Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties

primary project goal

The goal of this State University of New York (SUNY)–Buffalo project is to develop scalable membrane technology by engineering polymers to achieve superior hydrogen (H_2)/carbon dioxide (CO_2) separation properties in readily fabricated and easily deployed membranes for capture of CO_2 from coal-derived syngas. Specifically, the approach is to derive carbon molecular sieve (CMS) membranes from polybenzimidazole (PBI) doped with polyprotic acids, which should offer high H_2 permeance and H_2/CO_2 selectivity while retaining robust chemical stability at elevated operating temperature.

technical goals

- Develop CMS hollow fiber membranes (HFMs) having a H_2 permeance of 1,000 gas permeation units (GPU) and an H_2/CO_2 selectivity of 40 at 200–300°C.
- Fabricate small membrane modules and demonstrate membrane performance and durability via testing of the modules under simulated syngas flow at 0.01 kilowatt-electric (kWe) equivalency for 120 hours.
- Characterize a CMS membrane-based system able to capture 90% CO_2 from coal-derived syngas with 95% CO_2 purity at a cost of electricity 30% less than baseline capture approaches (Selexol) in the context of an integrated gasification combined cycle (IGCC) plant scenario.

technical content

Conventional methods for pre-combustion carbon capture consist mainly of solvent-based processes such as Selexol and Rectisol. Although enabling high levels of capture at high gas purity, these processes have high capital and operating costs and result in severe energy penalties. Membrane-based carbon capture is of continued interest as an alternative, given its potential advantages in simplicity, lower costs, and potential for large savings in energy use. Among membranes for separation of CO_2 from syngas, inorganic membranes such as palladium alloys, ceramics, metal-organic frameworks (MOFs), and graphene oxide have been evaluated, given their excellent H_2/CO_2 separation properties. However, they are faced with challenges in the cost and reliability, scale-up of membrane production, and module fabrication. In contrast, polymer-based membranes are much easier to implement than inorganic membranes, provided that the membrane materials demonstrate suitable separation properties. Production scale-up and module fabrication using polymeric membranes have been widely practiced, creating a substantial engineering knowledge base across

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Pre-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Carbon Molecular Sieve Hollow Fiber Membranes With Coal Syngas

participant:
State University of New York – Buffalo

project number:
FE0031636

predecessor projects:
N/A

NETL project manager:
Krista Hill
krista.hill@netl.doe.gov

principal investigator:
Haiqing Lin
State University of New York–Buffalo
haiqingl@buffalo.edu

partners:
Los Alamos National Laboratory; Trimeric Corporation

start date:
10.01.2018

percent complete:
95%

the polymer membrane industry. Building on this foundation, this work targeted development of scalable membranes by engineering polymers to achieve superior H_2/CO_2 separation properties.

Most work in H_2/CO_2 gas separations by polymeric membrane materials relies solely on strong size-sieving derived from the rigid polymer chains. Polymers available commercially in this class include examples like poly(p-phenylene oxide) (PPO), Matrimid, poly(bisphenol-A sulfone) (PSF), and cellulose acetate (CA). However, the commercially available polymers have low H_2 diffusivity and permeability, are limited by the permeability/selectivity trade-off, and are well below the Robeson upper bound, as illustrated in Figure 1.

