DEVELOPMENT OF HOLLOW FIBER CARBON MEMBRANES FROM POLY (P-PHENYLENE OXIDE) FOR GAS SEPARATION

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by

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In the Name of Allah, the Most Gracious, the Most Merciful

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LIST OF ABREVIATIONS

6FDA	Hexafluoroisopropylidene-2-bis(phthalic acid anhydride)
BTDA	3,3',4,4'-benzophenonetetracarboxylic dianhydride
BTDA	3,3',4,4'-benzophenonetetracarboxylic dianhydride
CMSM	Carbon molecular sieve membrane
DAM	Diamine monoxime
EA	Elemental analysis
F127	Pluronic F127
FFA	Furfuryl alcohol
FTIR	Fourier transform infrared spectroscopy
IR	Infrared
MWCNT	Multi-wall carbon nanotube
ODA	Octadecyl acrylate
ODPA	4,4′-oxidiphthalic anhydride
PAA	Poly(acrylic acid)
PAN	Polyacrylonitrile
PBI	Polybenzimidazole
PEG	Poly(ethylene glycol)
PEI	Polyetherimide
PFA	Poly(furfuryl alcohol)
PFR	Phenol formaldehyde novolac resin
PPESK	poly(phthalazinone ether sulfone ketone)
PPO	Poly(2,6-dimethyl-1,4-phenylene oxide) @ Poly(p-phenylene oxide)
PPOM	PPO polymeric membrane

PR	Phenolic resin
PVP	Poly(vinylpyrrolidone)
RF	Resorcinol–formaldehyde resin
SEM	Scanning electron microscopy
SPPO	Sulfonated PPO
TGA	Thermogravimetric analysis
XRD	X-ray diffraction

LIST OF SYMBOLS

A_m	Membrane's effective surface area (m^2)
A	Integrated area from GC input data (μV^2)
t_m	Thickness of membrane (m)
Q_i	Volumetric flow rate of gas i ($m^3.s^{-1}$)
Δp_i	Pressure difference of gas i (Pa)
$\alpha_{i/j,single}$	Ideal selectivity of gas *i* over gas *j*
$\alpha_{i/j,binary}$	Permselectivity of gas *i* over gas *j*
d	Crystallite size (nm)
$\dot{m}$	Gas flow rate of gas i ($mol.s^{-1}$)
l	Length of membrane fiber (m)
d	Crystallite size (Å)
k	Scherrer constant
B	Full width at half maximum
λ	X-ray wavelength of Cu (Å)
Θ	Bragg's angle (rad)
P_i	Permeability of gas i (Barrer)
S	Solubility (cm^3 (STP)/cm^3 CMS/psi)
D	Diffusivity (10^{-8} cm^2/s)
θ	Stage cut ratio
D_k	Knudsen diffusion (m^2/s)
r_p	pore radius (m)
M	gas molecular weight (kg/mol)
R	gas constant (8.3144 J/mol.K)

T	Temperature (K)
D_s	surface diffusion coefficient (m^2/s)
E_a	Energy of activation (kJ/mol)
D_{MS}	molecular sieving diffusion coefficient (m^2/s)
D^0	temperature-independent pre-exponential (m^2/s)

PEMBANGUNAN MEMBRAN KARBON GENTIAN BERONGGA BERASASKAN POLI (P-PHENILINA OKSIDA) UNTUK PEMISAHAN GAS

ABSTRAK

Pemisahan gas menggunakan teknologi membran telah mendapat perhatian dalam industri kimia berbanding pendekatan konvensional seperti proses kriogenik dan penjerapan buaian tekanan kerana pemisahan membran adalah cekap tenaga, sistem yang lebih ringkas dari segi mekanikal, dan boleh dikendalikan di bawah tekanan dan suhu yang lebih rendah. Disebabkan rintangan kimia yang terhad dan ketidakstabilan sifat fizik membran-membran polimer kini, membran karbon diperkenalkan. Walaubagaimanapun, pembangunan membran karbon terkini terlalu focus ke atas pembangunan bahan novel untuk mendapatkan keberkesanan pemisahan yang terbaik. Satu lagi faktor penting dan kritikal adalah kesinambungan untuk meneruskan pembangunan tersebut ke peringkat bernilai komersil yang merangkumi konfigurasi membran, prestasi dan pengoptimuman sintesis dan ujian pemisahan yang realistik, tapi malangnya, perkara-perkara tersebut sangat kurang dalam kajian-kajian lepas. Kajian ini berusaha untuk mengisi kekurangan tersebut dengan cara meneruskan pembangunan ke atas membran geronggang karbon yang dihasilkan daripada poli (p-phenilina oksida) (PPO) untuk pemisahan gas H_2/N_2, O_2/N_2 dan CO_2/CH_4. Membran gentian geronggang PPO (PPOM) telah ditemukan dimana ia dapat diterma-stabilkan pada suhu optimum 240 °C. Terma-stabil PPOM tersebut kemudiannya dirawat pada pelbagai keadaan pirolisis, iaitu suhu pirolisis, kadar pemanasan, dan tempoh rendaman terma bagi menghasilkan membran karbon. Prestasi membran karbon ditentukan dan dioptimumkan berdasar kebolehtelapan gas tunggal (H_2, N_2, O_2, CH_4

