MIXED MATRIX MEMBRANES INCORPORATED WITH PALLADIUM NANOPARTICLES FOR HYDROGEN SEPARATION

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by

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LIST OF ABBREVIATIONS

Ag	Argentum
Al	Aluminium
AlPO	Aluminophosphate
APTES	3-Aminopropyl)triethoxylsilane
ATR	Attenuated total reflection
Au	Gold
B	Boron
C	Carbon
CA	Cellulose acetate
Ce	Cerium
CH_4	Methane
CMS	Carbon molecular sieve
CO	Carbon monoxide
CO_2	Carbon dioxide
Cu	Copper
CVD/MOCVD	Chemical vapor deposition
DMAc	*N*,*N*-dimethylacetamide
DOE	Department of environment
EDX	Energy dispersive X-ray
EG	Ethylene glycol
EP	Electroless platting
EtOH	Ethanol
Fcc	Face centered cubic
FTIR	Fourier transformed infrared

GC	Gas chromatography
Gd	Gadolinium
GPU	Gas permeation unit
H	Hydrogen atom
H_2	Hydrogen gas
H_2O	Water
H_2PdCl_4	Dihydrogentetrachloropalladate
H_2S	Hydrogen sulphide
HCl	Hydrochloric acid
HDPE	High-density polyethylene
He	Helium
HFA	*4,4´*-(hexafluoro-isopropylidene)bis(benzoic acid)
HMA	2-hydroxy 5-methyl aniline
HVOF	High velocity oxy-fuel spraying
IPA	Isopropyl alcohol
LED	Light-emitting diode
LiCl	Lithium chloride
MeOH	Methanol
MdCl	Methane dichloride
MgO	Magnesium oxide
MMMs	Mixed matrix membranes
MMMSCFD	Million standard cubic feet per day
MOF	Metal organic framework
MSS	Molecular sieve silica
MWCNTs	Multi-walled carbon nanotubes
N_2	Nitrogen

NaOH	Sodium hydroxide
Ni	Nickel
O	Oxygen atom
O_2	Oxygen
PAMH	Proton-exchanged AMH-3
PBI	Polybenzimidazole
PBNPI	Poly(bisphenol A-co-4-nitrophthalic anhydride-co-1,3-phenylene diamine
PC	Polycarbonate
Pd	Palladium
$PdAc_2$	Palladium acetate
$PdCl_2$	Palladium chloride
PdHx	Palladium hydride
PDMS	Polydimethylsiloxane
PdO	Palladium oxide
PEG	Polyethylene glycol
PEI	Polyetherimide
PES	Polyethersulfone
PI	Polyimide
PILs	Proton conducting ionic liquids
PIM-1	Polymers of intrinsic microporosity
PMF	Poly(melamine *co*-formaldehyde)
PMP	Polymethylpentene
PPO	Polyphenylene Oxide
PSA	Pressure swing adsorption
PSf	Polysulfone

PSf-Ac	Polysulfone-acrylate
PSS	Porous stainless steel
Pt	Platinum
PVAc	Polyvinyl acetate
PVC	Polyvinyl chloride
PVD	Physical vapor deposition
PVDF	Polyvinylidene difluoride
PVP	Polyvinylpyrrolidone
PVTMS	Poly(vinyl trimethylsilane)
PXDA	*p*-Xylene diamine
S	Sulfur
SAPO	Silicoaluminophosphate
SEM	Scanning electron microscope
SMR	Steam methane reforming
SnO_2	Stannic oxide
TCD	Thermal conductive detector
TEM	Transmission electron micrographs
THF	Tetrahydrofuran
TiO_2	Titanium oxide
TPR	Temperature programmed reduction
TSA	Temperature swing adsorption
WGS	Water-gas shift reaction
XRD	X-ray diffraction
ZIF	Zeolite imidazolate framework
Y	Yttrium
Zr	Zirconium

LIST OF SYMBOLS

A	Membrane effective surface area
$\mathring{A}$	Kinetic diameter
A_m	Membrane area
E_p	Apparent activation energy
$H_{2\,pty}$	Hydrogen purity
$H_{2\,rcy}$	Hydrogen recovery
l	Membrane skin thickness
$n_{H2\,p}$	Molar flow rate of hydrogen in permeate
n_i	Molar flow rate of component *i*
n_{Tp}	Total molar flow rate
θ	The cut or fraction of feed permeate
p	Pressure
p_p	Total pressure in the low pressure (permeate) side
p_f	Total pressure in the high pressure (feed) side
Δp	Pressure difference across membrane
p_i	Partial pressure of gas component *i*
P	Pure gas permeability
P_i	Pure gas permeability of component *i*
P_i/l	Pure gas permeability of component *i* over thickness
P_o	Pre-exponential coefficients
Q_i	Volumetric flow rate of gas component *i*
R	Gas constant
R^2	Regression analysis

T	Temperature
T_g	Glass transition temperature
wt%	Percentage by weight
vol%	Percentage by volume
mol%	Percentage by mol
α_{ij}	Pure gas selectivity of component *i* over component *j*
i, *j*	Gas component H_2 and N_2 or H_2 and CO_2
f	Feed
r	Retentate
p	Permeate

MEMBRAN MATRIKS CAMPURAN DIPERBADANKAN DENGAN PARTIKEL PALLADIUM UNTUK PEMISAHAN HIDROGEN

ABSTRAK

Satu inovasi dalam pemilihan membran untuk hidrogen (H_2) memegang kunci penting kepada ekonomi hidrogen. Polimer adalah bahan yang paling praktikal dan menjimatkan untuk fabrikasi membran, tetapi penggunaan membran polimer termasuk polysulfone (PSf) dan polybenzimidazole (PBI) membran untuk pemisahan H_2 sentiasa terhad oleh "keseimbangan" antara pemilihan dan kebolehtelapan. Dalam kerja ini, nanopartikel Pd yang dimasukkan ke dalam membran PSf dan PBI mengatasi batasan disebut. Sebelum pengadunan, nanopartikel Pd telah disintesiskan secara kinetik dan distabilkan dalam mikroemulsi songsang oleh polyethylene glycol (PEG) atau Polyvinylpyrrolidone (PVP). PSf membran matriks campuran (MMMs) telah disediakan melalui fasa penyongsangan kering-basah manakala MMMs PBI yang padat telah disintesis melalui fasa penyongsangan kering. Keputusan X-ray diffraction (XRD) dan Energy dispersive X-ray (EDX) mengesahkan kemasukan nanopartikel Pd telah berjaya. PSf(Pd/PEG)_3 MMM menunjukkan prestasi pemilihan yang paling tinggi (pemilihan tulen H_2/N_2 : 21.69, pemilihan tulen H_2/CO_2 : 1.98 dan kebolehtelapan H_2: 161.84 Barrer) berbanding membran PSf yang dicampur dengan nanopartikel Pd dalam PEG yang lain. Penambahan PEG mendorong perubahan struktur seperti jari menjadi sel-sel tertutup dan pertumbuhan lapisan tebal. Kebolehtelapan H_2 yang besar telah dicapai dengan menggunakan 2 % nanopartikel Pd dalam PVP untuk membran PSf. (pemilihan Ideal H_2/N_2 : 20, pemilihan ideal H_2/CO_2 : 6.2 dan kebolehtelapan H_2 : 5781.07 Barrer). Peningkatan ini boleh dikaitkan dengan perubahan ruang kosong dalam polimer dan pertumbuhan lapisan padat yang disebabkan oleh PVP. Pada 200 °C, MMMs PBI dengan kestabilan haba yang luar biasa telah mencapai pemilihan H_2/CO_2 dan H_2/N_2 yang terbaik apabila 2 hingga 4 % nanopartikel Pd dalam PEG telah dimasukkan. Pemilihan H_2/CO_2 oleh membran PBI(Pd/PEG)_2 adalah 18.56 (kebolehtelapan H_2 : 53.22 Barrer) manakala pemilihan H_2/N_2 oleh membran PBI(Pd/PEG)_4 adalah 108.28 (kebolehtelapan H_2 : 62.40 Barrer). Pemilihan H_2 yang lebih tinggi telah dicapai dengan menggunakan PVP sebagai penstabil dalam PBI(Pd) MMMs