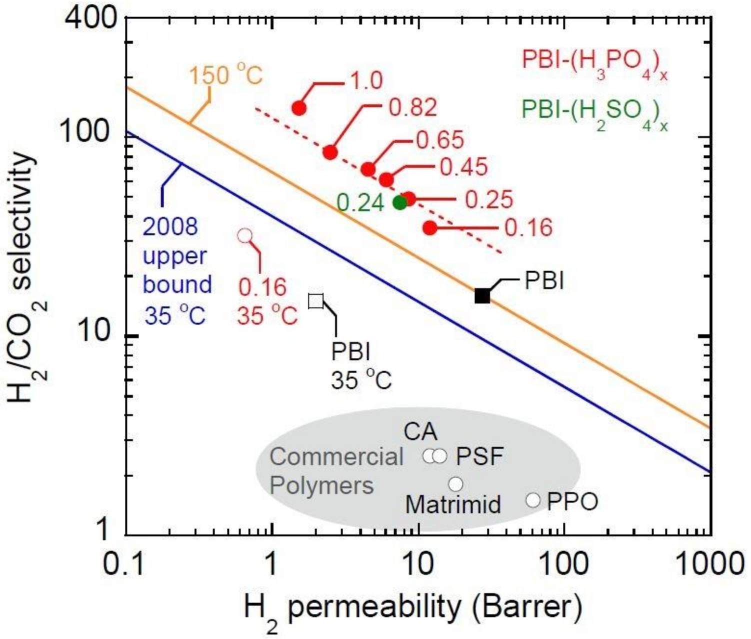

Figure 1: Pure-gas H_2/CO_2 separation performance of $PBI-(H_3PO_4)_X$ (x = 0.16-1.0) and $PBI-(H_2SO_4)_{0.24}$ at 150°C versus Robeson's upper bound at 35°C and 150°C.

The SUNY team has demonstrated considerable improvement in polymer membrane performance by doping the polymer PBI with polyprotic acids such as phosphoric acid (H_3PO_4) and sulfuric acid (H_2SO_4) to improve the size-sieving ability and H_2/CO_2 separation properties at 120–180°C. As shown in the upper part of Figure 1, increasing the H_3PO_4 doping level (defined as the molar ratio of H_3PO_4 to the PBI repeating units) decreases the pure-gas permeability and drastically increases the H_2/CO_2 selectivity at 150°C. For example, plain PBI shows an H_2/CO_2 selectivity of 16, while $PBI-(H_3PO_4)_{1.0}$ exhibits a remarkable selectivity of 140, which is much higher than that of any previously studied polymers. Phosphoric acid can strongly interact with multi-PBI chains via proton transfer from the acid to imidazole rings of PBI and hydrogen bonding, and thus it crosslinks the PBI. In comparison, a monoprotic acid such as hydrogen chloride (HCl) does not crosslink the PBI chains and has minimal effect on H_2/CO_2 separation properties.

SUNY's approach was to start with the already strongly size-sieving polymers (i.e., PBI doped with polyprotic acids [PPA]), and then carbonize them (by heating/pyrolysis at 500–800°C in inert nitrogen [N_2] for at least an hour) to increase both permeability and selectivity into a range suitable for commercial deployment. This approach is diagrammed in Figure 2, showing PBI being doped with the PPA pyrophosphoric acid, and then carbonized by pyrolysis. Carbonizing the acid-doped PBI results in CMS in which microcavities form, tending to increase gas permeability, and ultra-microporous necks increasing size-sieving ability.

