SRI International

2016 NETL CO_2 Capture Technology Project Review Meeting

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

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Energy and Environment Center

SRI International

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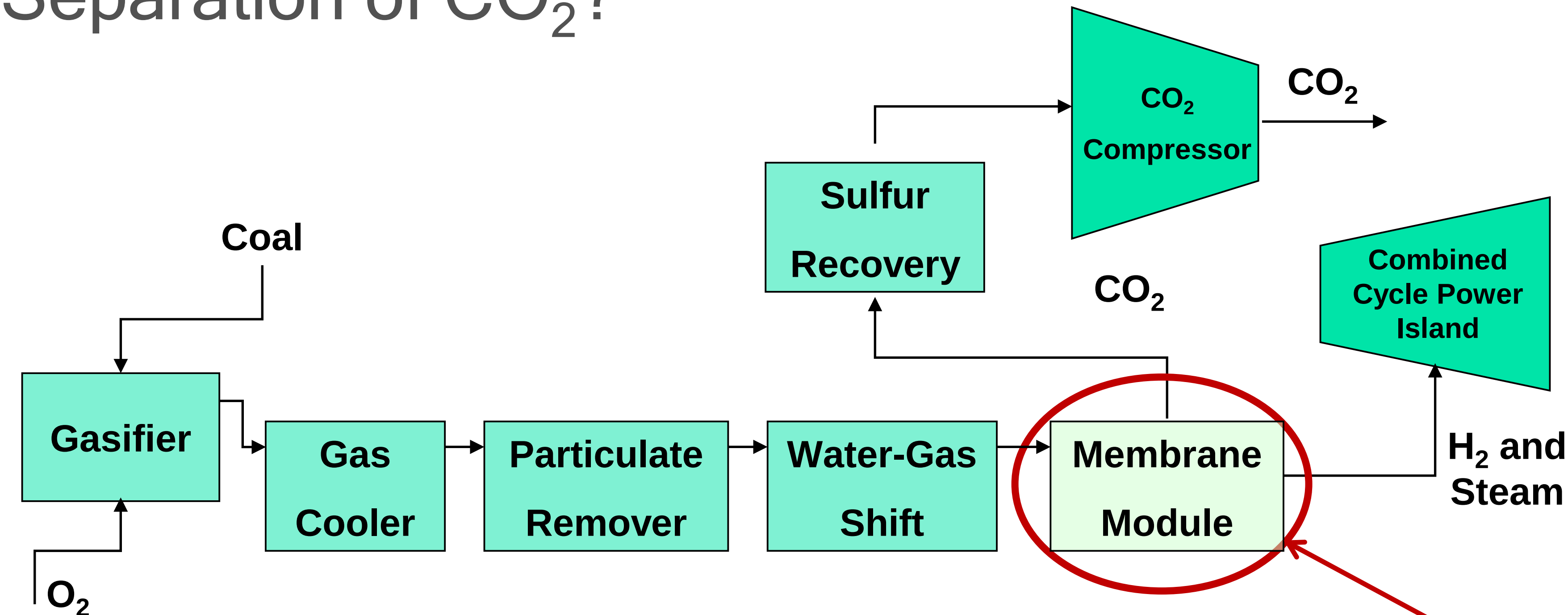
Project Overview and Technology Background

Why the High-Temperature Membrane Separation of CO_2?



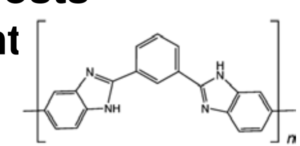
Note: PBI hollow fiber membrane (HFM) is a H_2O and H_2 transporting membrane

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 solvent
- Decreased capital costs
- Low maintenance



m-Polybenzimidazole (m-PBI)

The Road to the NCCC

Overcoming technical challenges

Format: Flat films of PBI

Advantage: Demonstrated excellent separation capability of PBI.
Disadvantage: Need different form factor to scale-up.

Format: PBI coated on metal substrate

Advantage: More surface area than flat sheets.
Disadvantage: Capital costs and footprint are excessive.

Format: Hollow fiber membranes with 2μ dense layer

Advantage: Typical format for gas separation membranes. Lower capital cost.
Disadvantage: Thickness of dense layer results in low permeance.

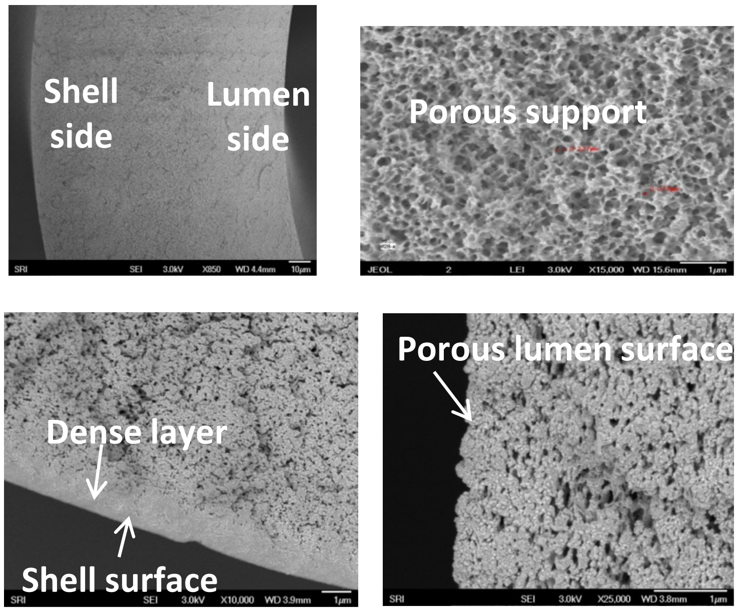
Format: Hollow fiber membranes with < 0.3μ dense layer

Advantage: Higher permeance due to thinner layer results in better economics and even lower capital costs.
Disadvantage: Reduction in selectivity but the trade-off is higher permeance with lower selectivity and acceptable performance.

