Critical Component/ Technology Gap in 21st Century Power Plant Gasification-Based Polygeneration: Advanced Ceramic Membranes/Modules for Ultra-Efficient H_2 Production/CO_2 Capture for Coal-Based Polygeneration Plants

primary project goal

Media and Process Technology Inc. (MPT), in collaboration with the University of Southern California, is advancing inorganic membrane technology for pre-combustion carbon dioxide (CO_2) capture from syngas in a gasification-based polygeneration plant. The primary project goal is two-fold: (1) to transition the current single-ended "candle filter" configuration of the ceramic membrane support to a dual-end (open both ends), full ceramic multiple-tube bundle configuration that will enable permeate sweep/purge capability; and (2) to develop the housing design for the dual-end bundles with emphasis on minimization of stresses associated with the membrane to housing seals and incorporation of multiple bundles into a pre-commercial-scale unit.

technical goals

- Demonstrate durability/robustness of the full ceramic multiple-tube membrane bundle and multi-bundle module at operating conditions of up to 400°C and at up to 800 pounds per square inch gauge (psig). Testing syngas flowrate is to be 10 standard cubic feet per minute (SCFM).
- Achieve the greater than 30% cost of electricity (COE) cost savings target for CO_2 capture relative to baseline capture costs.
- Develop, fabricate, and demonstrate a membrane module incorporating multiple membrane bundles in a series-parallel configuration with permeate purge capability.
- Conduct long term performance stability testing of multiple membrane bundles in the dual-end configuration.

technical content

Gasification-based polygeneration takes advantage of the primary gasification product, hydrogen (H_2), not only as fuel for power generation, but also a feedstock for chemicals production (specifically ammonia [NH_3] in this case) in conjunction with co-produced nitrogen (N_2). Polygeneration confers the ability to rapidly adjust

program area:
Point Source Carbon Capture

ending scale:
Small Pilot

application:
Pre-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Ceramic Membranes with Coal Syngas

participant:
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project number:
FE0031930

predecessor projects:
N/A

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University of Southern California

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percent complete:
40%

the plant output to market need, and enhances suitability of gasification-based processes in smaller-scale, distributed co-production facilities. Carbon capture from syngas is essential to yield H_2 for NH_3 synthesis or for decarbonized power generation in these cycles.

Conventionally, carbon capture is based on amine solvent-based capture (e.g., Selexol) requiring cooling of the syngas to low temperatures. However, plant efficiency can be greatly improved by H_2-CO_2 separations from warm syngas using alternative technology. MPT has developed an inorganic/ceramic membrane-based Dual-Stage Membrane Process (DSMP, DE-FE0013064), which eliminates the need for a high-cost conventional two-stage, Selexol-based CO_2 capture process. The membranes themselves consist of carbon molecular sieve, palladium, zeolites, or zeolitic imidazolate framework (ZIF) applied via thin active layer deposition on ceramic substrate. Membrane-based unit operation is recognized for its simplicity, modular configuration, and quick turn-up/turn-down, making it well suited for small-scale distributed production facilities. Figure 1 depicts the overall polygeneration cycle, in this case showing where the inorganic membrane-based warm/hot gas processing unit fits into the cycle for polygeneration of power and NH_3.

