Robust and Energy Efficient Dual-Stage Membrane-Based Process for Enhanced Carbon Dioxide Recovery

primary project goals

The Media and Process Technology Inc. (MPT) project objective has been to develop a dual-stage membrane-based process (DSMP) for pre-combustion carbon dioxide (CO_2) capture in an Integrated Gasification Combined Cycle (IGCC) power plant. The process utilizes MPT hydrogen (H_2)-selective carbon molecular sieve (CMS) membranes, in conjunction with conventional water gas shift (WGS) reactors, in the first stage for enhanced production and bulk recovery of H_2. Following cold gas clean-up, a palladium alloy-based membrane is used in the second stage for efficient residual hydrogen recovery from the high-pressure CO_2 gas stream just prior to sequestration.

technical goals

- Characterize the performance of the proposed CMS and Pd-alloy membrane technologies for H_2-CO_2 separations from simulated coal and biomass derived syngas in laboratory scale testing.
- Verify the membrane performance under extreme pressure conditions to qualify the technology for pre-combustion capture.
- Demonstrate the performance stability of the CMS and Pd-alloy multiple tube membrane bundles in actual gasifier syngas in bench-scale testing at the National Carbon Capture Center (NCCC).
- Develop the mathematical model from the performance database obtained in lab and bench-scale work.
- Perform techno-economic assessment (TEA) and environment, health, and safety (EH&S) analysis for the process using the performance database and models developed under this project.

technical content

The technological approach utilizes MPT's commercial ceramic tubular ultrafilter shown in Figure 1 as a support for the high performance H_2 selective membranes. Ultrathin CMS and Pd-alloy layers are deposited to form composite membranes and then packaged into high packing density multiple tube membrane elements as illustrated. In this bundle configuration, the membranes can be operated at high temperatures (up to 500 °C) and pressures (up to at least 1,200 pounds per square inch gauge [psig]) to support warm syngas cleanup in pre-combustion CO_2 capture.

technology maturity:

Bench-Scale, Actual Syngas (equivalent to 0.01 MW_e)

project focus:

Two-Stage Membrane Separation: Carbon Molecular Sieve Membrane Reactor followed by Pd-Based Membrane

participant:

Media and Process Technology, Inc.

project number:

FE0013064

predecessor projects:

FC26-07NT43057

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partners:

Technip USA Corporation, University of Southern California

start date:

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percent complete:

100%

Figure 1: MPT ceramic ultrafiltration membranes as supports for high performance H_2 selective CMS and Pd-alloy membranes shown packaged into multiple tube membrane elements

MPT's Dual Stage Membrane Process (DSMP) is illustrated in Figure 2. In the process, the CMS and Pd-alloy membranes are used in distinctly different roles, taking advantage of their specific performance capabilities, to deliver high H_2 and CO_2 recovery from IGCC gasifier syngas. In the DSMP, the CMS membrane is deployed in a multiple step serial arrangement with the WGS reactors in two roles, specifically, (i) to recover the bulk H_2 from the gasifier off-gas and (ii) to enhance the equilibrium conversion in WGS reactors to improve net power output. The CMS membrane is operated at temperatures in the range of 250–300 °C and no syngas pretreatment is necessary, making them complementary to the WGS reactors in terms of operating conditions window and reactor performance enhancement.

In the 1st Stage CMS membrane section, only about 85 percent of the H_2 is recovered due to the "low" pressure (~800 psig) of the syngas and excessive carbon losses to the permeate at higher H_2 recovery levels. Hence, considerable H_2 remains that must be recovered to deliver adequate power output and to meet the cost of capture targets. For this purpose, a Pd-Ag alloy membrane is used in the 2nd stage of the process. Due to the well-known deficiencies of the Pd-based membrane, most specifically its vulnerability to sulfur poisoning and the resultant irreversible damage, it is deployed downstream of the CO_2 compressors. At this location in the process, the syngas has been processed through the Cold Gas Cleanup Unit (CGCU) to remove various contaminants (Hg, sulfur, tar, water, etc.) as required for storage; thus, potential membrane poisons are eliminated. Hence, the major limitation of the Pd membrane technology is avoided while the major benefit, specifically its ultra-high (potentially infinite) selectivity of H_2-to-CO_2, is brought to bear. With the addition of this 2nd stage, >99 percent of the produced H_2 is ultimately recovered.

