

**IMPACT OF CROSS-LINKING POLYMER TO BRIDGE THE POROUS
MEMBRANE AND SELECTIVE LAYER IN MEMBRANE ABSORPTION**

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By

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LIST OF SYMBOLS

Symbol	Description	Unit
M	Molarity	mol/L
m_w	Weight of wet membrane	g
m_d	Weight of dry membrane	g
ρ_b	Density of butanol	g/cm ³
ρ_m	Density of PVDF membrane	g/cm ³
J_{CO_2}	Mass transfer rate of CO ₂	mol m ⁻² s ⁻¹
$Q_{g,in}$	The inlet of gas flow	mL/min
$Q_{g,r}$	The retentate of gas flow	mL/min
ρ_g	Density of the CO ₂ gas	g/mol
MW_g	Molecular weight of CO ₂	
A	Area of the membrane contacted	m ²
Greek letter		
ε	Porosity of the membrane	

LIST OF ABBREVIATIONS

AMP	2-amino-2-methyl-1-propanol
CF ₄	Carbon tetrafluoride
CNT	Carbon nanotubes
CO ₂	Carbon dioxide
DEA	Diethanolamine
DBP	Dibutyl phthalate
DMAc	N,N-Dimethylacetamide
DMF	N,N-Dimethylformamide
DMP	Dimethyl phthalate
EDA	Ethylenediamine
FTIR	Fourier transform infrared microscope
GO	Graphene oxide
H ₂	Hydrogen
LDPE	Low-density polyethylene
MDEA	Methyldiethanolamine
MGA	Membrane gas absorption
NaOH	Sodium hydroxide
NIPS	Non-solvent induced phase separation
NMP	N-Methyl-2-pyrrolidone
PEG	Polyethylene glycol
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride

SDG	Sustainable development goals
SEIPS	Solvent-evaporation phase separation
SF6	Sulfur hexafluoride
SEM	Scanning electron microscope
Sn	Tin
Tg	Glass transition temperature
TIPS	Temperature induced phase separation
UV	Ultraviolet
VIPS	Vapour induces phase separation
XeF2	Xenon difluoride
2P	2-pyrrolidinone

**KESAN POLIMER PENGHUBUNG SILANG UNTUK MENGHUBUNGAN
MEMBRAN POROS DAN LAPISAN SELEKTIF DALAM MEMBRAN
PENYERAPAN**

ABSTRAK

Teknologi penyerapan gas membran (MGA) telah menjadi alternatif menarik yang ditemui oleh penyelidik untuk memerangkap gas karbon dioksida (CO₂) daripada dibebaskan ke atmosfera. Pelbagai pengubahsuaian terhadap membran yang digunakan sebagai penyentuh dalam teknologi ini menjadi tumpuan para pengkaji untuk meningkatkan prestasi MGA. Dalam tesis ini, polyvinylidene fluoride (PVDF) telah digunakan sebagai membran untuk mengkaji kesan menghubung silang membran dan polimer dalam MGA. Membran porous PVDF telah dibuat melalui pemisahan fasa teraruh bukan pelarut (NIPS) atau lebih dikenali sebagai kaedah pemendakan rendaman.

Pengubahsuaian membran PVDF ini dilakukan dengan mencelupkan membran ke dalam polimer *chitosan*, *nylon*, *dopamine* dan *ethylenediamine* (EDA). Membran yang telah diubah suai akan dikaji untuk menentukan kebolehsaknaan membran yang diubah suai dalam MGA. FTIR, keliangan dan taburan saiz poros digunakan untuk mencirikan membran PVDF yang tidak diubah suai dan yang telah diubah suai. Imej SEM bagi membran PVDF yang telah diubah suai dengan polimer berbeza menunjukkan struktur poros yang sama seperti membran PVDF yang tidak diubah suai. Keliangan membran PVDF yang tidak diubah suai adalah 78.02%. Manakala, keliangan membran PVDF/Chitosan, PVDF/Nylon, PVDF/Dopamine and PVDF/EDA yang diperolehi adalah 81.28 %, 76.91 %, 81.75 % and 80.52 % bagi setiap membran. Taburan saiz poros membran yang diubah suai menunjukkan

perbezaan yang ketara daripada membran yang tidak diubah suai. Prestasi MGA bagi membran yang telah diubah suai adalah lebih rendah daripada membran PVDF yang tidak diubah suai.

Membran PVDF/EDA mempunyai prestasi MGA yang lebih baik dalam kalangan membran PVDF yang telah diubah suai dan digunakan untuk mengkaji kesan pelbagai parameter salutan EDA kepada prestasi MGA. Membran PVDF disalut dengan polimer EDA pada pelbagai suhu, masa dan kepekatan. Membran PVDF disalut dengan polimer EDA pada suhu 50°C dan 80°C. Prestasi MGA membrane PVDF/EDA pada suhu salutan 80°C adalah lebih tinggi daripada prestasi MGA membran PVDF/EDA pada suhu salutan yang lebih rendah. Masa salutan polimer EDA dimanipulasi kepada 30 minit, 60 minit dan 120 minit dan membran PVDF/EDA dengan masa salutan 120 minit mempunyai prestasi MGA yang terbaik. Manakala, kepekatan polimer EDA dipelbagaikan kepada 0.5 M, 1.7 M, dan 3.0 M dan begitu juga, membran PVDF/EDA pada kepekatan EDA yang lebih tinggi mempunyai prestasi MGA yang terbaik. Kajian ini menunjukkan bahawa menghubungkan silang polimer EDA pada membran PVDF porous memberi kesan kepada prestasi MGA.

