Bench-Scale Development of a Transformative Membrane Process For Pre-Combustion CO_2 Capture

primary project goals

Membrane Technology and Research, Inc. (MTR) and partners Susteon and the Energy and Environmental Research Center (EERC) are maturing technology based on a novel, hydrogen (H_2)-selective, multi-layer composite polymer membrane called Proteus™ for use in the separation of H_2 from post-shifted syngas. The current project focuses on the scale-up of a second-generation Proteus™ membrane, including fabrication of high-temperature prototype modules using Gen-2 membranes and validating module performance in laboratory tests. A prototype module test system will be designed, built, and installed at EERC for parametric and lifetime testing of the modules with actual coal-derived syngas. The process will be optimized, and a techno-economic analysis (TEA) will be updated based upon the results of testing.

technical goals

- Optimize the Gen-2 Proteus™ membrane and develop modules capable of operation up to 200°C.
- Demonstrate membrane module performance while processing coal-derived syngas during a field test at EERC by demonstrating an H_2/carbon dioxide (CO_2) selectivity = 30 and recovering 2.5 lb/h H_2 at 75% purity at a syngas flow rate of 20 lb/h.
- Advance the Gen-2 Proteus™ membrane pre-combustion membrane capture technology from Technology Readiness Level (TRL) 4 to TRL 5.
- Optimize processes for integrating membrane modules into the integrated gasification combined cycle (IGCC) process with carbon capture (including evaluating sulfur treatment options), showing the potential via a TEA to reduce the cost of capture by more than 30% compared to Selexol.

technical content

MTR is developing composite membranes for application in pre-combustion carbon capture where essential membrane characteristics include high H_2/CO_2 selectivity and high H_2 permeance rates. The MTR composite membrane for H_2 separation is called Proteus™. Figure 1 illustrates the membrane structure and some characteristic composite membrane layers. Note that the key to competitive industrial performance is a very thin selective layer, which is required to allow high gas fluxes (or permeances) for given membrane surface areas.

technology maturity:
Bench-Scale, Actual Syngas (equivalent to 0.015 MWe)

project focus:
Polymeric Membranes

participant:
Membrane Technology and Research, Inc.

project number:
FE0031632

predecessor projects:
FE0001124

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partners:
Susteon
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percent complete:
40%