PBI hollow fibers with < 0.3 μm dense layer can be commercialized

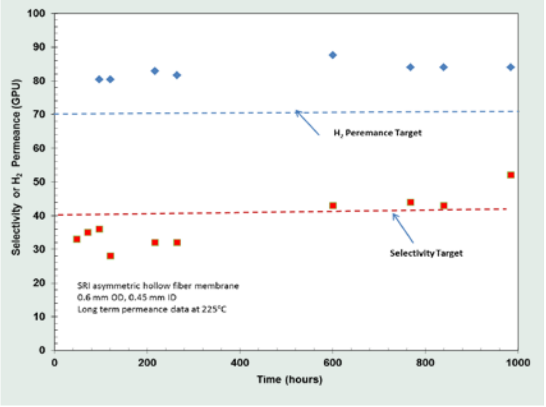
Previous Significant Achievements

- 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.

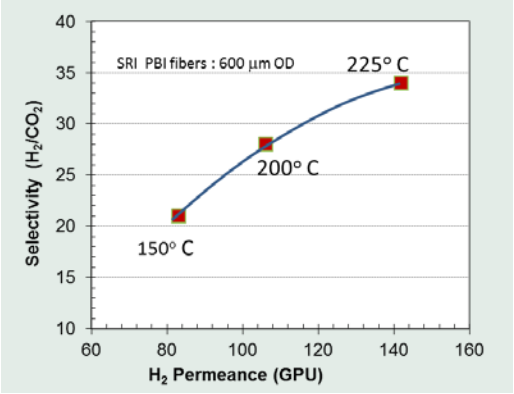


- **Membrane stability over 1000 hr**
- **H_2/CO_2 selectivities and their permanence data established for 1-µm dense layer.**

Selectivity= 40

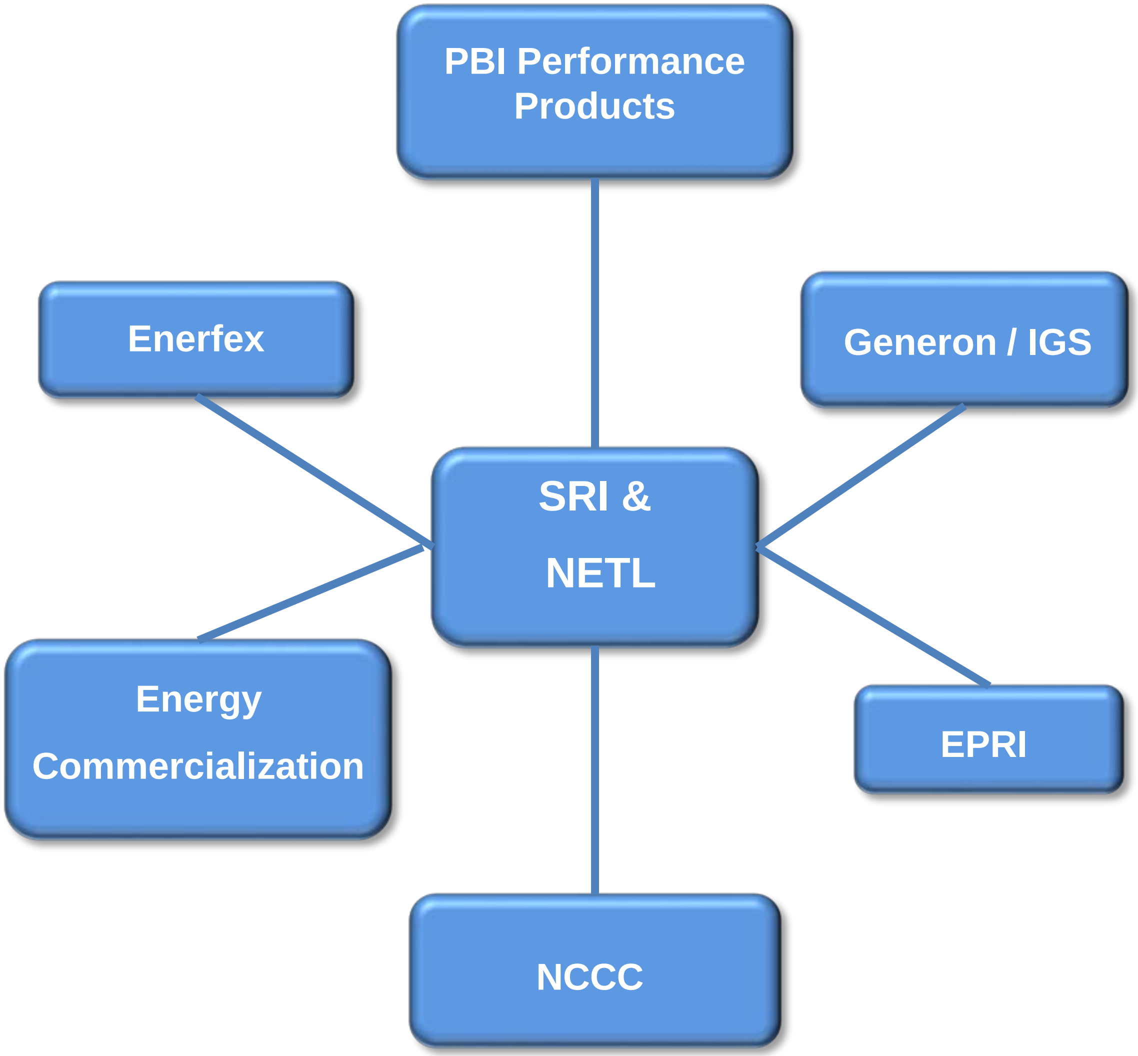


Measured H_2/CO_2 selectivity and H_2 permeance at 225°C for over 1000 hr.