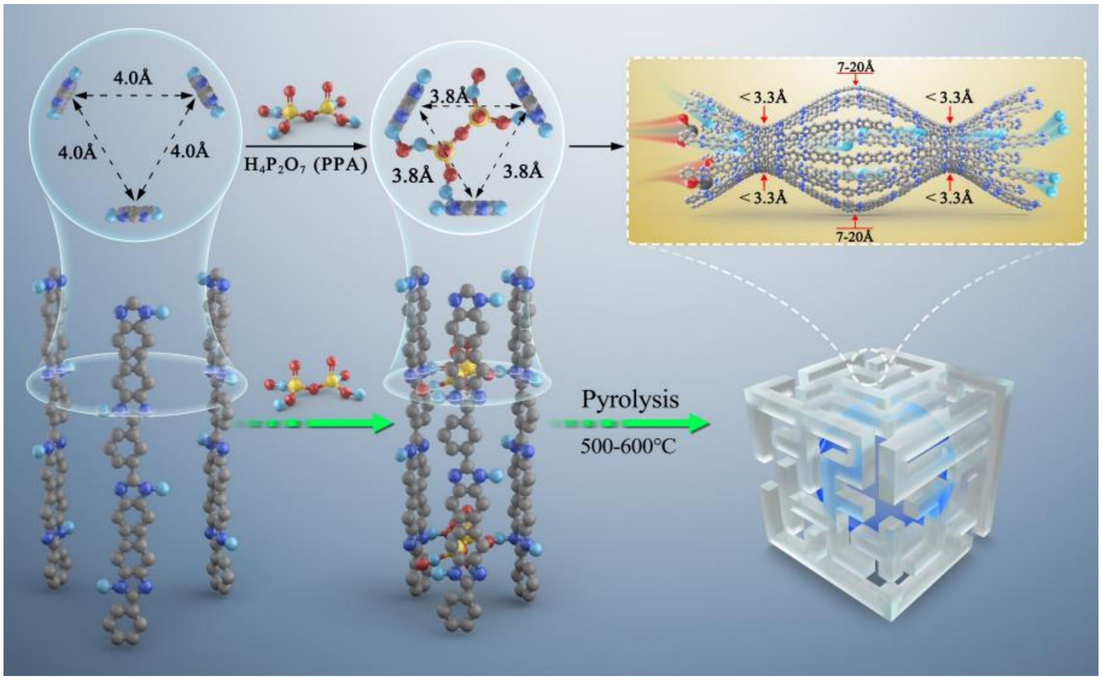

Figure 2: Steps to CMS membranes derived from PBI doped with polyprotic acids.

In past work, CMS membranes were made by carbonizing plain PBI. The pyrolysis increases the porosity and generates graphite-like structure. As shown in Figure 3 in blue, the carbonization of PBI substantially increases H_2 permeability while retaining or slightly increasing H_2/CO_2 selectivity at 100°C. All CMS samples have exhibited H_2/CO_2 separation properties above the upper bound. For example, pure PBI exhibits an H_2 permeability of 12 Barrer and an H_2/CO_2 selectivity of 14 at 100°C, while the CMS prepared by pyrolysis of PBI at 800°C shows an H_2 permeability of 670 Barrer (which is 50 times higher than pure PBI) and an H_2/CO_2 selectivity of 18 at 100°C.

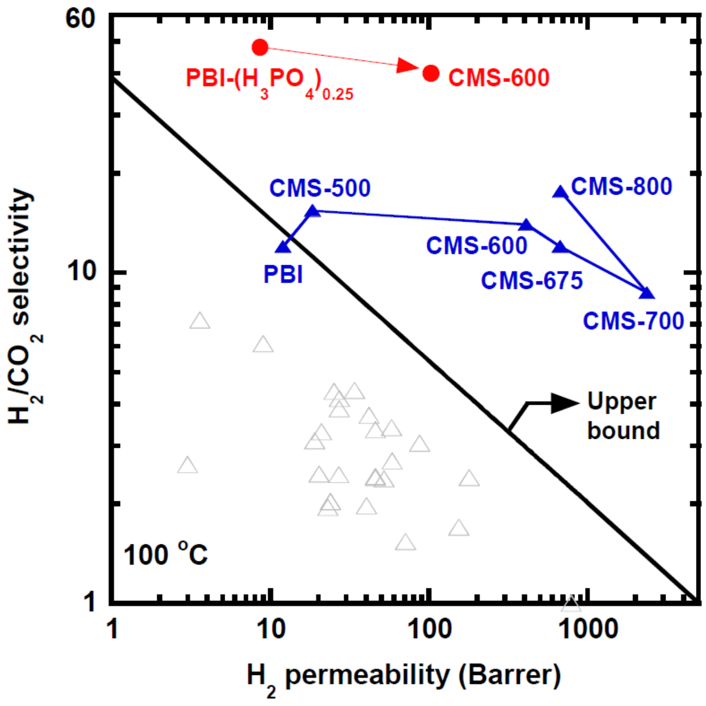

Figure 3: Improvement in membrane performance upon carbonization to CMS.

The SUNY team hypothesized that the CMS membranes would be able to meet targeted separation properties (H_2 permeance of 1,000 GPU and H_2/CO_2 selectivity of 40) if the starting polymers were PBI doped with polyprotic acids with strong size-sieving ability. For example, PBI-(H_3PO_4)$_{0.25}$ exhibits an H_2 permeability of 8.6 Barrer and an H_2/CO_2 selectivity of 48 at 150°C. The pyrolysis at 600°C increases the permeability to 100 Barrer while retaining an H_2/CO_2 selectivity of 40 at 100°C, as shown in red in Figure 3. During the pyrolysis, the H_3PO_4 gradually decomposes to polyphosphoric acid ($(HPO_3)_n$), retaining the rigid chains and strong molecular size-sieving ability.

