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

primary project goal

Membrane Technology and Research, Inc. (MTR) and partners Susteon and the Energy and Environmental Research Center (EERC) are maturing a 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. Project work is focused on the goal of scaling-up a second-generation Proteus membrane, including the fabrication of high-temperature prototype modules using second-generation (Gen-2) membranes and validating module performance in laboratory tests, followed by designing, constructing, and installing a prototype test system at EERC for parametric and lifetime testing of the modules with actual coal-derived syngas.

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 techno-economic analysis (TEA) to reduce the cost of capture by more than 30% compared to Selexol.

technical content

MTR has been 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 high temperature 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.

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Pre-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Composite Polymeric Membranes for CO_2 Capture from Coal Syngas

participant:
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FE0001124

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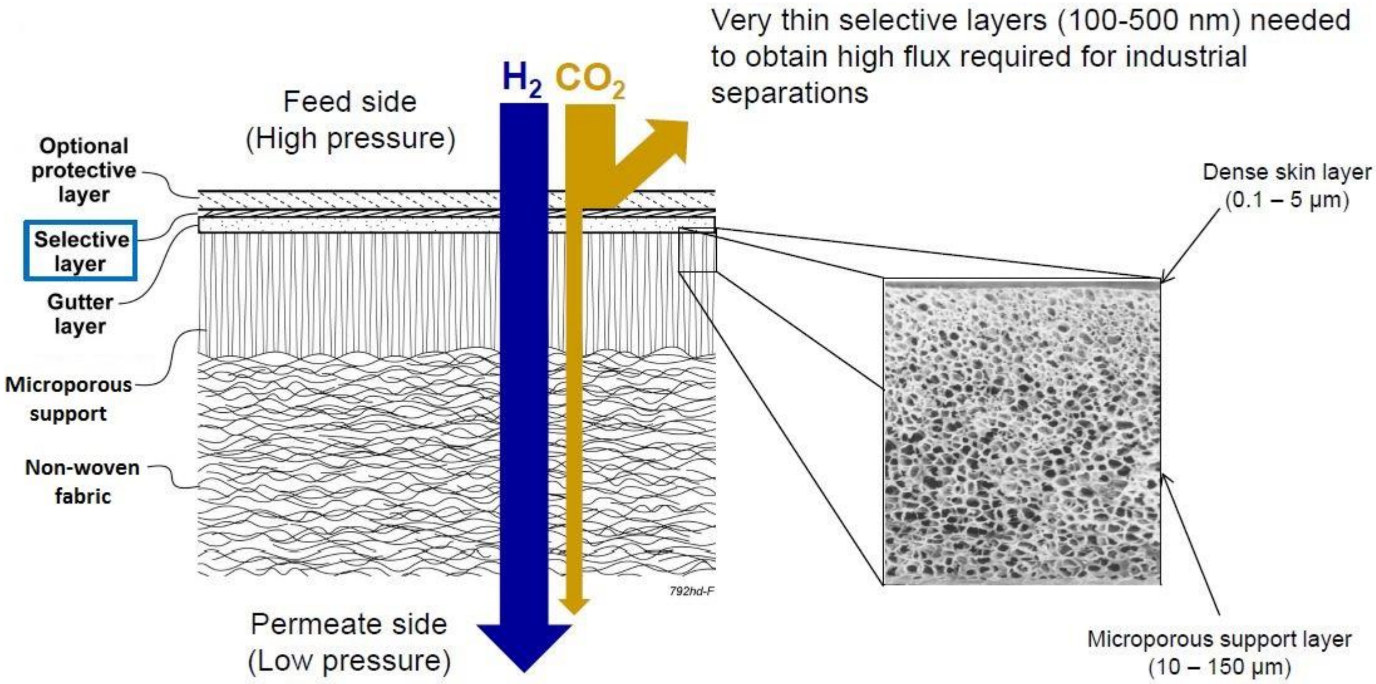

Figure 1: Proteus membrane multi-layer composite structure.

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 subsequently 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). A new membrane treatment technique has been developed that improves the membrane H_2/CO_2 selectivity; the optimized membrane has achieved a selectivity of 37, which exceeds the project success criteria of 30. This improved selectivity reduces 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.

