CO_2 ABSORPTION PERFORMANCE OF PVDF/ALUMINA HOLLOW FIBER MEMBRANE FOR MEMBRANE CONTACTOR APPLICATION

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Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

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DEDICATION

To my parents.

SHAMSUDIN BIN KASSIM

RAUDAH BINTI ARIFFIN

Those angels who were my most wonderful parents in the world.
The reason of what I become today.
Thanks for your support and continuous care.

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ABSTRACT

In this study, fabrication of composite polyvinylidene fluoride (PVDF) hollow fiber membrane for carbon dioxide (CO_2) absorption was successfully prepared via incorporating alumina clay as additive into polymer dope solution. 18 wt.% of PVDF hollow fiber membrane and 82wt. % of NMP was fabricated with various compositions of alumina clay (1 wt. %, 3 wt. % and 5 wt. %) via wet spinning process. The prepared membrane was characterized via contact angle and CO_2 absorption performance was conducted at various monoethanolamine (MEA) concentrations and liquid flow rates. The hollow fiber membrane sample with 5% of alumina content (S4) showed the highest value around 92.4° when characterized via contact angle. The high value of the contact angle showed that the membrane has a high hydrophobicity which capable of reducing membrane wetting. The CO_2 absorption at various flowrates and concentrations of MEA exhibited increasing trend of CO_2 absorption flux upon addition of alumina clay concentration. The highest value of CO_2 absorption flux recorded was 4.368×10^{-2} mol/m²s for the sample of PVDF/alumina with 5wt. % of alumina at 200 mL/min and 2M of MEA.

ABSTRAK

Dalam kajian ini, fabrikasi komposit polivinilidin florida (PVDF) membran gentian geronggang untuk penyerapan karbon dioksida (CO_2) telah berjaya disediakan melalui menggabungkan tanah liat alumina sebagai bahan tambahan ke dalam larutan polimer. 18wt. % membran gentian geronggang PVDF dan 82wt. % NMP telah difabrikasi dengan komposisi tanah liat alumina yang berlainan (1wt.%, 3wt.% dan 5wt.%) melalui proses putaran basah. Membran diciri melalui ujian sudut sesentuh dan prestasi penyerapan CO_2 telah dijalankan pada pelbagai kadar aliran cecair dan kepekatan monoethanolamine (MEA). Sampel membran gentian geronggang dengan 5% alumina (S4) menunjukkan nilai tertinggi sekitar 92.4 ° bagi ujian sudut sesentuh. Nilai tinggi sudut sesentuh menunjukkan bahawa membran mempunyai kehidrofobikan yang tinggi mampu mengurangkan pembasahan membran. Penyerapan CO_2 pada pelbagai kadar aliran dan kepekatan MEA mempamerkan trend peningkatan penyerapan CO_2 fluks dengan peningkatan kepekatan tanah liat alumina. Nilai tertinggi penyerapan CO_2 fluks direkodkan ialah 4.368×10^{-2} mol / m^2s untuk sampel PVDF / alumina dengan 5wt. % alumina pada kadar aliran 200 mL/min dan kepekatan 2M MEA.

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LIST OF ABBREVIATIONS

K_{OG}	Overall mass transfer resistance
k_G	Gas side mass transfer coefficient (m/s)
k_M	Membrane mass transfer coefficient (m/s)
k_L	Liquid side mass transfer coefficient (m/s)
d_i	Inner diameter of hollow fiber membrane (m)
d_M	Logarithmic mean diameter (m)
m	Distribution coefficient between gas and liquid phase
J_{CO2}	CO_2 absorption flux
C_{li}	Inlet liquid concentration (mol m^{-3})
C_{lo}	Outlet liquid concentration (mol m^{-3})
Q_1	Liquid flow rate (m^3s^{-1})
A_i	Inner surface of the hollow fiber membranes (m^2)
V	NaOH volume (m^3)
V_{sample}	Solution sample volume (m^3)
M	NaOH concentration (mol/L)
M_{CO2}	CO_2 concentration (mol/L)

LIST OF ABBREVIATIONS

$BaCl_2$	Barium Chloride
$BaCO_3$	Barium Carbonate
CO_2	Carbon dioxide
DEA	Diethanolamine
PEG400	Polyethylene Glycol
Al_2O_3	Aluminium oxide
HCl	Hydrochloric acid
LiCl	Lithium chloride
MDEA	Monodiethanolamine
MEA	Monoethanolamine
AMP	2-amino-2-methyl-1-propanol
NaOH	Sodium hydroxide
NMP	N-Methyl-2-pyrrolidone
PE	Polyethene
CHXN	Cyclohexanone
PG	Potassium glycinate
MEK	Methylethyl ketone
PP	Polypropylene
PS	Polysulfone
PTFE	Polytetrafluorethylene
PVDF	Polyvinylidene fluoride
PA	Phosphoric Acid
H_2O	Water
NaCl	Sodium chloride
S1	Hollow fiber membrane (without addition of alumina)
S2	Hollow fiber membrane with 1 wt. % alumina
S3	Hollow fiber membrane with 3 wt. % alumina
S4	Hollow fiber membrane with 5 wt. % alumina

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Carbon dioxide (CO_2) is a nonflammable, colorless, and odorless in any phase either gas or liquid. Current atmospheric CO_2 increase is caused by anthropogenic CO_2 emissions. Increasing CO_2 due to combustion of fossil fuels such as oil, natural gas and coal. About three quarters of this production is caused by burning fossil fuels (Prentice et al., 2001). About a quarter is due to the addition of vehicles, industry and human. In 2015, based on global CO_2 emission per region from fossil-fuel use and cement production, China released nearly 25000 million tonnes of CO_2 followed by other non-OECD1990 Europe countries about 13000 million tonnes CO_2 and Russian Federation by 12000 million tonnes of CO_2 (Olivier et al., 2015).

CO_2 is the primary gaseous element of the greenhouse gases in the atmosphere, indicating approximately 80% and contribute significantly to global warming (Rongwong et al., 2009). Industries manufacturing ammonia and urea produce wastewater that consumes high CO_2 concentrations (Agrahari et al., 2011). In plant, higher ratio of CO_2 to bicarbonate ion immediately declines pH of water, which causes corrosion of piping materials (Mansourizadeh and Ismail, 2012). The technique of removing CO_2 can be accomplished via numerous techniques which are pressure swing adsorption, cryogenic distillation, packed column and membrane technology (Simons et al., 2009; Zheng and DeMontigny, 2013). Lately, membrane contactor have received several attention because of its advantages including high contact area per unit volume, compatible to absorb CO_2, no loading and flooding constraints (Crespo et al., 1995).

Membrane contactor has the ability to perform mass transfer without dispersion of one phase within any other either gas/liquid mass transfer or liquid/liquid mass transfer, have a high operational flexibility and viable alternative for various applications (Stanojevi, 2003; Steenhoven et al., 1994). In membrane technologies more especially in hollow fiber membrane are extensively used nearly in all membrane processes, especially in ultrafiltration, microfiltration, gas permeation and pertraction via polymeric or liquid membranes. Currently, hollow fiber contactors have started to be used in membrane based methods in two phase contactors (Kert, 2005).

Hollow fiber membrane contactor indeed are more effective than others conventional absorption technologies but it also have several disadvantages such as tend to fouling for long term use, short lifetime, pretreatments needed to reduce fouling, and wetting problem whereby it can decline the efficiency of the membrane drastically (Criscuoli and Drioli, 2009). In order to prevent that problem, the membrane must be highly hydrophobic to avoid the membrane pore filled with aqueous absorbent solution.

Polyvinlylidene fluoride, polytetrafluoroethylene and polypropylene were considerably used for the preparation of microporous hydrophobic membranes utilized in membrane contactor. Among these polymers, only PVDF has an amazing solubility in many organic solvents (Hee et al., 2009). PVDF has been intensively studied due to its excellent bulk properties, along with high electric resistance as well as good thermos-stability, light weight and suitable process ability. Those properties have made PVDF increasingly more used in various fields which include filtration, air cleaning, and rechargeable batteries (Huang et al., 2010). Modification PVDF to turn out to be ceramic membranes are made from metal oxides, including alumina, zirconia, silica and so on, which are hydrophilic in nature due to the presence of hydroxyl (OH–) groups on the surface.

In the present study, the main objective is to produce of hydrophobic PVDF hollow fiber membrane with addition of alumina clay for CO_2 absorption via membrane contactor.

1.2 Motivation

The removal of CO_2 is vital in order to reduce the greenhouse effect hence to reduce the global warming. Based on the issues, many researchers began to look for innovation to reduce CO_2 emissions through the creation of a gas separation application. There are many traditional technologies for gas separation such pressure swing absorption, distillation column and gas-liquid extraction. However, each has disadvantages such as requiring large area to build and high cost of construction/maintenance. Meanwhile, membrane contactor is most appropriate in this century because of high contact area per unit volume, easy process integration and compatible to absorb CO_2.

1.3 Problem Statement

There are two problems that concern which are the release of CO_2 and corrosion in the pipeline. CO_2 is one of acidic gasses which need to expel from regular gas pipeline because it contributes to equipment corrosion. This is because corrosion will lead to produce a product which not in good quality. not only that, the addition of impurities if corrosion not prevented. Membrane wetting is the main problem of gas–liquid membrane contacting processes. The negative effects of membrane wetting on absorption performance and mass transfer resistance have been widely observed by researchers (Boributh et al., 2013; Lv et al., 2010). Membrane wetting influence by membrane characteristics, absorbent properties and operating conditions. Therefore, the need of it is essential to have hydrophobic polymer materials that withstand the membrane from getting wetted at prolong hour operation.