berbanding PBI(Pd) MMMs dengan PEG. Membran PBI (Pd/PVP)_1 dengan 1 % nanopartikel Pd dalam PVP mencapai pemilihan tulen H_2/CO_2 iaitu 19.73 dan pemilihan tulen H_2/N_2 iaitu 252.54 (kebolehtelapan H_2 : 32.41 Barrer). Kedua-dua membran PBI(Pd/PEG)_2 dan PBI (Pd/PVP)_1 melepasi had atas 'Robeson plot' dengan jayanya. Untuk membran PBI, pekali resapan bergantung kuat kepada suhu dengan sumbangan minimum oleh kelarutan dalam pemilihan gas dan kebolehtelapan. Tenaga pengaktifan dikurangkan dengan banyak oleh PBI MMMs dan ia boleh menandakan pengurangan penyebaran gas disebabkan oleh pengurangan dalam ruang kosong. Walau bagaimanapun, keutamaan penyerapan oleh H_2 dalam semua MMMs dengan nanopartikel Pd boleh berkaitan dengan interaksi antara H-Pd. Walaupun tingkah laku penyerapan berbeza antara gas tulen dan campuran disebabkan oleh tingkah laku pengangkutan, PBI(Pd/PVP)_1 MMMs telah menunjukkan peningkatan yang mengagumkan oleh H_2 di pengeluaran berbanding dengan membran PBI yang asal untuk nisbah 50/50. Ketulenan 98.7 % H_2 dicapai pada 90 % pemulihan H_2. Dalam kajian ini, pemuatan nanopartikel Pd dan suhu operasi memberi kesan kepada ketulenan dan pemulihan H_2 disebabkan perubahan pada kebolehtelapan dan pemilihan membran.

MIXED MATRIX MEMBRANES INCORPORATED WITH PALLADIUM NANOPARTICLES FOR HYDROGEN SEPARATION

ABSTRACT

An innovation in hydrogen (H_2) selective membrane holds the important key to hydrogen economy. Polymers are the most practical and economical material for membrane fabrication, but the application of polymeric membranes including polysulfone (PSf) and polybenzimidazole (PBI) membranes in H_2 separation is always limited by the "trade-off" between selectivity and permeability. In this work, Pd nanoparticles are incorporated into PSf and PBI membranes to overcome the mentioned limitations. Before blending, Pd nanoparticles were kinetically synthesized and stabilized in the inversed microemulsion of polyethylene glycol (PEG) or polyvinylpyrrolidone (PVP). The PSf mixed matrix membranes (MMMs) were prepared by dry-wet phase inversion while the dense PBI MMMs were synthesized by dry phase inversion. The X-ray diffraction (XRD) and Energy dispersive X-ray (EDX) results confirmed that the Pd nanoparticles incorporation was successful. The PSf(PEG/Pd)_3 MMM showed the highest separation performance (pure gas H_2/N_2 selectivity : 21.69, pure gas H_2/CO_2 selectivity: 1.98 and H_2 permeability : 161.84 Barrer) among the PSf membranes blended with Pd nanoparticles in PEG. The addition of PEG induced the changes of finger-like structure into closed cells and the growth of dense layer. High H_2 permeability was achieved using 2 wt% of Pd nanoparticles loading in PVP for PSf membrane (pure gas H_2/N_2 selectivity : 20, pure gas H_2/CO_2 selectivity : 6.2 and H_2 permeability : 5781.07 Barrer). The improvement could be related to the changes of free volume in polymer and the growth of dense layer caused by PVP. At 200°C, PBI MMMs with remarkable thermal stability achieved excellent H_2/CO_2 and H_2/N_2 selectivities when 2 to 4 wt% of Pd nanoparticles in PEG were incorporated. The H_2/CO_2 selectivity of PBI(Pd/PEG)_2 membrane was 18.56 (H_2 permeabillity : 53.22 Barrer) while the H_2/N_2 selectivity of PBI(Pd/PEG)_4 membrane was 108.28 (H_2 permeabillity: 62.40 Barrer). A higher selectivity of H_2 was achieved by using PVP as the stabilizer in PBI(Pd) MMMs in comparison to the PBI(Pd) MMMs with PEG. The PBI(Pd/PVP)_1 membrane with 1 wt% of Pd nanoparticles loading in PVP achieved

a pure gas H_2/CO_2 selectivity of 19.73 and a pure gas H_2/N_2 selectivity of 252.54 (H_2 permeabillity : 32.41 Barrer). Both PBI(Pd/PEG)_2 and PBI(Pd/PVP)_1 membranes surpass the upper bound of Robeson plot successfully. For PBI membranes, the diffusion coefficients depend on temperature strongly with minimal contribution of solubility into gas selectivity and permeability. The activation energy reduced greatly in PBI MMMs and it could signify the reduction of gas diffusion due to a drop in free volume. However, the preferential sorption of H_2 in all MMMs with Pd nanoparticles could be related to the H-Pd interaction. Eventhough the permeation behavior is different between pure and mixed gas permeation due to their transport behavior, the PBI(Pd/PVP)_1 MMMs for mixed gas showed an impressive improvement of H_2 in permeate compare to neat PBI membrane for 50/50 ratio. The 98.7 % H_2 purity was achieved at 90 % H_2 recovery. In this study, Pd nanoparticles loading and operating temperature gave significance effect on purity and recovery of H_2 due to the changes on permeability and selectivity of membrane.

CHAPTER ONE

INTRODUCTION

1.1 Hydrogen Demand and Production

Hydrogen (H_2) is a valuable commodity which has been widely considered to be an attractive energy carrier and storage medium with high gravimetric energy density (1.43×10^8 J/Kg) (Li et al., 2015). The demand for H_2 in fertilizer production, petroleum industry, fuel cell, transportation, energy storage and other applications is expected to increase from 168 million kg in 2013 to nearly 3.5 billion kg in 2030 (Martin, 2014). The demand is predicted to grow due to the strict regulatory norms to desulfurize petroleum products and search for a clean fuel option. H_2 is carbon free fuel and water is the only by-product. H_2 can be produced by the electrolysis of water using renewable energies such as wind, solar and water instead of the conventional production routes such as steam methane reforming, partial oxidation of oil and coal gasification. Biohydrogen can be also produced using photobiological systems, dark fermentation systems or hybrid systems (Bharathiraja et al., 2016).

