SRI International

2017 NETL CO_2 Capture Technology Project Review Meeting

Development of Pre-Combustion CO_2 Capture Process Using High-Temperature Polybenzimidazole (PBI) Hollow-Fiber Membranes (HFMs)

Indira S. Jayaweera

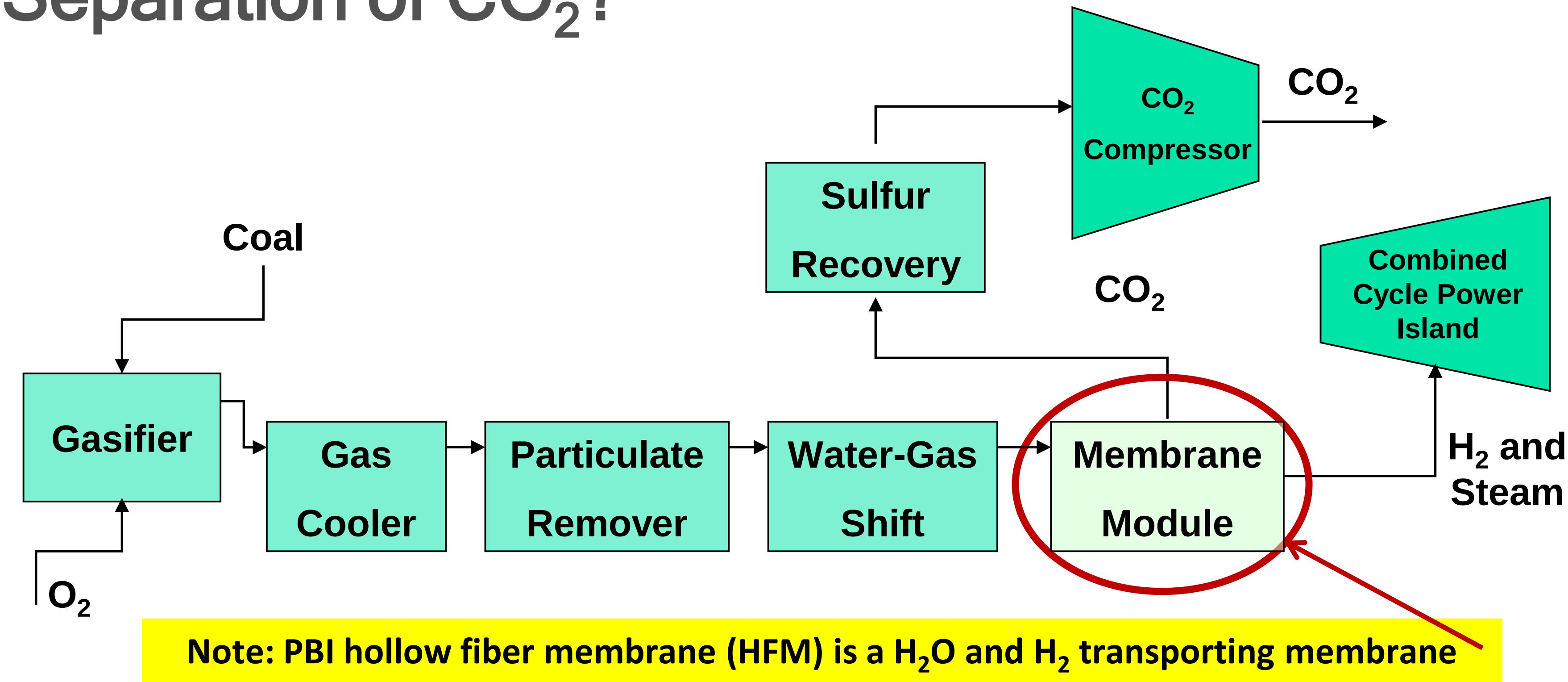
Sr. Staff Scientist and Program Manager

Energy and Environment Center

SRI International

August 21-25, 2017 • Omni William Penn Hotel• Pittsburgh, Pennsylvania

Why Use High-Temperature Membrane Separation of CO_2?

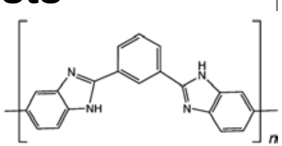


Characteristics of PBI Membranes

- PBI has an attractive combination of throughput and degree of separation
- Thermally stable up to ~ 300°C and sulfur tolerant
- Tested for 1000 hr at 225°C by SRI

Advantages of Membrane-Based Separation

- No need to cool syngas
- Reduced CO_2 compression costs
- Emission free, i.e., no solvents
- Decreased capital costs
- Low maintenance



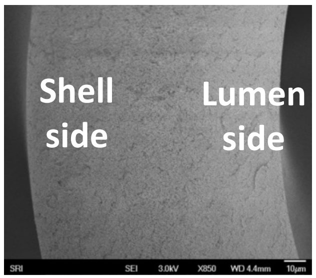
m-Polybenzimidazole (m-PBI)

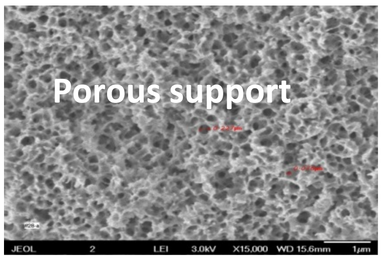
Membrane Development and Testing

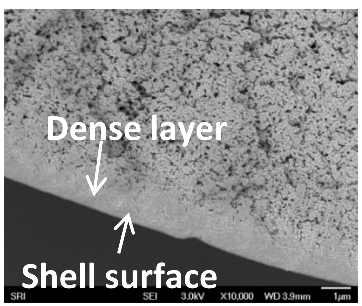
Previous Significant Achievements

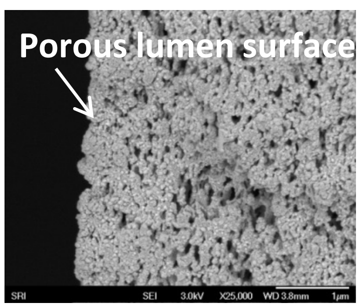
DOE Contract NO. DE-FC26-07NE43090

- Developed PBI polymer membrane to replace the original concept that used the PBI-coated porous stainless steel tubes.
- Developed new PBI formulation, installed a spinning line, and demonstrated defect-free fiber spinning with ~1-µm dense layer.