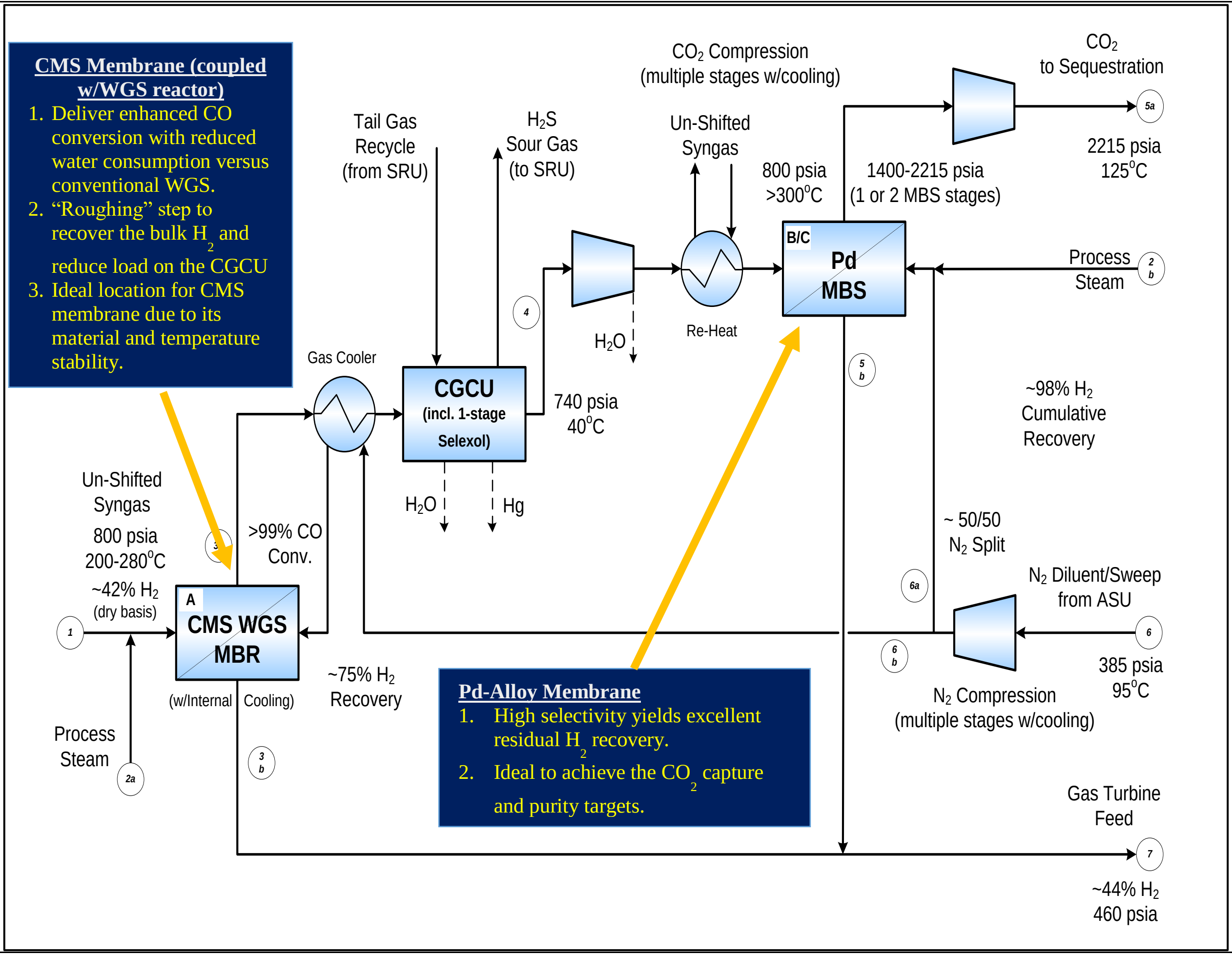

Figure 2: MPT Dual Stage Membrane Process for pre-combustion CO_2 capture

By replacing the dual-stage Selexol unit of the DOE baseline design with the proposed highly efficient and robust membrane technology, the DSMP achieves the DOE carbon capture targets, delivering 90 percent CO_2 capture at 94.5 percent purity, while producing higher net power output (+3 percent, 559 MW) at reduced cost of CO_2 captured (-14 percent, \$33.2/tonne) in comparison with the base case.