The fertilizers and petroleum industries are the largest H_2 users at the moment, consuming 50 % and 37 % of the total H_2 produced respectively (Bharathiraja et al., 2016). In 2014, Asia pacific became the largest market for H_2 consumption as shown in Figure 1.1 due to the growing demand for petroleum products from refineries with lower sulphur content. China is expected to consume a great amount of H_2 for fuel cell electric vehicles by enacting clean fuel regulations to achieve carbon emission target. Europe held the second largest market share

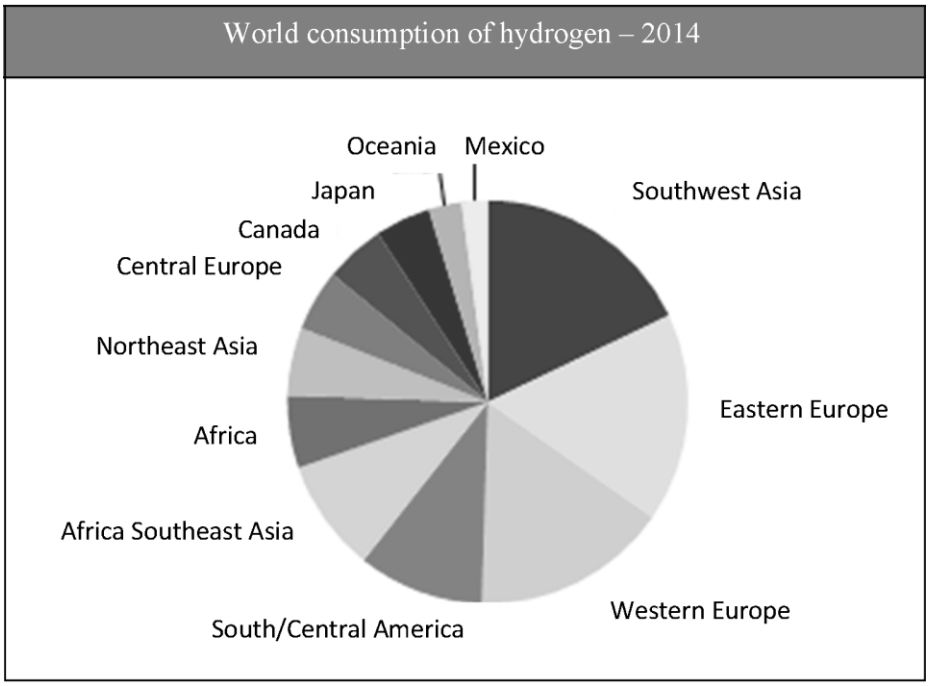

Figure 1.1: H_2 consumption worldwide in 2014 (Inc, 2015).

followed by North America. However, the H_2 demand of North America is expected to grow faster than the H_2 demand of Europe owing to the increased shale gas exploration (Research, 2016).

The supply chain of the H_2 starts from the primary energy sources which are further utilized for various generation, and application purposes as illustrated in Figure 1.2. The H_2 production plants can utilize the produced H_2 or further distribute H_2 to other market player for various applications. Some of the leading players in the H_2 market include Linde AG (Germany), Air Liquide SA (France), Air Products & Chemicals Inc. (U.S.), Praxair Inc. (U.S.), Airgas Inc. (U.S), and Hydrogenics Corp. (Canada).

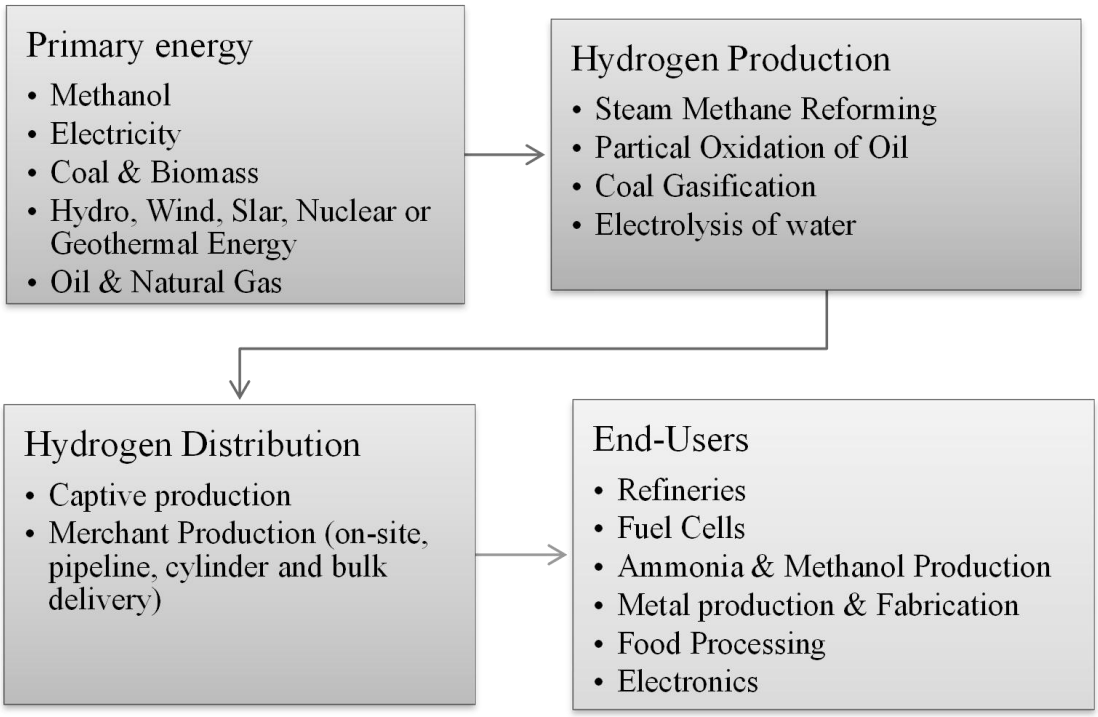

Figure 1.2: H_2 ecosystem (Markets, 2016).

Currently, around 49 % of the global H_2 demand is met by steam reforming using natural gas. Oil reforming contributes 29 % of the total H_2 generation while coal gasification contributes another 18 % of the total H_2 production (Inc, 2015). The remaining H_2 is produced from water electrolysis (3.9 %) and other sources (0.1 %) (Kalamaras and Efstathio, 2013). The dominant route for H_2 production at industrial scale involves the steam reforming of natural gas followed by gas purification. The common efficiency of steam reforming is 80 %. The production of H_2 by steam methane reforming (SMR) at a distributed scale is projected to be more cost effective compared to the central production of H_2 at large scale with delivery via compressed gas tube trailers or cryogenic trucks (Gupta, 2008). Steam reforming is typically conducted within a temperature range of 700 to 1000 °C and a pressure range of 3 to 25 bar. The reaction for SMR is shown in equation 1.1 (Liu et al., 2010).