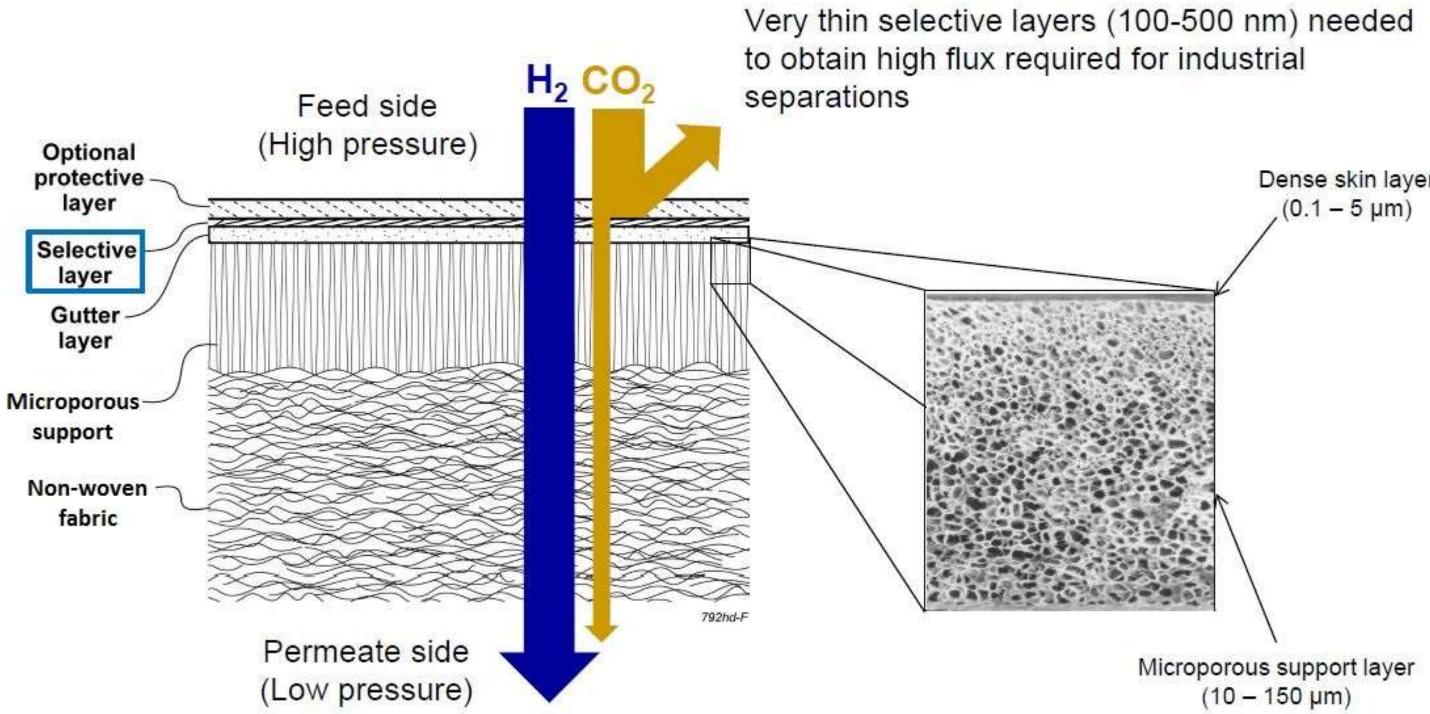

Figure 1: Proteus™ membrane multi-layer composite structure.

The H_2-selective Proteus™ membranes were first developed by MTR in work funded by the U.S. Department of Energy (DOE; DE-FE0001124). The first-generation membrane (Gen-1 Proteus™) had an upper temperature limit of 150°C. Semi-commercial modules made from this membrane demonstrated stable operation for extended periods in the presence of sulfur and other contaminants in slipstream tests of actual coal-derived syngas from an air-blown gasifier at the National Carbon Capture Center (NCCC). By the end of testing in 2017, Gen-1 Proteus™ was evaluated in more than 15 different gasification campaigns accumulating 5,500 hours of run time for membrane stamps or lab-scale modules and 3,625 hours for semi-commercial modules at NCCC.

The recently developed Gen-2 Proteus™ has a higher temperature limit compared to the Gen-1 membrane (200°C versus 150°C), which allows for better heat integration into pre-combustion processes. The Gen-2 membrane also has improved H_2/CO_2 selectivity compared to the Gen-1 membrane, with an average value of 32 measured in membrane stamp testing at NCCC (compared to 15 to 20 for Gen 1 in the same tests). In ongoing work, a new membrane treatment technique has been developed that improves the membrane H_2/CO_2 selectivity to 50, which significant exceeds the project success criteria of 30. This improved selectivity will reduce energy use and the required purification equipment size, thereby lowering operating and capital expenses.

To highlight the improved permeation performance of the Gen-2 Proteus™ membrane, Figure 2 compares the selectivity and permeance of this membrane with other polymers on a Robeson tradeoff plot.

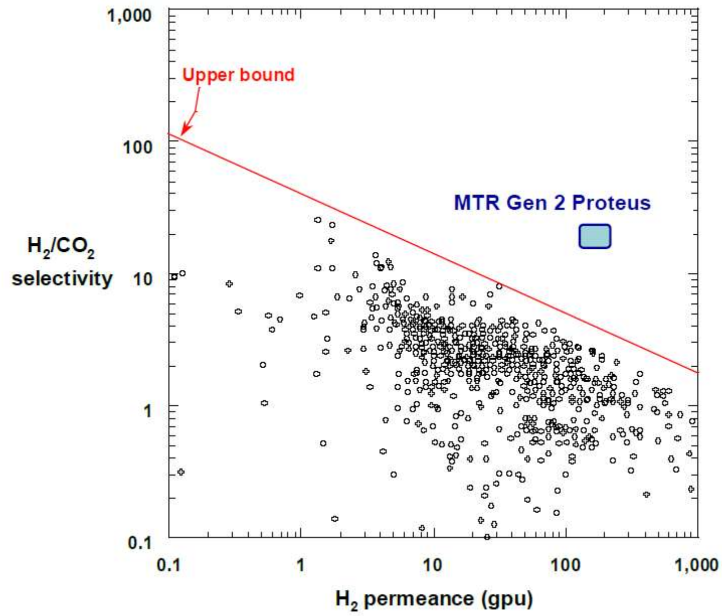

Figure 2: Robeson plot with Gen-2 Proteus™ membrane performance.