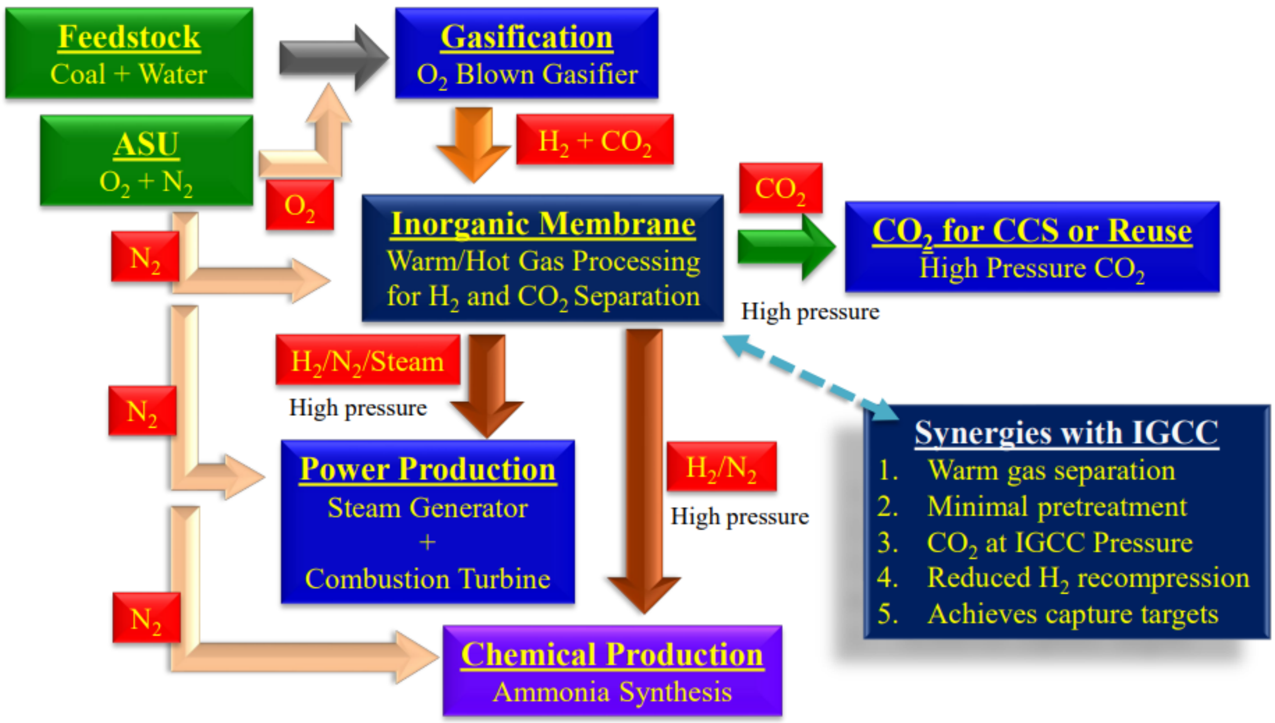

Figure 1: Inorganic membrane technology role in polygeneration cycle.

For the DSMP (and any membrane process in pre-combustion capture) to operate commercially, permeate sweep/purge with high-pressure N_2 (from the air separation unit [ASU]) and/or steam (from steam cycle of the power generating unit) is required. Unfortunately, this "permeate purge" capability is not currently available in large-format inorganic membranes rated for use at temperatures above approximately 200°C. MPT has prepared multiple-tube membrane bundles for high-temperature gas separation service (up to approximately 450°C; greater than 1,200 psig) that have been performance-demonstrated at the National Carbon Capture Center (NCCC). However, these bundles were fabricated in a "candle filter" configuration and are not permeate purgeable. Thus, the critical technology gap for the proposed process to be implemented commercially in polygeneration operation mode is the development of a purgeable inorganic membrane module. Such a module includes multiple dual-end open bundles in a series/parallel configuration, introducing additional technical challenges to be overcome such as inter-bundle sealing and shell-side feed flow distribution. Figure 2 depicts the concept for the permeate purgeable multiple bundle housing, bundles, and seals in question.