1.4 Objectives

The following is the objective of this research:

- To evaluate the effect of alumina compositions on PVDF/alumina hollow fiber membrane for CO_2 absorption at various flowrates and concentrations of liquid absorbent (MEA).

1.5 Scopes of Study

The following are the scopes of this research:

1) Preparation of 18 wt.% of PVDF solution dope with addition of alumina (1, 3 and 5wt. %).
2) Fabrication of a series of PVDF/alumina hollow fiber membrane via spinning process.
3) Characterization of PVDF hollow fiber via contact angle measurement.
4) CO_2 absorption test with liquid absorbent at different flowrates (50, 100, 150 and 200 mL/min) and concentrations (1M and 2 M).

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane Contactor

Membrane contactors are devices that uses porous hydrophobic membrane as a phase barrier allowing two fluids interface with each other for the purpose of mass transfer without diffusion of one phase into the other (Rongwong et al., 2009). Membrane contactors are a new membrane-based concept where a hydrophobic microporous membrane operates as contact medium between a feed stream and an extracting phase (Bernardo and Clarizia, 2013). It is difficult to introduce new technologies in industry especially in the field of separation technology but membrane contactor still get large demand for new improved processes (Klaassen et al., 2005).

In recent years, the applications of a hollow fiber membrane contactor has increased because it has the potential to degasify liquid streams and to overcome many of the problems and limitations (Agrahari et al., 2011). This approach takes advantage from the more efficient mass transfer achievable through the membrane pores with respect to conventional packing absorption towers (Bernardo and Clarizia, 2013). Membrane contactor is appropriate for use in gas exchange applications because it can give more significant productivity (Johnson, 1997). Table 2.1 shows advantages and disadvantages of membrane contactor.

Table 2.1: Advantages and Disadvantages of Membrane Contactor (Criscuoli and Drioli, 2009)

Advantages	Disadvantages
• Large surface area per volume • No foaming • No dispersion between phases • Reduced size and weight	• Wetting • Membrane fouling • Shell side by passing • Limited lifetime

Membrane contactor can provide large surface area per unit volume which is in range of 20-100 times higher than conventional equipment. The more interfacial area provided, the higher the efficient of membrane contactor and the smaller its size required for separation process (Crespo et al., 1995). Other advantage of membrane contactor is easy process integration. It is easy to combine membrane contactor before or after with other unit operation equipment. These hybrid process can be highly advantageous from a technical and economic point of view (Crespo et al., 1995).

Membrane contactor configuration can be divided into two type, which are flat and tubular. In flat configuration, there are another specific type which are plate and frame membrane and spiral wound membrane. For tubular configuration, hollow fiber membrane is the only one being used, but instead of being called hollow fiber membrane, it is also known as capillary or tubular membrane. Figure 2.1 shows typical membrane configuration that available in industry.

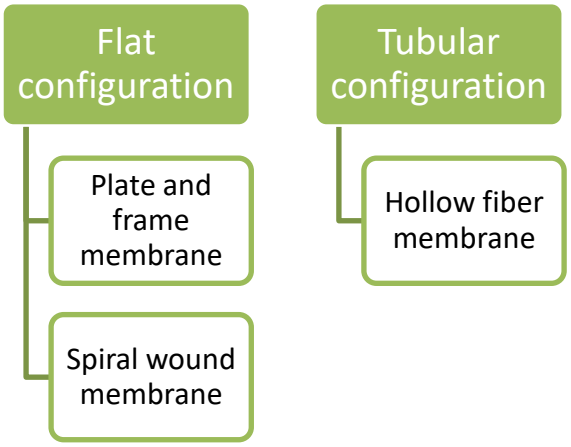


Figure 2.1: Typical Membrane Configuration that Available in Industry.

Hollow fiber membrane modules were significantly used in lots of applications seeing that last decade. Frequently, these modules are employed as contactor devices, inclusive of blood oxygenator, liquid–liquid extraction, and artificial gills (Wu and Chen, 2000). Hollow fiber membrane is to be preferred by the industry compared to others membrane due to its large surface area per unit volume (Lin et al., 2009). Hence, membrane contactor can increase the mass transfer between gas and liquid. Figure 2.2 shows the commercially available hollow fiber membrane module in the industry. The successful use of the membrane contactor process over the conventional absorption processes are largely dependent on the gas–liquid system, the types of membranes used and the operating conditions (Bottino et al., 2008).

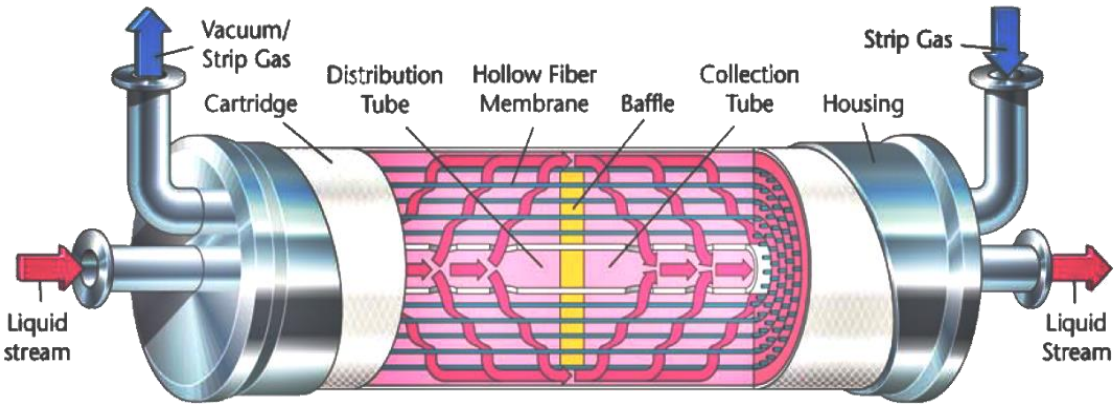
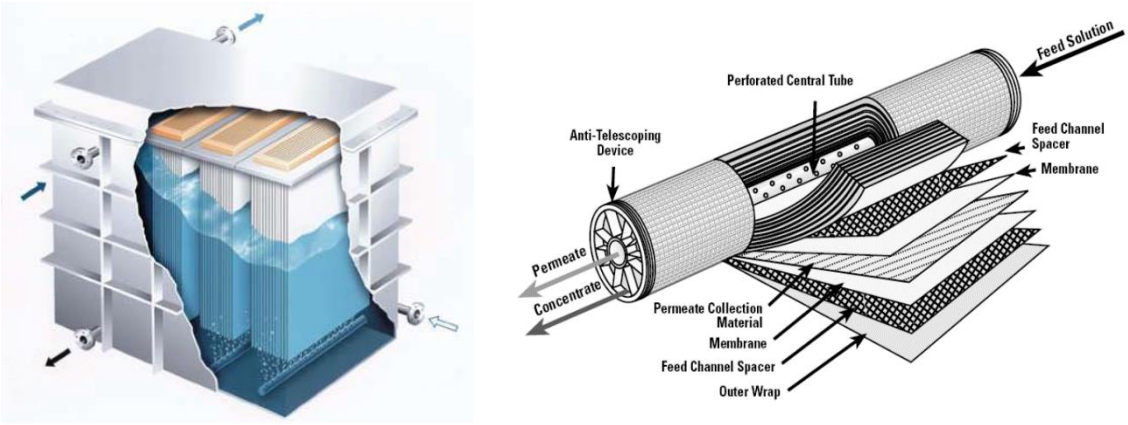


Figure 2.2: Hollow Fiber Membrane Contactor Module (Wiesler, 2004)

Generally, plate and frame membrane using a flat membrane and formed to be a cube or cuboid. Whereas, spiral wound membranes using a flat membrane but is formed into a cylinder by winding the flat membrane. Spiral wound membrane consist of four sheets wrapped around a central core of a perforated collecting tube as display in figure 2.3(b). The four sheets consist of the top sheet of an open separator grid for the feed channel spaces, membrane, permeate collection material and membrane (Geankoplis, 1993). Figure 2.3(a) shows the diagram of plate and frame membrane as one of type from flat configuration and meanwhile Figure 2.3(b) shows the of spiral wound membrane module as one of example for tubular configuration.



(a) (b)

Figure 2.3: (a) Plate and Frame Membrane Diagram (Wang and Zhou, 2013) and (b) Spiral Wound Membrane Module (Wagner, 2001).

Membrane contactor operating principle is based on the natural phenomenon of the capillary. The effect of surface tension causes the membrane is not wet, it because the liquid is prevented from entering the pores of membrane (Sengupta and Pittman, 2009). Definition of surface tension is the membrane quiet strong to support dense object (liquid) without getting wet (Ual and Sics, 2010). The gas stream is maintaining along one side of the membrane in the meantime absorption fluid is streaming at the opposite side of the membrane. As a consequence of the hydrophobicity of the membrane divider gas stage and absorption fluid are isolated from each (Klaassen et al, 2008). The basic principle of membrane separation is mainly the same although the membrane have different structure either porous or non-porous and either organic or inorganic (Stanojevi, 2003).

