Novel Carbon Dioxide-Selective Membranes for CO_2 Capture from Less than 1% CO_2 Sources

primary project goals

Ohio State University (OSU) is developing a cost-effective design and manufacturing process for new membranes and membrane modules that capture carbon dioxide (CO_2) from sources with less than 1% CO_2. Synthesis of novel CO_2-selective membranes using a nanoporous polyethersulfone (PES) polymer support and coating a top layer of thin, highly selective, yet permeable amine-containing polymer membrane will be performed. Pilot-size membranes will be used to fabricate at least three membrane modules for testing with the simulated gas mixture.

technical goals

- Synthesize and characterize membranes to obtain a CO_2 permeance of 1,800 gas permeation units (GPU) and a CO_2/nitrogen (N_2) selectivity of greater than 140.
- Fabricate a membrane prototype at least 14 inches in width and greater than 50 feet in length using the continuous membrane fabrication machine at OSU.
- Use prototype to fabricate at least three membrane modules and conduct pilot testing using a simulated gas mixture containing less than 1% CO_2.
- Perform an economic feasibility study.

technical content

OSU is continuing their work on developing novel CO_2-selective membranes that capture CO_2 from less than 1% CO_2 concentration sources. The membrane is inexpensive, consisting of a cost-effective nanoporous polymer support and a top layer coating of thin, highly selective, yet permeable amine-containing polymer membrane, as shown in Figure 1. The membrane modules are incorporated in a two-stage membrane process that would be implemented after the primary CO_2 capture system in a power plant, which has already captured greater than 90% CO_2 from flue gas. In the first membrane module, CO_2 is removed from the feed gas by using vacuum and the permeate stream is used as the feed for the second membrane module, where additional CO_2 is removed by vacuum such that the 90% capture and 95% purity targets are met.

technology maturity:

Pilot-Scale, Simulated Flue Gas

project focus:

Selective Membranes for <1% CO_2 Sources

participant:

Ohio State University

project number:

FE0026919

predecessor projects:

N/A

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partners:

TriSep Corporation;
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start date:

03.01.2016

percent complete:

100%

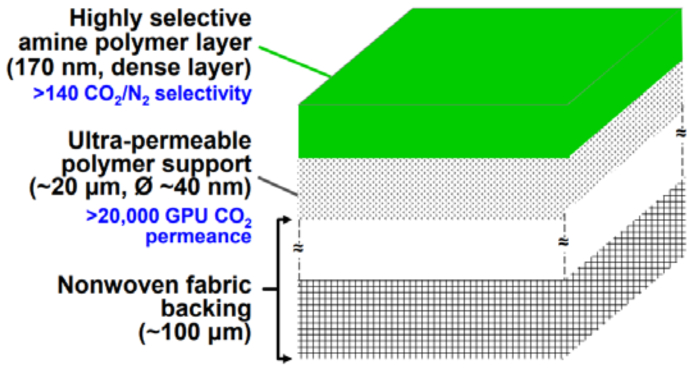

Figure 1: Selective amine polymer layer/polymer support.

Carbon dioxide permeates through the membrane via a facilitated transport mechanism where CO_2 reacts with amines reversibly to facilitate CO_2 transport, whereas N_2 cannot react with amines, resulting in very high CO_2/N_2 selectivity. The amine polymer layer contains mobile carriers that react with CO_2 to facilitate transport (Figure 2). The CO_2 flux increases as pressure increases until it reaches a saturation point in which CO_2 reacts with all carriers in the membrane. At low pressure (or low CO_2 concentration), more free carriers are available; therefore, the CO_2 permeance is higher due to greater CO_2 facilitation. Since sulfur dioxide (SO_2) permeates through the membrane, OSU proposes to add an SO_2 polishing step before the membrane process to remove SO_2 to less than 1 to 3 parts per million (ppm). A CO_2 permeance of 1,800 GPU and a CO_2/N_2 selectivity of greater than 140 using a simulated gas mixture containing less than 1% CO_2 are the target performance criteria for these membranes. New and improved membranes are synthesized, in which the polyamine layer is modified to achieve a higher CO_2 permeance and a hydrophilic agent is incorporated into the polymer support to improve its porosity, permeance, and adhesion. Membranes containing unhindered polyamine but with a thinner selective layer yielded a high CO_2 permeance of 2,299 GPU with a CO_2/N_2 selectivity of 179 at 67°C with 1% CO_2, which was the most permeable membrane developed during the project.