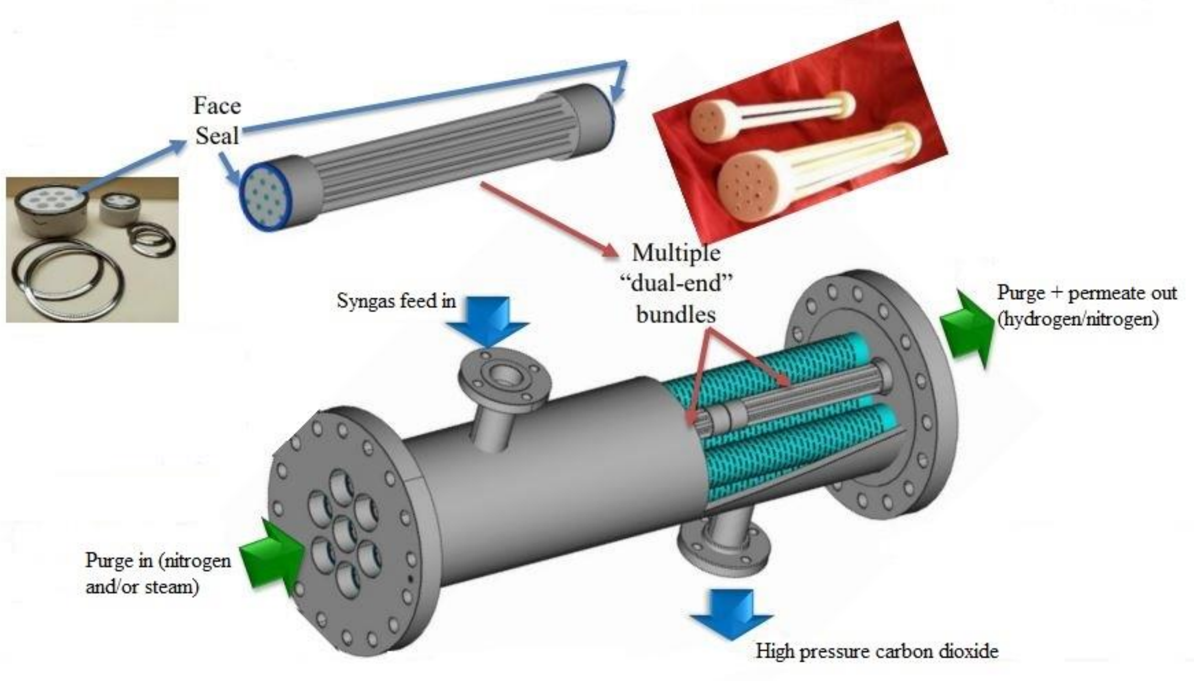

Figure 2: Permeate purgeable multiple bundle housing and seals.

Current technology development work consists of developing and fabricating a permeate purgeable multiple-tube bundle, with attention to the bundle housing with appropriate seals. Bundles sized up to 4-inch diameter and up to 38-inch length are ultimately targeted; a 1.5-, 2-, and 3-inch diameter, 38-inch dual-end bundle has been successfully fabricated.

A range of challenge tests to demonstrate bundle/housing stability are to be conducted, leading to long-term mechanical/performance stability testing (six to 12 months) at the target operating conditions. Computational fluid dynamics (CFD) modeling to simulate feed flow distribution is in process, with the idea of incorporating the CFD model into gas separation models, to use modeling to inform bundle/module configuration, and to verify mixed gas separation with model predictions. Figure 3 depicts some single-tube modeling results showing gas species concentrations.

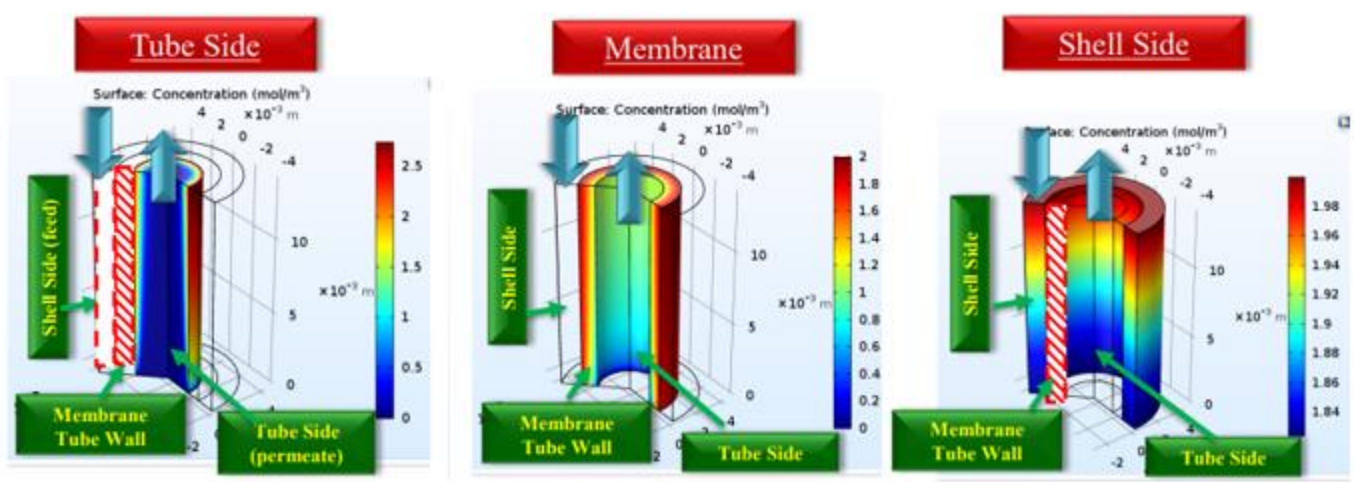

Figure 3: Single-tube membrane CFD gas concentration analysis.