dan CO_2) dan kememilihan unggul (H_2/N_2, O_2/N_2 dan CO_2/CH_4) dengan plot batasan atas Robeson 2008 sebagai rujukan. Kebolehtelapan gas tunggal dan kememilihan berubah dengan ketara apabila suhu pirolisis yang berbeza dikenakan. Berdasarkan kepada urutan diameter kinetic gas-gas tersebut, pengangkutan untuk gas-gas lengai menembusi membran karbon pada suhu pirolisis 600 °C dikuasai oleh mekanisma tapisan molekul dan kehadiran resapan permukaan oleh CO_2 dapat dikesan melalui membran karbon yang dipirolisis pada suhu 500 dan 700 °C. Sifat-sifat ini berkait rapat dengan struktur liang yang berliang mikro. Menaikkan kadar pemanasan meningkatkan kebolehtelapan gas-gas dan juga kememilihan unggul O_2/N_2, dan pada masa yang sama menurunkan kemimilihan unggul H_2/N_2 dan CO_2/CH_4. Memanjangkan tempoh rendaman terma telah sedikit menaikkan kebolehtelapan H_2 dan CO_2 dan kememilihan unggul H_2/N_2 dan CO_2/CH_4. Walaubagaimanapun, ia menurunkan kebolehtelapan O_2 dan kememilihan O_2/N_2 menunjukkan setiap pemisahan mempunyai kecenderungan terhadap struktur membran yang berbeza dimana ianya dapat diubah melalui formulasi pirolisis yang berbeza. Peningkatan ke atas membran karbon tersebut setelah proses optimasi adalah sebanyak 80, 9 dan 43 kali ganda untuk peningkatan kebolehtelapan H_2, CO_2 dan O_2 masing-masing dan 13, 1.3 dan 7 kali ganda untuk peningkatan kememilihan unggul H_2/N_2, CO_2/CH_4 dan O_2/N_2 masing-masing. Kebolehtelapan H_2 (268 Barrer) dan kememilihan H_2/N_2 (13) daripada ujian dwigas adalah lebih rendah daripada nilai kebolehtelapan gas tunggal H_2 dan kememilihan unggul H_2/N_2 disebabkan oleh rintangan yang tinggi daripada N2 dan pengutuban kepekatan. Kememilihan O_2/N_2 (13) adalah 70 % lebih rendah berbanding kememilihan unggul O_2/N_2 disebabkan persaingan pengangkutan gas dan pengutuban kepekatan. Kebolehtelapan O_2 (243 Barrer) untuk ujian dwigas adalah hampir sama dengan kebolehtelapan tunggal O_2. Kebolehtelapan CO_2 (1320 Barrer)

dan kememilihan CO_2/CH_4 daripada ujian dwigas adalah hampir sama dengan kebolehtelapan CO_2 dan kememilihan unggul CO_2/CH_4 yang diperoleh daripada ujian gas tunggal disebabkan oleh tarikan kuat CO_2 terhadap dinding liang membran karbon dan kesan penghalangan liang. Ketulenan dan perolehan H_2, O_2 dan CO_2 adalah 94% dan 9%, 57% dan 24%, dan 96% dan 8%, masing-masing. Kajian ini telah menunjukkan yang membran geronggang karbon telah berjaya dihasilkan dan dikaji. Pengoptimuman yang digunakan telah berjaya menggandakan prestasi pemisahan tanpa memerlukan penggubahan yang rumit atau penambahan bahan kedua. Prestasi pemisahan realistik mengesahkan yang membran karbon boleh memberikan keberkesanan pemisahan yang tinggi untuk O_2/N_2 dan CO_2/CH_4 berpandukan karakter pemisahan unggul tetapi rendah untuk H_2/N_2.

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ABSTRACT

Gas separation based on membrane technology has become more attractive in chemical industry compared to conventional approaches such as cryogenic process and pressure swing adsorption since membrane separations are energy-effective, mechanically simpler system, and can be operated under lower pressures and temperatures. Due to limited chemical resistance and physically unstability of current polymeric membranes, carbon membranes were introduced. However, the current development of carbon membranes have been too focus on novel material development to achieve state-of-the-art separation efficiency. Another important and critical factor is the continuity to further develop the membrane up to commercially valuable which includes the membrane configuration, performance and synthesis optimization and realistic separation tests, unfortunately, appeared very lacking in the literature. This study attempts to fill in the gaps by attempting to continue the development on a hollow fiber carbon membrane synthesized from poly(p-phynylene oxide) (PPO) for H_2/N_2, O_2/N_2 and CO_2/CH_4 gas separations. The PPO membrane (PPOM) was found to be acceptably thermostabilized at optimum temperature of 240 °C. The thermostabilized PPOM was then subjected to various pyrolysis conditions, which were pyrolysis temperature, heating rate, and thermal soak time to produce carbon membranes. The carbon membrane performances were determined and optimized based on their single gas permeabilities (H_2, N_2, O_2, CH_4, and CO_2) and ideal selectivities (H_2/N_2, O_2/N_2, and CO_2/CH_4) with Robeson's 2008 upperbounds as references. The permeabilities and ideal selectivity changed significantly when

different pyrolysis temperatures was applied. Based on the order of kinetic diameter of the gases, the transport of the inert gases through the carbon membrane pyrolyzed at 600 °C were dominated by molecular sieving mechanism and the presence of CO_2 surface diffusion was detected through the carbon membrane pyrolyzed at 500 and 700 °C. This properties are directly related to microporous pore structure. Increasing the heating rate increased the permeabilities of the gases and O_2/N_2 ideal selectivity, while decreased the H_2/N_2 and CO_2/CH_4 ideal selectivities. Increasing the thermal soak time slightly increased the H_2 and CO_2 permeabilities and H_2/N_2 and CO_2/CH_4 ideal selectivities. However, it decreased the O_2 permeability and O_2/N_2 ideal selectivity indicating that every separation has different preference of membrane structure which was changed through different pyrolysis formulation. Through the optimization using one-factor-at-time and Robeson's 2008 upperbound, the performances of H_2-H_2/N_2, O_2-O_2/N_2 and CO_2-CO_2/CH_4 were respectively found to be optimized at 1 °C/min (4 hours), 4 °C/min (0 hours) and 1 °C/min (4 hours). These optimized samples gave averaged H_2, O_2 and CO_2 permeabilities of 2868, 222 and 1205 Barrer, respectively with corresponding H_2/N_2, O_2/N_2, and CO_2/CH_4 ideal selectivities of 586, 40 and 195, respectively. The improvement on the carbon membranes after the optimization were recorded as 80, 9 and 43 times of increment for H_2, CO_2 and O_2 permeabilities and 13, 1.3 and 7 times of increment for H_2/N_2, CO_2/CH_4 and O_2/N_2 ideal selectivities, respectively. The H_2 permeability (268 Barrer) and H_2/N_2 permselectivity (13) from binary gas test were lower than their single H_2 permeability and H_2/N_2 ideal selectivity due to high resistance by N_2 and concentration polarization. The O_2/N_2 permselectivity (13) was 70% lower than the O_2/N_2 ideal selectivity due to competitive gas transport and concentration polarization. The O_2 permeability (243 Barrer) from binary gas test was almost equal to its O_2 single permeability. The CO_2 permeability (1320 Barrer)