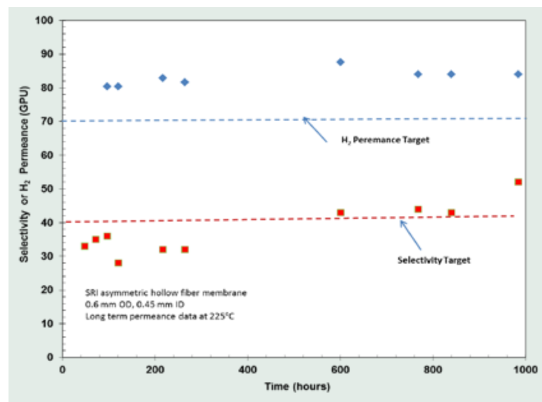




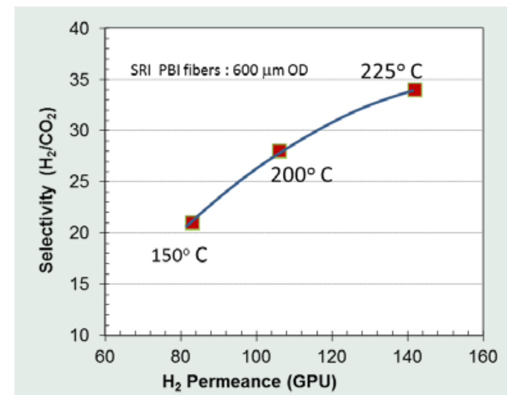


- **Membrane stability over 1000 hr**
- **H_2/CO_2 selectivities and their permanence data established for 1-µm dense layer.**

Selectivity= 40



Measured H_2/CO_2 selectivity and H_2 permeance at 225°C for over 1000 hr.



High-temperature/high-pressure PBI membrane performance for H_2 separation from syngas.

Predicted H_2 permeance for 0.1µm dense layer ~1000 GPU at 200℃

Current Project Budget and Team

- **Cooperative agreement grant with U.S. DOE (Contract No. DE-FE0012965)**
- **Period of Performance**:
  - Budget Period 1: 4-30-2014 through 10-31-15
  - Budget Period 2: 11-01-2015 through 12-31-17
- **Funding**:
  - U.S. Department of Energy: $2.299 million
  - Cost share: $0.575 million
  - Total: $2.875 million
- **NETL Project Manager**:
  - José D. Figueroa (current)
    Elaine Everitt (previous)

NETL

- Funding and technology oversight

SRI

- PBI membrane development
- Membrane testing

PBI Performance Products, Inc.

- Provides raw material

Generon, IGS

- Membrane fabrication scale-up
- Module fabrication

Enerfex, Inc.

- Membrane system modeling

Energy Commercialization

- Commercialization analysis

NCCC

- Gasifier facility test site

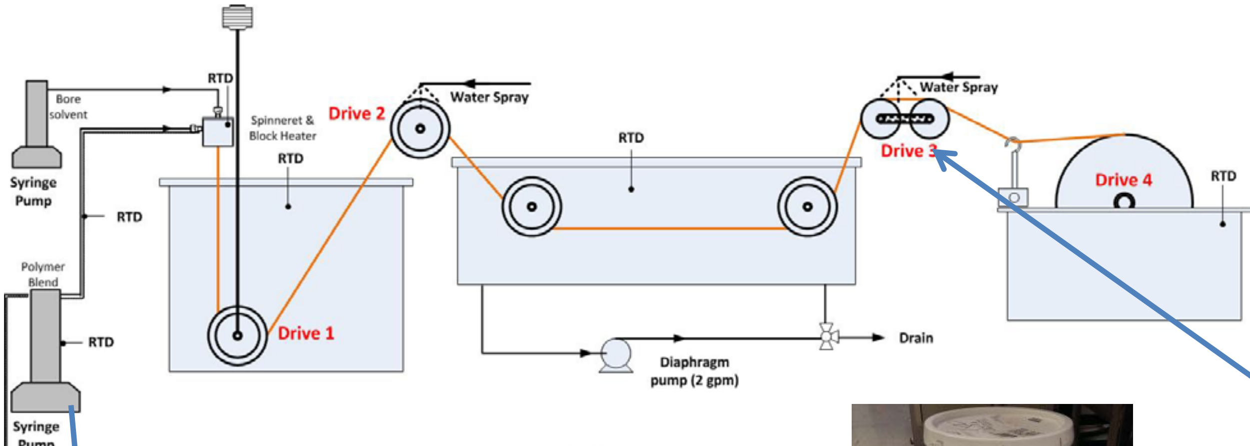
Project Objectives and Tasks

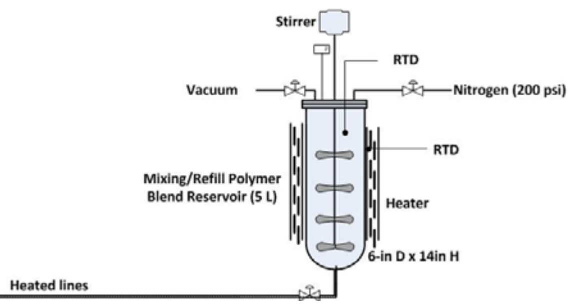
Project Objectives: Obtain sufficient *bench-scale data* to demonstrate the technical viability of the membrane system in an actual syngas feed stream. Utilize the data to evaluate the technical and economic viability of PBI-based membrane separation system to achieve NETL's Capture Program Performance Goals.

Project Tasks and Status

Task #	BP	Task	Status	Comments
1	1 & 2	Project management	Ongoing	On track
2	1	• Advanced development of asymmetric hollow-fiber spinning • Spinning defect-minimized fibers at km lengths • Assembly of multi-fiber modules 1-in, 2-in, 4-in modules • Installation of sub-scale fiber module test unit in laboratory • Conduct laboratory tests to generate parametric performance test database • Modeling of membrane performance • Technology transfer to initiate industrial scale fiber spinning • Design modification of the 50-kW_{th} skid design to house commercial membrane modules	Completed	
3	2	Modification of the 50-kW_{th} design and installation of a test skid at NCCC for the field tests	Completed	
4	2	Test the skid in a field setting using 50-lb/hr syngas stream from the gasifier at the NCCC and measure membrane performance	Completed	Post analysis on going
5 & 6	2	• Process techno-economic analysis (TEA) for ~550-MWe plant • Environmental health and safety (EH&S) analysis	Ongoing	On track
7	2	Decommission the system	TBD	