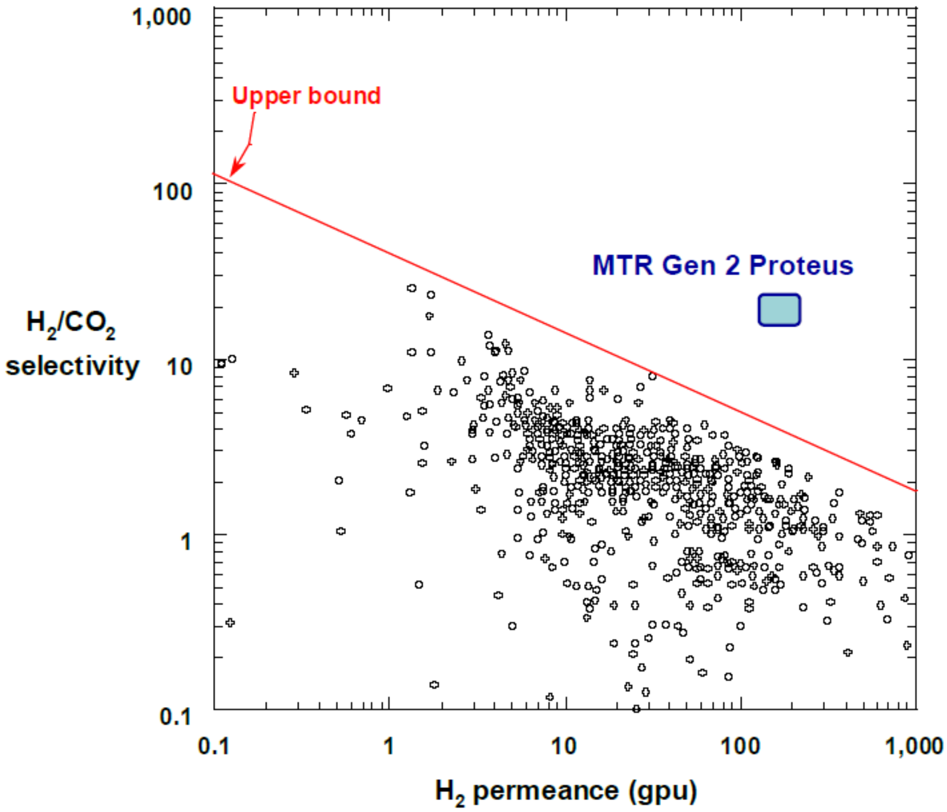

Figure 2: Robeson plot with Gen-2 Proteus membrane performance.

MTR has thoroughly tested the Gen-2 Proteus membrane to determine if all performance targets have been met. The membrane was both temperature- and pressure-cycled to verify robustness; gas permeance values were found to be very stable over multiple heating and cooling cycles, as shown in Figure 3. In addition, the membrane was pressure-cycled in nitrogen between 100 and 1,000 pounds per square inch gauge (psig); nitrogen permeance increased to 5 gas permeation units (GPU) at high pressure and consistently returned to 2 GPU at low pressure. The optimized Gen-2 Proteus membrane retained its high selectivity after operational cycling, showing the robustness of the membrane.

