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United Arab Emirates University

College of Engineering

Department of Chemical and Petroleum Engineering

EXPERIMENTAL INVESTIGATION OF CO_2 TRANSPORT THROUGH COMBINED MEMBRANE ABSORBER AND REGENERATOR

Nima Mohammadrasool Atbaei

This thesis is submitted in partial fulfillment of the requirements for the degree of
Master of Science in Chemical Engineering

Under the Supervision of Professor Mohamed H. Al-Marzouqi

November 2016

Declaration of Original Work

I, Nima Mohammadrasool Atbaei, the undersigned, a graduate student at the United Arab Emirates University (UAEU), and the author of this thesis entitled "*Experimental Investigation of CO_2 Transport through Combined Membrane Absorber and Regenerator*", hereby, solemnly declare that this thesis is my own original research work that has been done and prepared by me under the supervision of Professor Mohamed H. Al-Marzouqi, in the College of Engineering at UAEU. This work has not previously been presented or published, or formed the basis for the award of any academic degree, diploma or a similar title at this or any other university. Any materials borrowed from other sources (whether published or unpublished) and relied upon or included in my thesis have been properly cited and acknowledged in accordance with appropriate academic conventions. I further declare that there is no potential conflict of interest with respect to the research, data collection, authorship, presentation and/or publication of this thesis.

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Abstract

Greenhouse gases such as carbon dioxide have been known to contribute significantly to global warming, which in turn has resulted in serious global environmental problems. Carbon dioxide is the main gaseous contaminant in the atmosphere, representing about 80% of greenhouse gases. It is reported that half of the CO_2 emissions are produced by industry and power plants using fossil fuels such as coal-combustion power generators. These emissions create the need for low energy-consumption, and efficient technologies for the capture and removal of CO_2 from gas mixtures produced by industrial sources.

Conventional gas absorption processes for the removal of CO_2 including chemical absorption by alkanolamine solutions suffer from many drawbacks such as flooding, foaming, entraining, channeling, and high capital and operating costs. The effort of this research is to work on the possibilities of enhancing the efficiency of these processes to reduce the effect of their drawbacks by using Hollow fiber membrane Contactor (HFMC) as a new gas separation process.

In this study several membrane contactors such as homemade Polyvinylidenefluoride (PVDF), commercial Polytetrafluoroethylene (PTFE) and Perfluoroalkoxy alkane (PFA) were individually fabricated as an absorption process, the gas mixture of CO_2/N_2 flowed on one side of a hydrophobic microporous membrane while several liquid absorbent, such as Monoethanolamine (MEA), Diethanolamine (DEA) and Sodium Hydroxide (NaOH) flowed on the other side of membrane for comparison purpose. The CO_2 gaseous contaminant diffused from the gas phase to the membrane gas–liquid interface and is absorbed in the liquid.

The Result revealed that homemade PVDF has the highest removal rate and PFA has the lowest removal efficiency, in addition, although the removal performance by NaOH gave better removal efficiency, by contrast, it suffered from poor regeneration, therefore, DEA became more favorable in overall performance because of its higher regeneration rate. The effects of operation parameters such as gas and liquid flow rates and packing ratio on performance of CO_2 removal were analyzed. The results reveal that, regardless of the type of the membrane module used and liquid solvent, increase in liquid flow rate and packing ratio and a decrease in gas flow rate, give the best system performance in the absorption process.

The rich solution may be sent to another membrane contactor for stripping to remove the absorbed gases and regenerate the solvent. In the stripping unit the operating parameters such as temperature, gas flow rate and liquid follow rate were examined to investigate their effect on the stripping performance. Results determined that temperature has the focal effect on stripping performance regardless of the type of the solvent, increase in temperature increases stripping efficiency. In addition, higher stripping performance was found to be at high solvent liquid flow rate, low sweep gas flow rate. Using a suitable membrane configuration could be considered as a way to prevent wetting.

The generated lean solution is then recycled to the absorption unit and the CO_2 transport in combined absorber and stripper units were evaluated by time. Various membrane modules using several aqueous amine solutions such as MEA, DEA and NaOH at different heat of regeneration were examined to investigate their impact on membrane wetting and overall performance. Results revealed that DEA shows the optimum performance at high heat of regeneration. A mathematical model was applied to predict the CO_2 removal in gas liquid membrane contactor. Model results were in good agreement of the experimental data.

Keywords: Carbon dioxide captured, Gas liquid membrane contactors, Flue gas, Absorption, Regeneration, Close loop.

Title and Abstract (in Arabic)

دراسة معملية لعمليات امتصاص غاز ثاني أكسيد كربون من خلال المقاطع الغشائيه وإعادة تدويره

الملخص

كشفت النتائج أن الأغشية المصنعة محليا (PVDF) حققت أعلى معدل إزالة للغاز بينما النوع الآخر من الأغشية المستورده (PFA) حقق أدناها. إضافة إلى ذلك، تبين أن استخدام سائل هيدروكسيد الصوديوم أعطى نتائج كفاءة عالية في إزالة غاز ثاني أكسيد الكربون، ولكن في المقابل حقق أدنى مستوى في عمليات التدوير. لهذا تم تفضيل استخدام سائل (DEA) لتحقيقه نتائج واعدة في فصل الغاز و إعادة تدوير السائل المستخدم في عملية الفصل. هناك عدة دراسات شملت أهم العوامل التي تؤثر على عملية الفصل كمعدلات تدفق الغاز والسائل و نسبة إضافتها أودت إلى نتائج جديرة بالذكر، بينت هذه النتائج أنه بغض النظر عن نوع الأغشيه أو نوع المذيب المستخدم لإمتصاص الغاز، فإن تحقيق أعلى كفاءة للتقنية المستخدمة يعتمد على ارتفاع تدفق المذيب ونسبة الاضافة وانخفاض تدفق الغاز.قد يتم إرسال السائل المشبع بالغاز لوحدة أخرى لغرض فصل الغاز عن السائل وإعادة استخدام السائل مرة أخرى.

تم درتسة بعض العوامل كدرجة الحرارة، معدل تدفق الغاز والسائل تحت المجهر لفحص تأثيرها على كفاءة عملية التدوير. أظهرت النتائج أن عامل درجة الحرارة كان لها أثر واضح وكبير على كفاءة عملية التدوير حيث أن زيادة درجة الحرارة أدى إلى تحسين فصل الغاز عن السائل بغض النظر عن نوع السائل المذيب. إضافة إلى ذلك، فإن كفاءة فصل الغاز عن السائل تحسنت بزيادة معدل تدفق السائل وخفض معدل تدفق الغاز. يعتبر اختيار التصميم المناسب لإعداد القاطع الغشائي عامل مهم لمنع ظاهرة التبليل.

بعد عملية امتصاص غاز ثاني أكسيد الكربون يتم إرسال السائل المعالج إلى وحدة ادمصاص الغاز وبنفس الوقت يتم تقييم معدل إزالة غاز ثاني أكسيد الكربون من وحدتي الامتصاص والتدوير. شمل البحث عدة تجارب لدراسة تأثير بعض العوامل على ظاهرة التبليل وكفاءة العملية كتصنيع عدة نماذج للقواطع واستخدام عدة أنواع من السوائل المذيبة (MEA, DEA, NaOH) و ضبط درجات حرارة مختلفة. أثبتت النتائج أن سائل DEA أظهر الأداء

الأمثل لعمليات التدوير عند درجات حرارة عالية،كما تم تطبيق نموذج رياضي للتنبؤ بمعدلات إزالة الغاز في تقنية القواطع الغشائيه. وقد أوضح النموذج الرياضي نتائج تطابق النتائج العملية.

الكلمات المفتاحية: امتصاص غاز ثاني اكسيد الكربون، قواطع جوفاء تحتوي على ألياف غشائية،استخدام السوائل المذيبة، الامتصاص.

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At last but not least I must express my thanks to both my parents Mohammad Rasool Atbaei and Shirin Khosravi, for their lifelong love and devotion without which such work is nearly impossible to be completed.

Dedication

To my beloved parents and family

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List of Abbreviations

AMP	2-Amino-2-Methyl-1-Propanol
CAP	Chilled Ammonia Process
CCS	Carbon Dioxide Capture and Storage
CH_4	Methane
CO_2	Carbon Dioxide
DEA	Diethanolamine
EOR	Enhance Oil Recovery
GLMC	Gas Liquid Membrane Contactor
H_2S	Hydrogen Sulfide
HFMC	Hollow Fiber Membrane Contactor
IPCC	Intergovernmental Panel on Climate Change
KOH	Potassium Hydroxide
MDEA	N-methyldiethanolamine
MEA	Monoethanolamine
N_2	Nitrogen
Na_2CO_3	Sodium Carbonate
NaOH	Sodium Hydroxide
NH_3	Ammonia
NH_4HCO_3	Ammonium Carbonate
PE	Polyethylene
PFA	Perfluoroalkoxy Alkane
PG	Potassium Glycinate

PP	Polypropylene
PSA	Pressure Swing Adsorption
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidenefluoride
TG	Glass Transition Temperature of Fiber
TIPS	Thermally Induced Phase Separation
TM	Melting Point of Crystalline Polymer
TSA	Temperature Swing Adsorption

Chapter 1: Introduction

1.1 Overview

Fossil fuels such as oil, gas and coal are the main sources of energy. Carbon dioxide (CO_2) is the major greenhouse gas emitted as a byproduct of the fossil fuel combustion and causes air pollution (Rahbari-Sisakht, Ismail, Rana, & Matsuura, 2013). It is also reported that power plants that consume fossil fuels are producers of half of this CO_2 emission, therefore development of separation processes is highly recommended to remove and to recover the emitted CO_2 in such industries. In general there are many techniques for CO_2 removal such as; bubble columns, packed towers, venturi scrubber, and sieve tray.

Despite the fact that packed tower is widely known commercial process in CO_2 separation, it has some main disadvantages such as flooding, channeling, large-scale equipment and etc. As an alternative, hollow fiber membrane contactor (HFMC) offers a much larger contact area per unit volume compared to tray and packed columns, and has the advantages of no flooding, entrainment, and foaming restrictions on operational flow rates (Lin, Chiang, Hsieh, Li, & Tung, 2008). Hollow fiber membrane contactors (HFMC) are a promising alternative. Absorption/stripping of CO_2 occur in a membrane contactor when the gas stream contacts with the liquid phase flowing on the opposite side of the membrane. As long as HFMC is made modular, it is easy to be scaled up or down, and in comparison with conventional equipments, the associated problems can be effectively eliminated by absence of interpenetration of the two phases into each other (Li & Chen, 2005a).

In this technique, porous hydrophobic membrane acts as a barrier between gas and liquid phases and increases the contact area between the phases without dispersing one phase into another by having small equipment size, higher interfacial area, independent control of the gas and liquid flow rates. In this technique, fluids can be contacted on opposite sides of the membrane and at the mouth of each membrane pore, where the gas–liquid interface is formed. Mass transfer occurs by diffusion across the interface. As far as the membrane contactors offer high interfacial area per volume, membrane contactors are a compact device and can reduce energy consumption and require less in capital cost (Rahbari-Sisakht et al., 2013). Although HFMC is an alternative for CO_2 capture, there is still a long way to complete CO_2 separation process by considering that there are still some inherent problems exist in gas-liquid membrane contractor (GLMC) technology and these problems have to be improved.

The focus of this research is to study and investigate the potential and compare the required energy for various removal efficiencies of CO_2/N_2 via lean solvents and regenerating the rich solvents through absorption/stripping mechanism in a hollow fiber GLMC process. In this research, the gas mixture of CO_2/N_2 flows through one side of a hydrophobic microporous membrane, while the liquid absorbent flows through the other side. The gaseous contaminant diffuses from the gas phase to the gas-liquid interface and then it is absorbed by the liquid. The rich solution may be sent to another membrane contactor for stripping to remove the absorbed gases. The lean solution is then recycled through the absorption unit as shown in Figure 1.

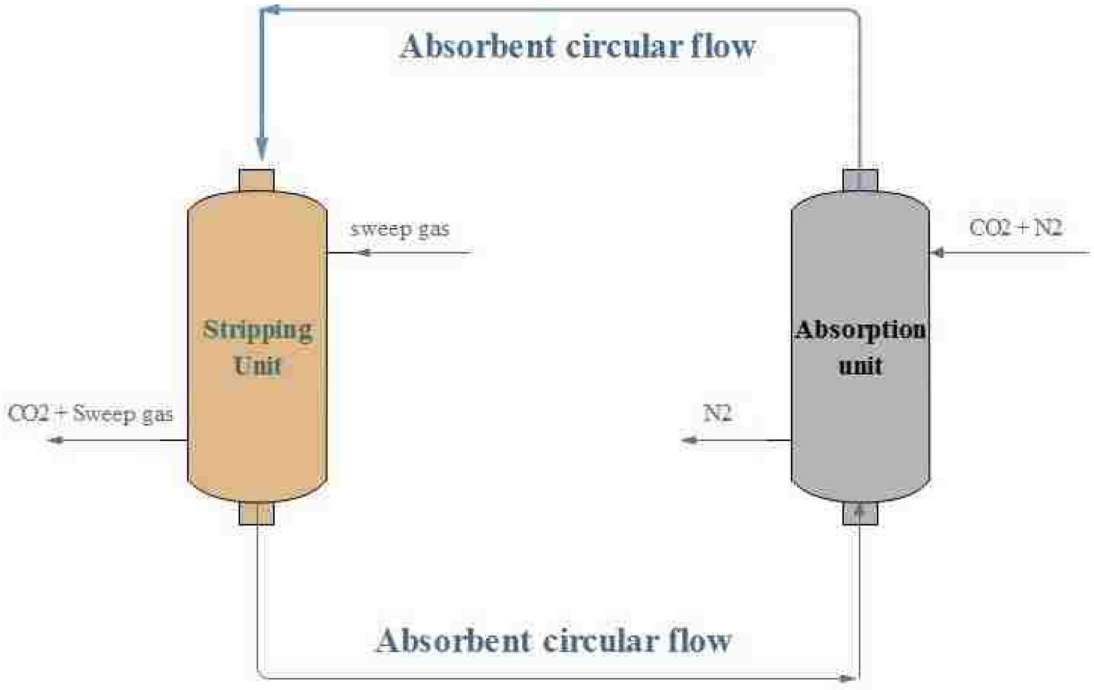

Figure 1: Membrane gas absorption/stripper process

1.2 Statement of the problem

Fossil fuels such as coal, oil and gas make-up the major part of energy resources worldwide. Carbon dioxide (CO_2) is the main cause of air pollution that comes from combustion of all fossil fuels. Therefore, the removal of CO_2 from industrial flue gas streams is essential. CO_2 removal is practiced using various techniques such as absorption into aqueous solution of alkanolamines using conventional equipment like packed columns, bubble columns, and spray columns. Liquid absorbents can be simply regenerated by heating of aqueous alkanolamines. Therefore, a simple and typical process for CO_2 capture may include two units, one for absorption and the other for desorption. Normally, the stripping processes are conducted slightly above ambient pressure and high temperature conditions. HFMC for CO_2 capture has been studied over the past few decades. Moreover, extensive studies were dedicated to absorption processes using HFMC. Apart from absorption, the membrane contactors can be also applied for desorption or regeneration of liquid absorbents (Khaisri, deMontigny, Tontiwachwuthikul, & Jiraratananon, 2011).

The energy consumed by the regeneration unit, counts for the major running costs of CO_2 separation processes. This has driven the researchers toward conducting various studies on CO_2 stripping using HFMC. Moreover the ambiguity in the optimal condition of this separation process opens up the area for more studies to commercialize the CO_2 absorption/stripping in GLMC.

1.3 Research objective

Experimental and theoretical results of GLMC as a CO_2 absorber/stripper have been reported by many researchers. Although there are many advantage for GLMC in CO_2 separation, there are still some inherent problems in GLMC technology that need to be resolved for successful commercialization of this technology. In contrast to wide current application of CO_2 absorption processes, CO_2 stripping has been implemented recently. While solvent regeneration is the most costly stage of the separation process, few documented results are reported in the open literature in this regards.

The objectives of this work are briefly described as follows:

1) Construction of polymer hollow fiber membrane modules which are suitable for both absorption and regeneration in GLMC applications using PFA (Perfluoroalkoxy alkane), PVDF (Polyvinylidene fluoride) and PTFE (Polytetrafluoroethylene) membrane fibers.

2) Construction of the experimental set-up.

3) Investigation and study of the CO_2 removal efficiency from gas mixture of CO_2/N_2 using PFA, PVDF, PTFE taking place in custom GLMC modules.

4) Conduct continuous experiments to study the regeneration of saturated DEA by stripping mechanism through lab-fabricated PTFE and PVDF gas liquid membrane contactor modules.

5) Develop a mathematical model for CO_2 absorption/stripping process in GLMC.

1.4 State of CO_2 absorption /stripping for GLMC

The hollow fiber membrane contactor (HFMC) has attained considerable attention in absorption/stripping of CO_2. As far as convectional process suffers from some drawbacks such as foaming, flooding and channeling, HFMC can easily overcomes these disadvantages due to the absence of interpenetration of the two phases into each other. The porous membrane acts as a fixed barrier and interface. Gas stream contacts with the liquid phase flowing through the opposite side of the membrane. The gas diffuses in the pores media and is absorbed in the liquid flowing on the other side. The membrane contactor can be easily scaled-up because of its modularity and can overcome problems associated with the conventional equipments (Li & Chen, 2005a).

In case of CO_2/N_2 separation, CO_2 diffuses thorough the pores of the membrane and is absorbed by selected absorption liquid. The absorption liquid is then sending to the stripping unit as the second module for stripping of CO_2 (Figure1). Removal efficiency of the CO_2 can be enhanced by selecting the appropriate types of absorption liquid and membrane morphology (polymer choice), and optimization of the operating conditions.

In the recent years, wide interest has been shown in the studding of polymeric membranes and among all, polyvinylidene fluoride (PVDF) tend to be more attractive. There are many methods to fabricate PVDF, and among those we used lab-fabricated PVDF by thermally induced phase separation (TIPS) method.

It should be considered that the performance of PVDF can be optimized by selecting the proper design factors during the fabrication. Since the thermal stability of PFA and PTFE are better than PVDF, they were selected for propose of removal efficiency comparisons. Liquid absorption can be either physical or chemical. There are many parameters that need to be considered in the selection of the appropriate liquid absorbent. A proper liquid absorbent must have; 1. High Reactivity with CO_2 (by having higher reactivity, we can have higher flux and absorption rate) 2. High surface tension (liquid must be unable to wet the membrane) 3. Chemical compatibility with the membrane material (it will directly affect on long-term stability of membrane module) 4. Lower vapor pressure and thermal conductivity (to avoid thermal degrading), 5. Easy to be regenerated (Li & Chen, 2005a).

The configuration of HFMC module such as design and length of the module with flow direction can significantly affect the overall mass transfer coefficient. Moreover, the operation conditions such as liquid and gas flow rates, type of the liquid absorbent, and temperature can also affect the performance of GLMC. Long term stability is another factor which plays an important role on performance of absorption and stripping in efficacy of GLMC. To overcome this issue, membrane break through pressure must be high. This depends on contact angle between liquid and membrane, surface tension of liquids, and pore size of membrane. Membrane wetting can be expected in cases where hydrophobic membranes and liquid solvents by high surface tension (that can cause large contact angles) are used. Obtaining a certain value of CO_2 removal efficiency might be challenging as it is needed to consider the optimization of many design parameters.

For the stripping stage of the process, the efficiency is affected by factors such as the nature of liquid solvent, the configuration of module and the operating conditions (liquid flow rate, rich solution temperature, etc). To improve the performance of CO_2 stripping, operating conditions need to be optimized in addition to the development of the proper fiber structure (e.g. PVDF, PTFE).

1.5 Outline of the research work

In this study three different hollow fiber membranes were used to construct the membrane module. These include: (1) custom PVDF which was fabricated via thermally induced phase separation (TIPS), (2) Commercial PTFE with two different structures and (3) Commercial PFA.

The experiments were carried out by an experimental set-up to investigate the effect of various parameters on the performance of GLMC in an absorption/stripping module. The separation of CO_2 from CO_2/N_2 mixture by using the fabricated hollow fiber membranes in a gas–liquid membrane contactor was studied. The potential of the process was investigated using different operating conditions and module configurations. Operating parameters such as temperature of the solvent stream, and liquid and gas flow rates were studied to investigate the performance of CO_2 removal and regeneration efficiency in a closed loop for various absorbent liquids. Finally, a mathematical model for CO_2 absorption in Gas liquid membrane contactor was developed.

1.6 Organization of the thesis

This thesis consists of six chapters: Chapter 1 includes an overview summary about this research work, statement of problems in CO_2 capturing and the major limitations currently being faced. Research objectives introduce the aim of this research with brief revision of the recent work done in the area of CO_2 removal and regeneration in absorption/stripping unit using GLMC, outline of the research and organization of this thesis. In Chapter 2, a general review of literature related to removal of CO_2, the major limitations of the recent technologies available, the advantages of GLMC and the factors that affect the overall CO_2 absorption/stripping performance in GLMC are discussed. Chapter 3 contains the experimental work by describing of module construction, CO_2 absorption/stripping experimental set-up and details of CO_2 flux and removal percentages. Chapter 4 includes results related to the effect of different module types on the CO_2 removal performance from gas mixture of CO_2/N_2 using different chemical solvents and operating conditions. The chapter then deals with stripping efficiency of CO_2 by changing the parameters and operating conditions. The chapter ends with an evaluating the effects of various parameters on the absorption/stripping process as a closed loop. In chapter 5 a mathematical model for CO_2 removal was developed. Finally chapter 6 provides the conclusions and recommendations.

Chapter 2: Literature Review

2.1 Introduction

It is well known that atmospheric carbon dioxide CO_2 has been increased recently due to the industrial activities, transportation and fossil fuels such as burning coal and oil. The excessive emission of CO_2 has been associated with the climate change (Thomas & Benson, 2015). According to the Intergovernmental Panel on Climate Change (IPCC), carbon dioxide is the main component of the greenhouse gas and its emission is directly associated with global warming which is nowadays a serious environmental concern. Hence the main global concern is to develop and improve the process of capturing CO_2 from various gas streams more efficiently in terms of both technical and economical aspects (Mehdipour, Keshavarz, Seraji, & Masoumi, 2014). For this reason, carbon dioxide capture and storage processes (CCS) are required. CCS is the process at which CO_2 is separated from the flue and natural gas resources. The CO_2 is then stored in various forms and it is isolated from the atmosphere (M. Wang, Lawal, Stephenson, Sidders, & Ramshaw, 2011). Petroleum industry is the major client that utilizes the separated CO_2 to Enhance Oil Recovery (EOR) from oil reservoirs. CO_2 captured from power plants can be applied in EOR when there is insufficient supply of CO_2. Figure 2 shows the recent technologies available for capturing the CO_2 while Figure 3 presents the most common CO_2 capturing and storage processes using amine solvents (Khalilpour et al., 2015).

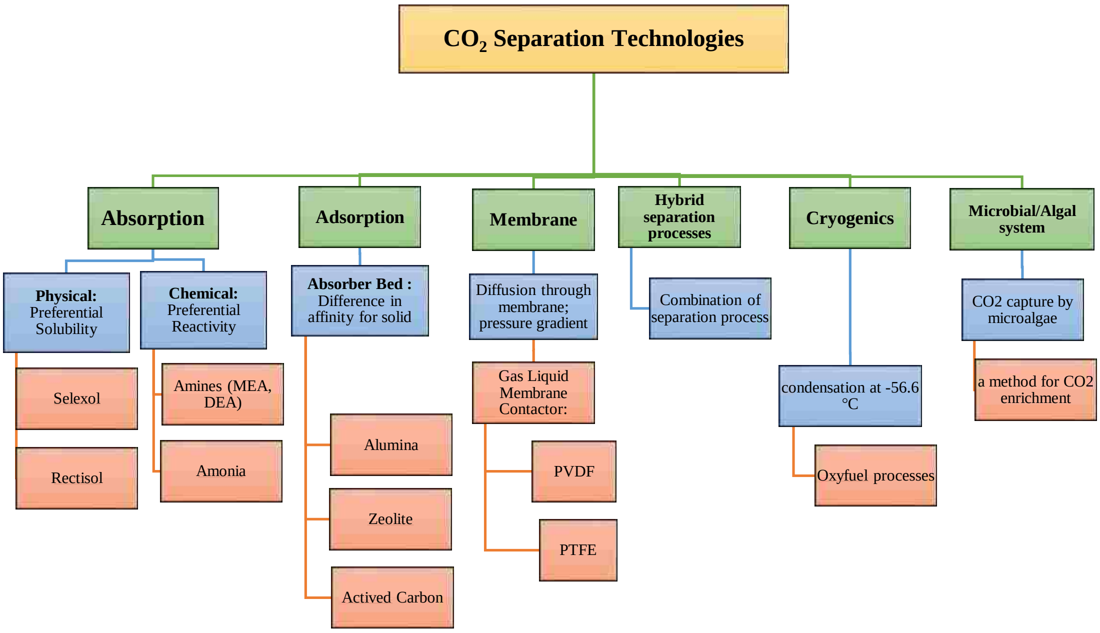

Figure 2: The availably technology for CO_2 capture

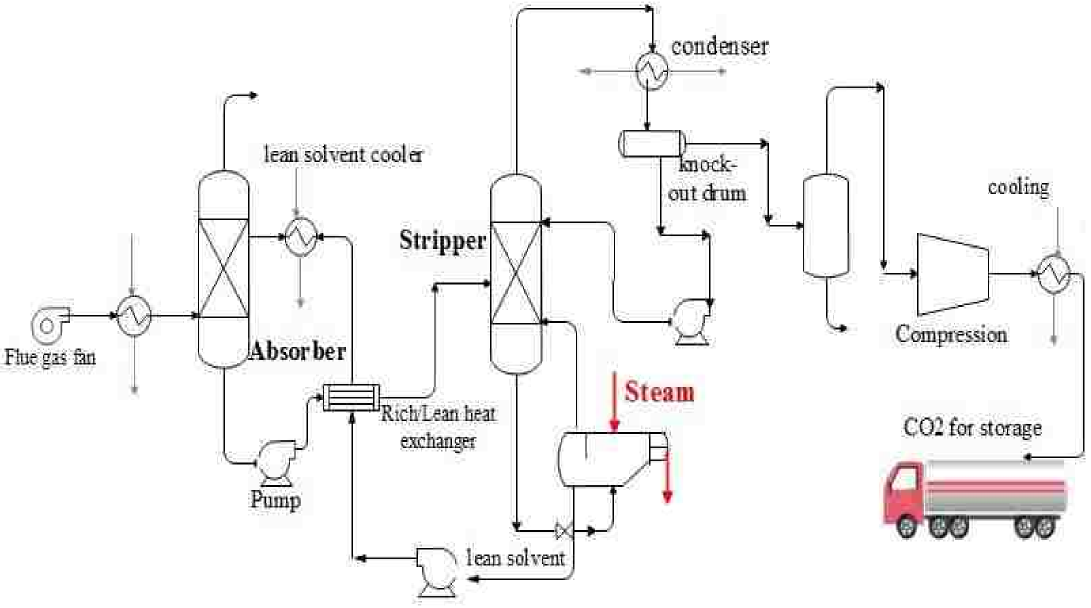

Figure 3: Common carbon capture process from flue gas

2.2 Post-combustion separation technologies

Post-combustion capture has been employed along with various separation technologies. This may include; (a) adsorption, (b) physical absorption; (c) chemical absorption, (d) cryogenics separation, (e) Microbial/Algal system and (f) membranes (M. Wang et al., 2011).

2.2.1 Adsorption process

Physical adsorption processes deal with gas, liquid and solid surface. Adsorbents like alumina, active carbon and metallic oxide can be used for CO_2 removal. These absorbents can be regenerated by pressure reduction (PSA: pressure swing adsorption) and application of heat (TSA: temperature swing adsorption) (M. Wang et al., 2011). In CO_2 capture, adsorption processes can be defined as the selective removal and adhesion of the component in the feed gas to the solid surface (Yang, 2013). Adsorption process has many advantages such as being simple to operate, easy to handle (as it exists in a solid form) and safe for the environment. Moreover, the regeneration part consumes less energy (Huang, Yang, Chinn, & Munson, 2003). However, nowadays physical adsorption may not be a good candidate for large scale applications for flue gas treatment. This is because most available adsorbents suffer from low adsorption capacity and selectivity. In addition, they need high CO_2 concentration to have a flue gas treated (M. Wang et al., 2011).

2.2.2 Absorption process

A wide range of commercial physical and chemical processes are available for CO_2 absorption.

2.2.2.1 Physical absorption process

Physical absorptions are processes at which the solvent only interacts physically with the dissolved gas. In these processes, the solvent is used as an absorbent with thermodynamic properties such that the relative absorption of CO_2 is more favored over the other components of the gas mixture (Shimekit & Hilmi, 2012). The operation of physical absorption of CO_2 by solvent is based on Henry's law. It needs low temperature and high pressure to absorb CO_2, on the other hand, to desorb the CO_2, temperature needs to be increased along with a reduction in the pressure. High CO_2 partial pressure is required for physical absorption processes. since pressurization flue gas consumes significant amount of energy, physical absorption may not be a good candidate for cases where the partial pressure of the CO_2 is less than 15% vol. (M. Wang et al., 2011). The absorption process usually takes place in counter current tower with the gas ascending and liquid turning upside down. The internals of tower are filled and packed by fitted trays as per our requirement to contact liquid and gas. Purisol, Rectisol and Selexol are the most common physical solvents (Rufford et al., 2012).

2.2.2.2 Chemical absorption process

Chemical absorption process is a well-established method for CO_2 separation in conventional towers by using alkanolamines solutions such as Monoethanolamine (MEA), Diethanolamine (DEA), N-methyldiethanolamine (MDEA) and 2-amino-2-methyl-1-propanol (AMP) (Mehdipour et al., 2014). The process consists of chemical reaction of CO_2 with the solvent to build a bonded component. Regeneration of solvent obtained from the CO_2 stream can be done by applying heat. Chemical absorption might be more promising in the CO_2 capture for industrial flue gases as long as the selectivity is high to produce pure CO_2 streams (M. Wang et al., 2011). The main concern in the design of a chemical absorption process is selecting the suitable solvent. Alkanolamines are the most common solvent used to capture CO_2 due to their high flexibility and CO_2 removal capability. Although these are widely available in industry they consume significant amount of energy for regeneration proposes which may cause thermal degradation. Ammonia as a cheap and widely available solvent is a good candidate that can overcome some of these issues (Mehdipour et al., 2014).

Chemical absorption processes may also cause corrosion in the separation units. Chemical solvents might also react with some corrosion inhibitors which ultimately results in reduction of CO_2 solvent loading. In this case, injection of antifoaming agents might be required to reduce the surface tension of the solvent and to ensure better contact between the solvent and the CO_2. Since the regenerated solution leaving the stripper is at its saturated temperature and it partially vaporizes in the suction pump, it might result in vibration and excessive wear of the pump impellers. Moreover, while all of the solvents cannot be recycled back to the absorber column, the disposal of the solvents causes environmental hazards and thus showed the common disadvantages of using the absorption process (Shimekit & Hilmi, 2012).

2.2.3 Cryogenics separation

Cryogenics separation is a process to separate CO_2 from flue gas streams by condensation at -56.6 °C. It is also well known as a low temperature distillation. This physical process is suitable for treating the flue gases with high concentration of CO_2 by considering the cost of refrigeration. Cryogenic process is normally used for purification of the gas mixture and capturing the CO_2 for Oxyfuel processes (M. Wang et al., 2011).

The major advantage of this process is the ability to purify and liquefy the gas stream with high concentration of CO_2 at low temperature to produce the liquid CO_2 in transportation purpose by pipeline. Since there is no chemical added, compression is not required. There are also some disadvantages in cryogenic method such as relatively high energy consumption for refrigeration, and the need to separate the water before any process to avoid blockages.

2.2.4 Microbial/Algal system

Biological capture of CO_2 by microalgae has attracted significant attention as an alternative strategy. Efficiency of microorganisms to CO_2 removal using solar energy has gained huge momentum than agrarian plants by almost 10 times greater. Some advantages of this process can be defined as: (1) direct use of solar energy (2) being environmental friendly (3) providing biomass material for human use such as: medical drugs, cosmetic, human food, biofuels (Pires, Alvim-Ferraz, Martins, & Simões, 2012). Capture of CO_2 from the air by microalgae cultivation can reduce the amount of CO_2, it is also more economic, and no regeneration is needed. This separation method may be located at any site and can be considered as a method for CO_2 enrichment (Rahaman, Cheng, Xu, Zhang, & Chen, 2011).

2.2.5 Hybrid separation processes

Hybrid separation process is an integration of one basic process with another. Usually, separation processes are composed of a single unit that can be either chemical or physical joint with the basic separation process. Since the two processes are combined, the efficiency of separation can be increased by overcoming the limitation in individual units. Combination of separation process with membrane and other processes is the most common hybrid separation process in the industry. It has been reported that the results of membrane-amine hybrid systems are much more promising in the economical aspects rather than the single system of membrane or single processes of amine (Shimekit & Hilmi, 2012).

2.2.6 Membrane contactors

Membrane contactor process became very popular during 1980s due to the several disadvantages of traditional processes. Membrane technology is widely available in gas separation processes (Mulder, 1996). Initially, specific non-porous polymer membranes were applied in gas separation processes, and then they were combined with conventional gas absorption processes. The combination of using conventional absorption process with selective membrane technology was then called gas liquid membrane contactor (GLMC). Gas liquid membrane contactor can easily overcome the problems that come from conventional methods. The physical barrier between gas and liquid in GLMC can overcome the problems of channeling, weeping, foaming, and entrainment. This physical barrier would prevent the mixing of the two different phases (M. Wang et al., 2011).

GLMC has been studied on many articles and there are many researches that were conducted to study a suitable configuration of membrane contactor. The major aim of these studies was to maintain the phases at different sides of the membrane. Mass transfer occurs at the interface by diffusion from one side to another. Small pressure drop is required for this diffusion. The overall process can be define in three steps: (1) transferring the solute gas from bulk gas phase to the gas-membrane surface (2) transferring the gas through the membrane pores (3) transferring from membrane–liquid interface into bulk of liquid. The main advantages of gas liquid membrane contactor include:

First: the two flow streams are independent and formation emulsion does not occur since dispersion of each fluid in the other one cannot happen. It is more flexible to work at low and high flow rates of liquid and gas where columns are subjected to flooding at high flow rates and unloading at low flow rate. Second: the other advantage that makes membrane contactors very popular among other contactors is the fact that there is a constant and large gas-liquid interfacial area which allows the performance to be more predictable. Third: it is easy to scale up and down. Fourth: low solvent hold up. Fifth: while there are some mechanically agitated by dispersing phase in columns, membrane contactor are free of moving parts (Al-Marzouqi, Marzouk, El-Naas, & Abdullatif, 2009).The efficiency of gas separation is determined by selectivity, membrane porosity and permeability of the membrane material.

Based on the pore structure, membranes may be classified into: porous, nonporous and asymmetric.

I. Porous membrane: permeate (absorption liquid) and membrane property (pore size and pore distribution) are the main factors in separation of gas mixture by porous membrane. A porous membrane is rigid and the pores are inter-connected. Porous membranes give a very high level of flux (rate of transport of the gases) but provide less selectivity (separation of gas from a mixture).

II. Non-porous membrane: separation of gas mixture by non-porous membrane occurred when there is a difference in diffusivity and solubility of gas molecules, therefore, selectivity and permeability is intrinsic properties of membrane material. Although the non-porous membranes offer high selectivity (separation of gas from a mixture), they give low flux.

III. Asymmetric membrane: asymmetric membranes consist of two structural layer: a thick and porous matrix layer which physically supports the skin, and a thin layer with dense selective skin. This combination brings the advantages of both porous and non-porous membranes (Mulder, 2000).

There are many open literature sources available to compare the separation processes of the gas streams. Table 1 shows a general comparison in advantages and disadvantage for separation processes. The main focus of this thesis is to work with porous membranes that are specifically fabricated for purpose of CO_2 absorption/stripping, therefore the detail is provided in the following section.