Oleh itu, kajian ini adalah potensi yang menarik untuk digunakan dalam teknologi MGA untuk mengurangkan pembebasan gas CO₂ ke atmosfera. Maka, kerja ini boleh dimajukan lagi untuk mempertingkatkan teknologi MGA dalam mengurangkan pembebasan gas CO₂ ke atmosfera dan menggalakkan matlamat pembangunan mampan matlamat 13 ke arah menghadapi perubahan iklim dengan tindakan segera dalam mengurangkan pembebasan gas CO₂.

IMPACT OF CROSS-LINKING POLYMER TO BRIDGE THE POROUS MEMBRANE AND SELECTIVE LAYER IN MEMBRANE ABSORPTION

ABSTRACT

The membrane gas absorption (MGA) technology has been an attractive alternative discovered by the researchers to remove the carbon dioxide (CO₂) gas from releasing into the atmosphere. Various modifications of the membranes used as the contactor in this technology has become the focus of the researchers to improve the MGA performance. In this thesis, polyvinylidene fluoride (PVDF) was used as the support membrane to study the effect of cross-linking the membrane and the polymers in MGA. A porous PVDF membrane was fabricated through the non-solvent induced phase separation (NIPS) or commonly known as the immersion precipitation method.

The modification of this PVDF membrane was done by dip-coating the membranes into chitosan, nylon, dopamine and ethylenediamine (EDA) polymers. The modified membranes were studied to determine the feasibility of the modified membranes in MGA. FTIR, porosity and pore size distribution were used to characterize the fabricated unmodified and modified PVDF membranes. The SEM images of the modified PVDF membranes with different polymers shown similar porous structures to the unmodified PVDF membrane. The porosity of the unmodified PVDF membrane obtained was 78.02%. Meanwhile, the porosity of PVDF/Chitosan, PVDF/Nylon, PVDF/Dopamine and PVDF/EDA membranes obtained were 81.28 %, 76.91 %, 81.75 % and 80.52 %, respectively. The pore size distribution of the modified membranes shown significant difference from the unmodified membrane. The MGA performances of the modified membranes were lower than the unmodified PVDF membrane.

PVDF/EDA membrane seemed to have the better MGA performance among the modified PVDF membranes and was used to study on the effect of various parameters of the EDA coating solution to the MGA performance. The PVDF membranes were coated with EDA polymer at various coating temperatures, times and concentrations. The PVDF membranes were coated with EDA polymer at coating temperature of 50°C and 80°C. The MGA performance of PVDF/EDA membrane coated at temperature of 80°C was higher than the MGA performance of PVDF/EDA membrane coated at lower temperature. The coating time of EDA polymer were varied to 30 mins, 60 mins and 120 mins and the PVDF/EDA membrane with coating time of 120 mins had the better MGA performance. Meanwhile, the coating concentration of EDA polymer were varied to 0.5 M, 1.7 M and 3.0 M and similarly, the PVDF/EDA membrane at higher EDA concentration had the better MGA performance. This study showed that the cross-linking of the EDA polymer on the porous PVDF membrane impacted the MGA performance.

Thus, it is an attractive potential to be employed in the MGA technology to reduce the emission of the CO₂ gas into the atmosphere. Thus, this work can be developed further to enhance the MGA technology in reducing the emission of the CO₂ gas into the atmosphere and promote the aim of sustainable development goal 13 towards coping with the climate change by urgent action in decreasing the emission of the CO₂ gas.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Nowadays, the emission of the carbon dioxide (CO₂) into the atmosphere has reached its highest concentration and poses to be the threat to the environment as well as to the human wellbeing. CO₂ is the largest component found in the greenhouse gases. The steadily increase in the concentration of CO₂ in the atmosphere will lead to the increase in the greenhouse effect. This will contribute to the global climate changes due to heat entrapped in the atmosphere. Figure 1.1 shows the trends in CO₂ in Malaysia in which it can be seen that the emission of the CO₂ is steadily increased year by year. Therefore, there is a requirement in removing CO₂ from the gas released into the atmosphere.

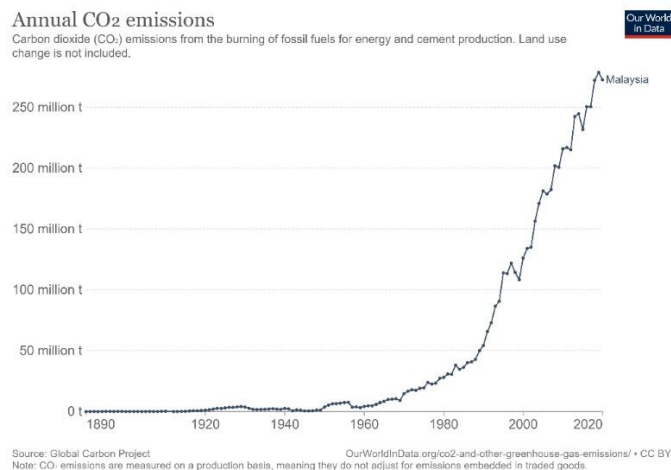


Figure 1.1 CO₂ emission in Malaysia (Malaysia: CO₂ Country Profile - Our World in Data, no date)

One of the methods in removing the CO₂ is by the absorption process in which the packed towers or bubble columns is used to remove the carbon dioxide gases from released to the atmosphere. Yet, this conventional method has its drawback in terms of its efficiency due to the flooding, loading, channelling and

foaming (Siagian et al., 2019). Thus, an alternative such as the membrane contactor is used to remove CO₂. Membrane contactor or membrane gas absorption integrates the conventional absorption method and membrane separation (Figueroa and Cuenca, 2018). The membrane acts a contactor to allow efficient mass transfer between liquid and gas phases (Himma and Wenten, 2017; Siagian et al., 2019).

