

**SYNTHESIS, CHARACTERIZATION AND OPTIMIZATION OF
SUPPORTED CARBON MOLECULAR SIEVE MEMBRANE FROM
POLYETHERIMIDE**

NOOR KHALILAH BINTI ABDUL RASHID

UNIVERSITI SAINS MALAYSIA

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SUPPORTED CARBON MOLECULAR SIEVE MEMBRANE FROM
POLYETHERIMIDE**

by

NOOR KHALILAH BINTI ABDUL RASHID

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Master of Science**

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LIST OF SYMBOLS

A	Surface area	m^2
b_0	Constant coefficient	
b_i	Coefficient for the linear effect	
b_{ii}	Coefficient for the quadratic effect	$\text{mole s}^{-1} \text{ m}^{-2} \text{ Pa}^{-1}$
b_{ij}	Coefficient for the interaction effect	
E_p	Activation energy	kJ mol^{-1}
N	Total number of experiment	
n	Number of factors	
n_c	Center run	
P	Pressure	Pa
Q	Gas flow rate	mol s^{-1}
R^2	Coefficient of determination	
r	Pore radius	
S	Solubility coefficient	
x_i, x_j	Factors (independent variables)	
Y	Response	
<i>Greek letters</i>		
Å	Angstrom unit	
α	Alpha (axial distance from center point which makes the design rotatable)	
β	Mean free path	
ε	Error	
γ	Permselectivity	
γ_D	Diffusion selectivity	
γ_S	Solubility selectivity	

LIST OF ABBREVIATION

ANOVA	Analysis of variance
BET	Brunauer-Emmet-Teller
BPDA	Biphenyltetracarboxylic dianhydride
CCD	Central composite design
CCF	Central composite face centered
CCI	Central composite Inscribed
CCR	Central composite rotatable
CH ₄	Methane
CMS	Carbon molecular sieve
cm	centimeter
CO	Carbon monoxide
CO ₂	Carbon dioxide
DMAC	Dimethylacetamide
DMF	Dimethylformamide
DoE	Design of experiment
EDX	Energy dispersive X-ray microanalysis
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
g	Gram
GPU	Gas permeation unit
H ₂	Hydrogen
H ₂ O	Water
H ₂ S	Hydrogen sulfide
He	Helium
HCN	Hydrogen cyanide
HCl	Acid hydrochloric
K	Kelvin
KBr	Potassium bromide
m	meter
MF	Microfiltration
mm	Millimeter

MPS	Metodologi permukaan sambutan
N ₂	Nitrogen
NH ₃	Ammonia
NH ₄ Cl	Ammonium chloride
nm	nanometer
NMP	N-methylpyrrolidone
O ₂	Oxygen
ODA	oxydianiline
Pa	Pascal
PAN	Polyacrylonitrile
PEG	Polyethylene glycol
PEI	Polyetherimide
PFA	Polyfurfuryl alcohol
PSA	Pressure swing adsorption
psi	Pressure unit
PVDC	Polyvinylidene chloride
rpm	Rotation per minute
RSM	Response surface methodology
s	second
TEM	Transmission electron microscopy
UF	Ultrafiltration
XRD	X-ray diffraction analysis
ZMS	Zeolite molecular sieve
°C	Degree celcius
3D	Three dimensional

SINTESIS, PENCIRIAN DAN PENGOPTIMUMAN MEMBRAN SARINGAN MOLEKULAR KARBON DARIPADA POLIETERIMID

ABSTRAK

Dalam kajian ini, membran saringan molekular karbon (SMK) telah berjaya disintesis daripada polieterimid. Cakera karbon berliang (diameter 20 mm, ketebalan 2.5 mm) sebagai penyokong telah disediakan terlebih dahulu daripada percampuran serbuk hitam karbon dan resin fenolik. Penyokong tersebut dilapisi dengan larutan polieterimid dan seterusnya melalui proses pirolisis pada suhu dan masa yang berbeza bagi menghasilkan lapisan saringan molekular. Metodologi permukaan sambutan (MPS) telah digunakan untuk menilai sumbangan parameter penyediaan ke atas respon peresapan pemilihan H_2/N_2 , CO_2/CH_4 dan O_2/N_2 . Keadaan penyediaan optimum untuk membran SMK telah diperolehi pada $722^\circ C$, 3 jam dan 7.92 wt% masing-masing untuk suhu pirolisis, masa pirolisis dan kepekatan polimer yang memberi keputusan 6.70, 4.32 dan 2.04 masing-masing untuk peresapan pemilihan H_2/N_2 , CO_2/CH_4 dan O_2/N_2 . Pencirian membran SMK mendedahkan kehadiran lapisan karbon mikroliang berserta pelbagai kumpulan berfungsi pada permukaan membran. Luas permukaan BET, isipadu mikroliang dan purata diameter liang membran SMK adalah masing-masing $342.01 \text{ m}^2/\text{g}$, $0.19 \text{ cm}^3/\text{g}$ dan 0.36 nm . Peresapan gas didapati meningkat dengan meningkatnya suhu peresapan dan tekanan masukan.