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H_{298} = 205.9 \text{ kJ/mol} \qquad (1.1)$$

Besides H_2, the reaction also produces about 12 % of carbon monoxide (CO), which can be further converted into carbon dioxide (CO_2) and H_2 through the water-gas shift reaction (WGS). For instance, the SMR plant in Pasadena, Texas produces H_2 at a rate of 80 million standard cubic feet per day (MMMSCFD) using the steam reforming and WGS reactions followed by pressure swing absorption to remove the remaining traces of CO, CO_2, steam and methane (CH_4) from H_2 (Reformer, 2013). In the small and large SMR plants, natural gas feedstock cost contributes up to 68 % of the final H_2 price and the remaining expenses compose of capital charges. According to Muradov and Veziroglu (2005), a typical H_2 plant with a production capacity of 1 million m^3 H_2/day releases around 0.3 - 0.4 million m^3 of CO_2 daily depending on the separation processes. The capture of CO_2 may induce additional cost, approximately 25 - 30 % (Hoseini and Wahid, 2016). The CO_2 and H_2 gases are produced according to the following stoichiometries (Liu et al., 2010);

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H_{298} = -41 \text{ kJ/mol} \qquad (1.2)$$

In partial oxidation, natural gas and oxygen (O_2) are introduced into a reactor at high pressure (15 - 30 atm). An exothermic oxidation reaction is initiated to form H_2 and CO. Similar to SMR, the formation of H_2 from CO is further accomplished via WGS. The use of catalyst can reduce the reaction temperature to 800 - 900 °C in catalytic partial oxidation. Equation 1.3 below shows the relevant stoichiometric equation for partial oxidation reaction (Liu et al., 2010).

$CH_4 + ½O_2 \rightarrow CO + 2H_2$ $\Delta H_{298} = -35.9$ kJ/mol (1.3)

Since the reaction is exothermic, no external heat supply is necessary and the capital cost is reduced. SMR and partial methane oxidation are well developed processes, the cost of H_2 production depend on the cost of natural gas greatly (Paul, 2014). Autothermal reforming further combines SMR and partial methane oxidation to achieve exothermic state with outlet temperature in the range of 950 to 1100 °C and pressure as high as 100 bar. WGS is required to convert CO into H_2, but the efficiency of autothermal reforming is limited by the gas purification step (Riis et al., 2006).

The partial oxidation of oil is another major route of H_2 production and it has been widely commercialized. Several modifications are required based on the feed composition and the reactor type. The catalytic or noncatalytic partial oxidation processes are exothermic due to the sufficient amount of oxygen added. The noncatalytic partial oxidation of heavy oil is conducted at high temperature (1100 - 1500 °C) while the catalytic partial oxidation of light hydrocarbon such as naphtha can be conducted at a lower temperature (600 - 900 °C) (Gupta, 2008). The syngas is shifted, desulfurized and methanated.

The H_2 production from coal gasification is also well-established, but it is only competitive with SMR when oil and gas price is high (Padró and Putsche, 1999). In coal gasification, the process involves the partial oxidation of coal using O_2 followed by steam reforming in a high pressure reactor. Two types of coal gasification processes are commercially used, name Koppers-Totzek process and

Texaco process. The Koppers-Totzek process is operated at atmospheric pressure while the Texaco process is operated at a pressure of 5.5 MPa. The syngas is then desulfurized, shifted and purified subsequently. Both processes result in H_2 product streams with purities of at least 97 % (Mirabal, 2003).

Although H_2 is considered a clean energy, 98 % of H_2 actually generated from fossil fuel as discussed earlier. At the present rate of fossil fuel consumption, the reserves are predicted to be finished in less than 50 years (Mclamb, 2011). The dependence on fossil fuels not only contributes climate change and global warming, but also causes a rapid exhaustion of natural energy sources. Hence, H_2 should be produced from clean and abundant resources using environmentally benign methods. Rohland et al., (1992) predicted that the renewable resources will meet 36 % of the total global energy demand by 2025, with H_2 contribution of 11 %. If the H_2 production technology is further improved, the use of coal and crude oil will drop to 36.7 % and 40.5 % respectively, by 2030.

H_2 can be generated from water and electricity through electrolysis, the reverse of the process used in a fuel cell. Water electrolysis has been extensively developed in recent years and supplying up to 4 % of current total H_2 production (Gupta, 2008). Water electrolysis is an electrochemical reaction which yields H_2 and O_2 and the charge carrier can be OH^-, H_3O^+ or O^{2-}. Alkaline electrolysis is a mature technology for H_2 production a large scale, but it only offers low current density and the system is highly corrosive. Polymer electrolyte membrane electrolysis with high power density is also commercially available at expensive price besides alkaline electrolysis. Furthermore, solid oxide electrolysis has been recently developed to

achieve high electrical efficiency (Götz et al., 2016). Water can be further electrolyzed using solar or wind energy to produce H_2 with minimum environmental impacts. However, the H_2 produced using water electrolysis is estimated to be much more expensive than the non-renewable H_2 discussed earlier (Gandía et al., 2013). The electrolysis usually loses 10 - 30 % of the input energy and 39 kWh of electricity is required to produce 1 kg of H_2 even 100 % efficiency is achieved (Gardner, 2009).

Through biomass conversion processes, H_2-containing gas can be produced similarly to coal gasification. The biomass particles undergo partial oxidation, resulting in gas and charcoal production at the temperature higher than 1000 K (Ni et al., 2006). Biomass gasification is categorized as thermochemical conversion which is the most widely practiced conversion pathway for H_2. Thermochemical conversion also includes pyrolysis, hydropyrolysis, reforming and liquefaction as shown in Figure 1.3. Pyrolysis and liquefaction convert biomass directly at high temperature to bio-oils, gases, and char, while steam reforming of bio-oil after fast pyrolysis requires noble metals as the catalyst (Mohanty et al., 2015). Typically, about 60 – 70 % of the weight of biomass is converted to bio-oil, while 13 - 15 % are from biochar and 13 – 25 % are from syngas.

