# Development and Testing of a High-Temperature PBI Hollow-Fiber Membrane Technology for Pre-Combustion $CO_2$ Capture

## primary project goal

SRI's overall goal is to develop a technically and economically viable carbon dioxide ($CO_2$) capture system based on a high-temperature polybenzimidazole (PBI) polymer hollow-fiber membrane separation technology. This is intended for deployment at elevated temperatures to separate hydrogen ($H_2$) and $CO_2$ in shifted syngas, enabling pre-combustion carbon capture in integrated gasification combined cycle (IGCC) power plants. The project goals are to extend previous work on PBI hollow-fiber membranes to further evaluate second-generation (Gen-2) fibers having improved selectivity through the development and field testing of Gen-2 PBI-based membrane modules on actual coal-derived syngas from an oxygen-blown gasifier.

## technical goals

- Produce at least 100 kilometers of Gen-2 fibers that provide an $H_2/CO_2$ selectivity of about 40 and $H_2$ permeance of 80–120 gas permeation units (GPU) at greater than 150°C at a 150 pounds per square inch (psi) pressure differential.
- Modify the existing 50-killowatt-thermal (kWth) bench-scale test skid (fabricated and used in FE0012965) with Gen-2 hollow-fiber modules of 4- to 6-inch diameter, and complete bench-skid acceptance testing for 50 hours achieving $H_2/CO_2$ selectivity greater than 35.
- Perform bench-scale testing at temperatures ≈225°C and up to a pressure of 30 bar under various operating conditions, including long-term steady-state conditions using actual coal-derived syngas (throughput equivalent to 50 kWth) from the entrained flow oxygen-fed gasifier at the University of Kentucky's Center for Applied Energy Research (CAER).
- Prepare techno-economic analysis (TEA) based on Gen-2 bench-scale testing results to re-evaluate technology performance to achieve DOE's pre-combustion capture targets.

## technical content

SRI's PBI membrane-based technology is being developed for high-temperature pre-combustion separation of $H_2$ from shifted syngas, leaving a high-concentration, high-pressure $CO_2$-rich stream in the retentate and yielding a high $H_2$-content permeate stream. SRI's membranes consist of asymmetric hollow-fiber PBI (molecular structure of the polymer shown in Figure 1), which is chemically and thermally stable at temperatures up to 300°C and pressures up to 55 atmospheres (atm; 800 pounds per square inch gauge [psig]). PBI membranes are also sulfur tolerant. These characteristics permit the use of the PBI membrane for $CO_2$ capture downstream of a sour water-gas shift (WGS) reactor without

**program area:**
Point Source Carbon Capture

**ending scale:**
Bench Scale

**application:**
Pre-Combustion Power Generation PSC

**key technology:**
Membranes

**project focus:**
PBI Polymer Membrane for $CO_2$ Capture from Coal Syngas

**participant:**
SRI International

**project number:**
FE0031633

**predecessor projects:**
FC26-07NT43090; FE0012965

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**partners:**
Enerfex Inc.; PBI Performance Products; University of Kentucky Research Foundation

**start date:**
10.01.2018

**percent complete:**
95%

requiring further gas cooling before the PBI membrane, significantly increasing plant efficiency. In addition, the $CO_2$ is recovered at high pressure, decreasing $CO_2$ compression requirements.

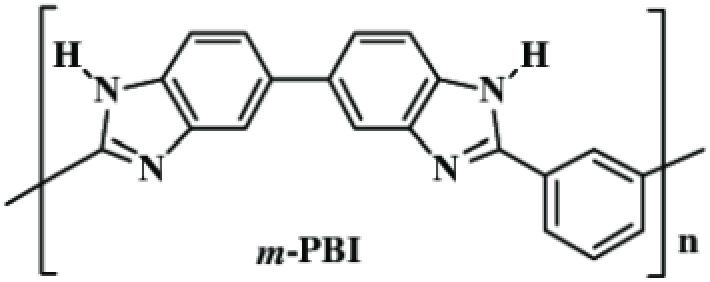



Figure 1: m-polybenzimidazole molecular structure.

Single-bore PBI-based hollow fibers have been shown to be highly durable, with near-constant levels of permeability and selectivity over the course of 330 days while in the presence of $H_2$, carbon monoxide (CO), methane ($CH_4$), nitrogen ($N_2$), $CO_2$, and hydrogen sulfide ($H_2S$) at 250°C. Therefore, PBI fiber modules can be successfully used in pre-combustion $CO_2$ capture applications.

PBI-based hollow fibers, as seen in various magnified views in Figure 2, offer a considerable advantage over coated stainless-steel tubes. They require as much as 24 times less membrane surface area and 305 times less membrane volume when using a 0.1–0.5 micrometer separation layer (the dense layer). Ease of large-scale manufacturability, high packing density, and the cost are notable advantages of hollow-fiber membrane systems.