Table 1: General detail in gas separation process (Baker, 2004)

Process	**Advantages**	**Disadvantages**
Absorption	**Matured and widely used technology for efficient % removal of acid gases**	*** Not economical as high partial pressure is needed while using physical absorbents** *** Long time requirement for purifying acid gas as low pressure is needed while using chemical solvents**
Adsorption	*** High purity of products can be achieved** *** Ease of adsorbent relocation to remote fields when * equipment size becomes a concern**	*** Recovery of product is lower** *** Relatively single pure product**
Membrane	*** Simplicity, veracity, low capital investment and operation** *** Stability at high pressure and High recovery of products** *** Good weight and space efficiency and Less environmental impact**	*** Recompression of permeate** *** Moderate purity**
Cryogenic	*** Relatively high recovery compared to other processes** *** Relatively high purity products**	*** Highly energy intensive for regeneration** *** Not economical to scale down to very small size**

2.3 Gas liquid membrane contactor separation system

Gas liquid membrane contactor (GLMC) is a well-known device for CO_2 capturing and regeneration which allows liquid and gas to have a direct contact without dispersing one phase in another for mass transfer purposes. The pores of the membrane act as a fixed barrier interface between these two phases. The separation process is a transfer of one or more components from the gas phase into the liquid phase. Liquid and gas phases are kept away from each other and small pressure drop is required for the mass transfer to occur (Naim, Ismail, & Mansourizadeh, 2012).

For the case of CO_2/N_2 separation shown in Figure 4, the CO_2 molecules diffuse from feed gas through the membrane porous media into the liquid absorbent.

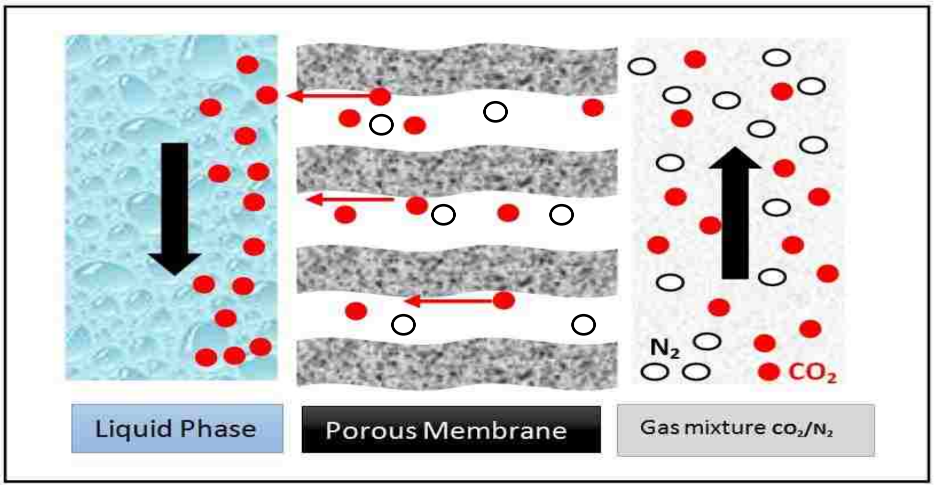

Figure 4: Schematic of CO_2 absorption through gas–liquid membrane contactor

Absorption process is categorized into physical and chemical processes. In a physical absorption process, gas component is physically dissolved, where in the chemical process, gas component reacts with the liquid phase. In order to design a GLMC using either physical or chemical absorption, details about solubilities and diffusivities of gas component need to be considered along with the reaction rates.

GLMC is a combination of absorption process and membrane technology which offers several advantages over the other conventional methods such as loading, weeping, flooding and foaming by having an independent control of gas and liquid flow rate and high surface per unit contactor. Due to these advantages, GLMC is commonly applied in the removal of acid gases from flue gas, natural gas and various gas streams of industrial processes (Amir Mansourizadeh, 2012).

The microporous GLMC device using hydrophobic flat Gore-Tex membrane of PTFE (Polytetrafluoroethylene) has been used for oxygenation of blood. The prepared PVDF (Polyvinylidenefluoride) is being applied for CO_2 capturing from gas streams (A. Mansourizadeh & Ismail, 2009). Beside the absorption, GLMC can also be a good candidate for desorption or regeneration of liquid absorbent. Basic mechanism of CO2 stripping through gas–liquid membrane contactor is shown in Figure 5.

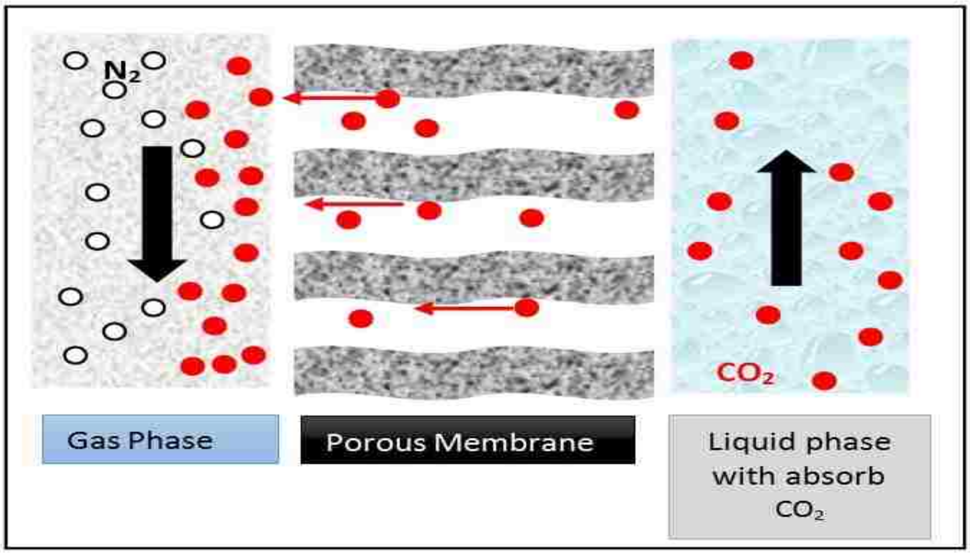

Figure 5: Basic schematic of CO_2 stripping by GLMC

In order to describe mass transfer process in GLMC, resistance in series model for Gas-Liquid system has been used. Figure 6 shows the cross section of hollow fiber membrane and Figure 7 is a schematic presentation of the overall mass transfer in GLMC along with resistances in GLMC system.

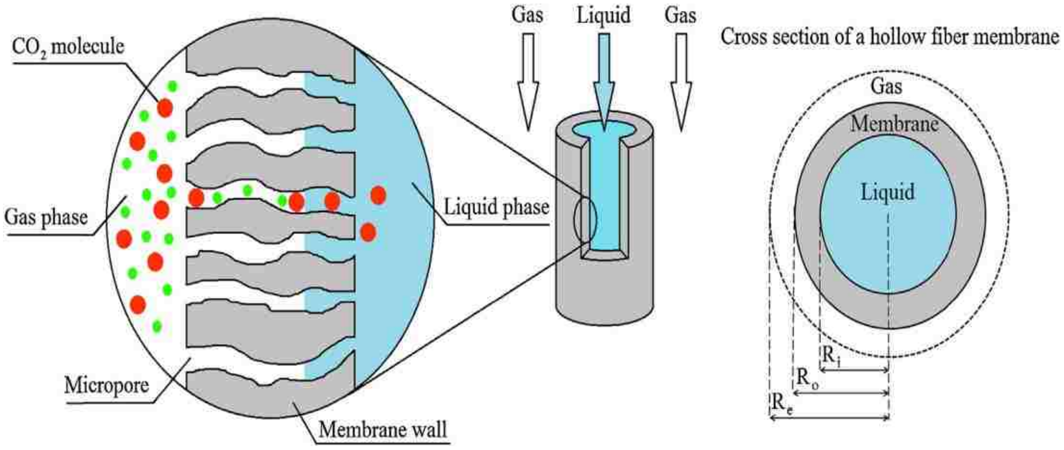

Figure 6: Schematic of cross section and mass transfer in GLMC (Mehdipour et al., 2014)

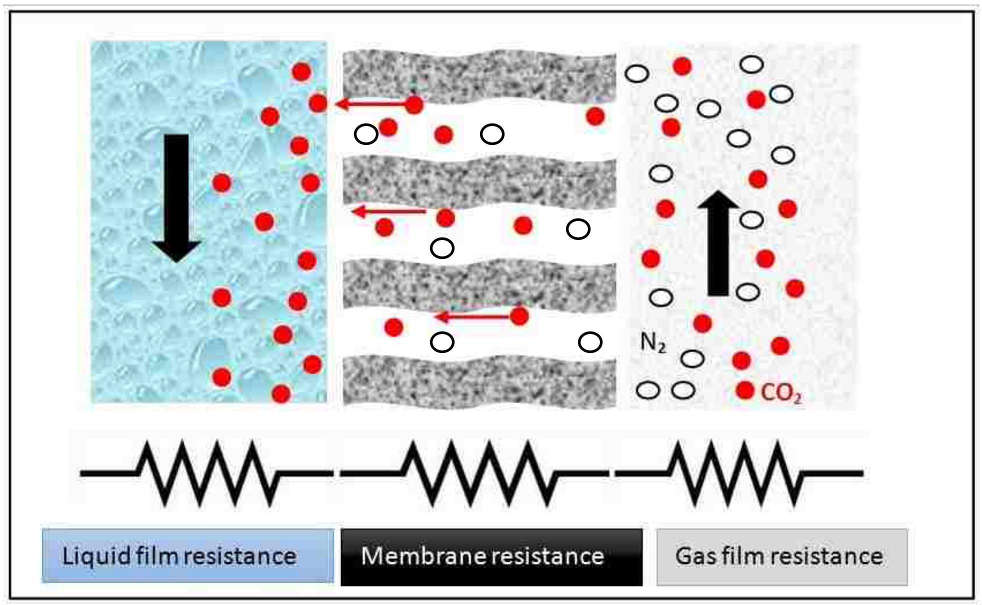

Figure 7: Overall mass transfer resistance in membrane hollow fiber contactor

Overall mass transfer resistance includes 3 resistances in series:

1. Gas phase resistance (1/ K_G)

2. Liquid phase resistance (1/ K_L)

3. Membrane resistance (1 / K_M)

$$J = K_{OG} (C_1 - C_2)$$

Where J is the flux, C_1 is the inlet concentration, C_2 is outlet concentration and K_{OG} is overall mass transfer with:

$$\frac{1}{K_{OG}} = \frac{d_o}{K_G\, d_i} + \frac{d_o}{K_M\, d_{lm}} + \frac{1}{m\, K_L}$$

K_G is the gas side mass transfer coefficient (m/s); K_M is the membrane mass transfer coefficient (m/s); K_L is the liquid phase mass transfer coefficient (m/s); d_o is the outer diameter of hollow fiber membrane (m); d_i is the inner diameter of hollow fiber membrane (m); d_{lm} is logarithmic mean diameter (m) and m is the distribution coefficient between gas and liquid phases (–). The individual mass transfer coefficients, K_G and K_L, are mainly determined by the geometry and flow conditions in the membrane contactor and the various correlations available (Mosadegh-Sedghi, Rodrigue, Brisson, & Iliuta, 2014).

2.4 Limitation and prevention - wetting mode

Membrane mass transfer resistance is directly related to wetting and it is contributes the most among other resistances. Wettability is mainly determined by membrane and absorbent properties and operating conditions. This would result in following modes; non-wet, partial wet and fully wet mode.

Figures 8, 9 and 10 show respectively the schematic of the non-wet, fully-wet and partially-wet modes in GLMC systems.

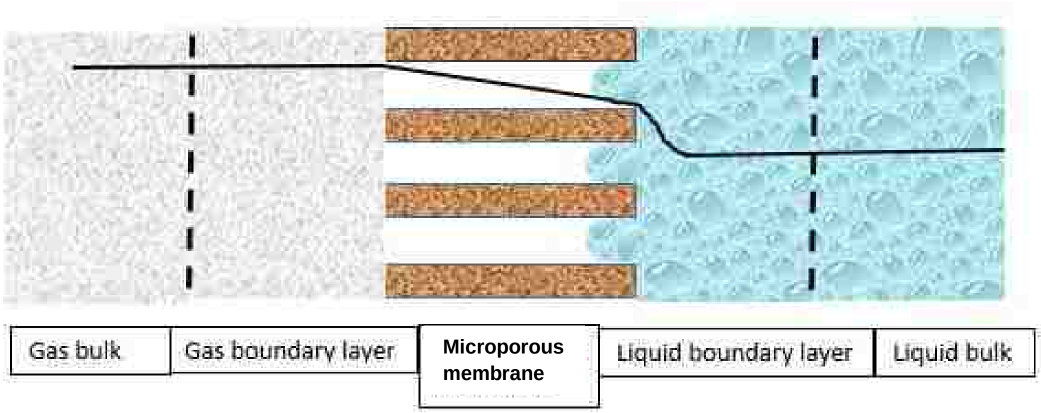

Figure 8: Non-wetting patterns (Mosadegh-Sedghi et al., 2014)

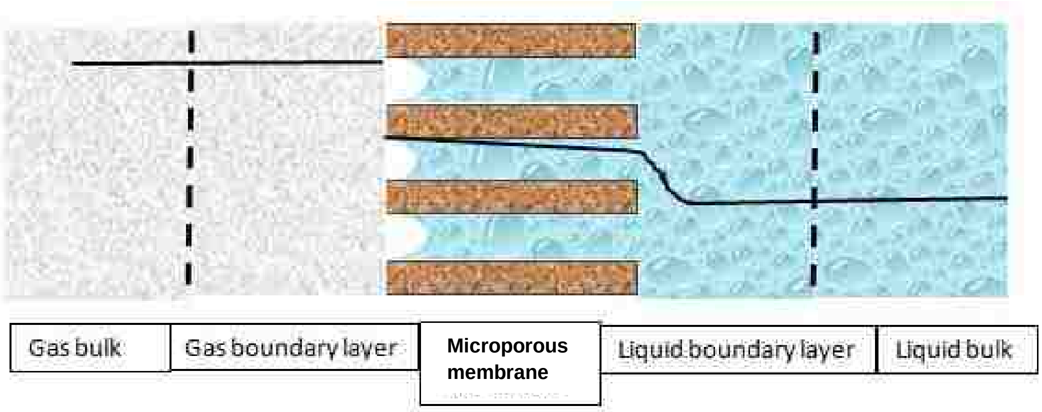

Figure 9: Overall wetting mode (Mosadegh-Sedghi et al., 2014)

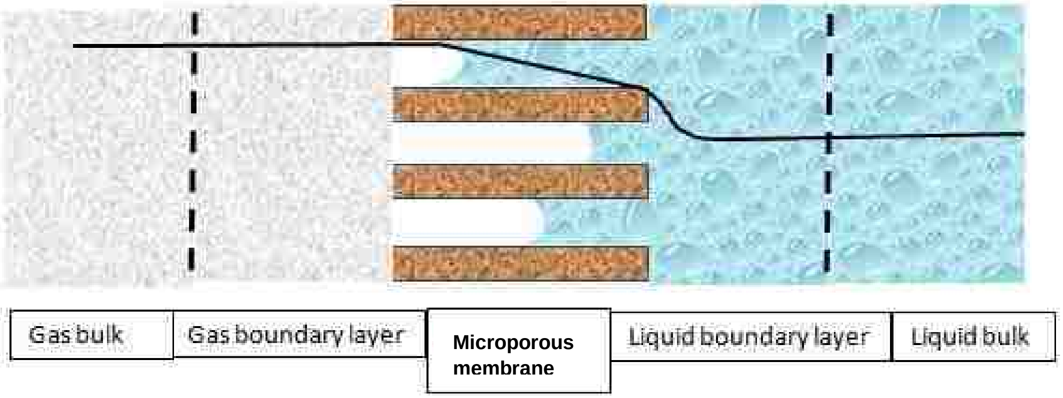

Figure 10: Partial-wetting mode (Mosadegh-Sedghi et al., 2014)

For highly hydrophilic membranes, non-wetted mode theoretically applies when all the pores are filled with gas. However, this phenomenon can be never observed in the practice. For membranes with low hydrophobicity, the pores are filled with liquid absorbent as shown in Figure 9, while in reality, the membrane pores are partially wetted with absorbent which can reduce the mass transfer coefficient (Mosadegh-Sedghi et al., 2014). As an example reported by Mansourizadeh & Mousavian, (2013), after 10 hours of running the experiment, there was a 26% reduction of the absorption flux when PVDF membrane contactor and DEA was used. In addition, A. Mansourizadeh, Ismail, & Matsuura, (2010) reported that after 150 hours of operation, the absorption flux was reduced by 23% in chemical (NaOH) and 30% in physical (water) when PVDF membrane contracture was used.

The minimum pressure required to make the membrane wet is called breakthrough pressure and it is defined as an entry pressure. It can be measured by observing the formation of first liquid drop on the other side of the membrane. For cylindrical pores by Laplace-young equation we have:

$$\Delta \mathrm{P} = \frac{2\ \sigma_{\mathrm{L}} \cos \Theta}{r_p}$$

Where σ_L, θ and r_P represent, respectively, the interfacial surface tension between the fluids, the contact angle between the liquid phase and the membrane, and the maximum membrane pore radius. However, most membranes do not have the cylindrical pores.

As per Laplace equation, the breakthrough pressure can be increased using membranes with smaller pore size and reducing the contact angle. Using a liquid with suitable surface tension and membrane with hydrophobic surface to have a large contact angle, can prevent a wetting on absorption process in membrane contactor (Mosadegh-Sedghi et al., 2014).

In general there are many factors that affect the mass transfer, by considering their categories along their specific wetting phase.

Here are some approaches that can be followed to prevent wetting of the membrane:

I. Surface modification of the membrane: hydrophobic modification in surface of membrane can result in having a non-wet membrane. A good example may be coating the membrane with very small permeable thin layer.
II. Using hydrophobic membrane: this will lead to large contact angles, and therefore reducing the chance of wetting.
III. Selection of denser membrane: although denser hollow fiber membrane offers a non-wet mode, it also provides greater flexibility in the pressure of the feed gas.
IV. Selection of the most suitable absorbent with surface tension: liquids with lower surface tension have a higher potential to leak through the porous membrane.
V. Optimization of operation conditions: mass transfer coefficient and wettabelity depend on several factors such as gas-liquid system, type of membrane and operation conditions like pressure, temperature (Li & Chen, 2005a).

2.5 Preparing and fabricating of GLMC membrane

Selection of the membrane material has a direct effect on absorption and chemical stability and therefore, it is the main part of GLMC fabricating. Membrane materials can be organic or inorganic. Inorganic (polymeric) materials may give better chemical and thermal stability and higher mechanical strength. Although ceramic materials for membrane are good candidates, their hydrophilic property may cause wetting of the membrane (A. Mansourizadeh & Ismail, 2009).

2.5.1 Characteristic of membrane

Since microporous membrane technology can offer large contact area per volume, from last decades it become most popular for gas separating rather than its conventional technique. Microporous membranes reduce 63%-65% of the size of gas absorber and stripping units. Table 2 shows the specific surface area for the common contactors used in separation processes (A. Mansourizadeh & Ismail, 2009).

Table 2: Specific surface area (m^2/m^3) (A. Mansourizadeh & Ismail, 2009)

contactor	specific surface are (m^2/m^3)
Free dispersion column	1-10
Mechanically agitated column	50-150
Packed column	100-800
Membrane contactor	1500-3000

Generally, various structures of membrane can result in different removal efficiencies. Therefore, characteristics of membrane are important in preparing the membrane. Nowadays, asymmetric membranes with very thin layer or symmetric hydrophobic porous membrane are used in GLMC process. Moreover the polymeric materials with high porosity are more popular. The common membrane characteristics are presented in Table 3 (A. Mansourizadeh & Ismail, 2009).

Table 3: Common membrane characteristics (A. Mansourizadeh & Ismail, 2009)

membrane type	OD (µm)	ID (µm)	pore size (µm)	porosity %	purpose
Polyethylene(PE)	706	482	-	82	CO_2 absorption with MEA solution
PP	300	270	0.015	30	CO_2 absorption with water, DEA and NAOH solutions
pp	442	344	0.02 - 0.2	> 45	CO_2 absorption with PG, MEA and MDEA solutions
pp	1000	600	0.265	79	CO_2 absorption with CORAL 20 solution
PVDF	907	607	0.04	-	H_2S and CO_2 absorption with Na_2CO_3 solution
Polytetrafluoroethylene (PTFE)	1700	1000	-	40	CO_2 absorption with MEA solution

2.5.2 Material selection of polymeric membrane

Among the various hydrophobic polymers, PP (polypropylene), PE (polyethylene) and PTFE (polytetrafluoroethylene) are the most popular membrane materials. PTFE is a good candidate because of its high resistance to wetting after several hours of running the experiment as well as being suitable for alkanolamine (Falk-Pedersen & Dannström, 1997). Recent studies show that PVDF has an excellent chemical and thermal resistance many of those justify the suitability of PVDF for alkanolamine applications. PVDFs have became more popular since they can be dissolved in organic solvents which makes them easy to prepare by phase-inversion method (Amir Mansourizadeh, 2012) (Rahim, Ghasem, & Al-Marzouqi, 2015) (Zhao et al., 2016) (Jampol'skij & Freeman, 2010).

To select a suitable membrane material, it is important to consider parameters such as wetting and long term stability. Likewise, since there are reactions between solvent and membrane, the chemical stability of membrane is relatively important. Since the process tends to operate at high temperature, thermal stability of membrane needs to be considered to avoid decomposition and degradation. The values of T_g (glass transition temperature of fiber) and T_m (melting point of crystalline polymer) can be used as parameters to define the nature of the membrane (A. Mansourizadeh & Ismail, 2009). Glass transition temperature for the common fibers used in membrane gas absorption are shown in Table 4 (Li & Chen, 2005a).

Table 4: Glass transition temperature for common fiber

Polymer	**Tg (◦C)**
Polytetrafluoroethylene	126
Polypropylene	-15
Polyethylene	-120
Polyether sulfone	230
Polysulfone	190
Polyvinilydenfluoride	-40
Polyimide(Kapton)	300

In general, the increase in T_g/T_m and crystallinity of membrane can enhance both thermal and chemical stability. H_2S separation from natural gas takes place in ambient temperature; therefore a moderate T_g is required for selection of membrane polymer. In contrast, for CO_2 removal from flue gas streams, separation takes place in higher temperature and thus requires membranes with higher T_g (above 100 °C) values. Fluorinated polymers may be potential candidates due to their chemical stability and hydrophobic porous nature (A. Mansourizadeh & Ismail, 2009).

Table 5 briefly presents the wetting possibility and its reason for the most common fibers (Li & Chen, 2005a).

Table 5: Wetting possibility for common fibers

Membrane	Absorption Liquid	Wettability	Cause of Wetting
PTFE	Aqueous MEA	+	Hydrophobicity of PTFE is not enough
PTFE	Aqueous amines	-	
PTFE	Aqueous MEA	+	Larger pore size of PTFE
PTFE	Aqueous KOH solutions	-	
PE	Aqueous MEA	+	Hydrophobicity of PE is not enough
PP	Aqueous NAOH solutions	+	Possible modification of pores by trace impurities and ionic species
PP	Aqueous alkanolamines	-	
pp	Aqueous amino acid salt solutions	-	
PP	Water, aqueous NAOH, Aqueous MEA	+	Not given, but possibly due to low surface tension of MEA, insufficient hydrophobicity and chemical instability of membrane
PP	Aqueous amines solutions	+	Cause of wetting was not given; PTFE is more chemically stable
PP	Aqueous NAOH solutions	-	
pp	Aqueous MDEA	+	Possibly the low surface tension of aqueous MDEA

2.5.3 Process of fabrication in polymeric porous membrane

In producing the porous membranes, materials are specifically selected to fulfill high chemical and thermal stabilities. There are various techniques for preparation of microporous membranes such as stretching, sintering, phase inversion and track-etching. Depending on the characteristics of the membrane required, the most suitable fabrication process is then selected (Drioli, Criscuoli, & Curcio, 2011).

The most common approaches for membrane fabrication are explained in the following sections:

2.5.3.1 Phase inversion

Phase inversion is a method to prepare porous and non-porous homogeneous polymer solutions which are transferred in control manner from liquid to solid. This transformation can be achieved by several ways:

a. Immersion precipitation: solution of polymer is immersed in coagulation bath (mostly water) which is non-solvent. Since there is an exchange in polymer solvent and non-solvent coagulation bath, precipitation and demixing occur.
b. Evaporation induced phase separation: the process is known as solution casting method. In this process polymer solution is dissolved into the solvent or a mixture of volatile non-solvent. The solvent is then allowed to be evaporated, therefore demixing and precipitation occur.
c. Vapor-induced phase separation: the polymer solution is exposed to atmosphere containing a non-solvent (mostly water). Demixing and precipitation occur since there is absorption and penetration of non-solvent.
d. Thermally induced phase separation (TIPS): the homogeneous solution is prepared by dissolving a polymer with a high boiling point into low molecular weight diluents. In this method quality of solvent usually decrease, by reducing the temperature. Once the precipitation and demixing occurred, solvent can be removed by evaporation, extraction or freeze drying.

2.5.3.2 Stretching

In this process, the polymer is heated to above the melting point and then extruded into thin sheets. The sheets are then made porous by means of stretching. Stretching is done in two steps; cold and hot stretching. First step (cold stretching) is used to nucleate the micro porous in pioneer film. The second step (hot stretching) is to control and increase the final pore structure of membrane. The main controlling parameter of porous structure is the physical properties of material such as melting point, crystallinity and conditions at which the process was applied. This technique is suitable for highly crystalline polymers (Lalia, Kochkodan, Hashaikeh, & Hilal, 2013).

2.5.3.3 Sintering

Sintering is a common and well known process for commercial production of symmetric membranes such as PP and PTFE. In this method, low solubility of solvent is required. The process includes particles with known compressed size that are then sintered at high temperature. While sintering, the particles contact each other and form the interface of the membrane pores.

2.5.3.4 Track-etching

The Track-etching is mainly used to fabricate PVDF. In this technique, foil or polymer film are subjected to high energy particles (metal ion) that are perpendicularly applied to the material. The process is then followed by etching alkaline bath or acid, therefore, cylindrical pores with homogeneously distributed pore sizes are shaped. Temperature and etching time are the main parameters used to determine the pore size and porosity during the preparation of the membrane (Liu, Hashim, Liu, Abed, & Li, 2011). This process is popular for its accurate control over the pore size distribution of the membrane which provides low porosity (almost 15%) and pore density (6 ×108 cm^{-2} for 50 nm and 2 ×107 cm^{-2} for 1 µm).

2.5.3.5 Electrospining

Electrospining is one of the most common techniques to fabricate porous membrane for the purposes of desalination and filtration. In this method, a high potential electric current is applied between a polymer solution droplet and a grounded collector. A charged liquid jet called ‘taylor cone’ is formed, once the electrostatic potential becomes sufficient enough to overcome the surface tension of the droplet (Lalia et al., 2013) as shown in Figure 11:

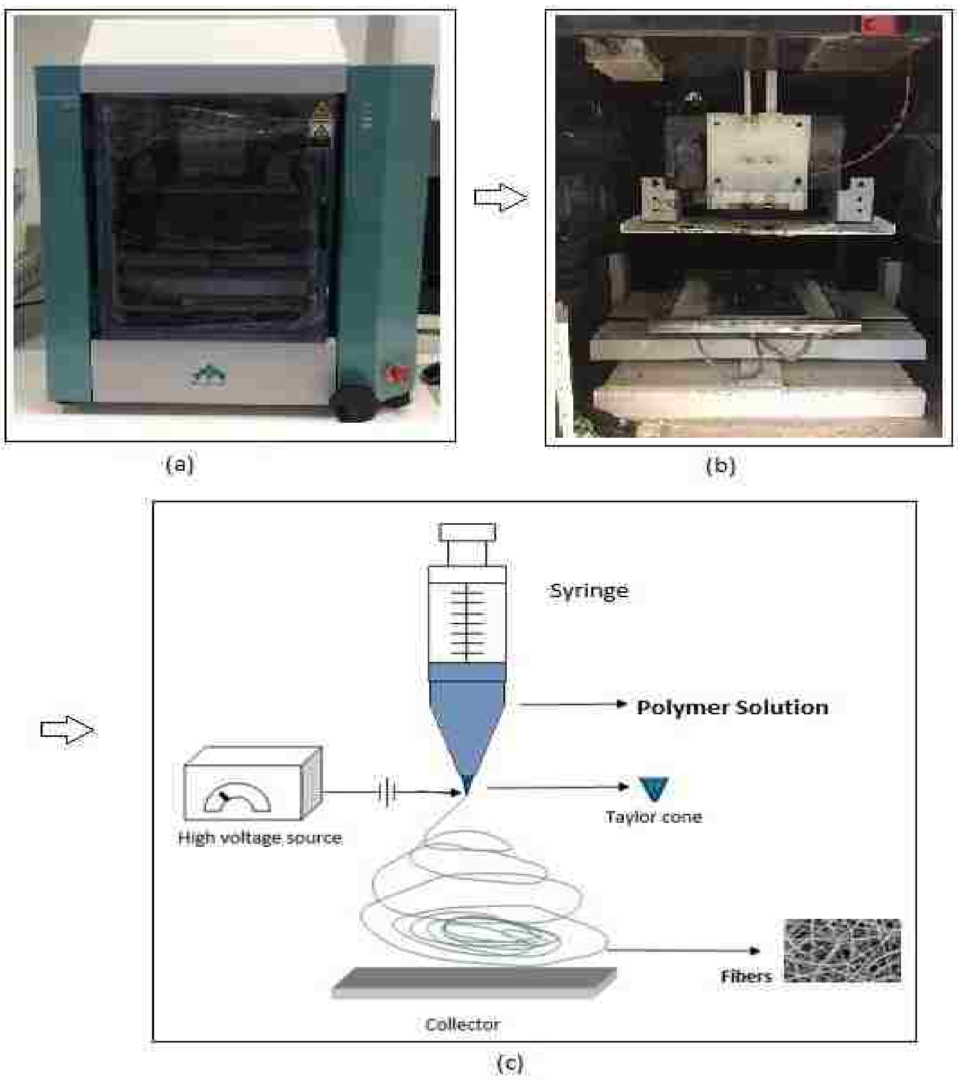

Figure 11: Schematic drawing of electrospining technique

In this technique, parameters like polymer concentration, composition of the coagulation bath, temperature and type of solvent significantly affect the membrane morphology.

2.6 Common liquid absorbents used in membrane contactor process

The absorption process is categorized into physical and chemical absorption. For the physical absorption, the gas component is physically dissolved in the liquid absorbent, while in the chemical absorption, gas components react chemically with a liquid. In order to design an absorber system, detailed knowledge of both physical and chemical behavior of the absorption process such as diffusivities, solubility of gas component and reaction rate are crucial.

Researchers have studied and tested various liquid absorbents in such membrane process technique. The criteria mentioned below, make solvents more suitable for the separation process:

I. High reactivity with CO_2: This provides a higher flux and absorption rate of the process. The resistance in liquid phase can be negligible because of chemical reaction.
II. Chemical compatibility: Due to the reaction between the membrane and the chemical solvent, the liquid absorbent must have compatibility with the membrane material to avoid wetting. This undesirable reaction might change the surface and structure of the fiber, and lead to the reduction of breakthrough pressure.
III. Surface tension: A higher surface tension prevents the wetting phenomenon.
IV. Thermal stability: An optimal thermal stability lowers the risk of thermal degradation.

V. Vapor pressure: Higher vapor pressure facilitates volatile solvents that penetrate through the pores of the membrane into the gas phase resulting in higher mass transfer resistance.

VI. Regeneration: Energy consumption required for the regeneration of liquid absorbents are proportionally related to the cost effectiveness of a project (Li & Chen, 2005a).

Absorption flux and removal efficiency in a chemical is higher than physical absorption for gas-liquid membrane contactors; therefore our study is more focused on common chemical absorbents.

2.6.1 Ammonia based solvent

Ammonia is relatively affordable and widely available in commercial industries. Ammonia, owing to its lower molecular weight, lower heat of reaction in absorption process and low energy consumption in regeneration process, provides high CO_2 absorption capacity compared to other solvents. In general, it is not as corrosive as MEA. Wang et al (2011) reported that CAP (Chilled Ammonia Process) at low temperature is a developed process of CO_2 absorption. Due to the high volatility of ammonia, a lower applied temperature would prevent loss of the solvent. Stripping operation temperature is mostly between 100-150 °C and operation pressure is between 2 to 136 atm. Energy consumption in ammonia-based processes is significantly lower than MEA-based solvents (M. Wang et al., 2011). Despite the series of middle reaction for aqueous ammonia with CO_2, the total reaction of ammonia and CO_2 can be described as:

$$NH_3 + H_2O + CO_2 \longrightarrow NH_4HCO_3$$

The product of ammonia reacting with CO_2 is ammonium carbonate (NH_4HCO_3) and it is a reversible reaction. Regeneration of ammonia is accomplished by applying heat to provide NH_3, H_2O and CO_2. In the scrubbing process, ammonia is not consumed since the NH_3 and H_2O can be recycled back to the process of CO_2 capture and CO_2 will be separated and recovered (Chen et al., 2012).

There are some issues with ammonia-based processes compared to amine-based, including the tendency of the membrane to be wetted by ammonia, thereby affecting mass transfer and causing a reduction in the efficiency of CO_2 removal in the long-term operation (Mosadegh-Sedghi et al., 2014). Since the NH_3 is highly volatile and its vapor pressure is high in both clean flue gas absorber and stream of CO_2 after regeneration, the slip level of ammonia is too high to be released in atmosphere or kept in CO_2 steam. As long as ammonia is highly volatile, it can become gaseous and leave the absorption column with treated gas. Another issue is the lower absorption rate of CO_2 in the ammonia absorbent liquid as compared to amine-based processes (Gale et al., 2011). Figure 12 shows the chemical structure of ammonia.

2.6.2 Amine based solvent

Treatment of industrial gas stream with alkanolamine has been used since almost 75 years ago. Based on the degree of substitution of nitrogen atoms and reaction with CO_2, amines are categorized into primary, secondary and tertiary. Different types of amine have different reaction mechanisms and kinetics. The chemical structure of amine determines the capability of CO_2 reaction and absorption (M. Wang et al., 2011).

Figure 12 shows the chemical structure of ammonia and the three types of primary, secondary and tertiary amine.

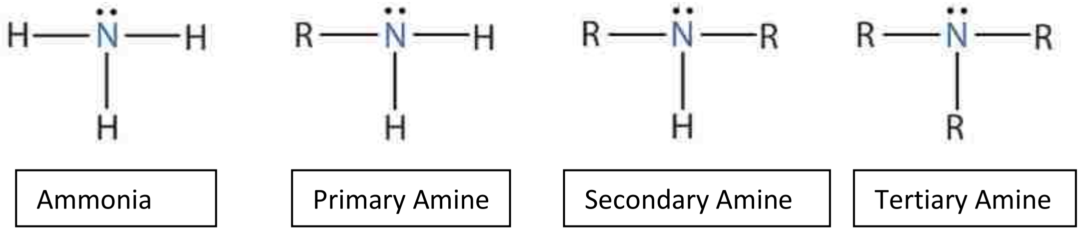

Figure 12: Shemical structure of ammonia and primary, secondary and tertiary amine

Primary and secondary alkanolamines react rapidly with CO_2 and form carbamates, while the reaction rate for tertiary alkanolamine with CO_2 is slow. Since tertiary alkanolamine do not have any hydrogen atom attached to the nitrogen, once they react, they become bicarbonates. Carbamates needs higher heat of reaction than bicarbonates. There is always a mix of tertiary with primary and secondary to reduce the cost of regeneration like MDEA. Sterically hindered amine is identified as a form of amine with a combination of primary and secondary amines attached to the tertiary carbon atom, in order to minimize the cost of regeneration. An example is 2-amino-2-methyl-1-proponol and 2-priperdineethanol (M. Wang et al., 2011).

In general, less corrosive and lower heat of regeneration is the advantages of secondary amines over primary amines. Tertiary amines are an alternative which is very beneficial to primary and secondary CO_2 bulk removal, due to having the lowest regeneration cost in heating, and low corrosive property (R. Wang, Li, & Liang, 2004).

Reaction mechanism in amine based

The purpose of this study is to work on amine-based solvents; therefore, our focus is centered on amine solutions, for the absorption and stripping processes.

a. Reaction mechanism in primary and secondary amine

The overall reaction of primary and secondary amines (R_1R_2NH) with CO_2 is described by the Zwitterion mechanism in 2 steps: firstly, the formation of an intermediate in Zwitterion by reaction between CO_2 and the amine, which is a reaction determination.

$$CO_2 + R_1R_2NH \overset{Zwitterion}{\Longleftrightarrow} R_1R_2^{+}NH + CO_2^{-}$$

Then the forming a carbamate ion and deprotonated base:

$$B + R_1R_2NH + CO_2^{-} \overset{carbamate}{\Longleftrightarrow} R_1R_2N\,CO_2^{-} + BH^{+}$$

$$R_1R_2NCOO^{-} \Leftrightarrow R_1R_2NH + HCO_3^{-}$$

$$HCO_3^{-} \Leftrightarrow CO_2 + OH^{-}$$

Assume Quasi-steady state , where B is a sign of H_2O, OH^{-} in aqueous solution (R. Wang et al., 2004). According to the pseudo-steady-state condition on Zwitterion, the reaction rate between CO_2 and amines is first order in amine, and first order in CO_2. The overall forward reaction can be defined as:

$$R_{CO_2} = \frac{K_2[CO_2][R_1R_2NH]}{1 + \left(\frac{K_{-1}}{K_{H_2O}[H_2O]}\right) + \left(\frac{K_{-1}}{K_{OH^-}[OH^-]}\right) + \left(\frac{K_{-1}}{K_{R_1R_2NH.}[R_1R_2NH]}\right)}$$

Where, $R_{CO_2}$is the rate of CO_2 reaction (mol m^2 s^{-1}), K_{-1} is the reverse first order reaction rate constant (s^{-1}), K_2 is the second order reaction rate constant (s^{-1}).