**SYNTHESIS, CHARACTERIZATION AND OPTIMIZATION OF
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ABSTRACT

In this work, carbon molecular sieve (CMS) membranes were successfully synthesis from polyetherimide. Porous carbon disks (diameter 20mm, thickness 2.5mm) as support were prepared first by agglomeration of fine powdered carbon black with phenolic resin. The polyetherimide solution was coated onto the support and then pyrolyzed at various temperatures and times to form molecular sieve layer. Response surface methodology (RSM) was used to evaluate the contribution of the preparation parameters onto responses which were permselectivity of H₂/N₂, CO₂/CH₄ and O₂/N₂. The optimum preparation conditions for the CMS membrane were obtained at 722°C, 3 hours and 7.92 wt% respectively for pyrolysis temperature, pyrolysis time and polymer concentration which gave result of 6.70, 4.32 and 2.04 for the H₂/N₂, CO₂/CH₄ and O₂/N₂ permselectivity, respectively. The characterization of CMS membrane reveals the existing of microporous carbon film with various functional groups exists on the surface. The BET surface area, micropore volume and average pore diameter of CMS membrane were 342.01 m²/g, 0.19 cm³/g and 0.36 nm, respectively. The gas permeation was found to increase with increase in permeation temperature and feed pressure.

CHAPTER ONE

INTRODUCTION

1.1 Membrane technology

Membrane technology is applied widely in water treatment, dairy industry, biomedical industry and gas purification. In water treatment, membranes make possible the water supply for millions of people in the world and care for the survival of the innumerable people suffering from kidney disease (Geiszler and Koros, 1996). Membranes were used in seawater desalination in the production of fresh water. The membrane bioreactor technology for waste water treatment has been developed based on the combination of the activated sludge process with biomass separation by membrane filtration. Furthermore, membrane technology has been used to refine proteins and transform a waste by-product from cheese production into a valuable product in dairy industry.

Artificial membranes are used in biomedical industry to treat blood for a broad variety of therapeutic purposes and maintain the patient's homeostasis. In gas purification, membranes were most widely in industry for hydrogen/nitrogen separation in ammonia plants, hydrogen/hydrocarbon separation in petrochemical application, separating nitrogen from air, carbon dioxide (CO₂) and water removal from natural gas, and organic vapor removal from air or nitrogen streams.

The market of membrane for gas separation application has grown for the past 20 years. The United State market for this membrane was \$2 billion in 2008. The market is expected to reach \$2.9 billion in 2013. Meanwhile, market for membrane used in liquid separation was \$400 million in 2008 and forecast to reach \$450 million in 2013 (Hanft, 2010).

1.2 Membrane gas separation

The acceptance of membrane technology in the gas separation industry since the early 1980s has boosted and stimulated both commercial and academic interest to further develop membranes that provide better separation performance with high thermal and chemical stability. Conventional gas separation systems such as cryogenic, catalytic and pressure swing adsorption are among the most demanding units in chemical process plants (David and Ismail, 2003).

Membrane gas separation presently provides raw components for a wide range of industrial chemical processes such as oxygen (O₂) and nitrogen (N₂) gas, which are momentarily the third and fifth largest bulk chemicals produced worldwide (Centeno and Fuertes, 2001). Other important separations are the recovery of hydrogen in the production of syngas, and dehydration-deacidification of natural gas. The type of gas separation membrane is shown in Figure 1.1. Membrane can be classified into polymeric membrane and inorganic membrane. Under polymeric membrane category can be divided into glassy membrane and rubbery membrane, while under inorganic membrane are carbon membrane and zeolite membrane.

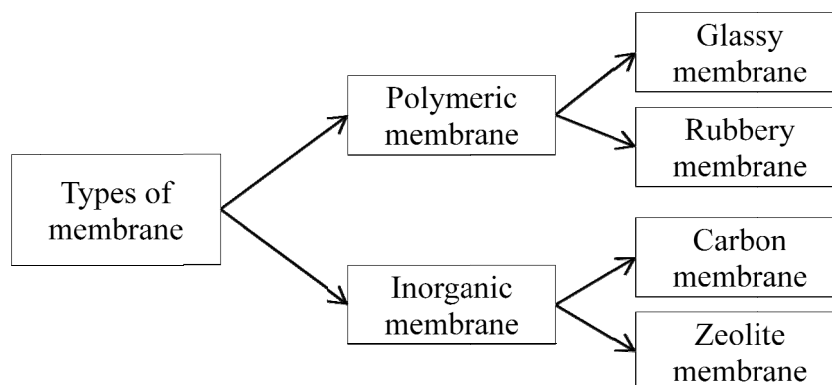


Figure 1.1: Type of membrane

Gas separation membranes are now widely used in variety of application areas as shown in Table 1.1. This is because of its advantages of low operation cost, low energy consumption, ease of operation, cost effectiveness even at low gas volumes and good weight and space efficiency.