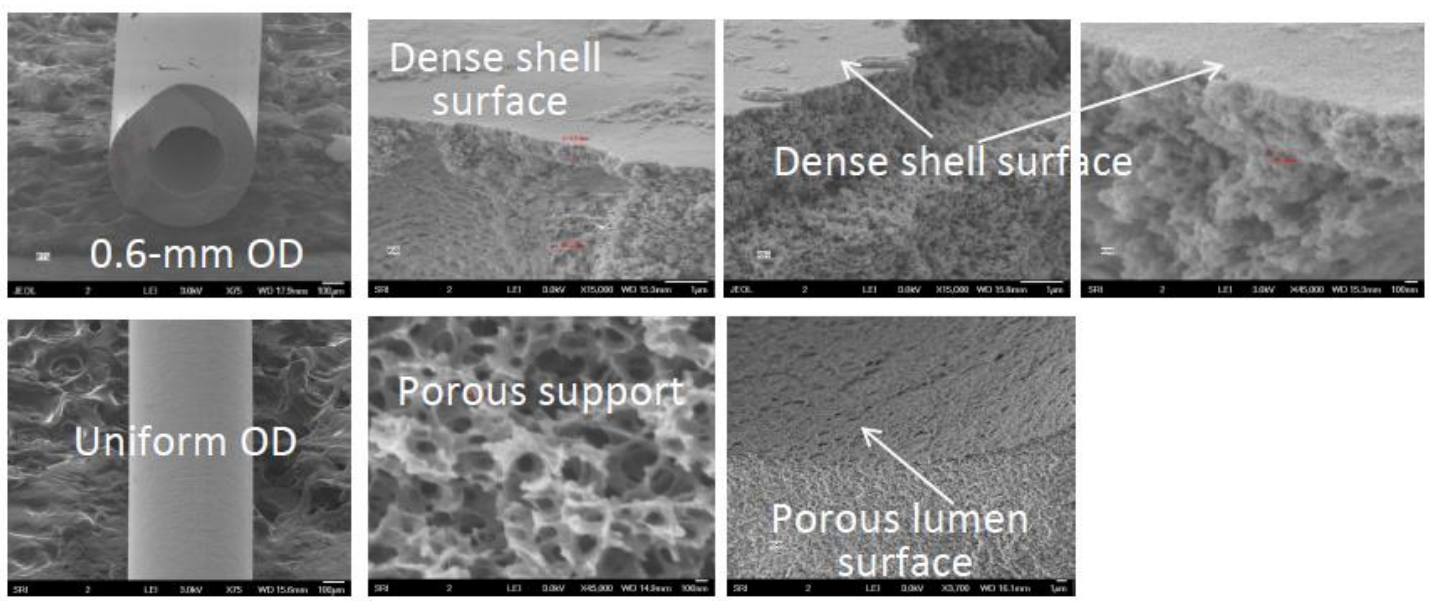



Figure 2: PBI hollow-fiber membranes and details of physical structure.

### Fiber Fabrication and Modules

Hollow-fiber membrane fabrication is accomplished in a spinning line as depicted in Figure 3. An important part of technology maturation involves improvements in fiber spinning technology enabling an improved and robust spinning process that can be transferred to industry. Improvements in the spinning line have enabled use of multiple coagulation solvents, increased productivity (one-gallon reservoir size), process monitoring and data collection, precise flow controls and draw ratios, optimization of fiber diameter, and optimization of the fiber dense-layer thickness.

SRI has been improving its developed protocols to enable spinning dense layer hollow-fiber membranes that are less than 0.3-µm in thickness, with outer diameters (ODs) of 450–650 µm. Figure 2 includes photographs of a hollow-fiber membrane well within this range, with around 0.1-µm dense layer fibers having approximately 600-µm OD. Optimization of OD and dense layer has been supported through testing of more than 100 fiber bundles (1-inch). Fabrication of the Gen-1 hollow-fiber membrane with a very thin, dense layer (less than 0.3 µm) in kilometer lengths has been accomplished with very good reproducibility. In previous work, more than 100 kilometers of Gen-1 fibers have been spun for both Generon and SRI modules (4-inch diameter size fiber modules). In the latest work, more than 10 kilometers of the improved performance Gen-2 fibers have been produced so far for deployment in the new modules to be used in upcoming testing at the University of Kentucky's CAER. Performance parameters for the Gen-2 membranes are shown in Table 1.