Process Scenarios

A simplified process flow diagram for carbon capture with membranes in an IGCC power cycle is depicted in Figure 3. Coal is converted by oxygen-based pressurized gasification resulting in a raw syngas. This syngas is shifted via the water-gas shift (WGS) reaction to produce syngas consisting mostly of H_2 and CO_2. This shifted syngas is introduced at the high-pressure feed side of the membrane capture unit. The high-partial pressure driving force, combined with a nitrogen (N_2) sweep on the lower-pressure permeate side of the membrane, causes selective H_2 permeation into the N_2 sweep, which serves as fuel gas in a combustion turbine. The high-pressure membrane retentate is enriched in CO_2 that can then be further purified, compressed, and sent to storage.

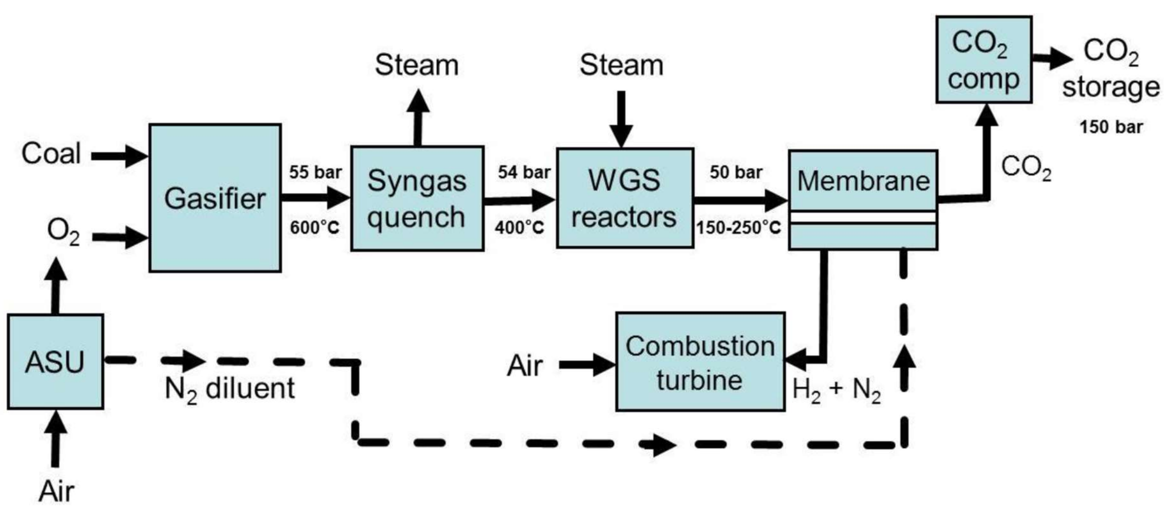

Figure 3: Overall process design for the pre-combustion capture membrane system.

Figure 4 shows additional process details for the MTR pre-combustion CO_2 capture process. After using the Proteus™ membrane to recover H_2, a series of steps are used to purify CO_2. These steps include (1) sulfur removal, (2) gas drying, (3) refrigeration to produce liquid CO_2, (4) additional CO_2 recovery with the MTR Polaris™ membrane, and (5) pumping liquid CO_2 to storage pressure. The CO_2 purity can be readily increased to greater than 99% in this process. In comparison to a baseline case (GE Gasifier with two-stage Selexol [i.e., Case 2 of DOE Bituminous Baselines Study]), prior studies showed that the MTR membrane process provides a 27-megawatt-electric (MWe) net power improvement and a 7.4% lower cost of energy (COE) using Gen-1 Proteus™ membrane properties. Both the warm (H_2 membrane) and cold (CO_2 membrane) portions of the MTR process have been validated in independent skid field tests at NCCC.