The membrane used in this process can be synthesized by various method such as electrospinning, stretching, track etching, matrix membrane and phase inversion methods. In fabricating the membrane, the morphology of the membrane produced is the most important as high porosity, smaller pore size and high hydrophobicity can lead to a high CO₂ absorption flux (Ahmad et al., 2018; Siagian et al., 2019).

Yet, the membrane contactor has its main challenge in which is the membrane wetting that can decrease the performance of CO₂ absorption in a long-term operation. The presence of membrane also imposes mass transfer resistance for CO₂ to be absorbed from the gas phase to the liquid phase absorbents. Thus, it is a must in modifying the membrane surface by crosslinking the membrane surface with a polymer that has higher affinity towards CO₂ to allow the gas to be easily diffused through the membrane pores and absorbed by the absorbent. The main scope of this research is to synthesize PVDF membrane for membrane gas absorption, study the polymer that can be used as a crosslinker to link PVDF membrane to another polymer and their variables that can affect the CO₂ absorption flux.

1.2 Problem Statement

From the literatures, the researchers had discovered that the abundant amount of CO₂ gas in the greenhouse gases contributes to the greenhouse effect. The greenhouse effect can cause the global temperature to rise, resulting to the melting of ice blocks in the Antarctic and risen the global sea level. Due to this, there will be a risk of flooding and the loss of the habitat in the Antarctic. Therefore, the researchers developed various methods to remove the CO₂ gas from released to the atmosphere. Membrane gas absorption technology is an attractive approach for the removal of CO₂ gas from releasing into the atmosphere. The membrane in this technology acts as the contactor between the liquid absorbent and gas phases.

However, this membrane generates limitation for the absorption of CO₂ by the absorbent. The presence of this membrane imposes a resistance for the mass transfer of gas phase into liquid phase (Li et al., 2020). Thus, CO₂ has difficulty to diffuse into the pore of the membrane. Modification treatment on the membrane surface will reduce the membrane resistance and maximize the amount of the CO₂ gas captured. One of the modification techniques is by coating the membrane surface with the CO₂ affinity nanofiller with a crosslinker polymer. In order to achieve this, the potential of different types of polymers to crosslink to the membrane will be investigated.

The crosslinker polymers can be coated on the membrane surface through the dip coating method. This method is the simplest surface treatment method to deposit the polymer on the membrane surface (Neacșu et al., 2016). Various parameters of the coating polymer can affect the CO₂ absorption flux, such as the coating temperature, coating time and coating concentration. Increasing in these parameters will lead to a denser membrane surface, which this can affect the membrane pore size and porosity (Jana et al., 2011). Therefore, these parameters can determine the CO₂ absorption flux

of the coated membrane. The challenge in crosslinking the polymer on the membrane is the risk of poor adhesion on the membrane surface due to the weak chemical interaction between the membrane and the coated layer (Liu et al., 2011; Nagandran et al., 2020). Hence, the coating of the crosslinker polymer at the optimum coating parameters is needed in order to make sure that it can be a proper bridge between the membrane surface and the CO₂ affinity nanofiller.

1.3 Research Objectives

1. To synthesis and characterize porous PVDF membrane.
2. To surface coating different cross-linking polymer on PVDF membrane.
3. To analyse the impact of coated layer on membrane gas absorption.

1.4 Scope of Study

The modification of the membrane in the membrane contractor technology has been widely studied to improve the CO₂ absorption flux during MGA operation. The modification of the membrane can be done by linking the membrane surface and the CO₂ affinity nanofiller with a crosslinker polymer. Thus, it is crucial to select the best polymer as the crosslinker and the optimum parameters for the crosslinker polymer to coat on the membrane surface. The scope of this project is to analyse the impact of the crosslinker polymer on the porous membrane in MGA operation.

The PVDF membrane is first fabricated via NIPS method prior to modify the membrane with crosslinker polymers. The prepared membranes are modified with different types of polymers which are chitosan, nylon, dopamine and EDA polymers

through dip-coating method. The characterization of the unmodified and modified PVDF membranes are carried out by FTIR analysis, SEM analysis, porosity and pore size distribution. The MGA operation for the unmodified and modified PVDF membranes are carried out for 3 hours to determine the crosslinker polymer that has the most preferable CO₂ absorption flux.

Then, the best crosslinker polymer is selected to study the impact of various coating parameters on the CO₂ absorption flux. The PVDF membrane prepared is modified with the selected polymer by manipulating the coating temperatures, the coating time of 30, 60 and 120 minutes and the coating concentration. These modified PVDF membranes at different coating parameters are subjected to the similar 3 hours of MGA operation to determine the CO₂ absorption flux.

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane Gas Absorption

Membrane gas absorption (MGA) is considered as a feasible alternative to capture carbon dioxide gases released from the processes such as the natural gas processing and the manufacturing of hydrogen and ammonia as compared to the conventional technology (Lv et al., 2013). Previously, most industries used the conventional chemical absorption equipment such as the packed towers or bubble columns to remove the carbon dioxide gases from released to the atmosphere (Lv et al., 2012).

However, the use of conventional equipment in the industries has shown undesirable outcome including high energy consumption caused by solvent regeneration, limitation on mass transfer area and flow rates due to the change in viscosity, and some of their problems in operation that leads to flooding, loading, channelling and foaming (Lv et al., 2013; Khalilpour et al., 2015; Siagian et al., 2019). Hence, the utilization of MGA technology in removal of carbon dioxide throughout the chemical industries is considered as one of the advantageous alternatives to overcome the drawbacks of the conventional gas absorption.

MGA technology is a hybrid operation that integrates the conventional gas absorption in which the liquid solvent offers high selectivity in capturing the gas and membrane separation with the additional of membrane (Khalilpour et al., 2015; Himma and Wenten, 2017). MGA operation is also known as the membrane contactor operation in which this operation uses a membrane that acts as a contactor between the

liquid and gas phases for better absorption performance. This alternative provides major benefits in energy and cost saving, flexible operation, linear scale-up and modularity as well as reducing the consumption of space for the operation due to its features of having a compact size that imparts high surface area to volume ratio and constant specific interfacial area in the operation (Lv et al., 2012; Himma and Wenten, 2017).