Since the concentration of OH^- in comparison to H_2O is low, the contribution of OH is negligible (R. Wang et al., 2004). The concentration and steric hindrance of amine are the main factor in determining the reaction rate, therefore the overall reaction rate in steady state approximation is (Kim & Yang, 2000):

$$R_{CO_2} = K_2[CO_2][R_1R_2NH]$$

In addition, under pseudo-first-order conditions with respect to CO_2, when the concentration of DEA is much in excess of that of CO_2, which means that the concentration ratio [DEA]/[CO_2] is at least 10, the reaction rate equation takes the form (Siemieniec, Kierzkowska-Pawlak, & Chacuk, 2011)

$$R_{CO_2} = -K_{ov}[CO_2]$$

Therefore, the observed pseudo-first-order reaction rate constant (k_{OV}) can be obtained by:

$$K_{ov} = \frac{K_2[R_1R_2NH]}{1 + \frac{K_{-1}}{K_{R_1R_2NH}[R_1R_2NH]}}$$

b. Reaction mechanism in tertiary amine

Since it was found that tertiary alkanolamine cannot directly react with CO_2, these amines have base-catalytic effect in the hydration of CO_2. The CO_2 is only physically absorbed, and fulfills the reaction mechanism which was proposed.

$$R_1R_2R_3N + CO_2 + H_2O \longrightarrow R_1R_2R_3NH^+ + HCO_3^-$$

The rate of reaction at low pH (less than 11) are neglected , however there is a direct reaction between CO_2 and tertiary amines at high pH (almost pH=13) (Awais, 2013).

Comparison between alkanolamines

Performance of CO_2 absorption and regeneration was analyzed (Z. Wang, Fang, Pan, Yan, & Luo, 2013) and the result showed that tertiary amine has better desorption or regeneration rate. However, it suffers from lower CO_2 absorption rate in comparison to other primary amines. It is well known that increases in the number of amine will enhance the absorption efficiency, while a substitution of methyl groups or hydroxyl groups to amines groups will improve the CO_2 regeneration.

2.6.3 Amino Acid Salts

Amino acid salts have been used for a long time in acid gas removal, and was recently developed for the purpose of CO_2 capture from the flue gas. It is reported that, the use of amino acid salt in the process of removal will bring 73% reduction in energy consumption compared to conventional MEA process. In addition, potassium salt increases the stability and resistance to degradation in comparison to the MEA processes. Amino acid salts have become more interesting due to their unique advantages such as low volatility, being environmentally friendly, having high resistance in degradation, its biodegradability, and lower energy consumption in the regeneration process. The reaction for amino acid salt with CO_2 is the same as alkanolamine (Dixon et al., 2013).

$$CO_2 + 2R - NH_2 \rightleftharpoons R\text{-}NHCOCO^- + R\text{-}NH_3^+$$

Since amino acid salts are in solid form for the CO_2 absorption process, it is difficult to select it as an alternative solution. Although amino acid salts are more expensive in comparison to alkanolamines, they are more remarkable in the CO_2 capturing process.

2.7 Key factors on design of gas liquid membrane contactor

Membrane contactors have been used and designed historically for filtration duties by the wrong definition that flow must be on the shell side of membrane. However, in the new design of the membrane contactor, flow needs to be on the side of membrane which gives a good mass transfer (Feron & Jansen, 2002). Module configuration is the main factor that relatively affects the mass transfer coefficient. Based on that, a membrane module can be designed by considering the regularity of fiber, packing density, and the relative flow direction (counter-current, co-current and cross-flow of two phases).

2.7.1 Criteria in design of membrane module relative to flow direction

Although structure of membrane porous media and their chemical aspects are important in the design of the membrane, flow pattern, configuration and geometry of module must also be considered. Typical form of module is a bunch of polymeric porous hollow fibers that are randomly filled and packed in parallel alignment into the shell side, same as the shell & tube heat exchanger (A. Mansourizadeh & Ismail, 2009). Depending on the direction of flow pattern in parallel (co-current, counter-current), the membrane module is designed and categorized into:

Cross flow module (Liqui-Cel)

The Cross-flow module integrates some baffles into the module design. The baffles in this module can provide higher mass transfer coefficients, minimize the shell side channeling, lowering the shell side pressure drop, and maintains normal velocity for the component at the membrane surface. This is an advantage in comparison to the Longitudinal flow module (Li & Chen, 2005a). Figures 13 & 14 illustrate the cross-flow module. Figure 13 shows the design provided by TNO-MEP while Figure 14 shows the cross-flow design by Dindore and versteeg (A. Mansourizadeh & Ismail, 2009)

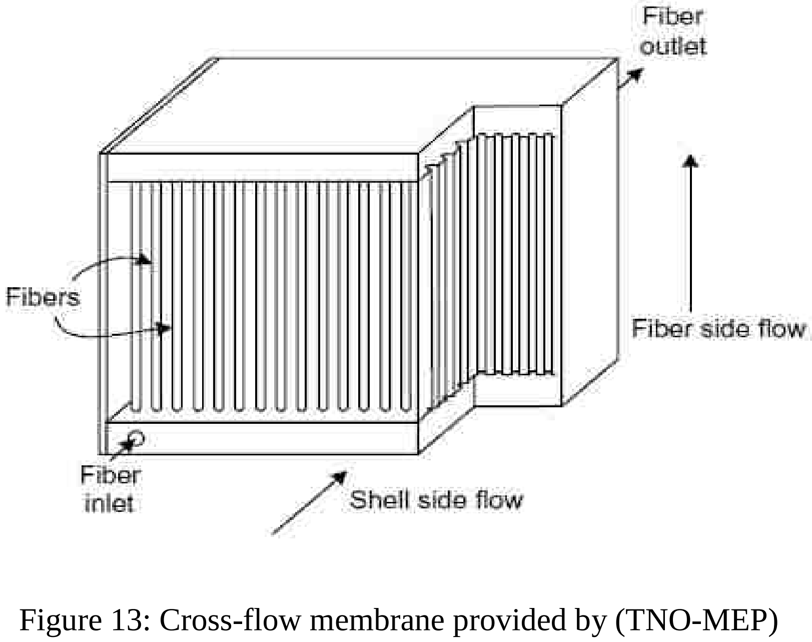

Figure 13: Cross-flow membrane provided by (TNO-MEP)

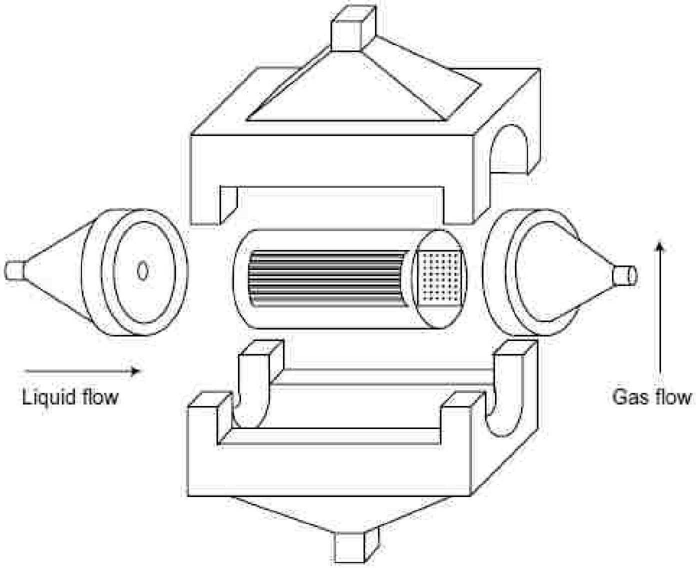

Figure 14: Cross-flow membranes designed by (Dindore and versteeg)

Longitudinal flow module

In the Longitudinal flow module, liquid and gas flow in parallel either co-current or counter-current to each other. Being simple to manufacture, and their ease of mass transfer are the advantages of the longitudinal flow module. Its main disadvantage is having moderate efficiency for mass transfer coefficient, which is lower than that of the cross-flow module. Fig 15 shows the schematic of longitudinal flow module (Li & Chen, 2005a).

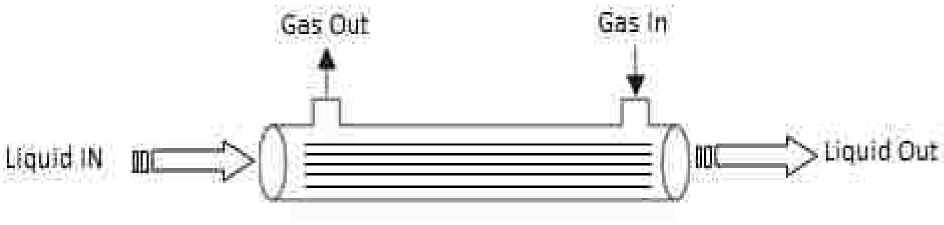

Figure 15: Parallel hollow fiber gas-liquid membrane contactor

Coiled module membrane contactor

Coiled module became more interesting nowadays by providing a curved channel as a secondary flow, in fluids for the purpose of nanofiltration and ultrafiltration membrane application. In addition, mass transfer and the capacity of the involved fluid become intensified. The ability of simultaneous development on mass transfer in both shell and lumen side is the advantage of the Coiled module against other methods. In general, there is insufficient research available about this module (A. Mansourizadeh & Ismail, 2009). Figure 16 shows the schematic of Coiled module membrane contactor.

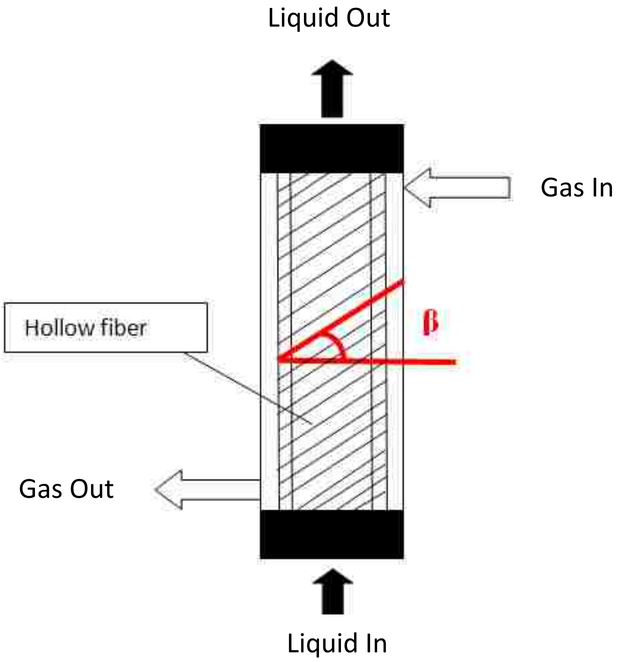

Figure 16: Schematic representation of Coiled module

Generally in HFMC, the performance of cross-flow operation is better than parallel-flow due to several advantages such as a lower shell-side pressure drop, and a higher mass transfer coefficient (Dindore & Versteeg, 2005). Result showed (K. L. Wang & Cussler, 1993) that baffled membrane modules can provide both of those advantages in the flow perpendicular to the well-spaced hallow fiber and counter-current contacting. Therefore, the performance of the cross-flow module is better than the longitudinal one.

Additional work has been done by (Rahim et al., 2015) and the result observed that for PVDF HFMC, the Cross-flow modules performed better than the Longitudinal flow modules, due to the aforementioned advantages. In that set up, counter-current mode was applied for CO_2 removal using 0.5M NAOH from a mixture of CO_2/CH_4. Liquid flowed on the lumen side of fiber while gas flowed in the shell side.

For laboratory purposes, the fabrication and preparation of parallel flow-mode is easier and preferred.

2.7.2 Effect of flow orientation via liquid and gas direction

In GLMC, liquid and gas phases flow in parallel to each other on the opposite side of the fiber. It is well known that counter-current flow has a better performance than other flow patterns since the driving force is more in mass transfer. DeMontigny, Tontiwachwuthikul, & Chakma, (2006) worked on the membrane system using absorption liquid of MEA in PP membrane to remove CO_2 from gas mixture of air + CO_2. The results showed that the counter-current mode has an average of 20% higher performance than co-current. In that set up, liquid was entered from the bottom and flowed up, while the gas stream flow direction was from top to bottom. A similar result was obtained (Rajabzadeh, Yoshimoto, Teramoto, Al-

Marzouqi, & Matsuyama, 2009) that mass transfer efficiency is 20% more for counter-current compared to co-current. Atchariyawut, et al, (2007) studied the CO_2 removal from a mixture of CO_2/CH_4 using water in GLMC system, and the results obtained showed that using the counter-current mode provides better performance than co-current mode.

another work done by Rahim et al.(2015) for the case of CO_2 absorption, using PVDF HFMC from a mixture of CO_2/CH_4 and 0.5M NaOH as an absorber. The gas stream was fed in the shell side and NaOH was supplied in the lumen side of the membrane module. There were three different modes applied to investigate the effect of flow direction on the performance of removal efficiency:

A. Co-current (gas and liquid flowed from bottom to top)

B. Co-current (gas and liquid flowed from top to bottom)

C. Counter-current (liquid from bottom to up, and gas in reverse from top to bottom)

It was observed that the removal performance in counter-current mode is almost 16% better than the co-current mode. Co-current mode of type B showed better result in comparison with type A.

In the case of CO_2 stripping, Rahim, et al.(2014) investigated the effect of liquid solvent flowing side, both in tube side or shell using 0.5M PG. The results obtained showed that liquid which flowed in the lumen side gave better stripping performance due to its lower packing density by almost 39% than the ones that flowed in the shell side.

2.7.3 Effect of liquid flow in fiber lumen side verse module shell side

In gas liquid membrane contactors, there are two types of flow pattern:

i. Liquid absorbent flows through shell side of module and gas stream feed through the tube side.

ii. Liquid absorbent flows in fiber lumen side of membrane module and gas stream through shell side of module.

While there are many researches for liquid flow through the lumen side, there is less research about liquid pass through shells side. They preferred the first mode since pre-filtration for the gas stream is needed for sending gas through lumen side. Pre-filtration is done to avoid the blocking inside of the fiber by contaminations that exist in the gas stream.

For the case of GLMC using PP fiber and MEA as an absorber to remove CO_2, it was reported (deMontigny et al., 2006) that small diameter of fibers preferred to send liquid through the shell side of membrane module. Since the cost of sending the liquid through the very small diameter of fiber is high, a moderate diameter of fiber is recommended. In the case for liquid absorbent flows through fiber lumen side, there will be 150-180% improvement in performance of GLMC. This phenomenon is due to the force by liquid to flow through lumen side of fiber. Therefore, the amount of bulk liquid that is not exposed to the membrane surface area reduced, and as a result, the absorption performance improves. A. Mansourizadeh & Ismail, (2009) preferred to apply the gas flow in tube side for the case of non-wetted mode condition and high packing density.

2.7.4 Effect of packing density

The membrane module packing density can be calculated by following equation as (Naim & Ismail, 2013):

$$\varphi = n_{\text{fibers}} \times \left(\frac{\text{OD}-\text{fiber}}{\text{ID}-\text{Module}}\right)^2$$

Where *n* is the number of fiber, *OD* is the outer diameter of hollow fiber, and *ID* is the inner diameter of the module.

In general, it is preferred to apply a bundle of fibers in the membrane module to increase the interfacial area and absorption capacity. It must be considered that small and narrow fibers might cause channeling around the fiber as the laminar flow applied in the shell side of the membrane may reduce the absorption capacity. In the case of pure CO_2-distilled water system by GLMC method using PVDF, an increase in the number of fibers from 10 and 30 to 50 by packing fraction respectively (2.6%, 7.7% and 13%) was reported, and it was observed the increase in CO_2 absorption flux (Naim & Ismail, 2013). The same result was also reported for CO_2 removal from pure CO_2 gas stream using pure water, and the results showed an increase in the packing density, which would increase the CO_2 flux.

Four PVDF hollow fibers with different number of fibers 10, 20, 30 and 40 were potted in the shell side of module by Rahim et al.(2015) to investigate the effect of packing ratio (respectively 12.1%, 24.2%, 36.3% and 48.4%) on the performance of CO_2 removal from a mixture of CO_2/CH_4. The liquid and gas flow rates were fixed using 0.5M NaOH in lumen side and gas in shell side. It was determined that packing density has a significant effect on mass transfer. Therefore, increasing the packing density will increase the overall removal efficiency.

2.7.5 Effect of membrane length

In the chemical reaction mode for GLMC, by increasing the membrane length at constant number and diameter of fiber, the residence time in liquid phase and surface area will increase. It should be considered that if the length of fiber is too long, there might be a saturation in liquid, and a reduction in the driving force for mass transfer and its efficiency (Ze & Sx, 2014). The effect of fiber length was studied (Boributh, Assabumrungrat, Laosiripojana, & Jiraratananon, 2011) for the ranges of fiber length from 25, 50 and 75 centimeters by pressure drop respectively, 1.5, 3 and 4.5 KPa. Although a higher number of fibers will increase the contact area and improve the overall absorption flux, the results obtained from this study noted that fibers with a longer length have less performance in CO_2 removal due to their higher pressure drop, which results in more wetting than the shorter one. It is concluded, therefore, that the design of HFMC is not only related to fiber length. Hence, to scale it up, overall improvement needs to be considered.

As per the Leveque equation:

For the physical absorption using a laminar and constant liquid flow rate in tube side, increasing the length of the fiber would increase the mass flux, but decrease the liquid mass transfer. Moreover, since the driving force at lower liquid velocity is less, the longer contact time between gas and liquid results the reverse effect on the overall performance. In conclusion, to enhance the overall performance of process by longer fiber, a higher liquid velocity is needed which might increase the pumping cost (Li & Chen, 2005a).

Rahim et al.(2015) used different lengths of hollow fiber (20, 26 and 32 cm) to investigate the effect of membrane length on the performance of CO_2 removal from a mixture of CH_4/CO_2, using 0.5 MNaOH and PVDF hollow fiber membrane contactor. Liquid absorbent was supplied on the lumen side, and the gas mixture on the shell side of the module. Although the length of fiber was increased, and results showed an increase in the removal efficiency, a pressure drop occurred which may need to be considered on the overall impact.

2.8 Influence of operation factors on the performance of CO_2 removal and regeneration in GLMC

In GLMC, there are some key operation parameters which effect mass transfer rate and overall performance of CO_2 absorption and stripping such as liquid and gas flow rate, temperature of liquid absorbent, and pressure. Operation conditions needs to be optimized in order to achieve optimum overall performance. Below is a summary of these parameters:

2.8.1 Effect of liquid flow rate

Liquid flow rate is perhaps the most important operation factor in GLMC, due to its influence on the mass transfer rate of CO_2. An increase in liquid flow rate will lead to an increase the mass transfer rate. This phenomenon occurs due to the fact that an increase in liquid flow rate causes a decrease in the thickness of the boundary layer in the liquid phase in the lumen side, which tends to reduce the resistance of the liquid phase. Therefore, there will be an increase in mass transfer, and higher diffusivity will be accrued (Yan et al., 2007). It should be considered that higher liquid flow rate tends to bring more wetting for the membrane contactor which would reduce the mass transfer rate, thus optimum liquid flow rate has to be applied. Moreover a higher liquid flow rate consumes more energy, which means a moderate liquid velocity is more affordable (Li & Chen, 2005a).

Many researchers have investigated the effect of liquid flow rate on the CO_2removal in GLMC. Yan et al.(2007) investigated the effect of liquid flow rate on the CO_2 removal using three different membrane contactors. Their experiment result reported that an increase in liquid flow rate will decrease the liquid phase resistance which leads to the increase in mass transfer rate, and better performance in CO_2 removal. It is also reported (Kim & Yang, 2000) that increasing liquid flow rate will increase mass transfer coefficient of CO_2 in membrane contactor. Results of the experiment by Mansourizadeh et al.(2010) confirmed that, for the case of physical and chemical CO_2 removal using water and NaOH, by increasing liquid flow rate, CO_2 flux increased in both absorbent. Similar result, were found (Mehdipour et al., 2014).

Liquid phase resistance is the controlling mass transfer rate in the stripping process as well as absorption process in the membrane contactor; therefore the liquid flow rate has a significant effect on CO_2 stripping performance. As per Khaisri et al.(2011), 90% of overall mass transfer accounts for liquid phase mass transfer resistance, consequently, at any temperature, an increase in liquid flow rate will increase the CO_2 desorption flux. This occurs because that increase in liquid flow rate will reduce the liquid film mass transfer resistance, leading to an increase in CO_2 stripping flux. It is further confirmed by Rahbari-Sisakht et al.(2014), as they used PVDF HFMC in purpose of CO_2 stripping using pure N_2 as a sweep gas and the resulting conclusion was that, an increase in liquid flow rate will increase the stripping flux and stripping efficiency, regardless of liquid temperature. Rahim et al.(2014) worked on the effect of liquid flow rate in the case of CO_2 stripping by PVDF using four different types of aqueous solvents. They found that at low temperature, increases in liquid flow rate reduce the stripping efficiency but at high temperature, by increasing liquid flow rate, stripping efficiency will increase. They explain this phenomenon happens due to two reasons; liquid phase boundary layer thickness and resistance time. To increase the overall stripping performance, both conditions have to be considered.

2.8.2 Effect of gas flow rate

Gas flow rate represents the total volume of gas stream feed to the membrane module in both absorption and desorption. Since gas flow rate has a significant effect on the performance of CO_2 removal, influence of gas velocity has been studied by many researchers. An increase in gas flow rate will increase the CO_2 mass transfer and reduce the resistance time of CO_2 in membrane contactor which would eventually cause a significantly decreased performance during CO_2 removal. Although increasing the gas flow rate decreases the overall performance of CO_2 removal, the amount of CO_2 absorbed into liquid phase will increase due to the increase in mass transfer rate (Yan et al., 2007).

Mehdipour et al.(2014) studied the effect of gas velocity on absorption performance in membrane separation, and their observation showed, despite an increase in absorption flux after increasing the gas flow rate, the CO_2 removal decreased.

Some researchers investigate the effect of gas flow rate on CO_2 stripping performance. Rahbari-Sisakht et al.(2014) studied the effect of sweep gas velocity on CO_2 flux and stripping efficiency using PVDF HFMC and pure N_2 as a sweep gas at liquid temperature of 80°c on the CO_2 stripping process; the result showed that by increasing the gas flow rate, CO_2 stripping flux increased but albeit not significantly.

It is also confirmed by (Khaisri et al., 2011) that, although an increase in the gas flow rate slightly changed the CO_2 stripping flux, the effect of gas flow rate was negligible since the liquid flow rate controlled the overall performance of CO_2 stripping. Moreover Rahim et al.(2014) confirmed that regardless of type of the solvent, sweep gas flow rates have no significant effect on the striping flux and efficiency.

2.8.3 Effect of liquid solvent temperature

The effect of liquid absorbent temperature on the performance of CO_2 removal (either chemical or physical absorption) relatively depends on solubility. The effect of solvent temperature both chemical and physical absorption was investigated by (Mansourizadeh et al., 2010), and the results conducted that although in chemical absorption an increase in solvent temperature increases the CO_2 absorption flux, in the physical absorption, the liquid absorbent's temperature has a reverse effect on CO_2 absorption flux. Furthermore Yan et al.(2007) studied the effect of temperature on CO_2 absorption using amine solution. As per results, enhance in solvent temperature will increase the reaction rate, and therefore, mass transfer and diffusion will increase. In contrast higher temperature result a reduction in CO_2 solubility and increase the absorbent evaporation (wetting) which is not suitable for the overall CO_2 removal. It can be said that an ambient temperature is favorable. Similar experiment result were observed by Mehdipour et al.(2014), who said that by increasing liquid temperature, the solvent reactivity increased, leading to higher CO_2 removal from the gas phase. In addition, it should be noted that in order to achieve the acceptable CO_2 removal, a moderate temperature is recommended.

Some researchers investigated the effect of liquid solvent temperature on stripping performance due to direct effect of liquid temperature on reaction rate and

CO_2 equilibrium partial pressure. As per Khaisri et al.(2011), by increasing the liquid solvent temperature (MEA), CO_2 stripping performance increased. Similar result were found by Rahim et al.(2014) and Rahbari-Sisakht et al.(2014). They studied the effect of absorbent liquid temperature on performance of CO_2 stripping using PVDF and the results showed that temperature of liquid solvent has a significant affect, and that the increase in temperature would result in an increase in CO_2 stripping flux due to reduction in solubility. Simioni, Kentish, & Stevens, (2011) studied the effect of temperature on CO_2 stripping using PTFE and their result confirmed that although increases in temperature of liquid solvent would increases the mass transfer coefficient, it would also increase the chance of getting wet into membrane pore. The calculation showed that up to 72% membrane was wetted, and this condensation of vapor in the membrane has a major impact on prevent facilitate of CO_2 transport. Therefore, it can be conducted that liquid phase temperature is the main operation factor on CO_2 stripping performance.

2.8.4 Effect of CO_2 pressure on performance of absorption/stripping

The pressure of a system and its reaction rate are free and independent from total mass transfer, which means an increase in CO_2 flux can enhance CO_2 concentration and driving force of absorption. Effect of CO_2 pressure has been studied for both chemical and physical absorption process in GLMC (A. Mansourizadeh et al., 2010). It was found that the effect of CO_2 pressure on physical absorption is more significant than the chemical; it means that reaction rate is not related to CO_2 concentration. The researchers increased CO_2 pressure from 1×10^5 to 6×10^5 Pa, and the flux was increased from 1.25×10^{-3} to 6.5×10^{-3}. On the other hand, in the chemical absorption, by increasing the CO_2 pressure, they observed a small increase in CO_2 flux. Since the liquid flow rate is steady, an increase in pressure caused an increase in concentration which caused liquid saturation in the lumen side of membrane module. Similar result was achieved by Mansourizadeh,(2012) and it shows that since solubility of CO_2 in water is related to liquid phase pressure, the effect of liquid pressure is more significant in physical absorption (increase in liquid pressure required an increase in the gas pressure).

In case of CO_2 stripping Rahim et al.(2014) investigated the effect of pressure in the exit liquid on CO_2 stripping flux. The result confirmed that regardless of type of the solvents, an increase in the exit liquid pressure, will increase the driving force of desorption and CO_2 concentration, which result in the increase in CO_2 stripping flux and efficiency. It should be considered that applying higher pressure might cause gradual wetting, therefore, liquid pressure must be below break through pressure.

2.8.5 Long term performance of CO_2 absorption

From an economic standpoint, long term stability in CO_2 removal is important and it is generally related to (1) Development in structure of membrane (high porous, small pore size) to avoid wetting, (2) Chemical and thermal stability, (3) Selection of chemical with high surface tension and (4) Non-volatile (Mansourizadeh & Ismail, 2009).

Mosadegh-Sedghi et al. (2014) investigated the long term stability in both physical and chemical absorption. Results showed that for case using pure water as a physical absorbent, performance of CO_2 flux remained the same during 12 days of operation; in contrast, by using amine as a chemical absorbent, there was a reduction in absorption flux that depended on surface tension and contact angle of liquid. Another work by Mansourizadeh et al.(2010) investigates the long term stability in both physical and chemical absorption over 150 hours, using PVDF HFMC in the case where liquid absorbent is sent in shell side and CO_2 on lumen side. Result obtained showed that in physical absorption using water, CO_2 flux decreased almost 30% in the first 23 hours due to partial wetting and capillary condensation of water vapor in membrane pore, and then remained constant the same. On the other hand, for the chemical absorption with NaOH, removal performance gradually reduced after 80 hours due to higher surface tension of NaOH. Therefore the pore enlargement leads gradual flux reduction.

2.8.6 Effect of hollow fiber membrane type

It is reported (Amir Mansourizadeh & Ismail, 2011) that CO_2 absorption flux in prepared PVDF is much more higher than membrane by PTFE at constant absorbent flow rate of 200 ml/min. Absorption flux for PVDF was almost 68% higher than PTFE. It is also confirmed Rajabzadeh et al.(2013) that the performance of gas absorption in the membrane by high porosity at the inner surface is higher than membrane with low porosity, due to the relation of gas-liquid contacts area with gas absorption rate.

Chapter 3: Experimental Work

3.1 Construction and preparation of Hollow Fiber Membrane Contactors

3.1.1 Preparing and arranging the polymer fiber

In this study, three different fibers (PTFE, PFA, and PVDF) were used to prepare the hollow fiber membrane contactor:

a) Polytetrafluoroethylene (PTFE) :

Two different types of porous PTFE hollow fiber were used in this study:

- The first type of PTFE was purchased from Markel Corporation Company (U.S.A) with an inner diameter of 1.00 mm and outer diameter of 1.6 mm, thickness of 0.3, and specific gravity of 0.96. Porosity was calculate by % porosity = $[1 - (\frac{Bulk\ density}{2.17})] \times 100$ formula and gave 55.76 %.

Figure 17 shows the cross section of the PTFE hollow fiber (US-made); it was captured by Motic microscope B1 Seri. The Figure shows how the inner and outer diameters of the fiber were measured.

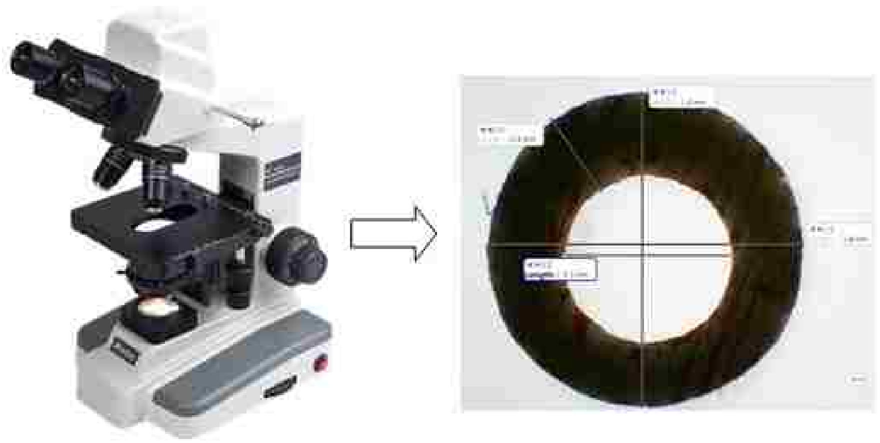

Figure 17: Schematic picture of PTFE – US made

- The second type of PTFE was purchased from a Chinese Company, the inner diameter is 0.9 mm and outer diameter is 2.1 mm and the tackiness is 0.6 mm. Figure 18 shows the cross section of the PTFE hollow fiber (China-made) that was captured by Motic microscope B1 Seri.

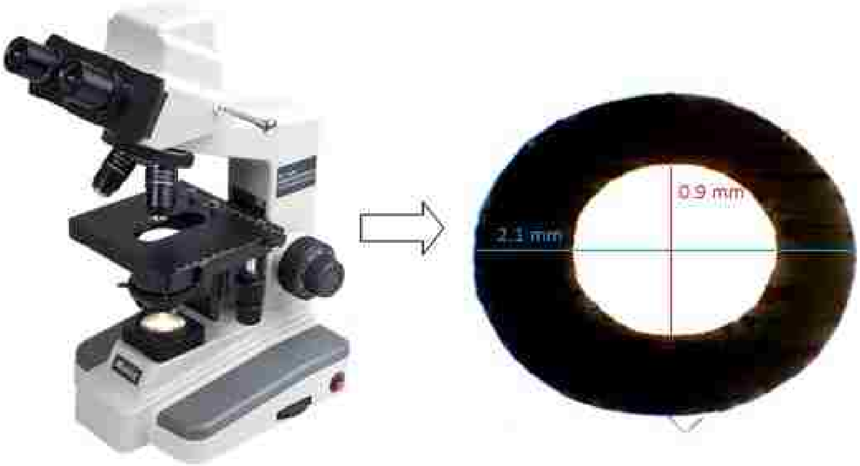

Figure 18: Schematic picture of PTFE – China made

b) Perfluoroalkoxy (PFA):

PFA was purchased from Entegris (Germany) company with the following specifications: inner diameter of 0.25 mm, outer diameter of 0.65 mm, thickens of 0.2 mm and overall porosity of 56.8 %.

c) Polyvinylidene difluoride (PVDF):

PVDF hollow fiber membrane contactor was fabricated in the lab by Thermally Induced Phase Separation (TIPS) method. The polymer material used is PVDF (solef®6020/1001) and it was purchased from Solvay (France) company. The chemicals used in the fabrication of the hollow fiber membrane were purchased from Sigma-Aldrich with purity more than 99%. The PVDF had the following specifications; inner diameter of 0.42 mm and outer diameter of 1.1 mm, thickens of 0.34 mm and porosity of 45.85 %.

3.1.2 Preparation and fabrication of gas-liquid membrane contactor

Lab-fabricated shell and tube Gas Liquid Membrane Contactors (GLMC) were prepared using Perspex glass as a shell and 3 different polymer fibers packed inside the Perspex glass acting as the tubes as shown in Figure 19:

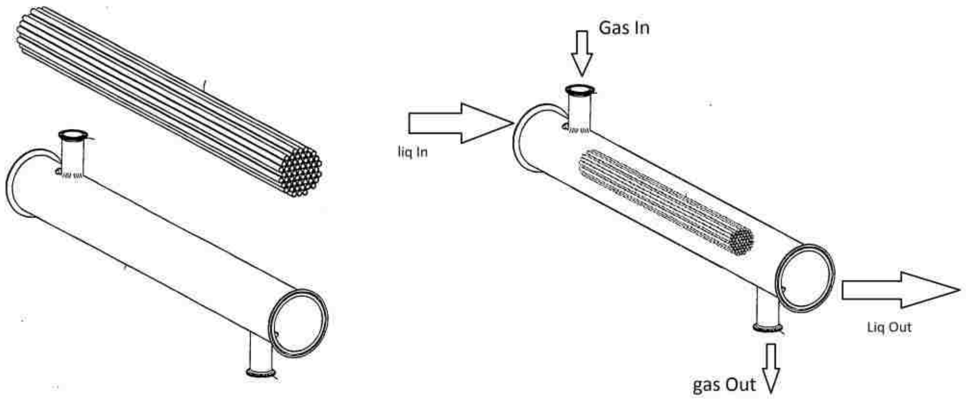

Figure 19: Schematic shell and tube GLMC

Perspex glass that was used as the shell for this HFMC was purchased from Signtrade L.L.C (U.A.E). It was cut in different lengths as needed and two holes as shown in Figure 19 were drilled to provide gas inlet and outlet in the shell. Fibers were tested before being placed in shell side of the membrane by keeping them in the water and then drying them right before use. To check the blockings and leaks, a simple procedure is to pass water through lumen side of fiber and checking whether the fiber is damaged. The required number of fibers which are ready for the use can be packed inside the shell as shown in fig 19. Modules then need to be filled from each side by applying epoxy provided by the local market such as 5 min rapid epoxy and 90 minute standard epoxy FEVICOl® Brand. Electrode caps were purchased from Signtrade L.L.C and were kept at the entry and exit pints of the tube for any connection purposes. It should to be considered that the constructed membranes have to be checked for any liquid and gas leakage before conducting the experiment.

Figure 20 shows the fabricated HFMC which is ready to be used.

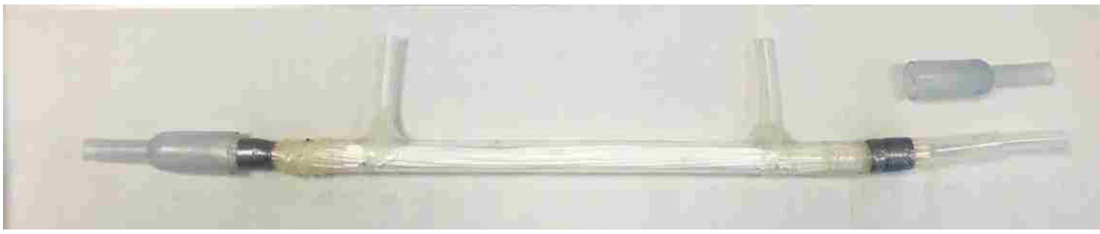

Figure 20: Lab-fabricated HFMC

3.2 Construction of the experimental set-up for individual absorption, stripping and combined absorption-stripping process

The chemicals (MEA, DEA and NaOH) were purchased from Sigma Aldrich Company (Germany Based) with purity more than 99%. Two gas cylinders one for nitrogen (99.9 % purity) and the second for gas mixture that contains: 80% vol. N_2 and 20% vol. CO_2 were purchased from Sharjah Oxygen, UAE. Masterflex platinum-cured silicone tube was purchased from Cole Parmer Industrial Company based in the UAE with variable diameters of 16, 18, and 25 mm for the connections and tubings.

