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ABSTRACT

THERMAL SWING MEMBRANE BASED METHOD FOR CO₂ CAPTURE FROM FLUE GAS

by Mukesh Kumar Kamad

Carbon dioxide, a greenhouse gas and a major contributor to global warming, is released in large amounts by flue gases. To limit climate change, such CO_2 emissions have to be reduced, CO₂ captured and sequestered. Conventional monoethanolamine (MEA)-based absorption techniques are costly due to high capital cost and high energy consumption since the absorbent has to be regenerated at a high temperature $\sim 120^{\circ}$ C. A temperature swing membrane absorption (TSMAB) process was described by Mulukutla et al. (2015) using a novel membrane contactor, novel absorbents and a cyclic process. In this device, the absorbent is on the shell side of a membrane device containing two commingled sets of hollow fiber membranes. One set consists of porous hydrophobic hollow fibers through which the feed gas at 25-50°C comes in for a while and CO₂ from this feed gas gets absorbed in the shell-side absorbent. After sometime when the absorbent gets saturated with CO₂ and CO₂ breaks through the other end of the membrane device, CO₂-containing feed gas introduction is stopped. The membrane device has another set of solid essentially impermeable hollow fibers through the bore of which hot water is then passed for some time at a temperature ~ 80-95°C to desorb the absorbed CO_2 from the absorbent into the bore of the porous hollow fibers. This purified CO₂ stream is taken out for some time. Once the desorption process is over, the TSMAB cycle is initiated again with the CO₂-containing feed gas coming in.

The device and absorbent used by Mulukutla et al. (2015) had many deficiencies. The absorbent had a very high viscosity; the thickness of the absorbent in between the two sets of hollow fibers was very high since only a few fibers were used; further the porous hollow fibers had a very large diameter (OD/ID, 925/691 μ m). In this research, porous hollow fibers have much smaller OD/ID, 300/240 μ m. The fibers were well packed in the device so that the film thickness for absorption was small and saturating it was quickly achieved. Further the viscosity of the absorbent namely, a very concentrated aqueous solution of N-Methyldiethanolamine (MDEA), is much lower than that of dendrimer-ionic liquid combination used by Mulukutla et al. (2015). This thesis has studied the behavior of such a device and its performance in a cyclic process of CO₂ absorption and desorption.

THERMAL SWING MEMBRANE BASED METHOD FOR CO₂ CAPTURE FROM FLUE GAS

by Mukesh Kumar Kamad

A Thesis Submitted to the Faculty of New Jersey Institute of Technology in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemical Engineering

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May 2017

APPROVAL PAGE

THERMAL SWING MEMBRANE BASED METHOD FOR CO₂ CAPTURE FROM FLUE GAS

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Dedicated to My loving parents, M.L Kamad and Kamla Devi Kamad

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LIST OF SYMBOLS

MDEA	Methyldiethanolamine
PZ	Piperazine
PE	Polyethylene
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidenefluoride
HFMC	Hollow Fiber Membrane Contactor
NaOH	Sodium Hydroxide

CHAPTER 1

INTRODUCTION

1.1 Background

Nearly 70% of the world's energy is derived from coal. Combustion of coal is one of the largest sources of CO₂ emission. Table 1.1 shows the CO₂ emission from various sources. Excess CO₂ in the atmosphere is responsible for Global Warming and is considered as a major challenge in the coming years. Carbon Capture and Storage (CCS) is a possible alternative to prevent accumulating large quantities of CO₂ in the atmosphere. Separation of CO₂ from fossil fuel power plant flue gas is a subject of concern for more than a decade. The following methods are widely used to remove CO₂ from flue gas e.g., amine absorption, adsorption and membrane separation. Conventional CO₂ absorption equipment (packed and tray towers, bubble columns, venturi scrubbers, and spray towers) suffer from several disadvantages such as large space occupancy, high capital cost, high tendency for corrosion, and a variety of operational problems including liquid channeling, foaming, flooding, and entrainment [2-4]. Mostly an aqueous MEA (monoethanolamine) solution is used in a packed tower to capture CO₂ which requires high heat in the regeneration step; flooding and loading are other issues related to this approach.

Separation of CO₂ using hollow fiber membranes is a good alternative to overcome the above mentioned problems as membranes have high operational flexibility and high interfacial area. Hollow fiber membranes are widely used in water treatment, desalination, cell culture, tissue engineering and gas separations. The first known application of a microporous membrane as a gas-liquid contacting device using hydrophobic flat Gore-Tex membranes of polytetrafluoroethylene was for oxygenation of blood by Esato and Eiseman, (1975). Tsuji et al. (1981) used hydrophobic microporous hollow fibers of polypropylene for blood oxygenation and CO_2 removal. Qi and Cussler (1985) proposed the method of CO_2 absorption in a hollow fiber membrane contactor using NaOH. Packed tower, spray tower and bubble column used for gas absorption are highly energy intensive. Gas dispersion in these devices is common and has many shortcomings. Sirkar (1992) reviewed recent literature and concluded that hollow fiber membranes based modules overcome these limitations and are highly selective. In addition, membranes involve low cost of operation, maintenance and labor cost. Kohl and Nielsen (1997) studied various (aqueous) solutions of alkanolamines for CO_2 removal on a large scale in the absorption and desorption process and found that alkanolamines are highly selective as compared to other solvents.

