Scale-up of PEEK Hollow Fiber Membrane Contactor for Post-combustion CO₂ Capture

Shiguang Li,^{*,a} Travis J. Pyrzynski,^a Naomi B. Klinghoffer,^a Timothy Tamale,^a Yongfang Zhong,^a James L. Aderhold,^a S. James Zhou,^a Howard S. Meyer,^a Yong Ding,^b and Benjamin Bikson^b

^a Gas Technology Institute, 1700 S. Mount Prospect Road, Des Plaines, IL 60018, USA

^b Air Liquide Advanced Separations, 35A Cabot Road, Woburn, MA 01801, USA

December 4, 2016

Revised: January 3, 2017

Abstract

Poly(ether ether ketone) (PEEK) hollow fiber membrane modules were scaled up from 2 inch diameter and 16 inch long to 4 inch diameter and 58 inch long (a factor of 90 increase in membrane area) for CO₂ capture from flue gases using a membrane contactor process, which combines advantageous features of both absorption and membrane processes. Field tests of a 4-inch-diameter module with activated methyldiethanolamine (aMDEA) solvent demonstrated greater than 90% CO₂ removal. The mass transfer coefficient in the absorption step was 1.2 (sec)⁻¹, which is over an order of magnitude greater than that of conventional column contactors. The membrane module was further scaled up from 4 inch to 8 inch diameter (a factor of 3 increase in membrane area). Single-gas permeation measurements indicated that 8-inch modules have an intrinsic CO₂ permeance as high as 2,150-2,670 GPU. One 8-inch-diameter module was tested in membrane contactor mode for CO₂ capture using a simulated flue gas. Carbon dioxide removal rate of 91.3% was achieved with a mass transfer coefficient of 1.5 (sec)⁻¹. Parametric tests indicated CO₂ flux and capture rate increased with increasing feed pressure, solvent flow velocity and solvent temperature. PEEK hollow fiber membrane contactor is effective in capturing CO₂ from low CO₂-concentration feeds, showing its high potential for natural gas flue gas CO₂ capture.

Keywords: gas separation; carbon capture; membrane contactor; CO₂ capture; polymer membrane; hollow fiber membrane; polyether ether ketone membrane

* Corresponding author: Shiguang.Li@gastechology.org; 847-544-3478 (phone); 847-544-3470 (fax)

1. Introduction

The greatest concern to climate change is the emission of greenhouse gases, especially CO₂ from fossil-fuel power plants. The amount of CO₂ attributed to the U.S. electric power sector is expected to increase by 11% from 2012 to 2040, although electric power generation from non-carbon sources (such as nuclear and renewable fuels) is projected to increase during this period [1]. Therefore, to address concerns about global climate change, CO₂ capture and storage is one of many approaches that is critical to significantly reducing domestic and global CO₂ emissions.

The US Department of Energy (DOE) has a goal of achieving 90% capture rate in existing plants with 95% CO₂ purity at a cost of \$40/tonne of CO₂ captured by 2025 [2]. To achieve this goal by any technological means is very difficult, because flue gas is hot, near atmospheric pressure, high in volume, and often contaminated with other impurities (O₂, SO_x, NO_x, and ash). Amine absorption is the current industry and DOE benchmark technology for capture of CO₂ from power plant flue gas. Residual oxygen in the flue gas is especially troublesome for conventional amine plants because of oxidative degradation of the amine. In addition, the heat duty of the stripper places a substantial burden on the steam supply. It is estimated that for every pound of CO₂ captured, 2 to 3 pounds of steam is required [3,4]. DOE/NETL systems analysis studies estimated that using aqueous monoethanolamine absorption process to capture 90% of the CO₂ from flue gas in existing plants will result in CO₂ capture cost of \$56/tonne (DOE Case 12) at the plant gate [5], which is above the 2025 DOE NETL Carbon Capture Program post-combustion capture cost goal (\$40/tonne of CO₂ captured). These factors result in enormous amine circulation rates, large equipment, and large energy requirements. Therefore, it is important to develop new advanced CO₂ capture technologies in order to maintain the cost-effectiveness of U.S. coal-fired power generation.

Through analysis and feasibility studies, Favre [6] reported that gas separation membranes are a technically and economically viable option for post-combustion CO₂ capture. Membranes are compact and can be retrofitted onto the tail end of a power-plant flue gas stream without complicated integration schemes. Conventional gas separation membrane process operates by a solution/diffusion mechanism, and the separation driving force is provided by the partial pressure difference of each component across the membrane. This process requires either flue gas compression, permeate sweep, application of permeate side vacuum, or a combination of these steps to provide the separation driving force required. Elaborate process design and optimization become prerequisite for conventional membrane processes in CO₂ capture from flue gases [7].

The main limitation of conventional membrane processes is the process pressure ratio (feed gas pressure/permeate gas pressure) limitation [8]. In practical gas separation applications, the pressure ratio across the membrane is usually between 5 and 15 [9]. When the membrane separation process is pressure ratio limited, the product CO₂ concentration will be limited even when the membrane selectivity is much larger than the pressure ratio. Thus, multiple membrane stages are required to generate greater than 95% pure CO₂ product (DOE's target) from flue gases using the conventional membrane process.

Membrane contactor process (also known as hybrid membrane/absorption process) combines advantageous features of both absorption and membrane processes to provide a cost-effective solution for CO₂ capture from flue gases. Hollow fiber membrane contactors for CO₂ capture, especially the absorption process, have been reported [10-14]. In this process, CO₂-containing gas passes through small-diameter membrane tubes (hollow fibers with porous walls) while a CO₂ selective solvent (typically an amine solution) flows on the shell side of the membrane. CO₂ permeates through the membrane and is absorbed in the solvent. The CO₂ rich solvent is regenerated and sent back to the membrane absorber.