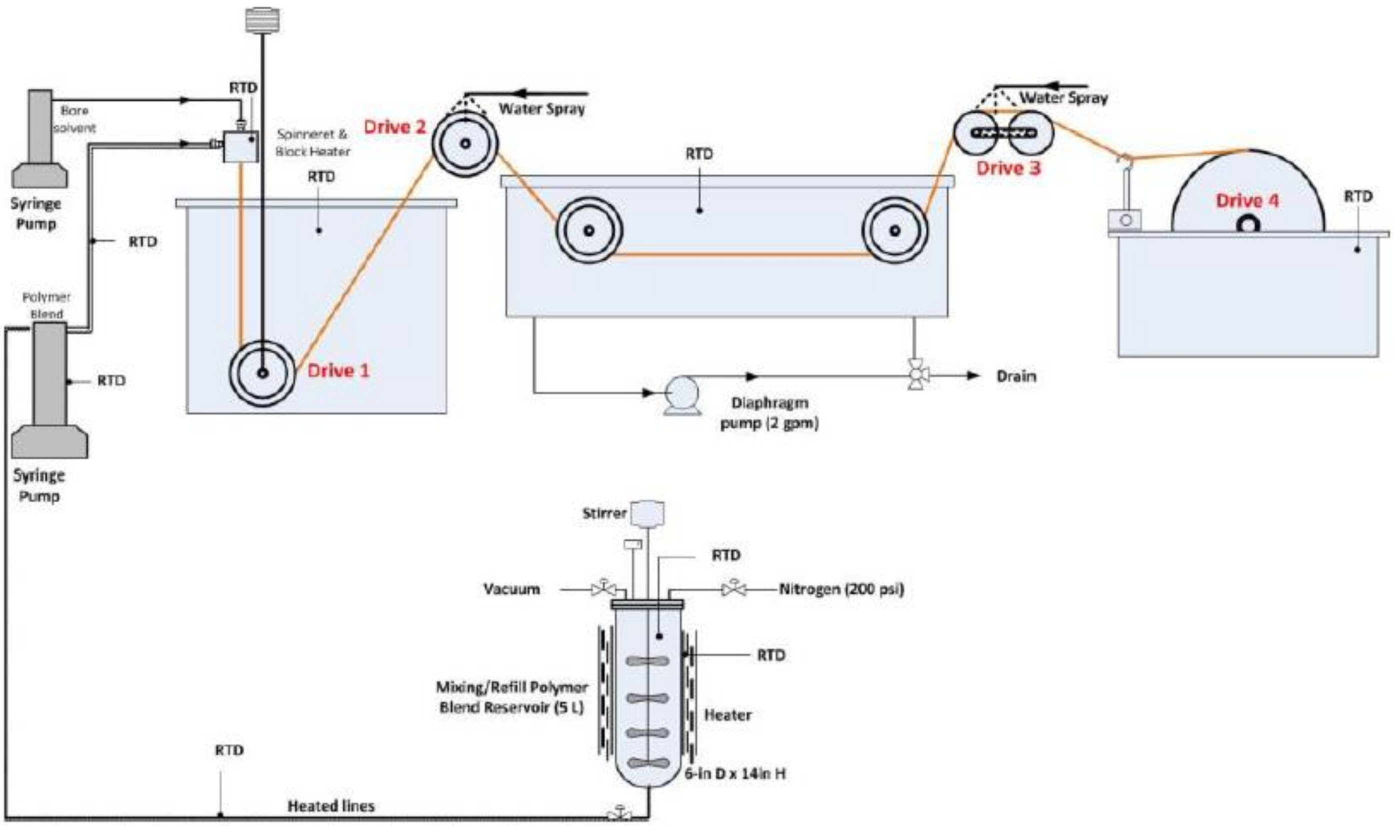



Figure 3: SRI hollow-fiber membrane spinning line.

Large bundles of hollow fibers are potted in tube sheet modules (currently in 4- or 6-inch diameters), which can then be assembled into larger-scale gas separation units/skid for process implementation. Figure 4 shows the cross-section of an actual 4-inch fiber module as fabricated at SRI (on the left); these are the type that had been incorporated in the bench-scale skid, which was deployed in past testing at the National Carbon Capture Center (NCCC) on a syngas slip stream. SRI fiber modules are designed for easy fabrication, easy handling, and easy drop-in replacement. A new tube sheet module design is being deployed (images on right side of Figure 4). These will enable faster module swapping and reduced gas bypass characteristics.