Karoor and Sirkar (1993) experimentally studied wetted and non-wetted modes of operation showed that there were no operational problems in either wetted or non-wetted modes of operation and concluded that for CO₂ absorption in water, the wetted mode of operation offers considerably higher resistance to mass transfer when compared to the non-wetted mode of operation. It is a liquid-phase- controlled process; thus filling the membrane pores with water increases the resistance to mass transfer. Increasing the contact area in a given module or the packing fraction for a given fiber size increases the CO₂ removal capacity.

Process	CO ₂ concentration in gas stream % by vol.	Number of sources	Emissions (MtCO ₂)	% of total CO ₂ emissions	Cumulative total CO ₂ emissions (%)	Average entissions/source (MtCO ₂ per source)
CO ₂ from fossil fuels or minerals						
Power						
Coal	12 to 15	2,025	7,984	59.69	59.69	3.94
Natural gas	3	985	759	5.68	65.37	0.77
Natural gas	7 to 10	743	752	5.62	70.99	1.01
Fuel oil	8	515	654	4.89	75.88	1.27
Fuel oil	3	593	326	2.43	78.31	0.55
Other fuels*	NA	79	61	0.45	78.77	0.77
Hydrogen	NA	2	3	0.02	78.79	1.27
Natural-gas sweetening						
	NA ^b	NA	50°	0.37	79.16	
Cement production						
Combined	20	1175	932	6.97	86.13	0.79
Refineries						
	3 to 13	638	798	5.97	92.09	1.25
Iron and steel industry						
Integrated steel mills	15	180	6304	4.71	96.81	3.50
Other processes ⁴	NA	89	16	0.12	96.92	0.17
Petrochemical industry						
Ethylene	12	240	258	1.93	98.85	1.08
Ammonia: process	100	194	113	0.84	99.70	0.58
Ammonia: fuel combustion	8	19	5	0.04	99.73	0.26
Ethylene oxide	100	17	3	0.02	99.75	0.15

Table 1.1 CO₂ Emission Sources

Source: Intergovernmental panel for climate change (IPCC).

Kosaraju et al. (2005) studied CO₂ absorption using a polyamidoamine (PAMAM) dendrimer of generation 0, in an aqueous solution using conventional Celgard polypropylene (PP) hollow fibers in an absorber, followed by a stripper to successfully resolve the issue of pore wetting. Hollow-fiber membrane contactors (HFMCs) are preferred over other various kinds of membranes since they have a much higher surface/volume ratio. In recent years, studies have been carried out on the different factors affecting HFMCs performance such as different absorbents, various polymers as a

membrane, and flow rate of gas and liquid. In the present study aqueous MDEA solution has been used for the bulk removal of carbon dioxide from flue gas. The advantage of a tertiary amine is based on the low consumption of amine per mole of CO_2 combined with the low heat of reaction of CO_2 (Table 1.2), which leads to higher rates of desorption and lower heats of regeneration in the stripper section of the hollow fiber membrane module. Zhang et al. (2014) investigated CO_2 capture by Methyldiethanolamine and 2-(1piperazinyl)-ethylamine in membranes and concluded that increase of the membrane length, number of fibers and porosity-to-tortuosity ratio had a positive effect on CO_2 capture. However, increase of the membrane thickness, inner fiber radius and inner module radius had a negative effect on CO_2 capture.

Membrane properties play a vital role in gas absorption method for CO_2 separation. Rajabzadeh et al. (2013) studied the impact of membrane porosity and pore size on CO_2 absorption performance using asymmetric HFMCs considering partial wetting of the membrane and concluded that a membrane with low porosity and smaller pore size showed a high CO_2 flux rate. Masoumi et al. (2014) experimentally analyzed that MDEA shows higher CO_2 capacity, thermal stability and less regeneration costs. Moreover, MDEA is less corrosive than other solvents, however it has a slower reaction rate with CO_2 . Zhu et al. (2012) performed experiments using MDEA solutions blended with an additive like MEA or PZ and reported that these blends provide a higher chemical reaction rate. Paul et al., (2009) concluded that PZ act as a promoter agent in the MDEA solution which shows a higher rate of reaction with CO_2 than that of non-activated MDEA. Bishnoi and Rochelle (2000, 2002) studied the kinetics of CO_2 with piperazine, reported CO_2 equilibrium data in aqueous piperazine solutions, determined experimental absorption rates of CO₂ into PZ activated MDEA solutions and used rigorous mass transfer model to correlate their results.