The specific surface area per volume for hollow fiber membrane contactors can be as high as ~1,000-9,000 m²/m³, which is up to two orders of magnitude greater than conventional contactors (free dispersion columns: ~3.0-35 m²/m³, packed and tray columns: 30-300 m²/m³, mechanically agitated columns: ~160-500 m²/m³) [15, 16]. Thus, the use of a membrane contactor instead of a conventional amine scrubber leads to a much smaller space requirement. This technology is well suited for new and existing pulverized coal-fired power plants due to the reduced footprint requirement and a much lower visual impact as well as providing more options for placement in the confines of existing plants.

In the hybrid membrane/absorption process, the permeate side partial pressure of CO₂ can be considered close to zero due to the chemical reaction of CO₂ with the absorption solvent, and thus overcomes the pressure ratio problem encountered by the conventional gas membrane process. Feed compression or permeate vacuum is not required to create the separation driving force for gas molecules to be transported through the membrane. The process selectivity for the hybrid membrane/absorption process is determined by the chemical affinity of the absorption solvent to CO₂. Therefore, high purity CO₂ product can be realized in a single stage.

In our previous study [17], the feasibility of utilizing PEEK membrane based hollow fiber contactor in combination with chemical solvents to separate and capture CO₂ from simulated flue

gases with high efficiency (at least 90% removal) has been successfully established via testing of 2-inch-diameter modules. Advanced hindered amines and promoted carbonate solvent have been used to minimize solvent degradation and lower regeneration energy requirements. Greater than 90% CO₂ capture with greater than 95% CO₂ purity has been achieved in one stage with activated methyldiethanolamine (aMDEA) solvent. The measured volumetric mass transfer coefficient for the 2-inch-diameter module was as high as 1.7 (sec)⁻¹, which is more than 20 times greater than the mass transfer coefficient of a packed column. The lab tests also indicated that the CO₂ capture performance was stable and not affected by flue gas contaminants, including O₂, NO₂, and SO₂, with aMDEA solvent. The PEEK hollow fiber membrane contactor provides a unique platform to maximize the benefits of new and advanced solvents including those currently supported the DOE,

In the current study, the PEEK membrane modules were scaled up from 2 inch diameter and 16 inch long to 4 inch diameter and 58 inch long (a factor of 90 increase in membrane area) for field testing, then further scaled to commercial-sized 8-inch diameter (another factor of 3 increase in membrane area). High CO₂ capture performances were observed for these modules, indicating scalability of the PEEK hollow fiber membrane contactor process.

2. Experimental Methods

2.1. Hollow Fiber Membrane Fabrication and Surface Modification

The hollow fiber membranes are manufactured from the best in class commercial engineered plastic, PEEK. Porous PEEK hollow fibers used in preparation of super-hydrophobic membranes were manufactured by a high temperature melt extrusion process. In this process, a mixture containing PEEK and PEI (polyether imide), was melt extruded to form a hollow fiber, which was then cooled in air and sent to reagent bath, where PEI was removed. The resulting product was porous PEEK fiber. The details of the process were described previously [18].

The super-hydrophobicity of the porous PEEK membrane was generated by surface modification with a functional perfluoro oligomer. Prior to grafting with the perfluoro oligomer the surface of the porous PEEK was functionalized with -OH groups by reacting ketone groups in the PEEK polymer backbone with monoethanolamine. The functionalized porous PEEK was prepared in a single step Reactive Porogen Removal process during porous PEEK fiber preparation according to US Patent 7,176,273 [19].

2.2. Membrane Module Fabrication and Characterization

Module design and construction have significant impacts on the overall gas mass transfer coefficient by minimizing liquid side resistance and maximizing the driving force. The following key design elements and development work have been carried out:

- 1) Four-port counter-current flow design, enabling optimum driving force for the acid gas absorption;
- 2) Computerized structural packing minimizing the absorption liquid malfow;
- 3) Optimum fiber packing density to minimize the liquid pressure drop and optimize the liquid flow turbulence;
- 4) Optimized winding patterns to promote the liquid side gas mass transport; and
- 5) Curved hollow fiber with enhanced gas phase mass transport.

The cartridge was potted by epoxy and sealed with O-rings and housed in a stainless steel pressure vessel. The non-leaking characteristics of membrane modules were determined by pressurizing a water/hexane mixture in the shell side of the module and observing if there was any liquid collection in the tube side. Any liquid collected on the tube side would indicate leakage of the membrane module.

The membrane's intrinsic gas permeation property for CO₂ was measured in a flow system shown in Figure 1. The CO₂ was fed to the tube side of the module. Flux was measured by a flow meter. The pressure normalized flux, permeance, is:

$$P = \frac{J}{\Delta p} \quad (1)$$

where J is the total steady state flux through the membrane and Δp is pressure differential between the tube and shell sides. Since the module has a cross-flow design, a log-mean pressure drop (Δp) was used to calculate the driving force from the partial pressures

$$\Delta p = \frac{(P_{f,i} - P_p) - (P_{f,o} - P_p)}{\ln[(P_{f,i} - P_p)/(P_{f,o} - P_p)]} \quad (2)$$

where $P_{f,i}$, $P_{f,o}$, and P_p are the pressures of gas feed inlet, gas feed outlet and the permeated gas, respectively. The pressure in the permeate side (P_p) was typically between 0 and 1.4 psig in our tests.