The principle of membrane contactor shows as Figure 2.4 where the CO_2 is absorbed by the aqueous amine solution (liquid absorbent). As the membrane is porous, gas permeation is still possible despite the presence of the membrane barrier. The CO_2 (and/or different gaseous additives) passes via the membrane pores right into a liquid. The driving force that moves the CO_2 gas is manipulated by pressure. Furthermore, the liquid absorption was nominated due to high affinity for CO_2, which the pores of membrane filled by CO_2 gas to the opposite side of membrane where it was absorbed in the liquid phase. (Klaassen et al., 2008). Upon entering the liquid, the CO_2 is absorbed by and reacts with components inside the liquid absorbent solution (Iversen et al., 1997).

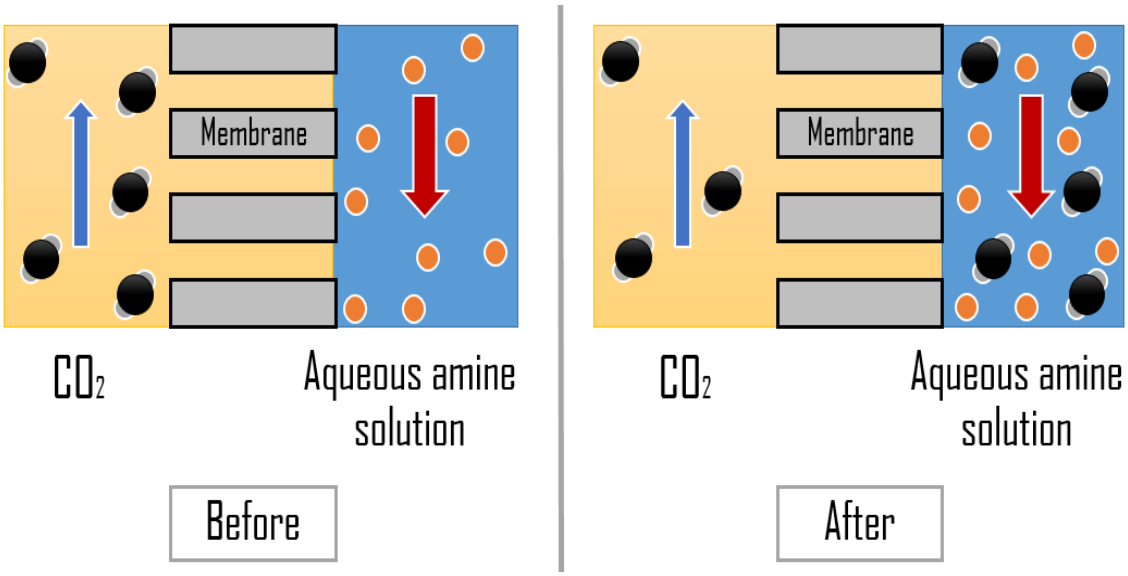


Figure 2.4: Principle of Membrane Contactor

2.2 Membrane Wetting

The membrane wetting by the liquid absorbents is vital problem in the process of gas liquid membrane contacting process (Rongwong et al., 2009). Theoretically, wetting is defined as the liquid absorbent filled the hydrophobic membrane pores hence increase the mass transfer resistance. The characteristic of hydrophilic is attracting toward the water and hydrophobic is vice versa. In this study, development and use of hydrophobic membrane is more effective to increase the absorption flux hence reduce the mass transfer resistance rather than use of hydrophilic membrane.

Membrane wetting by absorbents indications to an increase in mass transfer resistance and a reduce in CO_2 absorption performance during the membrane gas absorption process (Lv et al., 2010). There are two types of operation occur which are non-wetting mode and overall wetting mode (Lu et al., 2008). Figure 2.5 shows two types of wetting mode that often occurs in the membrane contactor.

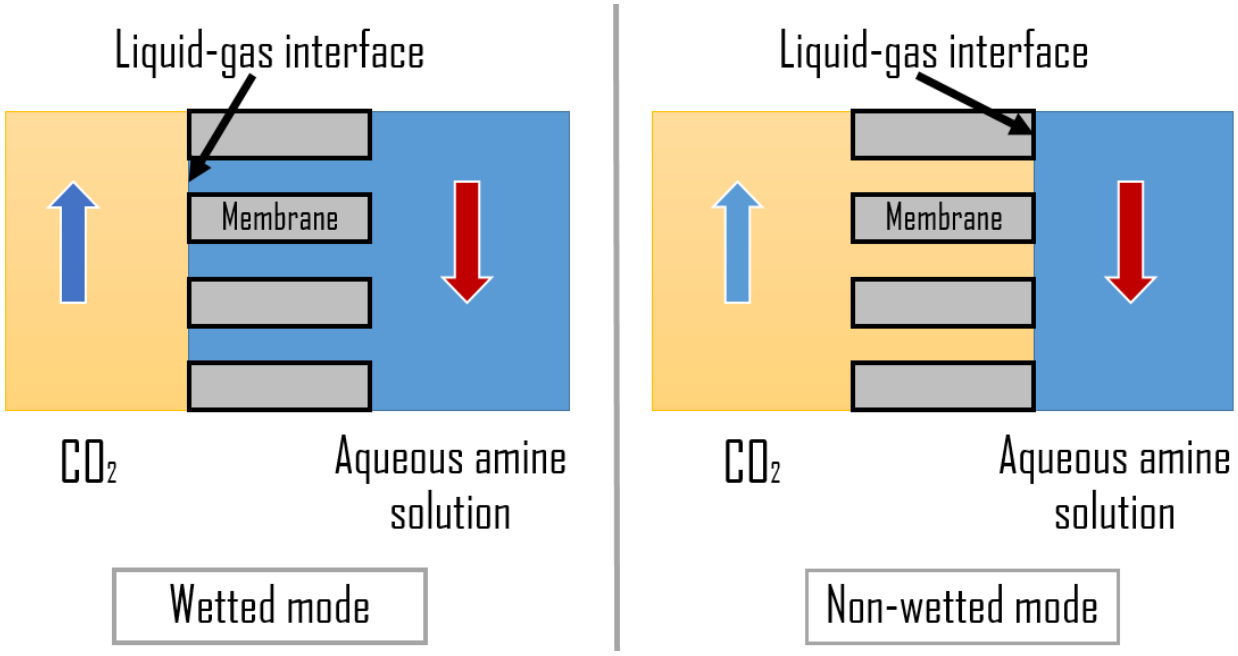


Figure 2.5: Two Types of Wetting Mode

After long term operation, hydrophobic membrane cannot keep their role to separate the two phase without dispersing each other anymore, then it changes to wetting mode. Normally, the operation for the hydrophobic membrane should be non-wetting mode however it generally tends to wet for long time period because the aqueous solution of organic compound. If membrane are wetted even in partially wetting mode, it will considerably increase the overall mass transfer resistance (Yan et al., 2007) .

Regarding to the theory, the overall mass transfer in a gas-liquid membrane contactor consists of three resistances in series which are the resistance of the gaseous phase boundary layer, the membrane resistance and the resistance of the liquid the phases boundary resistance (Mosadegh et al., 2014). The overall mass transfer resistance, based on given formula:

$$\frac{1}{K_{OG}} = \frac{d_O}{k_G\, d_i} + \frac{d_O}{k_M\, d_{IM}} + \frac{1}{m\, k_L} \qquad \textbf{(2.1)}$$

where,

K_{OG} = the overall mass transfer resistance

k_G = gas side mass transfer coefficient (m/s)

k_M = membrane mass transfer coefficient (m/s)

k_L = liquid side mass transfer coefficient (m/s)

d_i = inner diameter of hollow fiber membrane (m)

d_M = logarithmic mean diameter (m)

m = distribution coefficient between gas and liquid phase

Membrane wetting depends on several factors such as membrane characteristics, type of liquid absorbent and liquid flow rate (Boributh et al., 2013). Membranes characteristic include chemical properties of the membrane structure energy, pore size of membrane and porosity. Generally, membrane having lower surface energies have less wettability than those having higher surface energies (Mosadegh et al., 2014). The bigger size of pores of membrane is not good to be use because increasing diameter size of pores, the easier the liquid absorbent penetrate through the membrane pores. Besides, the higher the liquid flow rate, it is must easier for wetting to occurs (Wang et al., 2005).

However, there are also other reasons to be taken into consideration with regard to membrane wetting. Among of this problem are possible chemical reaction between the liquid absorbent and membrane material. Wang et al (2004) found that polypropylene (PP) membrane has a chemical effect when in contact with diethanolamine (DEA) solution which lead to penetration of liquid absorbent into pore of PP membrane. Besides, it was found that CO_2 gas contributed to plasticizing effect on the membrane material. (Porcheron and Drozdz, 2009).

One way to prevent the membrane wetting is to incorporate a compatible liquid absorbent with acceptable surface tension. Various types of liquid absorbent used in membrane contacting process may exhibit different phenomena of membrane wetting. Nowadays, the use of mixed amines as the liquid absorbent which promising approach because it could lead to an improvement in gas absorption and in reducing energy requirement for regeneration (Rongwong et al., 2009). This is because it has high reactivity and less corrosive with reasonable CO_2 absorption rate.

Another way to reduce membrane wetting by using the super-hydrophobic membrane which is this membrane has higher hydrophobicity than usually hydrophobic membrane and can stand prolong term operation due to surface tension effect. Besides, in order to prevent membrane wetting by decreasing the membrane pore size but it is not very effective. In addition, the membrane hydrophobicity also can be improved by pretreatment on the surface with fluoro-carbonic material (Lv et al., 2012).