Findings on performance of a commercially viable, purgeable module will inform a DSMP techno-economic analysis (TEA) for the polygeneration plant case. Both Carbon Molecular Sieve (CMS) and palladium alloy (Pd-Ag and Pd-Cu) have been previously performance-tested including multiple-tube membrane bundles at the NCCC. Membrane process parameters for these membranes (CMS Membrane #1 and Pd alloy Membrane #2) are summarized in Table 1A and 1B, respectively.

TABLE 1A: MEMBRANE PROCESS PARAMETERS

Materials Properties (Membrane #1)	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Carbon Molecular Sieve (CMS)	
Materials of Fabrication for Support Layer	—	Alumina	
Nominal Thickness of Selective Layer	µm	2 to 3	2 to 3
Membrane Geometry	—	Tubular	Tubular
Maximum Trans-Membrane Pressure	bar	>80	>80
Hours Tested without Significant Degradation	hour	>1,500 in coal gasifier syngas (NCCC)	>20,000
Manufacturing Cost for Membrane Material	$/m^2	2,400	<1,200
Membrane Performance (Membrane #1)			
Temperature	°C	250 to 300	250 to 300
H_2 Pressure Normalized Flux	GPU	350 to 750	350 to 750
H_2/H_2O Selectivity	—	2 to 4	2 to 4
H_2/CO_2 Selectivity	—	>50	>80
H_2/H_2S Selectivity	—	>100	>100
Sulfur Tolerance	ppm	>5,000	>5,000
Type of Measurement	—	Mixed gas and gasifier offgas (NCCC)	Same

TABLE 1B: MEMBRANE PROCESS PARAMETERS

Materials Properties (Membrane #2)	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Palladium Alloy	
Materials of Fabrication for Support Layer	—	Alumina	
Nominal Thickness of Selective Layer	µm	2 to 5	1 to 3
Membrane Geometry	—	Tubular	Tubular
Maximum Trans-Membrane Pressure	bar	>80	>80
Hours Tested without Significant Degradation	—	>35,000 hours in lab testing >150 in pre-treated coal gasifier syngas (NCCC)	>2,000 hours in laboratory simulated syngas
Manufacturing Cost for Membrane Material	$/m^2	9,500	<4,500
Membrane Performance (Membrane #2)			
Temperature	°C	350 to 450	350 to 450
H_2 Pressure Normalized Flux	GPU (at 20psig)	2,000 to >5,500	2,000 to >5,500
H_2/H_2O Selectivity	—	>3,000	>5,000
H_2/CO_2 Selectivity	—	>3,000	>5,000
H_2/H_2S Selectivity	—	NA (high)	NA (high)
Sulfur Tolerance	ppm	<50	<50
Type of Measurement	—	Mixed gas and pretreated gasifier offgas (NCCC)	Same
Proposed Module Design			
Flow Arrangement	—	Co-, counter-, or cross flow	
Packing Density	m^2/m^3	>450	
Shell-Side Fluid	—	Feed/retentate	

Syngas Gas Flowrate	kg/hr		—	
CO_2 Recovery, Purity, and Pressure	%/%/bar	>90	~95	>50
H_2 Recovery, Purity, and Pressure	%/%/bar	>98.8	>97	5 to 15
Pressure Drops Shell/Tube Side	bar		Unknown	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	Housing cost is estimated at ca. \$350 to \$700/m^2.		

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 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 co-current, 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 or retentate (syngas) stream.

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

Membrane Permeation Mechanism – CMS Membrane: Molecular Sieving; Pd Alloy Membrane: Solution-Diffusion.