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

Project Team



SRI
- PBI membrane fabrication research
- Membrane testing

PBI Performance Products, Inc.
- Provides raw material

Generon
- Membrane fabrication scale-up
- Module fabrication

Enerfex
- Membrane system modeling

Energy Commercialization
- Commercialization analysis

NCCC
- Gasifier facility test site

EPRI
- Electric power industry perspective

NETL
- Funding and technology oversight

Project Overview

- **Cooperative agreement grant with U.S. DOE-NETL**
  DE-FE0012965

- **Period of Performance**:
  - Budget Period 1: 4-30-2014 through 10-31-2015
  - Budget Period 2: 11-01-2015 through 01-31-2017
- Project Startup Meeting: 06-9-2014

- **Funding**:
  - U.S.: Department of Energy: $2.25 million
  - Cost share: $0.56 million
  - Total: $2.81 million

- **NETL Project Manager**:
  - José D. Figueroa (current); Elaine Everitt (previous)

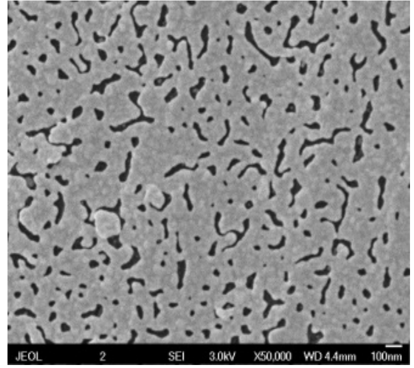
Objectives

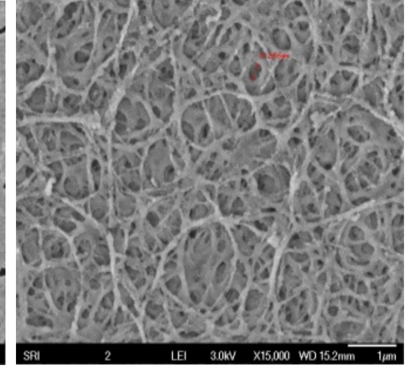
Program Objective:

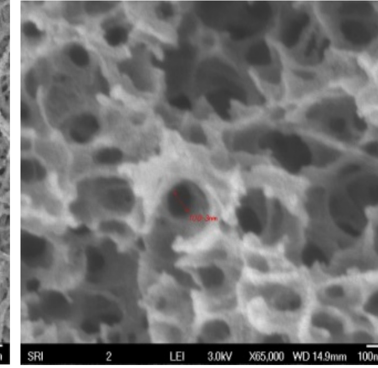
To develop polybenzimidazole (PBI) membrane-based H_2/CO_2 separation technology for Integrated Gasification Combined Cycle (IGCC) power plants that shows significant progress towards meeting the overall DOE Carbon Capture Program performance goal of 90% CO_2 capture rate at a cost of \$40/tonne of CO_2 captured by 2025.

Project Objectives:

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







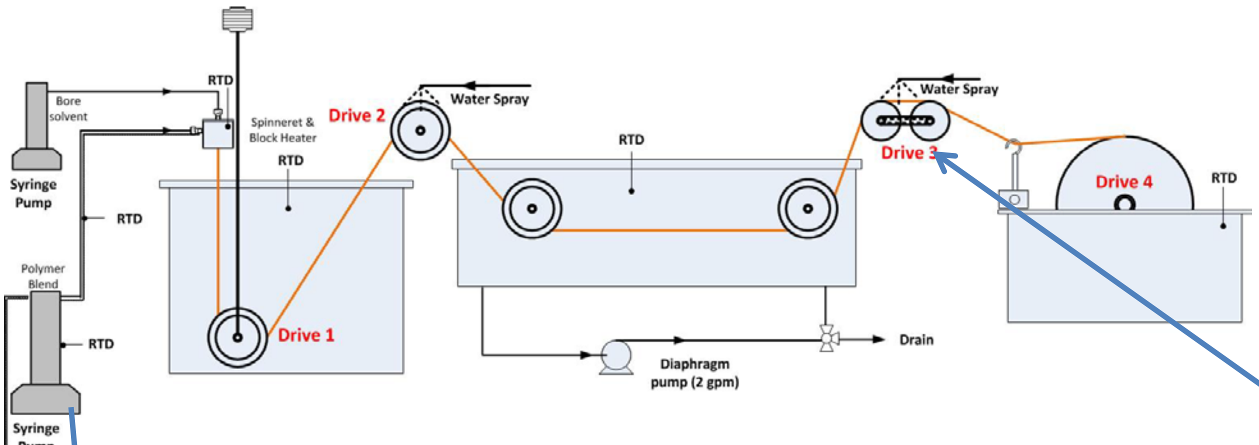
Progress of Current Program

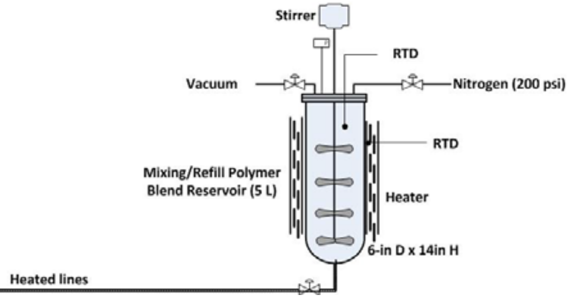
Project Tasks

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	Ongoing Ship by Oct. 2016	On track
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	Tests to begin in Nov. 2016	
5 & 6	2	• Process techno-economic analysis (TEA) for ~550 MWe Plant • Environmental health and safety (EH&S) analysis	Initiated	
7	2	Decommission the system		

Critical Challenge: Transfer of custom spinning procedures to standard industry spinning lines

New Spinning Line at SRI
(Installed in 2015)





Dope from
PBI Performance Products

Photograph of Drive 3

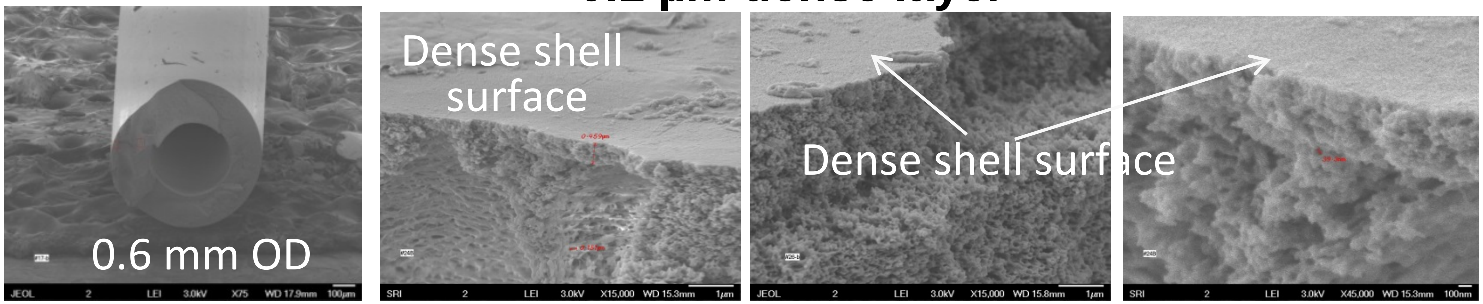
The new spinning line was crucial for developing an improved and robust spinning process that can be transferred to industry.