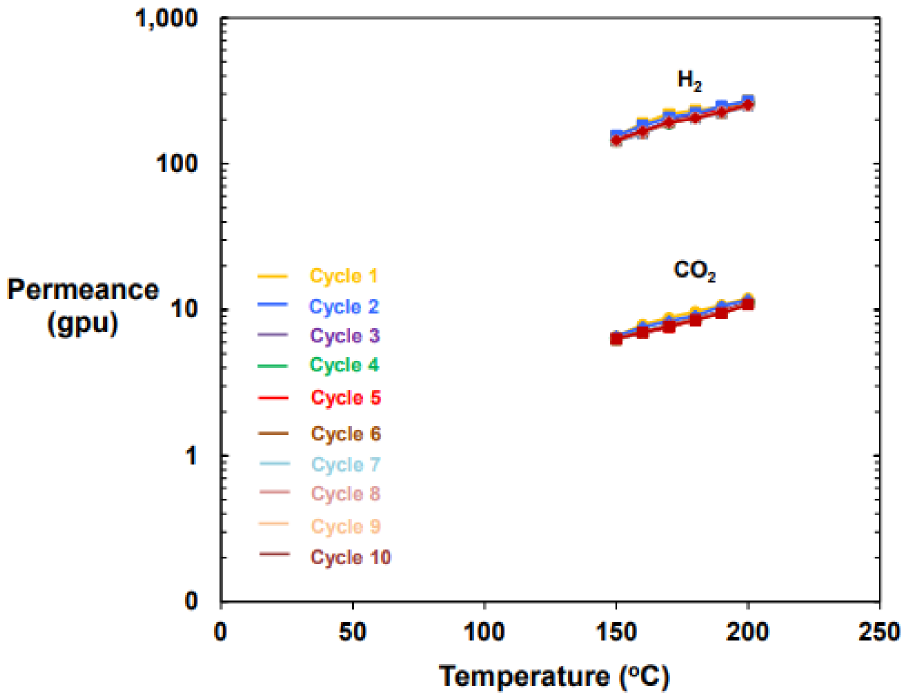

Figure 3: Gen-2 Proteus membrane temperature cycling results.

Process Scenarios

A simplified process flow diagram for carbon capture with membranes in an IGCC power cycle is depicted in Figure 4. 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.

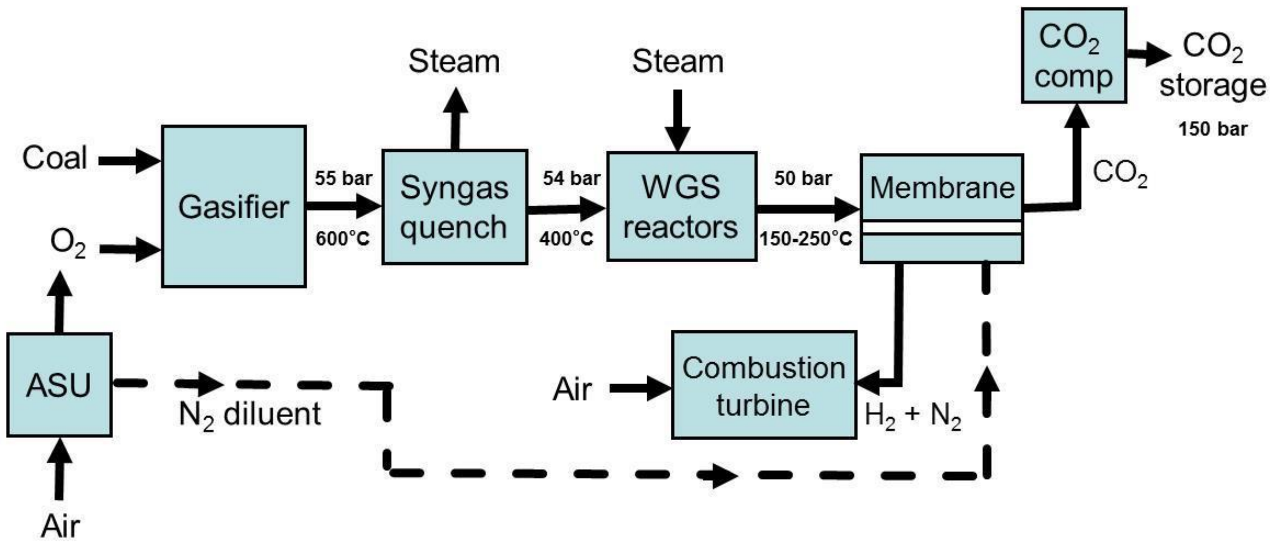

Figure 4: Overall process design for the pre-combustion capture membrane system.

Figure 5 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.