## TABLE 1: MEMBRANE PROCESS PARAMETERS

| Materials Properties | Units | Current R&D Value | Target R&D Value |
|---|---|---|---|
| Materials of Fabrication for Selective Layer | | PBI | PBI |
| Materials of Fabrication for Support Layer | | PBI | PBI |
| Nominal Thickness of Selective Layer | µm | 0.3–2 | <0.5 |
| Membrane Geometry | | hollow fiber | hollow fiber |
| Max Trans-Membrane Pressure | bar | ≈14 | >20 |
| Hours Tested without Significant Degradation | hr. | 1,000 | 1,000 |
| Manufacturing Cost for Membrane Material | $/m$^2$ | 30–80 | TBD |
| **Membrane Performance** | | | |
| Temperature | °C | 200–250 | 225 |

| | | | |
|---|---|---|---|
| $H_2$ Pressure Normalized Flux | GPU or equivalent | 80–120 | 80–120 |
| $H_2/H_2O$ Selectivity | — | <1 | <1 |
| $H_2/CO_2$ Selectivity (Dense layer thickness) | — | 40 (>1 µm) and 22 (<0.3 µm) | 40 (<0.3 µm) |
| $H_2/H_2S$ Selectivity (Dense layer thickness) | — | >200 (>1 µm) | >200 (<0.3 µm) |
| Sulfur Tolerance | ppm | 300 | 300 |
| Type of Measurement | | pure and mixed | mixed gases |
| **Proposed Module Design** | | *(for equipment developers)* | |
| Flow Arrangement | | countercurrent | |
| Packing Density | $m^2/m^3$ | >3,000 | |
| Shell-Side Fluid | | retentate or permeate | |
| Syngas Flowrate | kg/hr | 22 | |
| $CO_2$ Recovery, Purity, and Pressure | %/%/bar | TBD | |
| $H_2$ Recovery, Purity, and Pressure | %/%/bar | >98%, >49%, 30 bar | |
| Pressure Drops Shell/Tube Side* | bar | <0.007/0.03 | |
| Estimated Module Cost of Manufacturing and Installation | $\frac{\$}{kg/hr}$ | TBD | |

*A commercial 4-inch module design with 200 µm bore diameter and 28–48 bar feed pressure was assumed.

**Figure 4: Potted module cross-section (left-most); new tube sheet module design (right).**

### Testing Results

Results of testing PBI modules at NCCC on air-blown gasifier syngas have established performance characteristics of both the Gen-1 and Gen-2 PBI modules. Specifically, membrane element TS-1 (consisting of SRI Gen-1 fibers having GPU ~150, $H_2/CO_2$ selectivity ~25 at 150°C) was tested for about 500 hours. Membrane element TS-2 (consisting of SRI Gen-2 fibers having GPU ~100, $H_2/CO_2$ selectivity ~40 at 200°C, and at 200 psi) was tested for 48 hours. Figure 5 plots selectivity results of various testing runs for both Gen-1 and Gen-2 testing campaigns. Selectivity of Gen-2 shows definite improvement with potential for superior performance at target operating temperatures of approximately 200°C. Taken with gas permeance measurements (Figure 6), the Gen-2 modules evidence significant performance advantages over Gen-1.

