

Chapter four covers the results and discussions of the experimental data for the present study. This chapter is divided into four sections. In the first section, the characterization of the synthesized zeolite A membrane such as the XRD crystallograms, SEM micrographs and TGA analysis are covered. These characterizations are shown to reveal the microstructure and topology of the zeolite membrane. In the second section, the testing of the pervaporation rig and the process optimization studies for isopropanol aqueous solution using commercial membrane is presented. The design of experiments (DOE) results for the commercial membrane is presented and discussed. The optimum conditions for the pervaporation process are identified using DOE and the results for the verification test at these conditions are presented. Besides that, the effectiveness of pervaporation process in separating azeotropic mixture and the stability of the membrane during pervaporation is also being discussed in this section. In the third section, the performances for the synthesized zeolite membrane are being evaluated using the pervaporation experiments operated under the optimum conditions determined in the process

optimization studies. The effect of seeding on the membrane performance is being discussed and the performance of the synthesized zeolite A membrane and commercial membrane is compared. In the last section of this chapter, the separation parameters are determined from the experimental data by using the pervaporation transport equations. The separation parameters are used to predict the membrane performance in terms of permeation flux during the pervaporation process.

Chapter five presents the main conclusions obtained in the present study. This chapter ends with suggestions and recommendations for future studies in order to improve the present research works. These recommendations are given based on their significance and importance, taking into account the conclusions obtained in the present study.

## **CHAPTER TWO**

### **LITERATURE REVIEW**

#### **2.1 ROLE OF MEMBRANE IN PERVAPORATION**

Membranes have gained importance in chemical industries and are used in a broad range of applications. The systematic studies of membrane were traced as early as in the eighteenth centuries when membranes were only used as laboratory tools to develop physical or chemical theories and had no commercial or industrial applications (Baker, 2004). A membrane is a discrete, thin interface that moderates the permeation of a certain chemical species that is in contact with it. This interface may be molecularly homogeneous that is completely uniform in composition or structure or physically heterogeneous, for example containing holes or pores of finite dimensions or consisting of some form of layered structure (Baker, 2004). Different types of membranes are used for the pervaporation of organic compounds from aqueous solution. Three major categories are used. These are (a) organic membrane, broadly covers polymeric membranes, (b) inorganic membrane, covers ceramic membranes and (c) composite membrane, also called hybrid membrane and covers polymeric as well as inorganic membrane. Figure 2.1 shows the schematic representation of a supported membrane morphology used in the pervaporation process. The membrane which acts as the separating layer is coated on top of a porous support and allows only certain species to permeate through it selectively.

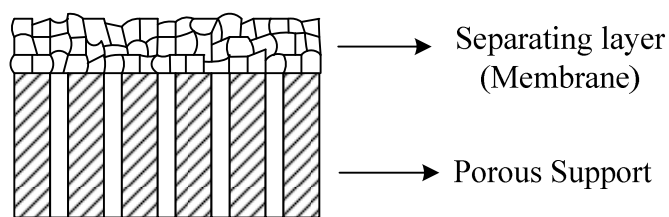


Figure 2.1: Schematic representation of a supported membrane morphology.

### 2.1.1 Polymeric Membrane

Most pervaporation membranes that are used in industrial applications are of polymeric type. Polymeric membranes are attractive because they are relatively economical to fabricate (Gimenes et al., 2007). Polymers such as poly(vinyl alcohol) (Hyder et al., 2006; Zhang et al., 2007), poly(vinylidene difluoride) (Hu et al., 2007), and poly(acrylic acid) (Huang et al., 2007b) are some of the materials used for preparing polymeric pervaporation membrane for the dehydration of alcohol and other solvents. Apart from that, chitosan (Hu et al., 2007; Kanti et al., 2004) is also one of the commonly used materials for polymeric membrane preparation because of its good film forming properties and chemical stability (Won et al., 2002). These polymeric membranes are good candidate owing to their water-permselectivity and high permeation fluxes (Liu et al., 2007). Polyacrylonitrile (Wang et al., 1996) and polytetrafluoroethylene (Liu et al., 2007) were reported using as support layers for these polymeric membranes. Sulzer Chemtech, Germany (Qiao et al., 2005) developed polymeric membrane that have a cross-linked poly(vinyl alcohol) selective layer and a porous polyacrylonitrile supporting layer cast on a polyphenylene sulfide non-woven fabric which are marketed for the dehydration of aqueous system. Hyder et al. (2006) prepared crosslinked poly(vinyl alcohol) membranes using two methods: (a) heating at 398 K (thermally crosslinked) and (b)

chemical reaction with glutaraldehyde at room temperature (chemically crosslinked). The pervaporation experiments of the ethanol-water mixture showed that the thermally crosslinked membrane gave a higher flux compared to the chemically crosslinked membrane. However, the selectivity of the thermally crosslinked membrane was lower as compared to the chemically crosslinked membrane.