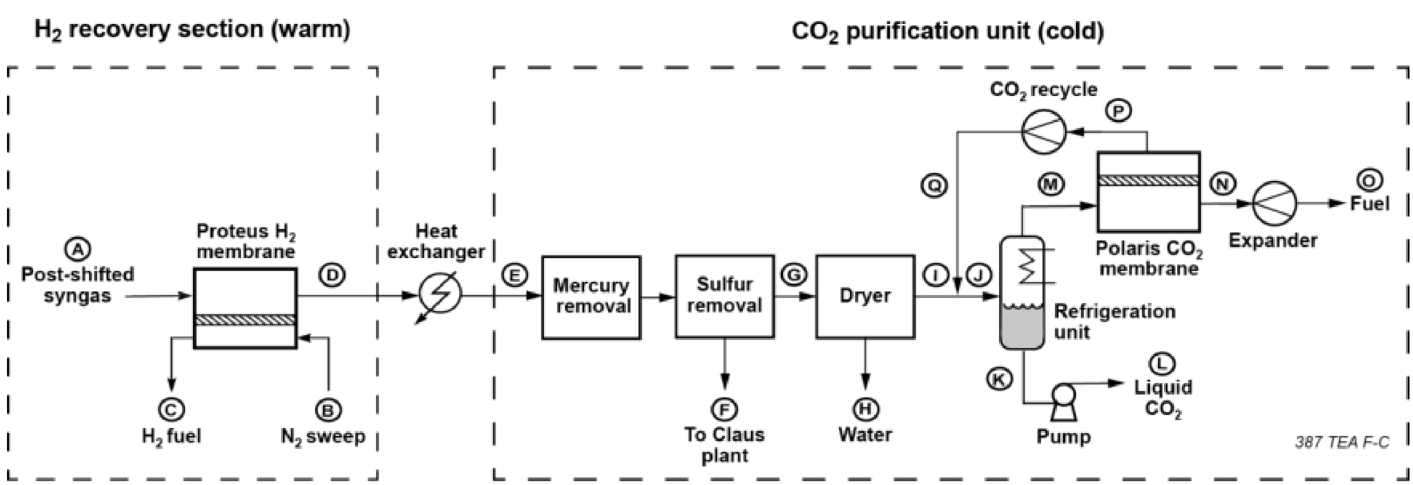

Figure 5: MTR dual-membrane process for H_2 recovery and CO_2 capture in IGCC power generation.

For industrial applications, Proteus membranes can 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 6 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.