and CO_2/CH_4 permselectivity from binary gas test were almost equal to their CO_2 permeability and CO_2/CH_4 ideal selectivity obtained from the single gas test due to strong CO_2 affinity towards the carbon membrane pore walls and pore blocking effect. The purities and recoveries of the H_2, O_2 and CO_2 were 94% and 9%, 57% and 24%, and 96% and 8%, respectively. This study has shown that, the carbon membrane has been successfully synthesized and studied. The optimization implemented has successfully multiplied the carbon membrane separation performance without the need of complicated modifications or additional materials. The realistic separation performance verified that the carbon membrane can indeed deliver high separation efficiency for O_2/N_2 and CO_2/CH_4 based on ideal separation characteristics but very poorly for H_2/N_2.

CHAPTER ONE
INTRODUCTION

Natural gas is one of valuable commodities in Malaysia and its production amounts to 1074 kboe/d (kilo barrel of oil equivalent per day). One of the challenges includes high content of CO_2 which is to be removed (Malaysian Gas Association, 2017). Another major production in Malaysia is ammonia which is located at three sites (Kertih, Bintulu and Gurun) with total capacity of 950 thousands metric tans per year to feed fertilizer manufacturing (Indexmundi, 2015). Haber-Bosch process is used to synthesize the ammonia through reaction between H_2 and N_2 gases at molar ratio of 3:1, under high temperature (400-500 °C) and pressure (100-200 bar) (Bland, 2015). Recovery and recycle of the unreacted H_2 and N_2 back into the process reactor requires effective separators and pre-cooling. The supply of N_2 comes from air separation (Appl, 2006). The air separation is usually accomplished using pressure swing adsorption units.

Gas separation is a technique to discriminate one gas from the others. Examples of current gas separation techniques are pressure swing adsorption, cryogenic distillation, amine absorption and membrane separation. Membrane technology grows as an attractive alternative for many gas separation industries (natural gas processing, landfill gas recovery, air separation, hydrogen recovery, etc.) (Paul and Yampol'skii, 1994; Vu et al., 2003). Due to economic competitiveness of other existing separation technology and the present challenges of aggressive separation environments, attempts towards finding robust membrane materials of high selectivities and permeabilities becomes important and attractive. (Koros and Mahajan, 2000; Vu et al., 2003).

1.1 Membrane separation

Membrane is a material with selective layer acting as an impermeable barrier between two phases of specific substances. It requires driving forces to allow the substances to pass through the barrier (Ismail et al., 2015). Membrane has single feed of input which contains mixture of components and two outputs as the result of the separation. The more permeable component is allowed to diffuse easily through the membrane layer as permeate whereas the less permeable is mostly rejected as retentate. The simplified diagram of the membrane separation process is shown in Figure 1.1.

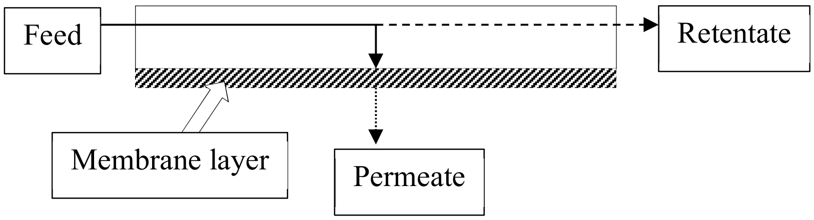

Figure 1.1 Simplified diagram of membrane separation process

In gas separation, the common driving force applied to diffuse through the membrane is pressure difference between feed and permeate sides (Huang et al., 2014). Other driving forces in various applications are the differences in temperatures (Cassano et al., 2008), electrical potentials (Pawlak et al., 2015) and concentrations (Cherif et al., 2015).

Membrane layer can be made porous or non-porous (dense), depending on synthesis methods and intended applications. Porous membranes are commonly utilized in microfiltration, ultrafiltration, nanofiltration, electrodialysis, pervaporation, and low-purity gas separations. On the other hand, reverse osmosis, high-purity gas separations or gas purifications utilize non-porous or dense membranes. In gas separation, the porous membranes serve only for low-purity separations such as in hydrogen recovery in which the selectivity ranges from low to moderate with high productivity (Li et al., 2016). Dense membranes offer superior separation efficiency but relatively poor in productivity such as palladium membrane for hydrogen purification and silver membrane for oxygen purification.

According to the average pore size, the porous membranes can be categorized into macropores (> 50 nm), mesopores (2 - 50 nm) and micropores (< 2 nm). Each pore size provides different transport mechanisms for the diffusing molecules through the membrane porous structure which results in different magnitudes of permeability and separability or selectivity. Macroporous membranes do not provide any gas separation capability. Mesoporous membranes allow greater permeability but mild selectivity whereas the microporous mostly provides lower permeability but excellent separability. Effective utilization of the mesoporous and microporous membranes is highly associated to the objectives and conditions of the separation process.