TABLE 1: MEMBRANE PROCESS PARAMETERS

<table>
<tr><th>Materials Properties</th><th>Units</th><th colspan="2">Current R&D Value</th><th colspan="2">Target R&D Value</th></tr>
<tr><td>Materials of Fabrication for Selective Layer</td><td>—</td><td colspan="4">carbon molecular sieve (CMS)</td></tr>
<tr><td>Materials of Fabrication for Support Layer</td><td>—</td><td colspan="4">alumina</td></tr>
<tr><td>Nominal Thickness of Selective Layer</td><td>µm</td><td colspan="2">2–3</td><td colspan="2">2–3</td></tr>
<tr><td>Membrane Geometry</td><td>—</td><td colspan="2">tubular</td><td colspan="2">tubular</td></tr>
<tr><td>Maximum Trans-Membrane Pressure</td><td>bar</td><td colspan="2">>82 bar</td><td colspan="2">>82 bar</td></tr>
<tr><td>Hours Tested without Significant Degradation</td><td>—</td><td colspan="2">>16,000 hours in lab,
>1,000 hours at NCCC</td><td colspan="2">—</td></tr>
<tr><td>Manufacturing Cost for Membrane Material</td><td>$/m²</td><td colspan="2"><1,200</td><td colspan="2"><750</td></tr>
<tr><th>Membrane Performance</th><th></th><th colspan="2"></th><th colspan="2"></th></tr>
<tr><td>Temperature</td><td>°C</td><td colspan="2">250–300</td><td colspan="2">250–300</td></tr>
<tr><td>H_2 Pressure Normalized Flux</td><td>GPU or equivalent</td><td colspan="2">500</td><td colspan="2">900</td></tr>
<tr><td>H_2/H_2O Selectivity</td><td>—</td><td colspan="2">2–4</td><td colspan="2">>3</td></tr>
<tr><td>H_2/CO_2 Selectivity</td><td>—</td><td colspan="2">35</td><td colspan="2">>50</td></tr>
<tr><td>H_2/H_2S Selectivity</td><td>—</td><td colspan="2">>100</td><td colspan="2">>100</td></tr>
<tr><td>Sulfur Tolerance</td><td>ppm</td><td colspan="2">>10,000</td><td colspan="2">>10,000</td></tr>
<tr><td>Type of Measurement</td><td>—</td><td colspan="2">mixed gas</td><td colspan="2">mixed gas</td></tr>
<tr><th>Proposed Module Design</th><th></th><th colspan="2"></th><th colspan="2"></th></tr>
<tr><td>Flow Arrangement</td><td>—</td><td colspan="4">co/counter-current or cross-flow</td></tr>
<tr><td>Packing Density</td><td>m²/m³</td><td colspan="4">>450</td></tr>
<tr><td>Shell-Side Fluid</td><td>—</td><td colspan="4">permeate</td></tr>
<tr><td>Syngas Gas Flowrate</td><td>kg/hr</td><td colspan="4">—</td></tr>
<tr><td>CO_2 Recovery, Purity, and Pressure</td><td>%/%/bar</td><td>90</td><td colspan="2">95</td><td>>60</td></tr>
<tr><td>H_2 Recovery, Purity, and Pressure</td><td>%/%/bar</td><td>.>80</td><td colspan="2">>90</td><td>Up to 20</td></tr>
<tr><td>Pressure Drops Shell/Tube Side</td><td>bar</td><td colspan="4">—</td></tr>
<tr><td>Estimated Module Cost of Manufacturing and Installation</td><td>$\frac{\$}{kg/hr}$</td><td colspan="4">1,500</td></tr>
</table>