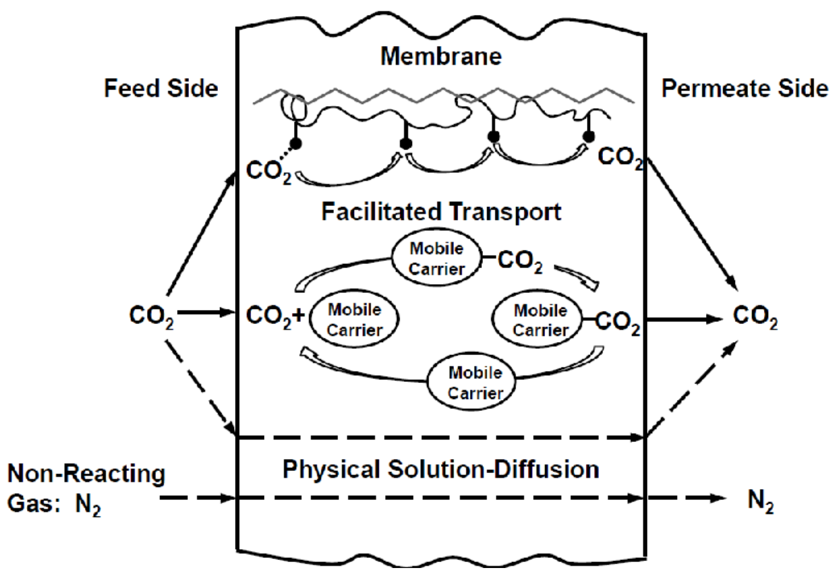

Figure 2: Facilitated transport on amine polymer layer.

The fabrication of the representative spiral-wound membrane modules for the performance testing at OSU was performed by using a multiple-leaf configuration for the membrane element (Figure 3). The number of membrane leaves was increased from six to seven pieces, while the length of each leaf was increased from 30 to 36 inches. Hence, the total membrane area was raised from 2 m^2 to 2.94 m^2. The spiral-wound membrane element was loaded in the stainless-steel housing to become the stainless-steel membrane module as shown in Figure 4.

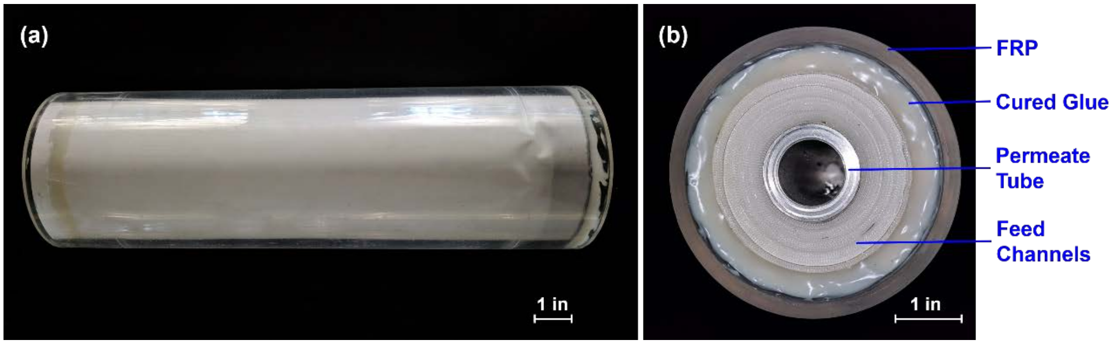

Figure 3: Images of a spiral-wound membrane element from (a) the side and (b) the end of the element.

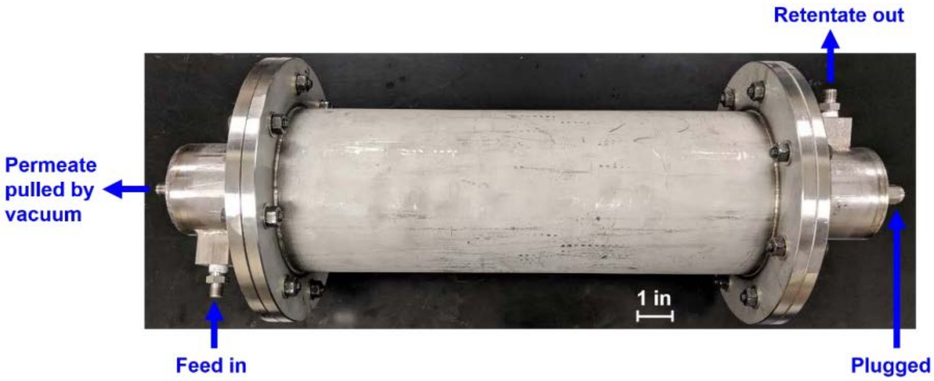

Figure 4: Image of an assembled stainless-steel spiral-wound membrane module.

A pneumatic unwinder was integrated into the existing module rolling machine. The new unwinder delivered the stack of membrane leaves to the central tube with better tension control. A schematic of the modified rolling machine is shown in Figure 5. Compared to the manual tension control, the modified machine ensured an even and steady rolling. This improved the membrane packing density and uniformity and minimized any feed gas channeling. In addition, the modified machine is capable of fabricating full-size commercial spiral-wound modules (8-inch diameter by 40-inch length).