A major drawback of these polymeric membranes is their limited solvent and temperature stability (van Veen et al., 2001). Swelling that occurs in polymeric membranes also tends to alter the membrane properties and generally leads to higher permeability and lower selectivity (Gallego-Lizon et al., 2002; Praptowidodo, 2005). Anjali-Devi and co-workers (2005) studied crosslinked chitosan membrane for feed composition comprising with 4–40 wt% water and found that an increase in feed water concentration increased the flux while decreased the selectivity. The preferential affinity of the membrane towards water causes swelling, thus allows a rapid permeation of feed molecules.

### **2.1.2 Inorganic Membrane**

In order to overcome the problems caused by polymeric membrane, considerable efforts have been put in the development of inorganic membrane, also called ceramic membranes made from silica, alumina or zeolite for pervaporation as these membranes show a better chemical, thermal and mechanical stability (Li, 2007). These membranes can be used for broad range of applications and at the same time have both high selectivity and permeability. The industrial use of ceramic membranes could lead to a higher product quality and broaden the application range of pervaporation. In particular, porous inorganic membranes exhibit high

permeabilities relative to dense membranes and high thermal stability relative to organic membranes (Burgraaf and Cot, 1996; Verkerk et al., 2001b).

Silica is known as a highly porous material and is preferable for a high flux inorganic membrane but it is not stable against water (Asaeda and Yamasaki, 2001). The addition of oxides such as  $ZrO_2$  and  $TiO_2$  is able to improve the stability of silica membrane towards water and alkali. Composite  $SiO_2$ - $ZrO_2$  can be put into thin porous membranes which have been found quite effective for the separation of aqueous organic mixtures by pervaporation (Urriaga et al., 2006). Yang and co-workers (2006) prepared five different types of microporous  $SiO_2$ - $ZrO_2$  ( $ZrO_2$ : 50 mol%) membranes by the sol-gel techniques and studied the pervaporation characteristics of aqueous solutions of organic chemicals. The pervaporation results suggested that the separation performance depends largely on the pore size and also on the interaction between the molecules and the pore wall. Van Veen and co-workers (2001) reported that the silica membrane performance could remain constant for a period of several weeks and can be operated at temperature above 100 °C with a much better acid stability.

Apart from the silica membrane, zeolite membranes have been attracting the attention of researchers in recent years. Several zeolites are known to separate organic molecules based on their properties of preferential adsorption, preferential diffusion or pure molecular sieving (Mohanty and McCormick, 1999). Zhou and co-workers (2005) studied the pervaporation properties of ZSM-5 type membranes in the separation of water-alcohol mixtures. The synthesized membrane consisted of about 40  $\mu m$  thick zeolite layer and exhibited high pervaporation selectivity of water

in methanol, ethanol, and isopropanol-water mixtures. The high performance silicalite-1 membranes were successfully synthesized by Chen and co-workers (2007a) by using the 'solution-filling' method. Pervaporation experiments were carried out using the synthesized silicalite-1 membranes for methanol-water, ethanol-water, 2-propanol-water and 1-propanol-water mixtures respectively. It was found out that the average total flux of membranes synthesized by using the 'solution-filling' method could be improved by about 90 %. Van Hoof and co-workers (2006) compared the dehydration performance of a commercial NaA-type zeolite membrane with the polymeric membranes for dehydration of the binary mixtures isopropanol-water, acetonitrile-water and methylethylketone(MEK)-water. For all the solvents that were tested, the polymeric membranes show the best dehydration properties with azeotrope, however the NaA-type zeolite membranes show the best separation properties at low water concentrations.