2.3. Lab Testing

[illegible]

Figure 2. Process flow diagram of the membrane contactor system used in lab testing. Yellow lines are gas and orange lines are liquid

Compared to packed columns, where a gas side pressure drop is typically about 50 mBar (0.73 psi) for CO₂ capture, our PEEK membrane contactor process can also operate at close to atmospheric pressure. The only requirement related to pressure of hollow fiber membrane contactor process is that the inlet flue gas pressure must be slightly higher than the ambient pressure in order to ensure uniform flue gas flow through the hollow fibers. In our lab tests, a blower (SPEEDAIRE, Model: SA 3300V) was used to boost room air with a flow rate up to 900 SLPM a discharge pressure up to 6 psig. Carbon dioxide from liquid CO₂ tanks was mixed with air to create a “simulated flue gas” and injected into the gas inlet of the absorber. The flow rate of CO₂ was controlled by a mass flow controller which can provide up to 600 SLPM of CO₂. This range of flow rates allowed us to change the inlet CO₂ concentration as needed. The inlet composition of the simulated flue gas was measured by a Horiba PG-350 flue gas analyzer.

The mixed gas was then directed to the tube side of the module (hollow fibers with porous walls), while a lean, CO₂ selective solvent was introduced to the shell side of the membrane. Carbon dioxide permeated through the membrane pores and was absorbed in the solvent. Activated methyldiethanolamine (aMDEA) with a piperazine to methyldiethanolamine ratio of 1:4 (wt.%) was used as solvent. Two concentrations (40 wt.% and 50 wt.% amine solution) were tested. The treated gas composition was measured by either by a Qubit S158 CO₂ analyzer (QUBIT SYSTEMS S158 IRGA Carbon Dioxide (CO₂) Analyzer, 0-10% range) or a Horiba PG-350 flue gas analyzer.

Rich, CO₂-laden solvent exited the top of the membrane module. The rich amine pump provided the driving force to circulate the solvent and to maintain the stream as a single, liquid phase until it reached the first heater. A once-through reboiler (Kettle reboiler shown in Figure 2) was used to allow the vaporized CO₂ to separate from the rich amine. Vapor exiting the reboiler flowed to a regeneration condenser, where the stream was cooled, and then to a high pressure vapor knockout, where water condensate was separated from the intermediate-pressure CO₂. The CO₂ vapor stream leaving this knockout (typically with a pressure of 50-72 psig) was depressurized to measure the flow rate and then vented to atmosphere.

“Moderately” rich amine, or mid-rich amine, exiting the once-through reboiler was then sent to the second heater, where the solvent was reheated to break CO₂-solvent bonding. The two-phase stream flows to the low-pressure separator, where water and additional CO₂ vaporize at this lower pressure. This vapor stream was cooled, and sent to a lower pressure vapor knockout, where water condensate was separated and sent back the lean amine drum. The CO₂ vapor stream leaving the

knockout (typically with a pressure of 3-10 psig) was depressurized to measure the flow rate and then vented to atmosphere.

Upon exiting the low-pressure separator, the hot lean amine was partially cooled through a cross-exchange with the cool, rich amine. This lean solvent was further cooled before being sent to the lean solvent drum. Solvent from the lean solvent drum was pumped to the membrane module for absorption to complete the liquid cycle.

The typical operating conditions for the integrated absorption/desorption lab testing are listed in Table 1. These operating conditions were similar to those typically employed in the field for CO₂ capture except the O₂ concentration was higher. For comparison to conventional contactors, volumetric mass transfer coefficient ($K_G A_v$, $(\text{sec})^{-1}$) was used in the current study.

Table 1. Operating conditions for integrated absorption/desorption lab testing.

Parameter	Condition
Membrane Absorption	
Membrane contactor surface area	11-32 m ²
Gas inlet temperature	18-27 °C
Gas flow rate	330-775 L/min
Feed gas composition	CO ₂ /balance air
Feed gas CO ₂ concentration	6.4-16.6 (vol.)%
Gas inlet pressure	3.3-5.9 psig
Solvent inlet temperature	18-40 °C
Solvent flow rate	2.0-5.5 L/min
Solvent composition	aMDEA/H ₂ O (40 wt.% or 50 wt.%)
Solvent inlet pressure	3.1-9.8 psig
Desorption	
Solvents	aMDEA/H ₂ O (40 wt.% or 50 wt.%)
Liquid flow rate	3.40-5.9 L/min
First stage flash temperature	119-128 °C
First stage flash pressure	50-72 psig
Second stage flash temperature	112-118 °C
Second stage flash pressure	15-30 psig

Figure 3. Process flow diagram of the membrane contactor system used in field testing.

2.4. Field Testing

The CO₂ capture performance of a 4-inch-diameter module M1 was tested in a coal-fired power plant (Midwest Generation's Will County Station located in Romeoville, IL). The process was identical to the lab testing with the following exceptions:

- 1) Real flue gas was used instead of simulated flue gas as feed gas; and
- 2) Membrane desorber was used as the first stage regeneration (Figure 3).

The typical operating conditions for the integrated absorption/desorption testing at the field are listed in Table 2.

Table 2. Operating conditions for the integrated absorption/desorption testing at the field.