Results of optimization of the acid type, composition, and pyrolysis temperature are depicted in Figure 4. The left side depicts results of doping with phosphoric acid at different proportions, while the right side shows results of doping with pyrophosphoric acid at different proportions, and before and after carbonization (respectively blue and red). A pyrolysis temperature of 600°C was found to be optimal. SUNY was able to achieve H_2 permeability of 200 Barrer with an H_2/CO_2 selectivity of 40 for pyrophosphic acid-doped, 600°C pyrolized PBI-PPA_x at x values of about 0.25.

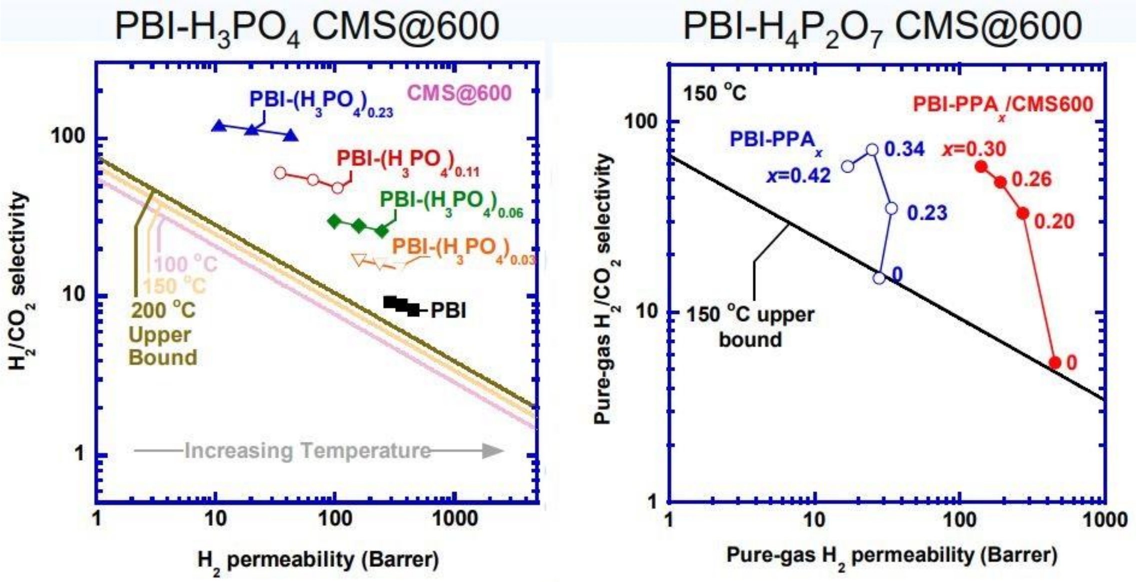

Figure 4: Improvement in membrane performance upon carbonization to CMS.

With this degree of permeability, HFMs with a selective layer thickness of 0.2 µm will achieve an H_2 permeance of 1,000 GPU and an H_2/CO_2 selectivity of 40. Los Alamos National Laboratory (LANL) has successfully fabricated nearly defect-free PBI HFMs with a 0.2 µm selective layer. Figure 5 shows images of (a) a base PBI HFM and (a') carbonized hollow fiber. This illustrates that the carbonized fiber retains the porous support morphology of the starting fiber.