### **2.1.3 Composite Membrane**

A novel membrane morphology emerging with the potential of future application is the composite membrane. Composite membranes are prepared by casting hydrophilic polymers on porous substrates (Liu et al., 2007). The porous support provides mechanical strength and the casting layer provides separation efficiency to the membrane. The introduction of cross-linked structure to hydrophilic membranes can significantly suppress excessive swelling of membranes in order to retain a high selectivity (Gimenes et al., 2007). The formation of organic-inorganic hybrid shows certain achievement on membrane stabilization in terms of thermal, chemical and mechanical properties (Gimenes et al., 2007; Liu et al., 2007). These membranes combine the superior separation performance of rigid adsorptive

inorganic materials and ideal membrane forming property of organic materials (Sun et al., 2008). Okumus and co-workers (2003) reported that permeation flux in the poly(acrylonitrile) (PAN)-based zeolite-filled membranes is increased about nine-fold with a loss of selectivity about seven-fold relative to homogeneous PAN membranes. Sun and co-workers (2008) prepared H-ZSM-5 filled chitosan membranes by incorporating H-ZSM-5 into chitosan. Improved pervaporation performance was reported (permeation flux of 230.96 g/m<sup>2</sup>h and separation factor of 153 for 90 wt% aqueous ethanol solution at 353K) compared with the chitosan control membrane with a permeation flux of 54.18 g/m<sup>2</sup>h and separation factor of 158 under identical experimental conditions. However the reduction of permeation flux is usually accompanied with the modified membranes (Gimenes et al., 2007; Liu et al., 2007).

Membrane plays an important role in pervaporation since pervaporation is a membrane separation process. Different kinds of membranes have its' own advantages and disadvantages. If pervaporation is used for the purpose of breaking an azeotrope, the polymeric membranes would be preferred since the polymeric membranes are cheaper and show higher fluxes and selectivities for azeotrope (Van Hoof et al., 2006). However, if low water concentration and harsh environment are involved, the inorganic membranes would be more preferred. For the successful implementation of membrane in industrial process, both membrane selectivity and permeability are important. Thus, the development of high flux, high selectivity and defect-free membranes is an important area of research.



## **2.2 ZEOLITE MEMBRANE SYNTHESIS**

Zeolite membranes that are synthesized so far has shown good separation performance, but the permeance is too low for practical application (Huang and Yang, 2008). One of the challenges for the preparation of zeolite membrane is to prepare zeolite membrane with high permeance while maintaining high separation selectivity. In order to obtain a better separation performance, zeolite membrane should be preferably made of pure zeolite crystals with uniform and small particle size. Several preparation methods are reported for the synthesis of zeolite membranes (Culfaz et al., 2006; Huang et al., 2004; Motuzas et al., 2006; Zah et al., 2006a). Majority of the zeolite membranes prepared are supported, due to their greater structural stability. The most frequently used supports are generally alumina and stainless steel tubes or discs. Alumina supports typically have pore diameters between 5 nm ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) and 200 nm ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>), and stainless steel supports pore diameters are typically between 0.5 and 4.0  $\mu$ m (Bowen et al., 2004a). Titania (TiO<sub>2</sub>) with a mean pore diameter of 0.12  $\mu$ m is also used as support by some of the researchers (van den Berg et al., 2003). Two critical stages occurred during the formation of supported zeolite membrane namely nucleation on the support followed by crystal growth to form a continuous zeolite film covering the support (McLeary et al., 2006).

### **2.2.1 Hydrothermal Synthesis**

Conventional hydrothermal synthesis (Kazemimoghadam and Mohammadi, 2006; Morigami et al., 2001; Zah et al., 2006a) is the most common method for zeolite membrane preparation and research carried out in recent years has resulted in improvements aimed to reduce the amount of defects in the synthesized membranes (Navajas et al., 2007). In this method, the porous support is immersed into the

synthesis solution. Membrane is formed on the surface of the support by direct crystallization. Bowen and co-workers (Bowen et al., 2003a) successfully synthesized high-quality, boron-substituted ZSM-5 zeolite membrane on Al<sub>2</sub>O<sub>3</sub>-coated SiC multi-channel monolith supports using the hydrothermal crystallization method. It was reported that the membranes effectively removed alcohols and acetone from 5 wt% organic-water binary feeds by pervaporation over a temperature range of 303–333 K. Zah and co-workers (2006b) studied the pervaporation properties of the NaA zeolite membrane synthesized by conventional hydrothermal synthesis with a variation in the crystallization time. The flow diagram for the membrane preparation is presented in Figure 2.2. It was reported that a fully crystalline membrane can be obtained at the crystallization time of 4 h.