3.2.1 Individual absorption process

Absorption performance and CO_2 removal by liquid absorbent in GLMC from CO_2/N_2 gas mixture was studied by flowing the gas stream in the shell side of the membrane at different flow rates. The flow rate was controlled by mass flow controller provided by Alicat Siencefic (U.S Based). Different kinds of aqueous solvents were used in the absorption process being supplied to the lumen side of the membrane contactor at different flow rate by counter-current flow. Liquid flow rates were controlled by Masterflex L/S Digital Pump purchased from Cole Parmer Industrial Company. CO_2 Analyzer (CAI – 600 Seri) was purchased from Gas

Analyzers (U.S.A) to measure the concentration of CO_2 in exit stream. Data logger or oscilloscope to generate signal and analyze the concentration was purchased from Pico Technology. To run the experiment, fresh solvents were prepared every time and data were collected once the resulted values were steady. For the better performance, counter-current flow direction was applied in this set-up. Figure 21 shows the schematic of set-up for the absorption process.

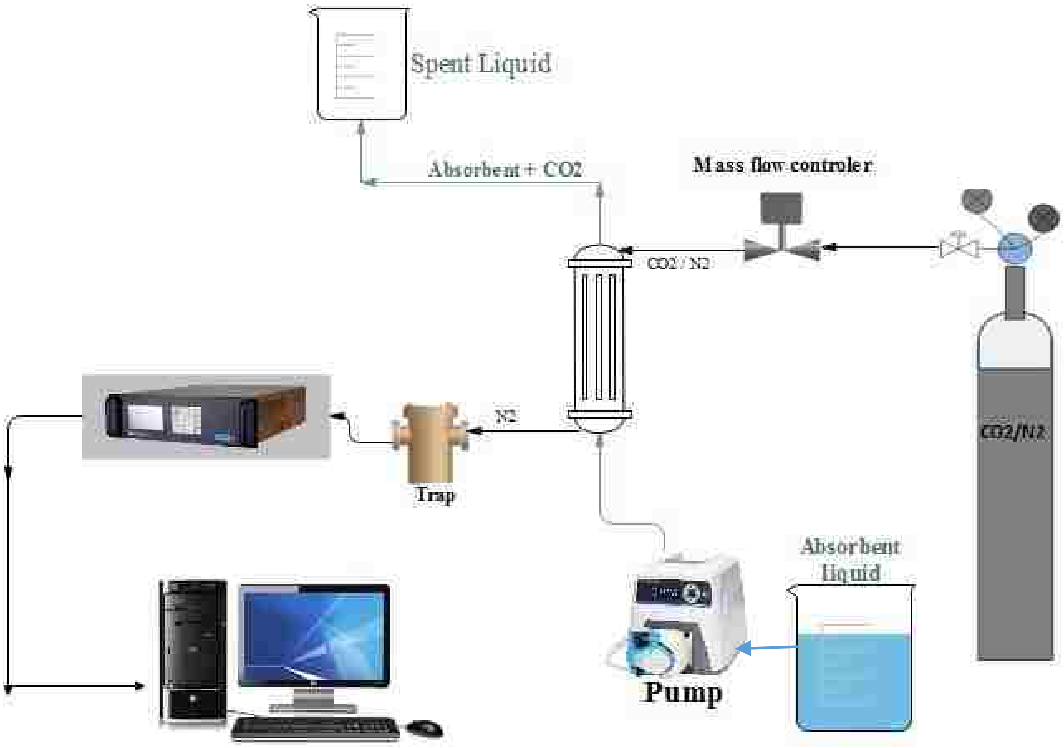

Figure 21: Schematic set-up of absorption process

The CO_2 absorption/stripping flux and efficiency can be calculated by:

$$J_{CO_2} = \frac{(C_i V_i - C_o V_o)}{A_i}$$

$$\eta\,(\%) = \frac{(C_i V_i - C_o V_o)}{C_i V_i} \times 100\%$$

Where, the J_{CO_2} is the flux of the module (mol/m^{2}s), η is efficiency, c_i and c_o are the feed gas concentration of CO_2 in absorption process. Moreover c_i and c_o represent respectively the concentration of CO_2 in inlet and outlet of liquid phase for the membrane stripping process (mol/m^3). The values of v_i and v_o are respectively the inlet and outlet feed gas flow rates in the absorption process while they are the liquid inlet and outlet flow rate in the stripping process. The value of A_i represents the inner surface of hollow fiber membrane (m^2).

3.2.2 Individual stripping process

For regeneration of the various liquids loaded by CO_2, stripping process was prepared. Different aqueous solutions were preloaded as a liquid feed stream until saturation achieved. The loaded liquids were then pumped by (Masterflex L/S pump) to the lumen side of membrane module. Figure 22 shows the set-up for the CO_2 loading by supplying pure CO_2 through the spiral tube placed inside the prepared solvent. The gas was continuously supplied until no further reduction in the value of pH was observed. The total process of CO_2 loading took approximately 3 hours. The saturated solvent was heated to different temperatures by using the feedback-controlled heater (WiseStir®). As a sweep gas, pure nitrogen (with 99.9% purity) was fed at different flow rate to the shell side of membrane module. Vacuum, water and steam were also used to compare the stripping performance. Counter-current flow was applied to provide the highest striping performance. Various samples were taken throughout the process to study the stripping efficiency. Double titration with Chittick apparatus method was applied to analyze and measure the concentration at inlet and outlet of the stripping module to determine the efficiency of the process.

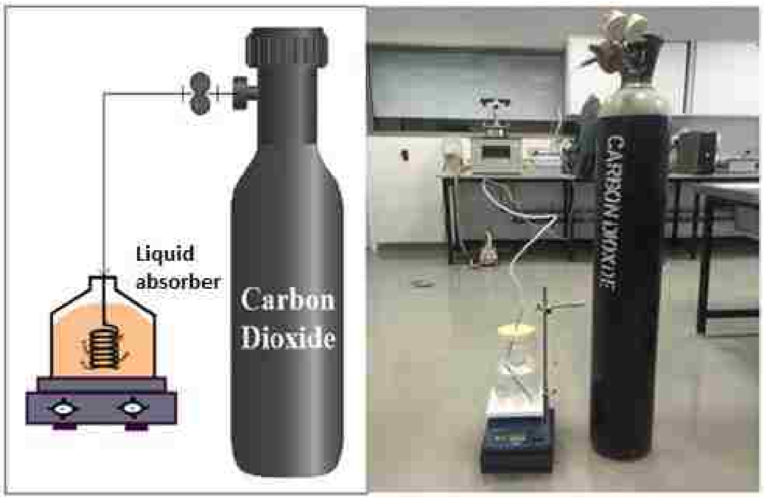

Figure 22: Schematic set-up of CO_2 loading

3.2.2.1 Chittick carbon dioxide apparatus method

The Chittick apparatus is an alternative titration approach used to determine the concentration of amine in the solution or measure the amount of captured (loaded) CO_2 that has been absorbed by amine solution (JI, Miksche, Rimpf, & Farthing, 2009). Fig 23 shows the schematic process and the designed set-up for Chittick carbon capture apparatus in the lab.

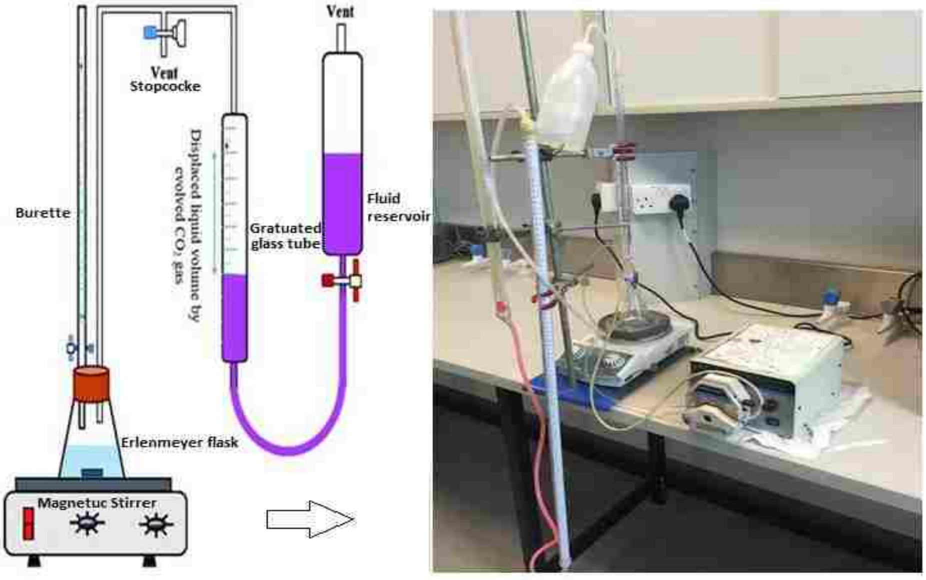

Figure 23: Schematic set-up of Chittick apparatus

5 to 25 ml of the amine solution was taken and placed in the reaction flask along with pH color indicator solution (methyl orange). The flask is then connected from one side to graduated U-Tube monometer and from other side to the open atmosphere. The hydrochloric acid (normally HCL with 1 M) is gently added from the 50 ml titration burette until the change in the color of solution observed. Addition of the HCL titrant would evolve the CO_2 from the solution. The magnet stirrer is used to agitate the reaction and keep the solution homogeneous. The process continues until no more CO_2 is liberated. Concentration of amine solution can be defined from the below titration equation:

$$C_1V_1 = C_2V_2$$

Where; C_1 and C_2 are respectively the concentration of amine and titrant in the solution in mole/liter (M), V_1 is the volume of sample solution (ml) and V_2 is the volume of titration (ml).

The amount of CO_2 absorbed by amine solution can be defined by below equation:

$$\alpha = \frac{\frac{VCO_2}{AB}}{\frac{C_1V_1}{B}} = \frac{\left[\frac{(V_{gas} - V_{acid})(p)(273\,K)}{(760 mmHg)(T)}\right]}{C_1V_1\,A}$$

Where; α is the ratio of CO_2 loading (mole CO_2/mole amine group)

A is conversion constant (22.41 liter/mole)

B is conversion constant (1000 ml/liter)

C_1 is concentration of amine solution in mole/liter (M)

P is barometric pressure (mmHg)

T is room temperature (K)

V_1 is sample volume of amine solution (ml)

V_{CO2} is volume of CO_2 collected (ml) at STP condition

V_{gas} is volume of displaced solution in the gas measuring tube (ml)

V_{acid} is volume of acid titrant (ml)

Figure 24 shows the experimental set-up for individual stripping process.

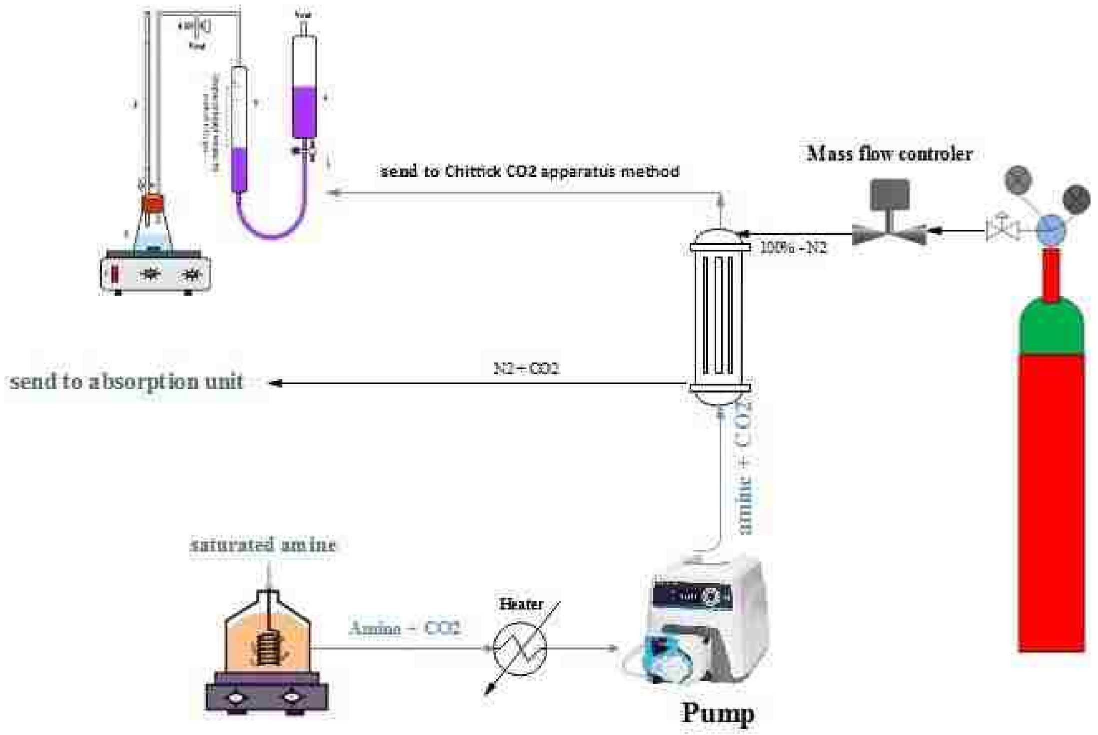

Figure 24: Schematic set up of stripping process

As per Figure 24, amine saturated by CO_2 was heated at various temperatures then it pumped through the bottom of GLMC and then flowed in lumen side of fibers. The amine is then produced from the top of the module and it is sent to the Chittick titration unit to measure the stripping efficiency. To assess the effect of sweeping fluids, pure nitrogen, water, steam and vacuum were separately studied. The various fluids were sent with a counter-current flow though the shell side of the module for the purpose of CO_2 stripping from the loaded amine.

3.2.3 Combined absorption and stripping process – Close loop

Experimental set-up of absorption/stripping membrane contactor system in a close-loop was constructed similar to the one shown in Figure 25.

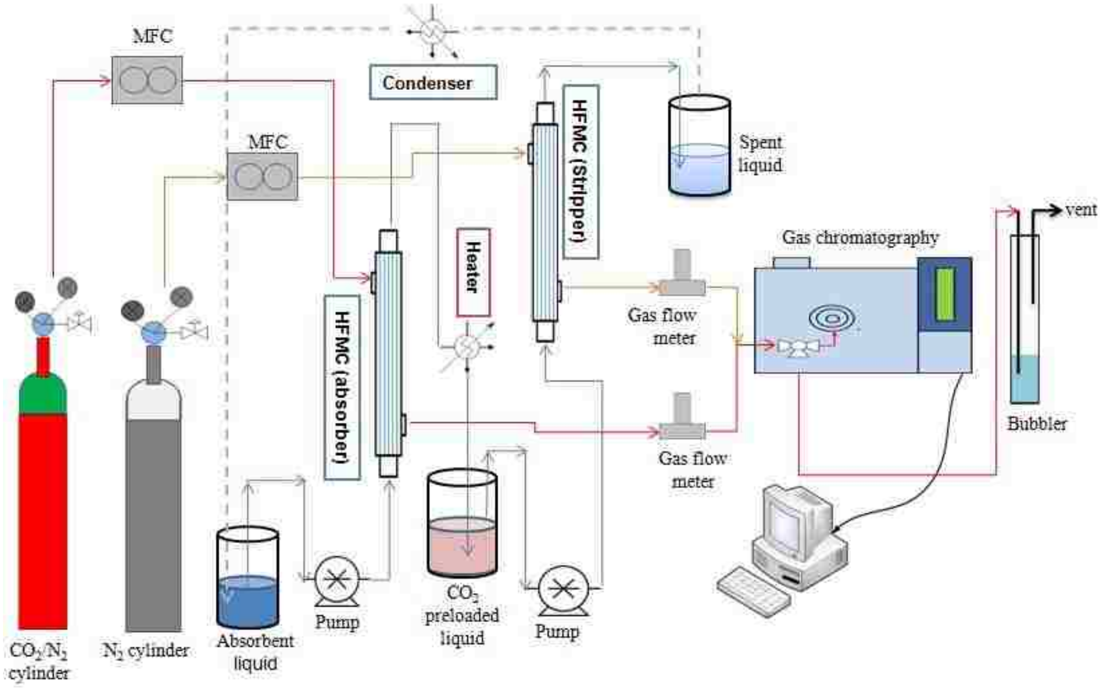

Figure 25: Flow diagram of GLMC as CO_2 absorber /stripper

The gaseous species are mixed with predetermined concentrations using mass flow controllers and then are fed at a certain flow rate to the constructed membrane absorber unit. The exit gas stream form absorption unit will be analyzed using the CO_2 analyzer or gas chromatography to determine the concentration of CO_2. The solvent is pumped to the membrane absorber in a counter-flow arrangement. The pressure and flow rates of gas and liquid phases are controlled by the control valves. In the absorber, the liquid pressure should be more than the pressure of the gas phase to avoid bubbling. In addition, the liquid pressure should be less than LEPw to avoid instantaneous wetting. The rich solvent leaving the absorber is then heated and pumped through the constructed stripping membrane. Nitrogen gas, vacuum, water and steam used as sweeping fluids in the stripping unit. The concentration of CO_2 is determined in the exit stream. The outlet stream of the stripping unit is then pumped back to the absorber in a closed-loop arrangement.

Chapter 4: Result and Discussion

Initial purpose of this work is to investigate the effect of different aqueous solvents via various types of hollow fiber membrane contactors on absorption in GLMC. Moreover individual stripping process and full absorption/stripping processes in closed loop were investigated. Operation parameters were changed during the experiment to Figure out the effect of those parameters such as liquid flow rate, gas flow rate, liquid temperature and the number of fibers on the performance of process.

4.1 Absorption and capture of CO_2 from a mixture of CO_2/N_2 using various HFMC via different aqueous solvent

For this aim, three different hollow fibers were used:

a. PFA HFMC
b. PTFE HFMC (different structure)
c. Custom PVDF prepared by TIPs method in HFMC

Three different absorbent liquids were used in the absorption/stripping process, they were the most common commercial amines such (MEA, DEA and NaOH). The effects of these solvents on process performance were compared. Although NaOH provides higher removal efficiency, it suffers from low regeneration rate, therefore, MEA and DEA becomes more remarkable amine because of their adequate CO_2 removal efficiency in absorption process and superior regeneration performance. The effects of membrane configuration, number of hollow fibers and the type of hollow fibers on CO_2 removal efficiency in GLMC were investigated.

4.1.1 Effect of different liquid absorbent in absorption process

4.1.1.1 Effect of different liquid absorbents in PFA HFMC

Effects of three different aqueous solution of 0.5M DEA, 0.5M MEA and 0.5M NaOH on absorption performance were studied. 50 number of PFA fibers were potted in shell side of module. Table 6 shows the specification of PFA HFMC:

Table 6: Specification of PFA membrane module

PFA	Value
Number of fiber	50
I.D of fiber (mm)	0.2
O.D of fiber (mm)	0.65
inner diameter of module (mm)	12
Effective length (cm)	19
Area (m^2)	0.00745
Porosity (%)	56.80%

A gas mixture consists of: 20% CO_2 & 80% N_2 by gas flow rate of 100 cm^3/min applied on shell side of module and there different absorbents liquid of DEA, MEA and NaOH were passed through lumen side of module in atmospheric pressure and ambient temperature. The removal percentage and CO_2 flux are given in Table 7:

Table 7: Removal percentage and CO_2 flux in absorption process in PFA HFMC

PFA - 50 Fiber								
GFR cm^3/min	**LFR ml/min**	**% CO_2 in**	**C in mol/lit**	**% CO_2 out**	**C out mol/lit**	**CO_2Flux (mol/m2 min)**	**% Removal**	**Absorbent**
100	20	20	0.00818	18.9	0.007729	0.00604	5.5	DEA
100	20	20	0.00818	18.9	0.007729	0.00604	5.5	MEA
100	20	20	0.00818	18.5	0.007565	0.00823	7.5	NAOH

4.1.1.2 Effect of different liquid absorbent in PTFE (US made)

The effect of three different aqueous solutions 0.5M DEA, 0.5M MEA, 0.5M NaOH on absorption performance is investigated. The module is constructed by potting 25 number of PTFE fibers in shell side module, the module effect length is 19 cm. Table 8 shows the specification of PTFE (US made):

Table 8: Specifications of PTFE (US) membrane module

PTFE - U.S made	**Value**
Number of fiber	25
I.D of fiber (mm)	1.00
O.D of fiber (mm)	1.60
inner diameter of module (mm)	12
Effective length (cm)	19
Area (m^2)	0.01492
Porosity (%)	55.76%

The gas mixture consists of: 20% CO_2 & 80% N_2 is used as the feed gas, the gas flow rate is 100 cm^3/min applied on shell side of module and three different absorbent liquids (0.5 M of DEA, MEA and NaOH) were passed through lumen side of module at atmospheric pressure and ambient temperature. The removal percentage and CO_2 flux are given in Table 9:

Table 9: Removal percentage and CO_2 flux in absorption process in PTFE (US made)

PTFE US Made- 25 Fiber								
GFR cm^3/min	**LFR ml/min**	**% CO_2 in**	**C in mol/lit**	**% CO_2 out**	**C out mol/lit**	**CO_2Flux (mol/m2 min)**	**% Removal**	**Absorbent**
100	20	20	0.00818	8.4	0.003435	0.03180	58.0	DEA
100	20	20	0.00819	3.3	0.001349	0.04579	83.5	MEA
100	20	20	0.00818	2.5	0.001022	0.09606	87.5	NAOH

4.1.1.3 Effect of different liquid absorbent on PTFE (China made)

The effects of three different aqueous solutions 0.5M DEA, 0.5M MEA, 0.5M NaOH on absorption performance were examined. 10 number of PTFE fibers were potted in shell side of module by effective length of 19 cm. Table 10 shows the specification of PTFE–China made:

Table 10: Specification of PTFE – China membrane module

PTFE - China made	Value
Number of fiber	10
I.D of fiber (mm)	0.9
O.D of fiber (mm)	2.1
inner diameter of module (mm)	12
Effective length (cm)	19
Area (m^2)	0.0053

Calculation of membrane effective area:

I.D = 0.9 mm and O.D = 2.1 mm therefore Area =2Πr (Inner diameter of the fiber)* h (length of the active fiber or length of active module)* N (number of fibers) so Area = (2*3.14*.0009*.19*10)/2 =0.0053

A gas mixture consists of: 20% CO_2 & 80% N_2 at gas flow rate of 100 cm^3/min is applied on the shell side of the module, three different absorbent liquids 0.5M DEA, MEA and NaOH were passing through lumen side of module in atmospheric pressure and ambient temperature. The removal percentage and CO_2 flux are given in the Table 11:

Table 11: Removal percentage and CO_2 flux in absorption process in PTFE (US made)

PTFE China Made - 10 Fiber								
GFR cm^3/min	**LFR ml/min**	**% CO_2 in**	**C in mol/lit**	**% CO_2 out**	**C out mol/lit**	**CO_2Flux (mol/m2 min)**	**% Removal**	**Absorbent**
100	20	20	0.00818	11.5	0.004703	0.06558	42.5	DEA
100	20	20	0.00818	6.3	0.002576	0.10571	68.5	MEA
100	20	20	0.00818	3.3	0.001349	0.12885	83.5	NAOH

4.1.1.4 Effect of different liquid absorbents using custom PVDF HFMC

The effects of three different aqueous solutions 0.5M DEA, 0.5M MEA, 0.5M NAOH on absorption performance were examined. 10 number of fabricated PVDF fibers were potted in shell side of module at effective length of 19 cm. The membrane inside diameter was 0.42mm and outer diameter was at 1.1 mm therefore,

The area = 2Π r (Inner diameter of the fiber)* h (length of the active fiber or length of active module)* N (number of fibers)

So the area = (2*3.14*.00042*.24*10)/2 =0.003165.

Table 12 shows the specification of custom PVDF:

Table 12: Specification of lab-made PVDF membrane module

28% concentration custom PVDF	Value
Number of fiber	10
I.D of fiber (mm)	0.42
O.D of fiber (mm)	1.1
Thickness (mm)	0.34
inner diameter of module (mm)	10
Effective length (cm)	24
Area (m^2)	0.003165
Porosity (%)	45.85%

A gas mixture consists of: 20% CO_2 & 80% N_2 at gas flow rate of 100 cm^3/min is applied on shell side of module and three different absorbent liquids 0.5M of DEA, MEA and NAOH were passing through lumen side of module at atmospheric pressure and ambient temperature. The removal percentage and CO_2 flux are given in the Table 13.

Table 13: Removal percentage and CO_2 flux in absorption process in PVDF

Lab-made PVDF - 10 fiber								
GFR cm^3/ min	**LFR ml/min**	**% CO_2 in**	**C in mol/lit**	**% CO_2 out**	**C out mol/lit**	**CO_2Flux (mol/m2 min)**	**% Removal**	**Absorbent**
100	20	20	0.00818	12.7	0.005193	0.09432	36.5	DEA
100	20	20	0.00818	8.4	0.003435	0.14988	58.0	MEA
100	20	20	0.00818	5.7	0.002331	0.18476	71.5	NaOH

The results presented in Figures 26 and 27, shown respectively, the CO_2 absorption efficiency and CO_2 absorption flux via change in absorbent liquid. As per Figure 26, regardless of the type of membrane module, NaOH has better removal efficiency than other solvents and DEA has the lowest removal efficiency. Figure 27 shows the absorption flux, and it says that regardless of the type of membrane module NaOH has the highest flux and DEA has the lowest rate of flux.

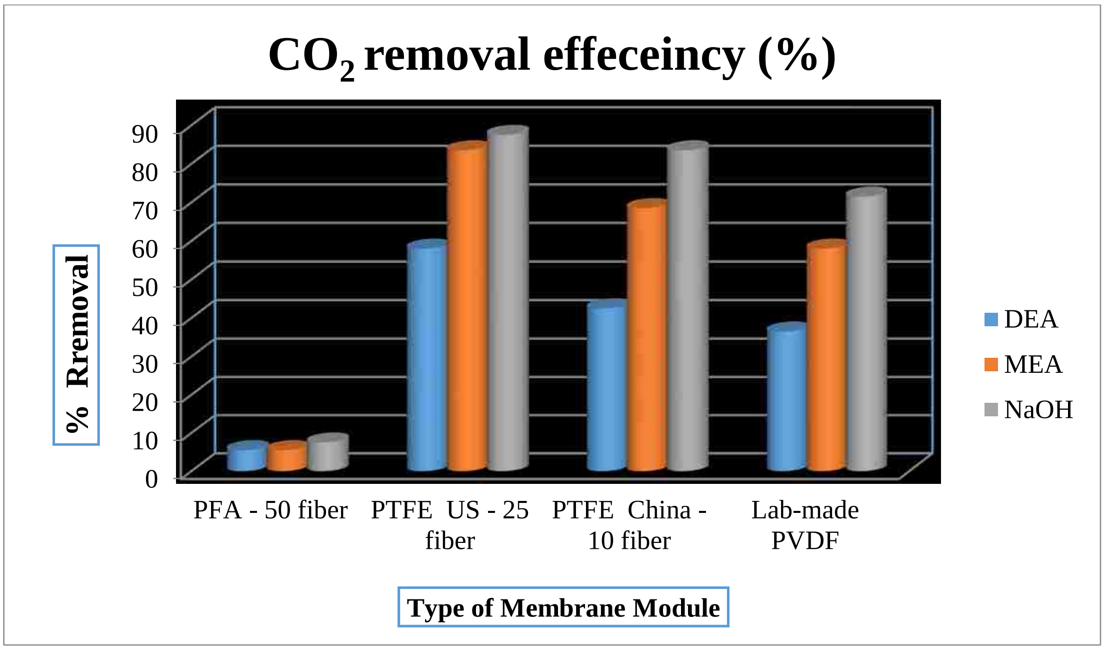

Figure 26: Effect of different solvent on the removal efficiency at constant liquid flow rate of 20 ml/min and Gas flow rate of 100 cm^3/min.

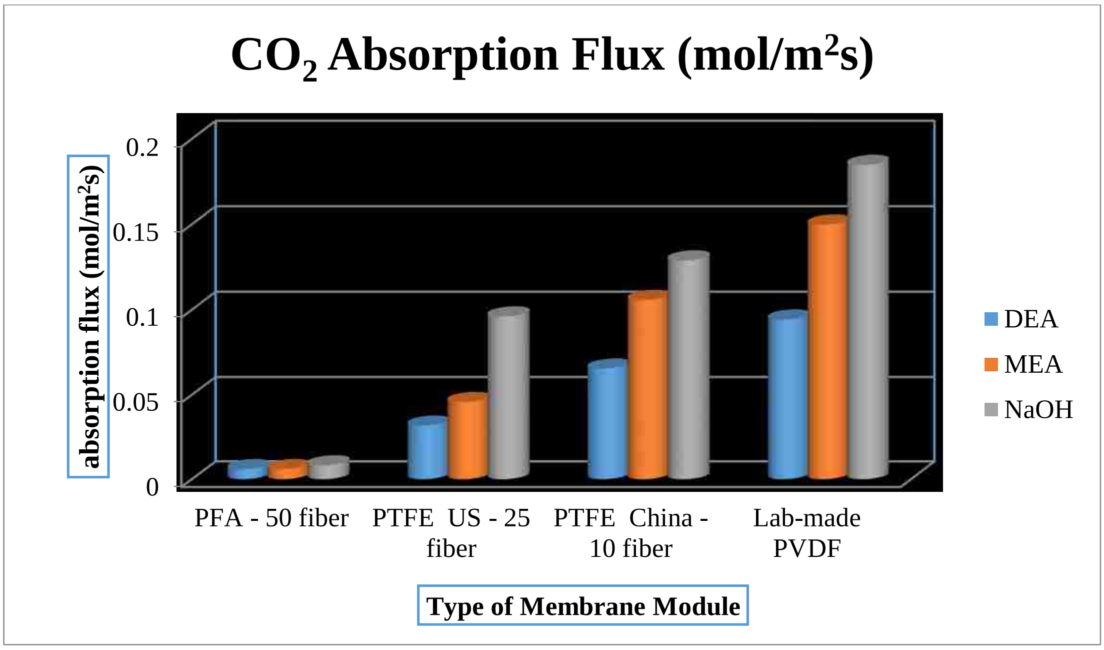

Figure 27: Effect of different solvent on the absorption Flux at constant liquid flow rate of 20 ml/min and Gas flow rate of 100 ml/min

4.1.2 Effect of different HFMC on the absorption performance

Five different membrane modules were constructed to Figure out the effect of different module configuration on the percent removal efficiency and absorption flux at specific liquid solvent.

4.1.2.1 Effect of different HFMC on the absorption performance for the case of DEA

A gas mixture consists of 20% CO_2 & 80% N_2 at gas flow rate of 100 ml/min is applied on shell side of module and then 0.5M DEA as an absorbent liquid passed through lumen side of module in atmospheric pressure and ambient temperature. The removal percentage and CO_2 flux using DEA are given in Figures 28 and 29:

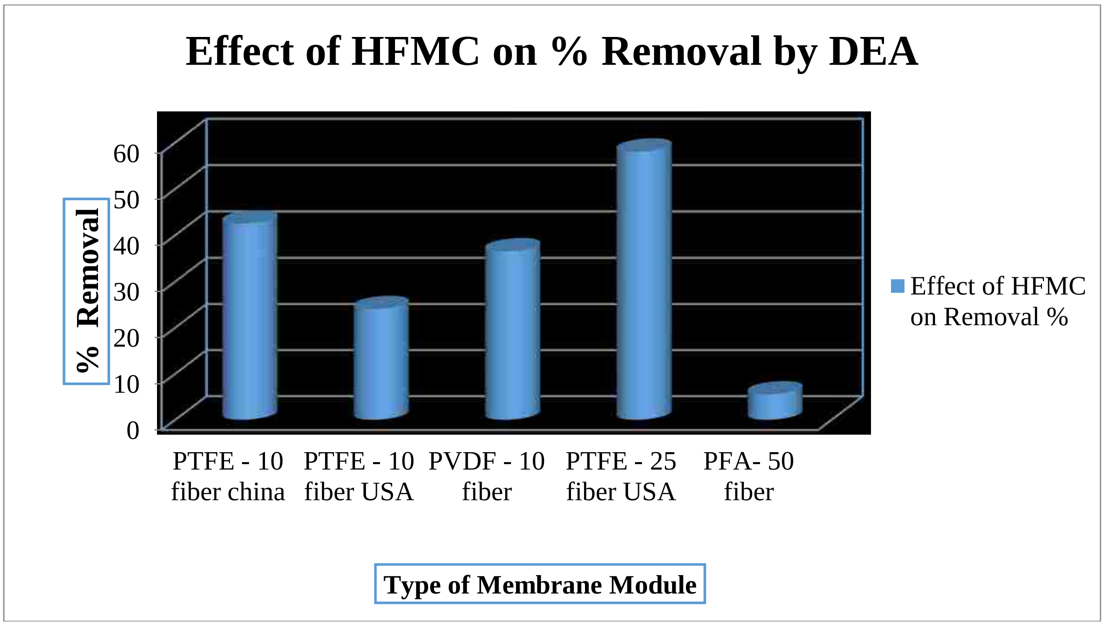

Figure 28: Effect of different HFMC on removal efficiency by using DEA at constant liquid flow rate of 20 ml/min and Gas flow rate of 100 cm^3/min

As shown in Figure 28, the highest removal efficiency is for module with 25 fibers of PTFE-US made; on the other hand module with PFA has the lowest removal performance. Actually change in the number of fiber, would change the effective area and packing ratio, therefore the percentage removal is unable to show the appropriate comparison for this specific operation condition, for this purpose absorption flux is giving the better approaches for the result.

As per Figure 29, The Lab-made PVDF fiber shows better performance in the CO_2 removal as stated by its higher absorption flux. In addition PFA shows the lowest absorption flux.

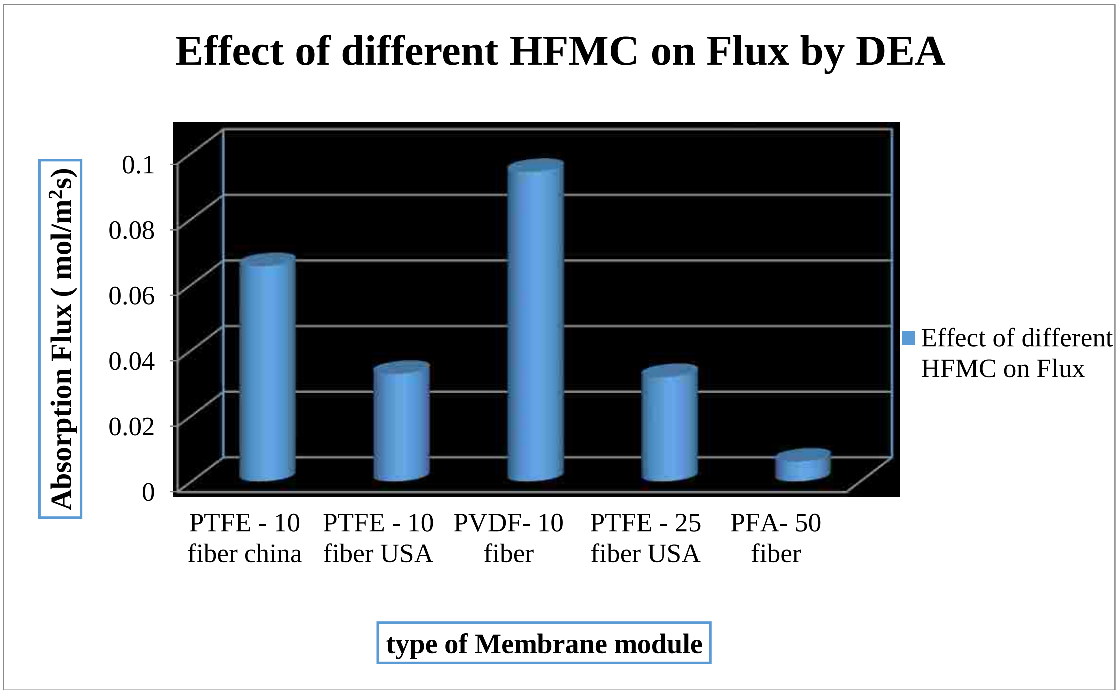

Figure 29: Effect of different HFMC on the absorption flux using 0.5M DEA at constant liquid flow rate of 20 ml/min and Gas flow rate of 100 ml/min

4.1.2.2 Effect of different HFMC on the absorption performance for the case of MEA

The gas mixture consists of (20% CO_2 & 80% N_2) at gas flow rate of 100 cm^3/min applied on shell side of module. 0.5M MEA used as the absorbent liquid and fed through lumen side of the module in atmospheric pressure and ambient temperature. The removal percentage and CO_2 flux at MEA are given in Figures 30 and 31:

As shown in Figure 30, the removal efficiency with module by 25 fiber of PTFE-US Made is the highest whereas PFA presents the lowest performance. As mentioned, since the numbers of fibers are difference, the effective area might be difference; therefore the percentage removal is not the appropriate factor in comparison for this specific operation condition, for this purpose absorption flux is giving the better approaches for the result.