Table 1.1: Gas membrane application areas (Abedini and Nezhadmoghadam, 2010)

Common gas separation	Application
O ₂ /N ₂	Oxygen enrichment, inert gas generation
H ₂ /Hydrocarbons	Refinery hydrogen recovery
H ₂ /N ₂	Ammonia purge gas
H ₂ /CO	Syngas ratio adjustment
CO ₂ /Hydrocarbons	Acid gas treatment, landfill gas upgrading
H ₂ O/Hydrocarbons	Natural gas dehydration
H ₂ S/Hydrocarbons	Sour gas treating
He/Hydrocarbons	Helium separation
He/N ₂	Helium recovery
Hydrocarbons/Air	Hydrocarbons recovery, pollution control
H ₂ O/Air	Air dehumification

Inorganic membrane concepts have been developed for gas separation such as carbon molecular sieve (CMS) membranes and zeolite molecular sieve (ZMS) membranes (Barsema, 2004). Inorganic membrane can basically be divided into microporous (pore size < 2nm), mesoporous (pore size 2 – 50 nm) and macroporous (pore size > 50 nm) types. Macroporous usually used as the support for microporous type of membrane in gas separation. CMS and ZMS membranes which are belong to microporous type of membrane consist of rigid pore structure with angstrom-level dimensions that allow the discrimination of gas molecules based on their molecular

dimensions. CMS membranes are produced from the pyrolysis of polymers meanwhile ZMS membranes are synthesized from aluminosilicate materials.

1.3 Carbon molecular sieve (CMS) membrane

CMS membrane is one type of porous inorganic membrane. CMS membrane was produced by pyrolysis of polymeric materials such as polyimide-based, phenolic resin and polyfurfuryl alcohol. CMS membrane are characterized by a very narrow microporosity of 0.3 – 0.6 nm which allows discrimination between gas molecules of different size. Polymers like polyimides are excellent precursors to CMS membrane with different configurations such as hollow fibers, supported disc, capillary tubes and unsupported carbon flat membranes (Fuentes *et al.*, 1999).

CMS membrane has the potential to overcome those problems facing from conventional polymeric membranes. CMS membrane was effective for separating gas mixtures with almost similar molecular sizes such as O₂/N₂, CO₂/CH₄ and CO₂/N₂. It has good mechanical strength and not suffers from compaction and swelling problems. Furthermore, the permeation properties of CMS membrane are not time dependent. This means that the operating life of CMS membranes is much greater than that of organic membranes. CMS membrane can being able to operate in environments that are generally prohibitive to polymeric materials, and they have superior stability in the presence of organic vapour or solvent and non-oxidizing acid or base environments. They are ideal for corrosive applications and are not overly affected by aggressive feeds. Moreover, CMS membrane has higher thermal stability than polymeric membranes. They are appropriate for application in high temperatures separation processes, with temperatures in the range of 500°C to 900°C. In contrast, organic polymer membranes cannot resist very high temperatures

and they begin to decompose or react with certain components (Ismail and David, 2003).

1.4 Polyetherimide (PEI)

PEI is an amorphous, amber-to-transparent high performance thermosetting polymer, combines high temperature resistance, rigidity, impact strength and creep resistance. The molecular formula of PEI is $C_{37} H_{24} O_6 N_2$ and the molecular weight is 592 g/mol. The glass transition temperature of PEI is 216°C. Its amorphous density at 25°C is 1.27 g/cc. Figure 1.2 represents the molecular structure of PEI.

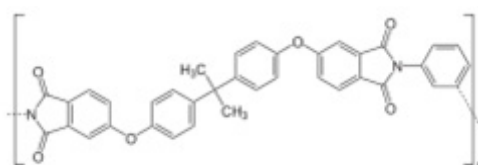


Figure 1.2: Molecular structure of PEI

1.5 Problem statement

Recent efforts to achieve economical and efficient membranes have resulted in a selection of new materials and an improvement in membrane preparation techniques in order to produce thinner and defect-free membranes. Polymeric membranes are used in practical industrial applications as they have reproducible processibility and reasonable gas selectivity. However, current polymeric membrane materials have reached a limit in their productivity-selectivity trade-off relationship and difficult to achieve significant improvement. Furthermore, polymeric membranes cannot operate in corrosive and high temperature environments.

To overcome this limitation, the interest is derived toward inorganic membranes due to their superior permeance-selectivity combination and suitable performance for high temperature or corrosive environment. Most of the inorganic membranes have better separation properties than polymeric membranes. Inorganic membranes, especially CMS membranes are research intensive due to their potential in surpassing the limit of polymeric membranes. CMS membranes have been recognized as promising and attractive gas separation materials due to their high flux and selectivity. Moreover, due to their rigidity, CMS membranes can retain their stability in aggressive (vapor or solvents, and nonoxidizing acids or bases) and adverse (high temperature and pressure operation) environments that too harsh for polymeric membranes. Numerous advantages and wide application of CMS membranes technology will definitely mean that they will become an important technology in this millennium.

Thus in this work, CMS membranes were prepared from polyetherimide for gas permeation study. The great potential and numerous advantages of CMS membranes will definitely lead to their wide application in the gas separation industry over the coming years. It is believed that CMS membranes gas separation technologies will break through the limitations and the weakness of polymeric membranes. Intensive research was carried out in order to produce CMS membranes suitable for gas application.