Another advantage of this technology is the absence of operational problems such as entrainment flooding, downflow flooding or weeping due to the elimination of the requirement for the phase dispersion between the gas and liquid during the absorption process (Lv et al., 2013). Therefore, MGA technology is an attractive alternative to be explored because of its economic benefits and potential in overcoming the limitations of the current technology applied in the industries that requires the carbon dioxide gas capture for a longer term.

2.1.1 Working Principle of Membrane Gas Absorption

The membrane in MGA acts as the contactor between the liquid and gas phases, providing more area for the liquid and gas phases to be in contact as well as it promotes the mass transfer between them (Himma and Wenten, 2017). This technology is the integration between the membrane separation and conventional absorption.

However, contrary to the other application of using membranes to perform separation process due to their selectivity to certain components, the membrane in this operation does not exhibit any selectivity and only acts as the support between the phases. Thus, the operation is highly dependent on the selectivity provided by the absorbent liquid to achieve a mixed gas separation (Li et al., 2020).

The selection of the solvent in this operation is as crucial as the solvent used in the conventional absorption in terms of the solvent capability in attracting and absorbing the gas as well as exhibits the ability to easily regenerated and high gas loading capacity. Generally, the membrane used is a hydrophobic porous membrane such as polypropylene (PP), polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) to prevent membrane wetting that lowers the mass transfer (Siagian et al., 2019). PVDF membrane is the most common membrane used as the contactor for its advantages of easily fabricated and low in cost (Siagian et al., 2019).

Figure 2.1 shows the schematic mechanism of MGA through porous membrane. From this, the working principle of the absorption process through the membrane can be described in which it involves three major steps for separating the gas. The first step is the transfer of gas to the membrane surface through a boundary layer of gas phase driven by the concentration difference. Then, the gas diffuses through the pores of the membrane to the other side of the membrane and lastly, the gas is absorbed into the absorbent liquid and carried away from the membrane contactor (Lv et al., 2013; Li et al., 2020). The diffusion of the gas through the porous membrane into the liquid absorbent creates mass transfer resistances including gas phase, liquid phase and membrane resistances that generates concentration profile (Li et al., 2020).

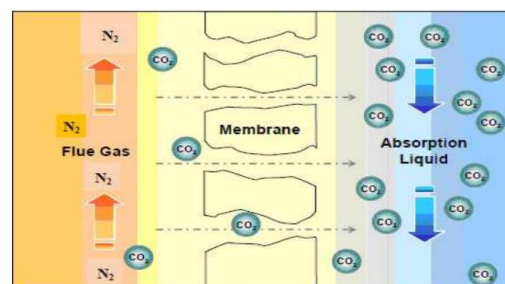


Figure 2.1 Schematic mechanism of membrane gas absorption through porous membrane (Lv et al., 2013)

2.1.2 Application of Membrane Gas Absorption

Nowadays, carbon dioxide (CO₂) emissions have reached its highest concentration in the atmosphere, posing a threat to the environment and human-wellbeing. CO₂ is the largest component found in the greenhouse gases. Thus, a steady increase in the concentration of CO₂ in the atmosphere will lead to the increase in the greenhouse effect. This will contribute to the high atmospheric pollution as well as one of the major causes for the global climate changes.

Amongst the chemical industries that releases the CO₂ gas, the natural gas processing industry is currently the main focus for the researchers to develop efficient and low-cost technology in removing the CO₂ gas from the natural gas (Ahmad et al., 2018). This is because it is reported that raw natural gas contains up to 30% in CO₂ (Siagian et al., 2019), surpassed other undesirable impurities including water, nitrogen and hydrogen sulphide. Hence, a large amount of the CO₂ exists in the natural gas resource, affecting the energy content of the natural gas, increasing the volume of the gas to be transported through the pipelines and causing pipeline corrosion.

Therefore, the employment of MGA process in the removal of CO₂ gas in power plant plants treatment is considered as an attractive alternative to the conventional absorption process due to its excellent mass transfer properties, high absorption rates, flexible operating conditions and low energy requirement. Because of its reported advantages, it is technically a viable and economically feasible technology for removal of CO₂ gas in a large-scale application (Lv et al., 2013).

PETRONAS Gas Processing Plant had utilized a pilot plant of the MGA operation in 2013 after a development study is conducted. The laboratory-scale study on the membrane contactor is carried out together with the Dalian Institute of Chemical

Physics (DICP). From this study, it is reported that the CO₂ gas exit from the plant is reduced to 1% of CO₂ gas from its feed that contain 10 to 70% of CO₂ gas (Chan et al., 2014). Moreover, the CO₂ removal efficiency is in the range of 89.71% to 98.85%, in which is a relatively high efficiency (Chan et al., 2014). This study proves that the MGA operation is suitable to be utilized in the removal of CO₂ gas from natural gas.

Moreover, PETRONAS Carigali Sdn. Bhd. also utilized the MGA operation for removing high CO₂ gas from hydrocarbon gas. This project is carried out on 2006 located offshore of the Peninsular Malaysia. In this project, the CO₂ gas exit from the outlet stream is reduced to 8% of CO₂ gas from its feed of raw gas that contain 32% of CO₂ gas (Faudzi et al., no date).

2.1.3 Factors Affecting Membrane Absorption

Previously, the membrane used for MGA were described as having no intrinsic selectivity to the gas, however, some properties exhibit by the membrane will be the factors that affect the mass transfer of the gas to the absorbent liquid. The physical properties of the membrane such as the pore size and porosity and the chemical property such as the hydrophobicity of the membrane can be the key factor affecting the gas absorption performance.