The hydrothermal synthesis method is easier to operate, but the synthesized membrane properties significantly depend on the characteristic of the support surface. It is usually difficult to prepare denser zeolite membrane by hydrothermal synthesis (Huang and Yang, 2008). This method usually needs long crystallization time of a few hours to a few days. The long crystallization time usually result in formation of impure zeolites (Xu et al., 2004). For example in the synthesis of NaA zeolite membrane, by-products such as gmelinite, chabazite and faujasite are formed (Yamazaki and Tsutsumi, 2000). Apart from that, due to the low heating rate and the inhomogeneous heating, zeolite crystals formed are not uniform in size as the zeolite nuclei do not form on the support surface simultaneously (Xu et al., 2004).

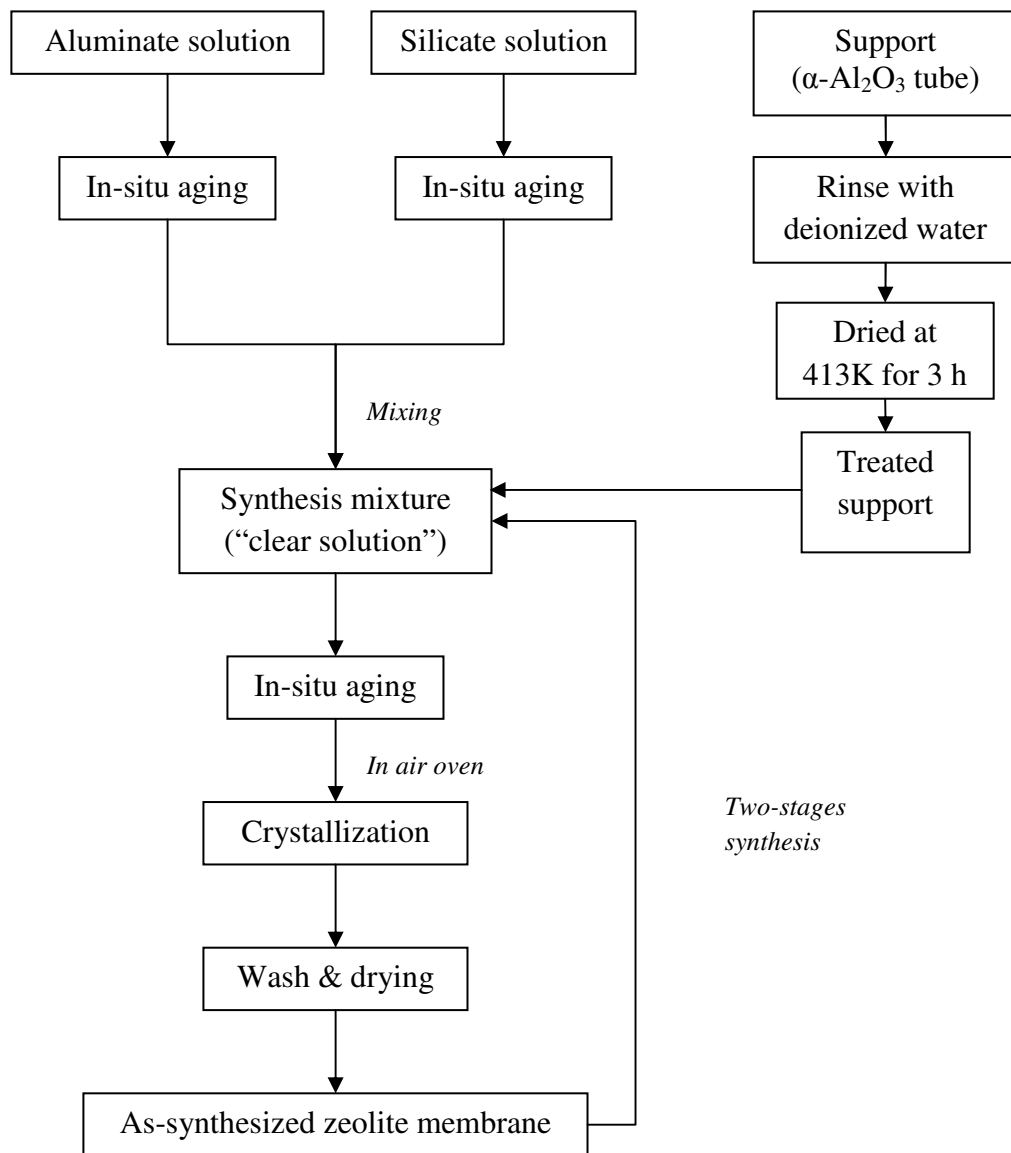


Figure 2.2: Flow diagram of the in-situ crystallization method for the synthesis of zeolite membrane (Zah et al., 2006a).