Another alternative of renewable H_2 production is the biological conversion which requires less energy than the thermochemical conversion methods mentioned earlier. The biologically generated H_2, or more commonly known as biohydrogen is of great interest due to its high energy content and sustainability. Biohydrogen can be biologically produced via a wide range of processes, such as direct biophotolysis, indirect biophotolysis, photo-fermentations and dark-fermentation. Direct

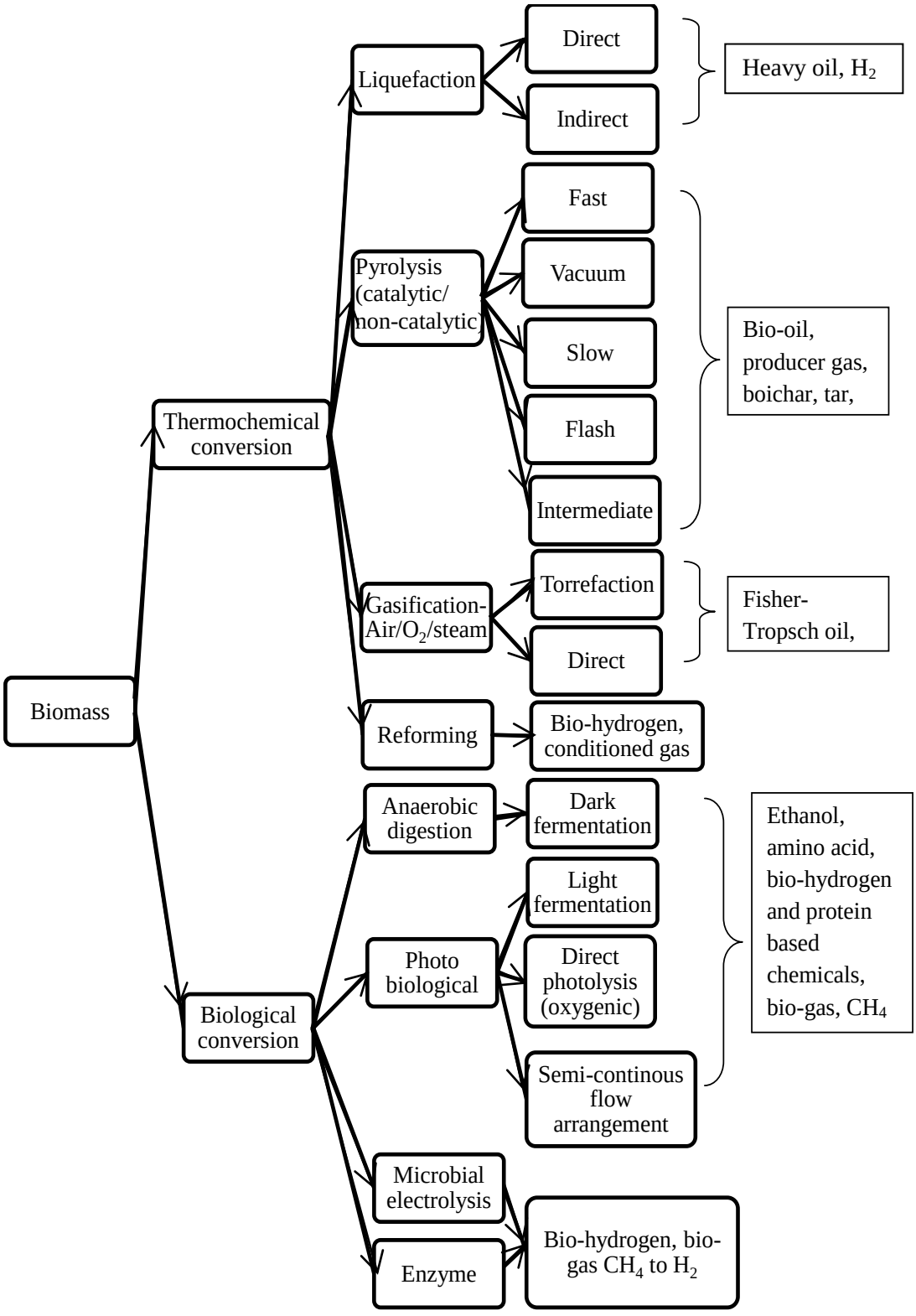

Figure 1.3: Different conversion routes of biomass into H_2 (Mohanty et al., 2015).

biophotolysis involves the photosynthetic reaction to convert solar energy into chemical energy using microalgae. The biophotolysis of water also can be indirectly achieved in serial reactions using cyanobacteria. H_2 production from microalgae is attractive since it produce H_2 from easily available water without the accumulation of CO_2 and more than 80 % of the theoretical solar energy conversion efficiency can be achieved. However, the H_2 production rate by cyanobacteria is few times higher than the H_2 production rate of green microalgae (Azwar et al., 2014). Equation for gasification of biomass is generally followed the reaction below (Balat et al., 2010);

Biomass + O_2 (or H_2O) →

$$CO, CO_2, H_2O, H_2, CH_4 + \text{other CHs} + \text{tar} + \text{char} + \text{ash} \qquad (1.4)$$

In photo fermentation, the photosynthetic bacteria such as Purple Non-Sulfur bacteria can produce H_2 from organic acids and alcohol under sunlight. Without sunlight, dark fermentation usually employs anaerobic bacterial as well as some microalgae to produce more fermentation products besides H_2, including CH_4, CO_2, CO and hydrogen sulphide (H_2S) from carbohydrates. Since a great amount of acetic acid and/or butyric acids is also produced in dark fermentation, the acid can be further used as the supply for a photo fermentative process in the integrated system (Gandía et al., 2013).

Taking the H_2 production cost of SMR as the basis ($2.08/kg), biomass pyrolysis and gasification appear to be viable since they only cost about $ 1.50 - 2.20 to produce 1 kg of H_2. Biological processes such as biophotolysis offers lower capital cost than SMR besides a reasonable production cost near to $2/kg. H_2 production through biomass conversion is considered a carbon-neutral option although carbon

exists in the process (Bartels, 2008). This is because CO_2 is used in the growth of H_2 feedstocks such as plants and microorganisms. According to the finding of United Nations Environment Programme (Chandak, 2010), 140 billion metric tons of biomass is generated every year from agriculture and it is equivalent to approximately 50 billion tons of oil. Hence, H_2 production using bioresources is expected to grow dramatically in the near future. Table 1.1 shows the typical composition of gases from various processes.

Table 1.1: Typical composition of gases from various processes (Liew et al., 2013).

Process	Composition vol%, dry basis					
	H_2	**CO_2**	**N_2**	**CH_4**	**CO**	**Other**
SMR	75.7	8.1	0.2	0.5	15.5	0.0
WGS	31.7	3.4	13.1	12.2	30.0	9.6
Coal Gasification	29.4	10.0	0.6	0.0	59.4	0.6
Partial Oxidation	46.0	4.3	1.4	0.3	47.0	1.0
Biomass Gasification	18.6	15.7	56.0	0.6	8.7	0.4
Biomass fermentation	4.4	16.5	56.8	4.2	14.7	3.4

1.2 Hydrogen Separation

Currently, a large number of H_2 production sites are designed for ammonia and methanol plants which require Nitrogen (N_2) : H_2 ratio of 3 : 1 and H_2 : CO ratio of 2 : 1, respectively. The ammonia synthesis reaction shown in equation (1.5) (Bartels, 2008).

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad \Delta H_{298} = 46.2 \text{ kJ/mol} \qquad (1.5)$$

It is customary to convert almost all CO to H_2 using WGS followed by CO_2 scrubbing and methanation for ammonia production, while CO_2 removal is not required for syngas utilization. However, the utilization of H_2 as the energy carrier in fuel cells for transportation and power generation requires H_2 with high purity. In addition, more alternatives for H_2 production using bioresources at low yield and rate have been developed in the recent years. H_2 separation and purification becomes an important topic.