Parameter	Condition
<i>Membrane Absorption</i>	
Membrane contactor surface area	11 m ²
Flue gas flow rate	120-220 SLPM
Flue gas inlet temperature	14-23 °C
Flue gas composition	Listed in “Results and Discussion” section
Flue gas inlet pressure	3.8-5.1 psig
Solvent flow rate	1-2 L/min
Solvent inlet temperature	16-21 °C
Solvent composition	aMDEA/H ₂ O (40 wt.%)
Solvent inlet pressure	2.4-4.0 psig
<i>Membrane Desorption</i>	
Solvents	aMDEA/H ₂ O (40 wt.%)
Liquid flow rate	1-2 L/min
Solvent flash vessel temperature	104-122 °C
Solvent flash vessel pressure	40-55 psig
Solvent pressure drop across the membrane	40 psig

Regeneration was carried out using a trans-membrane pressure drop method reported previously [20]. The rich solvent was feed to the shell side of the contactor. The CO₂ stripping rate as high as 2.8 kg/m²/h was observed for a 8 wt.% CO₂-loaded aMEDA solvent at 104 °C and with a trans-membrane pressure drop of 60 psi.

3. Results and Discussion

3.1. Membrane and Module Properties

Post-combustion CO₂ capture process conditions require development of hollow fibers with large diameter bore dimensions to minimize the feed side pressure drop; even a small increase in the gas side pressure drop can introduce a significant energy penalty on the entire power plant. The PEEK fiber dimensions manufactured in the current study were 0.44-0.72 mm outside diameter and 0.22-0.54 mm inside diameter (Table 3).

Table 3. Fiber dimensions.

Module	Cartridge diameter (inch/cm)	Fiber OD (mm)	Fiber ID (mm)
M1	4/10	0.44	0.22
M2	5/13	0.72	0.54
M3	8/20	0.71	0.54
M4	8/20	0.59	0.37

Membrane cartridge design and construction have significant impacts on the overall gas mass transport coefficient by minimizing liquid side resistance, maximizing the driving force and increasing the liquid side mass transport coefficient. Important design features of a cartridge include the regularity of fibers (poly-dispersity and spatial arrangements of fibers), packing density and the relative flow directions such as parallel, concurrently, counter-currently, and cross-flows of the two phases. In the current study, as shown in Figure 4, the fiber membrane cartridges were firstly scaled up from 2 inch diameter and 16 inch long to 4 inch diameter and 58 inch long (a factor of 90 increase in membrane area), and then from 4 inch to 8 inch diameter (another factor of 3 increase in membrane area).

Figure 4. Scale-up of membrane cartridge. **Figure 5.** Pressure shells for 2-inch-diameter and 8-inch-diameter cartridges.

The membrane cartridge was sealed with O-rings and housed in a stainless steel pressure vessel (Figure 5). In the current study, the hollow fiber membrane module was designed to operate with liquid on the shell side and gas flow on the bore side. Four-port counter-current flow design, enabling optimum driving force for CO₂ absorption.

High membrane intrinsic CO₂ permeance is important in attaining high CO₂ capture rates in membrane contactor mode. By modifying and optimizing membrane preparation procedures and module construction conditions, membrane intrinsic CO₂ permeances as high as 2,000-2,670 GPU (1 GPU = 10⁻⁶ cm³ (STP)/(cm²·s·cmHg)) were achieved as shown in Table 4. Table 4 also lists effective area and specific area of bundle for each of the modules fabricated.

Table 4. Intrinsic permeances for CO₂ through 4- to 8-inch-diameter modules.

Module	Cartridge diameter (inch/cm)	Membrane effective inside area (m ²)	Bundle porosity (%)	Specific area of bundle (m ² /m ³)	Module intrinsic CO ₂ permeance (GPU*)
M1	4/10	10.9	64.9	1,300	2,000
M2	5/13	12.5	71.1	1,030	-
M3	8/20	37.6	59.4	1,560	2,670
M4	8/20	31.8	63.5	2,620	2,150

*: 1 GPU = 10⁻⁶ cm³ (STP)/(cm²·s·cmHg).

3.2. Four-inch-diameter Module CO₂ Capture Performance

The CO₂ capture performance of the 4-inch-diameter module M1 was tested in a coal-fired power plant (Midwest Generation's Will County Station located in Romeoville, IL). The compositions of the flue gas upstream of the membrane absorber and treated gas downstream of the membrane absorber are shown in Table 5. The CO₂ removal rate and flux were 93.2% and 0.17 kg/(m²·h), respectively. Note that the local mass transfer coefficient changes along the membrane axial direction because the solvent loading gradually increases. Thus, the average mass transfer coefficient was obtained. The average volumetric mass transfer coefficient for CO₂ was 1.2 (sec)⁻¹, which was over one order of magnitude greater than those of conventional contactors with packed columns (0.0007 – 0.075 (sec)⁻¹) [15]. The NO_x concentration was 61.1 ppm in the feed and 24.1 ppm in the treated flue gas, respectively. Our previous study indicated that the CO₂ capture performance was not affected by flue gas contaminants, including O₂, NO₂, and SO₂, with the aMDEA solvent in the PEEK membrane contactor process [17] for the duration of the test.

Table 5. *Compositions for the feed flue gas and the treated gas.*

Component	Composition	
	Feed flue gas	Treated flue gas
CO ₂	9.06 vol.%	0.71 vol.%
NO _x	61.1 ppmv	24.1 ppmv
SO ₂	4.0 ppmv	4.0 ppmv
CO	6.0 ppmv	10.6 ppmv
O ₂	11.98 vol.%	16.02 vol.%
Balance	N ₂ , water vapor and trace elements	N ₂ , water vapor and trace elements

The overall volumetric mass transfer coefficient obtained for the 4-inch-diameter module M1 (1.2 (sec)^{-1}) was lower than that obtained previous for a 2-inch-diameter module (1.7 (sec)^{-1}) in the laboratory testing [17]. The overall resistance in membrane contactors comes from three parts: in the gas phase, in the membrane, and in the liquid phase. In the following section, each of these factors is analyzed to determine which resistance is responsible for the difference in mass transfer coefficients between the 2-inch-diameter and the 4-inch-diameter modules.