### 2.2.2 Secondary Growth Method

Coating the zeolite seeds on the support surface before hydrothermal synthesis (secondary growth method) is also an effective method to synthesize a high quality zeolite membrane. The secondary growth method exhibits advantages such as better control over membrane microstructure (thickness, orientation) and higher reproducibility (Boudreau et al., 1999; Huang and Yang, 2008). Therefore, the preparation of zeolite films using secondary growth of precursor particle layers has attracted considerable interest as a possible route to zeolite membrane synthesis (Ahn et al., 2006; Casado et al., 2003; Huang et al., 2004; Tiscareno-Lechuga et al., 2003; Xu et al., 2005). In this method loosely packed layer of zeolite seeds are attached on the support surface before the hydrothermal treatment. During the hydrothermal synthesis, dense membrane is being formed from the regrowth of the zeolite seeds. Until now, several methods have been practiced to deposit zeolite seeds on the support surface such as vacuum seeding (Huang et al., 2004), slip-coating (Tiscareno-Lechuga et al., 2003), rub-seeding (Ahn et al., 2006), and dip-coating (Xu et al., 2005). Sato and co-workers (Sato and Nakane, 2007) reported that high-flux NaA zeolite membrane could be developed by using the secondary growth method with dip-coat seeding. The synthesized NaA membranes exhibited high water flux ( $5.6 \text{ kg/m}^2 \cdot \text{h}$ ) for the pervaporative dehydration of 90 wt% ethanol-water mixture at 348K. Kyotani and co-workers (2007) studied the membrane surface morphologies of NaA zeolite membrane synthesized by secondary growth method by using different characterization method such as Fourier transform infrared attenuated total reflectance method (FTIR-ATR), grazing incidence  $2\theta$  scan X-ray diffraction analysis (GIXRD) and transmission electron microscopy (TEM) and scanning electron microscopy (SEM) combined with a focused ion beam (FIB) cross-section

specimen preparation technique. Information on the fine structure of the membrane which may affect the performance in pervaporative dehydration of ethanol/water system was obtained from their characterization studies.

Although the secondary growth method enables improved control of nucleation site location and density, by rendering the nature of support less importance for membrane growth with growth proceeding from a layer of seed crystals covering the support (McLeary et al., 2006), this preparation method is complicated being involved in multi-step synthesis and in some cases the use of binder might affect the layer properties (Huang et al., 2007a).

### **2.2.3 Continuous Flow Synthesis Method**

In recent years, the continuous flow synthesis method has been reported (Culfaz et al., 2006; Pera-Titus et al., 2006b; Richter et al., 2003) as an alternative techniques in the synthesis of inner-side zeolite membrane. Growing a layer of membrane in the inner side of the support is a challenging task for the preparation of zeolite membrane due to the low accessibility to the lumen of tubular supports (Pera-Titus et al., 2005). In the continuous flow synthesis method, the reactants are continuously supplied to the support surface. A continuous process is desirable for the reasons: (1) it is energy efficient by eliminating the high energy consumption that is required for repeated heat-up and cool down in batch crystallizers; (2) requires smaller equipment and possibly lower capital costs that are inherent in a continuous process as compared to a batch process at the same production rate; (3) produces a more uniform product because of the readily controlled operating conditions (Ju et al., 2006). Pera-Titus and co-workers (2008a) studied the synthesis of NaA zeolite

membrane on the inner side of porous titania (rutile) asymmetric tubular supports in a flow system. The scheme for the experimental set-up used for the zeolite membrane synthesis is shown in Figure 2.3. In this experimental set-up, the synthesis gel was continuously circulated in the lumen of the tubular support under the action of gravity. The synthesized membrane showed great ability to dehydrate ethanol-water mixtures (92 wt% ethanol) at 323K with separation factor up to 8500 and fluxes of  $1.2 \text{ kg/m}^2\cdot\text{h}$ .