2.3 Membrane Hydrophobicity

Hydrophobic surface is the surface having nano-scale roughness. Nano-roughened surface make lower water-solid contact area which is water perched on hydrophobic posts containing trapped air (Ma and Hill, 2006). There surface effectively repulse fluid, making it clump together since it is more pulled into itself than the surface. The membrane with higher hydrophobicity is more resistant to wetting (Lv et al., 2012). Figure 2.6 shows the nano-roughened surface at close range. The modification of membrane by increasing the hydrophobicity of the membrane can give more benefits to the industries especially in gas membrane absorption. Figure 2.7 shows the difference of each surface when contact with water.

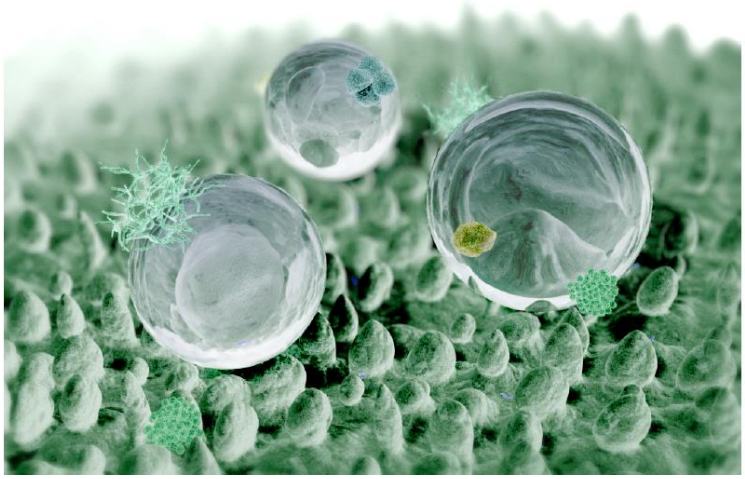


Figure 2.6: Nano-Roughened Surface (Mills et al., 2009)

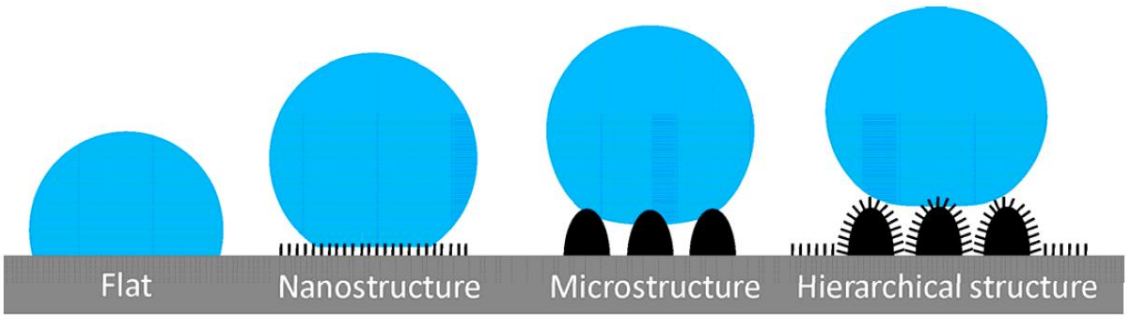


Figure 2.7: Difference of Each Surface When Contact with Water (Mills et al., 2009)

This is additionally referred to as the Lotus effect, when a droplet affecting on these sort of surfaces, it can completely bounce back like a versatile ball (Kumar and Maria, 2013). Based on Figure 2.7, the droplet of water contact with surface (hierarchical structure) is in good condition, the shape of droplet is exactly same like a ball shape. The membrane wetting by amine absorbents can be reduce the performance of membrane systems (Lv et al., 2012). In order to prevent wetting, membrane has high hydrophobicity was introduced to switch the usual hydrophobic membrane. A contact angle of less than 90° implies that the liquid will tend to wet the substrate and vice versa (Sengupta and Pittman, 2009).

2.4 Liquid Absorbent Criteria

In gas absorption, alkanolamines such as diethanolamine (DEA), n-methyldiethanolamine (MDEA), monoethanolamine (MEA) and 2-amino-2-methyl-1-propanol (AMP) are the most regularly utilized absorbents to capture CO_2 from various flue gases (Song et al., 2012). There are many more absorbent liquids other than alkanolamine. According to Lu et al. (2009) using pseudo-plastic fluids as absorbent in hollow fiber membrane contactor for determining the mass transfer coefficient. There is also the use of sodium hydroxide, sodium glycinate and distillate water as a liquid absorbent.

AMP is a primary amine in which the amino group is set a tertiary carbon atom. The carbarnate stability constant for a primary amine is much lower than those of other conventional amines (Kim and Yang, 2000). MDEA has fast kinetics of reaction and low absorbent regeneration energy with H_2S. Furthermore, at higher partial pressure MDEA has a higher CO_2 loading capacity than MEA but reacts slowly with CO_2 (Song et al., 2012). There are three criteria should have absorbent liquid so that gas absorption becomes more efficient Table 2.2 illustrated the criteria of liquid absorbent.

Table 2.2: List of Criteria of Liquid Absorbent (Li and Chen, 2005)

Criteria	Description
Surface tension	Liquid absorbent must be incapable to wet the membrane maintain the pores filled with gas even at high liquid pressure.
High reactivity with CO_2	Liquid absorbent should be high reactivity with CO_2 which can leads to high rate of absorption and mass fluxes.
Easiness of regeneration	This factor should be considered as normal liquid absorbent is recycled to be used over and over again in the process. it is easy to determine absorption efficiency and low CO_2 loading.

DEA has a lower heat of reaction with CO_2 and very good at low pressure condition. However, according to Galindo et al. (2012) disadvantages of DEA are slow kinetics, less reactive to sulphur components and their reaction products are not particularly corrosive. Meanwhile, MEA is recently used in various processes due to its low cost, low hydrocarbon solubility quick reaction kinetics with CO_2 and other advantageous characteristics (Song et al., 2012).

2.5 Polyvinlylidene Fluoride (PVDF)

In order to prevent aqueous absorbents from passing through membrane pores into the gas side, membrane used in membrane absorption is usually hydrophobic (Ghasem et al., 2012). Hydrophobic polymers such as polyproplene (PP), polyethylene (PE), polytetrafluoroethylene (PTFE), and poly (vinylidene fluoride) (PVDF) has widely been used for membrane contactor. Recently, polyvinylidene fluoride (PVDF) has received greatly consideration as a high-quality for hydrophobic polymeric membrane materials (Shi et al., 2007). Poly-vinylidene fluoride (PVDF) $(CH_2\text{-}CF_2)_n$ is a long chain, semi-crystalline (normally 50 to 55%) linear polymer (Adem et al., 2003). Figure 2.8 shows the chemical formula of PVDF. PDVF is produced by the emulsion polymerizarion of vinylidene fluoride monomer in the presence of the raw materials. In 1940s, first development of that process and was commercialized by Pennwalt in the 1960s.

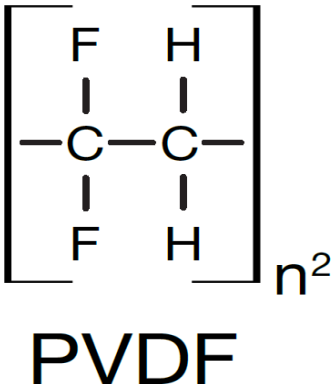


Figure 2.8: Chemical Formula PVDF (Coating and Fischer, 1997)

The membrane with higher hydrophobicity is more impervious to wetting, for example, PTFE shows great gas assimilation execution without membrane wetting by MEA aqueous for long time because of higher hydrophobicity but PTFE is restricted for high creation cost (Lv et al., 2011). PP and PTFE cannot be dissolved in common solvent at room temperature and need to use thermal methods, which is complicated processes to control the membrane structure (Mansourizadeh and Ismail, 2012).

Therefore, PVDF membrane remains the best option of membrane materials for some application. Figure 2.9 shows the PVDF in powder and pellet. The preferences utilizing PVDF membrane is easily dissolve in room temperature in a variety of solvent (Bottino et al., 2005). As a semi-crystalline polymer containing crystalline and rubbery phase, its crystalline phase provides thermal stability while the latter provides the desired membrane flexibility (Kong and Li, 2001).

(a)

(b)

Figure 2.9: (a) PVDF in Powder and (b) PVDF in Pellet (Coating and Fischer, 1997)

2.6 Ceramic Membranes (Addition Alumina Clay)

Due to their characteristics such as thermal stability, chemical resistance and mechanically more resistance, inorganic membranes have received a lot of attention (Choi et al., 2006; Gazagnes et al., 2007). Metal oxides, such as alumina, zirconia and silica are used to make ceramic membranes (Fang, Gao, Wang, & Chen, 2012). Metal oxide is hydrophilic in nature because of the presence of hydroxyl (OH-) group on the surface. According to that reasons, it avoids them to be utilized in other application except for membrane contactor, non-polar solvent extraction and vapour permeation (Koonaphapdeelert and Li, 2007).

Recently, it has been successfully adopted in preparing the inorganic aluminium oxide hollow fiber membrane. According to Liu and Li (2003) based on phase inversion characteristics, it provides a better permeability for a given thickness. Then, it can be served as a porous support for composite membrane formation and not only focus in separation process.