1.6 Objectives

The present research has the following objectives:

- 1) To develop CMS membrane from polyetherimide.
- 2) To determine the optimum CMS membrane preparation conditions including the pyrolysis temperature, pyrolysis time and polymer concentration using response surface methodology.
- 3) To characterize the optimum CMS membrane sample.
- 4) To study the performance of CMS membrane for single gas (H₂, CO₂, O₂, N₂ and CH₄) permeance and permselectivities.

1.7 Organization of the thesis

The thesis consists of five chapters, where each chapter represents an important build for general construction of the thesis. Chapter one presents an overview on the current status on the membrane industry. The needs to produce CMS membrane in the gas separation industry also included. Problem statement, objectives and the organization of the thesis are also highlighted. Chapter two provides background information and the theoretical basis relevant to this work, and a review of previous research done on CMS membrane. Chapter three presents list of materials used in the present research work. The experimental procedures, design of experimental for the CMS membrane, characterization of CMS membrane and gas permeation studies are explained. It followed by the schematic flow diagram showing the overall activities carried out in this research. Chapter four covered the results from the design of experimental used to prepare the CMS membrane, characterization of the optimized CMS membrane and gas permeation studies. Finally chapter five presents the conclusion that reflects the achievements of all the

objectives which were obtained throughout the study covering the recommendations for the future research. These recommendations offered the importance related to the present research.

CHAPTER TWO

LITERATURE REVIEW

2.1 Membrane classification

Membrane is barrier that allow for selective and specific permeation under conditions appropriate to their function (Figure 2.1). Porosity is an important characteristic of such membranes. Based on flux density and selectivity, membranes can be classified broadly into three classes which were porous, dense and asymmetric (Pandey and Chauhan, 2001).

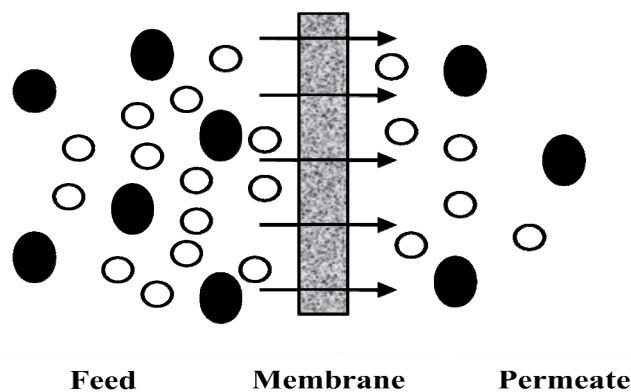


Figure 2.1: Schematic representation of the basic membrane separation principal

A porous membrane is a rigid and highly voided structure with randomly distributed inter-connected pores. The gases separation by porous membranes is mainly a function of the permeate character and membrane properties like the molecular size of the membrane and pore size distribution. In general, only those gases molecules that differ considerably in size can be separated effectively by these membranes. Porous membranes for gas separation can exhibit very high levels of flux but low in separation or selectivity.

Non-porous or dense membranes provide high selectivity or separation of gases from their mixtures but the rates of transport of the gases are usually low. In dense structure there is no intentional 'void space' with dimensions much larger than the atomic building blocks. An important property on dense membrane is that even permeants of similar sizes may be separated if their solubility in the membrane differs significantly. Dense membranes generally have an ideal selectivity in which only one species is transported.

Asymmetric membranes consist of two structurally distinct layers, one of which is a thin, dense selective skin or barrier layer and the other a thick, porous matrix (substructure) layer its main function is to provide a physical support for the thin skin.

2.2 CMS membrane

CMS membrane is porous type membrane, which permits effective size and shape separation between gas molecules (Singh and Koros, 1996). In addition, separation properties of CMS membrane can be finely adjusted to specific separation task by tailoring the microstructures through thermal and chemical treatments. The ability to tailor the structure and properties of CMS membranes holds much promise in application of these materials to gas separation problems (Pei *et al.*, 2004). Unlike the crystalline nature of the zeolite structure, CMS membranes are amorphous pore structure as shown in Figure 2.2. The turbostratic carbon structure is formed from the irregular packing of carbon sheets and pores are formed from packing imperfections in the material. The high porosity of these materials provides relatively high

permeances while the presence of the molecular sieving regions maintains the high selectivity (Perry, 2007).

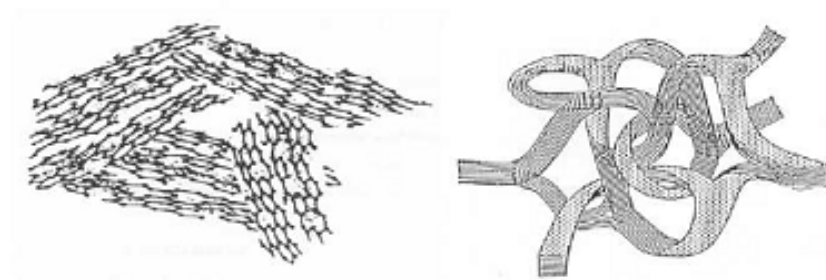


Figure 2.2: Amorphous and turbostratic structure of CMS (Perry, 2007)

CMS membrane has the greatest potential because of the ease of its formation. Different studies on CMS membrane have shown that these materials successfully compete with polymeric membranes and other porous inorganic membranes, such as silica- and zeolite-based membranes, in gas separation processes (Ismail and David, 2001).