1.2 Membrane application in gas separation

For decades, membrane technology has been advancing towards significant improvement in term of performance, materials, designs, and configurations. Gas separation membrane technology is highly competitive with the conventional separation technology such as cryogenic, amine absorption, and pressure swing adsorption (PSA). The membranes are claimed to be more cost-effective, energysaving, efficient in geometry, lightweight, simpler to operate and smaller space consumption (Zhang et al., 2009). Examples of gases separated using membranes are hydrogen, nitrogen, ammonia, oxygen, methane, and some hydrocarbon gases.

Figure 1.2 shows a simplified model of hydrocracking process adopting membrane technology to recover unreacted hydrogen during inert purge (Baker, 2002). Hydrocrackers function to break-down high-molecular-weight components, remove impurities, and to hydrogenate aromatics. In the presence of hydrogen and catalyst, heavy oil is cracked to C_{5+} hydrocarbons, but some unwanted byproducts which are methane, ethane, and propane are also produced from the reaction. The produced oil/gas mixture from the hydrocracker is then sent to a lower-pressure separator from which the C_{5+} product is removed. The unreacted hydrogen is recirculated back to the reactor. Methane, ethane, and propane accumulate in the recycle stream and must be removed as an inert purge. Commonly, every mol of light hydrocarbon purged from the reactor causes 3-4 mol of hydrogen lost altogetther. This lost are minimized by using membrane to recover the hydrogen from the light hydrocarbons and recycled back to the reactor.

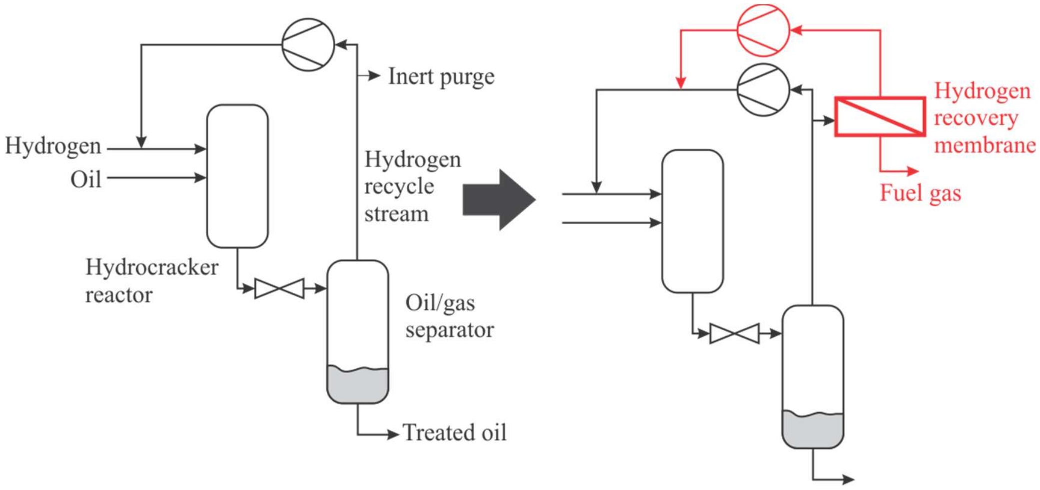

Figure 1.2 Simplified diagram of membrane technology adopted in hydrogen recovery process (Baker, 2004)

Membrane technology for gas separations was firstly implemented in 1980s where industrial-scale installation was accomplished by the Permea (Air Products). The installed membrane material was polysulfone which was integrated into ammonia plants for hydrogen recovery. Followed by such success, Cynara (Schlumberger) and Separex (Honeywell) introduced membranes made of cellulose acetate for CO_2 separation in natural gas stream. Generon fabricated membranes from poly(4-methyl-1-pentene)(TPX) to perform N_2/air separation. Two-thirds of gas separation market was dominated by the nitrogen separation from air and hydrogen from syngas (Baker, 2002). Table 1.1 shows some industrial separations using membrane systems and their suppliers.

Table 1.1 Industrial applications utilizing membrane system (Spillman, 1995)

Gas Separation	**Application**	**Manufacturer/supplier**	**Operating conditions**	**Issues and challenge**
O_2/N_2	Nitrogen generation, oxygen enrichment	Air Products (North America)(Hollow fiber) (Airproducts.com.my, 2018), Linde AG (Germany), Generon (USA)	25-35 °C, 1-15 bar (Alqaheem et al., 2017)	Low production capacity (10-25 tonnes daily) and purity (25-40% O_2) as compared to PSA (20-100 tonnes daily, >90% O_2 purity) (Chong et al., 2016)
H_2O/air	Air dehumidification	Ube Industries (USA), Air products (North America) (Hollow fiber)	Room condition (25-36 °C) (Zhang, 2010)	Extremely low water vapour permeability (Zhang, 2010).
H_2/hydrocarbon	Refinery hydrogen recovery	Air products (North America) (hollow fiber), Air Liquide (hollow fiber)	60 – 82 °C, 4 - 170 bar (Alqaheem et al., 2017)	Performance deteriorates significantly if carbon monoxide was presented in the feedstock (Alqaheem et al., 2017)

Table 1.1 *Continued*

Gas Separation	**Application**	**Manufacturer/supplier**	**Operating conditions**	**Issues and challenge**
H_2/co	Syngas ratio adjustment	Air products (north america) (hollow fiber), air liquide (hollow fiber)	60 – 82 °c, 14 - 170 bar (baker, 2008)	Require pretreatment to remove oil mist, particulate, as well as liquid to control condensation and excessive plasticization (baker, 2008)
H_2/N_2	Ammonia purge gas		<80 °C, <130 bar (Siavashi et al., 2014)	Requires pre-cooling treatment such as steam heater to prevent physical damage to the membrane (Air Liquide Advanced Separations, 2018); Siavashi et al., 2014) and trade-off behaviour between recovery and purity