Class	Alkanolamine	Am:CO2	$K_2^{ab}(T = 25^{\circ}C)$	Heat of solution of CO ₂ ^c	
	(Am)		[m ³ kmol ⁻¹ s ⁻¹]	KJ mol ⁻¹	
Primary	MEA	2:1	6.0	-82	
Secondary	DEA	2:1	1.3	-69	
Tertiary	MDEA	1:1	4. 10 ⁻³	-49	

Table 1.2 Characteristics of the Reaction between CO2 and MEA, DEA and MDEA

^aAssuming the reaction rate is given by $R_{CO2} = -k_2C_{Am}C_{CO2}$

^bTaken from Versteeg et al. [1996]

^cTaken from Carson et al. [2000]

Table1.3 Typical Properties of Coal-fired Flue Gas after SO₂ Scrubbing in Post Combustion

Flue gas	Composition	Kinetic Diameter (Å)
CO ₂	10-16 wt%	3.30
N ₂	70-75 wt%	3.64
H ₂ O	5-7 wt%	2.65
O ₂	3-4 wt%	3.45
СО	□20 ppm	3.75
NO _x	<400 ppm	
SO _x	<400 ppm	

Source: Deanna M. D'Alessandro Dr., Berend Smit Prof, Jeffrey R. Long Prof. *Carbon Dioxide Capture: Prospects for New Materials, Angew.* Chem.Int.Ed. 49 (2010) 6058-6082.

1.2 CO₂ Capture Technologies

Methods for CO₂ capture based on four large scale industrial processes producing CO₂ from fossil fuels are shown in Figure 2.1



Figure 1.1 Schematic representation of CO₂ capture systems [6].

1.2.1 Pre-Combustion Capture

In this method, CO_2 is separated from the fossil fuel (coal) prior to combustion. In the first step, fossil fuel i.e. coal is converted into synthesis gas, a mixture of CO and H₂. This synthesis gas is then sent to a water gas shift reactor where in the presence of steam it reacts to CO with steam to produce a mixture of CO_2 and H_2 . CO_2 is then separated from the (high pressure) gas mixture and H_2 is sent to the turbine to be combusted.



Figure 1.2 Schematic diagram of pre combustion capture.

This separation process of CO_2 from H_2 is likely to be more cost effective than post combustion capture due to the higher concentration and partial pressure of CO_2 .

Coal Gasification
Coal
$$\rightarrow$$
 CO + H₂ (1)

Water Gas shift reaction

$$CO + H_2O \rightarrow H_2 + CO_2$$
 (2)

Steam reforming $CH_4 + H_2O \rightarrow CO + H_2$ (3)

1.2.2 Post-combustion Capture

Post-combustion capture is widely used in industrial applications. CO₂ separation from flue gas mixtures is commercially practiced around the world as most of the energy is derived from the coal. Amine based solvents are more prevalent in the capture of CO₂ from flue gas. The process of CO₂ absorption from flue gas is shown schematically in Figure1.3. During the absorption process, the gas is contacted with a liquid phase containing amine, CO₂ diffuses and gets absorbed into the liquid. This liquid containing absorbed gas is sent to a desorber stage where the reaction is reversed, by increasing the temperature. The gas mixture containing CO_2 is separated from liquid as shown in the Figure 1.3.



Figure 1.3 Schematic of post combustion capture.

Source:http://www.energy.siemens.com/us/pool/hq/power-generation/power-plants/carbon-capture solutions/post-combustion-carbon capture/.

1.2.3 Oxy Fuel-combustion Capture

In the oxy-fuel combustion process pure oxygen is used for combustion instead of air, resulting in a flue gas that mainly contains CO_2 and H_2O which can be easily separated by cooling. The water is condensed and after phase separation the gas stream highly rich in CO_2 is obtained. However, oxygen separation is the most expensive part which is carried out at a low temperature. The oxy fuel combustion process is shown in figure 1.4



Figure 1.4 Schematic of oxy the fuel combustion capture. **Source**:https://www.netl.doe.gov/research/coal/energy-systems/advanced-combustion/oxy-combustion

1.3 Membrane Based Gas Absorption and Stripping

Gas absorption using membranes was developed for the purpose of reducing the cost and improving the performance of CO_2 capture. The membrane gas absorption process shown in Figure 1.5 allows selective gas molecules to pass through the pores and get absorbed in the liquid absorbent. In membrane based absorption and stripping process, there are two ways to introduce gas/liquid. In the first method, feed gas passes through the bore of the hollow fibers, and absorbent liquid is introduced from the shell side. In the second method,

absorbent liquid is introduced from the tube side i.e., bore of the fiber and gas is introduced on the shell side. Gas diffuses from the gas mixture to the gas-liquid interface via the membrane pores without high pressure and then contacts the liquid absorbent on the other side.