New Spinning Line Installed at SRI in 2015





Dope from
PBI Performance Products

Photograph of Drive 3

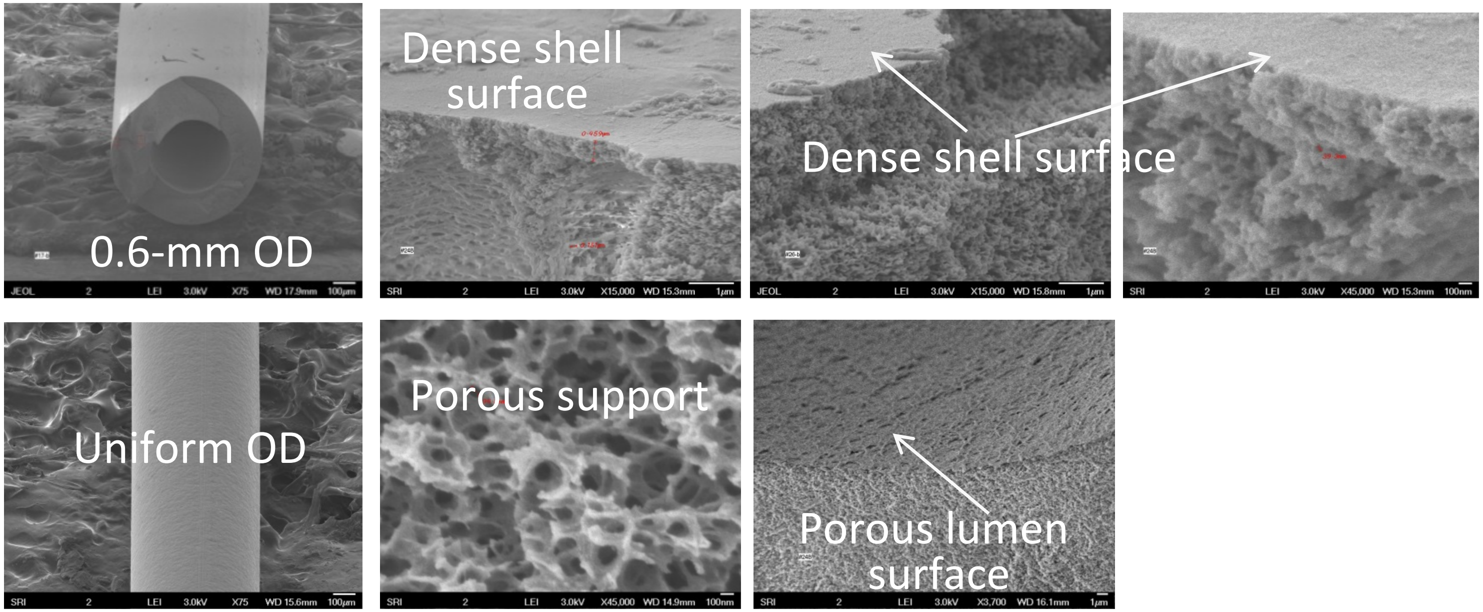
The new spinning line was crucial for developing an improved and robust spinning process that can be transferred to industry.

The new line enabled:

- Use of multiple coagulation solvents
- Optimization of fiber diameter
- Optimization of the fiber dense-layer thickness

Fabrication of Fibers with Good Reproducibility

Quality control is the KEY to success when scaling-up

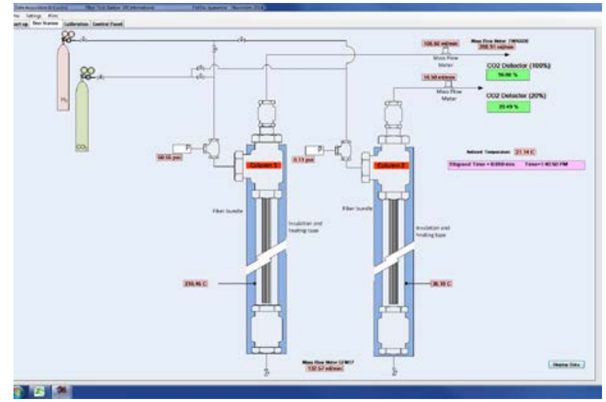


- **Developed protocols for spinning < 0.3-µm micron dense layer hollow-fiber membranes with membrane OD 450 to 650 µm. *ABOVE*: ~ 0.1-µm fibers with ~ 600-µm OD.**
- **Fabricated hollow-fiber membrane with a very thin, dense layer (< 0.3 µm) in kilometer lengths with <u>very good reproducibility</u>**
- **Tested more than 100 fiber bundles (1-in) for fiber-spinning optimization**
- **Spun > 100 km of fiber for both Generon and SRI modules (4-in)**

Achievements:
- **Dense-layer thickness reduced from 1 µm to < 0.3 µm**
- **Fiber diameter reduced from 1 mm to less than 600 µm**

Bench-Scale System for Fiber Performance Evaluation

Test Unit:
~ 1 kW_{th} capacity
(~ 0.16 m^2 fiber surface area)



Data Acquisition

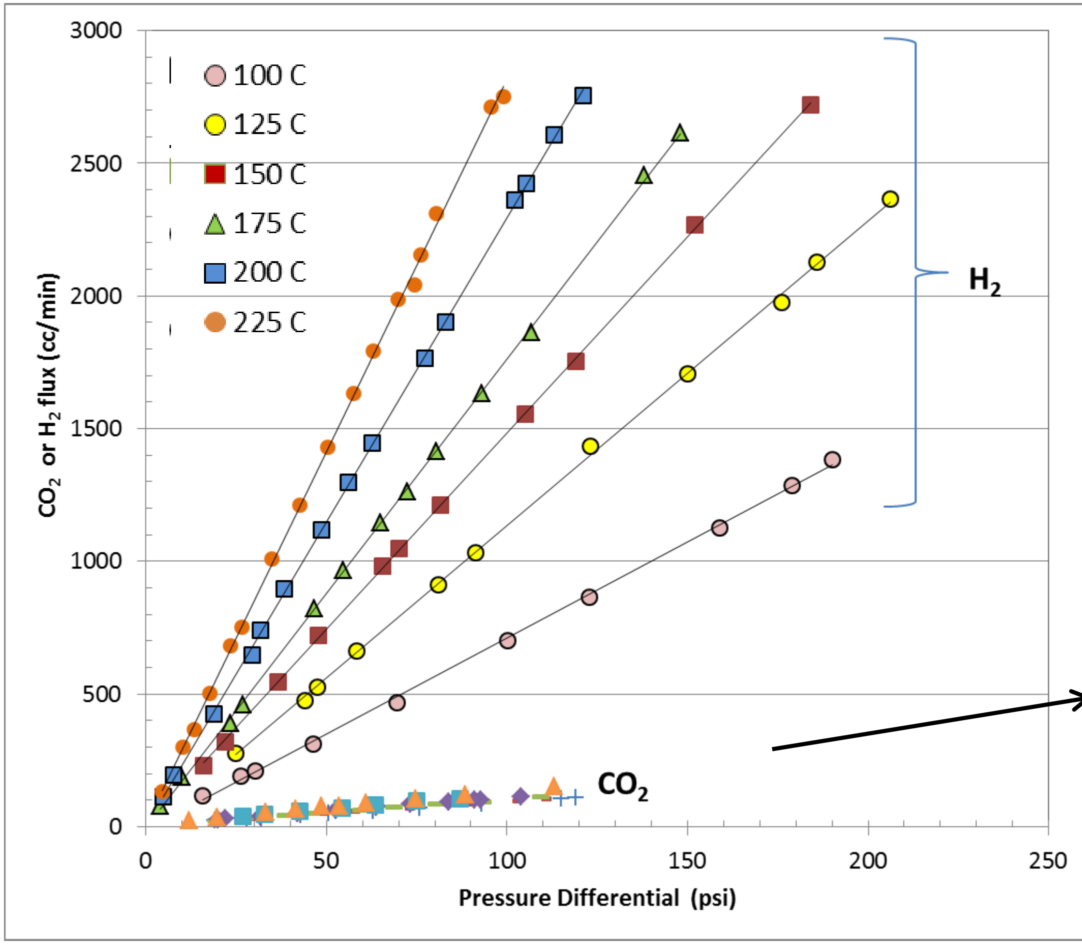
Feed Gas

- Single: CO_2, H_2,CO, and N_2
- Mixtures: CO_2/H_2, $CO_2/H_2/N_2$, $CO_2/H_2/CO$, and $CO_2/H_2/CO/N_2$
- Parameters varied: T, ΔP, composition, stage cut