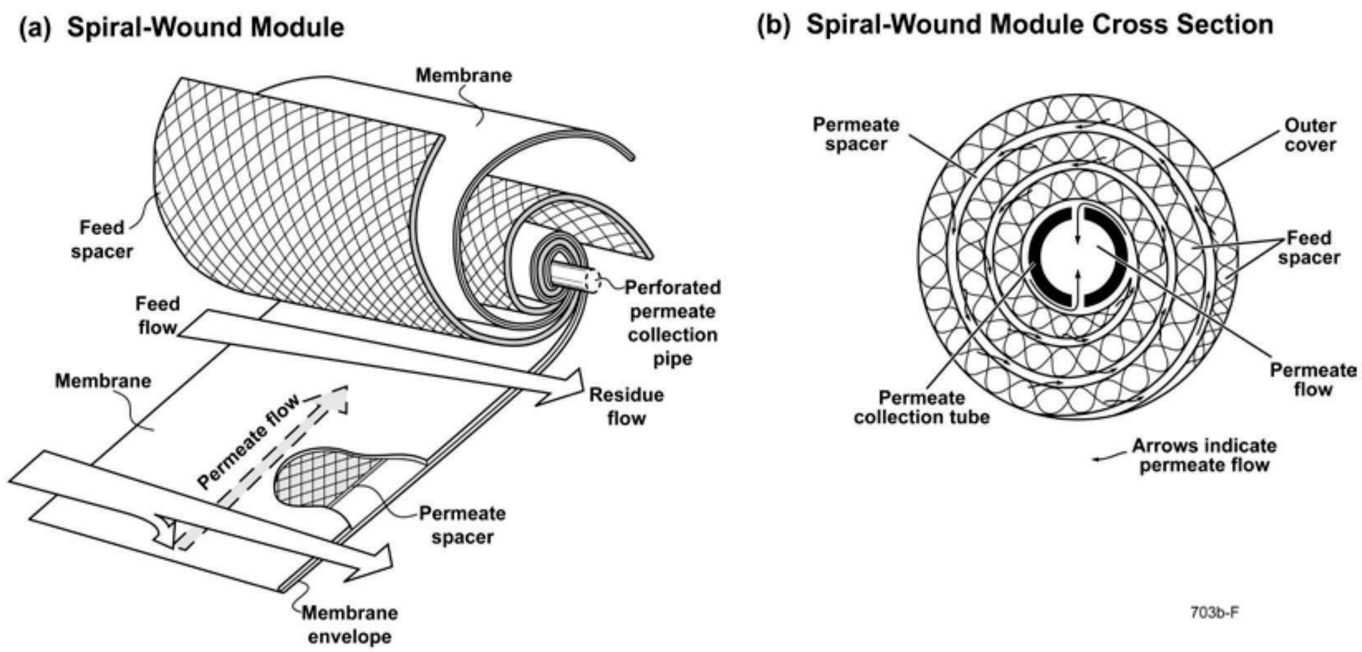

Figure 6: Schematic diagram of a spiral-wound membrane module.

Bench-Scale Field Testing

MTR constructed a bench-scale testing unit incorporating semi-commercial-scale spiral-wound modules. The bench-scale unit was deployed in field-testing at EERC in 2021. EERC's oxygen-blown fluidized bed gasifier supplied syngas for the testing; syngas conditions were as follows:

- 300 to 500 psig gas pressure.
- 30 to 35% H_2; 40 to 50% CO_2.
- Up to 3,000 parts per million (ppm) hydrogen sulfide (H_2S).

A full parametric test matrix of temperature and feed syngas pressures was completed in the testing. For assessment of operational robustness, modules were temperature-cycled up to a simulated process upset condition of 215°C at a syngas pressure of 300 psig. Initial and final 170°C H_2 permeance values were in excellent agreement with the MTR laboratory mixed gas value of 255 GPU, as shown in Figure 7. Overall, testing findings were encouraging, with post-field test examination of the modules finding no membrane pin-hole leaks, good membrane/spacer compatibility and spacers condition, glue lines intact, and no evidence found of module degradation due to high-temperature syngas exposure.