The history of alumina is familiar with the phrase of "alum" which is a compound of aluminium and potassium disulphate where it forms wherever schistose or clayey earth comes in react with sulphuric acid. Alum was known to Greeks and Romans who utilized it for at variance application such as astringent (Davis, 2010). To produce aluminium oxide that there are several methods that develop among Bayer method. Each user of aluminium oxide on the application it is already divided into several grades such as Table 2.3.

Table 2.3: Soda Impurity Level Required for Different Applications (Shirai et al., 2009)

Normal soda > 0.25%	**Intermediate soda 0.15-0.25%**	**Low soda 0.03-0.1%**	**High purity thermally reactive**
White wares Ceramics tile Glass Ceramics fibers	Electrical porcelain Grinding media	Spark plugs Laboratory wear Wear resistant components	Bio-ceramics Cutting tools Armour

2.7 Previous Work on Membrane Performance

The review by previous researcher demonstrated that the PVDF had been utilized as the polymer for their membrane and different type of liquid absorbent. Table 2.3 summarize the findings from previous researchers. It also shows that PVDF regularly fabricated for CO_2 absorption and shows a superior resistance of wetting contrasted. While DEA and MEA frequently applied for CO_2 absorption proved that MEA and DEA have a promising performance to be utilized as the liquid absorbent.

Table 2.4: Performance of Hollow Fiber Membrane Contactor Reported from Various Researchers

References	Membrane materials	Liquid absorbent	Process condition	Contact angle value (^{O})	CO_2 Absorption flux
(Ghasem et al., 2012)	PVDF/triacetin	NaOH	PVDF (28,30,32,34) wt.% shell side flow rate = 10 - 160 mL/min temperature = 298K pressure = atmospheric	28% = 107 30% = 115 32% = 117 34% = 118	For the entire range of tested gas volumetric flow rate, the 28% PVDF membrane shows the highest average percentage of CO_2 removal.
(Mansourizadeh et al., 2011)	1) PVDF + LiCl 2) PTFE	Distillate water	Temperature = 25° Absorbent flow rate (40 - 340 mL/min)	1) 111 ± 3 2) 123 ± 2	CO_2 flux of the prepared PVDF membrane (4.10×10^{-4} mol/m^2.s) is approximately 68% higher than the CO_2 flux of the PTFE membrane.
(Naim et al., 2011)	1) PVDF 2) PVDF + 3% LiCl 3) PVDF + 5% LiCl	DEA (99%)	Pressure = 300 kPa	1) 85 2) 80 3) 75	The increasing trend of fluxes was achieved with the increasing LiCl concentration. The highest stripping flux was obtained by 5% LiCl membrane at flow velocity of 0.45 m s^{-1} which was 1.61×10^{-2} mol/m^2.s.
(Rezaei et al., 2014)	PVDF + PA 1) M0 2) M1 3) M3 4) M5	Distillate water	Pg = 1×10^5 Pa Qg = 150ml/min Temperature = 26 ^{O}C	1) 80 ± 1.5 2) 84 ± 1.25 3) 88 ± 1.5 4) 99 ± 1.5	M5 = 9.7 × mol m^{-2}s^{-1} higher compared to other.
(Feng et al., 2006)	1) PVDF + PA 2) PVDF + glycerol 3) PVDF + distilled water	Distillate water	15 pieces of PVDF fibers with an effective length of 25 cm	Not involved contact angle measurement	The CO_2 absorption performance was in the sequence of #1>#2>#3 with

Table 2.4: Performance of Hollow Fiber Membrane Contactor Reported from Various Researchers (cont.).

References	Membrane materials	Liquid absorbent	Process condition	Contact angle value (^{O})	CO_2 Absorption flux
(Rongwong et al., 2009)	PVDF	1) Distillate water 2) MEA (1 M) 3) Sodium glycinate (1 M) 4) DEA (1 M) 5) AMP	Room temperature (30°) Gas flow rate = 200 mL/min	1) 91.77 2) 90.12 3) 93.91 4) 87.92 5) 86.95	SG > MEA > AMP > DEA > Water
(Mansourizadeh et al., 2011)	1) PVDF 2) PVDF/PEG400 3) PVDF/ethanol 4) PVDF/glycerol 5) PVDF/PA	Distillate water	Gas flow rate = 100 mL/min, Temperature = 25 ^{O}C, Liquid absorbent pressure = 120 kPa Feed gas stream pressure = 100 kPa	1) 85.2 ± 1.53 2) 84.9 ± 1.58 3) 88.8 ± 2.18 4) 84.1 ± 0.94 5) 84.4 ± 1.28	The PVDF/glycerol membrane was 7.9×10^{-4} mol/m^2.s presented higher CO_2 flux compared to the other membranes, which was approximately 30% higher than the flux of the plain PVDF membrane.
(Ahmad and Ramli, 2013)	1) PVDF 15.0wt. % + 85% NMP 2) PVDF 17.5wt. %+ 82.5% NMP 3) PVDF 20.0wt. %+ 80% NMP	2M of AMP	Room temperature	1) 90.5 ± 0.34 2) 84.1 ± 1.49 3) 76.5 ± 2.44	PVDF 15% + 85% NMP has the highest CO_2 removal efficiency around 40%.
(Lv et al., 2012)	1) PP 2) PP + CHXN 3) PP + MEK 4) PP + CHXN + MEK	MEA (99.5%)	Pressure = 0.1 Mpa Temperature = 20°C countercurrent flow	1) 122 2) 162 3) 149 4) 158	Not involved CO_2 absorption test.

Table 2.4: Performance of Hollow Fiber Membrane Contactor Reported from Various Researchers (cont.).

References	Membrane materials	Liquid absorbent	Process condition	Contact angle value (^{O})	CO_2 Absorption flux
(Franco et al, 2012)	PP	MEA (20 wt. %)	Gas flow rate = (1 – 6.1) L/min Liquid flow rate = (18-85) mL/min Pressure = 0.1 bar	117 ± 4	Not involved CO_2 absorption test.
(Mansourizadeh et al., 2010)	1)PVDF + PA 2) PVDF + LiCl.H_2O	Distillate water	Temperature = 25°C, Counter current mode, Absorbent velocity = 0.3 m/s	1) 86.10 ± 2.26 2) 86.71 ± 1.03	Not involved CO_2 absorption test.

* PP = Polypropylene, PVDF = Poly (vinylidene fluoride), CHXN = Cyclohexanone, MEK = Methylethyl ketone, MEA = Monoethnaolamine, DEA = Diethanolamine, AMP = 2-amino-2-methyl-1-propanol, LiCl = Lithium Chloride, PTFE = Polytetrafluoroethylene, PEG400 = Polyethylene Glycol, PA = Phosphoric Acid, H_2O = Water and NaCl = Sodium Chloride

CHAPTER 3

METHODOLOGY

3.1 Research Design

Figure 3.1 shows the research design that applied in this project. It consists of material selection, membrane preparation and membrane characterization through CO_2 absorption test in order to achieve the objective of the study.