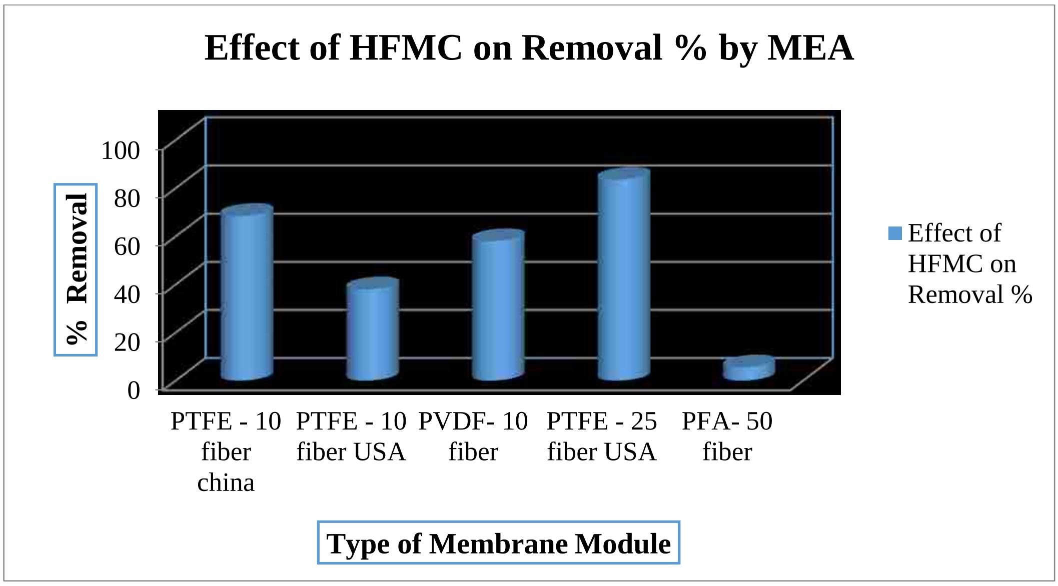

Figure 30: Effect of different HFMC on removal efficiency by using MEA at constant liquid flow rate of 20 ml/min and Gas flow rate of 100 cm^3/min

Figure 31 shows that homemade PVDF is the better fiber for the CO_2 removal as per its higher absorption flux using MEA. Moreover PFA remained to have the lowest absorption flux.

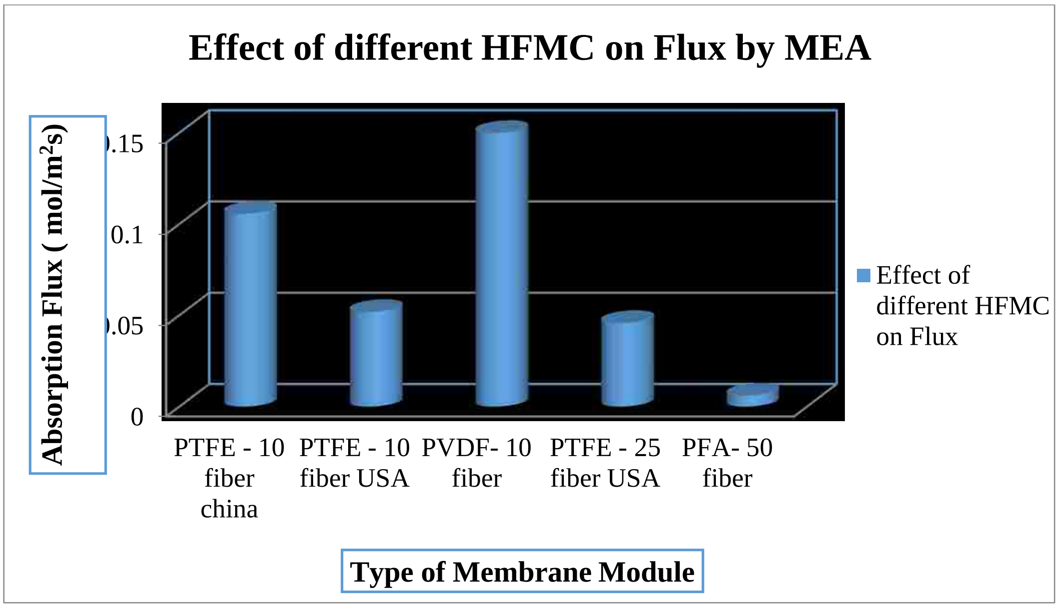

Figure 31: Effect of different HFMC on absorption flux by using MEA at constant liquid flow rate of 20 ml/min and Gas flow rate of 100 cm^3/min

4.1.2.3 Effect of different HFMC on the absorption performance for the case of NaOH

A gas mixture of (20% CO_2 & 80% N_2) flowing at the gas flow rate of 100 cm^3/min applied on shell side of module. 0.5M NaOH as an absorbent liquid passed through lumen side of module at atmospheric pressure and ambient temperature. The percentage of CO_2 removal and CO_2 flux for NaOH are given in Figures 32 and 33:

As shown in Figure 32, the removal efficiency in module with 25 fiber of PTFE-US Made and 10 fiber of PTFE-China are giving better removal efficiency. PFA has the lowest removal efficiency. As discussed, removal percentage is not a reliable factor for this specific experiment; consequently absorption flux is giving the better approaches. Accordingly to the Figure 33 lab-made PVDF is the better fiber for removal performance as per its higher absorption for the case using NaOH.

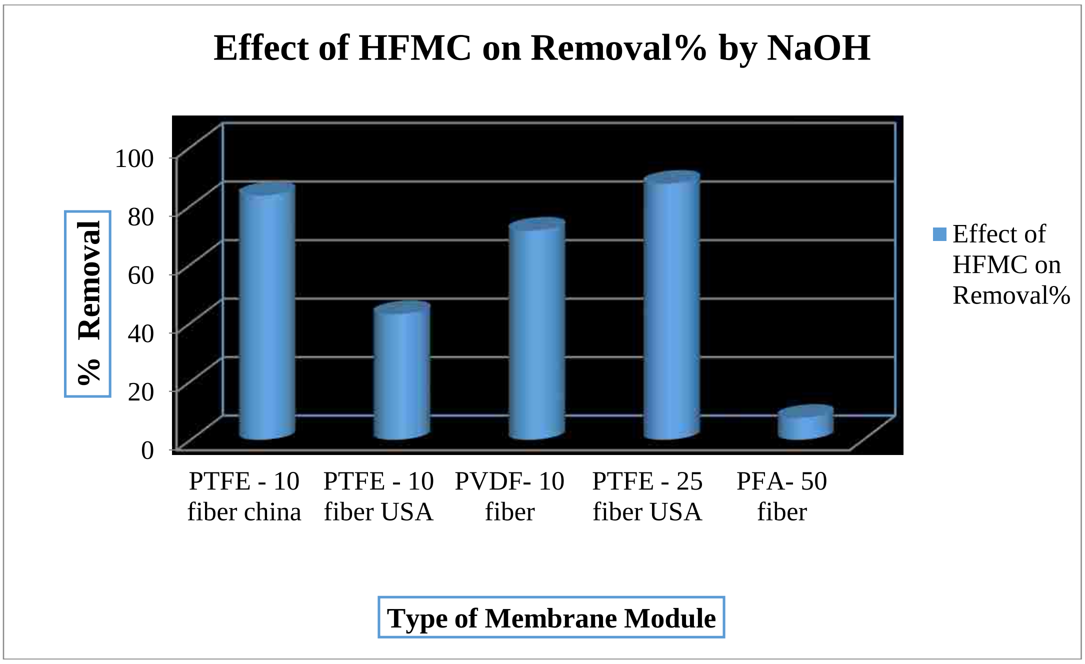

Figure 32: Effect of different HFMC on the absorption efficiency using NaOH at constant liquid flow rate of 20 ml/min and Gas flow rate of 100 cm^3/min

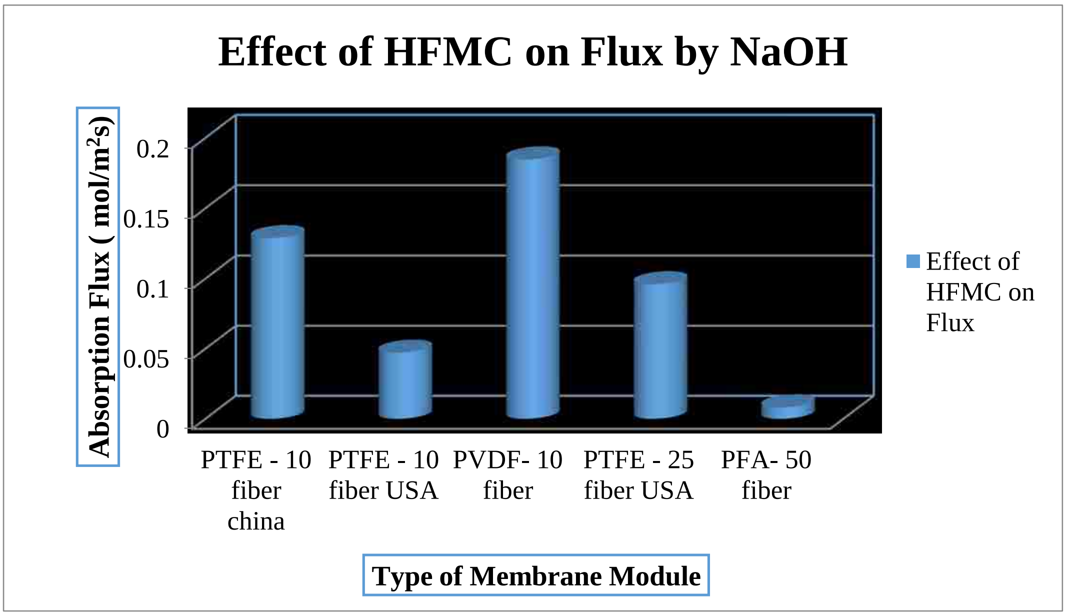

Figure 33: Effect of different HFMC on absorption flux by using NaOH at constant liquid flow rate of 20 ml/min and Gas flow rate of 100 cm^3/min.

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In general according to Figures 34 and 35, the lab-made PVDF is giving better removal performance due to its high CO_2 absorption flux and PFA is having the lowest flux and removal efficiency in ambient temperature and atmospheric pressure. It might need to be considered when the number of fibers and effective area different, the removal efficiency might get affected by this factor; therefore the removal efficacy becomes unreliable. Absorption flux is the only parameter to compare the removal performance;

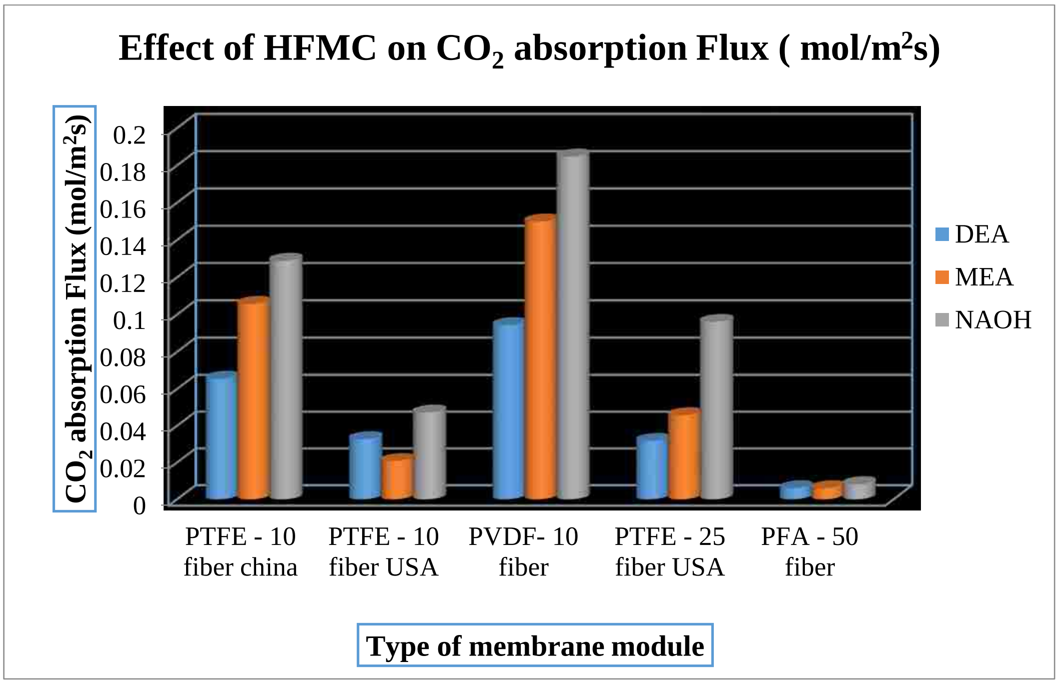

Figure 34: Effect of different HFMC on removal efficiency by using MEA, DEA and NAOH at constant liquid flow rate of 20 ml/min and Gas flow rate of 100 cm^3/min

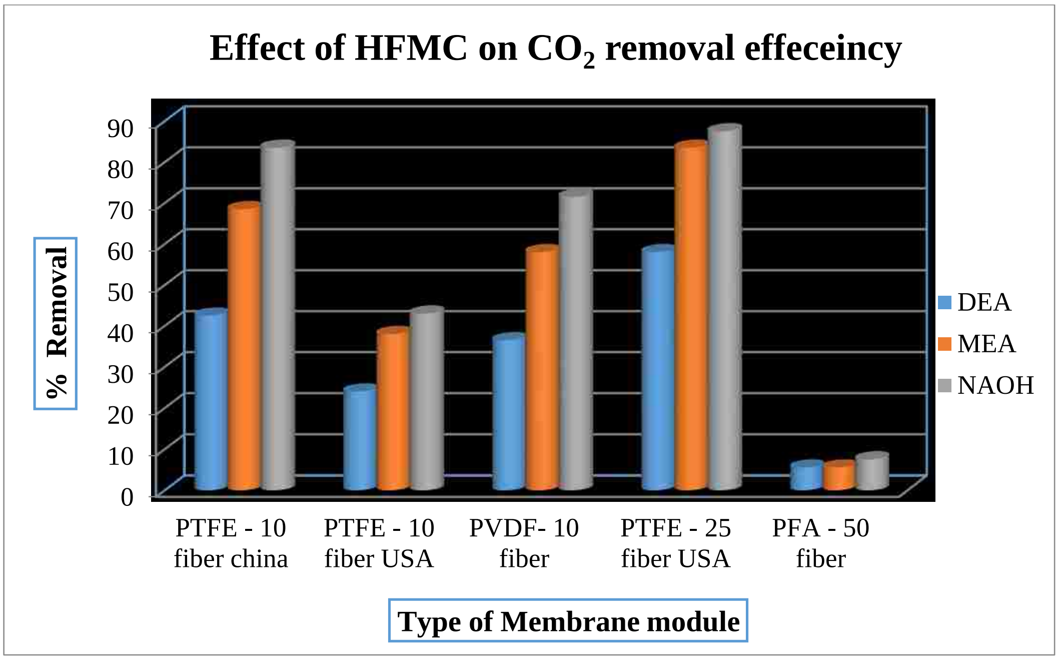

Figure 35: Effect of different HFMC on absorption efficiency by using MEA, DEA NaOH at constant liquid flow rate of 20 ml/min and Gas flow rate of 100 cm^3/min

4.1.3 Effect of liquid flow rate

In this case, the experimental setup contains three different absorbents liquid 0.5 M DEA, 0.5 M MEA and 0.5 M NaOH aqueous solution. Absorbents were sent to the lumen side of membrane module at different liquid flow rate from 5 ml/min to 20 ml/min at ambient temperature 298 K and atmospheric pressure. A gas mixture consist of (20% CO_2 and 80% N_2) was fed to shell side of gas-liquid membrane module at constant gas flow rate of 100 cm^3/min in ambient temperature 298 K and atmospheric pressure to investigate the effect of liquid flow rate on CO_2 removal performance ad flux .

4.1.3.1 Effect of liquid flow rate on removal efficiency

4.1.3.1.1 Effect of liquid flow rate on removal efficiency using DEA

0.5 M aqueous solution of DEA supplied on lumen side using different Gas-Liquid membrane contactor in different liquid flow rate from 5 ml/min to 20 ml/min at constant gas flow rate of 100 cm^3/min. Figure 36 shows the effect of liquid flow rate on Removal efficiency while DEA was used. As shown in Fig 36, regardless of type of module increase in liquid flow rate, will increase the removal efficiency.

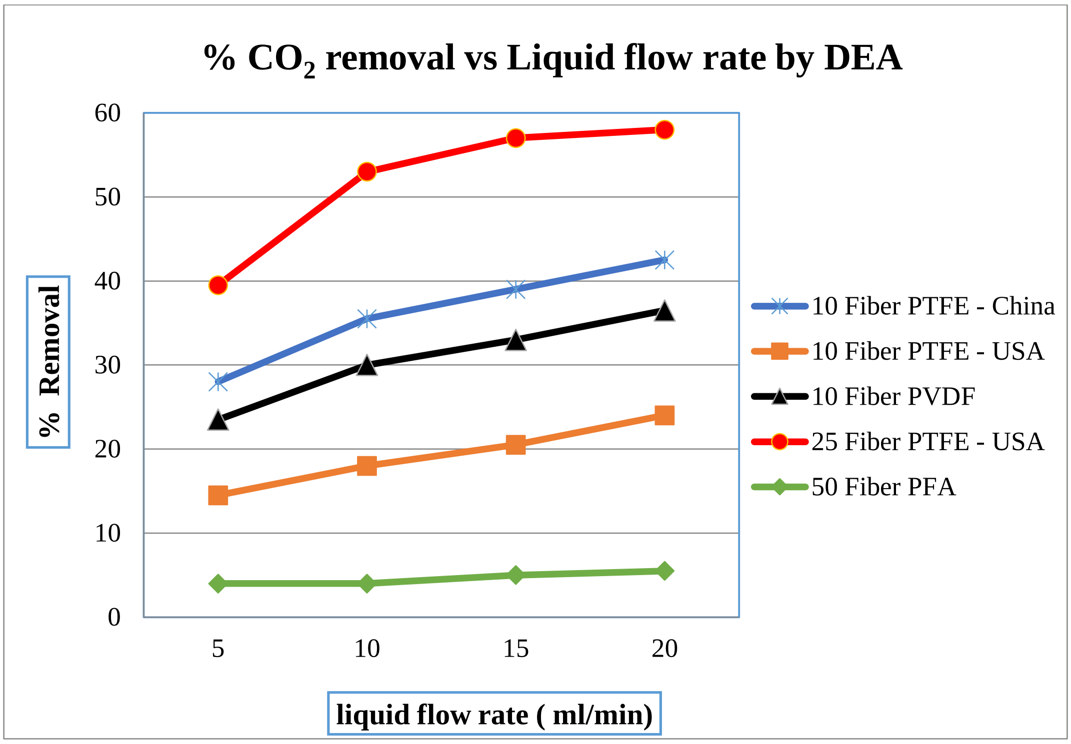

Figure 36: Effect of liquid flow rate on removal efficiency in GLMC using 0.5M DEA at constant gas flow rate of 100 cm^3/min

4.1.3.1.2 Effect of liquid flow rate on removal efficiency using MEA

0.5 M aqueous solution of MEA supplied on lumen side using different Gas-Liquid membrane contactor in different liquid flow rate from 5 ml/min to 20 ml/min at constant gas flow rate of 100 cm3/min. Figure 37 shows the effect of liquid flow rate on Removal efficiency while MEA was used. As shown in Figure 37, regardless of type of module increase in liquid flow rate, will increase the removal efficiency.

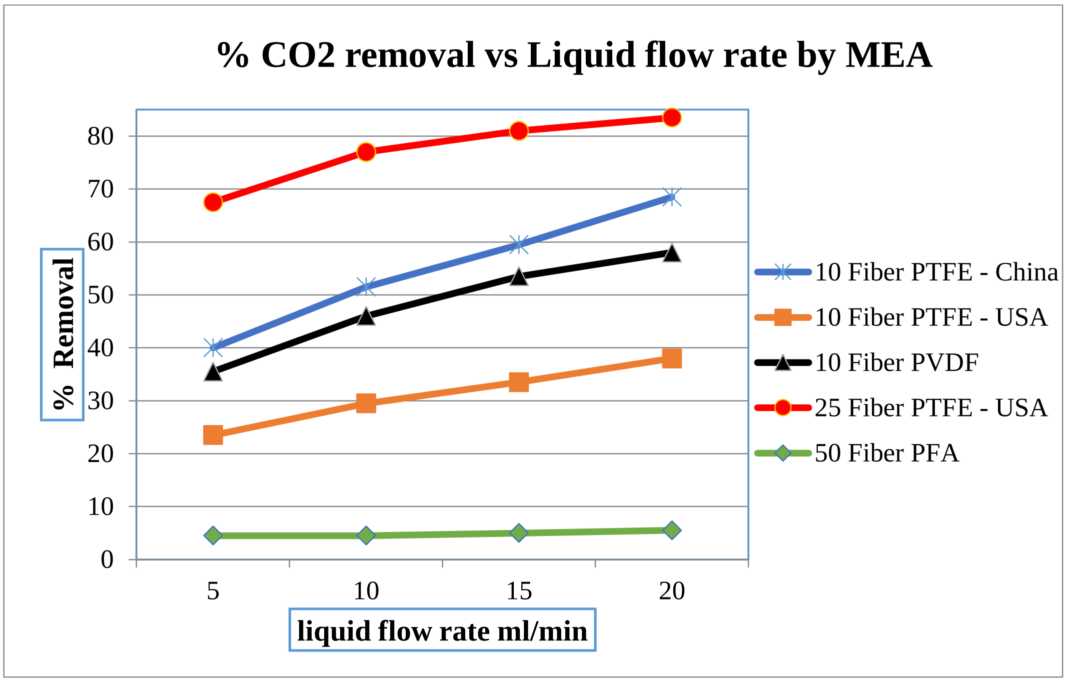

Figure 37: Effect of liquid flow rate on removal efficiency in GLMC using MEA 0.5 M with constant gas flow rate of 100 cm^3/min

4.1.3.1.3 Effect of liquid flow rate on removal efficiency using NaOH

0.5 M aqueous solution of NaOH supplied on lumen side using different gas-Liquid membrane contactor at different liquid flow rates from 5 ml/min to 20 ml/min at constant gas flow rate of 100 cm^3/min. Figure 38 shows the effect of liquid flow rate on Removal efficiency while using NaOH.

As shown in Figure 38, regardless of type of module increase in liquid flow rate, will increase the removal efficiency.

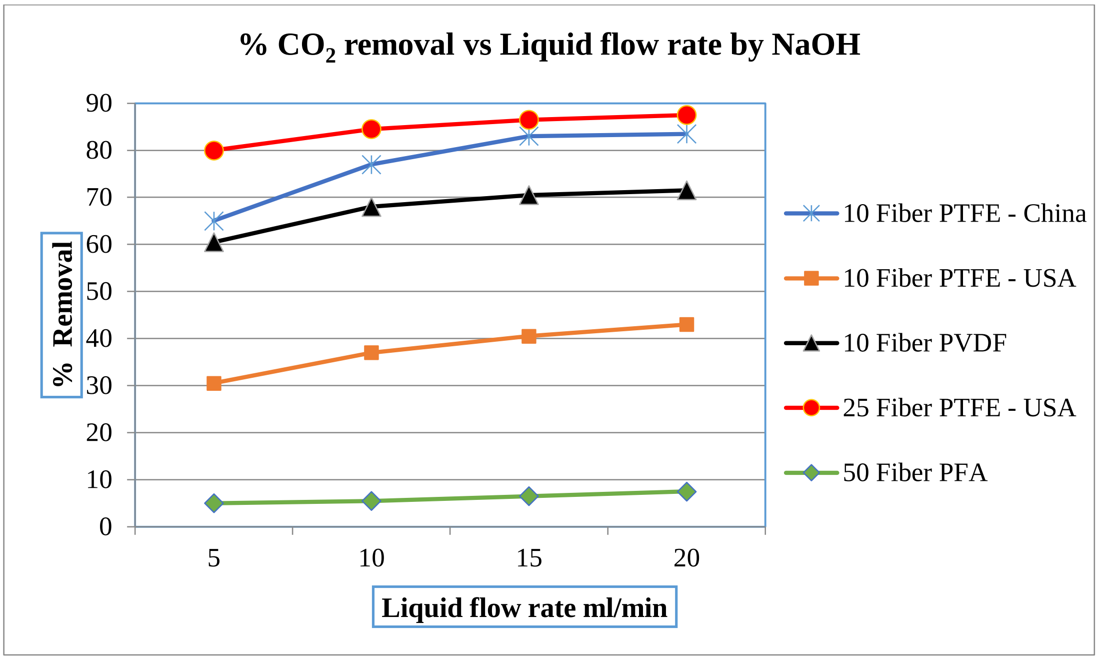

Figure 38: Effect of liquid flow rate on removal efficiency in GLMC using NAOH 0.5 M with constant gas flow rate of 100 cm^3/min

In general according to Figure 36, 37 and 38, regardless of type of membrane module and liquid type, increase in liquid flow rate, enhance the removal efficiency.

As per Figure 39, the effect of liquid flow rate is more significant for the removal performance with low removal efficiency rather than those with higher removal efficiency. As a result of that, while the removal efficiency using DEA is lower, therefore the increase in liquid flow rate significantly increase the removal efficiency compared to NaOH which has higher removal efficiency.

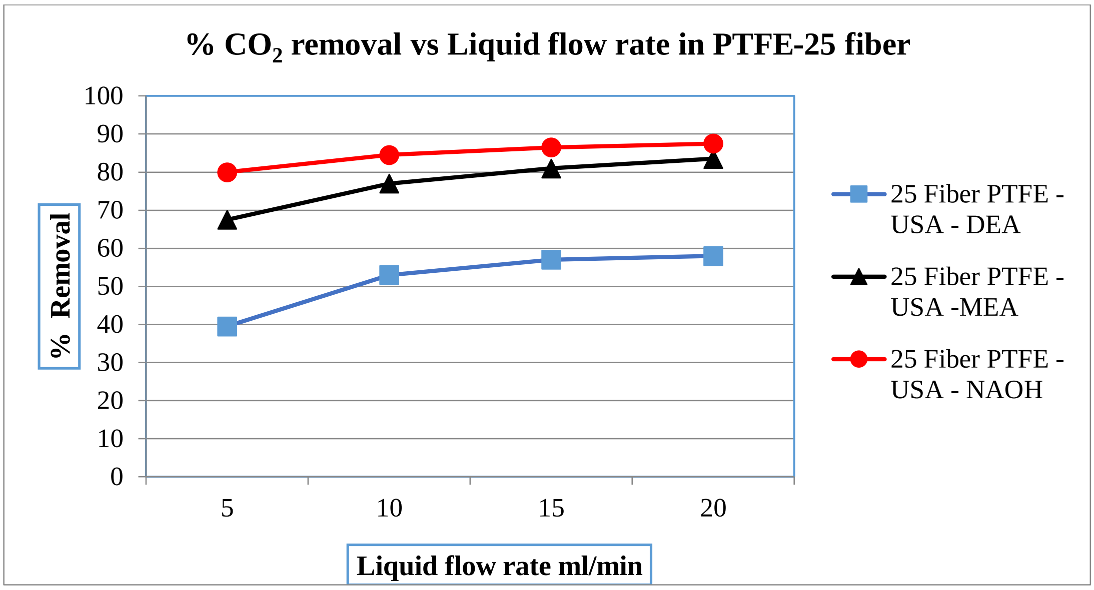

Figure 39: Effect of liquid flow rate on removal efficiency in GLMC with 25 fiber-PTFE using different 0.5 M aqueous solution with constant gas flow rate of 100 cm^3/min

4.1.3.2 Effect of liquid flow rate on CO_2 absorption flux

For this purpose, the same set up is ready for comparing the absorption flux. Three different absorbent liquids were used; 0.5 M aqueous solution of DEA, MEA and NaOH were used to send in lumen side of membrane module at different liquid flow rates of 5 ml/min to 20 ml/min at ambient temperature 298 K and atmospheric pressure. A gas mixture consist of 20% CO_2 and 80% N_2 was fed to shell side of gas-liquid membrane module at constant gas flow rate of 100 cm^3/min in ambient temperature 298 K and atmospheric pressure to investigate the effect of liquid flow rate on CO_2 absorption flux . Two types of membrane module were used for this experiment. Figure 40 and Figure 41 show the effect of liquid flow rate on CO_2 absorption flux.

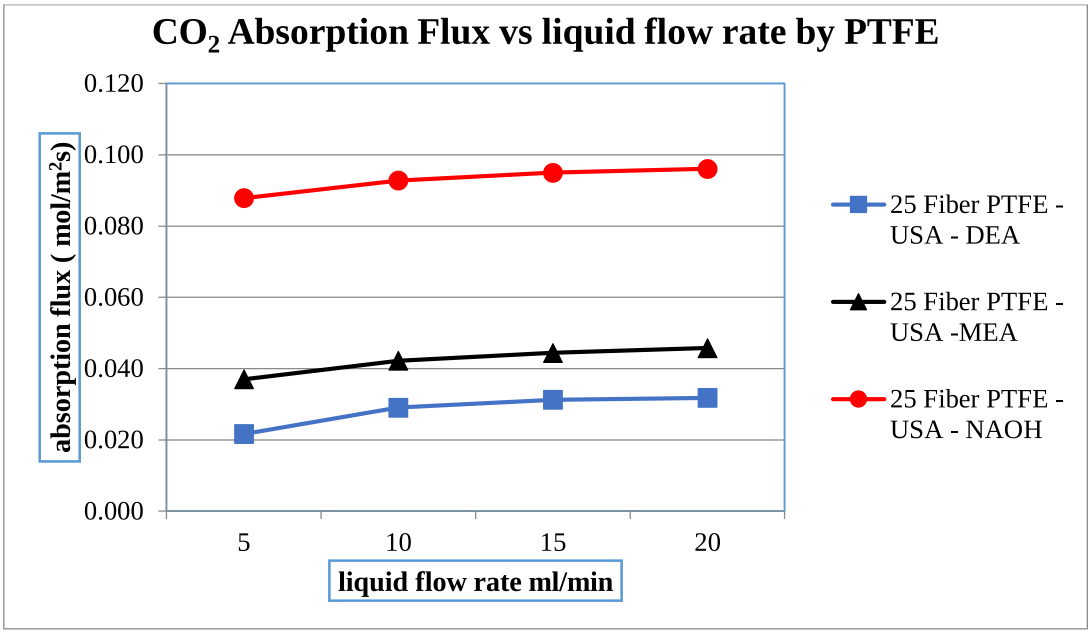

Figure 40: Effect of liquid flow rate on absorption flux for membrane contactor with 25 fiber-PTFE using different 0.5 M solution at constant gas flow rate of 100 ml/min

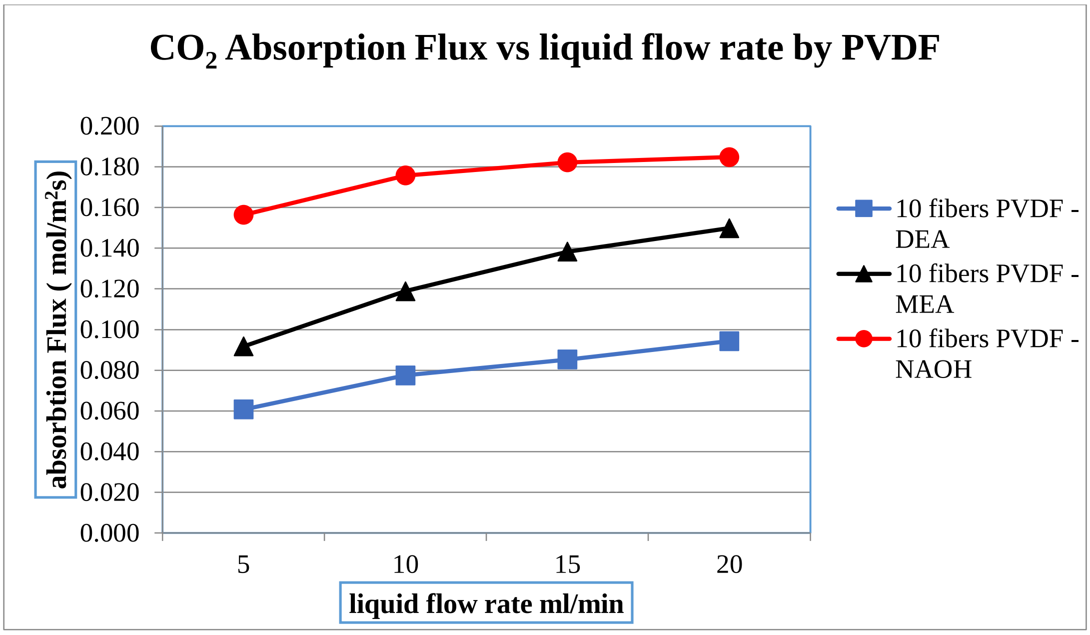

Figure 41: Effect of gas flow rate on absorption flux for membrane contactor with 10 fiber-PVDF using different 0.5 M solution at constant flow rate of 20 ml/min

As shown in Figure 40 and 41, the increase in liquid flow rate has significant affect on membrane module of PTFE rather than PVDF; in general increase in liquid flow rate will increase the absorption flux. The removal percentage and absorption flux is high with higher liquid flow rate due to reduced boundary layer thickness and its associated mass transfer resistance

4.1.4 Effect of gas flow rate

In this set up of experiment, there different absorbent liquid 0.5 M aqueous solution of DEA, MEA and NaOH were used to send in lumen side of membrane module at constant liquid flow rate of 20 ml/min in room temperature 298 K and atmospheric pressure. Gas mixture consist of 20% CO_2 and 80% N_2 was fed to the shell side of gas-liquid membrane module at different gas flow from 70 cm^3/min to 200 cm^3/min in ambient temperature 298 K and atmospheric pressure to investigate the effect of gas flow rate on CO_2 removal performance ad flux.

4.1.4.1 Effect of gas flow rate on removal efficiency

DEA:

0.5 M aqueous solution of DEA at constant flow rate of 20 ml/min is supplied to the lumen side of the membrane contactor using different gas-liquid hollow fiber membrane contactor. Figure 42 shows the effect of gas flow rate on carbon dioxide removal efficiency.

As shown in Figure 42, gas flow rate has a significant effect on removal efficiency and increase in gas flow rate will decrease the removal performance.

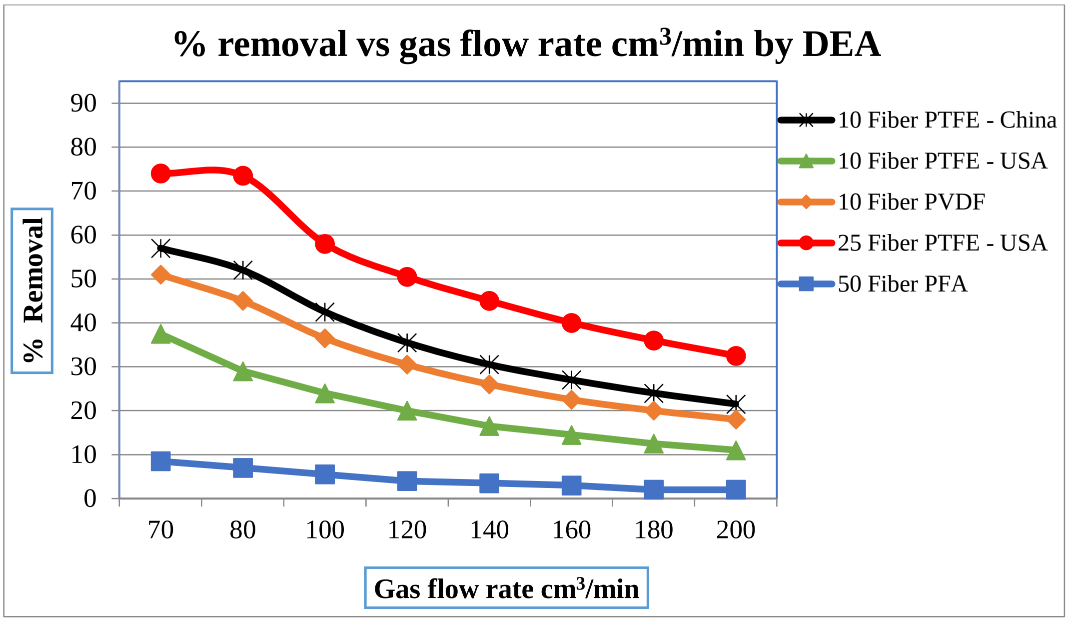

Figure 42: Effect of gas flow rate on removal efficiency in GLMC using 0.5 M DEA with constant liquid flow rate of 20 ml/min

MEA:

0.5 M aqueous solution of MEA supplied on lumen side using different gas-liquid hollow fiber membrane contactor. The Figure 43 shows the effect of gas flow rate on removal efficiency.