Table 1.1 *Continued*

Gas Separation	**Application**	**Manufacturer/supplier**	**Operating conditions**	**Issues and challenge**
CO_2/hydrocarbons	Acid gas treating, landfill gas upgrading	Schlumberger (US), Honeywell (US), Air products (North America)(Hollow fiber)	25-70 °C, 1-15 bar (Alqaheem et al., 2017)	Presence of heavy hydrocarbons caused significant drop in the selectivity (Alqaheem et al., 2017)
H_2O/hydrocarbons	Natural gas dehydration		Up to 95 bar, 71 °C (Alqaheem et al., 2017)	Requires pretreatment to remove particulate amd not economical for large volume treatment (Alqaheem et al., 2017)
H_2S/hydrocarbons	Sour gas treating		27-110 bar, <90 °C (Jahn et al., 2012)	Reduced efficiency in the presence of water, heavier hydrocarbons (ethane to pentane) and aromatic species (BTEX, benzene, toluene, ethylene benzene and xylenes) (Jahn et al., 2012)

Table 1.1 *Continued*

Gas Separation	**Application**	**Manufacturer/supplier**	**Operating conditions**	**Issues and challenge**
He/hydrocarbons He/N_2	Helium separations Helium recovery	Schlumberger (US), Honeywell (US), Air products (North America)(Hollow fiber)	< 150 °C, 3.5 bar (Sunarso et al., 2017)	Require multi-stage due to very low amount of He in the feedstock and instability in the presence of and highly adsorbable gases such as CO_2, heavier hydrocarbons (Sunarso et al., 2017)
Hydrocarbons/air	Pollution control, hydrocarbon recovery	GMT Membrantechnik GmbH (Germany)	< 80 °C, < 67 bar (Baker, 2008)	Very low selectivity and requires multi-stage membranes configuration (Baker, 2008)

Table 1.2 lists some technical aspects for current membrane systems (operated at low and high temperatures), pressure swing adsorption (PSA) and cryogenic process in H_2/N_2 separation. The higher the H_2 recovery and H_2 purity, the better the separation is. Membrane system operating at 120 °C has the highest recovery of H_2 which 91% whilst the H_2 recovery is highest when pressure swing adsorption is applied. The highest product flow rate (m^3/h) which is H_2 gas were obtained through the membrane system operating at 120 °C and cryogenic technology outperforming the other two systems. The power consumptions of the membrane systems were approximately 40-45% lower than PSA and cryogenic. However, the membrane systems require steam injection and very high consumption which are highly undesirable if compared to the lower consumption by cryogenic and none for pressure swing adsorption. Having said that, the cooling water required in both membrane operations are lower than both cryogenic and pressure swing adsorption, which slightly compensating the undesirable high steam consumption factor. The investment was estimated to be two times cheaper besides significantly small consumption of installation area. The membrane systems also consume less operating capital as shown by lower energy and mass intensities. The other superior advantages of membrane utilization is their effective productivity over footprint making it suitable for use in limited or isolated area. In overall, the membrane system outperforms the PSA and cryogenic technology.

Table 1.2 Comparison between membranes, pressure swing adsorption and cryogenic technology (Freeman and Yampolskii, 2010)

	Membrane system (80 °C)	Membrane system (120 °C)	Pressure swing adsorption	Cryogenic
H_2 recovery (%)	87	**91***	73	90
H_2 purity (%)	97	96	**98**	96
Product flow rate (m^3/h)	3257	**3375**	2643	**3375**
Power (kW)	**220**	**220**	370	390
Steam (kg/h)	230	400	-	**60**
Cooling water (t/h)	**38**	**38**	64	99
Investment (RM millions)	4.48	3.64	8.12	10.64
Installation area (m^2)	8	**5**	60	120
Energy intensity (kJ/ kg H_2)	2808	**2738**	5760	4853
Mass intensity (kg/ kg H_2)	136	**133**	277	342
Productivity/footprint, (kg H_2/ h m^2)	35	**58**	3.9	2.4

*Bolded numbers are the desired values

The separation of gases by membranes exploits the difference of the gas kinetic diameters, adsorption capabilities and affinity of the membrane materials towards the gas molecules. The separations of H_2/N_2, O_2/N_2 and CO_2/CH_4 using membranes can be accomplished since H_2 (2.89Å), N_2 (3.64Å), CO_2 (3.3 Å), CH_4 (3.8 Å), O_2 (3.46 Å) and N_2 (3.64 Å) have different kinetic diameters. The separation of CO_2 from other inert gases can also be accomplished based on their significant difference of adsorption capabilities towards certain membrane. Palladium and silver are used to exclusively attract and allow the diffusion of H_2 and O_2, respectively and completely reject other substances.

1.3 Membrane market and potential in gas separation

In 1994, the estimated market for industrial gases worldwide was $USD 26 billion with annual growth of 14% in Asia and 4% in the industrialized countries (Maier, 1998). Figure 1.3 projects the market of membrane in gas and liquid separation showing the consistency and continuous membrane technology utilization to 2015. It shows that, the growth of membrane technology is advancing particularly in liquid separation. The main implication of this development will also be affecting and giving mutual advantage to the gas separation as well. The total market was estimated to worth $2.3 billion, and the gas and other separation were almost $250 million in 2015.