Figure 1.5 Schematic of Membrane based Absorption process.

Gas and liquid are contacted at the immobilized gas-liquid interface on the membrane surface. The first method is known as a non-wetted method of operation and the second one is considered a wetted mode of operation. The gas absorption/stripping occurs at the gas-liquid interface.

In order to avoid bubbling and a dispersive mode of operation the gas pressure has to be lower than that of the liquid pressure. Unless a certain critical pressure (ΔP_{cr}) is exceeded by the liquid pressure over the gas pressure, the liquid does not enter the pores [4, 14]. This maximum allowable value of the differential pressure is defined as the breakthrough pressure. The present study is based on the non-wetted mode of operation. Figures 1.6A and 1.6B shows wetted and non-wetted mode of operation respectively.



(A) Non-wetted mode

(B) Wetted mode



Figure 1.6 A.) non-wetted mode (with gas filled pores); B.) wetted mode (with liquid filled pores) of operation.

If the microporous membrane could be modeled as a collection of parallel cylindrical pores of radius r_p, then the breakthrough pressure is related to other relevant variables by the Young-Laplace equation:

$$\Delta P cr = -\frac{2\gamma cos\theta}{r} \tag{1.1}$$

where γ is the surface tension of the absorbent liquid, θ is the contact angle and r is the pore radius.

$$\Delta P = P_{\text{liquid}} - P_{\text{gas}} \tag{1.2}$$

Unless the gas phase pressure is higher than that of the aqueous phase, the gas will not bubble into the aqueous solution. The requirement is that the liquid does not wet the membrane material. This does not spontaneously occur if $\Theta > 90^\circ$. Liquid penetration into the pores will then occur only if $\Delta P > \Delta P_{cr}$. If $\Delta P_{cr} > \Delta P > 0$ the gas/liquid interface will be "immobilized" at the liquid side pore opening as illustrated in Figure 1.6A. This is the desired situation when it comes to the application of the membrane in a CO₂/alkanolamine contactor. Thus, over the excess aqueous phase pressure range of 0 to ΔP_{cr} , the gas/liquid interface is immobilized at the pore mouth of the hydrophobic membrane on the solution side. Through such an interface, one or more gas species may be absorbed into the aqueous solution. Sirkar (1992) has reviewed non-dispersive gas absorption with the gas phase at a higher pressure by considering the wetting of the hydrophobic membrane via an exchange process and incorporating an aqueous solution in the membrane pores.

1.4 Advantages of Gas-Liquid Membrane Contactors

Gas separation through the hollow fiber membranes is more efficient than tray columns, packed columns, spray towers, etc. Membrane gas contactors/ modules require less regeneration energy and achieve a high degree of separation as compared to the traditional separation devices e.g. tray columns, packed columns, spray towers, etc. Porous membranes possess a high gas liquid contacting surface area per unit volume varying between 1500-3000 m²/m³, depending on the diameter and packing density of the hollow fiber but in case of conventional contactors the available contact area varies around 20-1000 m²/m³, which is considerably lower. Membrane contactors are capable of operating at high gas/liquid flow rate ratios. The gas and liquid flow are segregated from each other, there is no dispersion, entrainment, flooding, weeping etc. Moreover, high rates of mass transfer and heat transfer is offered by membranes, thereby it can achieve high selectivity and thus saves energy. Furthermore, membrane modules are easy to scale up due to the modular nature of the contactor.

1.5 CO₂ Removal Solvents – Membrane Processes

Nowadays different kinds of solvents are used in membrane modules for CO_2 removal. The essential parameters for absorbent selection are the reactivity, absorption ability and regeneration performance towards CO_2 and additional physicochemical parameters such as viscosity, surface tension and good compatibility with membrane materials (Yan et al., 2014).

Aqueous amine-based solutions are widely used in membrane processes for absorption of CO₂. The most commonly used solvent is MEA (monoethanolamine). Paul et al. (2008) and Zhang et al. (2010) performed experiments on the absorption and regeneration characteristics of different proportions of miscellaneous absorbents; adding small quantities of activators into the tertiary amine produced the best performance. Methyldiethanolamine (MDEA), which is a tertiary amine has found widespread use in bulk removal of CO₂. When compared with primary and secondary amines it has many advantages like relatively high capacity, small enthalpies of reaction with acid gases, a low vapor pressure and a low regeneration energy requirement. Donaldson and Nguyen (1980) proposed that CO₂ does not directly react with MDEA, the addition of small amounts of fast reacting amines is necessary to apply this process in the flue gas treatment. The experimental data confirmed this hypothesis.