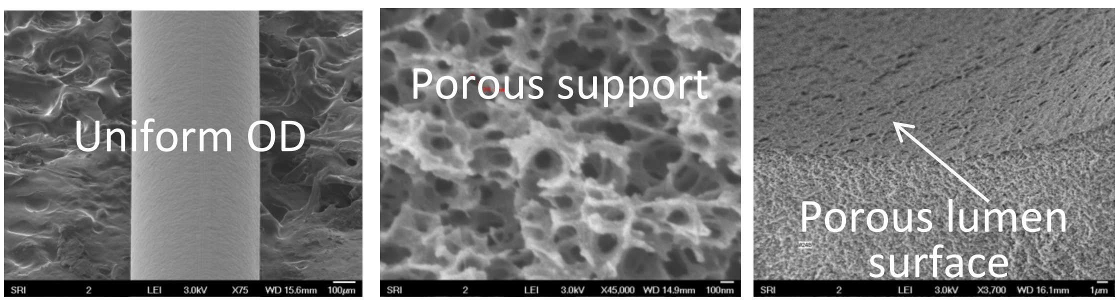
The new line enabled

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

Scaling-Up: Consistent Fiber a MUST

~ 0.1 μm dense layer



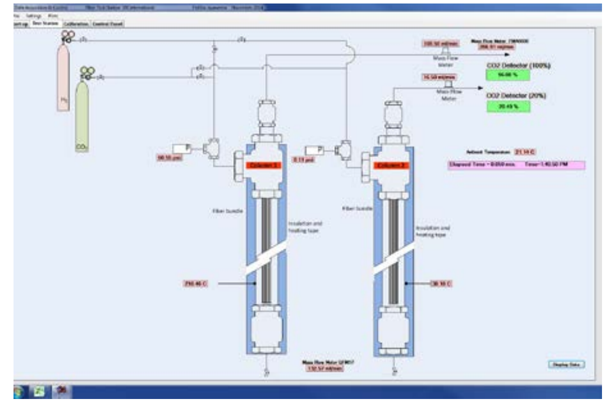


Main Focus:
Quality Control the KEY to scaling-up

- **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.**
- **Fabrication of 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 1-in fiber bundles for fiber-spinning optimization**
- **Spun > 50 km of fiber for both Generon and SRI modules**

Screening Fibers for Consistency

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

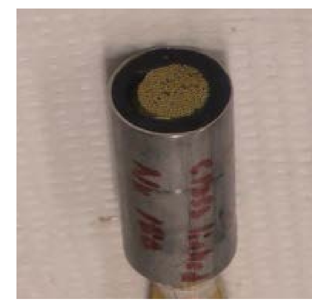


Data acquisition

Feed gas

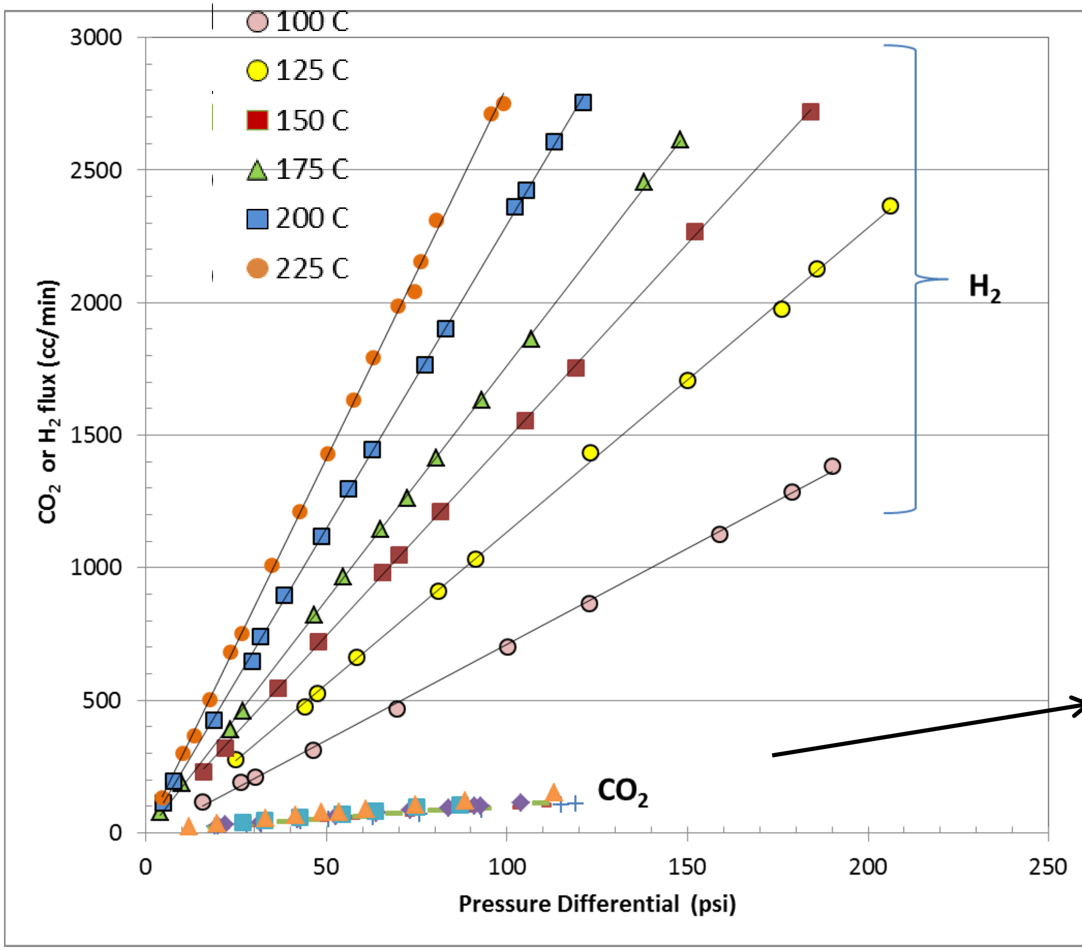
- Single :CO_2, H_2,CO and N_2
- Mixtures: CO_2/H_2, $CO_2/H_2/N_2$, $CO_2/H_2/CO$ and $CO_2/H_2/CO/N_2$
- Parameters varied: T, ΔP, composition, stage cut