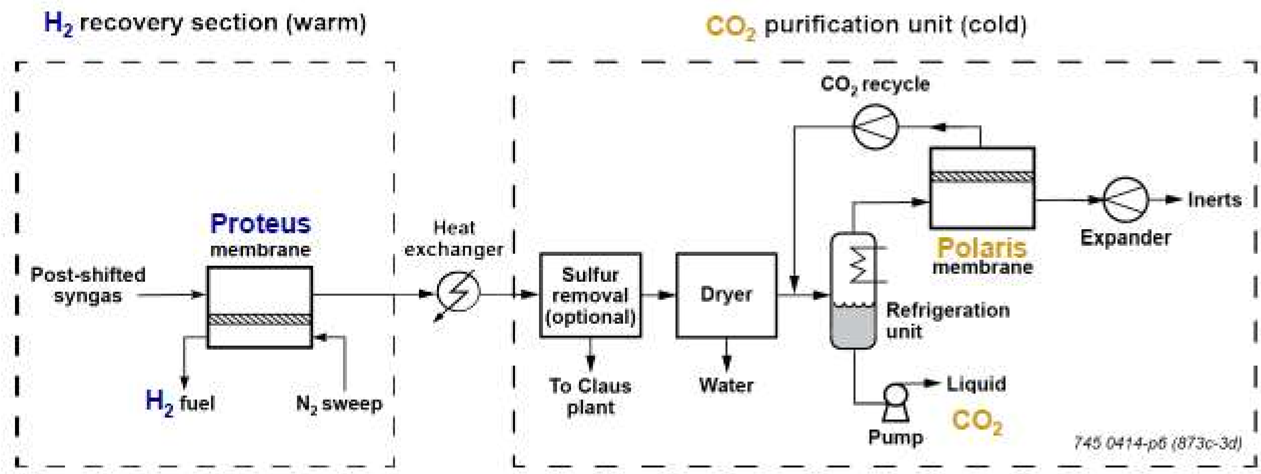

Figure 4: MTR dual-membrane process for H_2 recovery and CO_2 capture in IGCC power generation.

For industrial applications, Proteus™ membranes will be packed into spiral-wound membrane modules, a commonly used module design for commercial membrane installations. Spiral-wound modules are robust, resistant to fouling, and economical; they are used in 95% of the reverse osmosis (RO) desalination industry and more than 70% of the membrane market for CO_2 removal from natural gas. Figure 5 shows the general design features of a spiral-wound membrane module. The module consists of a permeate collection tube with a spiral formation of permeate spacers and feed spacers, allowing separated H_2 to be swept by N_2 on the permeate side and CO_2 retained on the feed site to flow through the device. In bench-scale work, modules have membrane area of 1 to 4 m^2, and accommodate gas flow of about 50 lb/h. Commercial modules have membrane area of 20 to 50 m^2, and accommodate gas flow of about 500 lb/h.