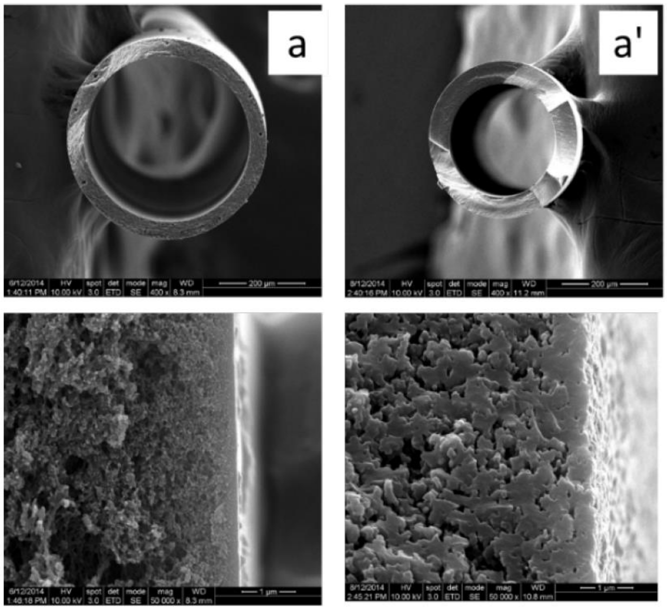

Figure 5: Scanning electron microscopy (SEM) images of PBI hollow fibers, before (left) and after (right) carbonization.

CMS membranes are intended for incorporation in hollow fiber modules for deployment in gas separation systems. LANL used the hollow fiber spinning system depicted in Figure 6 to fabricate the hollow fibers. A custom micro-machined spinneret forms the fiber. The steps resulting in CMS carbon fibers are also diagrammed.

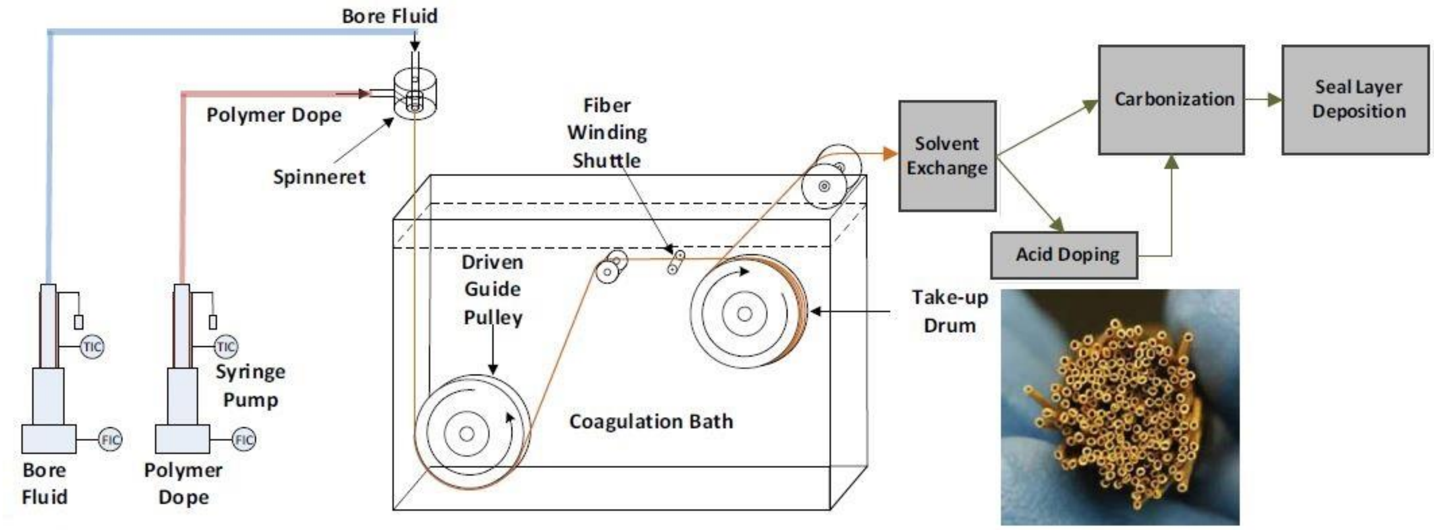

Figure 6: LANL lab-scale continuous hollow fiber spinning system.