Mixed gas analyzer



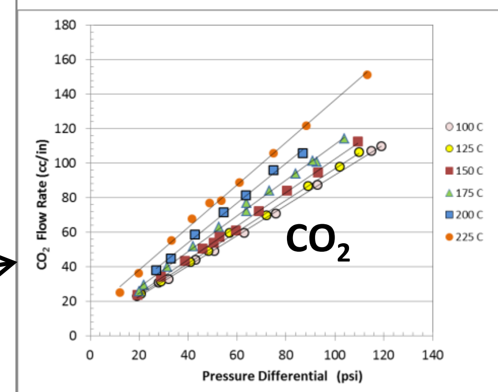
Samples:
Potted fiber bundles with 14” to18” in length, 100 fibers, and high packing density

PBI Fiber Withstands High Pressures and High Temperatures



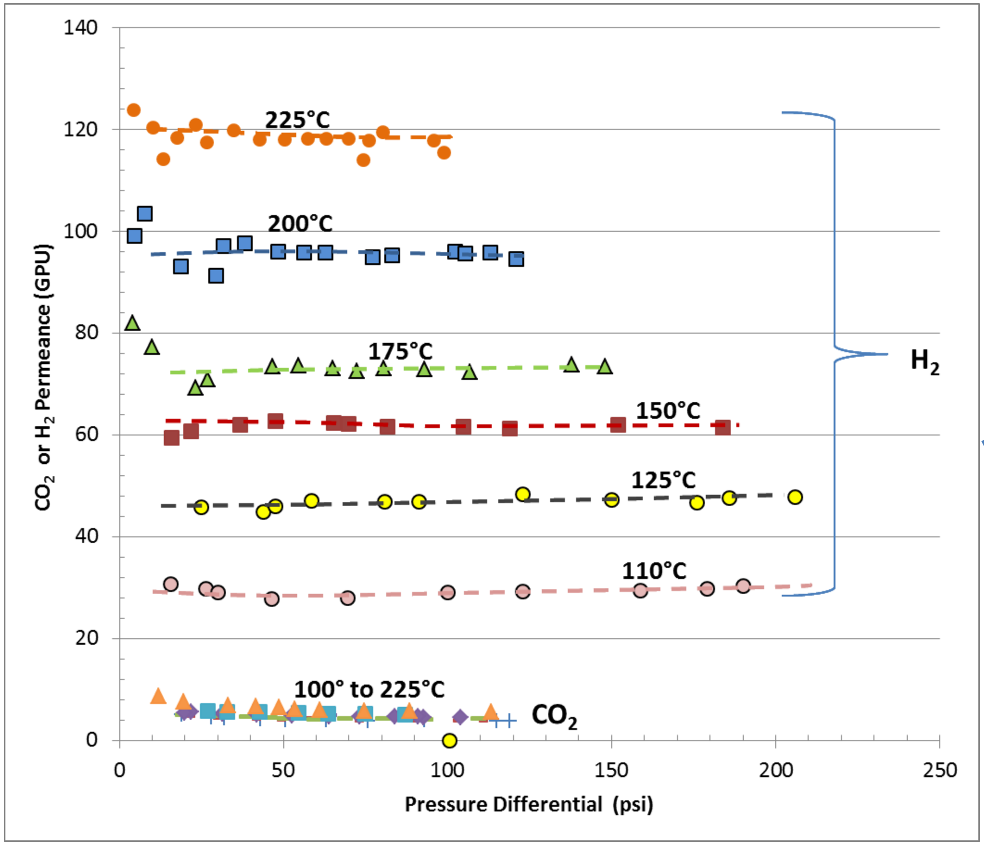
Mixed-gases

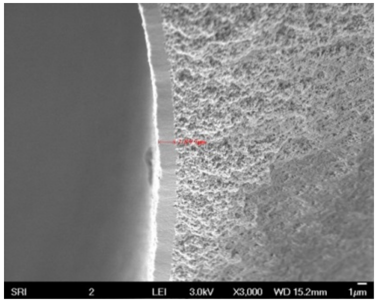
	Selectivity
H_2/CO_2	40
H_2/N_2	98
H_2/CO	103
H_2/H_2S	>200
225 ˚C and 200 psi ΔP	



Demonstrating Consistency and Operability:
<0.3 µm dense layer can operate at temperatures and pressures required