The resistance in the gas phase is typically very small compared to other two [21]. Also, gas velocity and residence time in the fibers of the 4-inch-diameter modules tested in the field were greater than those of the 2-inch modules tested in the lab (Table 6), which would lead to a slightly lower transport resistance in the gas phase. However, we obtained a lower mass transfer coefficient for the four inch, indicating the resistance in the gas phase was not the major factor that caused the difference in mass transfer coefficients between the two inch and the four inch.

Table 6. *Gas velocities and residence times in 2-inch and 4-inch module.*

Module	Gas velocity in fiber (m/s)	Gas residence time in fiber (s)
2-inch-diameter module [17]	3.3	0.12
4-inch-diameter module M1 (current study)	4.8	0.32

The resistance in the membrane phase is a function of membrane structure. The 4-inch-diameter module M1 had a membrane intrinsic CO₂ permeance of 2,000 GPU (Table 4), whereas the 2-inch-diameter module only had a membrane intrinsic CO₂ permeance of 1,000 GPU [17]. In contrast, the mass transfer coefficient obtained for the 4-inch-diameter module was 29% lower than that for the 2-inch-diameter module, indicating the difference in mass transfer coefficients between

the 2-inch-diameter and the 4-inch-diameter modules was not due to the resistance in the membrane phase.

The resistance in the liquid phase is a function of contactor module design, i.e. flow dynamics, and solvent characteristics. Table 7 shows that the liquid velocity in the 4-inch module was only 40% of the 2-inch module. Lower liquid velocity means less turbulence, which may cause a higher resistance in the liquid phase.

Table 7. Liquid flow rates and velocities in 2-inch-diameter and 4-inch-diameter modules.

Module	Liquid flow rate (L/min)	Liquid velocity in module (m/s)
2-inch-diameter module [17]	0.5	0.0097
4-inch-diameter module M1 (current study)	1.0	0.0039

Based on the analysis above, the lower mass transfer coefficient for the 4-inch-diameter module was likely due to the higher resistance in the liquid phase. Besides mass transfer coefficient, CO₂ loading of the rich solvent is another scaling parameter that should be considered in a practical operation; the higher CO₂ loading of the rich solvent, the lower amount of liquid to be heated, and thus reducing the energy demand for regeneration. Table 8 shows that the L/G ratio for the 4-inch-diameter module was only 10% of that for the 2-inch-diameter module. The rich solvent CO₂ loading was much higher in the four incher relative to the two incher. The rich solvent CO₂ loading of 5.2 wt.% in the fielding testing with 4-inch-diameter module was comparable to those of the packed columns in conventional absorption process.

Table 8. Flow conditions and rich solvent CO₂ loadings in 2-inch-diameter and 4-inch-diameter modules.

Module	Flue gas flow rate (L/min)	Gas side pressure drop (psi)	Liquid flow rate (L/min)	Liquid side pressure drop (psi)	L/G ratio (L/L)	Rich solvent CO ₂ loading (wt.%)
2-inch-diameter module [17]	12	1.6	0.5	1.3	0.042	0.6%
4-inch-diameter module M1 (current study)	245	4.1	1.0	2.5	0.0041	5.2%

3.3. CO₂ Capture Performance in Membrane Contactor for an 8-inch-diameter Module

After the field tests with the 4-inch-diameter module, the PEEK hollow fiber membrane modules were further scaled up to eight inch diameter. The 8-inch-diameter module M4 was tested

in membrane absorption for CO₂ capture using 40 wt.% and 50 wt.% aMDEA solvents. Carbon dioxide (from liquid CO₂ tanks) mixed with air was used as “simulated flue gas” in such lab tests.

A two-stage stripping process was used to regenerate the solvent. This regeneration process is particularly suited for regenerating CO₂ laden rich amine solvent in the post-combustion CO₂ capture process. CO₂ is collected at elevated pressure (around 50 psig) thus lowering the overall power requirement for CO₂ compression while regenerating the solvent for recirculating to the absorber side of the CO₂ capture process.

Table 9 shows that greater than 90% CO₂ removal rates were achieved with CO₂ mass transfer coefficients of 1.5 (sec)⁻¹ for both solvents.

Table 9. Carbon dioxide capture performance for an 8-inch-diameter module.

Solvent	CO ₂ removal rate	Volumetric mass transfer coefficient for CO ₂ ((sec) ⁻¹)
40 wt.% aMDEA	91.4%	1.5
50 wt.% aMDEA	91.3%	1.5

The liquid velocity in the 8-inch-diameter module M4 (0.0047 m/s) was slightly higher than that of the 4-inch-diameter module M1 (0.0039 m/s). So, the liquid side resistance was expected to be lower for the 8-inch-diameter as compared to the 4-inch-diameter module. Also, the 8-inch-diameter module M4 had a higher CO₂ intrinsic permeance (2,150 GPU) than the 4-inch-diameter module M1 (2,000 GPU), and thus M4 should have a lower membrane transport resistance. For a same solvent of 40 wt.% aMDEA, higher mass transfer coefficient for CO₂ was observed for the 8-inch diameter membrane (relative to the four inch) because of the lower resistances in the membrane and in the liquid phase.

Table 9 also shows that the 40 wt.% and 50 wt.% aMDEA solvents had the identical CO₂ capture performance at steady state. Simulation by ProTreat® indicates that the CO₂ saturation concentrations are 13.7 wt.% for the 40 wt.% aMDEA and 16.6 wt.% for the 50 wt.% aMDEA. Since the 50 wt.% aMDEA solvent has a potential to operate at higher CO₂ loading for the rich solvent, it was selected for further studies.