The pore size of the membrane is defined as the size of the pores present in the membrane, and these pores are the channels which gas diffuses to be absorbed by the absorbent. The pore size of the membrane directly affects the absorption flux. For instance, the smaller pore size of the membrane, the lower the possibility of membrane wetting (Ahmad et al., 2018). However, the pore size becomes the limitation factor to the diffusion coefficient as smaller pores have lower diffusion coefficient and low surface porosity. Additionally, the porosity of the membrane is also the key factor that

affects the gas absorption, because it is desirable for a membrane to possess high porosity due to the low mass transfer resistance (Siagian et al., 2019). Nevertheless, this characteristic also limits the gas absorption because high-porosity membrane and large pore sizes have a higher risk in membrane wetting, thus, decreasing the gas absorption flux.

The physical morphology of the membrane does play a role in the gas absorption performance, nonetheless, the chemical nature of the membrane, that is, the membrane hydrophobicity, directly impacts the absorption performance. Generally, it is desirable to use hydrophobic membrane in this operation to prevent membrane wetting. The hydrophobicity of the membrane can be determined by the water contact angle during the absorption process. When the contact angle is within 90° to 180° , the membrane is classified as hydrophobic meanwhile it is considered as superhydrophobic when the contact angle is above 150° (Mosadegh-Sedghi et al., 2014; Ahmad et al., 2018; Himma et al., 2019).

A high contact angle reduces the membrane wettability because the membrane tends to have non-wetting characteristic. This characteristic causes the liquid to stay away from the membrane surface (Mosadegh-Sedghi et al., 2014). Thus, no liquid is permitted into the membrane pores. This hydrophobicity of the membrane contributes to low degree of wetting as well as preventing the liquid from penetrating into membrane pores and reduces the membrane resistance imposed by the liquid phase, leading to high and stable absorption flux.

Ahmad et al. (2018) stated that the membrane with a smaller pore size will have lower risk of membrane wetting. A study conducted by Sea, Park and Lee (2002) compares CO_2 absorption flux on PVDF, PTFE and PP membranes with different pore diameter of 0.03, 1 and 0.25 μm , respectively. Although PTFE and PP has higher

hydrophobicity than PVDF, the CO₂ absorption flux of PVDF membrane is the highest. This proves that the membrane with smaller pore size and low hydrophobicity has higher membrane wetting resistance than the membrane with larger pore size and higher hydrophobicity (Ahmad et al., 2018).

2.1.4 Absorbents

As mentioned in the previous section, the selectivity of MGA is mainly provided by the absorbent liquid used in the process instead of the membrane. The selection of the absorbent must be taken into account in terms of its compatibility with the membrane, the selectivity, loading capacity of the desired gas and its chemical and physical properties such as its high surface tension, oxidation stability, volatility and high regeneration rate to achieve high rate of gas absorption and long-term performance (Ahmad et al., 2018). Another desirable feature of absorbents is that they are environmentally-friendly attributed to their low toxicity and can be recycled to reduce the operation cost.

The absorbent having high surface tension and viscosity is advantageous because it increases the contact angle of the liquid with the membrane surface and avoid penetrating the membrane pores (Mosadegh-Sedghi et al., 2014). Thus, these characteristics also reduce the tendency of the membrane wetting, leading to an increase in the CO₂ absorption flux. Moreover, the absorbent concentration has a significant impact to the CO₂ absorption. At high concentration of absorbent, the chemical reaction rate between CO₂ and the absorbent increases significantly (Siagian et al., 2019). Nonetheless, the high concentration of absorbent will limit the absorption flux because it is reported that increases in the MEA concentration leads to decline in CO₂ flux. Rongwong, Jiraratananon and Atchariyawut (2009) reported that the CO₂

absorption flux decreases by 19%, 23% and 26% of the initial flux when MEA concentrations used are 0.25 M, 0.5 M and 1 M, respectively. This is because their contact angle and surface tension decreases.

Currently alkanolamine solvents are the commercially available CO₂ absorbents widely used in the industries for examples monoethanolamine (MEA), diethanolamine (DEA), 2-amino-2-methyl-1-propanol (AMP) and methyldiethanolamine (MDEA) (Mosadegh-Sedghi et al., 2014; Ahmad et al., 2018). Alkanolamines are weak base, which forms weak chemical bonds when reacting with carbon dioxide. As for solvent regeneration, it is easy to break the chemical bonds through mild heating. MEA is the most common used absorbent for CO₂ gas absorption in a porous hydrophobic hollow fiber membrane contactor as it is cheaper and has acceptable carbon dioxide absorption in a low partial pressure of CO₂ gas (Kang and Cao, 2014).

2.2 Challenges on Current Membrane Gas Absorption Process

Although MGA is a promising option to counter the drawbacks of the conventional absorption method for example elimination of flooding, channelling and flexible operation. Nonetheless, the membrane used in this process introduced additional mass transfer resistance from the membrane that can affect the absorption performance over the prolong operation time. Moreover, this membrane resistance is associated to membrane degradation in the industrial application, which is the challenge in addition to the operating conditions over a long-term operation.

2.2.1 Degradation of Membrane

The property of the membrane introduced in the MGA process is susceptible to deteriorate over a long-term CO₂ absorption operation, especially when membrane pores are wetted by the liquid absorbents. Although the membrane used has hydrophobic characteristic, it is still a possibility for the absorbent to penetrate into the membrane pores during long-term operation.