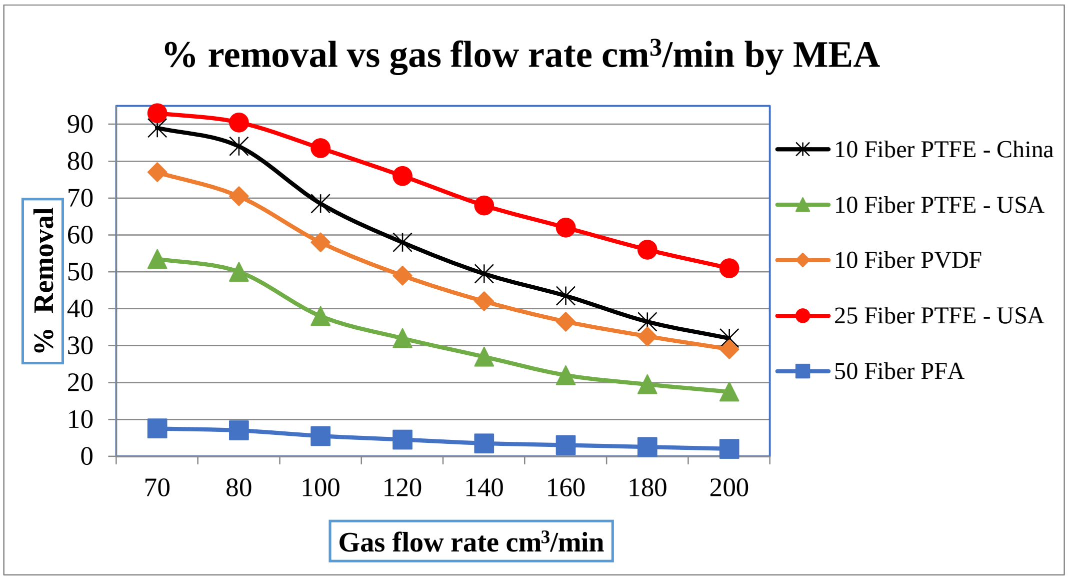

Figure 43: Effect of gas flow rate on removal efficiency in GLMC using 0.5 M MEA at constant liquid flow rate of 20 ml/min

NaOH:

0.5 M aqueous solution of NaOH supplied on lumen side using different gas-liquid hollow fiber membrane contactor, and the Figure 44 shows the effect gas flow rate on the CO_2 removal efficiency.

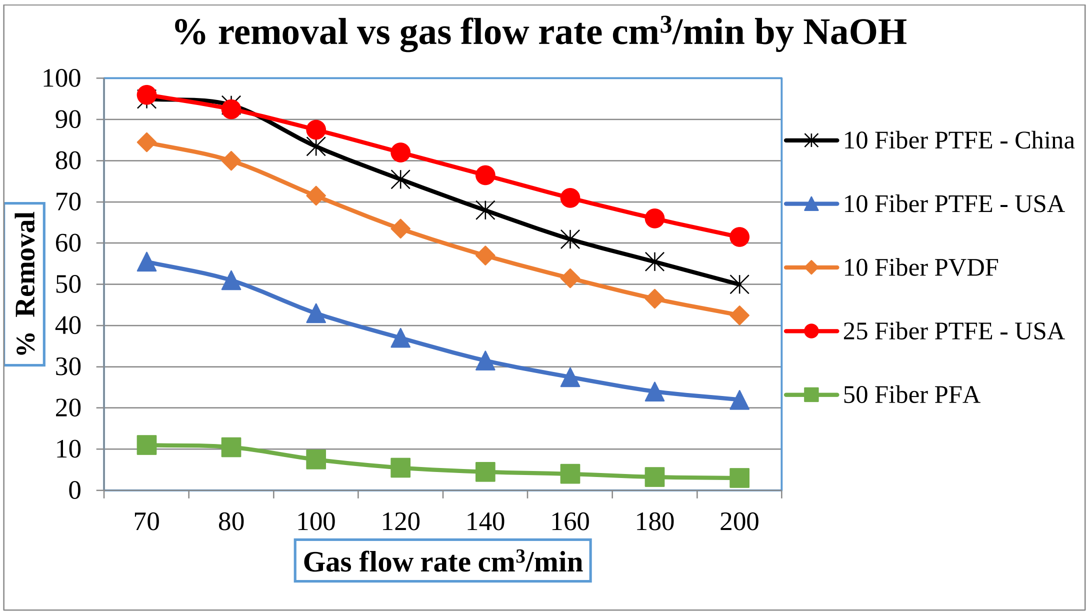

Figure 44: Effect of gas flow rate on removal efficiency in GLMC using 0.5 M DEA with constant flow rate of 20 ml/min

As shown in Figure 42, 43, 44, regardless of type of solvent, increase in gas flow rate will decrease the removal performance.

4.1.4.2 Effect of gas flow rate on absorption flux

Two different type of membrane modules were used for this aim at same set up to investigate the effect of gas flow rate on absorption flux. 0.5 M aqueous solution of DEA, MEA and NaOH supplied on lumen side using 25 fiber PTFE membrane contactor with 25 fibers potting in shell side and 10 fiber of homemade PVDF in shell side .solvent was at room temperature 298k at constant flow rate of 20 ml/min and Figures below shows the effect of gas flow on absorption flux.

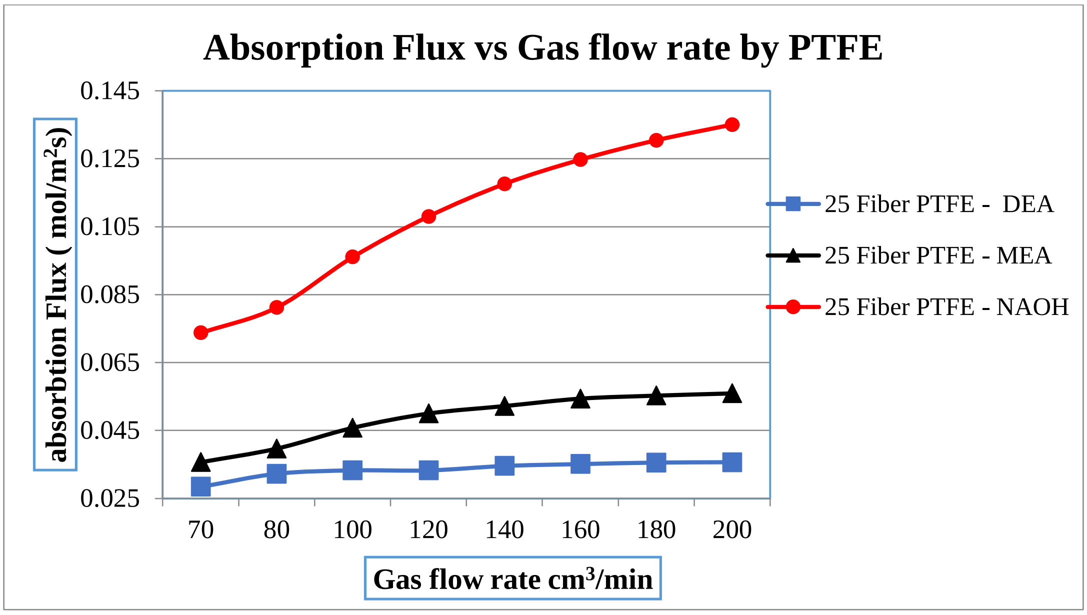

Figure 45: Effect of gas flow rate on absorption Flux 25fiber-PTFE membrane contactor using different 0.5 M solution with constant flow rate of 20 ml/min

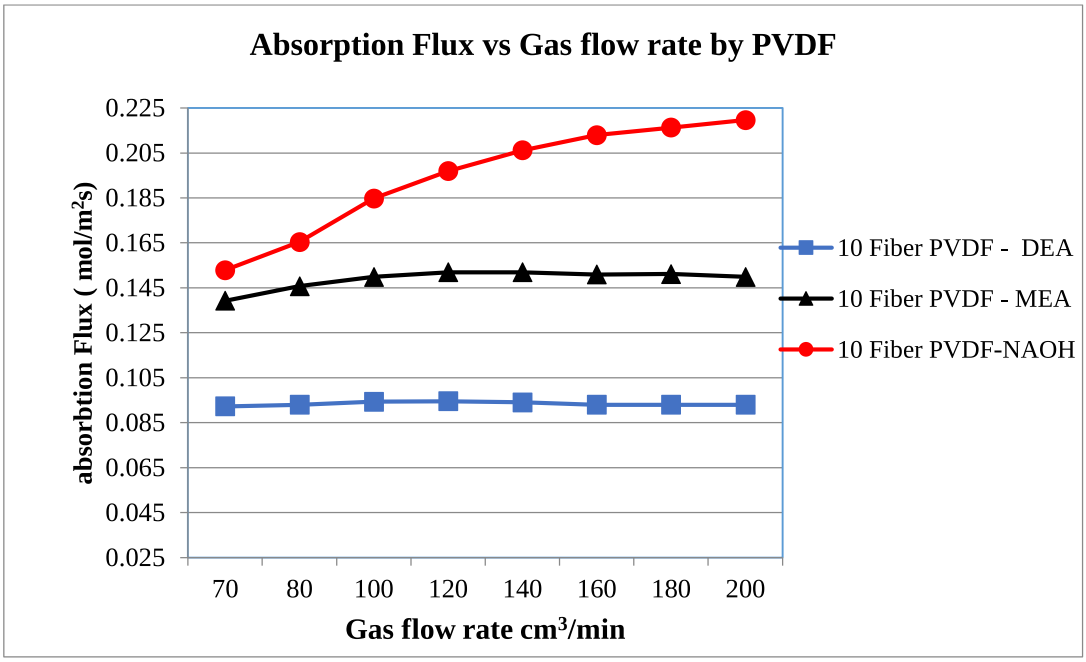

Figure 46: Effect of gas flow rate on absorption Flux 10 fiber-PVDF membrane contactor using different 0.5 M solution with constant flow rate of 20 ml/min

As shown in Figure 45 and 46, by increase in gas flow rate , we have slightly increase in the flux absorption for those solvent that have low removal performance but for those with high potential of removal , increase in gas flow rate will significantly increase the absorption flux.

Regardless of type of module, as shown in Figure 47, increase in gas flow rate will increase the absorption flux.

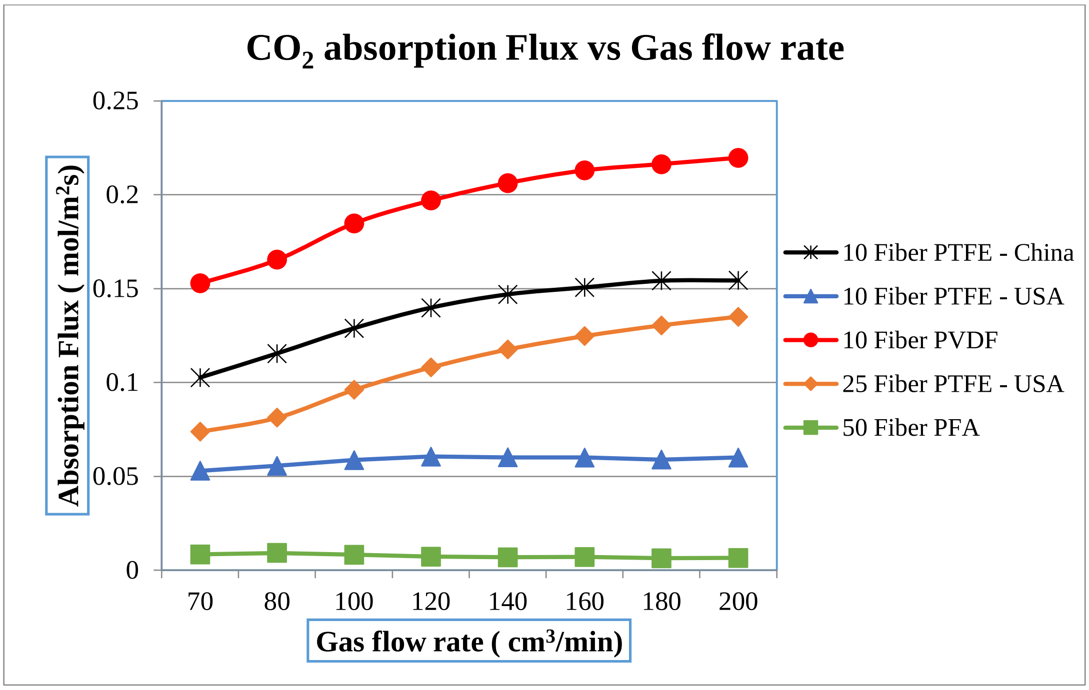

Figure 47: Effect of gas flow rate on absorption Flux in GLMC using 0.5M NaOH with constant flow rate of 20 ml/min

Overall, the flow rate of gas has a significant effect on performance of absorption regardless of the form in membrane module or absorbent liquid and it shows that increasing in flow rate of gas will reduce the removal efficiency.

Although by increasing in gas flow rate, the removal efficiency reduced, later on as per Figure 45, 46 and 47 it show that the flux increased by enhancing in the gas flow rate. This phenomenon is attributed to the fact that, increasing in gas flow rate, decreases the residence time of gas phase, therefore the contact time will be reduced. In addition increasing the flow rate of gas at the same time will increase the driving force in mass transfer since increase in velocity cause reduced in boundary layer and enhanced in mass transfer. Although by increasing in gas flow rate, the removal efficiency decrease, the rate of CO_2 captured and absorption flux increase. Moreover due to low contact time at higher gas flow rate, removal percentage goes down.

4.1.5 Effect of packing density

In this set up of experiment, Two different type of PTFE membrane module (10 and 25 number of fibers potted in shell side of membrane module) were used to investigate the effect of paccking ratio on absorption flux and removal effeceincy. A gas mixture of 20% CO_2 & 80% N_2 flowing at the gas flow rate of 100 cm^3/min applied on shell side of module and 0.5 M aqueous solution of DEA, MEA and NaOH supplied on lumen side of membrane module. Solvents were at ambient temperature 298k at constant flow rate of 20 ml/min. Figures 48 and 49 shows the effect of gas flow on absorption flux and removal efficiency.

Results was determined according to Figure 48 and 49 that packing density has a significant effect on mass transfer therefore increase in packing density will increase the overall removal efficiency.

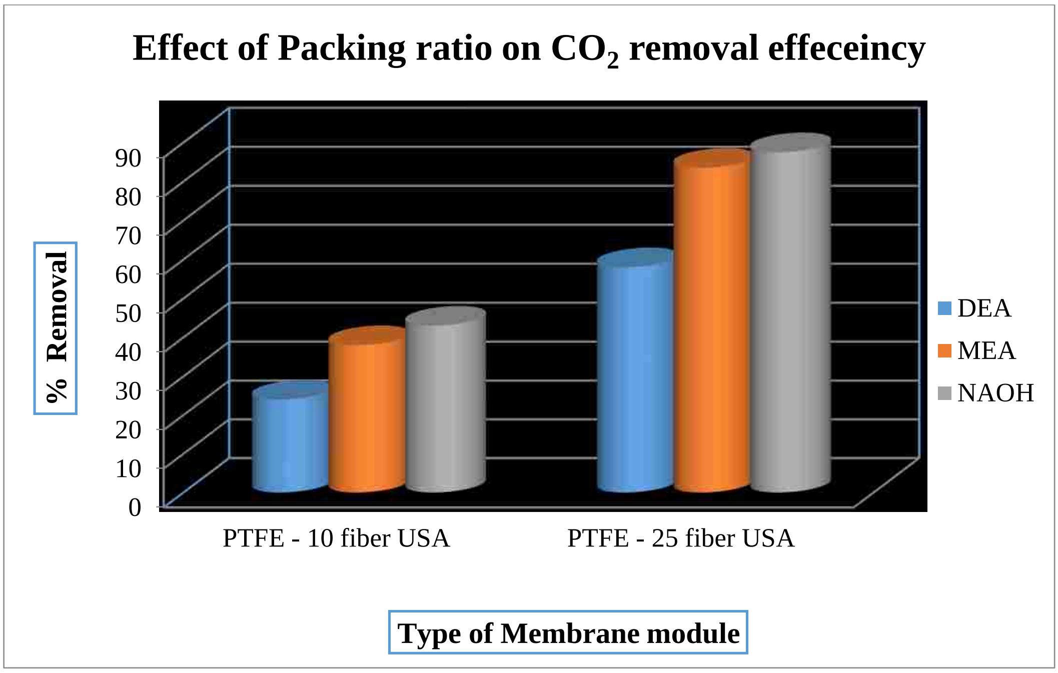

Figure 48: Effect of packing ratio on removal efficiency in GLMC using 0.5M DEA, MEA and NaOH with constant flow rate of 20 ml/min

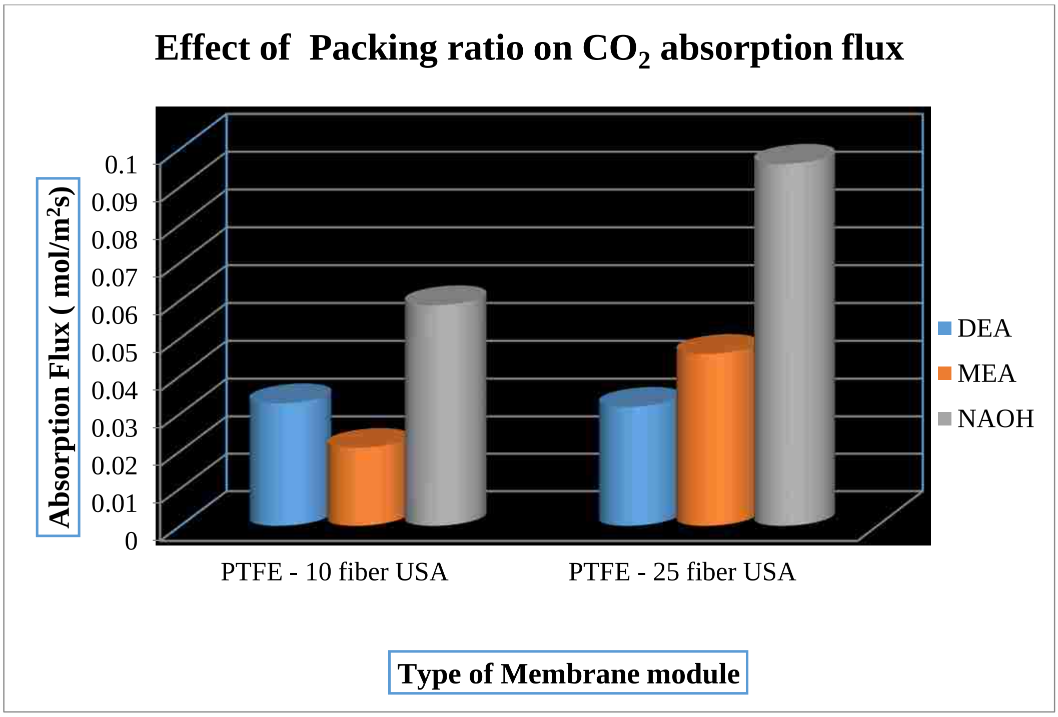

Figure 49: Effect of packing ratio on CO_2 absorption flux in GLMC using 0.5M DEA, MEA and NaOH with constant flow rate of 20 ml/min

4.1.6 Conclusions

In this part different hollow fiber GLMC were used with DEA, MEA and NaOH. The objectives were to investigate the effect of these aqueous solvents on the performance of the CO_2 removal and absorption flux. Also the effect of operation parameters such as liquid flow rate and gas flow rate were investigated and examined.

In general, results reveal that PFA has a poor CO_2 removal efficiency at atmospheric pressure and ambient temperature. Custom lab-made PVDF has the highest removal efficiency due to their specific structure of hollow fiber. According to the results concluded for this set up: PVDF >PTFE-China > PTFE-US > PFA.

The CO_2 removal was studied and the result obtained showed that the liquid absorbent has a significant effect on removal performance and can be summarized as: NAOH > MEA > DEA.

In addition, other parameters such as the regeneration rate and cost of the material might need to be considered in selecting the appropriate absorbent which will be reported in the next part.

Liquid flow rate has also significant effect on CO_2 removal performance for all types of hollow fiber and membrane modules in any liquid absorbent used. It is also reported that the effect of liquid flow rate is more significant in poor liquid absorbent rather than those with high removal efficiency. Based on the result obtained, the increase in liquid flow rate will increases the removal efficiency and absorption flux.

Gas flow rate also has a significant influence on removal percentage.

Although increase in gas flow rate reduces the removal percentage, it cause enhance in CO_2 flux due to increase in the amount of CO_2 being absorbed.

4.2 Stripping process of CO_2 using different HFMC via change in operation parameter

In this section 2 different types of HFMC were used. First module with 25 fibers of PTFE polymer (I.D of 1mm and O.D of 1.6 mm with inner area of 0.0149 m^2) and second consists of 10 fibers of lab-made PVDF (I.D of 0.42 mm and O.D of 1.1 mm with inner area of 0.003165 m^2). The idea is to compare the CO_2 stripping performance, by change in operation parameters such as temperature and sweep gas flow rate and investigate the effect of these parameters on stripping performance. Same as membrane module for absorption process (the Shell &Tube), was prepared. Counter-current flow direction applied. 1 M DEA aqueous solution as a rich solvent was saturated by CO_2 (method described on Figure 22) and then supplied in lumen side of module. Various sweep gas was sent through the shell side to have the better performance of stripping. To achieve steady state, experiment set up was running for almost 20 min, and then sample was collected to examine and calculate the stripping percentage by double titration.

4.2.1 Effect of hollow fiber membrane contactor (HFMC) types

Two different types of HFMC, module with 25 fibers PTFE (I.D=1mm, O.D=1.6 mm, and inner area=0.0149 m^2) and the second module with 10 fiber of lab-made PVDF (I.D= 0.42 mm, O.D= 1.1 mm and inner area=0.003165 m^2) were used.

Sample of 1M DEA was prepared and loaded by pure CO_2 and then was saturated (once the pH becomes steady at 7.3 and there is no more change in pH).

Saturated amine then sent through lumen side of module at liquid flow rate of 20 ml/min. Pure nitrogen was sent to shell side of module at gas flow rate of 200 cm^3/min. Samples were collected after each 20 min running of experiment and for accuracy purpose, two times titration were examined to get the mean of the result.

PTFE – 25 fiber

Stripping process applied on PTFE-25 fiber at three different temperatures of 24, 50 and 80 °C to investigate the performance of stripping at these temperatures. Table 14 shows the concentration of carbon dioxide in the exit stream and stripping efficiency using PTFE. Results show that as the temperature increased, concentration of carbon dioxide in the exit stream decreased, in other words, stripping efficiency increased.

Table 14: Stripping performance in PTFE at 24, 50 and 80°C

	Sample 1 volume (ml)	Vhcl	I gas	Vgas	no of moles co2	CO2 (mol/l)	Saturated
Flask 1	5	14	40.3	75.25991	0.002505	0.501077	T = 24 °c
Flask 2	5	12.5	39.1	73.01892	0.002475	0.495016	
Mean	5	13.25	39.7	74.13941	0.002490	0.498047	

	Sample 2 volume (ml)	Vhcl	I gas	Vgas	no of moles co2	CO2 (mol/l)	12.3522%
Flask 1	5	9.7	35.2	65.73570	0.002292	0.458346	T = 50 °c
Flask 2	5	11.3	33.2	62.00072	0.002074	0.414708	
Mean	5	10.5	34.2	63.86821	0.00218263	0.4365269	

	Sample 3 volume (ml)	Vhcl	I gas	Vgas	no of moles co2	CO2 (mol/l)	55.9240%
Flask 1	5	11.7	21.4	39.96432	0.001156	0.231189	T = 80 °c
Flask 2	5	12.5	20.3	37.91008	0.001039	0.207842	
Mean	5	12.1	20.85	38.9372	0.00109758	0.2195157	

PVDF – 10 fiber

Stripping process applied on PVDF-10 fiber at three different temperatures of 24, 50 and 80 °C to investigate the performance of stripping in these temperatures. Table 15 shows the stripping percentage and concentration of carbon dioxide in the exit stream using PVDF.

Table 15: Stripping performance in PVDF at 24, 50 and 80 °C

	Sample volume (ml)	Vhcl	l gas	Vgas	no of moles co2	CO2 (mol/l)	Saturated
Flask 1	5	13.2	43	80.30213	0.002744	0.548864	T = 24 °c
Flask 2	5	11.4	43.2	80.67563	0.002833	0.566642	
Mean	5	12.3	43.1	80.48888	0.002789	0.557753	

	Sample 2 volume (ml)	Vhcl	l gas	Vgas	no of moles co2	CO2 (mol/l)	18.1395%
Flask 1	5	11.9	36.15	67.50982	0.002274	0.454862	T = 50 °c
Flask 2	5	11.2	36	67.22969	0.002291	0.458297	
Mean	5	11.55	36.075	67.36976	0.0022829	0.4565794	

	Sample 3 volume (ml)	Vhcl	l gas	Vgas	no of moles co2	CO2 (mol/l)	48.393%
Flask 1	5	10.5	24.1	45.00654	0.001411	0.282247	T = 80 °c
Flask 2	5	11	25.1	46.87404	0.001467	0.293433	
Mean	5	10.75	24.6	45.94029	0.001439	0.287840	

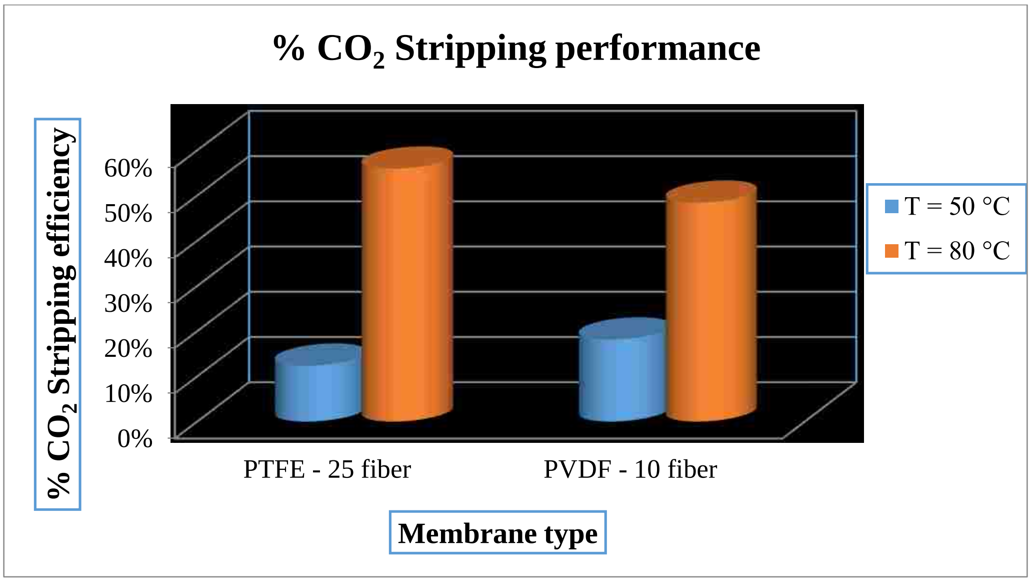

Figure 50: Effect of different HFMC on the stripping performance in T= 50 °C & T= 80 °C

As can be seen from Figure 50, PVDF provided better stripping performance at lower temperature, but PTFE is showing better performance at high temperature, this phenomenon is due to wetting. PVDF is getting wet faster than PTFE at higher temperature and it will effect on CO_2 stripping performance, therefore, operation parameter need to be considered on selecting of HFMC.

In addition, increase in liquid absorbent temperature significantly improve the overall stripping performance of PTFE than PVDF, therefore PTFE can be a good candidate for HFMC to operate at higher heat of regeneration.

4.2.2 Effect of various temperature of absorbent on stripping performance

Temperature is the main factor directly affected on stripping performance. Stripping efficiency and flux are a function of temperature. Since increase in temperature, enhance the reaction rate and cause unstable form of carbamate to release CO_2, therefore energy consumption becomes smaller and smaller. Regardless of type of the HFMC and solution type, increase in temperature will increase the stripping performances as shown in Figure 51.

The aim of this experiment is to investigate effect of liquid phase temperature on stripping performance. Three experiments were performed.

a. First run was performed using 25fiber of PTFE with I.D of 1 mm, O.D of 1.6 mm and inner surface area of 0.0149 m^2. 1M DEA loaded and saturated by CO_2 and then it was sent to the lumen side of module by liquid flow rate of 20 ml/min. Pure nitrogen at gas flow rate of 200 cm^3/min entered through the shell side of model. Samples were collected at different temperatures and double titration was done to get the result.
b. Second run was performed using lab-made PVDF with I.D of 0.42 mm, O.D of 1.1 mm and inner surface area of 0.003165 m^2. Sample of 1MDEA was loaded with pure CO_2 to be saturated, then it was sent through lumen side of module at liquid flow rate of 20 ml/min. Pure nitrogen was sent to the shell side of module at gas flow rate of 200 cm^3/min. Samples were collected at different temperatures to get the result by double titration method.
c. Third run was performed with 25fiber of PTFE with I.D of 1mm, O.D of 1.6 mm and inner membrane surface area of 0.0149 m^2. 1M DEA was saturated and sent to the lumen side of module at liquid flow rate of 20 ml/min.

Vacuum was used as a sweep gas and it was sent through shell side of module. Samples were collected at different temperatures. Figure 51 shows the effect of temperature on these there HFMC.

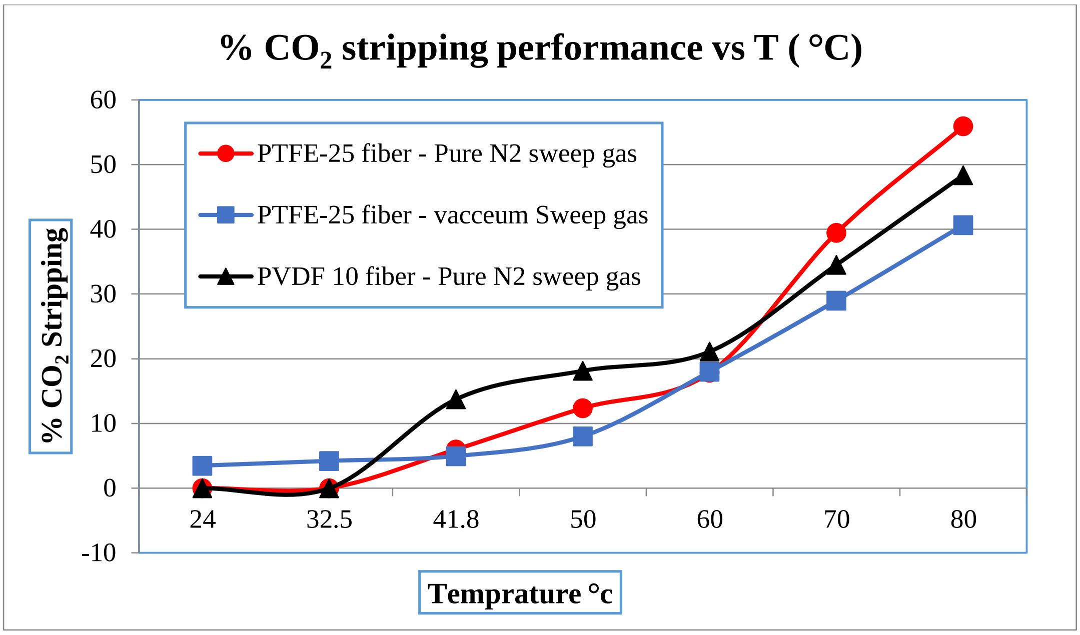

Figure 51: Effect of liquid phase temperature on CO_2 stripping performance

As shown from Figure 51 temperature is the main operating parameter which has strong impact on the CO_2 stripping performance. Regardless of type of module and different sweep gas used, overall, the increase in temperature will increase the performance of the CO_2 stripping.

4.2.3 Effect of sweep liquid flow rate on stripping performance

In this section, De-ionized water was used instead of sweep gas for stripping of CO_2 from saturated amine in various liquid flow rates. 25 fiber of PTFE were potted in the shell side of module. 1 M of DEA was prepared and saturated by CO_2 as we discussed previously and used as a rich amine. Saturated amine then sent through lumen side of module at constant temperature of 60°C and liquid flow rate of

20 cm^3/min. De-ionized water was sent at constant temperature of 32 °C at various liquid flow rates to the shell side of module. Counter-current applied in this set up. Samples were taken for double titration and Table 16 show the results.

Table 16: Effect of liquid absorbent flow rate on stripping performance in PTFE using saturated 1M DEA at 60°C

	Sample 1 volume (ml)	Vhcl	l gas	Vgas	no of moles co2	CO2 (mol/l)	Saturated
Flask 1	5	13.45	40.6	75.82015	0.002551	0.510159	
Flask 2	5	13.1	41.1	76.75390	0.002603	0.520659	
Mean	5	13.275	40.85	76.28703	0.002577	0.515409	

	Sample 2 volume (ml)	Vhcl	l gas	Vgas	no of moles co2	CO2 (mol/l)	**31.14%**
Flask 1	5	13.1	29.5	55.09100	0.001717	0.343467	DEA @ T : 60 °c water @ T : 32 °c & Flow rate : 20 cm3/min
Flask 2	5	7.5	28	52.28976	0.001832	0.366359	
Mean	5	10.3	28.75	53.69038	0.001775	0.354913	

	Sample 3 volume (ml)	Vhcl	l gas	Vgas	no of moles co2	CO2 (mol/l)	**20.16%**
Flask 1	5	13.2	34.1	63.68146	0.002065	0.412915	DEA @ T : 60 °c water @ T : 32 °c & Flow rate : 40 cm3/min
Flask 2	5	13.54	34.1	63.68146	0.002051	0.410134	
Mean	5	13.37	34.1	63.68146	0.002058	0.411524	

	Sample 4 volume (ml)	Vhcl	l gas	Vgas	no of moles co2	CO2 (mol/l)	**17.42%**
Flask 1	5	13.1	34.2	63.86821	0.002076	0.415260	DEA @ T : 60 °c water @ T : 32 °c & Flow rate : 60 cm3/min
Flask 2	5	15.8	37	69.09718	0.002180	0.435946	
Mean	5	14.45	35.6	66.4827	0.002128	0.425603	

	Sample 5 volume (ml)	Vhcl	l gas	Vgas	no of moles co2	CO2 (mol/l)	**16.40%**
Flask 1	5	14.1	36	67.22969	0.002173	0.434576	DEA @ T : 60 °c water @ T : 32 °c & Flow rate : 80 cm3/min
Flask 2	5	15	36	67.22969	0.002136	0.427214	
Mean	5	14.55	36	67.22969	0.002154	0.430895	

As per Figure 52, it shows that CO_2 stripping efficiency decreases by increasing in liquid flow rate which was used instead of sweep gas. Increase in liquid flow rate at low temperature reduces the efficiency of CO_2 stripping, while increasing the liquid flow rate at high temperature, will increase the CO_2 stripping performance.