Mixed Gas Analyzer

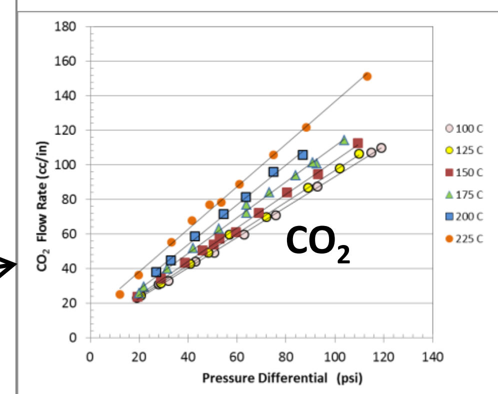
Samples:
Potted fiber bundles (100 fibers each) were 14- to 18-in long and had high packing densities

PBI Fiber Withstands High Pressures and High Temperatures



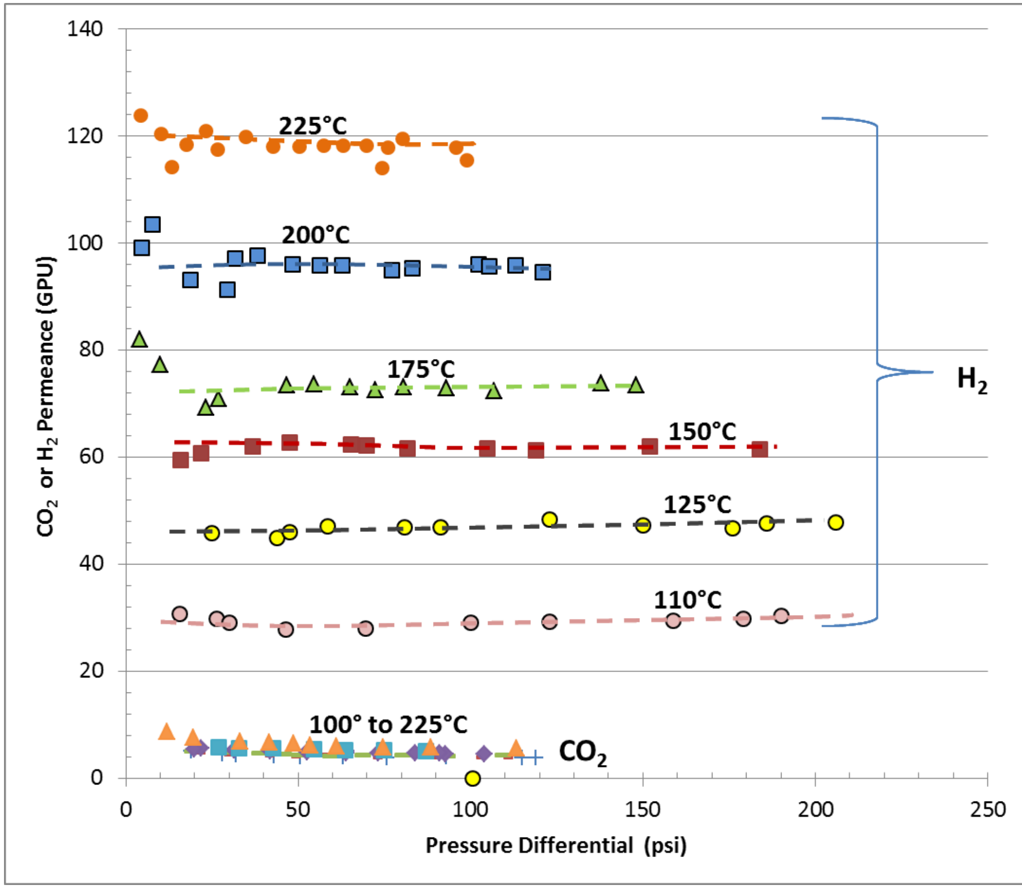
Mixed Gases

	Selectivity
H_2/CO_2	40
H_2/N_2	98
H_2/CO	103
H_2/H_2S	>200
225 ˚C and 200 psi ΔP	

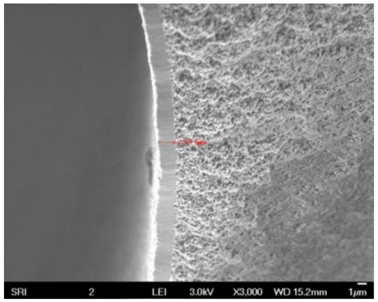


Observation: H_2/CO_2 selectivity increases with temperature up to 225 ° C.

Thinner Layer: Trade-off in Permeance and Selectivity is Acceptable



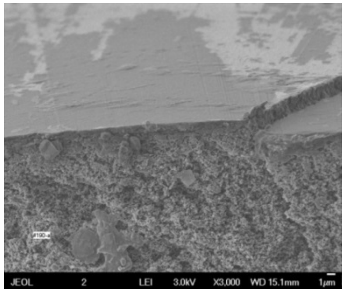
Performance monitored over a 3-month period with the HFM exposed to pressure swings of 1 to 15 atm and temperature swings of 20 to 225 °C.



Dense layer ~ 2 µm

H_2/CO_2 selectivity = ~ 40
H_2 permeance = 70 GPU

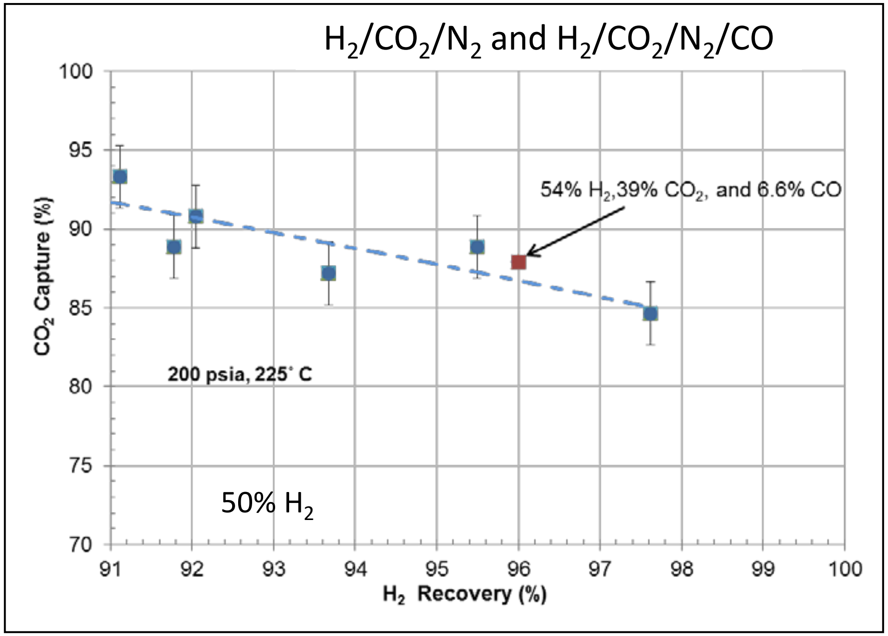
1 GPU = 10^{-6} cm^3 s^{-1} cm^{-2} Hg cm^{-1}