Pressure swing adsorption (PSA) is the most common method used in H_2 separation. PSA is conducted using at least two adsorbent beds. One of the bed captures the impurities (CO, CO_2, CH_4, and water (H_2O)) in the syngas stream or the product gas of WGS at high pressure (10 - 40 bar), while another bed releases the impurities at low pressure. In most of the applications, multiple beds are simultaneously utilized so that a continuous stream of H_2 with purity up to 99.9 % may be produced. The modern PSA units usually utilize 3 to 4 types of adsorbents to remove various kinds of impurities, namely silica gel or alumina for water separation, activated carbon for CO_2 capture as well as 5A zeolite for CH_4, CO and N_2 removal (Ritter and Ebner, 2007). Nowadays, PSA with 12 adsorbent columns is commonly found and PSA with up to 16 columns for H_2 recovery close to 90 % has been patented (Grande, 2012). Over 500 PSA plants including the world's largest PSA unit have been designed and supplied by Linde, ranging from small plant sizes of a few hundred Nm^3/h to a large scale plants of over 400 000 Nm^3/h feed gas flow (PSA, 2016). Temperature swing adsorption (TSA) is different from PSA in term of desorption only, but it is not widely used because of the relatively long time for heating and cooling of sorbents. Electrical swing adsorption has been proposed as

well, but it is currently at the development stage. Cryogenic separation processes purify H_2 at extremely low temperatures when the production of moderately pure H_2 and highly pure CO from syngas are required. These processes use the difference of boiling temperatures among the feed components to achieve separation. H_2 has a higher relatively volatility compared to other hydrocarbons, so a high H_2 recovery at moderate H_2 purities (95 % or less) can be achieved using a cryogenic system. Cryogenic separation processes are also applied to recover H_2 from other gas stream containing C_{2+} liquid products (Ritter and Ebner, 2007). However, cryogenic distillation is quite expensive.

On the other hand, membrane processes such as Polysep membrane systems and PRISM membrane systems have been developed by UOP and Monsanto, respectively. These membrane systems are now sold by Air Producs and Chemicals Inc. to recover H_2 from various refineries, petrochemical and chemical plants. Polymeric membranes, most likely polysulfone (PSf) in different shapes are utilized in both membrane separation systems. The spiral wound membranes are used in Polysep while the hollow fibers are used in PRISM. These membrane systems are able to achieve H_2 purity in the range of 70 to 99 vol.% with a H_2 recovery ranging from 70 to 95 % (Ritter et al., 2007). The H_2 permeates through the polymeric membranes via solution-diffusion and the preferential permeation of H_2 is achieved using the diffusivity selective membranes. This is because the kinetic diameter of H_2 (2.89 Å) is smaller than the kinetic diameter of other gases such as CO_2 (3.30 Å) (Li et al., 2015). An upper bound limit for the separation performance of polymeric membranes in H_2 purification can be predicted by Robenson. (2008) as shown in Figure 1.4. This upper bound shows the trade-off between permeability and

selectivity. This upper bound also represents the biggest challenge in gas separation using polymeric membranes (Ahmad and Hägg, 2013).

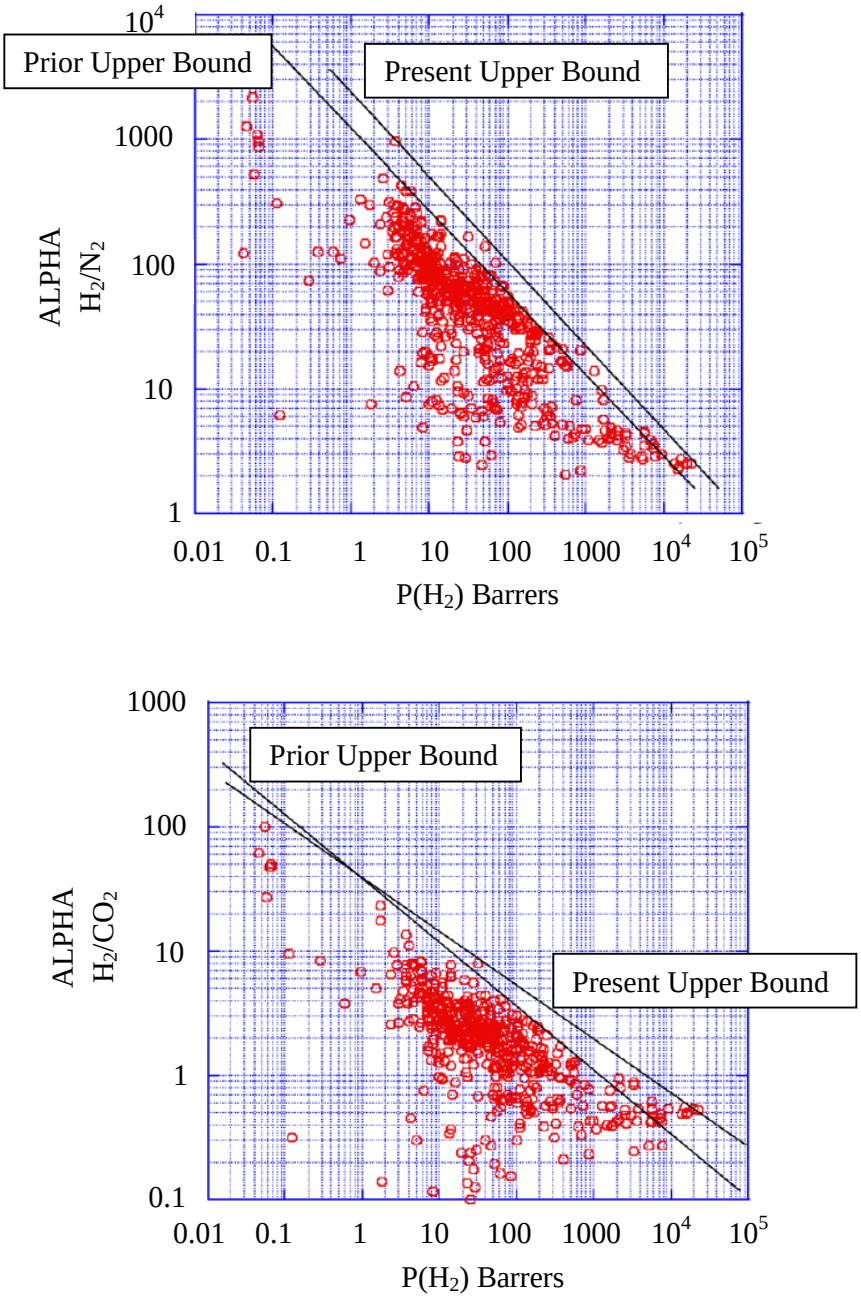

Figure 1.4: Upper bound correlation for H_2/N_2 and separation H_2/CO_2 (Robeson, 2008).

Table 1.2 below summarizes the performance comparison of H_2 separation by different separation process.

Table 1.2: The performance comparison of H_2 separation by different separation processes (Market, 2013).