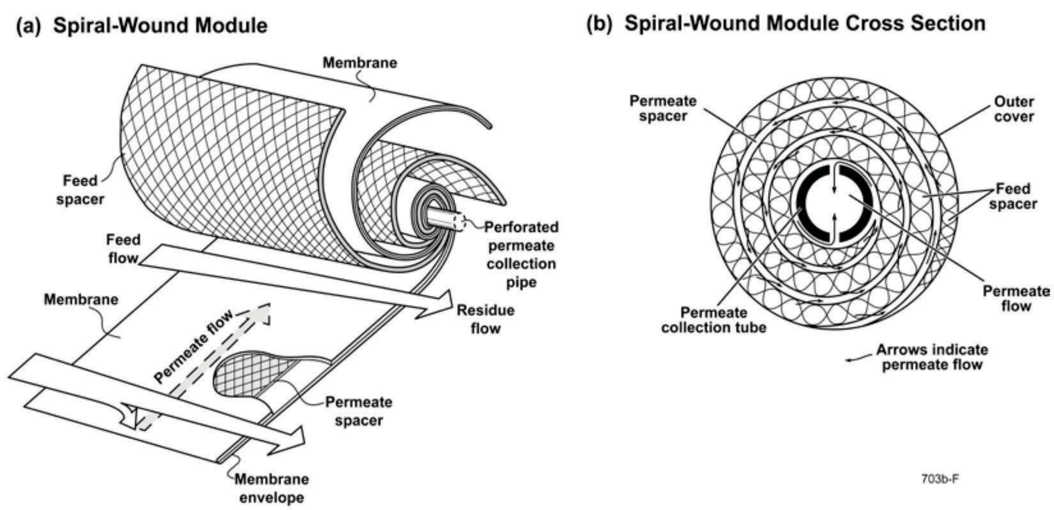

Figure 5: Schematic diagram of a spiral-wound membrane module.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value		Target R&D Value
Materials of Fabrication for Selective Layer	—	Proprietary polymers		
Materials of Fabrication for Support Layer	—	Proprietary polymers		
Nominal Thickness of Selective Layer	µm	< 1 micron		< 1 micron
Membrane Geometry	—	Flat sheet		Flat sheet
Maximum Trans-Membrane Pressure	bar	75		75
Hours Tested without Significant Degradation	—	1 month		3 months
Manufacturing Cost for Membrane Material	$\$/m^2$	500		250
Membrane Performance				
Temperature	°C	200		200
H_2 Pressure Normalized Flux	GPU	225		200
H_2/H_2O Selectivity	—	0.4		0.4
H_2/CO_2 Selectivity	—	50		30
H_2/H_2S Selectivity	—	>50		50
Sulfur Tolerance	ppm	Inert to Sulfur		Inert to Sulfur
Type of Measurement	—	mixed-gas		mixed-gas
Proposed Module Design				
Flow Arrangement	—	Spiral-wound modules		
Packing Density	m^2/m^3	1,000		
Shell-Side Fluid	—	Syngas		
Syngas Gas Flowrate	kg/hr	717,000		
CO_2 Recovery, Purity, and Pressure	%/%/bar	90	99.5	152.7
H_2 Recovery, Purity, and Pressure	%/%/bar	99.4	44 % in N_2 as fuel	30
Pressure Drops Shell/Tube Side	bar	feed: 1 /sweep: 1		
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	15		

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 atmosphere [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 = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

***Type of Measurement* –** Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in syngas.

***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 concurrent, 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* –** Syngas.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Permeation through the Proteus™ membrane occurs by the passive solution-diffusion mechanism.

Contaminant Resistance – The MTR membranes and membrane module components are compatible with the species found in coal-derived syngas. This is one of the major findings from syngas field tests conducted at NCCC between 2009 and 2017 for both the Polaris™ (5,200 cumulative hours online) and Proteus™ (9,125 cumulative hours online) membranes.

Syngas Pretreatment Requirements – The MTR pre-combustion CO_2 capture membrane process design does not require syngas pretreatment.

Membrane Replacement Requirements – The target membrane module lifetime is three years, which is at the conservative end of the typical industrial gas separation module lifetime of three to five years.

Waste Streams Generated – No additional waste streams are generated when adding the MTR pre-combustion CO_2 capture system to an IGCC process. Similar to the stand-alone IGCC process, water removed from the MTR process can be recycled to process demand and the removed sulfur species can be sent to a Claus plant for processing. The high-purity CO_2 product can be used for enhanced oil recovery or other industrial applications.

technology advantages

- The Proteus™ membrane allows separation of H_2 from syngas at elevated temperatures. This ability to operate warm/hot reduces the need for heat exchange (e.g., membrane modules operate at a higher temperature than conventional acid gas removal processes like Selexol, reducing the need for syngas cooling and water condensation).
- A membrane system does not contain moving parts or involve chemical reactions, making it simple to operate and maintain.
- The membrane material has a high tolerance to acid gases and is inert to all primary syngas species.
- The membrane capture system has a compact footprint and low energy cost.
- The membrane capture system permeates water in syngas (increase mass to turbine and reduces CO_2 dehydration costs).
- Membrane modules downstream from pressurized WGS maintain CO_2 effluent at pressure; therefore, less compression of CO_2 product is required compared to conventional acid gas removal processes.
- The proposed N_2 sweep on the H_2 permeate side increases the partial-pressure driving force for separation and decreases the required membrane area.

R&D challenges

- Countercurrent sweep module design could result in several potential inefficiencies, including sweep-side pressure drop, concentration polarization, poor utilization of the membrane area due to module geometry, and non-countercurrent flow patterns.
- Feed and permeate side pressure drops could lead to excessive energy losses if modules are not designed properly.
- Membrane module cost reductions will be needed if the technology is to become economically viable.
- Scale-up and integration issues are a possibility given the large number of membranes needed to service a 550-MWe plant.

status

A second-generation Proteus™ membrane has been made with performance that exceeds H_2/CO_2 selectivity targets, and robust membrane module components have been identified for use in syngas environments at high temperatures. Development work underway includes mixed-gas module testing at MTR and fabrication of a field test skid for prototype commercial-scale module testing on oxygen-blown, gasifier-produced syngas at EERC.

available reports/technical papers/presentations

"*Bench-Scale Development of a Transformative Membrane Process for Pre-Combustion CO_2 Capture*," presented by Jay Kniep, Membrane Technology and Research, Inc., 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019.

"*Bench-Scale Development of a Transformative Membrane Process for Pre-Combustion CO_2 Capture*," presented by Jay Kniep, Membrane Technology and Research, Inc., 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018.

"*Bench-Scale Development of a Transformative Membrane Process for Pre-Combustion CO_2 Capture*," Project kick-off meeting presentation, December 2018.

"*Novel Polymer Membrane Process for Pre-combustion CO_2 Capture from Coal-fired Syngas*," Final Report for DE-FE0001124, Membrane Technology and Research, Inc., December 2011.