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

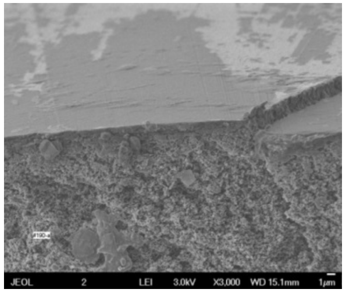




Dense layer ~ 2 µm

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

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

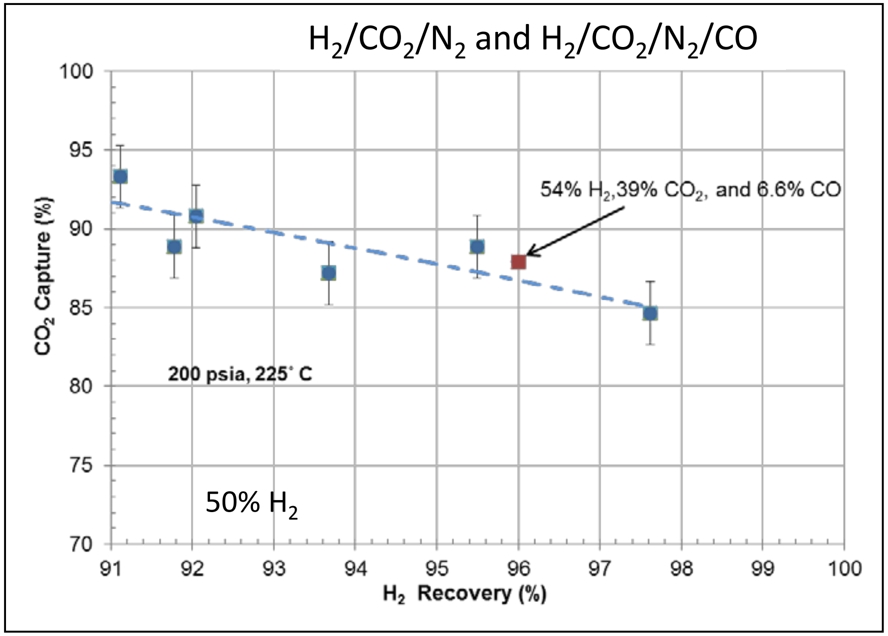


Dense layer ≤ 0.3 µm

H_2/CO_2 selectivity = 22 ±2
H_2 permeance = 120 GPU

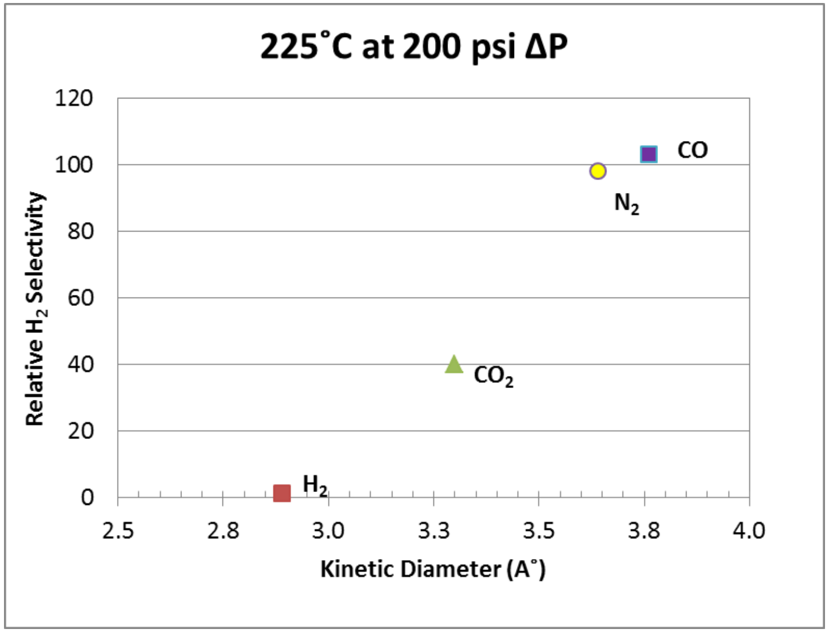
Performance monitored over a 3-month period with the HFM exposed to pressure swings of 1 to 15 atm and temperature swings of 20 to 225 °C.

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)

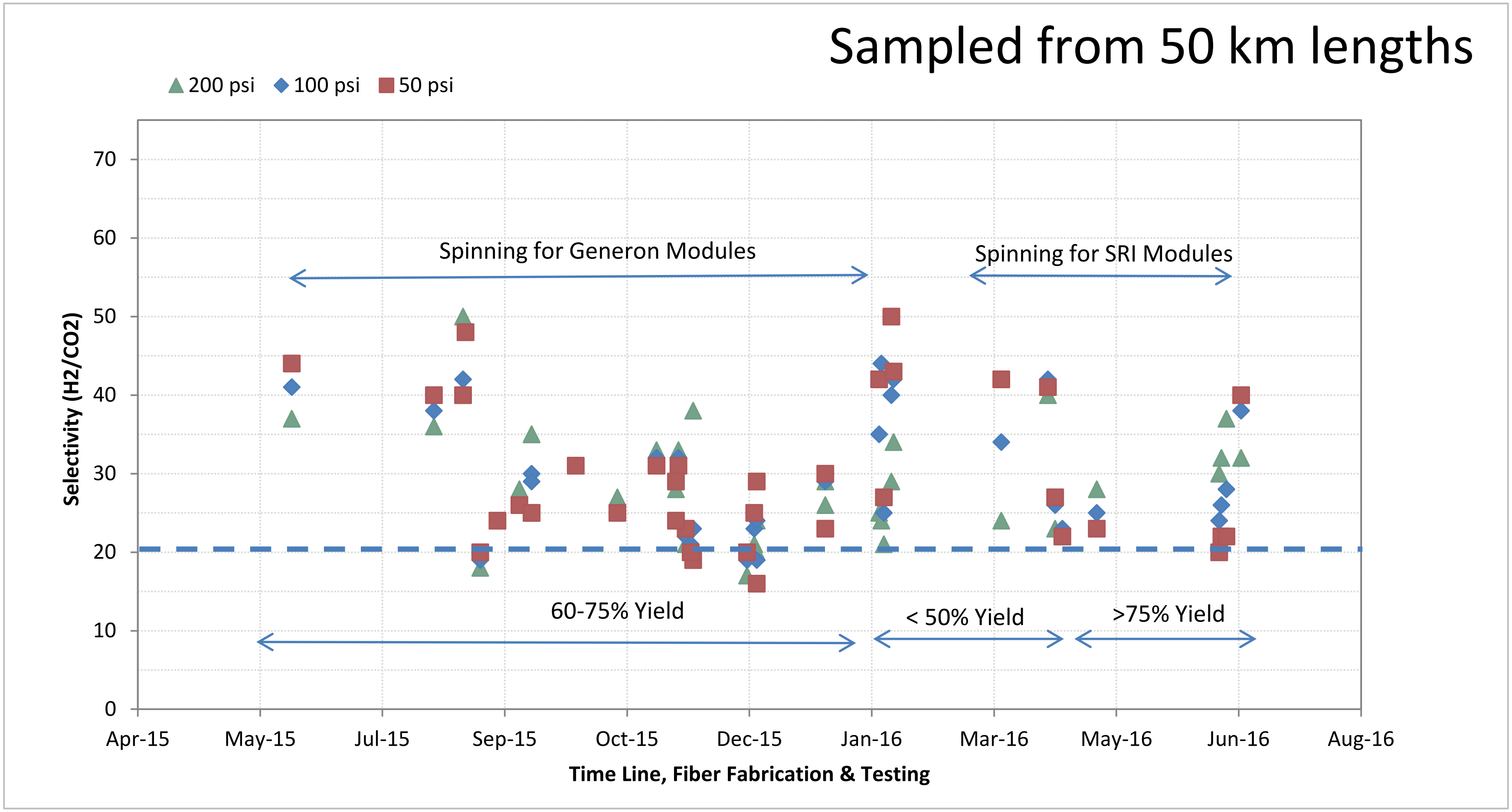


Relationship between H_2 separation factor and the kinetic diameter of the component gases.