The wetting properties are divided into three, as shown in Figure 2.2. The first one is the non-wetting category. In this mode, there is only gas phase inside in the membrane pores, which is the most desirable mode because the membrane phase resistance is relatively low in the overall mass transfer resistance (Fig 2.2a). Thus, the CO₂ absorption flux in this mode is higher than the other two modes. Over a certain period of operation, the liquid will penetrate into the membrane pores and partially fills them (Fig 2.2c). This mode is classified as partially-wetting mode. When the operation is carried out for a prolonged period, the liquid will gradually and completely fill the membrane (Fig. 2.2b). This is the fully-wetting mode and it is the most undesirable mode in MGA. These two modes change the membrane morphology by reducing the surface hydrophobicity and increasing the membrane resistance to the overall mass transfer resistances, resulting in a rapid decline in the absorption efficiency (Mosadegh-Sedghi et al., 2014). Also, it is reported that during long-term operation, the membrane pore sizes enlarged due to the interaction between the membrane and absorbent, resulting in a greater degree of membrane wetting (Himma and Wenten, 2017).

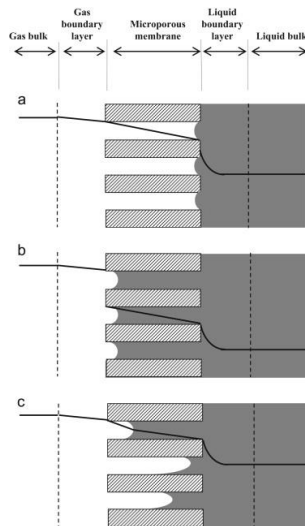


Figure 2.2 Wetting properties in a hydrophobic porous membrane: (a) non-wetting mode, (b) fully-wetting mode and (c) partially wetting mode (Mosadegh-Sedghi et al., 2014)

Moreover, the membrane used is easily affected by the absorbent used, because the compatibility of the absorbent and membrane is as crucial as the selectivity of the absorbent to the desired gas. An absorbent compatible with the membrane type used in the MGA process can prevent the membrane from degrading in terms of the morphological damage, colour changes, swelling and dissolution of the membrane used (Siagian et al., 2019). The suitability of the absorbent used need to be carefully considered, because the solvent may react with the polymeric membrane and cause enlargement of the membrane, thereby increasing the risk of membrane wetting.

It has been reported that even at low concentration of absorbent, PVDF membrane will degrade due to the adhesion by NaOH for long-term operation (Kang and Cao, 2014). Liu et al. (2011) reported that NaOH solution chemically attacked the surface of PVDF membrane and break down the hydrofluorocarbon bond. The dehydrofluorination in the polymeric chain forms carbon-carbon double bonds, resulting to discolouration of PVDF membrane and reduced in mechanical strength (Awanis Hashim, Liu and Li, 2011; Liu et al., 2011).

Fouling phenomena for MGA is not as severe as that of membrane filtration, however, this fouling phenomena has become a major concern in the coal-fired power plant. In the power plant industry, pollutants exist in the flue gas stream, such as dust and suspended particles deposited on the surface and the pores of the porous membrane, leading to a serious pore plugging and reduced CO₂ removal efficiency. Therefore, it is necessary to improve the membrane surface property to avoid degradation of the membrane over a long period of operation, leading to low CO₂ absorption flux and high operating cost.

Many studies have been conducted on the membrane pore enlargement due to the interaction between the membrane and absorbent. Fang et al. (2012) reported that the pore diameter of polypropylene membrane increased from 0.082 μm to 0.105 μm in CO₂ stripping process by using MEA solution. Mosadegh-Sedghi et al. (2012) also reported that the pore size of polyethylene membrane increases after 30 days of interaction between the membrane and MEA solution. MEA has the lowest surface tension. Therefore, it can easily penetrate the membrane pores and push the membrane wall, resulting to enlargement of the pore size (Mosadegh-Sedghi et al., 2012).

2.2.2 Operating Conditions

Apart from the interaction between the membrane and absorbents that degrades the surface properties of the membrane, such as reduction in surface hydrophobicity and membrane pore sizes, as well as membrane fouling and swelling, the operating conditions of the absorption process can also lead to membrane degradation.

The operating condition on the liquid side of the MGA process will affect the membrane performance, such as the pressure and flowrates. All these operating conditions can cause gas bubble formation, wetting by the absorbents and decreases

the residence time and gas absorption simultaneously (Mosadegh-Sedghi et al., 2014; Ahmad et al., 2018). The parameters such as absorbent concentration and membrane porosity can affect the absorption performance by increasing the rate of gas absorbed.

The other parameters such as gas velocity and initial CO₂ concentration can decrease the absorption efficiency significantly (Nakhjiri et al., 2018). It has been reported that increasing the concentration of the absorbents will result in a decrease in the CO₂ absorption flux (Ahmad et al., 2018). This is because a higher concentration of absorbents that exceeds the maximum allowable value causes membrane wetting to occur. Faiz and Al-Marzouqi (2010) demonstrated that no wetting occurs at 0.1 M of MEA while, membrane wetting occurs at 0.5 M of MEA due to the decrease in surface tension.

Although MGA process is usually operated at low-pressure such as at atmospheric pressure, this become a challenge in the gas sweetening process as the feed gas is usually fed at 50 bar (Kang and Cao, 2014). In this situation, the pressure on the liquid side needs to be higher than the gas side to avoid the formation of bubble, resulting in a significant reduction in absorption efficiency and loss of valuable components in the gas.

Furthermore, the liquid side pressure is influenced by the liquid flowrates. The increased in liquid flowrates leads to an increase in pressure on the liquid side, resulting in a higher trans-membrane pressure. Hence, the liquid easily penetrates the membrane pores and gradually wet the membrane pores until the membrane pores are fully wetted, resulting in a decrease in the gas absorption flux (Mosadegh-Sedghi et al., 2014). Therefore, it is necessary to control the operating conditions of the operation to prevent the decline in the gas absorption efficiency in the long-term operation.