1.6 Significance of Blended Amine Solvents- Piperazine Activated MDEA

Nowadays tertiary amines are widely used in industry for absorption and removal of CO_2 from process gases. The tertiary amines have zero reactivity towards CO_2 ; addition of a promoter is highly desired in order to carry out the reaction. The promoter can be primary or secondary amine i.e., Piperazine (PZ). By adding a small amount of PZ a high rate of absorption is achieved in the absorber while a low energy of regeneration is required in the stripper. So, the success of these solvents is due to the high rate of reaction coupled with a low heat of reaction result in higher absorption capacity of the tertiary amine and lower energy consumption. In the present study, PZ activated MDEA blend is used for CO_2 removal. Wagner et al.(1982) patented this blend for successfully removing a high capacity of CO_2 from ammonia plants.



Donaldson and Nguyen [10] proposed that the reaction can be described on the basis of base catalysis of the CO₂ hydration. This catalytic effect is based on the formation of a hydrogen bond between the amine and water. This weakens the bond between the hydroxyl group (OH) and hydrogen, and then increases the water nucleophilic reactivity toward carbon dioxide.

1.7 Objective of this Thesis

To overcome the shortcomings of many existing approaches, two hollow fiber membrane based module technique for CO_2 absorption and stripping is presented here. The basic objectives are:

1. To identify a solvent that can achieve high rate of CO₂ absorption and require low regeneration energy.

2. To demonstrate the advantages of low viscosity solvent and successful removal of bulk of the CO₂ and its recovery in CO₂ concentrated stream.

3. To design a two hollow fiber membrane module for carrying out rapid TSMAB in a highly absorptive solvent.

CHAPTER 2

EXPERIMENTAL

2.1 Approach

The objective is to study the absorption-stripping behavior of CO₂ in a particular solvent using a hollow fiber membrane module, two types of solution were used as an absorbent, one with aqueous MDEA and the other with MDEA with a very small amount of piperazine. A gaseous mixture of 14% CO₂, 2% O₂ and remainder nitrogen was used as a feed gas. In this experiment, the feed gas was humidified and passed through the lumen of a hollow fiber and absorbent solution was introduced from the shell side of membrane module and completely filled up before passing the feed gas.

2.2 Materials and Chemicals

The two-hollow-fiber-set arranged in an alternate fashion and having a packing density around 33% was fabricated using a cylindrical PTFE plastic shell, having an ID of 0.47 cm; two Y-fittings at each end were potted with West System # 105 Epoxy Resin and # 209 Extra Slow Hardener. The length of tubing for making this module was 16 inch. After curing the connector for shell side absorbent for one day with epoxy (C-4: resin; D: activator; weight ratio:4/1; Beacon Chemicals, Mt. Vernon, NY), a second layer was applied through the nearest shell side outlet using a glass dropper. Once the epoxy was dry, porous PP and solid PEEK fibers were then inserted into the membrane device through the arms of the Y-fittings. Forty-six 40.64 cm long hydrophobic porous hollow fibers of polypropylene combined with another forty-six solid non-porous fibers of PEEK were inserted in a 40.64 cm long tube for the CO_2 absorption and desorption. The properties of the porous and solid hollow fibers employed in the two-fiber set up are listed in Table 2.1.

Membrane	ID of the Fiber (μm)	OD of the Fiber (µm)	Pore size (µm)	Porosity
PPa	240	300	0.03	0.4
Solid PEEK	420	575	NA	NA

Table 2.1 Properties of the hollow fibers used in the two-fiber set up membrane module

ID = Internal Diameter; OD = Outside Diameter. PP = Polypropylene

a = Supplied by Applied Membrane technology, MN.

Before initiation of the experimental procedure, the membrane modules were tested for any leakage. To test for any leakage, the shell side of the module was filled with deionized water. Water at 10-15 psig (103.4-172.3 kPa) was passed for about 1-2 hours. There was no leakage of water through the potting, so the module was considered leakfree. Nitrogen gas was passed to dry the fibers inside the membrane module through the tube and shell side for some time to completely dry these hydrophobic fibers.

2.3 Experimental Setup

The materials, equipment and chemicals used for the experiments are as follows:

- Polypropylene hollow fibers (Applied Membrane Technology, Minnetonka, MN)
- PEEK solid hollow fibers (Applied Membrane Technology, Minnetonka, MN)
- Multiple channel flow controller (Model 8274, Matheson, E. Rutherford, NJ)
- Mass flow transducer (Model 8102-1452 FM, Matheson, E. Rutherford, NJ)
- Micro pump (Model No.7144-04, Cole Palmer Instrument Co., IL)
- CO₂ analyzer model no. 906 (Quantek Instruments)

- Compressed Nitrogen gas (Matheson, Rutherford, NJ)
- 14% CO₂ gas mixture ,2% Oxygen and 84% Nitrogen Certified Standard (Matheson, Rutherford, NJ)
- N-Methyldiethanolamine (Fisher Scientific, IL)
- Piperazine (Sigma Aldrich, Milwaukee, WI)
- Gear Pump Controller (Model no. 491581, Cole Palmer Instrument Co., IL)
- Digi sense Temperature Controller (Cole Parmer, IL)



Figure 2.1 Two hollow fiber membrane set up for the absorption and desorption process.