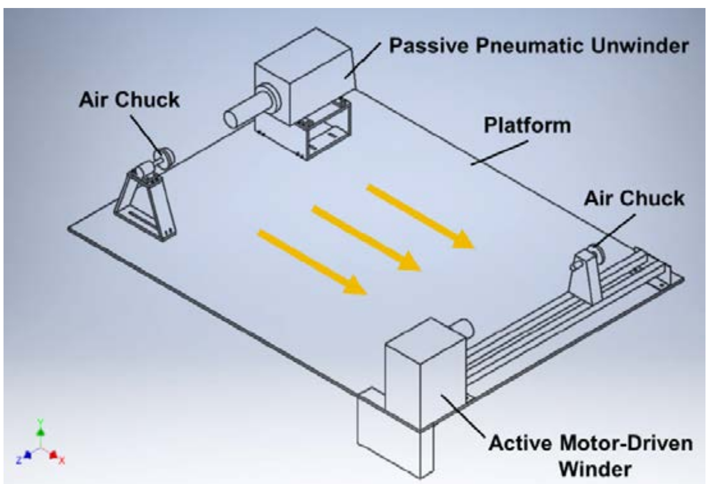

Figure 5: Schematic of spiral-wound membrane element rolling machine with tension control.

The two-stage membrane process is shown in Figure 6. The feed gas, containing less than 1% CO_2, is pressurized by Blower 1 to 4 atmosphere (atm) and passed to Membrane Stage 1. This stage produces a CO_2-depeleted retentate, with 90% CO_2 from the feed removed, and a CO_2-rich permeate, containing 15 to 20% CO_2 on dry basis. A vacuum of 0.2 to 0.3 atm is pulled on the permeate side of this stage to increase the transmembrane driving force. The permeate is re-compressed by Blower 2 to 4 atm and passed to Membrane Stage 2. This stage further enriches the CO_2 to greater than 95% purity in the permeate; the remaining CO_2 in the retentate is recycled back to the feed of Membrane Stage 1. A vacuum of 0.2 to 0.3 atm is also pulled on the permeate side. The vacuum discharge is eventually compressed to 150 atm for transport and storage.

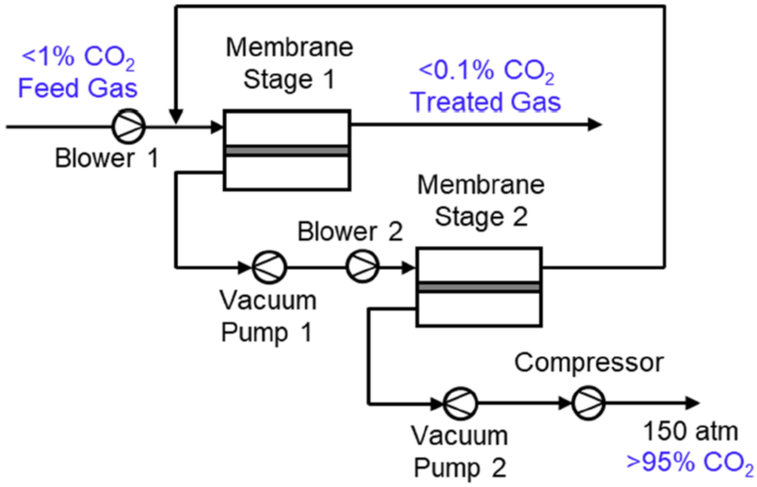

Figure 6: Schematic of the two-stage membrane process.

The techno-economic analysis (TEA) was updated. The membrane synthesized recently resulted in an estimated capture cost of $246/tonne (which takes into consideration the varying CO_2 permeance), and a cost of electricity (COE) increase of 17.9%.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Fixed and mobile amine carriers as the membrane matrix	
Materials of Fabrication for Support Layer	—	Nanoporous polyethersulfone	
Nominal Thickness of Selective Layer	nm	100–200	100–170
Membrane Geometry	—	Flat sheet	Flat sheet
Max Trans-Membrane Pressure	bar	10	10
Hours Tested without Significant Degradation	—	1,900	1,200
Manufacturing Cost for Membrane Material	$/m^2	10	<10
Membrane Performance			
Temperature	°C	57–67	57–87
CO_2 Pressure Normalized Flux	GPU or equivalent	2,299	2,200
CO_2/H_2O Selectivity	—	About 1	About 1
CO_2/N_2 Selectivity	—	140–200	150–225
CO_2/SO_2 Selectivity	—	About 1	About 1
CO_2/H_2 Selectivity	—	About 100	About 100
Type of Measurement	—	Simulated gas mixture	Simulated gas mixture
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	Countercurrent spiral wound	
Packing Density	m^2/m^3	1,800	
Shell-Side Fluid	—	Permeate containing CO_2 (vacuum is used on the permeate side)	
Flue Gas Flowrate	kg/hr	4.346	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%, >95%, 152 bar	
Pressure Drops Shell/Tube Side	bar	0 bar/m permeate/0.07 bar/m feed	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	$500/(kg/hr), $32/m^2 or $246/tonne CO_2 capture cost	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.35 × 10^{-10} mol/(m^2-s-Pa) (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (hydrogen [H_2]-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