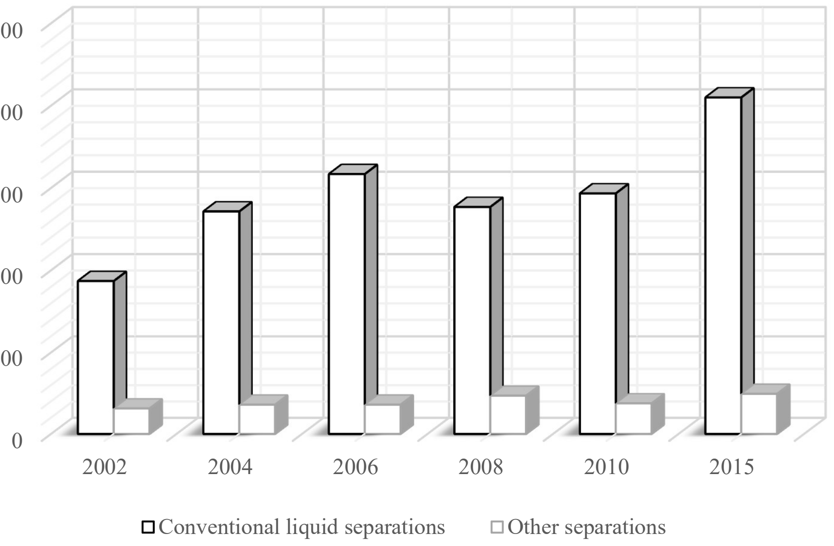

Figure 1.3 Estimation of membrane US market in liquid and gas separation in 2002-2015 (Research, 2010)

The advancement of membrane separations currently continue particularly in natural gas industry (Ismail, 2015). In natural gas separation field, amine absorption has been preferable since its earlier developed technology and dominates 90% compared to other separation technology including the membrane. This natural gas business has driven the worldwide market for separation equipment worth $$5billion/year but the membrane technology only has less than 5% share that focuses on CO_2 removal (Baker and Lokhandwala, 2008).

The separation of CO_2 from natural gas using membrane has positively grown tenfold since 1990 to a $150 million/year business in 2000. It is predicted that, other field of gas separation such as CO_2/nitrogen separations (flue gas carbon capture and sequestration), CO_2/hydrogen and oxygen/air separation (IGCC syngas production and oxycombustion) will also be following the merging trend of this technology with ten and even hundreds of billions dollars investment in the next two or three decades (Baker, 2002).

1.4 Problem statement

Conventional gas separation technology includes cryogenic, amine absorption and pressure swing adsorption. These technology has several drawbacks such as high operational cost and energy consumption especially for higher removal of impurities, complex control, and space-consuming. Membrane technology emerges as an alternative separation method that fully utilizes a unique and simple separation approach yet is highly efficient in term of operational energy, cost, and space requirement.

Polymeric membranes such as cellulose acetate have been widely known and applied at industrial scale for H_2 recovery in ammonia plant. However, polymeric membranes are limited to low operating temperature, pressure and chemically vulnerable. An installation of cooling or pre-treatment units are required to secure the polymeric membranes from the damage. Membrane experts in various membrane field have identified these limitations and listed out some of improvement required in gas separation membranes which include the fabrication of thin-skinned layers of unsupported and supported membranes, high O_2/N_2 selectivity or oxygen selective, acid-resistant materials, and a proper methodology for the selection of effective separation materials (Baker, 2010).

Inorganic membranes such as metal, ceramic, zeolite, glass and carbon membranes were introduced to solve some limitations of the polymeric membranes. Particularly by using carbon membranes which are inert materials as well as chemical-resistant in high operating pressure and temperature. Carbon membranes deliver competitive gas permeability and very high selectivity. They are producible as very thin layers of either unsupported hollow fiber or supported membranes (Cheng et al., 2014). Carbon membranes are able to discriminate gas molecules with almost similar kinetic diameters such as O_2 and N_2 due to its molecular sieving pore structure which is a very critical separation characteristic (Barsema et al., 2005).

The development of carbon membranes recently has been focusing on exploration of new precursor materials and blend of materials to produce new composite precursor materials. Normally the configuration of the membrane produced from such development studies are small unsupported or supported thin films that suit the lab scale to ease the testing and obtain accurate results. There are only few works that focused on the development of carbon membranes in a form of commercial hollow fiber which might share the same material precursors but provide different outcomes due to different synthesis method, configuration and dimension. Based on literature review, it is estimated that there are only 23% of reports working on carbon membranes in a form of hollow fiber. There are a lot of rooms for improvement in term of performance so it is reasonably competitive with the unsupported thin film and supported carbon membranes. Due to the various benefits of hollow fiber configuration, the research and development in this field deserve similar attention.

Thermostabilization process is to cross-link polymer chain so the structure can withstand high temperature treatment (David and Ismail, 2003). Thermostabilization study is critical when thermoplastic polymer was selected for carbon membrane conversion. Failure to determine the appropriate temperature and formulation would cause the carbon membrane unobtainable, defective, poorly reproducible, and inconsistent physical resemblance. Previous study has reported that the thermostabilization highly depends on the polymer amorphous and crystalline states (Gupta and Harrison, 1997). These phase compositions are sensitive and easily changes when different chemicals and synthesis methods of polymer are applied (Khulbe et al., 2000). Uncontrolled thermostabilization led to melting down and coalescing of fibers. Non-optimized thermostabilization also caused excessive weight-loss during pyrolysis with inferior physical properties (Gupta and Harrison, 1997). Thermostabilization study was very popular in the development of poly-acrylonitrile fiber and carbon fiber. However, a study that focus on thermostabilization of PPO has yet reported when it is significantly critical in delivering successful conversion from polymer into carbon phase in carbon membrane development.

In carbon membrane study, the popular approaches in the improvement of the performance are either development of new material precursor and modifications using the existences. These two routes, however, does not always end up with the intended performance improvements, and led to significant decline in performances (Shifflett and Foley, 2000; Li et al., 2015; Zhang et al., 2015; Yoshimune et al., 2005) particularly when both the responses, which are permeability and selectivity, are simultaneously plotted and measured against Robeson's upperbounds (Robeson, 2008). This is because, there have been no clear correlation between the polymer precursor microstructure and carbonized structure performances since the other synthesis parameters, which are the membrane configuration and pyrolysis parameters, are highly influencing the final outcomes as well (Fauzi, 2011). Modifications are mostly producing trade-off behaviours which either increased the permeability at the expense of selectivity or vice versa when it is highly expected to increase both (Husseini et al., 2014, Fu et al, 2015). Another improvement approach is synthesis technique which generally involved the thin film formation as supported formats by reducing the thickness and improve reproducibility. However, the previous study reported that reduction came with very low in separation factor and risked defectives (Cheng et al., 2014; Tanco et al., 2015).