Source: T. Mulukutla, J. Chau, D. Singh, G. Obuskovic, K.K Sirkar, *Novel Membrane Contactor for CO*₂ removal from flue gas by Temperature Swing Absorption, J. Membrane Science 493(2015) 321-328

2.4 Experimental Procedure for the Rapid Temperature Swing Absorption

First of all, the device became ready after complete cured with epoxy for several days. In the first set of studies, the simulated flue gas was allowed to pass through with the aq. MDEA solution at 25°C; for the second set the flue gas was allowed to pass through with the MDEA/PZ solution at 25°C. MDEA was obtained from Fisher Scientific Inc. and PZ was obtained from Sigma Aldrich. The absorbent solution was introduced from the shell side of the hollow fiber membrane-based device to carry out the thermal swing absorption (TSAB) process. The volume of the absorbent liquid required to fill the membrane module was 28.8 cm³ (ρ = 1.038 gm/ cm³; weight of absorbent = 37.67 gm).

The experimental setup is shown in Figure 2.1; a photo is shown in figure 2.2A and 2.2B. PTFE tubing having 3/8" OD and 5/16" ID and 16" length was used to make the membrane module. The humidified flue gas mixture of composition 14.1% CO₂, 1.98% O₂ and the rest N₂ (Welco CGI Gas Technologies, Newark, NJ) was introduced into the membrane module from the gas cylinder into the lumen of the porous hollow fibers in the membrane module. The schematic of the TSMAB system is shown in the figure 2.1. Feed gas flow rate was controlled by a Multi-channel Mass flow Controller Model 8248A and Mass flow Controller Transducer Model (MTRN-1002-SA, 72 Matheson TRI-GAS, Montgomeryville, PA).

Absorption Step: During this process, the simulated flue gas was passed through the lumen of the porous hollow fibers in the membrane module; in this non-wetted mode of operation gas diffuses into the shell side absorbent liquid and carbon dioxide concentrations in the treated flue gas stream and the stripped gas stream were monitored continuously by a solid-state IR- based CO₂ analyzer (Model 906, Quantek Instruments, Grafton, MA) connected at the gas outlet of the two fiber module. Complete capture of CO_2 from the flue gas took place until the onset of the CO_2 breakthrough, followed by a quicker increase in CO_2 concentration in the outlet gas as observed in the CO_2 analyzer. The feed gas was further allowed to pass through the fibers until the liquid absorbent was completely saturated as indicated by the feed CO_2 concentration of 14.1% appearing at the module outlet at which time the feed gas flow was stopped completely. The two gas valves at the inlet and the outlet of the two-fiber system were then closed, Mulukutla et al. (2014).

Desorption Process: In this process, hot water from a constant temperature reservoir heated to 90°C was passed through the lumen of the solid PEEK hollow fibers. The polymeric solid hollow fibers function as an extremely efficient heat transfer device and are ideal for rapid heating of the absorbent liquid residing in the inter-fiber space between the two sets of hollow fibers. In addition, these solid hollow fibers are also capable of absorbing the exothermic heat of reaction released during CO₂ absorption in the shell side absorbent liquid by passing cold water through their lumen to achieve isothermal absorption. The thermocouples at the inlet and the outlet of the solid PEEK fibers were connected to the temperature sensor to record the inlet and the outlet water temperature. As the reaction between CO_2 and MDEA is reversible, hot water had been passed for about 10 min, to desorb the gas from the sorbent, i.e., the absorbed CO_2 gas. After passing the hot water for 10 min, the two inlet and the outlet gas valves were quickly opened. The CO_2 concentration in the treated gas stream was recorded by the CO₂ analyzer. The highest concentration recorded on the analyzer was noted. After the sorption run, the bed was completely regenerated by passing the sweep nitrogen gas maintaining the same bed

temperature as in the experiment for about 40 min, to make it ready for the next sorption run.

A). Experimental Set-up of the thermal swing membrane absorption process.



B). Membrane Module



Figure 2.2 A) Experimental set up of the thermal swing membrane absorption process. B) Membrane Module.