Features	**PSA**	**Cryogenics**	**Membranes**
H_2 purity	99.9 % +	90.0 – 96.0 %	90.0 - 98.0 %
H_2 recovery	75 – 92 %	90 – 98 %	85 – 95 %
Feed pressure	10 – 40 bar	>5 - 75 bar	20 – 160 bar
Feed H_2 content	>40 %	>10 %	> 25 – 50 %
H_2 product pressure	Feed pressure	Feed / low pressure	<<Feed pressure
H_2 capacity	1 – 200 MMscfd	5 – 60 MMscfd	< 50 MMscfd
Pretreatment requirements	None	CO_2, H_2O removal	Minimum
Multiple products	No	Liquid HCs	No

The selection of H_2 separation techniques depends on several factors when they are integrated into the existing process such as SMR and coal gasification. The major factors are the process conditions (temperature and pressure), the product purity and recovery as well as the flexibility and efficiency of separation technique. However, biohydrogen requires the different selection criteria of H_2 separation techniques from SMR and gasification. This is because most of the biological production routes of H_2 involve the low temperature and pressure at a wide range of production scale. Among the separation techniques, membrane separation appears to be attractive especially when the options of H_2 production using bioresources have grown over the years. Membrane separation offers: (1) high energy efficiency, (2)

cost effectiveness per foot print, (3) simplicity in operation, and (4) environmentally friendly (Shao et al., 2009). More importantly, a wide spectrum of membrane material is available to fit different gas composition at varied temperature and pressure.

Besides polymeric membranes, palladium (Pd) based membranes are attractive alternatives to PSA and cryogenic separation. Pd based membrane was first commercialized by Johnson Matthey in 1964 to purify a H_2 rich-stream (Falco et al., 2011). A H_2 generator comprising of Pd membrane reactor fed with a methanol/water mixture was also developed by Johnson Matthey. However, Johnson Matthey which makes many gas purification products suited to light-emitting diode (LED) and compound semiconductor manufacturing exited the gas purification market. Johnson Matthey closed down the facility in West Chester, Pennsylvania in 2013 due to the slowdown in LED fabrication market (Johnson, 2013). Nevertheless, other companies continue to develop Pd based membranes for H_2 production and separation. For instance, Pall Corporation offers Pd-based membranes which are developed under the collaboration with Colorado School of Mines (Membrane, no date). Green Hydrotec has commercialized H_2 generator equipped with catalytic heater and Pd membrane tube in reformer (Hydrotec, 2010), while Fraunhofer IST is working with Plansee SE and Linde to develop Pd membranes on porous metal support (IST, 2012). The thickness of Pd membranes on support is typically in the order of 50 - 100 μm. The H_2 flux through Pd membranes is inversely proportional to the membrane thickness. Hence, the reduction of membrane thickness is important. The permeation of H_2 via Pd membrane involves the reversible adsorption of H_2 molecules at the Pd surface, followed by the rapid dissociation and diffusion of H^+

ions into the metal lattice (Lewis, 1967). The permeated H^+ ions recombine and desorbed from the Pd membrane. The Pd membranes work in a temperature range of 300 - 600 °C and they achieve a very high selectivity (>1000) and permeance compared to other types of membranes. Unfortunately, Pd is relatively expensive and Pd alloy membranes have been further developed (Al-Mufachi et al., 2015).

The H_2 separation using membranes should not further increase the cost of H_2 production and hinders the development of H_2 economy. H_2 separation using a membrane system with a cost less than $\$1080/m^2$ is the target of US Department of Energy (DOE) (Phair and Badwal, 2006). Besides economic consideration, the membrane should be selected based on the properties of product gas such as composition, pressure and temperature. The selectivity and the gas permeance of a membrane are the basic properties evaluated during the selection. The membrane separation system is more efficient by incorporating the membrane with higher selectivity, so that a lower driving force (pressure ratio) is required and a cheaper operating cost is accomplished. A smaller membrane area is needed when a membrane with higher permeance is selected, leading to a reduced capital cost. Without the satisfactory selectivity and permeance, the permeate gas needs to be recompressed and recycled back to the membrane separation system designed with multiple stages. The recycle cascades require additional compressor and it is highly energy demanding. Therefore, it may overturn the economic advantages of membrane-based separations compared to PSA or cryogenic distillation. With the satisfactory selectivity and permeance, H_2 separation membranes showed great potential to reduce separation cost by over 30 % compared to PSA (Gupta, 2008).

1.3 Problem Statement

Asian countries produce almost 85 % biomass waste in the world and the waste mainly located in Malaysia and Indonesia (Pudukudy et al., 2014). Hence, H_2 production from the biomass waste is expected to grow in this region. Gasification (Samiran et al., 2016) and fermentation (Ahmad et al., 2016) are the most extensively studied methods for H_2 production from oil palm waste and palm oil mill effluent, respectively. Currently, no membrane meets all the criteria required in the purification of H_2 produced from biomass. Pd membranes can be easily integrated into the gasification plant because Pd membranes can separate H_2 from CO_2 within the high temperature range of 300 - 600 °C (Al-Mufachi et al., 2015). H_2-embrittlement cracking only occurs when Pd membranes are used in H_2 separation below 300 °C and 20 bar (Falco et al., 2011). However, Pd membranes are not the perfect solution due to the high cost of Pd and alloys. Polymeric membrane can be used to purify the biohydrogen at low temperature and pressure, but most of the polymeric membranes including PSf membrane cannot surpass the Robeson upper bound limit for H_2 separation from N_2 or CO_2.

In recent years, mixed matrix membranes (MMMs) have been extensively studied and developed (Li et al., 2015). MMMs comprise of dispersed particles and the continuous polymer matrix to surpass the Robeson upper bound limit. The solution-diffusion limitation of the polymeric membranes could be easily overcome by incorporating various types of zeolites, silica, carbon molecular sieves, carbon nanotubes, and metal organic frameworks (Li et al., 2015). Pd nanoparcticles are proposed to be incorporated into PSf membrane in this work in order to develop MMMs that separate H_2 satisfactory and economically. However, the use of Pd

nanoparticles to engineer MMMs for gas separation has not been reported to the best knowledge. The Pd nanoparticles have been incorporated into polymeric matrix as catalyst (Emin et al., 2014, Gu et al., 2015). In addition, they have been used in H_2 sensing (Wadell et al., 2014) and supported on porous absorbent for H_2 storage (Konda and Chen, 2016). In the development of the H_2 selective MMMs, Pd nanoparticles appear to be a promising choice since they have high affinity for H_2 sorption. Pd nanoparticles are able to absorb large volumetric quantities of H_2 at room temperature and atmospheric temperature by forming palladium hydride (PdHx) (Konda and Chen, 2016).

The improvement on the separation performance of MMMs not only depends on the selection of inorganic particle, but also relies on the loading of inorganic particle. Particle agglomeration can cause the adverse effects on membrane separation performance. Membrane separation is also affected by the nature and degree of interfacial adhesion between the polymer and particles. Unlike other inorganic filler, Pd nanoparticles can be kinetically stabilized using electrostatic and/ or steric forces of a stabilizer without affecting the functionality and surface area of Pd nanoparticles. More importantly, the stabilizers such as polyvinylpyrrolidone (PVP) or polyethylene glycol (PEG) can introduce microvoids between polymeric matrix and Pd fillers to avoid pore blockage or diffusion hindrance. These stabilizers are common additive in gas separation membranes as well (Loloei et al., 2015, Aroon et al., 2010). Thus, it is proposed to utilize the Pd nanoparticles in appropriate stabilizers to attain the desired nanoparticles size and prevent from aggregating and allow one to isolate the nanoparticles.