In the absence of intramodule cooling in the membrane absorber, the rich amine accepted the CO₂ heat of absorption such that the rich amine exiting the modules had a higher temperature than the lean amine entering the module. The theoretical temperature increase is calculated here to compare with the measured temperature.

The heat generated by the reaction was calculated using the following equation:

$$Q_{rxn} = \dot{m}C_p\Delta T \quad (3)$$

Where

Q_{rxn} = heat of reaction

$\dot{m}$ = mass flow rate of solvent

C_p = specific heat capacity

ΔT = temperature change

In this case, the heat of reaction is calculated based on Equation 4:

$$Q_{rxn} = \dot{m}\Delta H \quad (4)$$

Where

ΔH = enthalpy of reaction

$\dot{m}$ = flow rate of CO₂ reacted

The parameters and values used in the calculation are listed in Table 10.

Table 10. Parameters and values used in the calculation of heat generated by reaction.

Parameter	Value	Unit	Source
C _p for 50 wt% aMDEA	3.29	kJ/kg-K	HYSYS simulation
$\dot{m}$ (solvent)	3.91	L/min	Experimental data
Solvent density	1.05	kg/L	HYSYS simulation
$\dot{m}$ (CO ₂ reacted)	2.7	mol/min	Experimental data
ΔH	76	kJ/mol	Svensson et al. [22] modified for our CO ₂ loading

Assumptions are:

- C_p is constant/independent of temperature; and
- No heat losses (they are calculated next, this is the baseline case).

Based on the above values, the ΔT calculated was 15.2 °C. The heat generation was 2.9 kW.

In our system, the inlet temperature to the absorber is 20 °C, so the outlet temperature would be 35.2 °C.

Heat loss from the absorber to the surroundings are calculated using Equation 6, accounting for conductive heat losses. Convective heat losses are assumed to be negligible, since the air is stagnant. Radiative heat loss was calculated but was determined to be negligible (<0.1% of conductive losses) so is not discussed here.

$$q = \bar{h}A(T_s - T_\infty) \quad (5)$$

Where

$$\bar{h} = \frac{k}{D} \bar{Nu}_D \quad (6)$$

$$\bar{Nu}_D = \left(0.60 + \frac{0.387 Ra_D^{1/6}}{\left[1 + (0.559 / Pr)^{9/6} \right]^{1/4}} \right)^2 \quad (7)$$

$$Ra_D = \frac{g\beta(T_s - T_\infty)D^3}{\nu\alpha} \quad (8)$$

$$Pr = \frac{\nu}{\alpha} \quad (9)$$

Where

A = surface area of absorber

h = heat transfer coefficient

D = diameter of absorber

k = heat transfer coefficient

g = gravitational constant

β = thermal expansion coefficient

ν = kinematic viscosity

α = thermal diffusivity

T_s = surface temperature of absorber

T_∞ = ambient temperature

The parameters and values used in the calculation are listed in Table 11.

Table 11. Parameters and values used in heat loss calculation.

Parameter	Value	Unit	Source
k (air)	0.0243	W/m•K	Incropera et al. [23]
T_s	21	°C	Measured
T_{inf}	4	°C	Measured
D	21	cm	From manufacturer
g	9.8	m/s ²	
β	0.00361	K ⁻¹	Calculated (from ambient temp)
ν	1.37E-05	m ² /s	Incropera et al. [23]
α	1.92E-05	m ² /s	Incropera et al. [23]

This calculation gives a heat loss of 60.5 W, which is 2.1% of the total heat generated. This would decrease the delta T by 0.94 °C, to give a delta T of 14.3 °C. The final outlet temperature would then be 34.3 °C. The measured outlet temperature was 29.2 °C.

Zaidiza et al. [24] recently reported an adiabatic modelling of CO₂ capture by amine solvents using membrane contactors. They compared the modelling results to those from an isothermal model and investigated the influence of heat release on contactor performance. Similar modelling was conducted in our study. A separate CO₂ capture experiment was run and relative humidities of the gas inlet and outlet were monitored. Because dry carbon dioxide (from liquid CO₂ tanks) mixed with air was used as simulated flue gas, the relative humidity was between 49.4% and 52.0% (Table 12). The outlet of the gas was saturated with water (relative humidity = 100%). This is because the liquid side had a higher temperature than the gas side (Table 12), and thus the water vapor pressure was higher in the liquid side, which provided a driving force for the permeation of water vapor from the liquid side to the gas side. Therefore, the measured lower temperature (relative to the theoretical temperature calculated above, i.e. 34.3 °C) of the liquid outlet was due to the phase change of water from liquid to vapor.

Table 12. Temperatures and relative humidities for a separate CO₂ capture test.

Sampling number	Gas inlet		Gas outlet		Liquid inlet temperature (°C)	Liquid inlet temperature (°C)
	Temperature (°C)	Relative humidity (%)	Temperature (°C)	Relative humidity (%)		
1	28.8	52.0	28.8	100	30.4	36.0
2	29.2	49.4	28.9	100	30.6	36.1

Liquid water was collected in the knockout vessel located in the downstream of the membrane absorber, indicating condensation is a potential issue. In the field, the real flue gas is saturated with water vapor. To avoid the condensation issue, the liquid temperature needs to be controlled lower than the flue gas temperature or the flue gas needs to be pretreated to decrease the humidity.