The main drawback of CMS membrane is their complicated in preparation and precursor used are expensive (Koros and Mahajan, 2000). As consequences, an immediate challenge faced by membrane scientists is to develop “simple and novel” approaches to control membrane microporous morphology and to fabricate CMS membranes with superior separation performance. They need to find a more economical material than those being used such as polyimides (Suda and Haraya, 1997; Fuertes and Centeno, 1998b), cellulose acetate (Soffer *et al.*, 1987), polyvinylidene chloride (PVDC) (Centeno and Fuertes, 2000) and polyfurfuryl alcohol (PFA) (Shiflett and Foley, 2000).

Aromatic polyimides based CMS membranes have been extensively used as gas separation membranes owing their structurally durable and good gas separation properties. It retains a number of valuable physio-mechanical and chemical

properties by versatile combinations of dianhydrides and diamines. In addition they have excellent thermal stability at high temperature up to 1200°C. For these reasons, aromatic polyimides have been investigated as CMS membrane precursor (Ho *et al.*, 2004).

2.3 CMS membrane configuration

CMS membranes can be divided into two categories which are unsupported and supported. Unsupported membranes have two different configurations which are flat (film) and hollow fiber/capillary while supported membranes consisted of two configurations which are flat and tube. Figure 2.3 shows the configurations of CMS membranes:

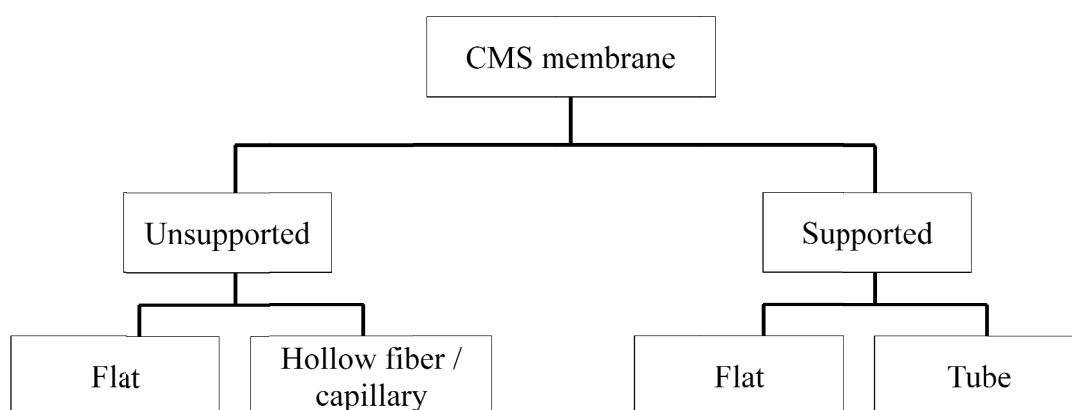


Figure 2.3: Configuration of CMS membrane

Supported membranes are formed by casting a thin layer of precursor material on a surface and then pyrolyzing. The support surface is typically a porous inorganic flat sheet or tubular structure. Unsupported membranes are formed in similar fashion to polymer membranes with the additional step of pyrolysis after the membrane has been formed (Perry, 2007).

A flat sheet membrane is looked like a sheet of paper. The main advantages of the flat sheet membrane modules are ease of cleaning, the possibility of replacing defective membrane elements and the ability to handle viscous feeds and suspension.

The hollow fiber configuration (Figure 2.4) is the most common configuration for microfiltration (MF) and ultrafiltration (UF). The hollow fibers are 0.5 – 1.5 mm (less than 5 mm) in diameter and several thousands of hollow fibers are packed into a module. The most important merit of hollow fiber membranes is that extensive pretreatment is not needed as the membrane can be backwashed (backflushed) automatically by changing the direction of flow of the permeate stream. In hollow fiber filtration process, no phase change is involved and consequently, need no latent heat. This makes the hollow fiber membranes have the potential to replace some unit operations which consume heat, such as distillation or evaporation column. Since the basic principal of hollow fiber is filtration, it does not create any waste from its operation except the unwanted component in the feed stream. This can help to decrease the cost of operation to handle the waste. Moreover, hollow fiber has large membrane surface per module volume. Hence, the size of hollow fiber is smaller than other type of membrane but can give higher performance. Furthermore, hollow fiber is a flexible membrane and low operation cost compare to other types of unit operation.