For high temperature separation, glassy membranes including PSf membrane age faster at higher temperature and experience permeability loss (Huang and Paul, 2005). The thinner membranes tend to age faster than the thick membranes. Hence, the application of glassy membranes such as PSf membrane is limited by the high temperature of H_2 rich gas produced from biomass gasification. The investigation of temperature effects on Pd nanoparticles dispersed in polymer matrix is also limited by these reasons. Polybenzimidazole (PBI) with a very high melting point should be selected to engineer MMMs for the separation of H_2 from hot gas. Although conventional PBI showed high selectivity, its closed and packed structure is the major constrain for the gas permeation. Hence, it is also interesting to study the effects of different stabilizers of Pd nanoparticles such as PEG and PVP which work as the membrane additives on PBI membranes (Loloei et al., 2015). The incorporation of Pd nanoparticles into PBI thin film allows further investigation of the temperatures effects on the functionality of Pd nanoparticles dispersed in polymer matrix. The application of Pd in H_2 storage and separation are affected by temperature as reported by many works (Sheng et al., 2014, Falco et al., 2011), but the effects of temperature on MMMs incorporated with Pd nanoparticles in H_2 separation remain unknown.

1.4 Objectives

The present research has the following objectives:

1. To synthesize and characterize PSf and PBI membrane incorporated with Pd nanoparticles.
2. To study the effects of Pd nanoparticles, stabilizer and temperature on the H_2 separation performance of PSf and PBI MMMs.

3. To perform a feasibility study using mathematical model in H_2 purification for biohydrogen system using Polymath software.

1.5 Scope of Study

This study basically focuses on the development of MMMs incorporated with Pd nanoparticles for H_2 separation. The Pd nanoparticles were synthesized using the inversed microemulsion. There were two stabilizers used in this study, namely PEG and PVP. These polymers were chosen by considering the stability of Pd colloid precursor, the solvent and the ability of the polymer to stabilize the reduced Pd nanoparticles. The synthesized Pd nanoparticles were characterized using Transmission Electron Micrographs (TEM), X-ray Diffraction (XRD) and Temperature Programmed Reduction (TPR) before being blended into PSf polymer matrix. The MMMs incorporated with Pd nanoparticles were synthesized using the common method, phase inversion. The Pd nanoparticles were blended into the polymer solution prior to casting and phase inversion.

The common H_2 separation membrane material, PSf has been chosen as the first polymer matrix to develop the MMMs. The Pd nanoparticles synthesized using PEG and PVP as the stabilizer were separately incorporated into the PSf matrix to form two types of PSf(Pd) MMMs. Besides the effects of stabilizer, the effects of Pd nanoparticles loading on membrane properties were studied using TPR, XRD, Fourier Transform Infrared (FTIR) Spectroscopy, Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX). The control membrane, the neat PSf membrane was also synthesized and characterized to compare the effects of stabilizers and Pd loading on PSf MMMs. PSf(Pd/PEG) and PSf(Pd/PVP) MMMs

were further tested for gas separation to study the compatibility of PSf polymer, PEG or PVP stabilizer and Pd nanoparticles. In addition, the separation test was used to determine the appropriate loading of Pd nanoparticles in PSf. The separation of H_2 from N_2 and CO_2 gases using MMMs membrane were the second focus in this study.

In order to improve the separation performance of MMMs and their stability at the high temperature (100 - 150 °C), PBI has been chosen as the second polymer. Similar to the PSf MMMs, the Pd nanoparticles synthesized using stabilizer such as PEG and PVP was incorporated in the PBI matrix to form PBI MMMs. The compatibility between PBI matrix, PEG or PVP stabilizer and Pd nanoparticles were studied. Besides the effects of stabilizer, the effects of Pd loading on the membrane morphology and separation performance were investigated. The effects of temperature on H_2 separation performance of a selected PBI(Pd) MMMs were also considered. All the fabricated PBI(Pd) MMMs were characterized via XRD, SEM, FTIR, EDX and TPR. The chosen PBI MMMs (selected based on their separation performance) were further tested at high operating temperature (200 - 300 °C) to study the effects of temperature.

In addition, the feasibility of PBI(Pd) MMMs in the purification of H_2 produced from fermentation and biomass gasification were mathematically evaluated. The membrane feasibility was measured in terms of membrane area, product purity and gas recovery.

1.6 Organization of the Thesis

This thesis comprises of five chapters as listed in the table of content. It provides all the details and findings of this research. Each chapter contains the important knowledge and information as listed below.

Chapter one (Introduction) presents the overview of H_2 demand in various applications and their production using different routes as well as resources. The comparison between the conventional separation methods and the advantages using membrane separation has been highlighted. Besides the polymeric membranes, the general overview on Pd membranes and their application in H_2 separation have been briefly described to give a fundamental view. Next, the problem statements of the study are also being discussed. Then, the research objectives are listed and the scopes of study are thoroughly explained. Lastly, the organization of the thesis is specified in the last section of this chapter.

Chapter two (Literature Review) is devoted to an extensive literature review from previous to recent studies. The first part of the literature focuses H_2 selective membrane. Subsections of this part explain the general overview on PSf and PBI as membrane material including its characteristic and their separation performance. Next, the overview on inorganic membrane based on dense metallic and microporous membrane has also been explained. The review is focused further on the MMMs for H_2 separation, which involve the incorporation of different type of filler. A review study was done on the effect of stabilizer, filler loading and high operating temperature on MMMs performance. In the next section, the application of membrane in biohydrogen system has been discussed. The last segment gives

attention on Pd nanoparticles which involves the discussion on their uses and synthesis method.

Chapter three (Research Methodology) presents the detail of materials and chemicals used through this research study. This is followed by the detailed experimental procedures, which include the synthesis of Pd nanoparticles, the fabrication of PSf and PBI MMMs, characterization method and gas performance analysis. Details on the experimental set up are also elaborated in this chapter. In the last section, the mathematically model and membrane process simulation are listed.

Chapter four (Result and Discussion) is the core of this thesis, which address the three objectives as listed in Chapter 1. The research findings and results are presented and extensively discussed. The first section, presented the preparation and characterization of PSf MMMs incorporated with Pd nanoparticles by using PEG and PVP as stabilizer. The second section investigated the effect of stabilizer and Pd nanoparticles on the performance of PSf MMMs in H_2 separation. The third section presented the preparation and characterization of PBI MMM with Pd stabilized by PEG and PVP. The last section discussed the effects of Pd, stabilizer and temperature on the H_2 separation performance of PBI MMMs. Besides, a feasibility study on H_2 purification that been conducted based on fermentation and gasification system also has been studied in this section.

Chapter five (Conclusions and Recommendation) concludes all the major findings obtained in the result and discussions in this present study. At the end of the

thesis, suggestion, recommendation that describe future improvements on present study are presented.