2.3 Synthesizing Membranes

Researchers had adopted various methods in synthesizing the membranes to be used in MGA process such as electrospinning method, stretching method, track etching method, matrix membrane and phase inversion method. The sections following will discussed on the methods of synthesizing the membranes.

2.3.1 Electrospinning

Electrospinning is a method that produce porous membrane by electrostatically spinning the melt or solution polymers. This method produces sub-micro to nano-scale fibrous membranes, which are highly porous with high permeability, high specific surface area to unit volume, controllable membrane thickness, interconnected pore and high surface roughness. It contributes to the hydrophobicity of the membrane, which is an essential characteristic to has in gas absorption (Liu et al., 2011; Kang and Cao, 2014; Himma et al., 2019; Tan and Rodrigue, 2019). This method can be applied in the membrane fabrication for various fields, such as water filtration and gas separation.

Figure 2.3 shows the setup of the electrospinning method consist of a high voltage power supply, a collector and a spinneret in vertical and horizontal positions (Tan and Rodrigue, 2019).

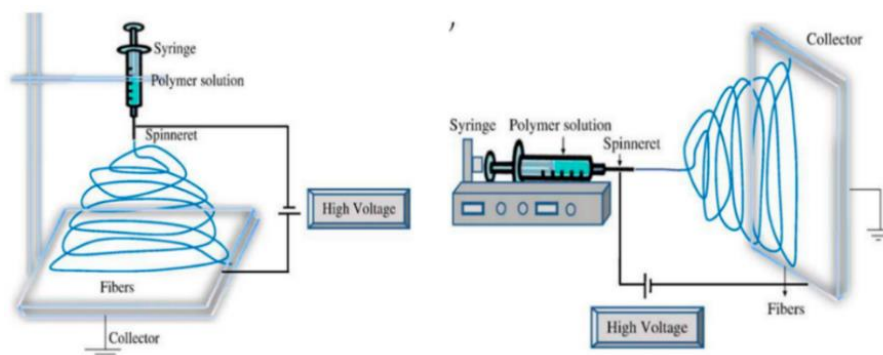


Figure 2.3 Electrospinning apparatus setup in the vertical (left) and horizontal (right) positions (Tan and Rodrigue, 2019)

The steps of fabricating a membrane by using this method are: (i) placing melt or solution polymer into the capillary tube; (ii) applying an electric field at the tip of the capillary and a grounded collector; (iii) due to the strong electric field, of the polymer solution will change from hemispherical shape to conical shape (Taylor cone), (iv) the polymer fluid is ejected from the tip and continuous polymeric fibres forms a porous membrane.

Al-Qadhi et al. (2015) fabricates a superhydrophobic polysulfone membrane by using electrospinning method. The contact angle of the membrane fabricated at the lowest polymer concentration, 5% is 160° , thereby this membrane can be classified as superhydrophobic. The presence of the bead on the fiber structure fabricated by this method also increases the surface and water contact angle.

However, this method has low and limited capacity to produce membrane and unable to produce membrane of various shapes. Moreover, this technique has the drawbacks of solution accumulation and toxicity, limited selection of solvent, high mass loss by the solvent evaporation and limitation process parameters such as humidity in the electrospinning chamber.

2.3.2 Stretching

Stretching is a technique that stretched the porous membrane to enlarge its pores. The pores are enlarged by stretching the membrane perpendicular to the voids' direction until the film almost has small rupture. This membrane produced by this method has high porosity and a high ratio of the void volume to total membrane volume (Tasselli, 2014). Also, this method promotes the membrane to transform from the crystalline phase to solid phase and then recrystallization of the polymer chains by stretching and annealing. Through this method, the membrane properties such as the

tensile strength is improved but the maximum elongation before tearing is reduced (Tang et al., 2020).

This method has four stages that occurs one after another, in which it starts with melt-extrusion stage. In this step, polymers are mixed and melted to form a film with desired morphology. Then, the annealing stage is carried out at high temperature approximately 130°C before the film undergoes stretching stage (Tang et al., 2020). During the stretching stage, the membrane is separated from the lamellae and forms pores by cold-stretching. The size of the pores is increased by hot-stretching (Komaladewi et al., 2018). Lastly, the heat-setting stage allows the polymer chain crystallized to obtain highly porous membrane. Figure 2.4 shows the SEM photo of the membrane cross-section fabricated by stretching method. At 20 mm/min stretching ratio, the mean pore size of membrane is 268.7 nm which is higher than the original membrane (Tang et al., 2020). The porosity and tensile strength are also much higher than the original membrane.

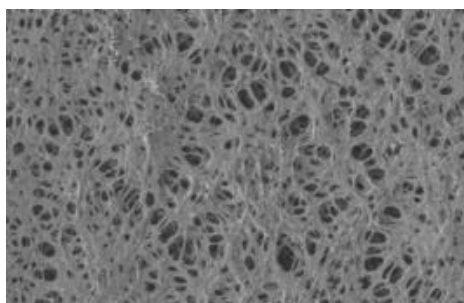


Figure 2.4 SEM of the membrane inner surface produced by stretching method (Tang et al., 2020)

This method has several drawbacks. For instance, the physical properties of the membrane such as, the molecular configuration will cause the annealing process to take place over a longer time. It is because higher polymeric chain will contribute to higher molecular weight and high glass transition temperature (T_g). Therefore, require

higher temperature and longer residence time for the annealing process (Komaladewi et al., 2018). Moreover, the researchers still face some issues in tracking the melt dynamics and the nature of the transient phenomena due to the lack of facilities.