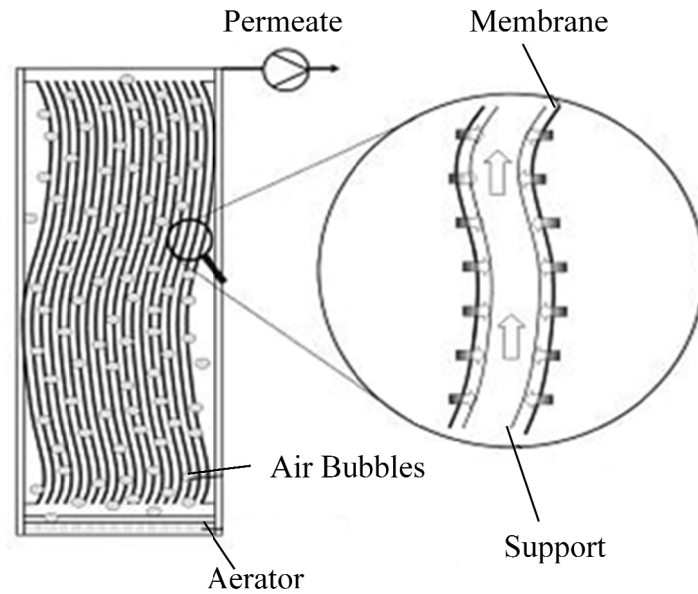


Figure 2.4: Schematic view of a hollow fiber membrane module (Li *et al.*, 2008)

The tubular configuration (Figure 2.5) is an extension of the hollow fiber, but with larger diameter (up to 25 mm) tubes. The advantage of tubular membrane is that easy to clean mechanically. However, tubular membranes are more costly than hollow fiber membrane module. The tubular configuration is widely used in the food and beverage industries.

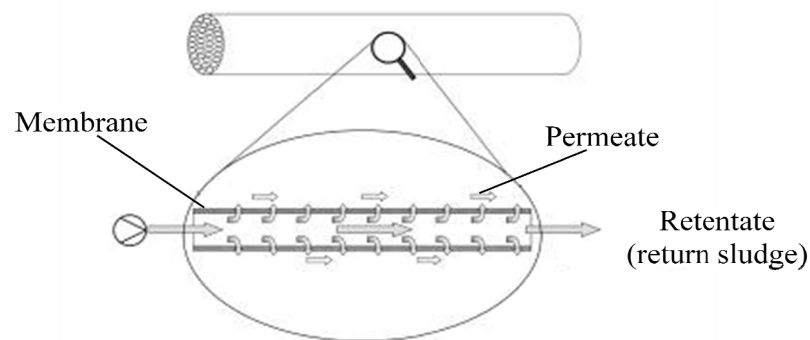


Figure 2.5: Schematic view of a tubular membrane module (Li *et al.*, 2008)

2.4 Synthesis of CMS membrane

A growing interest can be seen in the synthesis of CMS membrane mainly because of their chemical and thermal stability. A distinctive feature is that the

controlled pyrolysis of a precursor can yield a series of CMS membrane that possess micropores of desired dimension. Nevertheless, the factors such as pyrolysis temperature, pyrolysis time and polymer concentration determining the microstructure and gas permeation properties of CMS membrane.

2.4.1 Precursor

The choice of the precursor is the first important factor since pyrolysis of different precursors may bring about different kinds of CMS membrane (Suda and Haraya, 1997). Suitable precursor materials for CMS membrane production will not cause any pore-holes or cracks to appear after the pyrolysis step. CMS membrane can be produced through the pyrolysis process of suitable carbon-containing materials such as thermosetting polymer, polyimides and derivatives (Barbosa-Coutinho *et al.*, 2003).

A thermosetting polymer can often withstand high temperature and neither liquefies nor softens during any stage of pyrolysis. A variety of thermosetting polymers have been used to produce CMS membrane. Koresh and Soffer (1983) produced first hollow-fiber CMS membrane by pyrolyzing cellulose hollow fibers. Other polymers that have been used to produce CMS membranes including polyacrylonitrile (PAN) (David and Ismail, 2003), phenolic resin (Fuertes and Menendez, 2002), polyfurfuryl alcohol (PFA) (Shiflett and Foley, 2001), and poly(vinylidene)-based polymers (Centeno and Fuertes, 2000).

Polyimides and their derivatives are among the most stable classes of polymers and good precursors for glassy carbon membrane (Geiszler and Koros, 1996). Jones and Koros (1994) reported that the good carbon membranes, in terms of

both separation and mechanical properties, were produced from the pyrolysis of aromatic polyimides. Moreover, Hatori *et al.* (2001) found that polyimide blended with polyethylene glycol (PEG) was also a good precursor for porous carbon membranes. Polyimides are rigid, high melting point, high glass transition temperature and thermally stable (Vu *et al.*, 2003). Normally, polyimide was synthesized with different type of dianhydrides and diamines monomers (Figure 2.6) in order to tailor the CMS membrane properties.

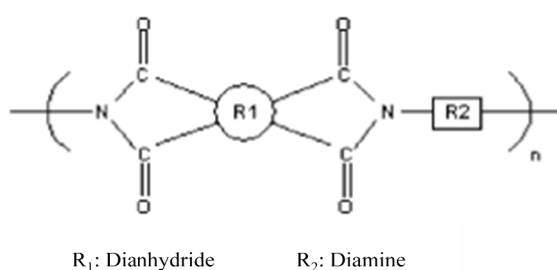


Figure 2.6: Basic molecular structure of polyimides (Saufi and Ismail, 2004)

A typical synthesis of polyimide might involve separately suspending powder 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 4,4'-oxydianiline (ODA) in a solvent such as N,N'-dimethylacetamide (DMAC) and adding each suspension together drop wise under an inert environment to produce a homogenous polyamic acid solution (Shiflett and Foley, 2001). Then, the polyamic acid was subjected to an imidization process, which transforms it into polyimide polymer.