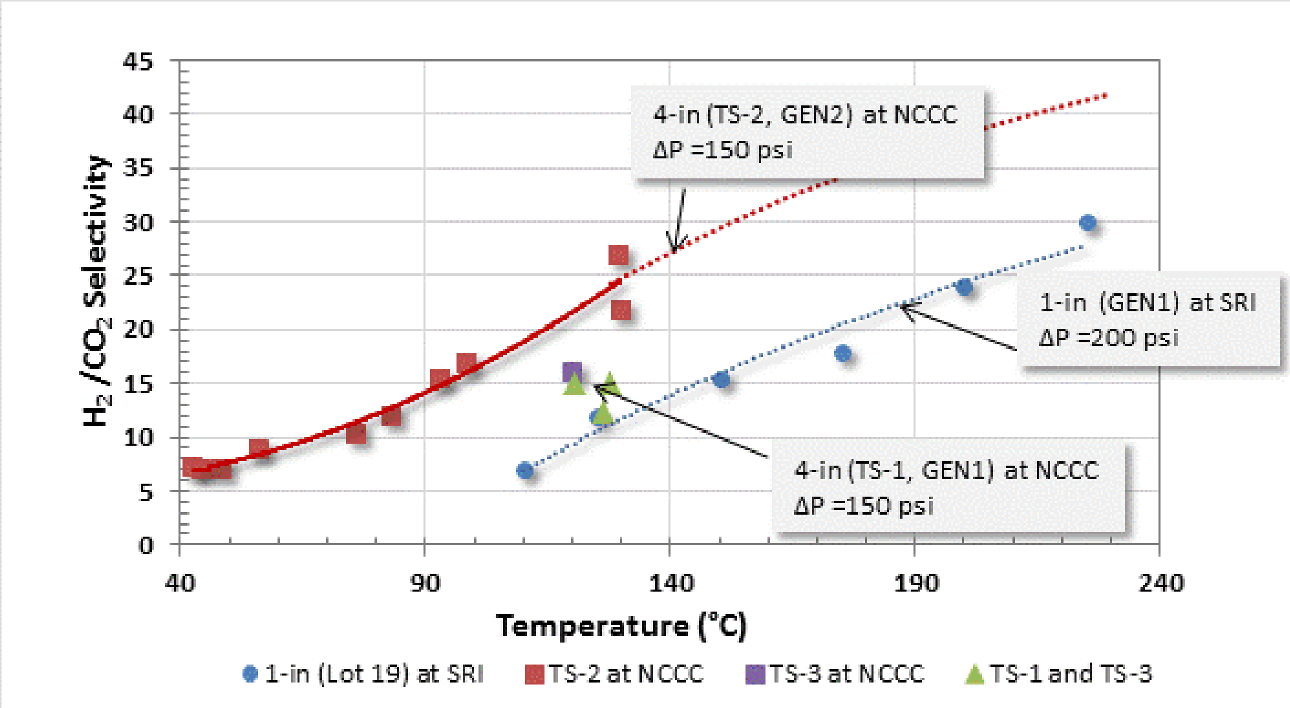



Figure 5: Comparison of measured $H_2/CO_2$ selectivity for Gen-1 and Gen-2 PBI modules.

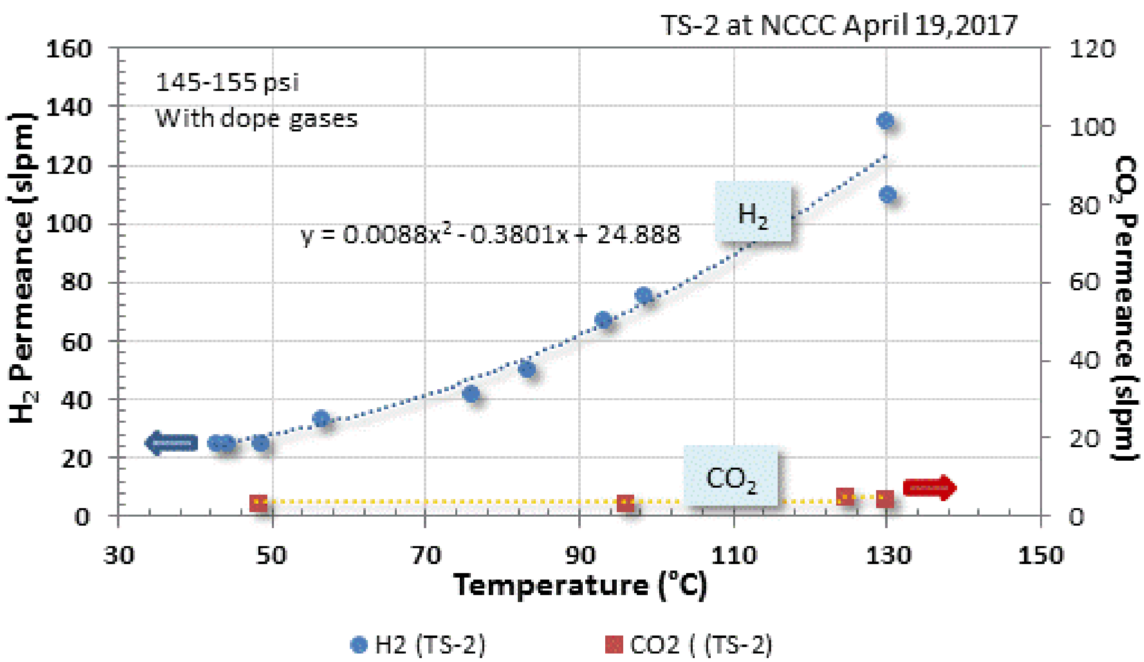



Figure 6: Measured $H_2$ and $CO_2$ permeances for the Gen-2 module at varying temperatures under a pressure differential of 145–155 psi.

## Preliminary Techno-Economic Analysis Findings

SRI has previously made estimations of cost of electricity (COE) reductions that should be possible by application of the PBI membrane technology in process implementation in the context of an IGCC power plant cycle. From testing of Gen-1 and Gen-2 membranes, performance parameters have been quantified. Given expected Gen-1 and Gen-2 gas selectivities and different gas permeance assumptions, it is possible that the PBI membrane technology can meet National Energy Technology Laboratory (NETL) targets, assuming the membrane system has capital cost reductions that are expected to emerge in industrial-scale economies and savings associated with high levels of system optimization, which are anticipated as higher Technology Readiness Levels (TRLs) are attained. Current research and development (R&D) techno-economic data is shown in Table 2.

## TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

| Economic Values | Units | Current R&D Value | Target R&D Value |
|---|---|---|---|
| Cost of Carbon Captured | \$/tonne $CO_2$ | \$32 | <\$32 |
| Cost of Carbon Avoided | \$/tonne $CO_2$ | — | — |
| Capital Expenditures | \$/MWhr | \$75 | TBD |
| Operating Expenditures | \$/MWhr | \$60 | TBD |
| Cost of Electricity | \$/MWhr | \$135* | <\$135 |

* >99% hydrogen recovery with 90% $CO_2$ capture.

### 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

***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 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 = $3.3464 \times 10^{-6}$ 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*** – Molecular sieving and activated diffusion.

***Contaminant Resistance*** – PBI is resistant to acidic contaminants.

***Syngas Pretreatment Requirements*** – Tar removed.

***Membrane Replacement Requirements*** – Required frequency of membrane replacement to be determined.

***Waste Streams Generated*** – Gaseous waste stream generated includes $CO_2$ and $H_2S$ separated from the syngas. This stream will be further treated to remove $H_2S$.

***Process Design Concept*** – Flowsheet/block flow diagram is shown in Figure 7. Note that the PBI hollow-fiber membrane is both a water and $H_2$ transporting membrane, so most water vapor/steam in the shifted syngas will segregate into the permeate stream along with the $H_2$.

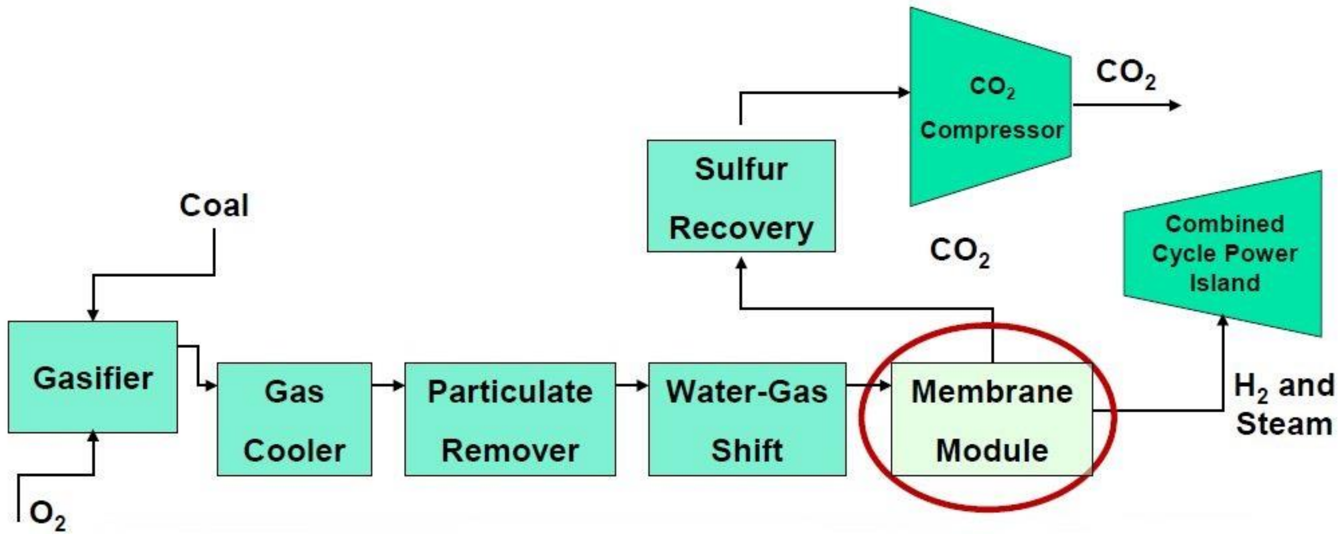



Figure 7: Flowsheet/block flow diagram showing PBI membrane module integration in the IGCC plant process.

***Proposed Module Integration*** – Module design is tubular with 4-inch diameter and 36-inch length. Figure 8 shows the simulated module performance: the pressure, temperature, and composition of the gas entering the module, assuming $H_2/CO_2$ selectivity of 40. Note that the module feed gas is from an oxygen-blown gasifier with a shifted syngas feed to the membrane. In an oxygen-blown gasifier (assumed in TEA), the permeate recovers 98.4% of the feed $H_2$ and the retentate captures 90% of the feed $CO_2$. The retentate stream is further processed in a Claus plant to remove $H_2S$ and a catalytic oxidizer to convert CO and $CH_4$ to $CO_2$ and $H_2$ to water ($H_2O$). The final retentate dry basis $CO_2$ purity is 96.88%.