Dense layer ≤ 0.3 µm

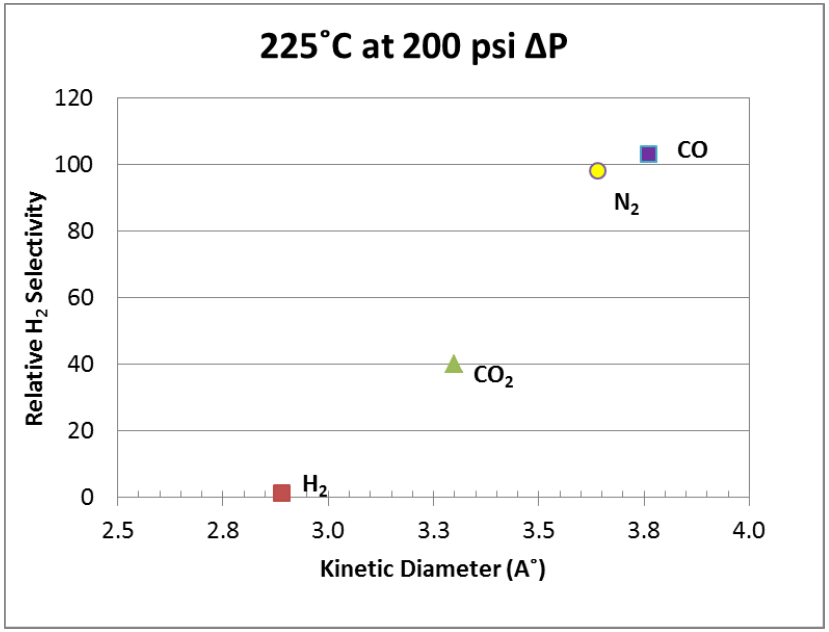
H_2/CO_2 selectivity = 25 ±2
H_2 permeance = 120 GPU

Results From Mixed-Gas Testing



Varied CO_2 concentration

H_2 recovery and CO_2 capture at 225˚C and at a ΔP value of 200 psi (stage cut > 0.5).
H_2 /CO_2 Selectivity = 40



Relationship between H_2 separation factor and the kinetic diameter of the component gases.

Observation: No observable interference from the presence of CO on H_2

>95% H_2 recovery is possible without a cascade with selectivity of 40 for H_2/CO_2 and helps keep capital costs down

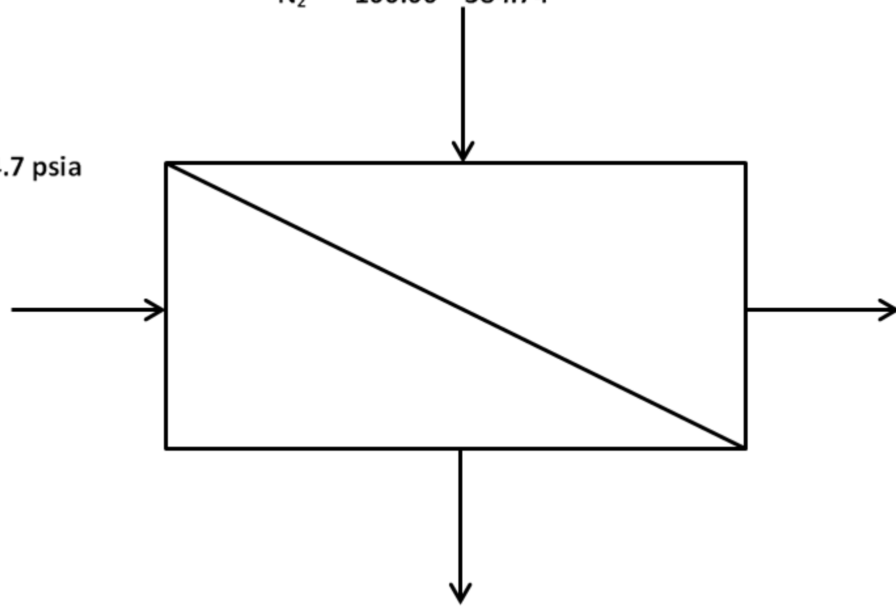
Simulation Results with H_2/CO_2 Selectivity of 25

N2 sweep (N2SWP) at 15.1 psia

	%	slpm
N_2	100.00	384.74

Feed (WGSGAS) at 214.7 psia

	%	slpm
CO_2	7.33	44.69
CO	0.87	5.30
CH_4	0.49	2.99
N_2	35.62	217.19
H_2	55.48	338.28
H_2O	0.21	1.28
	100.00	609.73



Permeate (H2FL) at 15.0 psia

	%	slpm
CO_2	0.69	4.96
CO	0.03	0.19
CH_4	0.01	0.05
N_2	0.37	2.63
H_2	44.95	321.73
H_2O	0.17	1.23
N2 SWP	53.78	384.74
	100.00	715.53

Retentate (CO2CAP) at 210.9 psia

	%	slpm
CO_2	14.25	39.73
CO	1.83	5.12
CH_4	1.05	2.93
N_2	76.92	214.56
H_2	5.93	16.55
H_2O	0.02	0.05
	100.00	278.94

Membrane parameters

- H_2 Permeance = 120 GPU
- H_2/CO_2 Selectivity = 25
- Dense layer thickness = 0.3
- Membrane area = 14.6 m^2

89% CO_2 capture
95% H_2 recovery

The data from modeling and bench-scale test data are used in designing 4-in modules and the 50-kw $_{th}$ test skid

Module Preparation and Testing at NCCC

Fabrication of Large Modules: 2- and 4-in Modules

Protoype 2-in module

Trimmed cross-section

Actual 4-in module assembled at Generon (8/6/16)

Actual 2-in module

- A protocol was developed for potting PBI HFM without dry spots
- The method was implemented in 2-in module fabrication
  - Challenges identified
- An updated method was implemented for 4-in modules

Fabrication of Large Modules at SRI: 4-inch

Photograph of 5000 fibers (5 m^2) arranged for potting at SRI

4-in sleeve for fiber potting

Potted 4-in fiber module cross-section (early design)

SRI fiber modules are designed for:

- -Easy fabrication
- -Easy handling
- -Easy drop-in replacement

Designed for Deployment in Industrial Environments

A photograph of the PBI skid in October 2016

Built for flexible operation, fully automated system

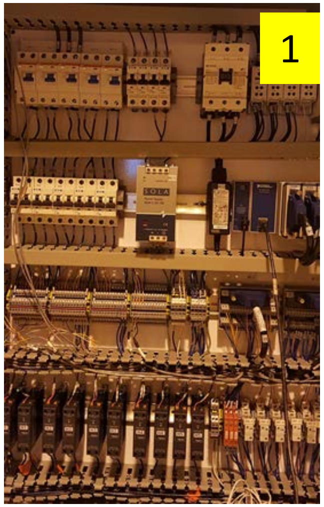
- Testing of commercial or custom membranes
- Testing of spiral-wound or hollow-fiber-based modules
- Testing of up to four modules
- Testing of individual modules
- Single-stage and dual-stage operation