		Composition						
		vol%					ppmv	
Pressure	Temperature	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7 psia	135°F	0.99	17.25	78.62	2.34	0.80	42	74

Other Parameter Descriptions:

Membrane Permeation Mechanism – Facilitated transport using chemical reaction to enhance separation.

Contaminant Resistance – 3 ppm SO_2 and 3 to 7% oxygen (O_2).

Flue Gas Pretreatment Requirements – SO_2 polishing step (with 5% sodium hydroxide [NaOH]) to have 1 to 3 ppm SO_2.

Membrane Replacement Requirements – About once every four years.

Waste Streams Generated – No additional waste streams generated.

technology advantages

- Energy-efficient technology.
- Low-cost membrane (less than \$2.00/ft^2).
- High CO_2/N_2 selectivity due to amine polymer layer.
- Facilitated transport mechanism allows for increase in CO_2 permeance at low CO_2 concentrations.
- Membrane stability.
- Hydrophilic additives in polymer support improve membrane performance.

R&D challenges

- Achieving very high membrane performance (CO_2 permeance of 1,800 GPU and CO_2/N_2 selectivity of greater than 140).
- Membrane stability in presence of contaminants.
- Requires two membrane stages.

status

Spiral-wound prototype membrane module with an active membrane area of 2.94 m^2 was tested with a simulated residual flue gas at 4 atm and 67°C. The membrane module showed a CO_2 permeance of 1,921 GPU and a CO_2/N_2 selectivity of 209 with 1% CO_2. The module showed good stability with 3 ppm SO_2. The TEA showed a CO_2 capture cost of $246/tonne, which is a 17.9% increase in COE. The project has concluded.

available reports/technical papers/presentations

Ho, W., Han, Y., "Novel CO_2-Selective Membranes for CO_2 Capture from <1% CO_2 Sources," Final project review meeting presentation, Pittsburgh, PA, October 2019. *https://www.netl.doe.gov/projects/plp-download.aspx?id=17279&filename=DE-FE0026919_Project%20Final%20Review%20Meeting%2010-28-19.pdf*.

Ho, W., Han, Y., "Novel CO_2-Selective Membranes for CO_2 Capture from <1% CO_2 Sources," presented at the 2019 NETL CCUS Integrated Project Review Meeting, Pittsburgh, PA, August 2019. *https://www.netl.doe.gov/projects/plp-download.aspx?id=17322&filename=FE0026919_OSU_2019%20NETL%20CCUS%20project%20review%20meeting.pdf*.

Ho, W., Han, Y., "Novel CO_2-Selective Membranes for CO_2 Capture from <1% CO_2 Sources," presented at the 2018 NETL CO2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=13108&filename=Y-Han-OSU-Membrane-Capture-from-less-than-1--CO2-Sources.pdf*.

Ho, W., "Novel CO_2-Selective Membranes for CO_2 Capture from <1% CO_2 Sources," presented at the 2018 NETL continuation application status meeting, Pittsburgh, PA, February 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=13105&filename=FE0026919-Mtg-021918.pdf*.

Ho, W., "Novel CO_2-Selective Membranes for CO_2 Capture from <1% CO_2 Sources," presented at the 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/2-Tuesday/W-Ho-OSU-Capture-from-less-than-1--CO2-Sources.pdf*.

Ho, W., "Novel CO_2-Selective Membranes for CO_2 Capture from <1% CO_2 Sources," Continuation Application Status Meeting, Pittsburgh, PA, February 2017. *https://www.netl.doe.gov/projects/plp-download.aspx?id=13107&filename=DE-FE0026919-Continuation-Application-Status-Mtg-2-27-17.pdf*.

Ho, W. "Novel CO_2-Selective Membranes for CO_2 Capture from <1% CO_2 Sources," presented at the 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/projects/plp-download.aspx?id=13109&filename=W-Ho-OSU-CO2-Selective-Membranes.pdf*.

Ho, W., "Novel CO_2-Selective Membranes for CO_2 Capture from <1% CO_2 Sources," Project Kickoff Meeting presentation, April 2016. *https://www.netl.doe.gov/projects/plp-download.aspx?id=13106&filename=DE-FE0026919-Project-Kick-off-Meeting.pdf*.