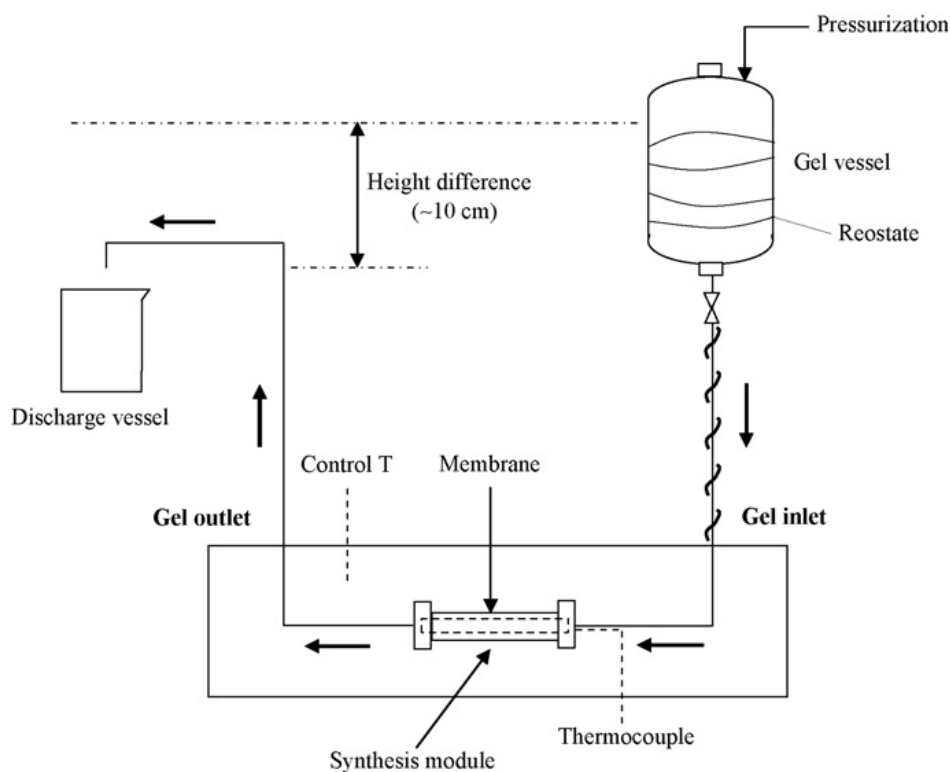


Figure 2.3: Scheme of the continuous flow system used for inner-side NaA zeolite membrane synthesis. Adapted from ref. (Pera-Titus et al., 2008a).

#### 2.2.4 Microwave Synthesis

Recently, the microwave synthesis has been reported for the synthesis of zeolite membranes (Chen et al., 2005; Li et al., 2006; Motuzas et al., 2006; Xu et al., 2001). Compared with the conventional hydrothermal synthesis, microwave synthesis has the advantages of short synthesis time, broad synthesis composition, small zeolite particle size, narrow particle size distribution and high purity (Huang and Yang, 2007; Xu et al., 2004). In microwave processing, energy is supplied by electromagnetic field directly to the material, thus is more efficient in transferring thermal energy to a volume of material than conventional thermal processing which transport heat through surface of the material by convection, conduction and radiation (Bonaccorsi and Proverbio, 2003). However, only few studies on microwave synthesis have been reported to date. For instance, Li and co-workers (2007c) studied the synthesis of LTA zeolite membrane (NaA zeolite membrane) by using the “in-situ aging - microwave synthesis” method. Before microwave heating, the autoclave with support and synthesis mixture was put in an air-oven for aging. It was reported that the synthesized LTA zeolite membranes failed in pervaporation at high water concentration although they possessed excellent long-term stability in vapor permeation. It was also found that the damage of LTA zeolite membrane by water mainly occurred in the grain boundary layer. Huang and Yang (2007) successfully prepared uniform and dense NaA zeolite membrane by using the hydrothermal synthesis method together with microwave heating and conventional heating. Figure 2.4 shows the schematic diagram for the membrane preparation. The separation factor of 10,000 and a flux of  $1.44 \text{ kg/m}^2\cdot\text{h}$  was obtained by using this synthesis method. Bonaccorsi and Proverbio (2003) obtained pure NaA zeolite membrane in a total processing time of 1 h by exposing the reaction mixture to a