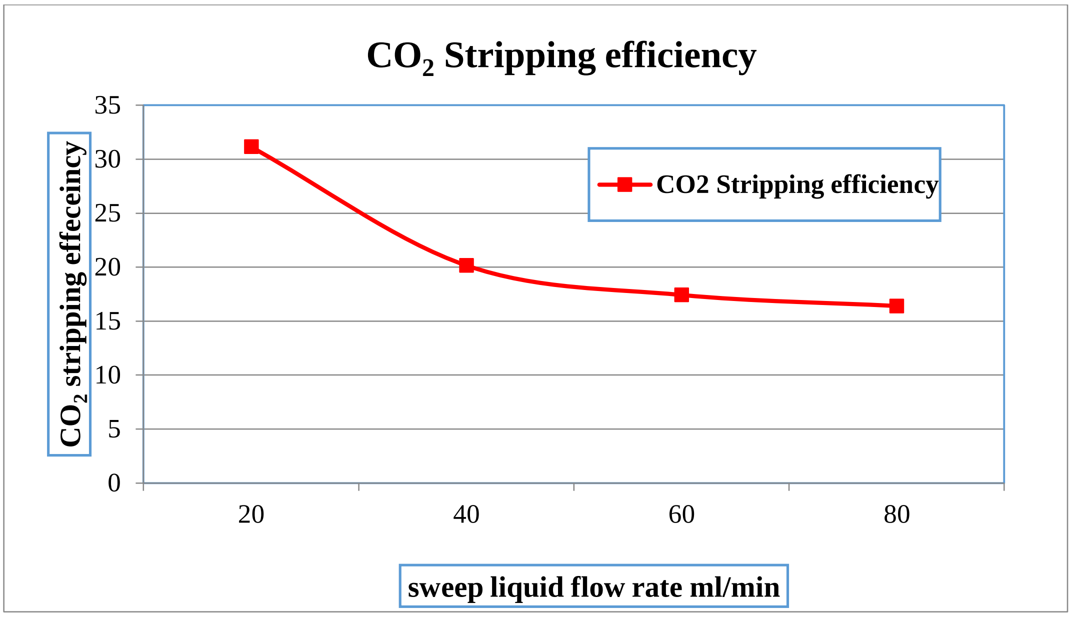

Figure 52: Effect of sweep liquid flow rate on stripping performance in PTFE using saturated DEA at 60°C

4.2.4 Effect of sweep gas flow rate on stripping performance

In this section, vacuum was used instead of the sweep fluid for stripping of CO_2 from saturated amine. 25 fiber of PTFE were potted in the shell side of the module.1 M DEA was prepared and saturated by CO_2 loading method as we discussed previously and it was used as a rich amine. Saturated amine then was sent to lumen side of module at constant temperature of 60°C and liquid flow rate of 20 cm^3/min. Vacuum was sent at various gas flow rate to shell side of module. Counter-current applied in this set up. Samples were taken for double titration. The results are shown in Table 17.

Table 17: Effect of sweep gas flow rate on stripping performance in PTFE using saturated DEA at 60°C

	Sample 1 volume (ml)	Vhcl	I gas	Vgas	no of moles co2	CO2 (mol/l)	saturated
Flask 1	5	13.45	40.6	75.82015	0.002551	0.510159	
Flask 2	5	13.1	41.1	76.75390	0.002603	0.520659	
Mean	5	13.275	40.85	76.28703	0.002577	0.515409	

	Sample 2 (on volume (ml)	Vhcl	I gas	Vgas	no of moles co2	CO2 (mol/l)	**16.26%**
Flask 1	5	15.5	36.1	67.41644	0.002123	0.424652	T = 60 °c Vacuum Flow rate : 250 cm3/min
Flask 2	5	15.3	36.9	68.91044	0.002193	0.438508	
Mean	5	15.4	36.5	68.16344	0.002158	0.43158	

	Sample 3 (on volume (ml)	Vhcl	I gas	Vgas	no of moles co2	CO2 (mol/l)	**18.20%**
Flask 1	5	15.15	36.2	67.60319	0.002145	0.429042	T = 60 °c Vacuum Flow rate : 450 cm3/min
Flask 2	5	15.2	35.25	65.82907	0.002071	0.414122	
Mean	5	15.175	35.725	66.71613	0.002108	0.421582	

	Sample 4 (on volume (ml)	Vhcl	I gas	Vgas	no of moles co2	CO2 (mol/l)	**18.39%**
Flask 1	5	15.02	35.1	65.54895	0.002067	0.413303	T = 60 °c Vacuum Flow rate : 700 cm3/min
Flask 2	5	13.7	35.35	66.01582	0.002140	0.427919	
Mean	5	14.36	35.225	65.78239	0.002103	0.420611	

	Sample 5 (on volume (ml)	Vhcl	I gas	Vgas	no of moles co2	CO2 (mol/l)	**19.14%**
Flask 1	5	13.6	34.2	63.86821	0.002056	0.411170	T = 60 °c Vacuum Flow rate : 1000 cm3/min
Flask 2	5	14.1	35.2	65.73570	0.002112	0.422356	
Mean	5	13.85	34.7	64.80195	0.002084	0.416763	

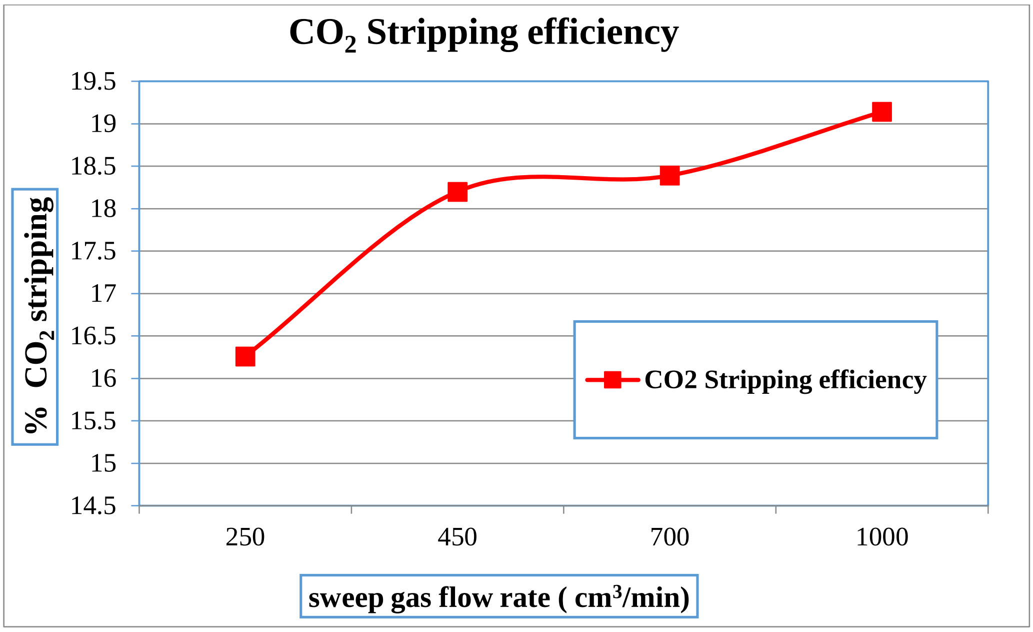

Figure 53: Effect of sweep gas flow rate on the stripping performance using PTFE by saturated DEA at 60°C

As shown in Figure 53, increase in flow rate for vacuum will increase the stripping performance. In case of Using N_2 as a sweep gas, by change in gas flow rate, there was not significant effect on stripping efficiency.

4.2.5 Effect of using steam instead N_2 as sweep gas

In this section, steam was used instead of sweep gas for the CO_2 stripping from saturated amine. 25 fibers of PTFE were potted in the shell side of module.

1 M DEA was prepared and saturated by CO_2 loading process as we discussed previously and then used as a rich amine. The saturated amine was sent to the lumen side of module at ambient temperature and constant liquid flow rate of 20 ml/min. Steam was obtained by steam generator and then it was sent at 200-300 ml/min flow rate to the shell side of module. Counter-current operation mode was applied in this experimental setup. Samples were taken for double titration. Since

using the steam at its high temperature causes earlier wetting, the experiment was performed twice for accuracy purpose. Sample after the first experiment run was taken for titration, and then module was dried and then it was used for second running of experiment. The experiment was run at the same condition and the sample was taken for double titration. Table 18 shows the result.

Table 18: Effect of using the steam as sweep gas on the stripping performance in PTFE using saturated DEA

	Sample 1 volume (ml)	Vhcl	I gas	Vgas	no of moles co2	CO2 (mol/l)	**DEA - 1 M - Saturated**	**Stripping 56.66%**
Flask 1	5	8.2	43.75	81.70275	0.003006	0.601218		
Flask 2	5	6.4	40.3	75.25991	0.002816	0.563242		
Mean	5	7.3	42.025	78.48133	0.002911	0.582230		
	Sample 2 volume (ml)	Vhcl	I gas	Vgas	no of moles co2	CO2 (mol/l)	**first sample**	
Flask 1	5	8.2	38.1	38.10000	0.001223	0.244568		
Flask 2	5	8.3	39.25	39.25000	0.001266	0.253156		
Mean	5	8.25	38.675	38.67500	0.001244	0.248862		
	Sample 3 volume (ml)	Vhcl	I gas	Vgas	no of moles co2	CO2 (mol/l)	**second sample module was dried and then tried again**	
Flask 1	5	8.2	35.1	38.10000	0.001223	0.244568		
Flask 2	5	7.3	33.1	39.25000	0.001307	0.261336		
Mean	5	7.75	34.1	38.67500	0.001265	0.252952		

As shown in table 18, we conducted that stripping efficiency is approximately 56.66% using steam for this specific type of GLMC.

4.2.6 Conclusion

Several operating parameters need to be considered in stripping process by membrane module. Optimum performance and overall satisfaction required considering long term stability, since some parameters are giving the better result in short term, while they are not satisfied with long term applicant. In general, regardless of type of HFMC or type of solution, stripping performance increase with temperature, but it needs to consider that, membrane can get easily wet at highest temperature. Due to capability of being wet at high temperature, a moderate temperature is recommended. As shown in Figure 50, PVDF is giving better result in low temperature for stripping performance, while at higher temperature; PTFE is giving better result for stripping efficiency. Here is the result of some experiment to see how difference in parameter condition, change the performance of CO_2 stripping. As shown water gives the lowest stripping performance, while the steam gives the higher stripping efficiency.

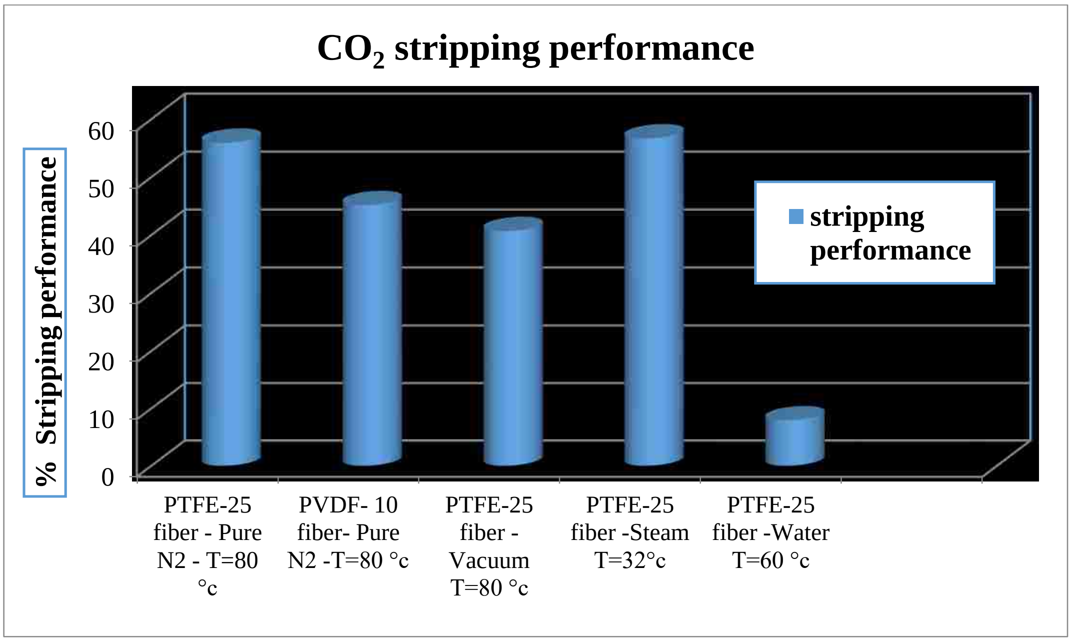

Figure 54: Stripping performance using various HFMC at different operation condition

4.3 Combined absorbing/stripping process of CO_2 removal and regeneration via different chemical absorbent using PTFE HFMC

To construct the experimental set up, The PTFE fiber was used for construction of membrane module. 25 fibers were packed inside the shell side of Perspex glass like shell and tube heat exchanger. For each experiment two modules needed. One act as absorber and the other as a stripper, Figure 55 and 56 show the experimental set-up of absorption/stripping membrane contactor system in a close-loop respectively schematic and practical in our lab.

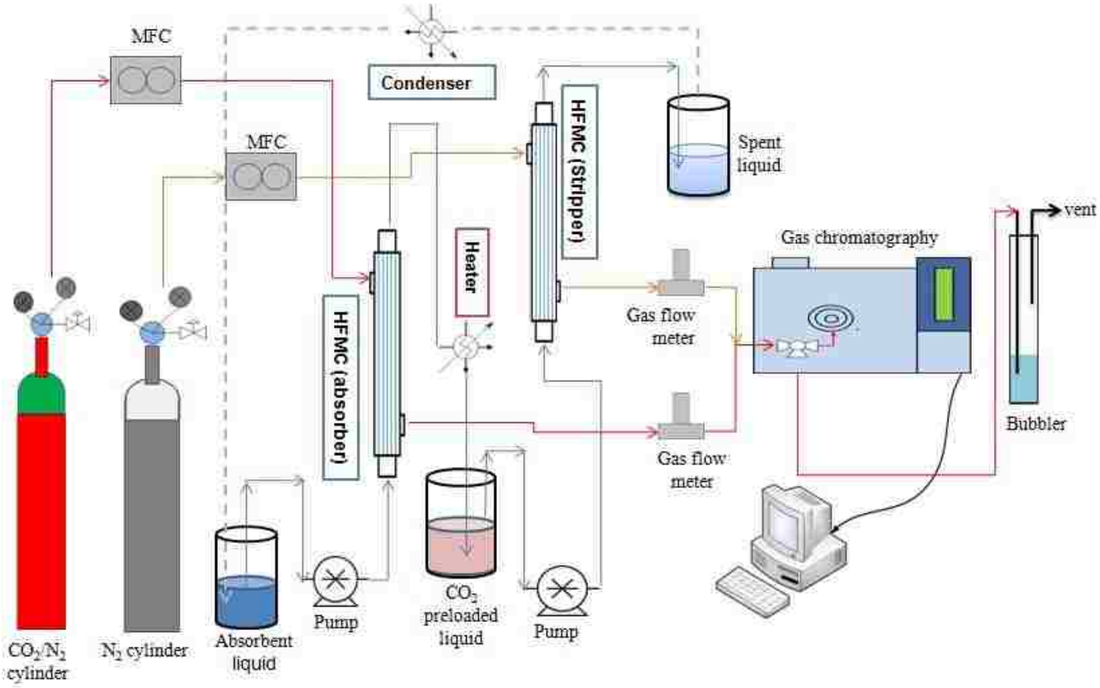

Figure 55 : Flow diagram of gas liquid membrane contactor as CO_2 absorber/stripper

Figure 56: Practical gas- liquid membrane contactors as CO_2 absorber/stripper

The gaseous mixture of (20% CO_2 & 80% N_2) was fed by mass flow controls at 100 ml/min flow rate to the shell side of membrane absorber unit. The exit gas stream in absorber unit analyzed by CO_2 analyzer/gas chromatography every 30min to determine the concentration of CO_2 in outlet. Several solvents such 0.5M DEA, 0.5M MEA and 0.5M NaOH pumped counter current to the lumen side of membrane absorber unit to remove CO_2 from gas mixture. In the absorber, the liquid pressure should be more than gas phase pressure to avoid bubbling. In addition, the liquid pressure should be less than LEPw to avoid instantaneous wetting. The rich solvent leaving the absorber was heated, and then was pumped to the membrane stripper unit which is 25 fibers of PTFE. Nitrogen used as a sweep gas in the stripping unit at constant flow rate of 200 ml/min. The outlet liquid stream from the stripping unit then cooled down and pumped back to the absorber in a closed-loop system. This experiment was run in two different temperature and using various aqueous solution to investigate CO_2 removal from gas mixture using both modules in a closed-loop system.

4.3.1 Effect of using different amines in the combined process at ambient temperature

In this setup, a close loop experiment for absorption and stripping experiment were performed at room temperature for almost 390 minute using 0.5M DEA, 0.5M MEA and 0.5M NaOH and data was conducted as shown in table 19.

Table 19: Effect of using different amines in full absorption/striping process at ambient temperature

Time Min	Concentration of CO_2 from 20% CO_2 -by DEA 0.5 M	Concentration of CO_2 from 20% CO_2 -by MEA 0.5 M	Concentration of CO_2 from 20% CO_2 -by NAOH 0.5 M	Removal % DEA 0.5 M	Removal % MEA 0.5 M	Removal % NAOH 0.5 M
0	8.7	6.8	5.9	57	66	71
15	9	6.9	6	55	66	70
30	10.7	7.1	6.6	47	65	67
60	11.8	9.2	7.2	41	54	64
90	13.4	10.7	8.2	33	47	59
120	14.1	11.8	9.4	30	41	53
150	14.8	12.8	12.2	26	36	39
180	15.1	13.9	15.6	25	31	22
210	15.7	14.6	16.6	22	27	17
240	16.1	15.5	17.1	20	23	15
270	16.8	16.4	17.4	16	18	13
300	17.1	17	17.7	15	15	12
330	17.5	17.4	18.1	13	13	9
360	17.7	17.7	19	12	12	5
390		18	19.1		10	4

Absorption process was at ambient temperature: Mixture of (20% CO_2 & 80% N_2), Solvents: 0.5 M DEA, 0.5 M MEA and 0.5 M NaOH, liquid flow rate: 20 ml/min and gas flow rate: 100 ml/min.

Stripping process was at ambient temperature: Pure N_2 100% used, liquid flow rate was at 20 ml/min and gas flow rate at 200 ml/min.

Figure 57 shows the behavior of using these three amines in close system of absorption/stripping at ambient temperature. As shown, although NaOH has better removal efficiency at the beginning, it has poor overall regeneration efficiency when compared to other solvents. Decrease in removal efficiency is due to the high tendency of NaOH in saturating which effect on membrane wetting after a while. Although MEA has better removal efficiency in compare to DEA, there is no significant difference in using MEA and DEA at ambient temperature since both are getting saturated at the same time,

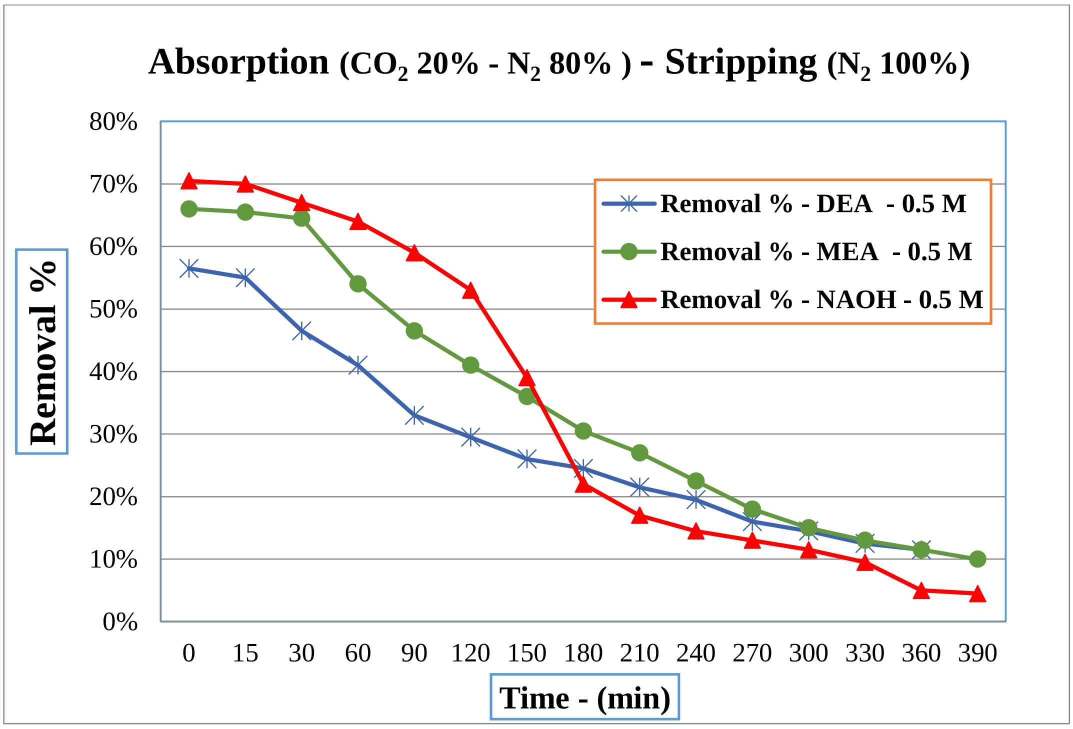

Figure 57: CO_2 removal and stripping in close gas liquid membrane contactor at ambient temperature using 0.5M DEA, MEA and NaOH and nitrogen as sweep gas

4.3.2 Effect of using different amines in combined absorption/stripping process when liquid absorbent is at T= 48.5 °C for stripping process

In this set up, a close loop for absorption and stripping experiment were performed for almost 7 hours using 0.5M DEA, 0.5M MEA and 0.5M NaOH, and data was conducted as shown in table 20. Rich amine receive from absorber unit was heated by a heater to reaches to 48.5 °C then sent to stripping unit. The exit liquid from stripper then cooled down to room temperature then sent to absorption unit to avoid wetting in absorption part and increase the performance of full process.

Table 20: Effect of using different amines in combined absorption/striping process at liquid absorbent in T= 48.5 °C for stripping

Time Min	Concentration of CO_2 from 20% CO2 - by DEA 0.5 M	Concentration of CO_2 from 20% CO2 - by MEA 0.5 M	Concentration of CO_2 from 20% CO2 - by NAOH 0.5 M	Removal % - DEA - 0.5 M - 48.5 'c	Removal % - MEA - 0.5 M - 48.5 'c	Removal % - NAOH - 0.5 M - 48.5 'c
0	9.6	7.9	5.5	52	61	73
15	9.8	8.2	5.6	51	59	72
30	10.3	9.4	6.1	49	53	70
60	11.8	10.2	7	41	49	65
90	12.9	11.1	8.4	36	45	58
120	13.4	12.4	10	33	38	50
150	13.8	13	11.9	31	35	41
180	14.2	13.7	13.9	29	32	31
210	14.4	14.2	14.9	28	29	26
240	14.6	14.9	16	27	26	20
270	14.95	15.6	16.9	25	22	16
300	15.3	16.1	17.7	24	20	12
330	15.5	16.6	18.1	23	17	9
360	15.85	16.9	18.3	21	16	9
390		17.3	18.5		14	8

Absorption at ambient temperature: Mixture of (20% CO_2 & 80% N_2). Solvents: 0.5 M DEA, 0.5 M MEA and 0.5 M NAOH. Liquid flow rate is 20 ml/min while gas flow rate is constant at 100 ml/min.

Stripping process while liquid absorbent is at T= 48.5 °C and Pure 100% N_2 was used. Liquid flow rate: 20 ml/min and gas flow rate: 200 ml/min.

Figure 58 shows the behavior of using these three amines in a closed system of absorption/stripping at T= 48.5°C. As per Figure 58, again it shows although NaOH has a better removal efficiency but it suffer from poor regeneration efficiency in compare to other solvents, DEA is having better performance as it spend more time to reach the saturation and it's the overall performance is better than other solvent.

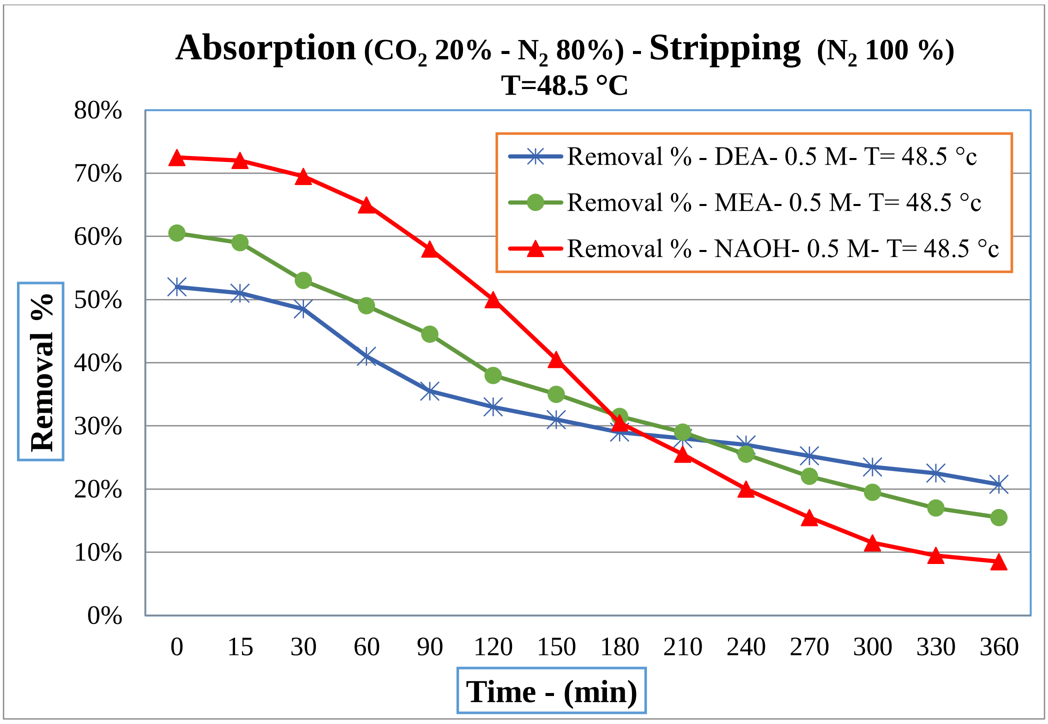

Figure 58: Flow diagram of gas liquid membrane contactor as CO_2 absorber/stripper at T= 48.5 °C

Conclusion

Although some solvents have better removal efficiency, they suffer from poor regeneration performance; therefore, to select the chemical solvent, several factors need to be considered. As per this experiment, although DEA has a lower removal percentage at the beginning in compare to other solution, by contrast, it gives better results the in overall process of full absorption/stripping process. Also it shows that, to have a better performance it needs to heat the rich amine comes from absorber and then send to stripping unit since the stripping performance is very poor at low temperature and it affect on full process. Since temperature is the main factor in full close loop process, each solvent were compared at two different temperatures to see their impact.

4.3.3 Effect of temperature by time in combined absorption/stripping process when the temperature of rich amine in only stripping process has changed

In this set up, a close loop of absorption and stripping was performed using module with 25 fibers PTFE when 0.5 M DEA was used as a rich amine. Two different temperature applied on the rich amine comes from absorption unit, T_1= 23 °C & T_2= 48.5 °C and then sent to stripping unit. The experiment was running for almost 6 hours and the experimental results were collected every 30 min.

Absorption process was at ambient temperature, mixture of (20% CO_2 & 80% N_2) was sent to shell side of membrane module at gas flow rate100 ml/min and 0.5 M DEA aqueous solvent were pumped at liquid flow rate of20 ml/min to the lumen side of fibers.

In stripping process, rich amine from absorber unit was heated to two different temperature (T_1= 24°C & T_2= 48.5°C) and then sent to lumen side of membrane fiber at liquid flow rate: 20 ml/min. Pure N_2 100% was fed to shell side of membrane module at gas flow rate of 200 ml/min. Figure 59 shows the behavior removal/stripping performance in close loop for 360 minute of running experiment when using DEA.

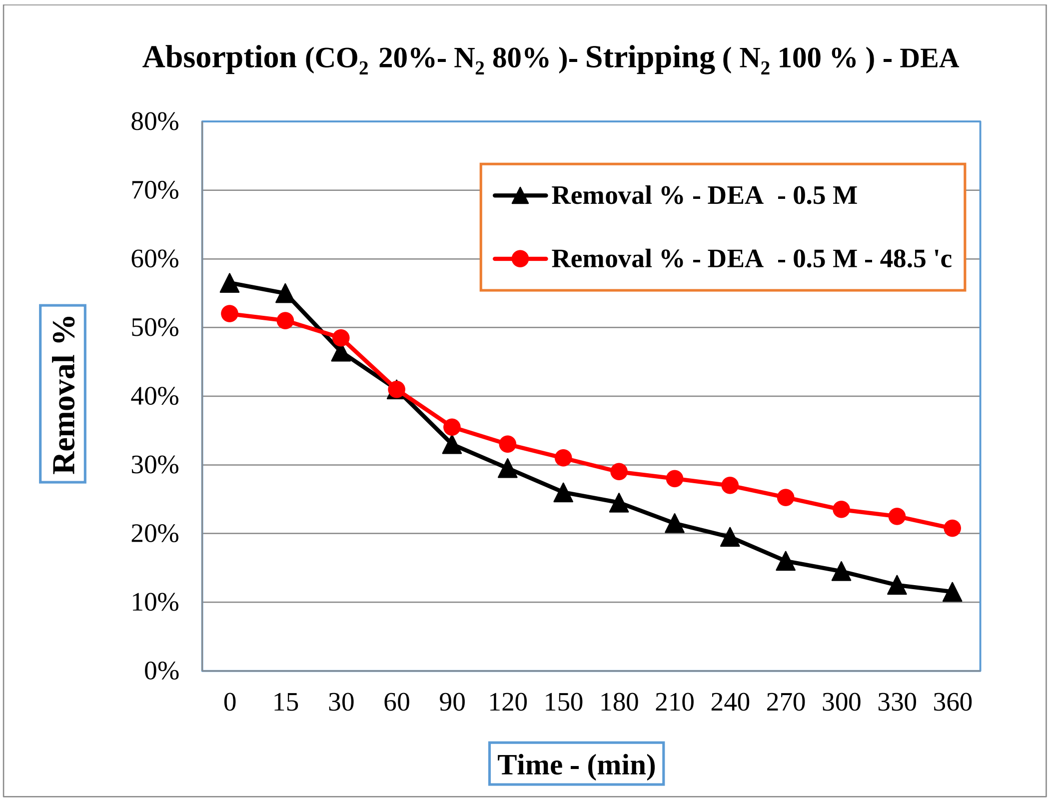

Figure 59: Effect of temperature in full absorption/stripping process by increasing temperature of rich DEA amine in stripping process only

In this set up, a close loop of absorption and stripping was performed using module with 25 fibers PTFE when 0.5 M MEA was used as a rich amine. Two different temperature applied on the rich amine comes from absorption unit, T_1= 23 °C & T_2= 48.5 °C and then sent to stripping unit. The experiment was running for almost 7 hours and the experimental results were collected every 30 min.

Absorption process was at ambient temperature, mixture of (20% CO_2 & 80% N_2) was sent to shell side of membrane module at gas flow rate100 ml/min and 0.5 M MEA aqueous solvent were pumped at liquid flow rate of 20 ml/min to the lumen side of fibers. In stripping process, rich amine from absorber unit was heated to two different temperature (T_1= 24°C & T_2= 48.5°C) and then sent to lumen side of membrane fiber at liquid flow rate: 20 ml/min. Pure N_2 100% was fed to shell side of membrane module at gas flow rate of 200 ml/min. Figure 60 shows the behavior removal/stripping performance in close loop for 390 minute of running experiment when using MEA.

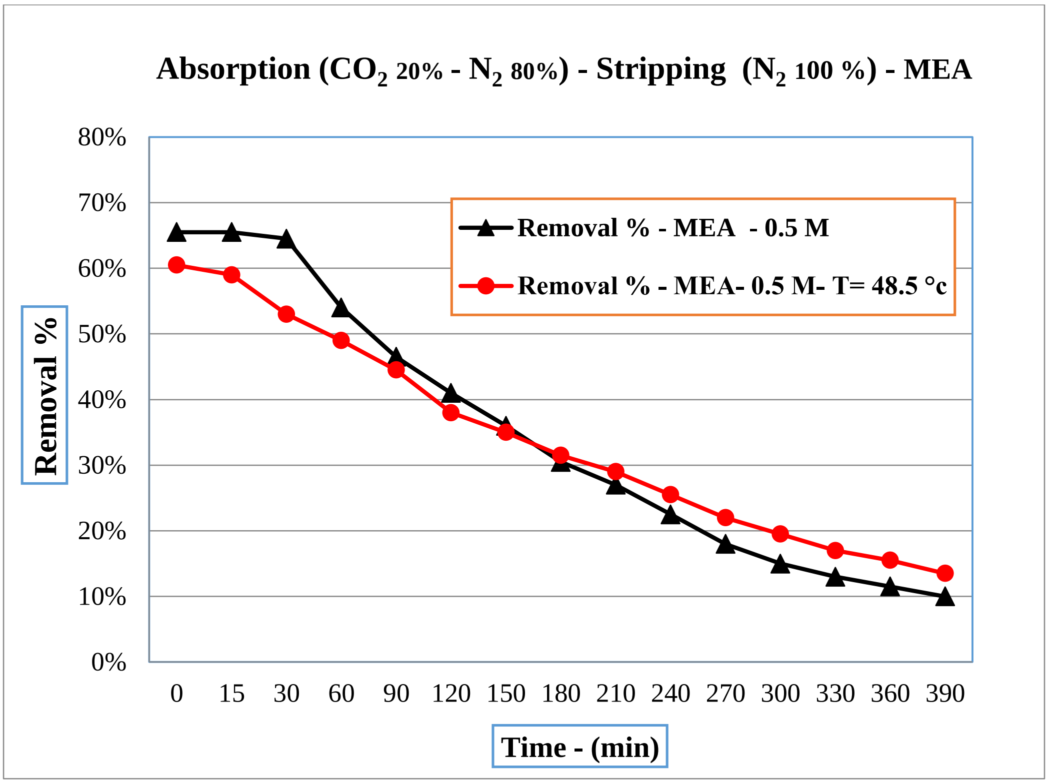

Figure 60: Effect of temperature in full absorption/stripping process by increasing temperature of rich MEA amine in stripping process only

In this set up, a close loop of absorption and stripping was performed using module with 25 fibers PTFE when 0.5 M NaOH was used as a rich amine. Two different temperature applied on the rich amine comes from absorption unit, T_1= 23 °C & T_2= 48.5 °C and then sent to stripping unit. The experiment was running for almost 7 hours and the experimental results were collected every 30 min.

Absorption process was at ambient temperature, mixture of (20% CO_2 & 80% N_2) was sent to shell side of membrane module at gas flow rate100 ml/min and 0.5 M NaOH aqueous solvent were pumped at liquid flow rate of 20 ml/min to the lumen side of fibers. In stripping process, rich amine from absorber unit was heated to two different temperature (T_1= 24°C & T_2= 48.5°C) and then sent to lumen side of membrane fiber at liquid flow rate: 20 ml/min. Pure N_2 100% was fed to shell side of membrane module at gas flow rate of 200 ml/min. Figure 61 shows the behavior removal/stripping performance in close loop for 390 minute of running experiment when using NaOH.

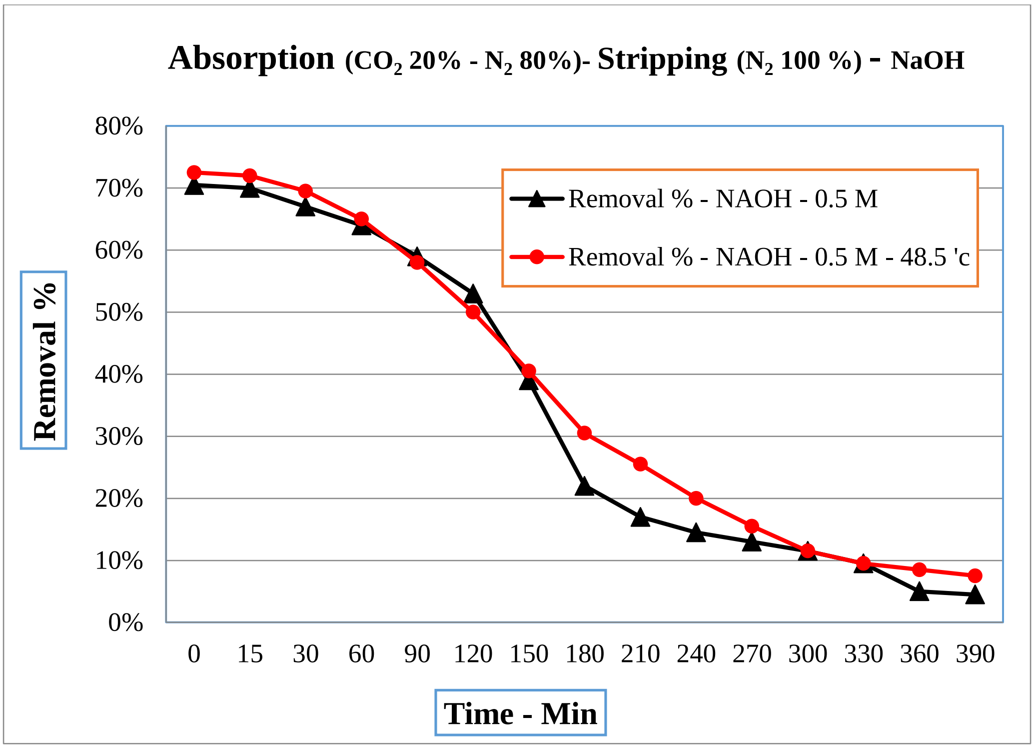

Figure 61: Effect of temperature in full absorption/stripping process by increasing temperature of rich NaOH amine in stripping process only.