The composition of the gas entering the module is shown below:

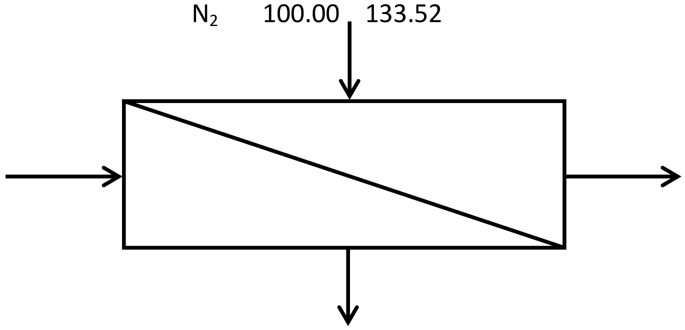
| Pressure | Temperature | Composition | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | vol% | | | | | | |
| psia | °F | $CO_2$ | CO | $CH_4$ | $N_2$ | $H_2$ | $H_2O$ | $H_2S$ |
| 691.1 | 437 | 31.01 | 0.67 | 0.07 | 0.96 | 43.83 | 22.99 | 0.47 |

$N_2$ sweep at 30 psia

| | % | slpm |
|---|---|---|
| $N_2$ | 100.00 | 133.52 |

Feed at 691.6 psia

| | % | slpm |
|---|---|---|
| $CO_2$ | 31.01 | 218.82 |
| CO | 0.67 | 4.73 |
| $CH_4$ | 0.07 | 0.49 |
| $N_2$ | 0.96 | 6.77 |
| $H_2$ | 43.83 | 309.28 |
| $H_2O$ | 22.99 | 162.23 |
| $H_2S$ | 0.47 | 3.32 |
| | 100.00 | 705.64 |



Permeate at 30 psia

| | % | slpm |
|---|---|---|
| $CO_2$ | 3.54 | 21.96 |
| CO | 0.03 | 0.19 |
| $CH_4$ | 0.00 | 0.01 |
| $N_2$ | 0.05 | 0.29 |
| $H_2$ | 49.10 | 304.44 |
| $H_2O$ | 25.75 | 159.69 |
| $H_2S$ | 0.00 | 0.01 |
| $N_2$ swp | 21.53 | 133.52 |
| | 100.00 | 620.11 |

Retentate at 691.1 psia

| | % | slpm |
|---|---|---|
| $CO_2$ | 89.87 | 196.86 |
| CO | 2.07 | 4.54 |
| $CH_4$ | 0.22 | 0.48 |
| $N_2$ | 2.96 | 6.48 |
| $H_2$ | 2.21 | 4.84 |
| $H_2O$ | 1.16 | 2.54 |
| $H_2S$ | 1.51 | 3.31 |
| | 100.00 | 219.05 |

Membrane parameters:

- $H_2$ permeance = 80 GPU
- $H_2/CO_2$ Selectivity = 40
- Dense layer thickness = 1.0 µm
- Membrane area = 8.5 $m^2$

Operating parameters:

- Feed temperature = 437°F
- 50 kWth Shifted Syngas Feed
- Permeate $H_2$ recovery = 98.4%
- Retentate $CO_2$ capture* = 90.0%

* Retentate $CO_2$ dry basis purity = 96.88% after $H_2S$ removal and catalytic oxidation of CO, $H_2$ and $CH_4$

**Figure 8: Simulation of a PBI module performance with an oxygen-blown gasifier and a 50-kWth shifted syngas feed.**

## technology advantages

- PBI combines both useful throughput (permeability) and degree of separation (selectivity).
- PBI is thermally stable up to 300°C and is sulfur tolerant.
- PBI asymmetric hollow fibers can be fabricated at increasingly small diameters, allowing increased fiber packing densities in modules realistically consistent with 7,000 $m^2$ of membrane surface area per $m^3$ of module volume.
- Membrane gas separation systems have reduced costs for syngas cooling.
- Membrane gas separation systems should result in reduced $CO_2$ compression costs.
- Membrane gas separation systems are emissions-free (i.e., they use no solvents such as amines).
- Membrane gas separation systems may have decreased capital costs (assuming membrane costs are managed).
- Membrane gas separation systems have relatively low maintenance demands.
- Membrane gas separation systems are scalable and modular.

## R&D challenges

- Maintaining fiber and module fabrication quality/performance (avoiding membrane pinholes, macrovoids, module seal integrity) in scale-up/transfer of technology to larger-scale manufacturing.
- Designing and synthesizing materials structure and configurations.
- Integration and optimization of membrane-based $CO_2$ separation systems in coal gasification-based plants.