SUNY manipulated the PBI-CMS HFM fabrication process to optimize HFM H_2/CO_2 separation performance. Figure 7a shows the H_2 permeance and H_2/CO_2 selectivity for a series of PBI-CMS HFMs fabricated under varied conditions. The project goal of 1,000 GPU H_2 permeance and H_2/CO_2 selectivity of 40 was definitively attained along the measured points under gas permeation testing at 250°C. Figure 7b shows the influence of temperature on the H_2/CO_2 separation performance of asymmetric PBI-CMS HFMs. The ideal H_2, CO_2, and N_2 permeance increases as the temperature increases from 150 to 300°C. The highest H_2 permeance of 1,090 GPU and H_2/CO_2 selectivity of 57 was measured at 300°C, which substantially exceeds the project goal.

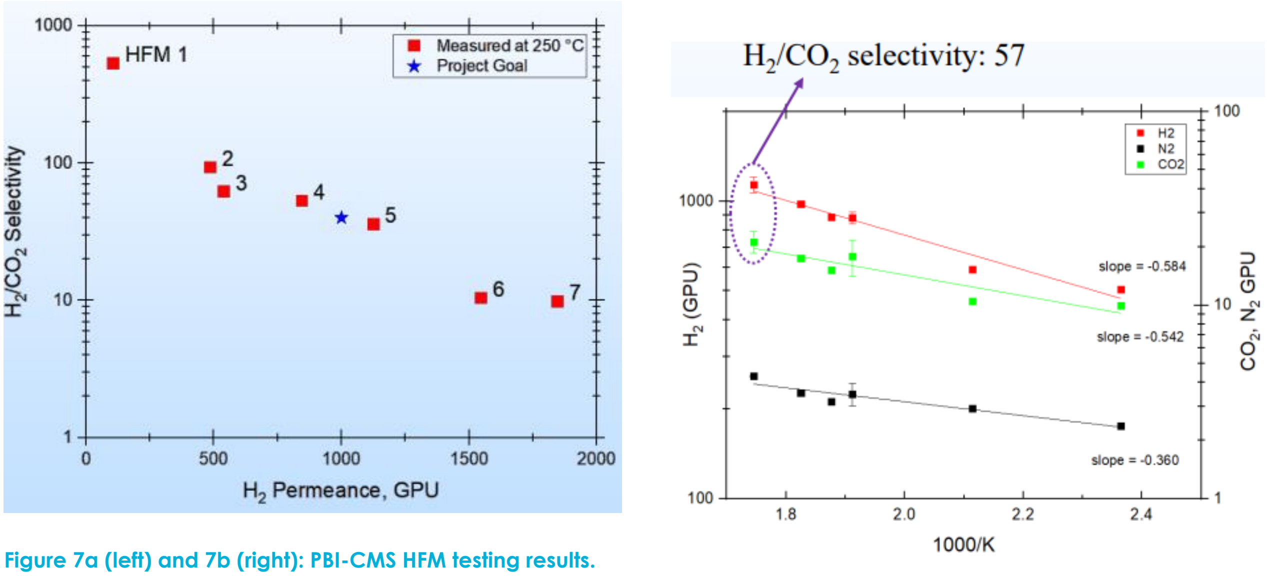

Figure 7a (left) and 7b (right): PBI-CMS HFM testing results.

Process implementation of CMS membrane modules would follow the basic flow diagram shown in Figure 8. Shifted syngas (1) containing mostly H_2 and CO_2 passes through membrane modules. Hydrogen selectively permeates and is swept away by N_2 (3), which is available in large quantities from the air separation unit producing oxygen for coal gasification (not shown on this figure). The H_2 and N_2 mixture comprises fuel gas (4) to be combusted in the power turbine. Retentate from the membrane modules is conditioned, dewatered, and compressed/pumped into liquid CO_2 for storage or use (2). With the CMS membranes able to withstand increased operating temperature of 200–300°C (as opposed to more conventional limit of 150°C), there is reduced cost of cooling syngas upstream of the membrane separation step, while improved permeability and selectivity afforded by the PBI-CMS HFMs reduces CO_2 processing costs downstream. These benefits combine to offer better economics for CO_2 capture than conventional approaches.