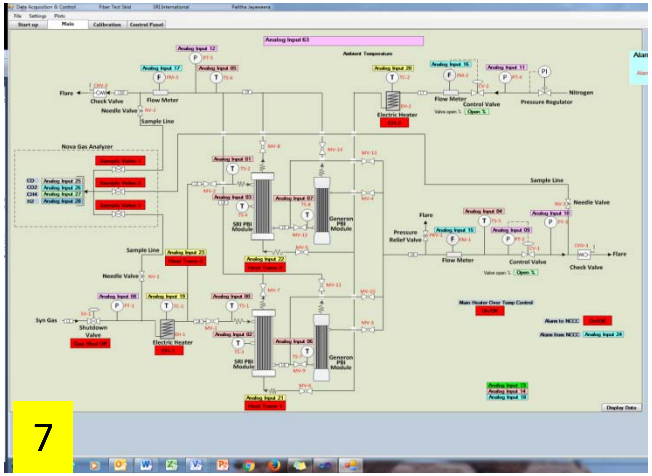
This skid could accommodate 6-8 modules each with 0.2 t-CO_2 per day capacity

This is an excellent example of a modular system

The skid was commissioned and tested at SRI in November 2016.

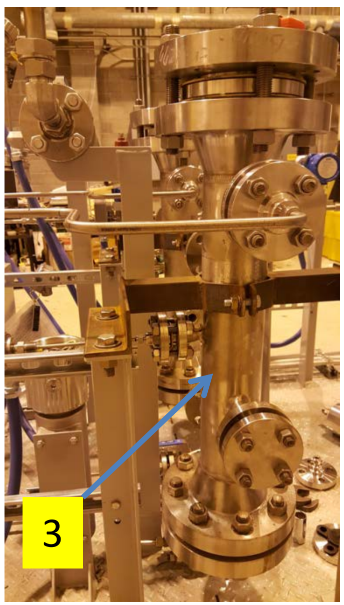
Membrane Skid Components





Selected Skid Components

1. Electronic panel
2. Flow meter, RTD
3. Vessel for SRI HFM module
4. Back-pressure control valve
5. Gas-stream heater
6. Feed-gas shut-off valve
7. Process control display



Skid Installation and Testing at the NCCC

Photograph of the skid being loaded on a truck for transportation to the NCCC (March 2017)

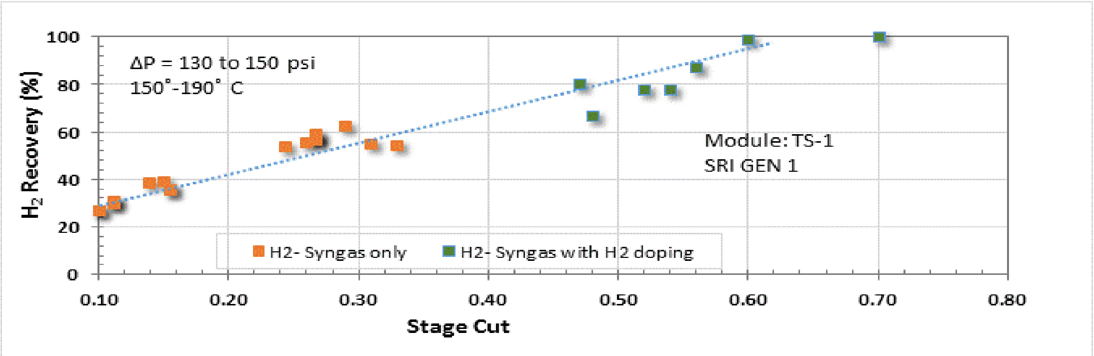
Photograph of the skid installed at the NCCC (April 2017)

After the PBI membrane skid was transferred to the NCCC in March 2017, the test campaign was conducted in April 2017.

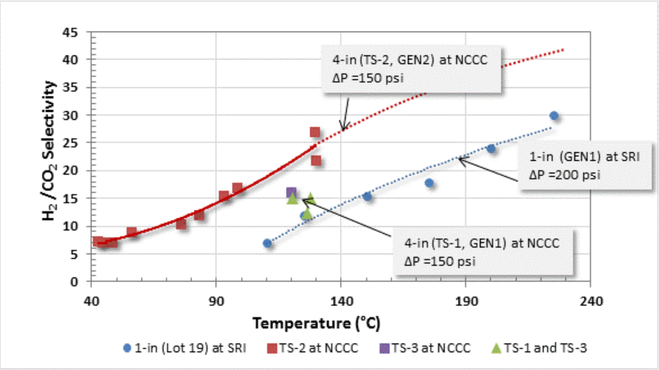
Test Results

Sample parametric matrix for generating data for the performance database

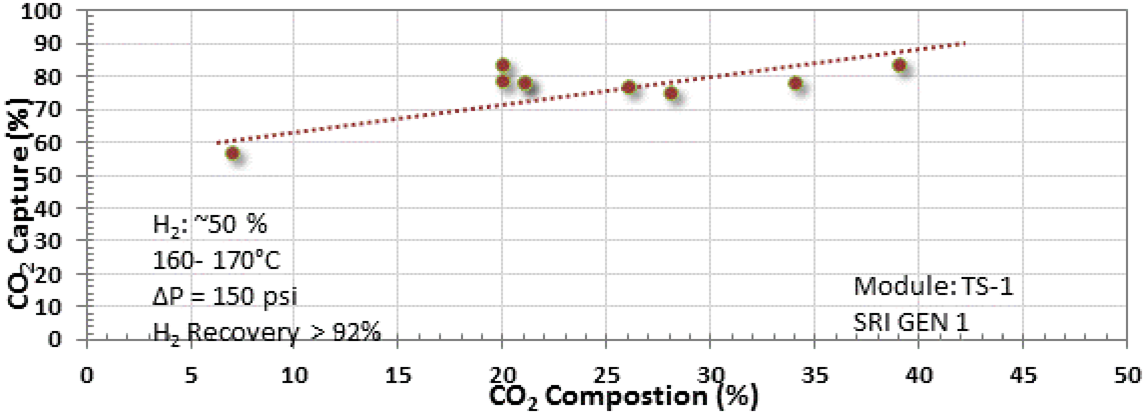
Test Parameter	Range	Unit
Temperature	80 to 215	°C
Pressure	50 to 170	psig
Gas composition	Variable	slpm
Stage cut	0.2-0.7	
H_2 in syngas	12 to 50	%
CO_2 in syngas	5 to 40	%



Observed hydrogen recovery with varying stage cuts in the temperature range 150˚ – 190˚C and pressure differentials of 130 to 150 psi for the syngas-only condition and for syngas with doped with H_2