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

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

Excellent Performance from Test Modules



Expected Average selectivity H_2/CO_2 from large-scale modules is closer to 30

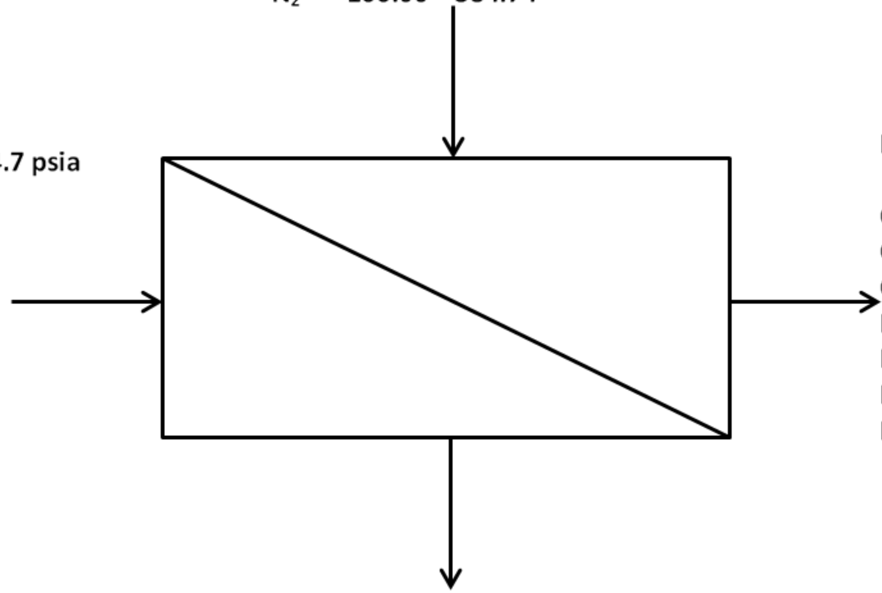
Simulation Results Look Good

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

Fabrication of Large Modules: 2-in, 4-in Modules (Generon modules)

Protoype 2-in module

Trimmed cross-section

Actual 4-in module assembling at Generon (8/6/2016)

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**
  - **Generon modules are expected in September 2016**

Fabrication of Large Modules (SRI modules)

~8,000 fibers

~6.5 m^2

Sufficient fiber for a single module fabrication

Fabrication of Large Modules : 2-in, 4-in SRI Modules (Continued)

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

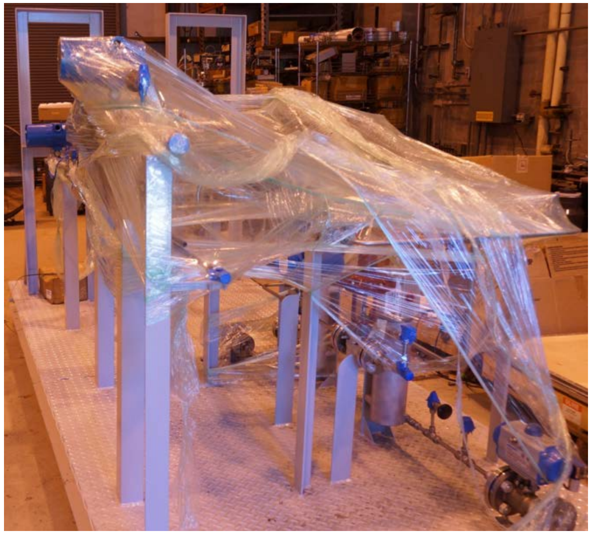
SRI fiber modules are designed for:

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

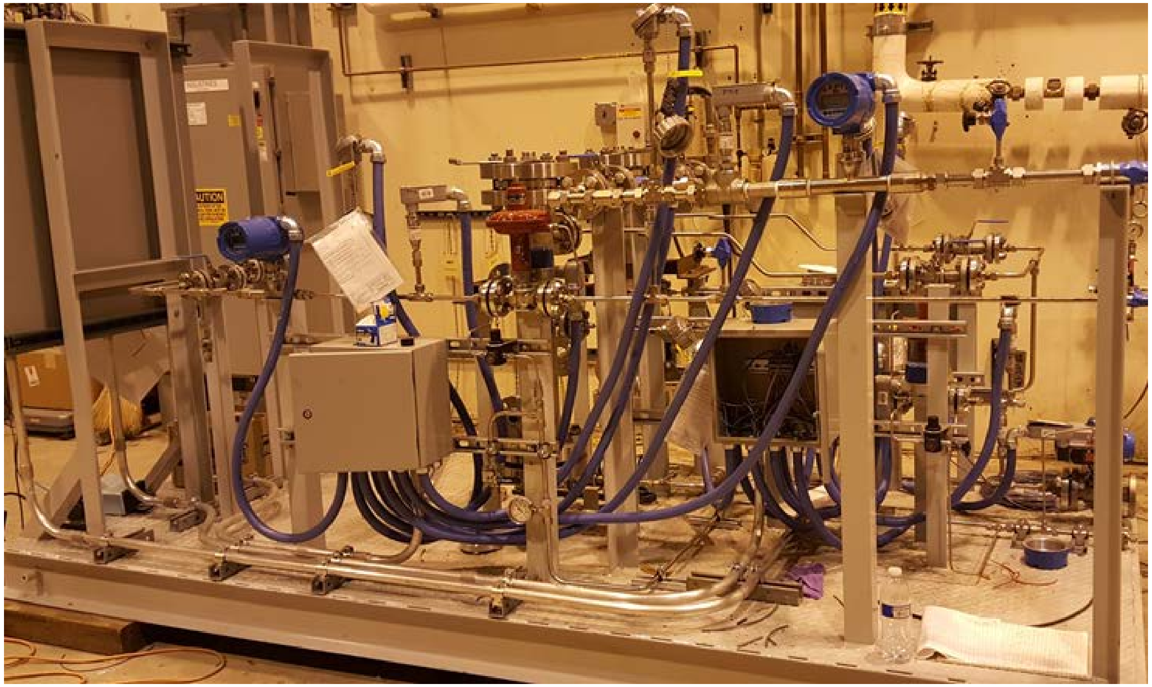
Preparing for NCCC Testing

Test unit (50 kW_{th}) installation and commissioning at NCCC

- Installation of the test unit at NCCC
- Short-term and longer-duration testing (225 °C, ~ 200 psi)