To skip the guess works on producing very high performance carbon membrane which comes with commercially accepted configuration, a convincing approach which is optimization utilizing the previous valuable knowledge and findings should be considered. So far, the performance optimization in carbon membrane has been limited to single parameters commonly pyrolysis temperature. Numerous studies has shown other pyrolysis parameters namely heating rate and thermal soak times have great significance in defining the carbon membrane microstructure and corresponding performances. However, a stage by stage optimization on those parameters simultaneously have yet to be reported. This absence is expected due to the major concern on the reproducibility issue of the carbon membrane itself, especially for carbon membranes synthesized using coating. The optimization itself requires intensive lab work and enormous amounts of samples and duplicates to produce convincing trends with minimal errors and draw sound conclusions. Besides that, previous study has shown that the correlation between permeability and selectivity plotted against Robeson's upperbound corresponding to different pyrolysis temperature produced no simple curve (Hayashi et al., 1997). The optimal performances and conditions has to be selected manually based on observation on the Robeson's plot and commercially attractive regions. One-factor-at-one-time is expected to be able to allow the optimization and selection simultaneously executed and draw sufficient and reasonable conclusion.

Carbon membranes have been reported to possess surprisingly higher ideal selectivity and permeability than polymeric and other inorganic membranes, especially for popular gas separations which are H_2/N_2 (Tanco et al., 2015), O_2/N_2 (Rao et al., 2008) and CO_2/CH_4 (Li et al., 2012). Most studies in the carbon membrane have been lingering around single gas permeability and ideal selectivity tests and calculations (Salleh et al., 2015; Lin et al., 2015; Chen et al., 2017). These measurements are suitable when it is used as comparative study to justify the differences before and after modifications implemented on the membrane or differences between different synthesis parameters or additional treatments. However, it is highly inaccurate to justify the separability of the membrane, particularly when it involves non-adsorbable gases or diffusions that have no specific interactions between the gases and the membrane pore walls. Real separation involves more complex interactions between the competing gases and membrane pore walls resulting significantly different results and conclusions on the membrane separability. This is a major restriction that significantly hinder the progress, continuity and commercial development in carbon membrane technology. To overcome this issue, real separation study should be conducted to prove the high ideal separation factors of the carbon membranes. Another issue in the real separation study itself is too much focus on the purity gain and neglecting the importance of recovery in which the retentate flow rate was set as high as its concentration changes from the feed become insignificant (Kruse et al., 2016; Jiao et al., 2017). This displacement can be overcame by introducing stage cut studies on the membrane real separation study.

In this work, an attempt was made to develop and optimize the carbon molecular sieve membrane from poly(*p*-phenylene oxide) (PPO) for gas separations of H_2/N_2, O_2/N_2 and CO_2/CH_4. Robeson’s 2008 upperbound was fully utilized to assist in producing carbon membranes with balanced performance between productivity and separability.

1.5 Research objective

This study is carried out in order to achieve the following objectives;

1. To synthesize and characterize hollow fiber polymeric membrane, thermostabilized membrane, and carbon membranes from poly(*p*-phenylene oxide) (PPO)
2. To analyze the effect of thermostabilization temperature on the PPO membrane properties
3. To analyze and optimize the effect of pyrolysis conditions (pyrolysis temperature, heating rate, and thermal soak time) on carbon membrane properties and ideal separation performances
4. To analyze and assess the performance of optimized carbon membranes in separations of binary gas mixtures of H_2/N_2, O_2/N_2 and CO_2/CH_4

1.6 Scope of study

Based on the limitations and gaps in the literature, this study focused on the development of hollow fiber carbon membrane from PPO which is optimized stage by stage to improve the ideal separation characteristics. In the first stage, the PPO hollow fiber was synthesized to a level it is highly reproducible in which it is measured by five gases; H_2, N_2, O_2, CH_4 and CO_2. Being unable to produce highly reproducible or consistent PPO hollow fiber will raise a lot of issues during optimization process rendering the data and results unacceptable error margins. The PPO was characterized accordingly to understand its ideal separation characteristics, morphology, thermal stability, microstructure and surface chemistry.

The next important part is to determine the right or optimal thermostabilization temperature in which thermogravimetric analysis was used to observe weight changes. This is a crucial step so the PPO can be converted to carbon material successfully with minimum deformation in terms of the carbon material physical dimensions. Excessive thermostabilization caused degradation and decomposition, while insufficiency caused deformed or inability to form fine carbon materials. The conversion process was studied and thermostabilized PPOM was accordingly characterized at different temperatures. The heating rate of 1 °C/min and minimum 1 hour of thermal soak time was applied. The temperatures were varied from 160 to 280 °C. Direct physical observation and testing was conducted to extract sufficient information and identify changes at microstructural level.