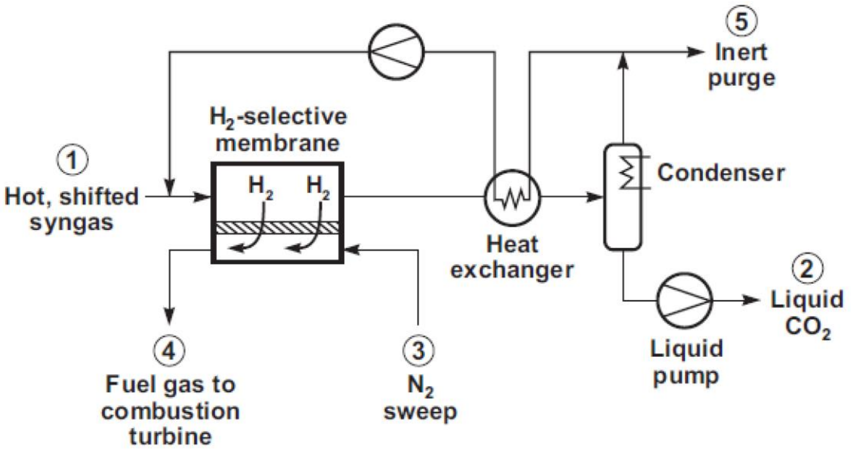

Figure 8: Membrane process integration in process cycle.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value *	Target R&D Value
Materials of Fabrication for Selective Layer	—	carbonized acid-doped PBI	carbonized acid-doped PBI
Materials of Fabrication for Support Layer	—	plain PBI	plain PBI
Nominal Thickness of Selective Layer	µm	0.2	0.2
Membrane Geometry	—	hollow fiber	hollow fiber
Maximum Trans-Membrane Pressure	bar	20	50
Hours Tested without Significant Degradation	h	120	120
Manufacturing Cost for Membrane Material	$\$/\text{m}^2$	20	20
Membrane Performance			
Temperature	°C	150	200-300
CO_2 Pressure Normalized Flux	GPU or equivalent	200	1,000
CO_2/H_2O Selectivity	—	0.5	0.5
CO_2/H_2 Selectivity	—	0.025	0.017
CO_2/H_2S Selectivity	—	2	2
Sulfur Tolerance	ppm	20	20
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design			
Flow Arrangement	—	Countercurrent	
Packing Density	m^2/m^3	~1,000	
Shell-Side Fluid	—	Permeate, CO_2-rich flow	
Syngas Gas Flowrate	kg/hr	~960,000	
CO_2 Recovery, Purity, and Pressure	%/%/bar	94.3 43.6 50.4	
H_2 Recovery, Purity, and Pressure	%/%/bar	72.8 41.9 32	
Pressure Drops Shell/Tube Side	bar	1/1	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	~4.0	

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 – Physical solution-diffusion.

Contaminant Resistance – Membranes are resistant to chemicals in the syngas.

Syngas Pretreatment Requirements – Removal of particles.

Membrane Replacement Requirements – Module lifetime is three to five years.

Waste Streams Generated – Water vapor will permeate with H_2, and the water stream will be produced after the H_2 combustion.

Proposed Module Design – See Figure 8. The pressure, temperature, and composition of the gas entering the membrane module are as follows:

Pressure	Temperature	Composition						
psia	°F	vol%						ppmv
		CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
756	432	30.8	0.6	0.76	0.44	43.7	23.3	4700

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	43.01	—
Cost of Carbon Avoided	\$/tonne CO_2	60.74	—
Capital Expenditures	\$/MWhr	60.9[1]	60.9
Operating Expenditures	\$/MWhr	25.5/52.5[2]	52.5
Cost of Electricity	\$/MWhr	113.5/121.3[3]	—

[1] Capital Cost Factor*Total Overnight Capital/MWh-net

[2] without fuel / with fuel

[3] without transportation, storage and monitoring costs / with transportation, storage and monitoring costs

Definitions:

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

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The cost of Carbon Captured and Carbon Avoided in Table 2 are based on the supercritical, pulverized coal reference plant Case B12A, found in the "Cost and Performance Baseline for Fossil Energy Plants Volume 1a: Bituminous Coal (PC) and Natural Gas to Electricity Revision 3" report (https://www.netl.doe.gov/energy-analysis/details?id=729). The Cost of Carbon Captured excludes the costs for transportation, storage, and monitoring. The Cost of Carbon Avoided includes the costs for transportation storage, and monitoring.