CHAPTER 3

RESULTS AND DISCUSSION

MDEA is a tertiary amine. The reaction mechanisms of tertiary amines are different from primary and secondary amines. The following reactions occur during the CO₂ absorption into aqueous MDEA solutions (Donaldson and Nguyen, 1980; Rinker et al., 1995). MDEA [CH₃CH₂(CH₂CH₂OH)₂N] can be represented as R₃N. The reactions of MDEA, H₂O and CO₂ are as follows.

$$CO_2 + R_3N + H_2O \xleftarrow{k_{21}K_1} R_3NH^+ + HCO_3^-$$

(3.1)

$$CO_2 + OH^- \xleftarrow{k_{21}K_2} HCO_3^-$$
 (3.2)

$$HCO_{3}^{-} + OH^{-} \xleftarrow{K_{2}} CO_{3}^{2-} + H_{2}O$$

$$(3.3)$$

$$R_3NH^+ + OH^- \longleftrightarrow R_3N + H_2O$$
 (3.4)

$$2H_2O \xleftarrow{K_2} OH^- + H_3O^+$$

(3.5)

The rate of reactions (1) and (2) can be expressed as:

$$r_{1} = k_{21} [CO_{2}] [R_{3}N] - \frac{k_{21}}{K_{1}} [R_{3}NH^{+}] [HCO_{3}^{-}]$$
(3.6)

$$r_2 = k_{22} [CO_2] [OH^-] - \frac{k_{22}}{K_2} [HCO_3^-]$$
(3.7)

where

$$K_{1} = \frac{[R_{3}NH^{+}][HCO_{3}^{-}]}{[CO_{2}][R_{3}N]}$$
(3.8)

$$K_{2} = \frac{[HCO_{3}^{-}]}{[CO_{2}][OH^{-}]}$$
(3.9)

In reactions (3-5) only proton exchange occurs and these reactions can be treated as very fast ("instantaneous"). Equilibrium constants for these reactions are as follows:

$$K_{3} = \frac{[CO_{3}^{2-}]}{[HCO_{3}^{2}][OH^{-}]}$$
(3.10)

$$K_{4} = \frac{[R_{3}N]}{[R_{3}NH^{+}][OH^{-}]}$$
(3.11)

$$K_{5} = [OH^{-}][H_{3}O^{+}]$$
 (3.12)

3.1 Calculation of Amount of Water Required to Facilitate the Reaction

It has been widely accepted that CO_2 does not react directly with tertiary amines. In order to facilitate this reaction; the presence of water is desired. An approximate estimation of the grams of water needed is made and absorption experiments with moisture are performed.

Stoichiometrically, 1 mole of MDEA consumes 1 mole of CO₂ and consumes 1 mole of water.

$$\frac{-\text{NMDEA}}{1} = \frac{-\text{NCO2}}{1} = \frac{-\text{NH2O}}{1}$$
(3.13)

For 1g of absorbent 85 wt.%

Moles of MDEA = 0.85/119 = 7.1mmol

Moles of water to complete the reaction = $-\frac{\text{NMDEA}}{1} = -\frac{\text{NH2O}}{1}$

Therefore, Wt. of water required = 7.1 mmol * 18 = 0.127 gm for 1 g mol of CO₂.

3.2 CO₂ Absorption in the Two-hollow Fiber Membrane Module

The breakthrough performance was studied for different humidified feed gas flow rates. The absorption process was allowed to take place at 25°C. The CO₂ breakthrough performance by the two fiber beds at different feed gas flow rates had been noted for two different kinds of absorbent solutions. In the first set of studies, the flue gas was allowed to pass through aq. MDEA at 25°C. In the second set, the flue gas was allowed to pass through the aq. MDEA/PZ at 25°C. The bed is maintained at 25°C for both the studies.

The breakthrough performance for the first set of studies was carried out at four different feed gas flow rates i.e. 7,15,20,25 cm³/min as shown in Figure 3.1. The behavior of the curve is different at different flow rates. When the inlet humidified feed gas temperature was at 25°C and the bed temperature of 25 °C, there was a wide spread in the CO₂ breakthrough curve as seen for the flow rate of 7cm³/min when compared with 25 cm³/min.

The CO₂ breakthrough curve is very sharp for 25 and 15 cm³/min due to the fast diffusion of CO₂ gas in the shell-side absorbent liquid. At the onset, it takes only a few seconds to start CO₂ absorption in the liquid. This is due to the low viscosity of the absorbent liquid, higher packing density and low OD of hollow fibers. At the flow rate of 7 cm³/min, the liquid takes a longer time to get saturated as compared to other flow rates and there is significant spreading of the curve over the length of time. The CO₂ bed breakthrough times for the feed gas flow rates 7, 15, 20 and 25 cm³/min were 1.35, 1, 0.49 and 0.35 minutes respectively for the bed and feed gas at room temperature. The presence of water is highly desired as tertiary amines get activated in the presence of water in order to react with the CO₂. At lower gas flow rates, it takes longer time to reach the

breakthrough. By increasing the flow rate, the time taken to reach the breakthrough decreases markedly and the absorption rate also increases. So, gas flow conditions play a vital role in achieving the desired separation in a shorter time.