## status

Field-testing of the bench-scale skid was started in October 2021 and is continuing through June 2022. The goal is to operate the skid up to 300 hours under the operating conditions and test the performance of the membrane modules with syngas from the gasifier at the host site.

An updated TEA and Technology Maturation Plan (TMP) will be provided after testing concludes in June 2022.

## available reports/technical papers/presentations

"Development and Testing of a High-Temperature PBI Hollow-Fiber Membrane Technology for Pre-Combustion $CO_2$ Capture." Presented by Indira Jayaweera and Michael Wales, SRI International, 2021 NETL Carbon Management Research Project Review Meeting. Pittsburgh, PA. August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Jayaweera_0.pdf*

"Development and Testing of a High-temperature PBI Hollow-fiber Membrane Technology for Pre-combustion $CO_2$ Capture," presented by Elisabeth Perea, SRI International, 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting - Capture and Utilization Sessions, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/E-Peria-SRI-High-Temperature-PBI.pdf*

"Development and Testing of a High-temperature PBI Hollow-Fiber Membrane Technology for Pre-Combustion $CO_2$ Capture," presented by Indira Jayaweera, SRI International, Final Project Review (FE0012965) and Project Kickoff (FE0031633), January 2019. *https://netl.doe.gov/projects/plp-download.aspx?id=10555&filename=Development+and+Testing+of+a+High-Temperature+PBI+Hollow-Fiber+Membrane+Technology+for+Pre-Combustion+CO2+Capture.pdf*

"Development and Testing of Polybenzimidazole (PBI) Hollow-Fiber Membrane Technology for Pre-Combustion $CO_2$ Capture (FE0031633)," presented by Indira Jayaweera, SRI International, 2018 NETL $CO_2$ Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/I-Jayaweera-SRI-Hollow-Fiber-Membrane.pdf*

"Development of a Pre-Combustion $CO_2$ Capture Process Using High-Temperature PBI Hollow Fiber Membranes," presented by Indira S. Jayaweera, SRI International, 2017 NETL $CO_2$ Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/sites/default/files/2017-12/2I-S-Jayaweera2-SRI-PBI-Hollow-Fiber-Membranes.pdf*

"Development of Pre-Combustion $CO_2$ Capture Process Using High-Temperature PBI Hollow-Fiber Membranes (HFMs)," presented by Indira S. Jayaweera, SRI International, 2016 NETL $CO_2$ Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/sites/default/files/2017-12/I-Jayaweera-SRI-PBI-Hollow-Fiber-Membranes.pdf*

"Development of Pre-Combustion $CO_2$ Capture Process Using High-Temperature PBI Hollow-Fiber Membranes," presented by Indira S. Jayaweera, SRI International, 2015 NETL $CO_2$ Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File Library/Events/2015/co2captureproceedings/I-Jayaweera-SRI-High-Temperature-PBI-HF-Membranes-for-Pre-c.pdf*

"Development of a Pre-Combustion Carbon Dioxide Capture Process Using High Temperature Polybenzimidazole Hollow-Fiber Membrane," presented by Gopala Krishnan, SRI International, 2014 NETL $CO_2$ Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File Library/Events/2014/2014 NETL CO2 Capture/G-Krishnan-SRI-PBI-Hollow-Fiber-Membranes.pdf*

"Development of a Pre-Combustion Carbon Dioxide Capture Process Using High Temperature Polybenzimidazole Hollow-Fiber Membrane Fact Sheet," July 2014. *https://www.netl.doe.gov/sites/default/files/2017-12/FE0012965.pdf*

"Development of a Pre-Combustion $CO_2$ Capture Process Using High-Temperature PBI Hollow-Fiber Membranes," Project Kickoff Meeting Presentation, Pittsburgh, PA, June 9, 2014. *https://www.netl.doe.gov/sites/default/files/2017-12/DE-FE0012965-Kickoff-Meeting-June-2014.pdf*

Krishnan, G.; Steele, D.; O'Brien, K.; Callahan, R.; Berchtold, K.; and Figueroa, J., "Simulation of a Process to Capture $CO_2$ From IGCC Syngas Using a High Temperature PBI Membrane," *Energy Procedia*, Volume 1, Issue 1, February 2009, pp. 4079-4088.

Gopala Krishnan; Indira Jayaweera; Angel Sanjurjo; Kevin O'Brien; Richard Callahan; Kathryn Berchtold; Daryl-Lynn Roberts; and Will Johnson," Fabrication and Scale-up of Polybenzimidazole (PBI) Membrane Based System for Precombustion-Based Capture of Carbon Dioxide," DOE Contract Number: FC26-07NT43090, 2012-March 31. *http://www.osti.gov/scitech/biblio/1050227*