4.3.4 Conclusion

As shown in Figure 59, 60 and 61, the overall performance of closed loop absorption/stripping process is getting better by increase the temperature of rich amine comes from absorbent unit. It is also shown that the time period for amine saturation is longer at higher temperature rather than ambient temperature. As per this experimental work, results revealed that, although DEA has a lower removal percentage at beginning of experiment, it has more potential in regeneration and shows better performance compared to other solvent. Therefore, to select the optimum solvent, DEA will reduce the cost of regeneration as long as it is getting longer time to be saturated. On the other hand, although NaOH has the highest removal efficiency at beginning, it suffers from poor regeneration and it is not a good candidate for close loop of absorption/stripping process.

Chapter 5: Modeling and Simulation

5.1 Introduction

Several techniques are available for the separation of CO_2 from flue gas streams at present, such as chemical and physical absorption, solid adsorption, carbon molecular sieve adsorption, cryogenic distillation, membrane separation and other novel methods (Granite & O’Brien, 2005) and (Li & Chen, 2005b). Among these methods, the most well established method is to separate CO_2 from gas stream by absorption into alkanolamines solutions using conventional contactor equipment such as packed or tray columns (NATO Advanced Study Institute on Membrane Processes in Separation and Purification, Crespo, & Böddeker, 1994). In packed towers or columns, CO_2 contacts the absorbent to form a weak complex and the aqueous solution is then transferred to a regenerating unit to release CO_2 by heating. After this, the solution is cooled and re-circulated to the absorption equipment. Although chemical absorption technology has large commercial significance, the technology is energy-consuming and not easy to operate because of some frequent problems including foaming, flooding, channeling and entrainment. Membrane gas absorption technology uses hollow fiber membrane contactors to absorb CO_2 from flue gas into solvent. By contrast, chemical absorption technology uses random or structured packed columns to capture CO_2 from flue gas into solvent. Hydrophobic microporous membranes are used to form a permeable barrier between the liquid and gas phases; Absorbent liquid offers the CO_2 selectivity; liquid phase and gas phase are not directly contacted; main driving force is the differential concentration of CO_2 between gas and liquid phase; membrane pores must be completely filled by gas.

Liquid phase and gas phase are not directly contacted. Avoid the conventional problems such as flooding, foaming, channeling and entrainment in packed column, membrane device has larger contact area. Reduction over 70% in size and 66% in weight compared with conventional columns. The interfacial area is known and constant. It does not depend on the operating conditions such as temperature and liquid flow rate. As a result, it is easier to predict the performance of a membrane contactor (Kim & Yang, 2000) .Potential problems of membrane gas absorption are membrane wetting. Main difficulty is how to prevent the membrane wetting in the long-term operations. This can be achieved by using hydrophobic membranes through surface modification of membrane, composite membrane, selection of denser hollow fiber membrane; selection of liquid with suitable surface tension and optimizing the operating conditions. An amino acid salt Diethanolamine (DEA) was found to have high tension, high reactivity with CO_2, and chemical compatibility with membrane material and easiness of regeneration (Yan et al., 2007).

In this chapter, experiments on carbon dioxide capture from flue gas using (nitrogen) using polymeric Polytetrafluoroethylene (PTFE) hollow fiber membrane contactors were conducted. Absorbent including aqueous Diethanolamine (DEA) solution has been proposed for separation of CO_2 from flue gas because of its high surface tension than water and hence lower potential of membrane wetting. A two-dimensional mathematical model has been employed to predict concentration profiles in the liquid, membrane and gas phases. The model equations were based on "non-wetted mode" in which the gas mixture filled the membrane pores for counter-current gas-liquid contact. Axial and radial diffusion inside the hollow fiber membrane, through the membrane skin, and within the shell side of the contactor were considered in the model. Furthermore, the model was validated with the experimental results obtained for carbon dioxide removal from CO_2/N_2 gas mixture using Polytetrafluoroethylene (PTFE) membrane contactor. The effect of inlet gas and liquid temperature on the membrane performance was investigated. The modeling predictions were in good agreement with the experimental results.

5.2 Modeling of membrane contactor

A steady state mathematical model that described the material balance has been carried out on a shell-and-tube membrane contactor system shown in Figure 62.

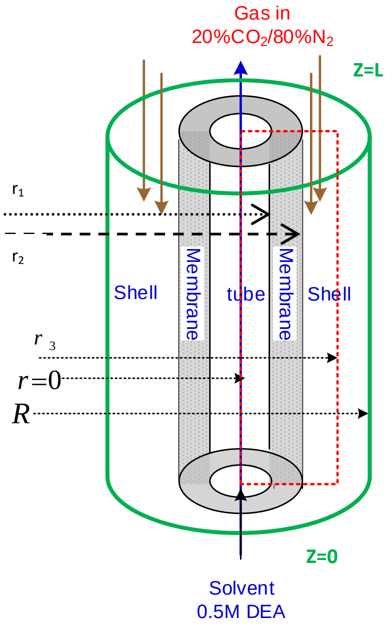

Figure 62: Schematic diagram of the hollow fiber section used in modeling the membrane contactor

The model is developed for a segment of a hollow fiber, as shown in Fig. 62, through which the solvent flows with a fully developed laminar parabolic velocity profile. The fiber is surrounded by a laminar gas flow in an opposite direction to that of the liquid. Based on Happel's free surface model, only portion of the fluid surrounding the fiber is considered which may be approximated as circular cross section. Thus, symmetry may be considered at the outer portion of the fluid surrounding the fiber (at $r = r_3$). The steady state continuity equation for each species during the simultaneous mass transfer and chemical reaction in a reactive absorption system can be expressed as:

5.2.1 Shell side (gas phase)

The steady state material balance for the transport of gas mixture in the shell side may be written as follows (*i* = CO_2 and N_2):

$$D_{i,s}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{i.s}}{\partial r}\right)+\frac{\partial^2 C_{i,s}}{\partial z^2}\right]=\frac{\partial}{\partial z}\left(V_{zs}C_{i,s}\right)+\frac{1}{r}\frac{\partial}{\partial r}\left(rv_{rs}C_{i,s}\right)$$

Considering the active area around each fiber calculated from the hypothetical radius bearing in mind a hexagonal–shaped unit cell of the fiber assembly around each fiber.

$$r_3 = r_2\sqrt{1/(1-\varphi)}$$

Where φ is the volume void fraction of the membrane contactor module. Assuming Happel’s free surface model, the boundary conditions:

$$r = r_2,\ C_{i,s} = C_{i,m}$$

$$r = r_3,\ -\frac{\partial C_{i,s}}{\partial r} = 0$$

$$z = 0, -\frac{\partial C_{i,s}}{\partial r} = 0$$

$$z = L, \mathrm{C}_{\mathrm{CO}_{2,s}} = \mathrm{C}^{\circ}_{\mathrm{CO}_2} \;\;,\; \mathrm{C}_{N_{2,s}} = \mathrm{C}^{\circ}_{N_2}$$

5.2.2 Membrane section

The steady state material balance for the transport of CO_2 and N_2 across the membrane skin layer for non-wetting mode of operation is considered to be due to diffusion only; no reactions are taking place in the gas filled pores (i = CO_2 and N_2).

$$D_{i,m}\left[\frac{\partial^2 C_{i,m}}{\partial r^2} + \frac{1}{r}\frac{\partial C_{i,m}}{\partial r} + \frac{\partial^2 C_{i,m}}{\partial z^2}\right] = 0$$

Boundary conditions:

$$r = r_1, \;\; C_{i,m} = C_{i,t} / m_i$$

$$r = r_2, \; C_{i,m} = C_{i,s}$$

$$z = 0, \; z = L, \; \frac{\partial C_{i,m}}{\partial z} = 0$$

Where m_i is the solubility of CO_2 and N_2 in aqueous DEA solution.

5.2.3 Tube side (liquid phase)

The steady state material balance for the transport of CO_2 and aqueous DEA in the lumen side of the hollow fiber membrane tubes is considered to be due to diffusion, convection and reaction as well (Ghasem, Al-Marzouqi, & Abdul Rahim, 2013):

$$D_{i,t}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{i,t}}{\partial r}\right)+\frac{\partial^2 C_{i,t}}{\partial z^2}\right]+r_{i,t}=\frac{\partial}{\partial z}\left(v_{zt}C_{i,t}\right)+\frac{1}{r}\frac{\partial}{\partial r}\left(rv_{rt}C_{i,t}\right)$$

Where the subscript "*i*" indicates carbon dioxide and DEA. In aqueous DEA solutions the corresponding reactions are taking place:

$$R_1R_2NH^+COO^- + R_1R_2NH \xrightarrow{k_{R_1R_2NH}} R_1R_2NCOO^- + R_1R_2NH_2^+$$

$$R_1R_2NH^+COO^- + H_2O \xrightarrow{k_{H_2O}} R_1R_2NCOO^- + H_3O^+$$

$$R_1R_2NH^+COO^- + OH^- \xrightarrow{k_{OH-}} R_1R_2NCOO^- + H_2O$$

In this mechanism, a quasi-steady state condition for the zwitterion concentration is assumed. It means that the zwitterion concentration is constant in time and very small comparing with concentrations of substrates and products. In this situation the overall forward reaction rate equation for this reaction can be expressed as:

$$r=\frac{k_2[CO_2][R_1R_2NH]}{1+\dfrac{k_{-1}}{(k_{H_2O}[H_2O]+k_{OH-}[OH^-]+k_{R_1R_2NH}[R_1R_2NH]}}$$

In aqueous DEA the contribution of hydroxyl ion to the deprotonation of the zwitterion can be neglected due to its very low concentration.(Versteeg & van Swaaij, 1988) Moreover, most of the researchers neglected the contribution of water to the deprotonation of the zwitterion so the equation is reduced to:

$$r = \frac{k_2[CO_2][R_1R_2NH]}{1 + \dfrac{k_{-1}}{k_{R_1R_2NH}[R_1R_2NH]}}$$

Under pseudo-first-order conditions with respect to CO_2, when the concentration of DEA is much in excess of that of CO_2, which means that the concentration ratio [DEA]/[CO_2] is at least 10, the reaction rate equation takes the form (Siemieniec et al., 2011):

$$r_{CO_2} = -k_{ov}\ CO_2$$

Therefore, the observed pseudo-first-order reaction rate constant (K_{OV}) can be obtained by:

$$k_{ov} = \frac{k_2[R_1R_2NH]}{1 + \dfrac{k_{-1}}{k_{R_1R_2NH}[R_1R_2NH]}}$$

Kinetics rate data for CO_2 into aqueous DEA solutions were analyzed to determine the kinetics parameters associated with the reaction. The effect of concentration of the aqueous solution of DEA on the kinetics of reaction between DEA and CO_2 was studied at 293, 298, 303 and 313 K. As expected, for a given amine concentration, the reaction kinetics increases when the temperature increases. Moreover, for a given temperature, the k_{OV} values increase when amine concentration increases. The obtained values of the pseudo-first-order reaction rate constant k_{OV} are presented in Table 21 (Siemieniec et al., 2011). The effect of DEA concentration and temperature on K_{OV} is shown in Figure 63.

Table 21: The pseudo-first-order reaction rate constant K_{OV} (Siemieniec et al., 2011).

DEA [kmol/m^3]	kov			
	293K	**298K**	**303K**	**313K**
0.167	26.7	36.0	44.3	65.2
0.200	38.1	42.8	58.2	88.5
0.250	59.3	72.7	99.0	137.8
0.300	83.4	98.7	135.9	198.1
0.333	101.6	120.2	163.7	228.3
0.375	114.2	137.2	174.4	240.5
0.400	124.4	148.8	184.5	291.8
0.429	133.8	175.7	217.9	333.1
0.455	142.4	184.5	226.5	341.4
0.474	167.0	197.7	248.0	346.7
0.500	172.8	236.5	255.6	408.0

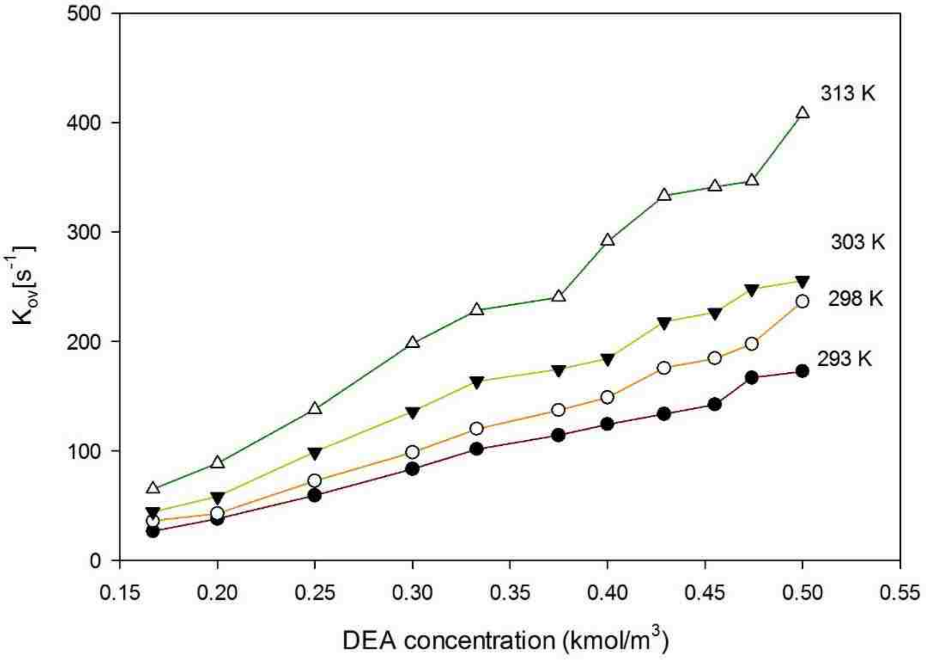

Figure 63: Effect of DEA concentration and temperature on K_{ov}.

Boundary conditions

The boundary conditions for liquid flowing in lumen side of the fibers (*i* = CO_2 and DEA):

$$r = 0, \; -\frac{\partial C_{i,t}}{\partial r} = 0$$

$$r = r_1, \; C_{i,t} = m_i C_{i.m}$$

$$z = 0, \; C_{DEA,t} = C_{DEA}^{o}$$

$$z = L, \; -\frac{\partial C_{i,t}}{\partial z} = 0$$

5.3 Results and discussion

Figure 64 shows the effect of gas flow rate at fixed other operating conditions on percent removal of CO_2 and its removal flux. The diagram reveals that % CO_2 removal decreased with increases inlet gas flow rate, by contrast, its removal flux increases, as the flux is based on amount of CO_2 removed within specific time. As inlet gas flow rate increased at fixed liquid flow rate, more CO_2 enters the shell side of the membrane contactor and since the amount of DEA available in the fixed liquid flow rate is not enough to react with the abundant available of carbon dioxide the concentration of CO_2 in the exit gas stream increased and the percent removal decreased. As the flux is based on the amount of CO_2 absorbed per area per time, the amount of CO_2 being absorbed increased as the inlet gas flow rate increased, accordingly, the rate of CO_2 removal flux increased.

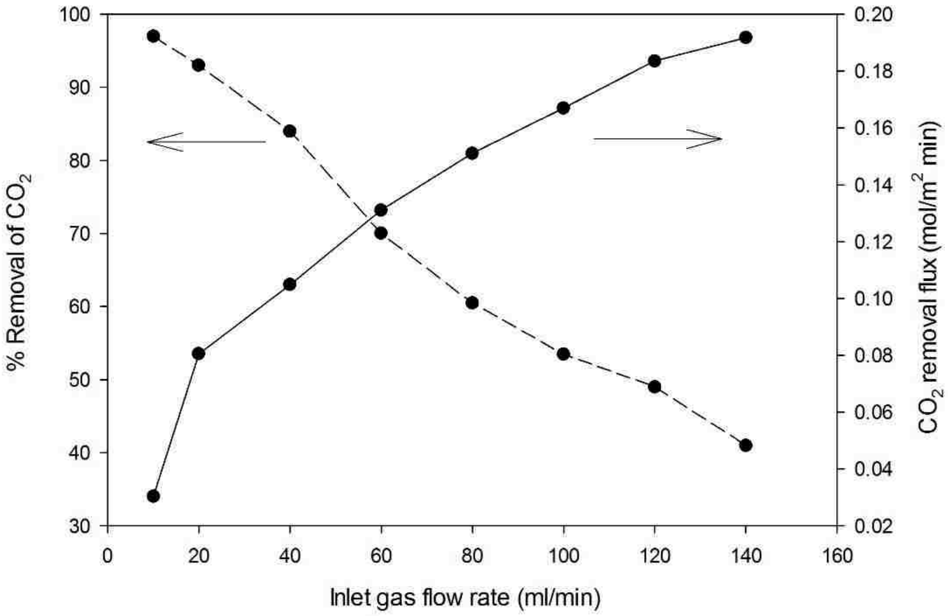

Figure 64: Effect of inlet gas flow rate in the membrane shell side on percent CO_2 removal and flux, liquid flow rate of 10 ml/min

Figure 65 shows the effect of liquid flow rate at different inlet gas flow rate. The diagram disclosed that the percent removal of CO_2 increases slightly with inlet liquid flow rate at high gas flow rate (40 and 60 ml/min), this occurrence is due to the abundant concentration of CO_2 and the starvation of carbon dioxide for more DEA to react with. By contrast, at low gas flow rate (10 and 20 ml/min), the effect of liquid flow rate is insignificant. This is attributed to the fact that at low gas flow rate the CO_2 is already consumed at low liquid flow rate and addition of extra solvent is considered as an excess and is not needed, accordingly, no effect on CO_2 percent removal is observed.

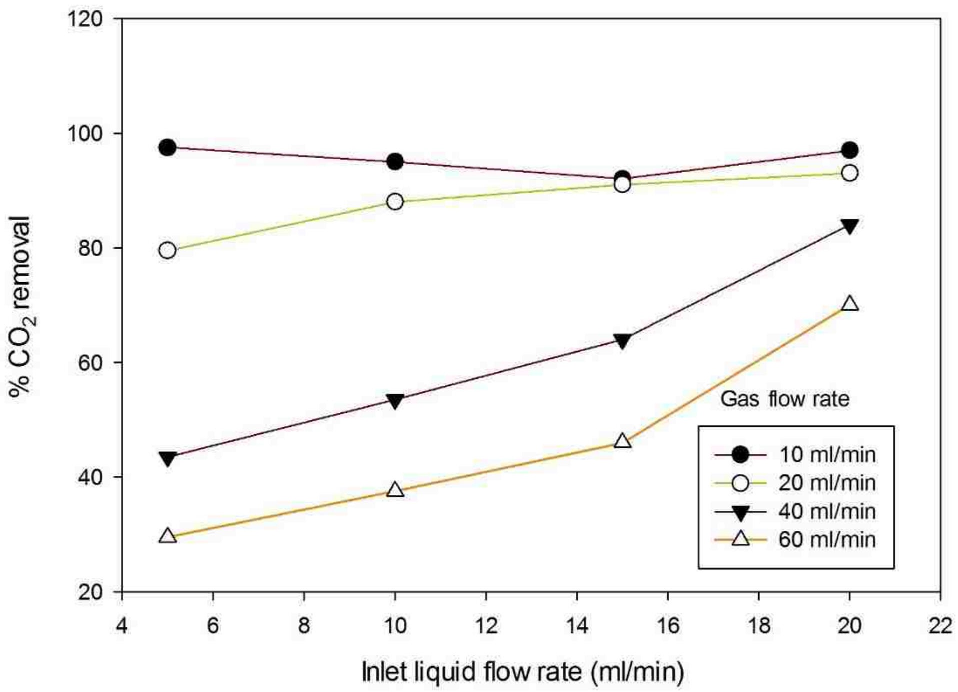

Figure 65: Effect of inlet liquid flow rate in the membrane tube side at various gas flow rates on percent CO_2 removal

5.4 Model predictions

The representation of the vector of the total flux (diffusive and convective) of CO_2 in the tube, membrane and shell side of the contactor is shown in Fig. 66. The gas mixture flows in the shell side from one side of the contactor (z = L) where the concentration of CO_2 is the highest (CO_2, 20%), whereas the solvent flows from the other side (z = 0) in the tube side where the concentration of CO_2 is assumed to be zero (CO_2, 0%). As the gas flows through the shell side, it moves to the membrane due to the concentration difference, and then it is absorbed by the moving solvent flowing in the tube side.

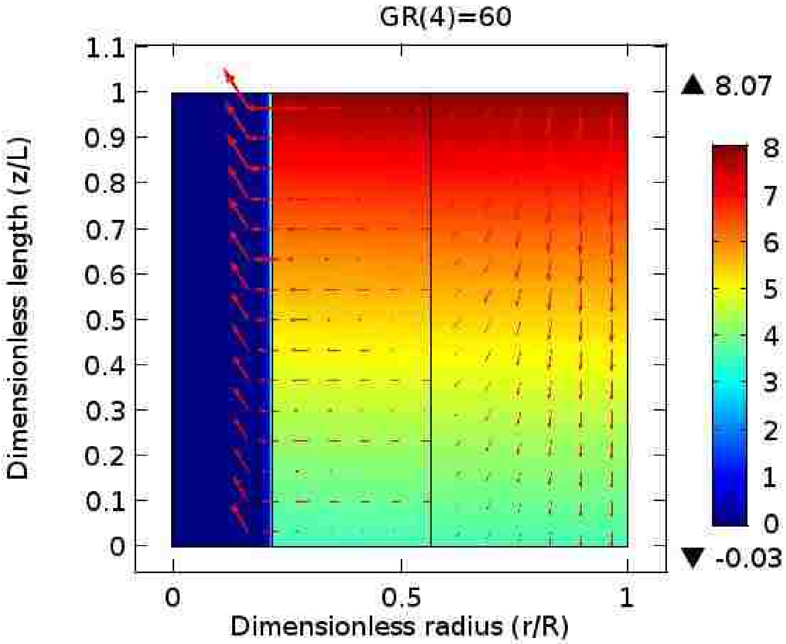

Figure 66: A representation of the total flux in the membrane contactor

The effect of inlet gas flow rate on the CO_2 concentration profile is shown in the surface diagrams (Figure 66-70) are for membrane modules inlet gas flow rate 10, 20, 40, and 60 ml/min, respectively. The Figures show that as gas flow rate increase the concentration of CO_2 in exit gas stream increased. This is attributed to the decrease in residence time and the increase of the total inlet amount of carbon dioxide due to increased inlet gas flow rate.

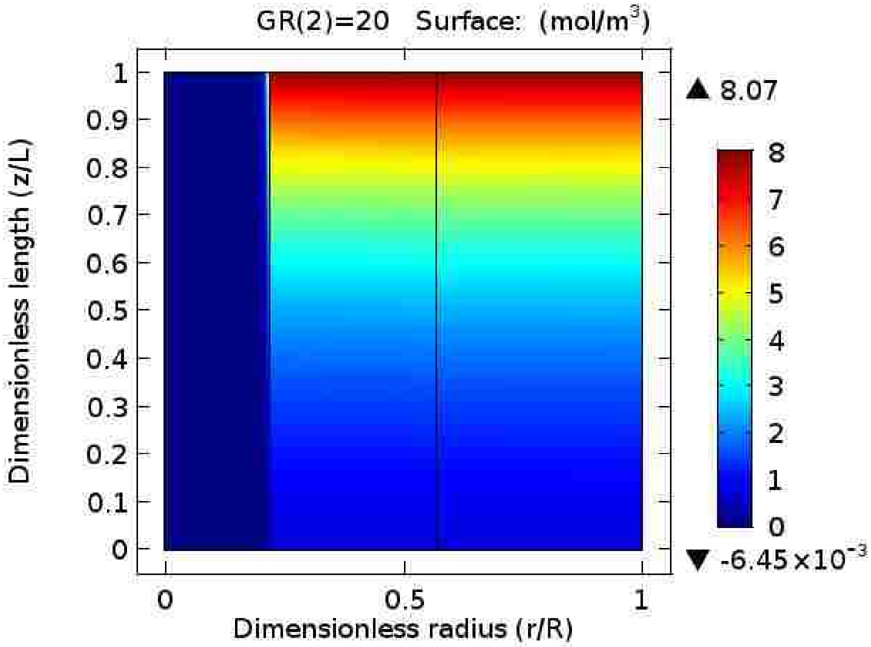

Figure 67: Surface plot for CO_2 concentration at liquid flow rate 10 ml/min and gas flow rate 20 ml/min

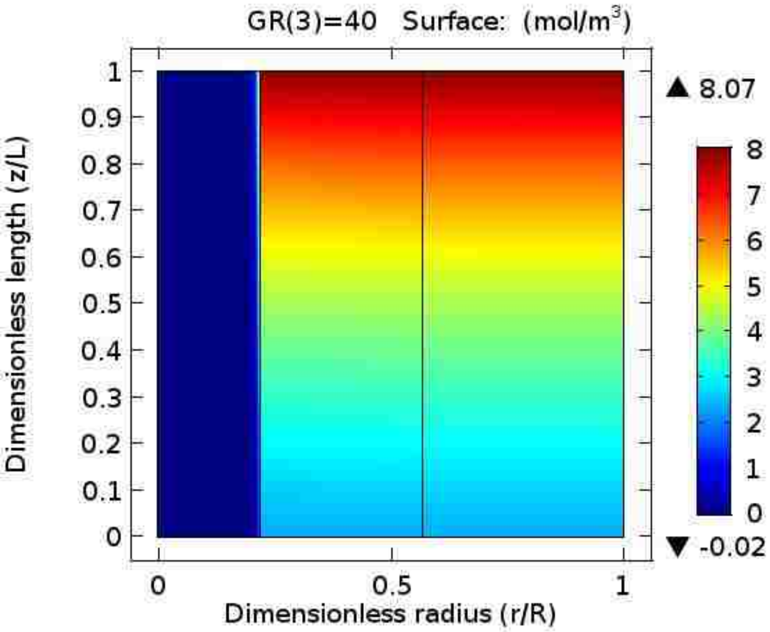

Figure 68: Surface plot for CO_2 concentration at liquid flow rate 10 ml/min and gas flow rate 40 ml/min

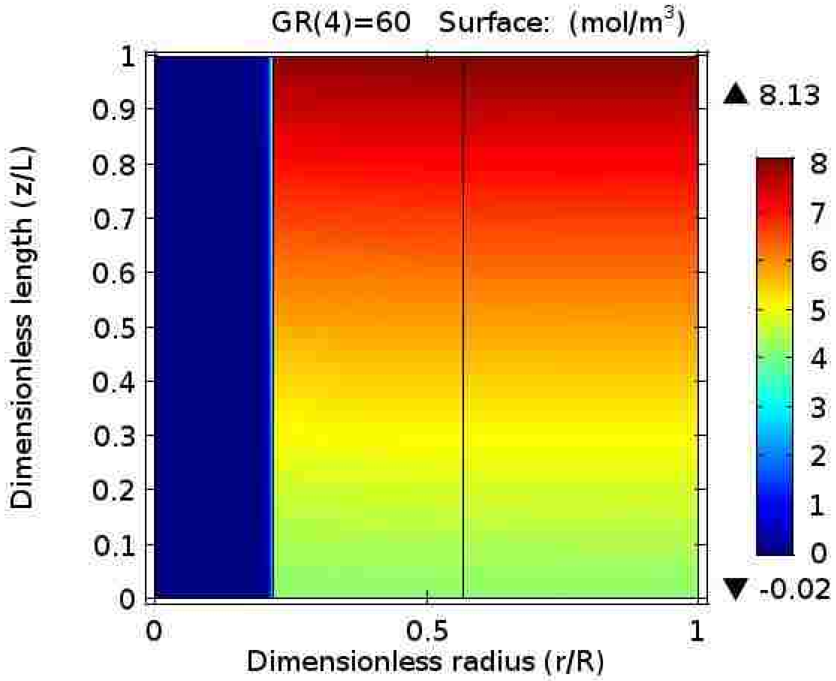

Figure 69: Surface plot for CO_2 concentration at liquid flow rate 10 ml/min and gas flow rate 60 ml/min.

Figures 67, 68 and 69 show the model predicted CO_2 concentration at the gas-membrane interface along the membrane length at variable gas feed rate (20, 40, 60 ml/min) and fixed feed liquid flow rate 10 ml/min. The diagram depicts that, the carbon dioxide concentration decreases with membrane length. The decrease in the acid gas concentration is attributed to the continuous consumption of CO_2 due to reaction with DEA. At fixed dimensionless concentration, the CO_2 consumption rate decreases with the increase of gas feed rate. This is expected due to the decrease in gas residence time. Figures 70 and 71 depict the CO_2 concentration and the percent removal of CO_2 along the dimensionless length of the membrane contactor. The percent removal decreased as inlet gas flow rate increased.

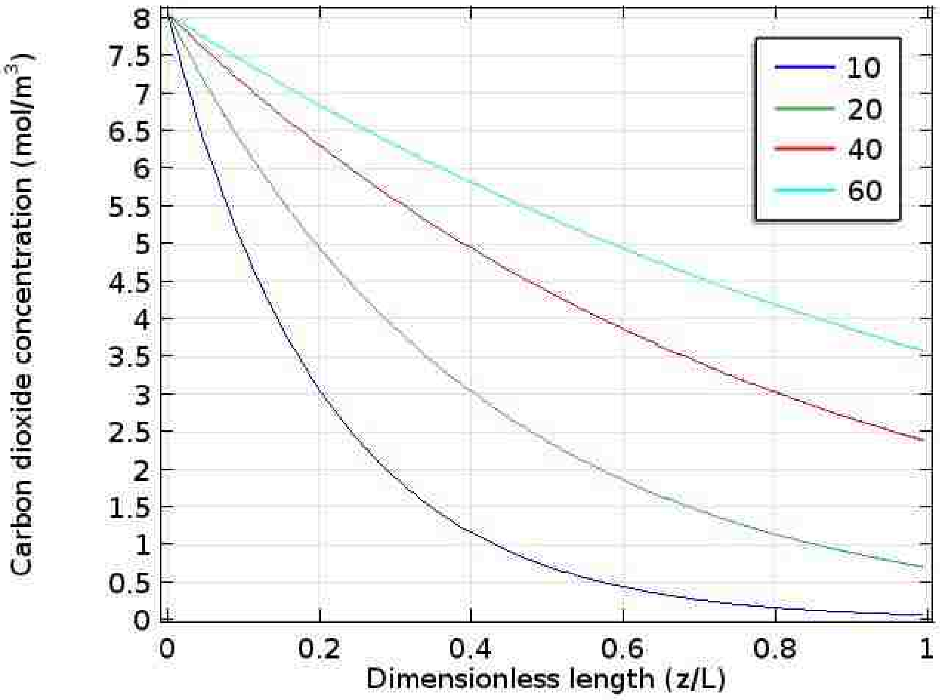

Figure 70: Effect of inlet gas flow rate on exit CO_2 concentration at fixed liquid flow rate of 10 ml/min. 20% CO_2 & 80% N_2 inlet gas flow rate

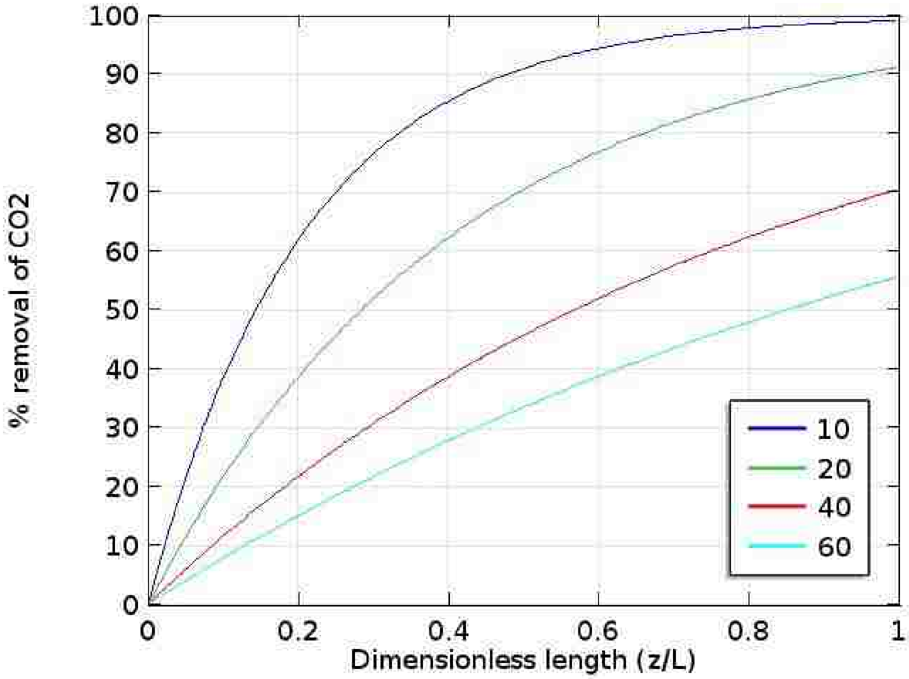

Figure 71: Effect of inlet gas flow rate on percent CO_2 removal, at fixed liquid flow rate of 10 ml/min. 20% CO_2 & 80% N_2 inlet gas flow rate.

5.5 Conclusion

Carbon dioxide was successfully captured from flue gas through gas-liquid hollow fiber membrane contactor using aqueous Diethanolamine (DEA) solution as solvent. A two-dimensional mathematical that describes the inert removal process via gas liquid membrane contactor was employed. Experimental results reveal that complete removal of CO_2 from flue gas can be achieved. The effect of increase in liquid flow rate at fixed gas flow rate shows insignificant effect at low inlet gas flow rate, by contrast, at high inlet gas flow rate the increase in liquid flow rate leads to slight increase in percent removal of CO_2. The effect of increase gas flow rate at fixed inlet liquid feed rate decreases CO_2 percent removal with increase gas flow rate, by contrast, CO_2 removal flux rate increases.

Chapter 6: Conclusions and Recommendation

6.1 Conclusion

The objective of the present work was to experimentally investigate the CO_2 separation form gas mixture contain (20% CO_2 & 80% N_2) using GLMC as an alternative to the conventional absorption/stripping process. Several membrane contactors such as PVDF, PTFE and PFA were individually fabricated in order to study the potential of CO_2 removal from gas mixture of CO_2/N_2 in GLMC using various liquid absorbent such as MEA, DEA and NaOH. Results showed that PVDF has more removal efficiency than PTFE, PFA has the lowest removal efficiency. NaOH gave better removal efficiency but suffered from poor regeneration, therefore DEA is more favorable because it has moderate removal performance and higher regeneration efficiency. Operating parameters such as liquid flow rate, gas flow rate, packing ratio were studied and the results obtained, regardless of type of membrane module and liquid absorbent, high liquid flow rate and packing ratio and lower gas flow rate provide high removal rate.

In stripping unit, varied operating conditions were studied to approach optimum performance. Parameters such as temperature, liquid and gas flow rates were changed and the results revealed that temperature has the main effect on stripping efficiency, regardless of type of membrane module used; increase in temperature will increase the stripping performance.

In addition, high CO_2 stripping rate was found to be at lower sweep gas and liquid absorbent flow rate. The CO_2 stripping efficiency decreased by increasing in liquid flow rate which was used instead of sweep gas by considering that increase in liquid flow rate at low temperature reduces the efficiency of CO_2 stripping, while increasing the liquid flow rate at high temperature, will increase the CO_2 stripping performance.

CO_2 transport through combined absorption/stripping units was evaluated by time. Several chemical solvents such MEA, DEA and NaOH at different heat of regeneration were examined and it was found that optimum overall process performance occurred at high heat of regeneration, respectively, for DEA>MEA>NaOH.

6.2 Recommended future work

1. Develop the study in CO_2 removal adding ionic liquid at different operation condition.
2. Perform CO_2 capture by applying different polymer fiber in order to avoid wetting of the membrane at higher temperature.
3. Work on other kind of liquid solvent with higher regeneration rate to optimize the overall performance.

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