TABLE 2: MEMBRANE PROCESS PARAMETERS

<table>
<tr><th>Materials Properties</th><th>Units</th><th colspan="2">Current R&D Value</th><th colspan="2">Target R&D Value</th></tr>
<tr><td>Materials of Fabrication for Selective Layer</td><td>—</td><td colspan="4">palladium-alloy</td></tr>
<tr><td>Materials of Fabrication for Support Layer</td><td>—</td><td colspan="4">alumina</td></tr>
<tr><td>Nominal Thickness of Selective Layer</td><td>µm</td><td colspan="2">2 to 5</td><td colspan="2">2 to 5</td></tr>
<tr><td>Membrane Geometry</td><td>—</td><td colspan="2">tubular</td><td colspan="2">tubular</td></tr>
<tr><td>Maximum Trans-Membrane Pressure</td><td>bar</td><td colspan="2">>82</td><td colspan="2">>82</td></tr>
<tr><td>Hours Tested without Significant Degradation</td><td>—</td><td colspan="2">>35,000 hours lab
150 hours at NCCC</td><td colspan="2">—</td></tr>
<tr><td>Manufacturing Cost for Membrane Material</td><td>$/m²</td><td colspan="2">1,800</td><td colspan="2"><1,000</td></tr>
<tr><th colspan="6">Membrane Performance</th></tr>
<tr><td>Temperature</td><td>°C</td><td colspan="2">250 to 400</td><td colspan="2">250 to 400</td></tr>
<tr><td>H_2 Pressure Normalized Flux</td><td>GPU or equivalent</td><td colspan="2">2,000 to >5,000</td><td colspan="2">1,000 to >5,000</td></tr>
<tr><td>H_2/H_2O Selectivity</td><td>—</td><td colspan="2">1,000 to >5,000</td><td colspan="2">1,000 to >5,000</td></tr>
<tr><td>H_2/CO_2 Selectivity</td><td>—</td><td colspan="2">1,000 to >5,000</td><td colspan="2">1,000 to >5,000</td></tr>
<tr><td>H_2/H_2S Selectivity</td><td>—</td><td colspan="2">N/A</td><td colspan="2">N/A</td></tr>
<tr><td>Sulfur Tolerance</td><td>ppm</td><td colspan="2"><10</td><td colspan="2"><10</td></tr>
<tr><td>Type of Measurement</td><td>—</td><td colspan="2">mixed gas.</td><td colspan="2">mixed gas</td></tr>
<tr><th colspan="6">Proposed Module Design</th></tr>
<tr><td>Flow Arrangement</td><td>—</td><td colspan="4">co- or counter-current</td></tr>
<tr><td>Packing Density</td><td>m²/m³</td><td colspan="4">450</td></tr>
<tr><td>Shell-Side Fluid</td><td>—</td><td colspan="4">feed/retentate</td></tr>
<tr><td>Syngas Gas Flowrate</td><td>kg/hr</td><td colspan="4"></td></tr>
<tr><td>CO_2 Recovery, Purity, and Pressure</td><td>%/%/bar</td><td>>99</td><td colspan="2">93 to 94</td><td>>1,000</td></tr>
<tr><td>H_2 Recovery, Purity, and Pressure</td><td>%/%/bar</td><td>>99</td><td colspan="2">>99</td><td>1.2</td></tr>
<tr><td>Pressure Drops Shell/Tube Side</td><td>bar</td><td colspan="4">N/A</td></tr>
<tr><td>Estimated Module Cost of Manufacturing and Installation</td><td>$\frac{\$}{\text{kg/hr}}$</td><td colspan="4">260</td></tr>
</table>

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; projected permeance and selectivities should be for mixture of gases found in pre-conditioned 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 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 (H_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 – CMS: molecular sieving. Pd-alloy: H_2 dissolution and permeation.

Contaminant Resistance –.CMS: stable in gasifier raw syngas testing conducted at NCCC. Pd-alloy: stable in gasifier syngas with the removal of sulfur and tar species.

Syngas Pretreatment Requirements – CMS: No syngas pretreatment required. Pd-alloy: sulfur and tar-like species removal required.

Membrane Replacement Requirements – Unknown but lifetimes of >16,000 hours for the CMS and >35,000 hours for the Pd-alloy membranes have been demonstrated with no apparent loss in performance.

Waste Streams Generated – None.

Process Design Concept – See Figure 2.

Proposed Module Integration –

Membrane Material	Pressure psia	Temperature °F	Composition vol%						Composition ppmv
			CO_2	CO	CH_4	N_2, Ar	H_2	H_2O	H_2S
CMS	800	440–540	27.4	5.5	<1	~1	40.8	24.5	>5,000
Pd-alloy	>1,000	480–570	87.8	0.5	<1	~3	8.4	0.17	<10