Contaminant Resistance – CMS Membrane: Resistant to all coal/biomass gasifier off-gas contaminants; Pd Alloy Membrane: Sulfur species are a significant problem. Unknown for other gas phase contaminants.

Syngas Pretreatment Requirements – CMS Membrane: None except upstream particulate removal at >50µm.

Pd Alloy Membrane: Desulfurization required.

Membrane Replacement Requirements – Unknown; assume 10 years.

Waste Streams Generated – None.

Process Design Concept – See Figure 1.

Proposed Module Design – See Figure 2. Composition of gas entering the membrane subsystem is assumed to be:

Pressure	Temperature	Composition						
		vol%						ppmv
psig	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
800	550	27	6	<1	<1	41	25	500

TABLE 2: INDUSTRIAL PLANT CARBON CAPTURE / DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	33.2	21.5
Capital Expenditures	\$/tonne CO_2	644	644
Operating Expenditures	\$/tonne CO_2	26.3	26.3

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – This work has been developed using Case B5B of DOE/NETL Report 2015/1727 – "Cost and Performance Baseline for Fossil Energy Plants," Volume 1b Rev 2b, July 31, 2015, GEE IGCC with CO_2 Capture as the base case.

Scale of Validation of Technology Used in TEA – Testing was conducted at the NCCC with pilot scale multiple tube membrane bundles at gasifier syngas feed rates up to 5 scfm.

technology advantages

- Inorganic membranes have been demonstrated to be highly effective for and ideally suited to pre-combustion capture.
- Warm gas removal of CO_2, sulfur, and contaminants minimizes gas recompression demand and improves process efficiency.
- Potential for greater than 40% reduction in COE versus baseline amine solvent-based capture.
- DSMP modified polygeneration cycle is well suited to co-production of NH_3.

R&D challenges

- Permeate purge capability with nitrogen or steam is assumed in various technoeconomic analyses, but not yet available in practice.
- Multiple bundle housing design concerns and restrictions: minimizing stress between the ceramic membrane bundles and steel housing, and maintaining bundle interconnects that maintain axial compression.
- Multiple bundle feed flow maldistribution (shell side) resulting in poor mixed gas performance. CFD modeling is being developed for the configuration shown in Figure 2.

status

Dual-ended multiple-tube membrane bundle fabrication scale-up is in process with increasing diameters (1.5-inch and 2-inch diameter scales to 3 inches) being worked on, along with thermal cycling challenge testing. There has been a successful test of a prototype high-temperature testing rig to 400°C and 800 psig. CFD model development and testing continues.

available reports/technical papers/presentations

"Critical Component/Technology Gap in 21st Century Power Plant Gasification Based Poly-Generation: Advanced Ceramic Membranes/Modules for Ultra Efficient H_2 Production/CO_2 Capture for Coal-Based Poly-generation Plants," Project Budget Period 1 Review Meeting, March 11, 2022. *https://www.netl.doe.gov/projects/plp-download.aspx?id=13015&filename=Critical+Component%2fTechnology+Gap+in+21st+Century+Power+Plant+Gasification+Based+Poly-*

generation%3a+++Advanced+Ceramic+Membranes%2fModules+for+Ultra+Efficient++H2+Production%2fCO2+Capture+for+Coal-Based+Poly-generation+Plants.pdf.

"Critical Component/Technology Gap in 21st Century Power Plant Gasification Based Poly-Generation: Advanced Ceramic Membranes/Modules for Ultra Efficient H_2 Production/CO_2 Capture for Coal-Based Poly-generation Plants," Presented by Richard Ciora, Media and Process Technology, Inc., 2021 NETL Carbon Management Research Project Review Meeting, August 13, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Ciora.pdf.*

"Critical Component/Technology Gap in Coal FIRST Gasification Based Poly-generation: Advanced Ceramic Membranes/ Modules for Ultra Efficient H_2 Production/CO_2 Capture for Coal-Based Poly-generation Plants," Project Kickoff Meeting, November 5, 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11008&filename=Critical+Component%2fTechnology+Gap+in+Coal+FIRST++Gasification+Based+Poly-generation%3a+++Advanced+Ceramic+Membranes%2fModules+for+Ultra+Efficient++H2+Production%2fCO2+Capture+for+Coal-Based+Poly-generation+Plants.pdf.*