Figure 3.1 CO_2 breakthrough experiments with humidified feed gas at various flow rates using Aqueous MDEA. Feed gas flow rate temperature (FGT) at 25°C with bed temperature (BT) at 25°C.



Figure 3.2 CO₂ breakthrough experiments with humidified feed gas at various flow rates using MDEA/PZ. Feed gas flow rate temperature (FGT) at 25°C with bed temperature (BT) at 25°C.

In the second set of studies with MDEA/PZ used as an absorbent, the absorption rate is higher and the curve is much sharper as compared to the aqueous MDEA absorbent although the time taken to reach the breakthrough had increased a little. The breakthrough time for the feed gas flow rates 15, 20 and 25 cm³/min was approximately closer, with the difference of a few seconds. This is because the chemical reaction of PZ with CO₂ is a fast reaction compared to the aqueous MDEA. The CO₂ bed breakthrough times for the feed gas flow rates 10, 15, 20 and 25 cm³/min were 2, 1.15, 0.18 and 0.17 minutes, respectively for the room temperature bed and feed gas temperature.

These curves give a useful indication of the amount of CO_2 uptake and by integrating the area under the curve and subtracting it from the total area one can provide the CO_2 sorption capacities of all the above experiments calculated from the CO_2 breakthrough curves. The volume of CO_2 captured in each experiment was calculated from which the number of mmol of CO_2 absorbed was calculated using ideal gas law. Most of the CO_2 is captured till the onset of the bed breakthrough, followed by partial capture of CO_2 . Happel (1959) introduced the concept of free surface approximation which assumes a cylindrical envelope of fluid surrounds each fiber; the external boundary of this envelope is a line of symmetry, it has been observed that the mass transfer takes place only in this portion of the fibers. By calculating the happel radius and thereby calculating the volume gives us the amount of liquid around the hollow fiber, and it covers about 0.34 gm of the solvent. Happel radius calculations are provided in Appendix.

Feed Gas Type	Absorption Temperature (°C)	Feed Gas Flow rate (cm ³ /min)	Mmol of CO ₂ Captured mmol	Mmol of CO2 per gram of Absorbent(Total Volume)	Mmol of CO2 per gram of Absorbent (Happel-radius)
Wet	25	7	1	0.027	2.9
Wet	25	15	1.1	0.029	3.2
Wet	25	20	1.3	0.035	3.8
Wet	25	25	0.9	0.024	2.6

Table 3.1 CO₂ Uptake by the Two-fiber Sorbent Bed using Aqueous MDEA

Table 3.2 CO₂ Uptake by the Two-fiber Sorbent Bed using MDEA/PZ

Feed Gas Type	Absorption Temperature (°C)	Feed Gas Flow rate (cm ³ /min)	Mmol of CO2 Captured (mmol)	Mmol of CO2 per gram of Absorbent (Total Volume)	Mmol of CO ₂ per gram of Absorbent (Happel-radius)
Wet	25	10	1.2	0.032	3.5
Wet	25	15	0.8	0.021	2.3
Wet	25	20	1	0.027	2.9
Wet	25	25	0.9	0.024	2.6

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

In the present study, the fiber packing is quite tight, which restricted the ease with which fluid is distributed across the fiber bundle. This results in reduced liquid layer thickness and reduced CO_2 absorption capacity. The differences in fiber sizing has adverse effects on module performance because smaller fibers behave like regions with smaller than average inter-fiber spacing. If the fiber packing is spaced at little extent and not so tightly packed, then there will be uniform distribution of absorbent liquid over all the surface of the fibers. This will enhance the absorption rate and will provide longer saturation.

The shell side liquid entry and exit port should be designed with proper design considerations. If the ports are not designed well, the region where the fluid is distributed across the fiber bundle (and collected at the opposite end) can extend over a significant portion of the module.

APPENDIX

Calculation of Happel radius

To calculate the happel radius, first, we need to calculate the volume between the two radii.

Outer radius of PP hollow fiber = $r_o = 0.0300/2 = 0.0150$ cm.

Active length of the fiber = L = 40.6 cm.

Shell radius of the module = $r_s = 0.47$ cm.

Number of PP fibers = 46.

Happel radius $r_e = (1/1-\epsilon)^{0.5}$. r_o

Where
$$\varepsilon = 1 - N\left(\frac{\pi ro^2}{\pi rs^2}\right)$$

= $1 - \frac{(46 * 0.015 * 0.015)}{0.47 * 0.47}$
= $1 - \frac{0.0104}{0.220}$
= 0.952

 $\mathbf{r}_{\rm e} = (1/1 - 0.952)^{0.5} * 0.0105$

= 0.068 cm

Volume between the fibers = $\pi L (r_e^2 - r_o^2)$

$$= 127.4 (0.0046 - 0.002)$$
$$= 0.33 \text{ cm}^3$$

Density of the liquid = 1.04 g/cm³

Wt. of the liquid = 0.34 gm

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