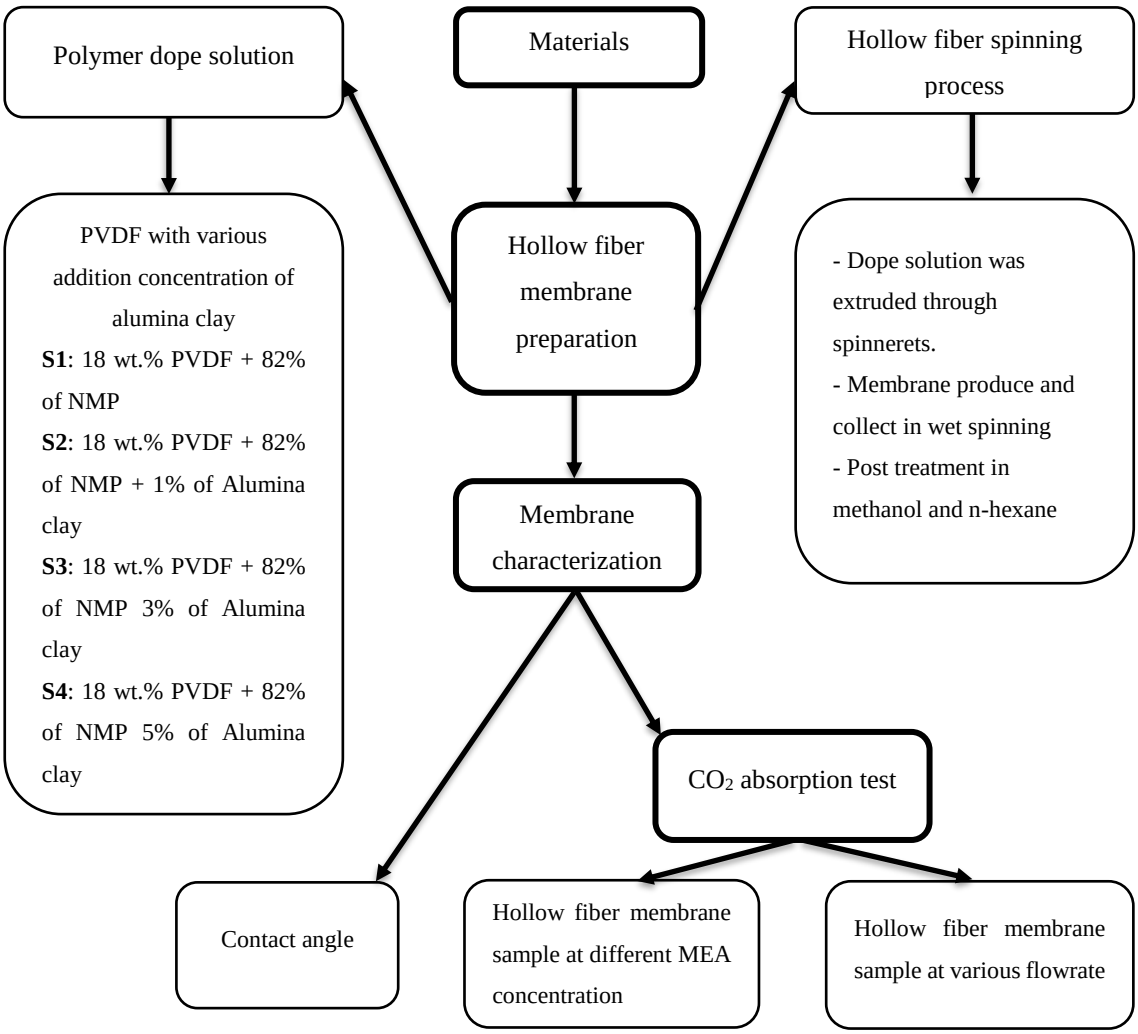


Figure 3.1: Research Design on PVDF/alumina Hollow Fiber Membrane

3.2 Materials

Polyvinlylidene fluoride (PVDF) polymer in form of pellets was used. N-Methyl-2-pyrrolidone (NMP) and monoethanolamine (MEA) from Merck were used as solvent and liquid absorbent respectively. Alumina clay was used as a non-solvent additive in the polymer solution. Methanol (99.9%) (Merck) and n-hexane (99.9%) (Merck) were used as post-treatment solution for hollow fiber membrane. Tab water was used as a coagulation bath medium. Other material such as barium chloride (BaCl), sodium hydroxide (NaOH) and hydrochloric acid (HCl) was used in double titration method.

3.3 Fabrication of PVDF Hollow Fiber Membrane via Spinning Process

The PVDF pellets was dried in a vacuum oven around 60°-70°C for 1 day period to remove the moisture content (Hou et al., 2012) . The PVDF pellets was dissolved in NMP solution with addition of alumina clay except for plain sample to become the dope solution. The spinning dope solution of alumina was stirred consistently at 60-70°C for several hours. The PVDF dope solution was extruded through spinnerets to produce hollow fiber membrane at specific spinning condition which is in Table 3.1. The spun hollow fiber was immersed in water for 3 days to remove residual solvent (Mansourizadeh and Ismail, 2008). The dried membrane were then post treated at room temperature by methanol and n-hexane to reduce fiber shrinkage and pore collapse (Wongchitphimon et al., 2011). Table 3.2 showed the weight percentage of composite (alumina) to create dope solution.

Table 3.1: PVDF Hollow Fiber Spinning Conditions (Naim et al., 2012)

Bore flowrate (ml/min)	2.0
Dope extrusion rate (ml/min)	4.0
Bore fluid composition (wt%)	NMP/H_2O : 80/20
Coagulation medium	Tap water
Spinneret OD/ID (mm/mm)	1.0/0.5
Air gap distance (cm)	0
Spinning dope temperature (°C)	25
External coagulation temperature (°C)	25

Table 3.2: Polymer Dope Composition

Spinning dope	**HF_1**	**HF_2**	**HF_3**	**HF_4**
PVDF (wt.%)	18	18	18	18
Alumina clay (wt.%)	0	1	3	5
NMP (wt.%)	82	82	82	82

3.4 Characterization of PVDF/alumina Hollow Fiber Membrane

3.4.1 Contact Angle Measurement

PVDF/alumina was characterized using contact angle measurement. A sample of hollow fibers was dried in a vacuum oven at 60°C for 12 hours. Deionized water was dropped onto the hollow fiber membrane samples from a needle on a micro-syringe during the test. A picture of the drop was captured after the drop set onto the sample. All the experiments were carried out at temperature of 25°C. The contact angles could be calculated by the software through analyzing the shape of the drop. The contact angle θ was an average of 10 measurements.

3.4.2 CO_2 Absorption Test

CO_2 absorption test was conducted via membrane contactor module which consists of 10 hollow fiber membranes. The test was carried out in counter current flow where pure CO_2 was employed as the feed gas stream through the lumen side of the membrane at 1.8×10^5 Pa pressure and various liquid flow rate. Meanwhile, MEA as the liquid absorbent was flow through the shell side of the module in contact with the skin layer of the membrane. The pressure of the MEA was controlled at 0.2×10^5 Pa higher than CO_2 pressure to prevent bubble formation in the liquid phase. Figure 3.2 showed the schematic diagram of membrane contactor system for CO_2 absorption test. It consists of MEA liquid at inlet and outlet, membrane contactor module and CO_2 gas tank.

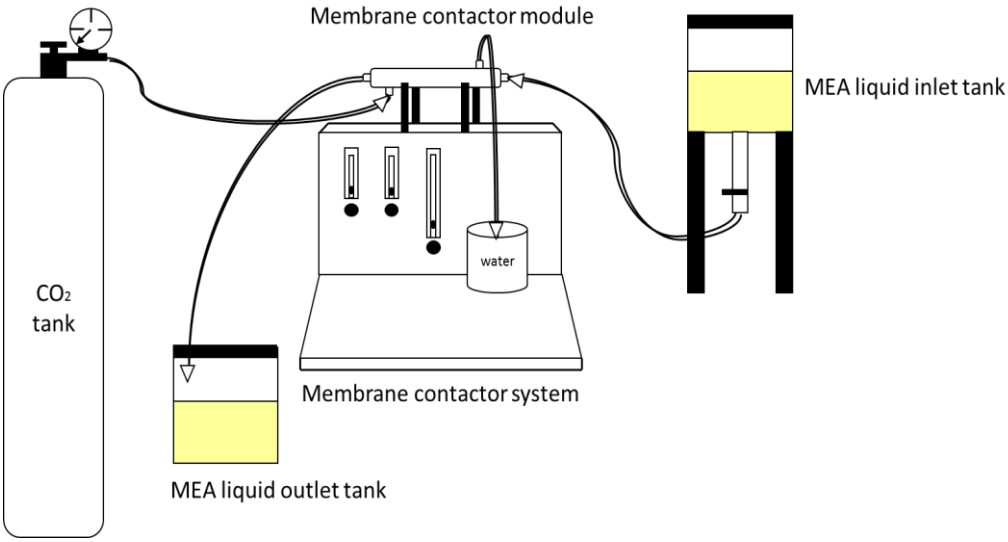


Figure 3.2: Schematic Diagram of Membrane Contactor System

The concentration of both inlet and outlet liquid were used to calculate the CO_2 absorption flux as follows:

$$J_{CO_2} = \frac{(C_{li} - C_{lo}) \times Q_1}{A_i} \quad \textbf{(3.1)}$$

Where J_{CO_2} is the CO_2 absorption flux (mol/m2s), $(C_{li} - C_{lo})$ is the liquid phase CO_2 concentrations (mol/m3) at inlet and outlet, Q_1 is liquid flow rate (m^3/s), and A_i is inner surface of the hollow fiber membranes (m^2).

CO_2 absorption efficiency of the membrane module can be calculated as:

$$\eta\ (\%) = (1 - \frac{C_{li}}{C_{lo}} \times 100) \quad \textbf{(3.2)}$$

3.5 Double Titration Method

At equilibrium, an outlet liquid sample was withdrawn from the membrane contactor system into a cylinder containing excess 1.0 M NaOH solution, thus converting free dissolved CO_2 into the non-volatile ionic species. An excess amount of barium chloride ($BaCl_2$) solution is then added to the solution. The solution is shaken well to permit all absorbed (physically and chemically) CO_2 to precipitate the carbonate as barium carbonate ($BaCO_3$). The excess NaOH was titrated with 1.0M HCl solution using phenolphthalein as the indicator where the colour of solution changes from purple to colourless. Then by using methyl orange as the indicator, the solution changes from colourless to light yellow. The solution was carefully titrated again with 1.0 M HCl until it the colour change to bright orange, which is titration end point. The amount of HCl added can be used to calculate the solubility of CO_2 in terms of the moles of CO_2 per mole of amine (Li and Chang, 1994).

$$BaCO_3\ (s) + 2\ HCl\ (aq) \longrightarrow BaCl\ (aq) + H_2O\ (l) + CO_2\ (g) \qquad \textbf{(2.3)}$$

The CO_2 concentration in the solution was calculated as:

$$M_{HCl} = M_{CO_2} \qquad \textbf{(2.4)}$$

$$M_1 = \frac{\frac{M_{HCl}}{2} \times V_{HCl}}{V_{sample}} \qquad \textbf{(2.5)}$$

where M_{HCl} and M_{CO_2} is the molarity of the solution containing HCl and CO_2, M_1 is the concentration of liquid containing absorbed CO_2, V_{HCl} is the value of HCl added into the solution until titration end point was obtained and V_{sample} is the initial value of the liquid sample withdrawn from the system.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Contact Angle Measurement

Table 4.1 showed the result for contact angle at different composition of alumina. Plain PVDF contact angle was 85.6 °, which is the lowest value compared to others. According to the table, the membrane with 1wt.%, 3wt.% and 5wt.% of alumina shows 86.1 °, 86.8° and 92.4° respectively. S4 (5% alumina) have highest degree of contact angle among the others. Contact angle is one of the regular approaches to wettability of a surface membrane (Yuliwati and Ismail, 2011). Theoretically, the degree of contact angle increase due to hydrophobicity of membrane also increase thus it can lower the wettability of membrane and can withstand wetting at prolong hour operation.