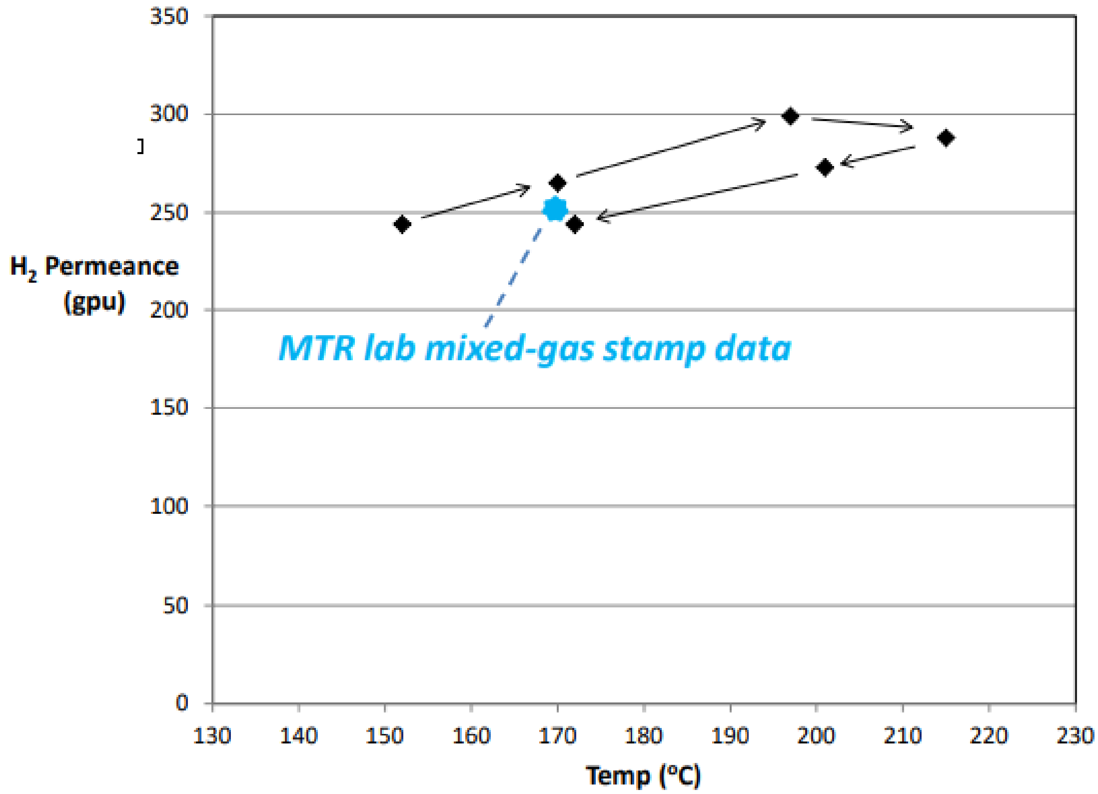

Figure 7: Influence of temperature on H_2 permeance during EERC field test of the Gen-2 Proteus module.

Technoeconomic Analysis

The TEA for this project is assuming the configuration of the reference plant B5B found in the Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity Rev. 4. Gen-2 Proteus membrane performance numbers being used in the TEA were validated during a bench-scale field test (TRL-5) at the EERC with an oxygen-blown fluidized bed gasifier as the coal-derived syngas source.

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 or equivalent	275		200
H_2/H_2O Selectivity	—	0.4		0.4
H_2/CO_2 Selectivity	—	37		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 desulfurized 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 – Either the permeate (CO_2-rich) or retentate (syngas) stream.

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

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.

Proposed Module Design – Spiral-wound modules; see Figure 6.

The pressure, temperature, and composition of the gas entering the membrane module are as follows:

Pressure	Temperature	Composition						
		vol%						ppmv
psia	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
740	392	40.73	1.19	0.01	0.77	55.79	0.18	6230

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, 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 possible given the large number of modules 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. The membrane was incorporated in near-commercial-scale robust membrane modules, which were deployed in a bench-scale field-test skid for evaluation of capture performance on oxygen-blown, gasifier-produced, high-temperature syngas at EERC. The membrane and module were found to perform robustly and maintained durability after exposure to the sulfur-containing syngas. Field test data analysis has been completed and the results are currently being incorporated into the final TEA.

available reports/technical papers/presentations

“Bench-Scale Development of a Transformative Membrane Process For Pre-Combustion CO2 Capture,” presented by Jay Kniep, Membrane Technology and Research, Inc., DOE NETL Virtual Review Meeting, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Kniep.pdf*.

“Bench-Scale Development of a Transformative Membrane Process for Pre-Combustion CO2 Capture,” Membrane Technology and Research, Inc., Project Budget Period 2 Meeting Presentation, September 2020. *https://netl.doe.gov/projects/plp-download.aspx?id=10546&filename=Bench-Scale+Development+of+a+Transformative+Membrane+Process+for+Pre-Combustion+CO2+Capture.pptx.*

“Bench-Scale Development of a Transformative Membrane Process for Pre-Combustion CO2 Capture,” presented by Jay Kniep, Membrane Technology and Research, Inc., 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/J-Kniep-MTR-Precombustion-Membrane.pdf*.

“Bench-Scale Development of a Transformative Membrane Process for Pre-Combustion CO2 Capture,” presented by Jay Kniep, Membrane Technology and Research, Inc., 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/J-Kniep-MTR-Transformative-Membrane-Process.pdf*.

“Bench-Scale Development of a Transformative Membrane Process for Pre-Combustion CO2 Capture,” Project kickoff meeting presentation, December 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10543&filename=Bench-Scale+Development+of+a+Transformative+Membrane+Process+for+Pre-Combustion+CO2+Capture+.pdf.*

“Novel Polymer Membrane Process for Pre-combustion CO2 Capture from Coal-fired Syngas,” Final Report for DE-FE0001124, Membrane Technology and Research, Inc., December 2011. *https://www.osti.gov/servlets/purl/1080044.*