The costs for the current R&D case are based on Case B5B, found in the "Cost and Performance Baseline for Fossil Energy Plants Volume 1b: Bituminous Coal (IGCC) to Electricity Revision 2b – Year Dollar Update" report (https://www.netl.doe.gov/energy-analysis/details?id=1033).

Costs for the current R&D case and reference cases were adjusted to a cost basis of June 2011 US Dollars. Costs reported in Table 2 are in June 2011 US Dollars.

Scale of Validation of Technology Used in TEA – Laboratory scale experiments were conducted to assess the membrane technology performance. The TEA is a conceptual study on a full-scale power plant using the laboratory-measured performance metrics.

technology advantages

- The capability of CMS membranes with high permeance and selectivity to operate at high temperature eliminates the need for syngas cooling and avoids water vapor loss, which improves energy and cost efficiency of the carbon capture process.
- The simplicity of the membrane structure lowers its manufacturing cost.
- A membrane system does not contain moving parts or involve chemical reactions, conferring some operation and maintenance (O&M) advantages.
- The membrane material has a high tolerance to acid gases and is inert to all primary syngas species.
- Membrane capture systems (particularly those based on HFM modules) have compact footprint.

R&D challenges

- Assuring polymer performance and properties.
- Feed and permeate side pressure drops may lead to excessive energy losses.
- Cost reductions for the membrane module materials will be needed if the technology is to become economically viable.
- Durability and gas integrity of membrane modules (gas seals, fouling).
- Scale-up and integration issues (and operational complications from multiple vacuum pumps and valves and complicated ductwork in multiple flow banks) likely given the large number of membranes needed to service a 550-megawatt-electric (MWe) plant.

status

Many project activities are complete. However, evaluation of PBI-CMS HFMs in wet simulated syngas as a function of operating conditions and feed gas composition, study of membrane reactor-based WGS reaction, and techno-economic analysis (TEA) of the capture system in IGCC plant context continue.

available reports/technical papers/presentations

"Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties," presented by Haiqing Lin and Leiqing Hu, University at

Buffalo, 2021 NETL Carbon Management Research Project Review Meeting, August 16, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Lin.pdf*

"Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties," BP1 Project Review Meeting, March 27, 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10574&filename=+Development+of+Carbon+Molecular+Sieves+Hollow+Fiber+Membranes+Based+on+Polybenzimidazole+Doped+with+Polyprotic+Acids+with+Superior+H2%2fCO2+Separation+Properties.pdf*

"Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties," presentation by Haiqing Lin, SUNY Buffalo, 2019 NETL CCUS Integrated Project Review Meeting. Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/H-Lin-UB-SUNY-Carbon-Hollow-Fiber.pdf*

"Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties," project kickoff meeting presentation, November 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10570&filename=Development+of+Carbon+Molecular+Sieves+Hollow+Fiber+Membranes+Based+on+Polybenzimidazole+Doped+with+Polyprotic+Acids+with+Superior+H2%2fCO2+Separation+Properties.pdf*

"Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties," presented by Haiqing Lin, State University of New York (SUNY) at Buffalo, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA. August 2018. *https://netl.doe.gov/sites/default/files/netl-file/H-Lin-SUNY-Carbon-Molecular-Sieves.pdf*

"Unexpectedly Strong Size-Sieving Ability in Carbonized Polybenzimidazole for Membrane H_2/CO_2 Separation," M. Omidvar, H. Nguyen, L. Huang, C.M. Doherty, A.J. Hill, C.M. Stafford, X. Feng, M.T. Swihart, and H. Lin, ACS Appl. Mater. & Interfaces, 11 (50), 47365-47372 (2019).

"Ultraselective Carbon Molecular Sieve Membranes with Unprecedented Performance for H_2/CO_2 Separation for Pre-combustion CO_2 Capture," presented by Hien Nguyen, State University of New York (SUNY) at Buffalo, 2019 Materials Research Society, Boston, MA. December 2019.