technology advantages

- The proposed DSMP matches specific capabilities and properties of the CMS (high material stability) and Pd-alloy (high H_2 selectivity) membranes to different separation requirements at separate stages in the process, enabling efficient gas separations performance.
- The proposed DSMP delivers significant cost savings in cost of CO_2 captured due to reduced capital and parasitic compression costs relative to conventional technology. Further, since significant H_2 recovery is achieved in the first stage, the required size and cost of the cold gas cleanup unit is significantly reduced due to the nearly 50 percent reduction in gas volume processed.
- The CMS membranes exhibited excellent performance stability in the presence of untreated gasifier syngas in testing conducted at the NCCC. This makes them highly suitable for first-stage service in pre-combustion H_2 and CO_2 gas production and separations.
- The Pd-alloy membranes were also demonstrated to be highly stable in second stage residual H_2 recovery following cold gas clean-up prior to CO_2 sequestration. The high selectivity of the Pd-alloy permitted excellent residual H_2 recovery to achieve CO_2 capture and purity targets at higher power output and lower cost of CO_2 captured.
- By limiting the Pd-alloy membrane to residual H_2 recovery and fabricating it as an ultra-thin film on a ceramic support, the Pd metal demand/consumption is significantly reduced over CO_2 capture schemes that rely solely on Pd membrane use in flat sheet geometry, thereby addressing both issues of the very high cost and limited availability of Pd metal.

R&D challenges

- Develop the multiple tube membrane bundle suitable for the high-pressure gas processing.
- Fabricate CMS and Pd-alloy membrane bundles for bench-scale testing at the NCCC.
- Demonstrate performance stability of the multiple tube membrane bundles in actual gasifier syngas at the NCCC.
- Develop the mathematical model and confirm applicability to the proposed process in live gas testing.

status

Multiple tube CMS and Pd-alloy membrane bundles were tested at NCCC, exposed to synthetic and actual coal gasifier syngas for hundreds of hours, and found to be stable in this environment. Given this and their stability at elevated temperature and pressure, the technology is expected to be viable for CO_2 capture in IGCC process scenarios. Techno-economic analysis of proposed DSMP in pre-combustion CO_2 capture for an IGCC power has been completed. The TEA shows that net power production is improved by 3 percent and the cost of CO_2 captured is reduced by 14 percent over the NETL base plant case (IGCC with dual stage Selexol CO_2 capture). An EH&S assessment has been completed for the proposed process, and based upon this assessment, there is no reason to believe that a production process and operation meeting the EH&S satisfaction cannot be established to commercialize the proposed technology and process.

available reports/technical papers/presentations

"*Robust and Energy Efficient Dual-Stage Membrane-Based Process for Enhanced CO_2 Recovery*," presented by Richard Ciora, Media and Process Technology, Inc., 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017.

"*Robust and Energy Efficient Dual-Stage Membrane-Based Process for Enhanced CO_2 Recovery*," presented by Richard Ciora, Media and Process Technology, Inc., 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016.

"*Robust and Energy Efficient Dual-Stage Membrane-Based Process for Enhanced CO_2 Recovery*," presented by Richard Ciora, Media and Process Technology, Inc., 2015 NETL CO_2 Capture Technology, Pittsburgh, PA, June 2015.

"*Robust and Energy Efficient Dual-Stage Membrane-Based Process for Enhanced CO_2 Recovery*," presented by Richard Ciora, Media and Process Technology, Inc., 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014.

"*Robust and Energy Efficient Dual-Stage Membrane-Based Process for Enhanced CO_2 Capture*," NETL Fact Sheet, February 2014.

"*Robust & Energy Efficient Dual-Stage Membrane-Based Process for Enhanced Carbon Dioxide Recovery*," Project Kickoff Meeting Presentation.

Doug Parsley, Richard J. Ciora, Jr., Diane L. Flowers, John Laukaitaus, Amy Chen, Paul K.T. Liu, Jiang Yu, Muhammad Sahimi, Alex Bonsu, Theodore T. Tsotsis, "Field evaluation of carbon molecular sieve membranes for the separation and purification of hydrogen from coal-and biomass-derived syngas", *J. Membrane Science*, *450, 81* (2014)

M. Abdollah, J. Yu, H.T. Hwang, P.K.T. Liu, R.J. Ciora Jr., M. Sahimi, T. Tsotsis, "Process Intensification in Hydrogen Production from Biomass Derived Syngas", Ind. Eng. Chem. Res., **49**, 10986, (2010).

Abdollahi, M., et al., "Hydrogen Production from Syngas, using a Catalytic Membrane Reactor," presented at the North American Membrane Society, Charleston, SC, June 2009.

Abdollahi, M., et al., "Integrated One-Box Process for Hydrogen Production from Syngas," presented at the 2009 Annual Meeting, American Institute of Chemical Engineers (AIChE), November 2009.