3.4. Effects of Operation Parameters

Operation parameters, such as flue gas feed pressure, solvent flow velocity, solvent temperature and CO₂ feed concentration in the flue gas, were investigated using the 8-inch-diameter module M4 in conjunction with the 50 wt.% aMDEA solvent. Carbon dioxide mixed with air was used as simulated flue gas. A two-stage stripping process was used to regenerate the solvent. During

these tests, the gas side pressure drops were between 1.6 and 2.7 psi, whereas the liquid side pressure drops were between 1.3 and 4.1 psi.

3.4.1. Flue Gas Feed Pressure

The CO₂ capture flux increased with increasing feed pressure of the simulated flue gas (Figure 6) because the gradient of CO₂ partial pressures between the gas side and the liquid side increased. As a result, the CO₂ removal rate increased from 85.7% to 93.5% as feed pressure increased from 2.6 to 5.9 psig.

Figure 6. CO₂ flux and removal rate of a simulated flue gas at 23 °C as a function of gas feed pressure. Gas side: 14% CO₂/balance air, and air flow rate of 340 SLPM; liquid side: 6.9 psig inlet pressure, 21 °C inlet temperature, and 4 L/min flow rate.

3.4.2. Solvent Flow Velocity

Figure 7 shows that the CO₂ flux increase with increasing solvent flow velocity. This is because the increase in solvent flow velocity increases turbulence for mass transport, and thus decreases the liquid side resistance based on a modeling study by Wang et al. [25]. Due to the increase in CO₂ flux, the CO₂ removal rate increased from 86.3% to 91.1%.

Figure 7. CO₂ flux and removal rate of a simulated flue gas at 22 °C as a function of solvent flow velocity. Gas side: 14% CO₂/balance air, 3.4 psig pressure and air flow rate of 340 SLPM; liquid side: 5.0-8.8 psig inlet pressure, 22 °C inlet temperature, and 2-5.5 L/min flow rate.

3.4.3. Solvent Temperature

As shown in Figure 8, the CO₂ flux increased with increasing solvent temperature. This is attributed to two reasons: 1) the increase in reaction rate, and 2) the decrease in liquid side resistance since the solvent viscosity decreased from 12.8 to 7.4 cP as solvent temperature increased from 22 °C to 40 °C per HYSYS simulation. As a result, the CO₂ removal rate increased with increasing solvent temperature.

Figure 8. CO₂ flux and removal rate of a simulated flue gas at 22 °C as a function of solvent temperature. Gas side: 14% CO₂/balance air, 3.6 psig and air flow rate fixed at 340 SLPM; liquid side: 6.1-6.9 psig inlet pressure, and 4.0 L/min flow rate.

3.4.4. Carbon Dioxide Feed Concentration

When the CO₂ feed concentration in the flue gas is decreased at 23 °C, the CO₂ flux decreased, as shown in Figure 9, because the driving force decreased due to the decrease in CO₂ partial pressure. The CO₂ removal rate (Figure 9), however, increased with decreasing CO₂ feed concentration. For a 6.4 vol.% CO₂ feed, the CO₂ removal rate was 93.4% and the treated gas had a CO₂ concentration as low as 0.45 vol.%.

Figure 9. CO₂ flux and removal rate at 23 °C as a function of CO₂ feed concentration. Gas side: 3.4 psig inlet pressure, and air flow rate fixed at 340 SLPM; liquid side: 7.0 psig inlet pressure, 22 °C inlet temperature, and 4 L/min flow rate.

In a membrane contactor, due to the chemical interaction of CO₂ with the absorption solvent, the permeate side partial pressure of CO₂ is essentially close to zero. Therefore, driving force always exists for the transport of CO₂ from the gas side to the liquid side. This overcomes the pressure ratio problem encountered by the conventional gas separation membrane configurations. The results shown in Figure 9 indicated that our PEEK hollow fiber membrane contactor process can also be effectively used in CO₂ capture from lower CO₂ concentration flue gases, such as natural-gas-fired flue gases.

In our previously study [17], PEEK membrane contactor stability was investigated by continuously performing CO₂ capture through a two-inch-diameter module with aMDEA solvent for 120 hours. Good mechanical stability and stable permeation properties of the module were observed. The stability of the 8-inch-diameter module will be investigated by a continuous, steady-state operation for a minimum of two months in the field at the National Carbon Capture Center.

4. Summary

- PEEK hollow fiber membrane modules were scaled up from 2 inch diameter and 16 inch length to 4 inch diameter and 58 inch length (a factor of 90 increase in membrane area) for CO₂ capture from flue gases using membrane contactor process
- Field test of a 4-inch-diameter module with aMDEA solvent demonstrated a 93.2% CO₂ removal for a flue gas containing 9.06 vol.% CO₂. The mass transfer coefficient in the absorption step was 1.2 (sec)⁻¹, which is over an order of magnitude greater than that of conventional column contactors.
- PEEK membrane module was further scaled up from 4 inch to 8 inch diameter (a factor 3 increase in membrane area). Single-gas permeation measurements indicated that 8-inch modules had an intrinsic CO₂ permeance as high as 2,150-2,670 GPU.
- One 8-inch-diameter module was tested in membrane contactor mode for CO₂ capture using a simulated flue gas. Carbon dioxide removal rate of 91.3% was achieved with a mass transfer coefficient of 1.5 (sec)⁻¹.
- Parametric tests indicated CO₂ flux and capture rate increased with increasing feed pressure, solvent flow velocity and solvent temperature. PEEK hollow fiber membrane contactor is effective in capturing CO₂ from low CO₂-concentration feeds, making it high potential for natural gas flue gas CO₂ capture.