One of common commercial polyimides used for preparing CMS membranes is Kapton (DuPont trademark) polyimide. Hatori *et al.* (1992) had successfully prepared CMS film with homogenous fine pores and without cracks by carbonizing Kapton film at 800°C. Kapton polyimide was also successfully carbonized in the form of a capillary membrane which can retain high gas permselectivity even at high temperature (Petersen *et al.*, 1997). The membrane exhibited a high permselectivity

for H₂/N₂ of 170 at 250°C. Study on Kapton polyimide-based carbon membrane showed that the permselectivities for O₂/N₂, CO₂/CH₄ and CO₂/N₂ are 4, 16 and 9, respectively at 25°C (Fuertes *et al.*, 1999).

Another economical polyimide used to form carbon membrane is polyetherimide (PEI), which is manufactured by General Electric under trade name of Ultem[®] 1000. This material has been used to prepare carbon membranes due to its superior strength and chemical resistance (Sedigh *et al.*, 2000). An early work regarding the use of PEI as a precursor was disclosed by Fuertes and Centeno (1998a). They had prepared supported PEI carbon film by casting in only one step, which gave the permselectivity values of 7.4, 121, 25 and 15 for O₂/N₂, He/N₂, CO₂/CH₄ and CO₂/N₂, respectively, at 25°C.

Sedigh *et al.* (1999) prepared CMS membranes by dip-coated a PEI film inside a ceramic tube and then carbonized it at 600°C under flowing argon for 4 hours. They had investigated the transport characteristics of their PEI-based CMS membrane using single gases (CH₄, H₂, CO₂), binary mixtures (CO₂/CH₄, H₂/CH₄, CO₂/H₂), and also ternary mixtures of CO₂/H₂/CH₄. CO₂/CH₄ separation factors as high as 145 for the equimolar binary and 155 for the ternary mixture. Barbosa-Countinho *et al.* (2003) had prepared PEI carbon hollow fiber membrane for use as a catalyst supports in a membrane reactor. They had investigated pyrolysis process parameters as well as stabilization parameters to find an optimum condition for preparing PEI-based carbon membranes.

2.4.2 Pretreatment conditions

The CMS membrane precursor is often subjected to pretreatment before undergo the pyrolysis process. This step can ensure the stability of the precursor and the preservation of its structure during pyrolysis. Pretreatment can be divided into *physical* and *chemical* methods. Physical pretreatments consist of stretching or drawing hollow fiber membranes prior to pyrolysis. In contrast, chemical pretreatments involve some chemical reagents, which are applied to the polymeric precursor. Sometimes the precursor is subjected to more than one pretreatment method to achieve the desired properties in a CMS membrane. The most important and popular pretreatment method employed by previous researchers have been the oxidation treatment. It can be stated that, in membrane fabrication process, a heat assisted oxidation treatment in oxygen, air or an oxidative atmosphere is involved. Preoxidation can form crosslinks in the polymer structure and therefore increase the thermal stability of the precursor.

2.4.2.1 Physical pretreatment

Stretching or drawing is categorized as a physical pretreatment and usually involves the hollow fiber precursor only. This technique is adapted from the fabrication of carbon fiber and is sometimes referred to as a post-spinning treatment. An ideal post-spinning modification scheme would allow the removal of surface defects, attenuation of variations in filament diameter, and an enhanced retention of molecular orientation prior to heat treatment in order to obtain fibers with a good balance of stiffness and strength.

Draw ratios are preferably as high as possible within the range in which the structure of fiber is not ruptured. Typical upper limits of the total draw ratio around

80% of the draw ratio at which fiber break occurs. Drawing can also take place during the spinning process to no more than a few times the original length of the fibers. This offers an advantage in that the pore systems obtained after the spinning process can be preserved to a larger extent in the carbon membrane and thus ensure greater dimensional stability.

Stretching PAN precursor fibers in the preoxidation stabilization stage results in an increase in the Young's modulus of the final carbon fiber. Since the dipole-dipole interactions among the nitrile groups obstruct the molecular chains from becoming fully oriented during stretching, a reduction of these interactions can make the drawing process more effective. In particular, the introduction of solvent molecules or heat has been cited as an effective means of decreasing these interactions in PAN molecules.

2.4.2.2 Chemical pretreatment

Pretreatment of a membrane with certain chemicals can enhance uniformity of the pore system formed during pyrolysis. Among the chemicals commonly used for chemical pretreatment are hydrazine, dimethylformamide (DMF), hydrochloric acid and ammonium chloride. During the manufacture of porous carbon membrane by Schindler and Maier (1990), an acrylic precursor was subjected to a pretreatment with an aqueous solution of hydrazine. They found that this pretreatment improved the dimensional stability of the membrane during the subsequent processing steps and, in particular, that the tar formation and clogging of the pores could be prevented during these steps. Very good results were obtained for acrylic using a pretreatment with 80% hydrazine hydrate for 30 minutes at a solution temperature of 90°C.