Table 4.1: Result Contact Angle at Different Composition of Alumina clay

Hollow fiber membrane sample	Angle contact angle (°)
S1	85.6
S2	86.1
S3	86.8
S4	92.40

4.2 CO_2 Absorption Test

This absorption experiment was conducted with 1 M and 2 M of MEA as liquid absorbent at different liquid flow rates. Based on Figure 4.1, it showed that membrane samples with increasing alumina concentration resulted higher CO_2 absorption flux with increment of liquid flow rate. Meanwhile, similar trend was observed for CO_2 absorption efficiency as the alumina concentration increased. The highest CO_2 absorption efficiency of 42% was obtained for PVDF + 5% alumina, in the meantime the highest CO_2 absorption flux recorded was 2.88×10^{-2} mol/m².s at 1.0 M of MEA. Compared with plain PVDF at the highest flow rates the CO_2 absorption flux only 0.06384×10^{-2} mol/m².s and CO_2 absorption efficiency was 4%. CO_2 absorption flux is normally associated with mass transfer resistance. Upon increasing liquid absorbent flow rates, the liquid flow resistance towards the membrane side was reduced. Thus, the mass transfer of CO_2 gas from the gas phase to the liquid phase was less hindered by the low mass transfer resistance at the liquid side.

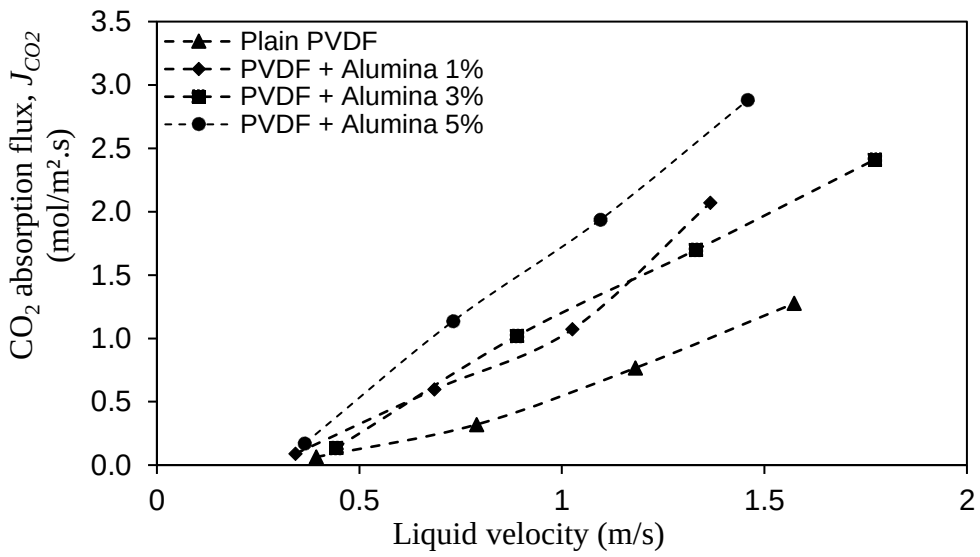


Figure 4.1: CO_2 Absorption Flux, J_{CO_2} (mol/m^2.s) vs Liquid Velocity (m/s) for Different Composition of Alumina clay at 1M of MEA

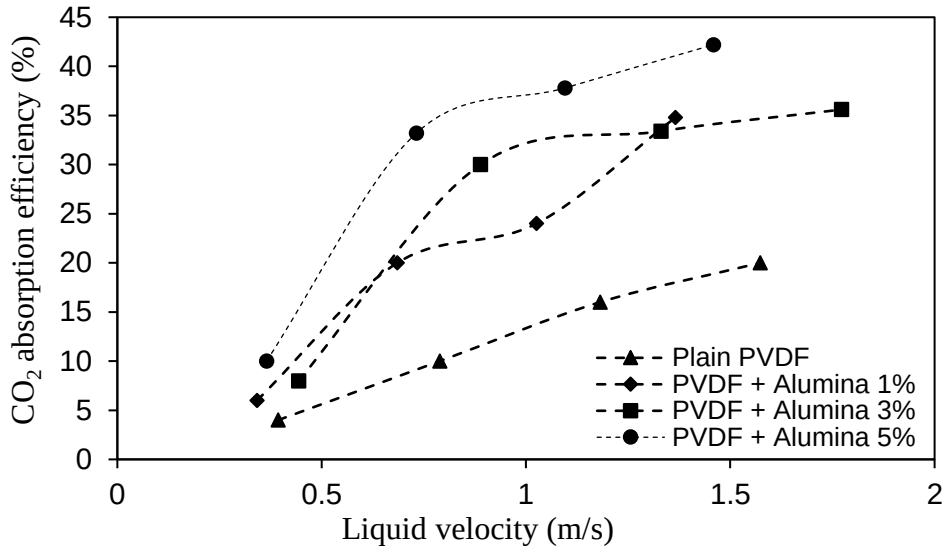


Figure 4.2: CO_2 Absorption Efficiency (%) vs Liquid Velocity (m/s) for Different Composition of Alumina clay at 1M of MEA

While the experiment with 2.0 M of MEA as a liquid absorbent shown by Figure 4.3, CO_2 absorption flux increased with the addition of alumina concentration. It illustrated the CO_2 absorption flux S4 (5% alumina) have the highest absorption flux of 4.368×10^{-2} mol/m².s followed by the S3 (3% alumina) at the highest velocity is 3.927×10^{-2} mol/m².s. Figure 4.4 represented CO_2 absorption efficiency against liquid velocity. As the result, CO_2 absorption efficiency obtained was 46%, meanwhile the plain PVDF membrane resulted only 20%. This described that the higher the concentration of liquid absorbent, the more CO_2 gas is absorbed. The CO_2 absorption seems to be substantially enhanced when the initial concentration of the absorbent solution is increased Nevertheless, higher absorbent concentration could have harmful side effects to the hollow fiber membrane material as well as corrosion in the other metallic components (Boucif et al., 2008).

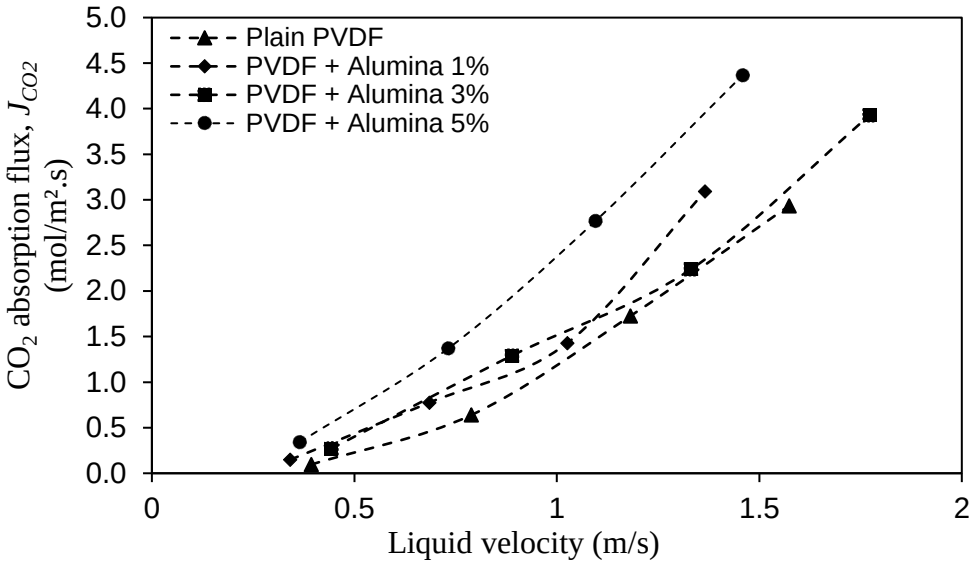


Figure 4.3: Absorption Flux, J_{CO_2} (mol/m^2.s) vs Liquid Velocity (m/s) for Different Composition of Alumina clay at 2M of MEA

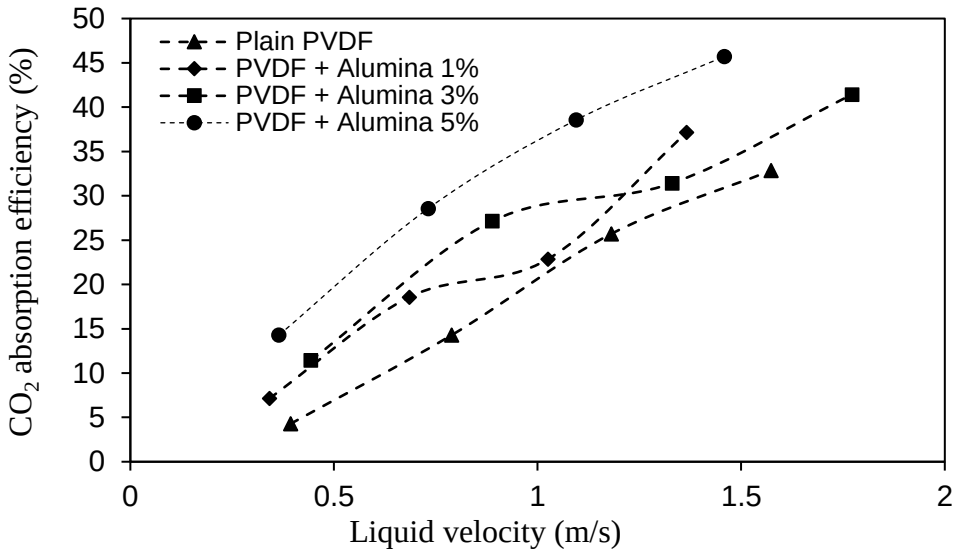


Figure 4.4: Absorption Efficiency (%) vs Liquid Velocity (m/s) for Different Composition of Alumina clay at 2M of MEA