After the suitable thermostabilization temperature was determined accordingly, attempt to produce optimized hollow fiber carbon membrane using the determined thermostabilization temperature was initiated by applying different pyrolysis temperatures which were 500, 600 and 700 °C. The thermal soak time and heating rate was pre-determined at 15 mins and 1 °C/min, respectively. The 500 °C was determined as the minimum pyrolysis temperature. The 700 °C was decided as the maximum temperature since the ideal performances of the carbon membranes showed declination at the temperature. The produced carbon membranes were tested using single permeabilities of H_2, N_2, O_2, CH_4 and CO_2 and ideal selectivities of H_2/N_2, O_2/N_2, and CO_2/CH_4 were averaged and calculated. The experiment was repeated using three batches of polymer solutions produced from different times and the reproducibility of the carbon membrane was observed using error bar. The carbon membranes produced using different pyrolysis temperature were plotted against Robeson's upperbounds of

H_2/N_2, O_2/N_2 and CO_2/CH_4. Using this approach, the optimum pyrolysis temperature was determined for the next optimization stage. The carbon membranes were also characterized in terms of their morphologies, crystalline structure and surface chemistry.

As the optimum pyrolysis temperature was satisfactorily determined, a wide range of heating rate was applied on the carbon membrane. The heating rate were 1, 2, 3, 4, 5, 7, 10°C/min. The maximum heating rate was determined at 10 °C/min as it is the maximum rate the furnace is capable to cope up to achieve high pyrolysis temperature. The pyrolysis temperature was the optimal settings obtained from the previous experiment and the thermal soak time was pre-determined at 15 mins. The produced carbon membranes were then tested using single permeabilities of H_2, N_2, O_2, CH_4 and CO_2 and ideal selectivities of H_2/N_2, O_2/N_2, and CO_2/CH_4 were averaged and calculated. Thermogravimetric analysis was used to detected any variation of weight loss as different heating rates were applied as it could provide insights on the microstructural formation. After the error bar margins were satisfied, Robeson's upperbounds were used to determine the optimum heating rate unique to different separation characteristics of H_2/N_2, O_2/N_2, and CO_2/CH_4.

After the optimal heating rates were determined for each ideal separation characteristics, the next optimization was focused on the thermal soak time. The different thermal soak times were 0, ¼, ½, 1, 2, 4 and 8 hours. The pyrolysis temperature was the optimal setting obtained in the previous experiment, and the heating rate was the optimal setting determined in the previous experiment, and both settings are unique to each separation characteristic. The produced carbon membranes were then tested according to their pre-determined optimal separation characteristics obtained from the heating rate optimization experiments. The experiments were repeated using three batches of polymer solutions and the results were averaged and presented. Robeson's upperbounds were again used to find the optimal balance between permeabilities and ideal selectivities. The effects of heating rate and thermal soak time were studied simultaneously in terms of the crystalline structure, weight loss, physical dimension changes, and pore structure. At this stage, optimum formulations of carbon membranes unique to ideal separation of H_2/N_2, O_2/N_2, and CO_2/CH_4, in terms of pyrolysis temperature, heating rate, and thermal soak time, were obtained. The formulation was used to prepare carbon membranes for real separation study using binary mixture of H_2/N_2, O_2/N_2, and CO_2/CH_4.

The binary mixture was conducted to identify the separability of the developed carbon membranes and its margin between the ideal and real separation values. The H_2/N_2 ratio was determined at 68:32 vol/vol. The O_2/N_2 ratio was determined at 21:79 vol/vol. The CO_2/CH_4 ratio was determined at 35:65 vol/vol. The carbon membranes for each separation was produced using their corresponding optimal formulations determined in the previous experiments. On each binary study, the stage cut was varied from approximately 1-2% and increased gradually to 40-50%. The 1-2% was the lowest stage cut in which the retentate was almost equal to the feed concentration. Lower stage cut would produce separation without recovery. The 40-50% stage cut was the highest stage the experimental rig can achieve since the flux of the carbon membrane was very slow. Plot of the feeds, retentates and permeates against stage cuts were plotted in form of permeabilities for H_2/N_2, O_2/N_2, and CO_2/CH_4 separation characteristics. The H_2/N_2, O_2/N_2, and CO_2/CH_4 permselectivities of permeate and the

N_2/H_2, N_2/O_2 and CH_4/CO_2 permselectivities of the retentate were plotted as well against the different stage cuts.

1.7 Thesis organization

This thesis covers five chapters. Chapter One (Introduction) briefly gives the general overview of membrane technology, problem statement and research objectives. Chapter Two (Literature Review) focused on theory of gas transport in membrane, carbon membrane materials, synthesis method and configuration, and gas separation performances. Chapter Three (Methodology) describes the materials used, fabrication equipment and procedures of the hollow fiber membranes, characterization, single and binary mixture permeation tests. Chapter Four (Results and Discussion) presents the experimental result analysis and discussion. It covers the synthesis and characterization of PPO membrane, thermostabilized PPO membrane, and carbon membranes as well as ideal and mixture gas separation performances. Chapter Five (Conclusions and Recommendations) concludes the findings and some recommendations for improvement for future work to widen the horizon of knowledge in the current research.

CHAPTER TWO

LITERATURE REVIEW

This chapter reviews earlier studies in carbon membranes applied for gas separation particularly in H_2/N_2, O_2/N_2 and CO_2/CH_4 separation. It provides basic information of the recent development of carbon membrane preparation and precursors used for the carbon conversion. In the early section, transport mechanisms in membranes are introduced, particularly porous membranes since many of the terms in the section are widely used in the following sections and chapters. The next section is the introduction of carbon membrane and its unique turbostractic structure, providing background information established so far on the mechanism of the carbon membrane being able to deliver both high permeability and selectivity. A brief discussion on the reactions of polymer conversion into carbon is covered in the next section. After that, polymer precursors being used currently in the production of carbon membrane is categorized and analyzed. The performances of non-modified and modified polymers are evaluated and compared to determine the extent of performances contributed by the additional modifications. After that, this chapter also discusses the preparation of carbon membrane and the effects of the various pyrolysis conditions on the carbon membrane performances that have been reported so far. The final section includes the discussion on binary mixture and stage cut on membrane separation which are very critical in determining the realistic gas separation performance. This chapter is concluded by a research gap that requires to be investigated in the field of carbon membrane which then subjected in this study.