Acknowledgments

We gratefully acknowledge support by the US Department of Energy (Contract Numbers DE-FE-0004787 and DE-FE-0012829) and Illinois Clean Coal Institute (ICCI). We thank DOE/NETL Project Manager, José Figueroa, for his assistance and many valuable discussions. We also thank Dennis Leppin for his help in obtaining property data for the aMDEA solvent using ProTreat.

References

- [1] Annual Energy Outlook 2014 with Projections to 2040, Report # DOE/EIA-0383(2014), April 2014.
- [2] DOE NETL, Funding Opportunity Number: DE-FOA-0000785.

- [3] T. Guenther, Power Plant CO₂ Capture Overview, LRGCC, March 2008.
- [4] M. Ramezan, et al., Carbon Dioxide Capture from Existing Coal-Fired Power Plants, Final Report, DOE/NETL-401/110907, Nov. 2007.
- [5] “Updated Costs (June 2011 Basis) for Selected Bituminous Baseline Cases.” August 2012. DOE/NETL-341/082312.
- [6] E. Favre, Carbon dioxide recovery from post-combustion processes: Can gas permeation membranes compete with absorption? *J. Membr. Sci.* 294 (2007) 50-59.
- [7] T. C. Merkel, H. Q. Lin, X. T. Wei, R. Baker, Power plant post-combustion carbon dioxide capture: An opportunity for membranes. *Journal of Membrane Science*, 359 (2010) 126-139.
- [8] Y. Yampolskii, et al. *Materials Science of Membranes for Gas and Vapor Separation*, John Wiley and Sons, 2006.
- [9] R. W. Baker, *Membrane Technology and Applications*, 2nd ed., John Wiley & Sons Ltd., Chichester, England, 2004, p. 544.
- [10] S. Khaisri, D. deMontigny, P. Tontiwachwuthikul, R. Jiraratananon, Comparing membrane resistance and absorption performance of three different membranes in a gas absorption membrane contactor, *Sep. Purif. Technol.* 65 (2009) 290–297.
- [11] D. deMontigny, P. Tontiwachwuthikul, A. Chakma, Using polypropylene and polytetrafluoroethylene membranes in a membrane contactor for CO₂ absorption, *J. Membr. Sci.* 277 (2006) 99–107.
- [12] N. Nishikawa, M. Ishibashi, H. Ohta, N. Akutsu, H. Matsumoto, T. Kamata, H. Kitamura, CO₂ removal by hollow fiber gas–liquid contactor, *Energy Convers. Manage.* 36 (1995) 415–418.
- [13] D. deMontigny, P. Tontiwachwuthikul, A. Chakma, Comparing the absorption performance of packed columns and membrane contactors, *Ind. Eng. Chem. Res.* 44 (2005) 5726–5732.
- [14] J.L. Li, B.H. Chen, Review of CO₂ absorption using chemical solvents in hollow fiber membrane contactors, *Sep. Purif. Technol.* 41 (2005) 109–122.
- [15] B.W. Reed, et al., Chapter 10: Membrane Contactors, in: *Membrane Separations Technology: Principles and Applications*, R.D. Noble and S.A. Stern, eds., Elsevier Science B.V., 1995, p. 478.
- [16] R. P. Lively, M. Dose, L. Xu, J.R. Johnson, K. Zhang, J. Vaughn, M. E. Lydon, J. A. Thompson, J. S. Lee, L. Liu, Z. Hu, M. Realff, W. J. Koros, A High-Flux Polyimide As a Contender for CO₂ Recovery From Flue Gas, 2012 North American Membrane Society Meeting, June 9-13, 2012, New Orleans, LA, USA.

- [17] S. Li, D. Rocha, S.J. Zhou, H.S. Meyer, B. Bikson and Y. Ding, Post-combustion CO₂ capture using super-hydrophobic, polyether ether ketone, hollow fiber membrane contactors, *J. Membr. Sci.*, (2013) 79-86.
- [18] Y. Ding, B. Bikson, Preparation and characterization of semi-crystalline poly(ether ether ketone) hollow fiber membranes, *J. Membr. Sci.* 357 (2010) 192-198.
- [19] Y. Yuan, Y. Ding, Functionalized porous poly(aryl ether ketone) materials and their use, US Patent 7,176,273, Feb 13, 2007.
- [20] S. James Zhou, Shiguang Li, Howard Meyer, Yong Ding and Ben Bikson, "Hybrid Membrane/Absorption Process for Post-combustion CO₂ Capture," DOE NETL CO₂ Capture Technology Meeting, July 8-11, 2013, Pittsburgh, PA, USA.
- [21] P.T. Nguyena, E. Lasseguette, Y. Medina-Gonzalez, J.C. Remigy, D. Roizarda, E. Favrea, A dense membrane contactor for intensified CO₂ gas/liquid absorption in post-combustion capture, *J. Membr. Sci.* 377 (2011) 261- 272.
- [22] H. Svensson, C. Hulteberg, H. T. Karlsson, Heat of absorption of CO₂ in aqueous solutions of N-methyldiethanolamine and piperazine, *International Journal of Greenhouse Gas Control*, 17 (2013) 89–98.
- [23] Incropera et al. "Fundamentals of Heat and Mass Transfer", Wiley, Hoboken NJ, 2002.
- [24] D. A. Zaidiza, B. Belaissaoui, S. Rode, T. Neveux, C. Makhloufi, C. Castel, D. Roizard, E. Favre, [Adiabatic modelling of CO₂ capture by amine solvents using membrane contactors](#), *J. Membr. Sci.* 493 (2015) 106-119.
- [25] R. Wang, D.F. Li, D.T. Liang, Modeling of CO₂ capture by three typical amine solutions in hollow fiber membrane contactors, *Chemical Engineering and Processing* 43 (2004) 849–856.