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

CO_2 absorption performance of PVDF/alumina hollow fiber membrane was successfully achieved via contact angle and absorption test using membrane contactor system. Modification plain PVDF membrane to PVDF/alumina clay have showed potential result through the degree of contact angle, CO_2 absorption efficiency and the CO_2 absorption test via membrane contactor system to reduce CO_2 emissions. As shown in the CO_2 absorption test, experiment carried out at different concentration of MEA, different velocity of MEA and the different composition of alumina clay. From the experiment, contact angle, efficiency of absorption and CO_2 absorption flux performance incline as the composition of alumina increased when liquid velocities increased due to reduce mass transfer resistance in the liquid side. Based on the experiment, the initial concentration of the liquid absorbent solution has a higher impact on the gaseous outlet concentration. The CO_2 absorption appears to be significantly enhanced when the preliminary concentration of the absorbent solution is increased, however higher absorbent concentration could have caused side consequences consisting of erosion of the pores and skin of the membrane and it is able to have harmful damages as well as corrosion if applied for long hour operation. It is expected that membrane contactor with PVDF/alumina hollow fiber membrane has the potential to be applied in the industry for CO_2 removal.

5.2 Recommendation

Throughout this project, there are numerous issues which have been identified, which may be improved in the future to enhance the CO_2 absorption: -

- To accurately read the liquid and gas flowrate during the experiment, both measuring device should be replaced with a digital device to ensure that the flowrate measurement is constantly accurate and precise.
- It is recommended to let the membrane contactor machine operate for 30 minutes in order to eliminate any air bubble in liquid MEA channel an to ensure the system has reached a stable state.
- Titration method ought to be carried out in a careful manner to avoid the excess HCl mixed with the MEA solution when doing titration. This is due to the fact extra HCl solution will tend to change the orange colour to pink colour instantaneously. It will lead to inaccurate determination of CO_2 absorption flux.
- MEA tank should be prepared with proper amount of 1M aqueous MEA and ensure it is tightly closed to avoid any external air absorbed by the liquid absorbent before performing the CO_2 absorption test via membrane contactor system.

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APPENDICES

APPENDIX A: Details on membrane module

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Membrane contactor module	• 10 fibers in module • Std module • Liquid flow in thee lumen • Gas low on the shell side
Operating condition	• Liquid pressure = 1.0 bar • Gas pressure = 0.8 bar • Temperature = room temp.
Concentration liquid absorbent	• 1M of MEA • 2M of MEA
Concentration HCl	• 1M of HCl
Concentration NaOH	• 1M of NaOH
Module inner diameter	• 1.0 cm
Total length	• 29.2 cm
Effective length	• 16 cm

APPENDIX B: Dimension of the sample membrane

Sample	Outer dia (µm)	Inner dia (µm)	Cross Sectional Area
Plain PVDF	768	519	2.11641E-06
PVDF + Alumina 1%	753	557	2.43767E-06
PVDF + Alumina 3%	711	489	1.87881E-06
PVDF + Alumina 5%	770	539	2.28267E-06

APPENDIX C: Data of CO_2 absorption flux for all PVDF/alumina membrane at various flowrate and 1M of MEA

Liq velocity (m/s)	Sample	Liq. f/r	Amount of HCl added (ml)	Cin (mol/m3)	C outlet (mol/m^3)	Ai	Ql	Absorption flux, J_{CO2}	Absorption efficiency (%)
0.393591432	Plain PVDF	50	4.1	50	48	0.002609829	0.000000833	0.06384	4
0.78907286		100	5.233	50	45	0.002609829	0.00000167	0.31994	10
1.181246796		150	6.3	50	42	0.002609829	0.0000025	0.76633	16
1.573420732		200	7.4	50	40	0.002609829	0.00000333	1.27595	20

Liq velocity (m/s)	Sample	Liq. f/r	Amount of HCl added (ml)	Cin (mol/m3)	C outlet (mol/m^3)	Ai	Ql	Absorption flux, J_{CO2}	Absorption efficiency (%)
0.341719657	PVDF + Alumina 1%	50	4.8	50	47	0.002800914	0.000000833	0.08922	6
0.685080224		100	5.866	50	40	0.002800914	0.00000167	0.59623	20
1.025569198		150	6.9	50	38	0.002800914	0.0000025	1.07108	24
1.366058172		200	7.66	50	32.6	0.002800914	0.00000333	2.06868	35

Liq velocity (m/s)	Sample	Liq. f/r	Amount of HCl added (ml)	Cin (mol/m3)	C outlet (mol/m^3)	Ai	Ql	Absorption flux, J_{CO2}	Absorption efficiency (%)
0.443366253	PVDF + Alumina 3%	50	6.5	50	46	0.002458971	0.000000833	0.13550	8
0.888861516		100	7.4	50	35	0.002458971	0.00000167	1.01872	30
1.330631012		150	8	50	33.3	0.002458971	0.0000025	1.69786	33
1.772400508		200	8.5	50	32.2	0.002458971	0.00000333	2.41052	36

Liq velocity (m/s)	Sample	Liq. f/r	Amount of HCl added (ml)	Cin (mol/m3)	C outlet (mol/m^3)	Ai	Ql	Absorption flux, J_{CO2}	Absorption efficiency (%)
0.364924332	PVDF + Alumina 5%	50	7.43	50	45	0.00243936	0.000000833	0.17074	10
0.731601001		100	8.53	50	33.4	0.00243936	0.00000167	1.13645	33
1.09521108		150	9.5	50	31.1	0.00243936	0.0000025	1.93698	38
1.458821159		200	9.8	50	28.9	0.00243936	0.00000333	2.88039	42

APPENDIX D: Data of CO_2 absorption flux for all PVDF/alumina membrane at various flowrate and 2M of MEA

Liq velocity (m/s)	Sample	Liq. f/r	Amount of HCl added (ml)	Cin (mol/m3)	C outlet (mol/m^3)	Ai	Ql	Absorption flux, J_{CO2}	Absorption efficiency (%)
0.393591432	Plain PVDF	50	9.733	70	67	0.002609829	0.000000833	0.09575	4
0.78907286		100	10	70	60	0.002609829	0.00000167	0.63989	14
1.181246796		150	11.9	70	52	0.002609829	0.0000025	1.72425	26
1.573420732		200	13	70	47	0.002609829	0.00000333	2.93468	33

Liq velocity (m/s)	Sample	Liq. f/r	Amount of HCl added (ml)	Cin (mol/m3)	C outlet (mol/m^3)	Ai	Ql	Absorption flux, J_{CO2}	Absorption efficiency (%)
0.341719657	PVDF + Alumina 1%	50	13.83	70	65	0.002800914	0.000000833	0.14870	7
0.685080224		100	14.4	70	57	0.002800914	0.00000167	0.77510	19
1.025569198		150	15.13	70	54	0.002800914	0.0000025	1.42811	23
1.366058172		200	15.8	70	44	0.002800914	0.00000333	3.09113	37

Liq velocity (m/s)	Sample	Liq. f/r	Amount of HCl added (ml)	Cin (mol/m3)	C $_{outlet}$ (mol/m^3)	Ai	Ql	Absorption flux, J_{CO2}	Absorption efficiency (%)
0.443366253	PVDF + Alumina 3%	50	15.7	70	62	0.002458971	0.000000833	0.27101	11
0.888861516		100	16.46	70	51	0.002458971	0.00000167	1.29038	27
1.330631012		150	17.06	70	48	0.002458971	0.0000025	2.23671	31
1.772400508		200	17.8	70	41	0.002458971	0.00000333	3.92725	41

Liq velocity (m/s)	Sample	Liq. f/r	Amount of HCl added (ml)	Cin (mol/m3)	C $_{outlet}$ (mol/m^3)	Ai	Ql	Absorption flux, J_{CO2}	Absorption efficiency (%)
0.364924332	PVDF + Alumina 5%	50	17.1	70	60	0.00243936	0.000000833	0.34148	14
0.731601001		100	17.8	70	50	0.00243936	0.00000167	1.36921	29
1.09521108		150	18.7	70	43	0.00243936	0.0000025	2.76712	39
1.458821159		200	19.6	70	38	0.00243936	0.00000333	4.36836	46

APPENDIX E: Membrane contactor arrangement

APPENDIX F: Double titration result change of colour

First titration:

Colour of solution after 5 drops of 1M NaOH, 2 drops of BaCl and 1 drop of phenolphthalein

Colour of solution obtained after first titration with 1M of HCl

Second titration:

Color of solution when added with 1 methyl orange

Color of solution occurred after second titration with 1 M of HCl