2.3.3 Track Etching

Track etching method is a technique that breaks the chemical bonds in the polymer and releases a small volatile compound (such as H₂, CO₂ and hydrocarbons) to form pores in the polymer. Membranes produced by this method are generally conducive to uniform pore size, shape, location and density, resulting in a wider range of pore sizes and density. Moreover, this method can be applied in various industrial fields such as the filtration, separation and energy conversion.

This method first exposes the polymeric membrane to irradiation, such as electrons or X-ray irradiation, perpendicularly to the surface of the membrane, and then damages the polymer chains along the track. Next, the ion-radiated membrane is etched in a suitable solution to dissolve the ion tracks and enlarged the pores to form an uniform porous membrane (Tasselli, 2014; Ismail, Khulbe and Matsuura, 2015; Tan and Rodrigue, 2019).

Figure 2.5 shows the SEM photo of the membrane surface produced by this method. The pore size of PVDF membrane irradiated with Sn ion in vacuum is 398 nm with cylindrical and open pore structures (Grasselli and Betz, 2005). The etching process of this study take place at 75°C and the total energy used is 2.75 MeV/amu (Grasselli and Betz, 2005; Tan and Rodrigue, 2019).

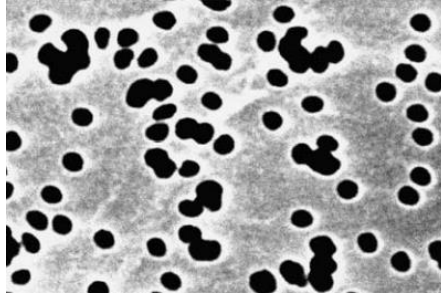


Figure 2.5 SEM of the membrane surface produced by track etching method

(Grasselli and Betz, 2005)

However, the drawbacks of this method overshadow its advantages whereas the porosity of the membrane produced can only achieve approximately 5% to 10% (Tasselli, 2014), which is not conducive to the field of filtration and separation, such as the removal CO₂ gas. Furthermore, this method is not common in the industrial fields because it is by far the most complex method used to produce porous membrane (Shiohara, Prieto-Simon and Voelcker, 2021). Additionally, the relatively small membrane thickness contributes to increase the surface area to volume ratio, which results in the loss ions and molecules from the interaction between the molecules and the membrane wall.

2.3.4 Mixed Matrix Membrane

In recent years, the manufacture of matrix membranes have attracted researchers to further develop them to obtain a higher efficiency in purification process especially in removing the CO₂ gas released into the atmosphere. The matrix membrane has porous fillers in the membrane, such as functional groups, zeolites and any other porous organic fillers that can interact with the desired gas and increases the permeability of the gas through the membrane. Moreover, the gas separation performance through the membrane can be improved when the additives are also incorporated to the matrix membrane.

The incorporation of the fillers in the membrane contributes to the membrane selectivity to the desired gas, attracting the gas closer to the membrane to quickly remove the gas. This characteristic is favourable in MGA because the closer the gas to the membrane, the easier the gas to be absorbed by the absorbent. Furthermore, the porous fillers provide higher surface area and occupy the space in the polymer to improve the performance of the matrix membrane.

A variety of methods can be used to fabricate the matrix membrane in the laboratory-scale research, such as physical blending, sol-gel method, infiltration, polymerization and layer-by-layer method. The common used methods are physical blending and sol-gel method, in which fillers are introduced into the membrane by mixing or dispersing before the polymer is solidified. The difference between these methods is that the sol-gel method has both sol-gel reaction and polymer solidification occurs simultaneously, rather than just polymer solidification (Ismail, Khulbe and Matsuura, 2015). The fillers of the sol-gel method are incorporated during the membrane formation process, rather than before the membrane formation like physical blending.

The major drawback of this mixed matrix membrane is that the fillers, especially the inorganic fillers, need to be compatible with the polymer to avoid gaps in the membrane, resulting the loss of selectivity (Hunger et al., 2012; Khalilpour et al., 2015). Low mass loading and poor permeability through the membrane can also occur in the matrix membrane, due to the high density and low pore volumes of the inorganic fillers. The low pore volumes of the fillers will result in a low porosity of the membrane, thus, decreasing the gas absorption performance of the membrane. Similar to the electrospinning method, the process of fabricating this membrane is expensive, and the membrane itself has yet to be used on the large-scale application,

so the true potential and industrial disadvantages of this membrane remain to be explored (Khalilpour et al., 2015).

2.3.5 Phase Inversion

The most widely used method of producing porous membrane for MGA is by phase inversion. Phase inversion methods are classified into four types, which are non-solvent induced phase separation (NIPS) or commonly known as immersion precipitation, temperature induced phase separation (TIPS), solvent-evaporation phase separation (SEIPS) and vapour induces phase separation (VIPS).

There are only three methods commonly used in practical production of gas-absorbing porous membrane: NIPS, TIPS and VIPS. SEIPS is not conducive to be used in producing porous membrane for MGA because it is a complicated process and uses liquid monomers in membrane formation, rather than polymer (Tan and Rodrigue, 2019). Table 2.1 shows the differences of between the NIPS, TIPS and VIPS methods.

Table 2.1 Comparison between NIPS, TIPS and VIPS

Methods	NIPS	TIPS	VIPS
Solvent or diluent used	Common organic solvents for examples N,N-Dimethylacetamide (DMAc), N,N-Dimethylformamide (DMF), N-Methyl-2-pyrrolidone (NMP), Acetone, etc.	Triacetin, sulfolane, dimethyl phthalate (DMP), dibutyl phthalate (DBP), etc.	Common organic solvents for examples N,N-Dimethylformamide (DMF), N-Methyl-2-pyrrolidone (NMP), 2-pyrrolidinone (2P), etc.
Non-solvent used	Water in liquid phase	None	Water in gas phase
Membrane morphology	Wide pore size but weak mechanical properties	Narrow pore size and high	Variety of membrane morphologies for