Comparison of measured H_2/CO_2 selectivity for GEN-1 and GEN-2 modules



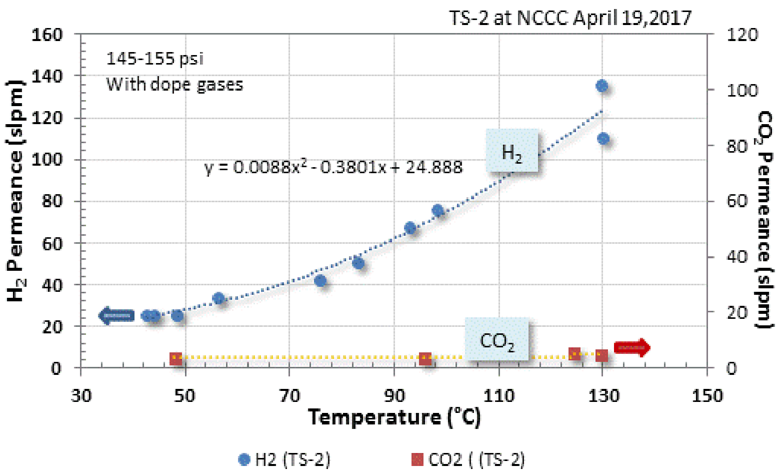
Observed CO_2 capture with varying feed CO_2 composition under fixed hydrogen composition at the temperature range 150 – 190˚C and a pressure differential ~ 150 psi for the TS-1 membrane

Modules tested:

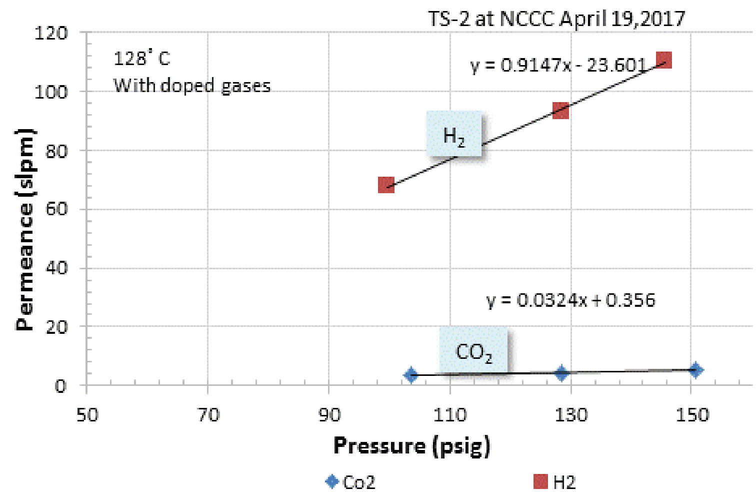
- Membrane element TS-1 consisting of SRI GEN-1 fibers (GPU~150, H_2/CO_2 selectivity ~ 25 at 150˚C) for ~ 500 hr
- Membrane element TS-2 consisting of SRI GEN-2 fibers (GPU ~ 100 , H_2/CO_2 selectivity ~ 40 at 200˚C, 200 psi) for ~ 48 hr

Test Results (continued)

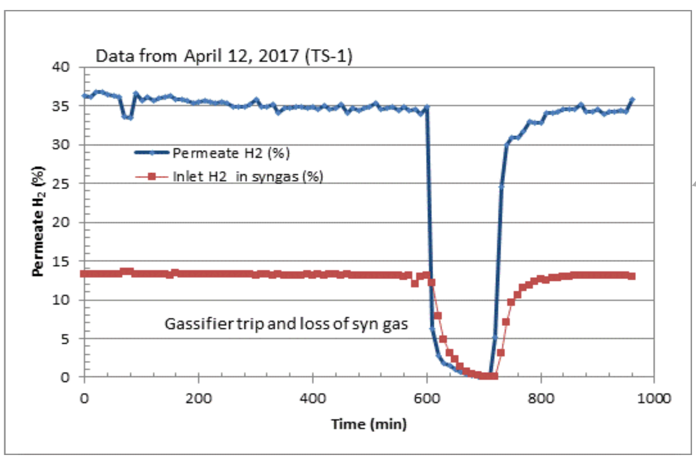
Effect of temperature and pressure on permeance



Measured H_2 and CO_2 permeances at the NCCC for the TS-2 (GEN-2) module at varying temperatures under a pressure differential of 145 to 155 psi.



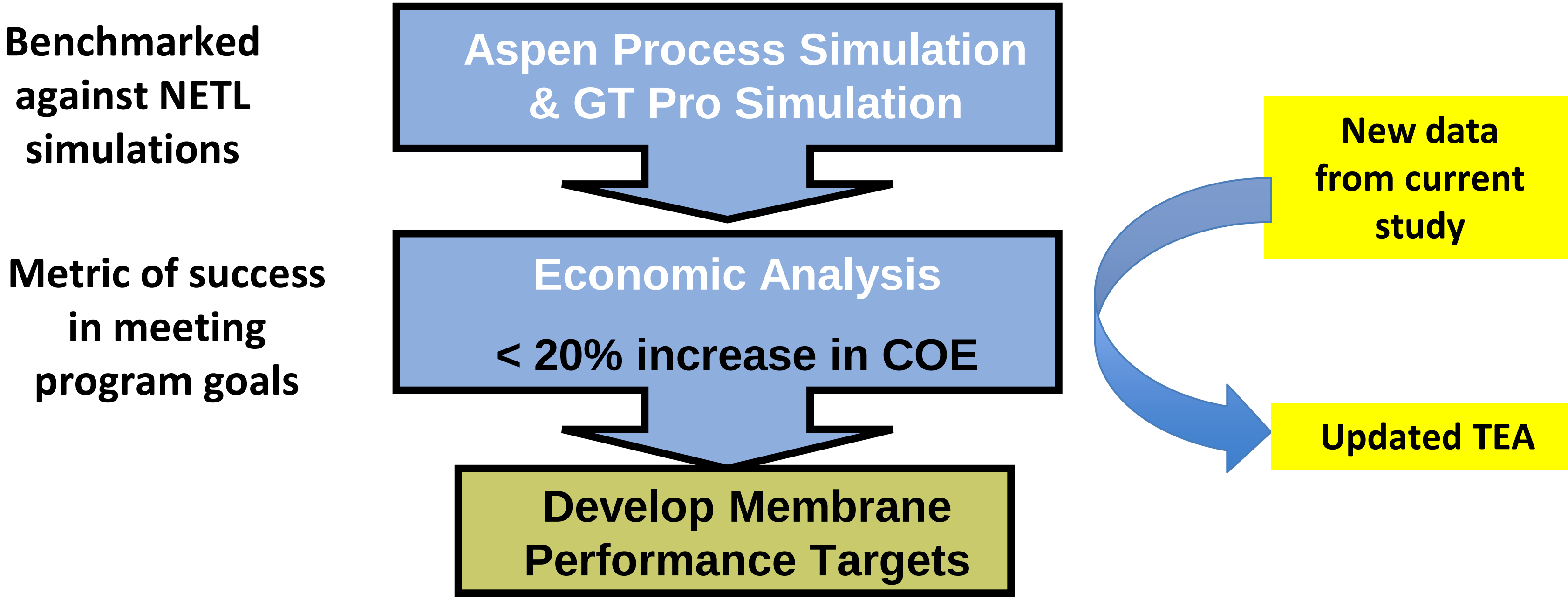
Measured H_2 and CO_2 permeances at the NCCC for the TS-2 (GEN-2) module with varying pressures at 128˚C