During the chemical pretreatment, the membrane is fully immersed in the appropriate solution. After that, the membrane is washed and dried before it is fed to the first heat treatment station. In certain cases, it has also been proven that it may be advantageous to evacuate the pores of the membrane by applying a low air pressure, and subsequently fill with nitrogen gas at normal pressure prior to pretreatment with an aqueous solution. By this way, one can obtain membranes with higher carbon content than made from precursor which pores were still filled with air during the pretreatment.

Another type of chemical pretreatment involves using of mineral acids and acidic salts such as phosphoric acid and diammonium hydrogen phosphates as catalyst before pyrolysis. However, the preparation of carbon hollow fiber membranes with pyrolysis catalysts causes certain problems. In carbon hollow fibers, pyrolysis must take place uniformly both inside and outside of the fiber, and pitting must be avoided because the selectivity of the membrane depends strongly on the uniformity of the pores produced during pyrolysis. Pitting occurs immediately if the catalyst is not uniformly distributed throughout the fiber, due to locally catalyzed oxidation on the surface.

2.4.2.3 Oxidation pretreatment

Certain membrane precursors underwent softening during the pyrolysis step, and the resulting CMS membrane had a low membrane performance (Kusuki *et al.*, 1997). Therefore, the oxidation step is intended to prevent the melting or fusion of the membranes and to avoid excessive volatilization of elemental carbon in the subsequent pyrolysis step, thus maximizing the final carbon yield from the precursor. The oxidation treatment is considered very important and can has a substantial

influence on the resulting performance of a CMS membrane. Oxidation pretreatment can be applied at very different ranges of thermal soak times, depending largely on the precursor used. In all cases, the aim is the same that is to contribute to the stabilization of the asymmetric structure of the precursor and provide sufficient dimensional stability to withstand the high temperatures of the pyrolysis steps.

David and Ismail (2003) have shown that the thermal stability of polyacrylonitrile (PAN) hollow fiber membranes is improved when the precursors were heated to 250°C in air or oxygen for 30 minutes. The results suggested that stabilization in an inert atmosphere can cyclize PAN, while stabilization in an oxidative environment both cyclizes and oxidizes the structure.

Okamoto *et al.* (1999) formed CMS membrane from asymmetric polyimide hollow fibers formed from BPDA and aromatic diamines. They pretreated the fibers by heating to 400°C in atmospheric air for 30 minutes. The pretreatment was necessary to maintain the asymmetric structure of the precursor. Otherwise, the precursor softened and the CMS membrane has a low separation performance.

Centeno and Fuertes (2000) analyzed the effect of oxidative pretreatment on separation performance of supported poly(vinylidene chloride-co-vinyl chloride) based CMS membrane. The films were oxidized in air at 150 or 200°C for up to 2.5 days before pyrolysis. Membranes oxidized at 200°C for 6 hours showed a decreased permeance but increase in selectivity, while those treated at 150°C for 2.5 days had increased permeance and decreased selectivity. Therefore, the results showed that oxidative pretreatment conditions must be optimized for a given precursor but may improve the CMS membrane properties. Table 2.1 lists selected oxidation pretreatment applied to different precursors by various researchers.

Table 2.1: Preoxidation conditions of selected precursors for CMS membrane

Precursor	Configuration	Temperature and time	References
Acrylonitrile	Hollow fiber	200 – 300°C, 3 hours, air 180 – 350°C, 1 – 20 minutes, air	Yoneyama and Nishihara (1992) Schindler and Maier (1990)
Polyacrylonitrile (PAN)	Hollow fiber	250°C, 30 minutes, air/O ₂	David and Ismail (2003)
	Hollow fiber	265°C, 30 minutes, air/N ₂	Linkov <i>et al.</i> (1994)
Coal tar pitch	Plate	200 - 260°C, 120 minutes, O ₂	Liang <i>et al.</i> (1999)
Phenolic resin	Supported film	150 – 300°C, 2 hours, air	Centeno and Fuertes (2001)
Polyfurfuryl alcohol (PFA)	Supported film	90°C, 3 hours, air	Chen and Yang (1994)
Polyimide	Hollow fiber	400°C, 30 minutes, air	Okomoto <i>et al.</i> (1999)
	Hollow fiber	300°C, 1 hour, air	Barsema <i>et al.</i> (2002)

2.4.3 Pyrolysis

Pyrolysis (sometimes referred as carbonization) is a process which a suitable carbon precursor is heated in a controlled atmosphere (vacuum or inert) to the pyrolysis temperature at a specific heating rate for a sufficiently thermal soak time. The pyrolysis process is conventionally used for the production of porous carbon fibers, and causes the product to have a certain microporosity of molecular dimensions that is responsible for the molecular sieve properties.

This process removes most of the heteroatoms originally present in the macromolecules whilst leaving behind a stiff and cross-linked carbon matrix with an amorphous porous structure created by evolution of gaseous products and the rearrangements of the molecular structure of the starting precursor during the