TS-1 module performance on April 12

Membrane modules performed very well under gasifier offset conditions and reverted back to original performance levels once the gasifier returned to normal operation

Process Economics



Process design and engineering study:

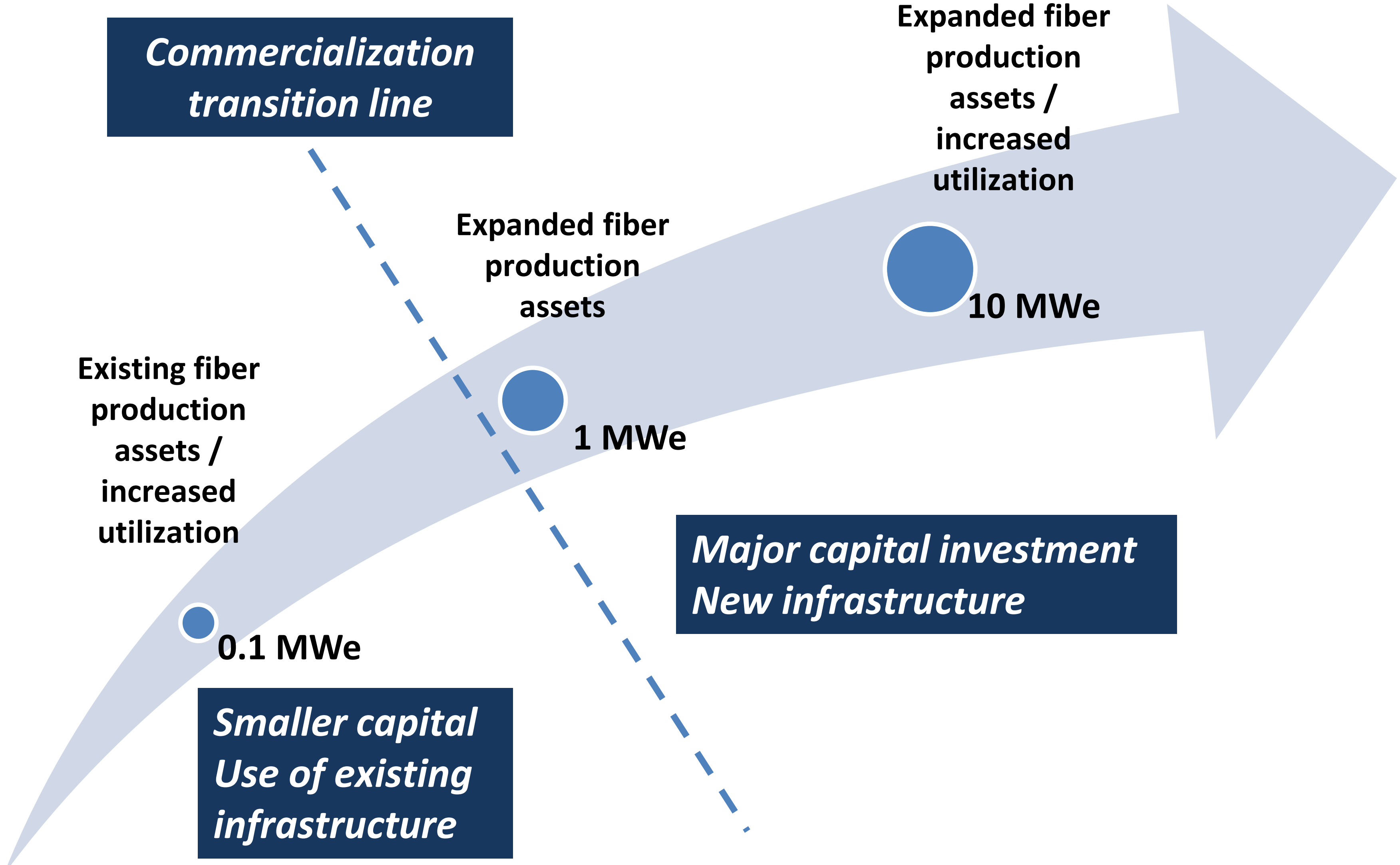
- Determine how the high-temperature hollow-fiber PBI membrane process concept would work if incorporated into a nominal 550-MWe gasification-based power plant with CCS.
- Use an IGCC process based on a GE-oxygen-blown gasifier and Selexol-based CO_2 removal as the base case.
- Perform the work in collaboration with Enerfex, Inc.

The cost estimation has shown that the CO_2 capture cost for combined process would be < $40 /tonne of CO_2 captured compared to $52/tonne of CO_2 captured for IGCC with the baseline technology, Selexol.

PBI HFMs: Transitioning From Lab to Field

- PBI HFMs can be produced at km lengths with minimal defects at SRI
- More than 100 1-in modules tested (equivalent fiber length > 50 kW_{th})
- Upper limit for H_2/CO_2 selectivity is ~ 40.
- Membrane test systems reach steady-state operation very rapidly (within a few minutes)
- 50 kW_{th} skid fabricated and tested at the NCCC
  - During the G5 gasifier run, SRI operated the PBI membrane skid for more than 600 hours; most of the system components were at 200˚C, and the valves and the control devices performed as designed.
  - The TS-1 module was tested for about 500 hr with syngas, syngas doped with H_2 and CO_2, and the TS-2 module was tested for about 48 hr. With syngas alone, the TS-1 module showed a greater than 3-fold H_2 stream enrichment even at temperatures below 170°C.
  - Membrane modules performed very well under gasifier offset conditions.
  - The current testing confirms that greater than 90% recovery of CO_2 is possible at operating temperatures > 190°C.
  - Because we planned in advance and had the support of the NCCC staff, we were able to operate the skid over the complete window of gasifier operation time.
- Potential Future Work
  - Begin long-term testing of GEN-2 modules
  - Start longer-term stability testing of two epoxy types
  - Install and test 8-in modules

The Road to Small and Large Pilots



US Patent 9,321,015 Issued on April 26, 2016

Acknowledgements

- Jose Figueroa, Elaine Everitt, Lynn Bricket, and others at NETL
- SRI Team: Srini Bhamidi, Regina Elmore, Xiao Wang, Indira Jayaweera, Palitha Jayaweera, Bill Olson, Gopala Krishnan, Marcy Berding, and Chris Lantman
- Richard Callahan (Enerfex, Inc.)
- Kevin O’Brien (Energy Commercialization, LLC)
- Greg Copeland and Mike Gruende (PBI Performance Products)
- John Jensvold and his team (Generon IGS)
- The staff at the NCCC

Disclaimer

This presentation includes an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

SRI International

Contact:

Dr. Indira Jayaweera

indira.jayaweera@sri.com

1-650-859-4042

Thank You

Headquarters
333 Ravenswood Avenue
Menlo Park, CA 94025
+1.650.859.2000

Additional U.S. and
international locations

www.sri.com