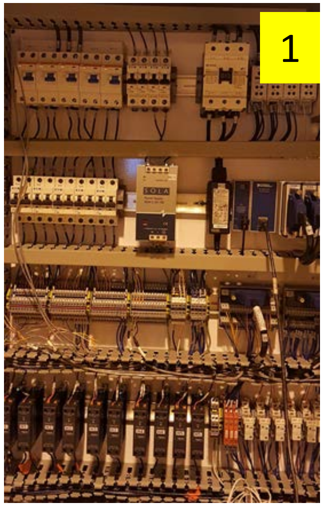


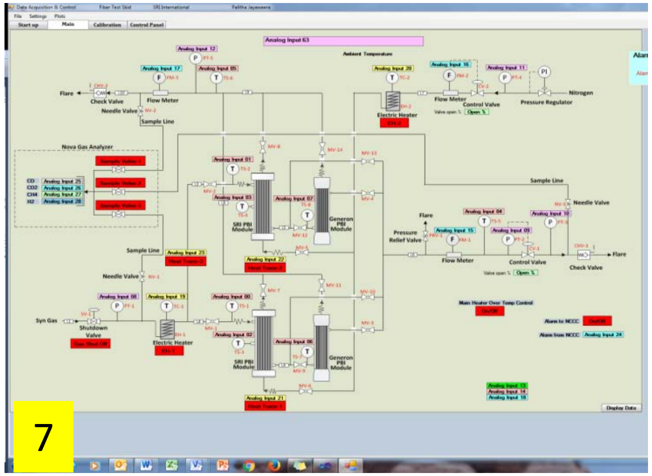
Skid as arrived (February 2016)



Electronic components installation in June 2016

Membrane Skid for NCCC



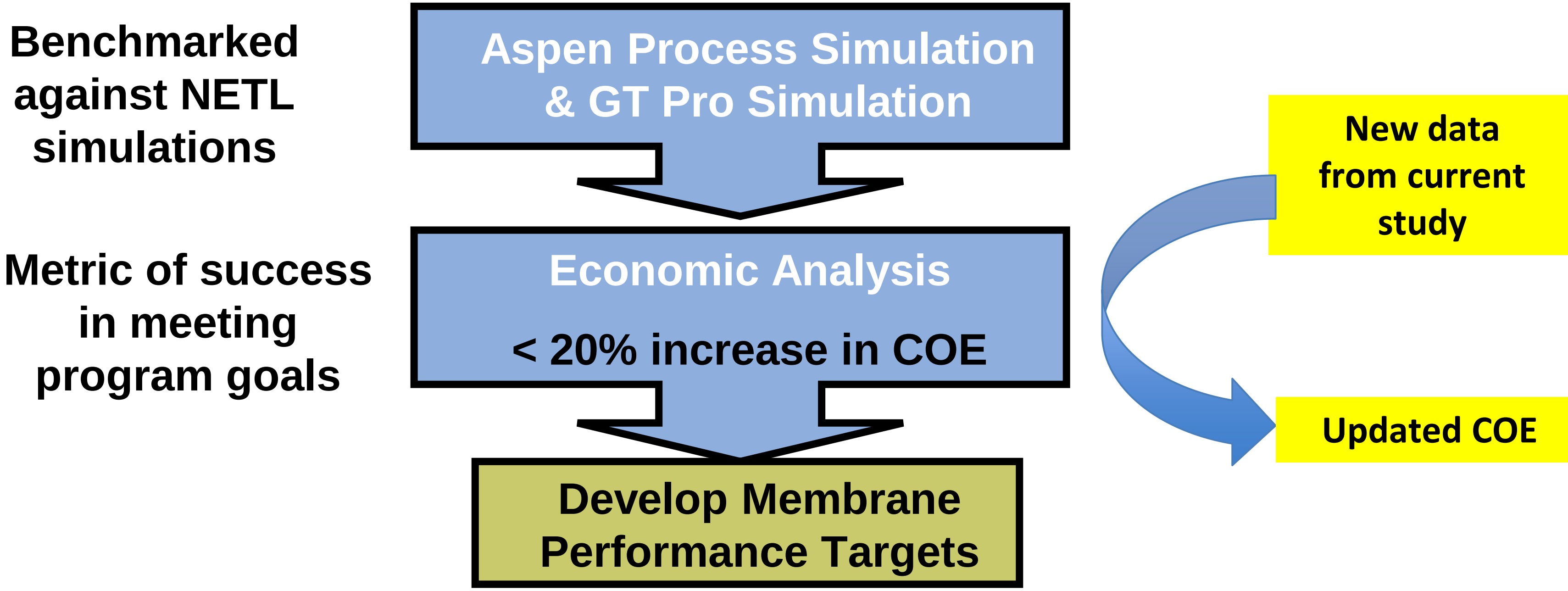


Selected Skid Components

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 will be commissioned shortly at SRI and moved to NCCC in October for testing with Syngas in November 2016.

Process Economics



Process design and engineering study:

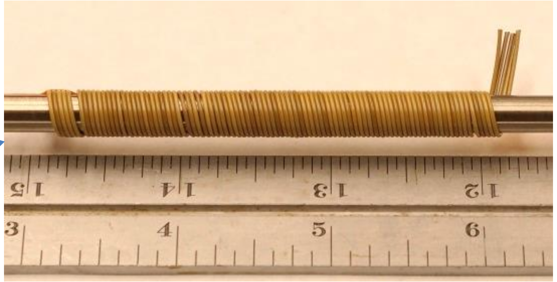
- Determine how the high temperature hollow-fiber PBI membrane process concept would be if incorporated into a nominal 550-MWe gasification-based power plant with CCS.
- Use an IGCC process based on a GE-oxygen-blown gasifier and selexol-based CO_2 removal as the base case.
- Perform the work in collaboration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

The preliminary estimations show that the CO_2 capture cost for combined process would be ~ \$39 /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 modules (1-in) 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 is fabricated
  - System shakedown testing at SRI August 2016 to September 2016.
  - System Installation at NCCC site October 2016
  - System testing to start in November 2016.

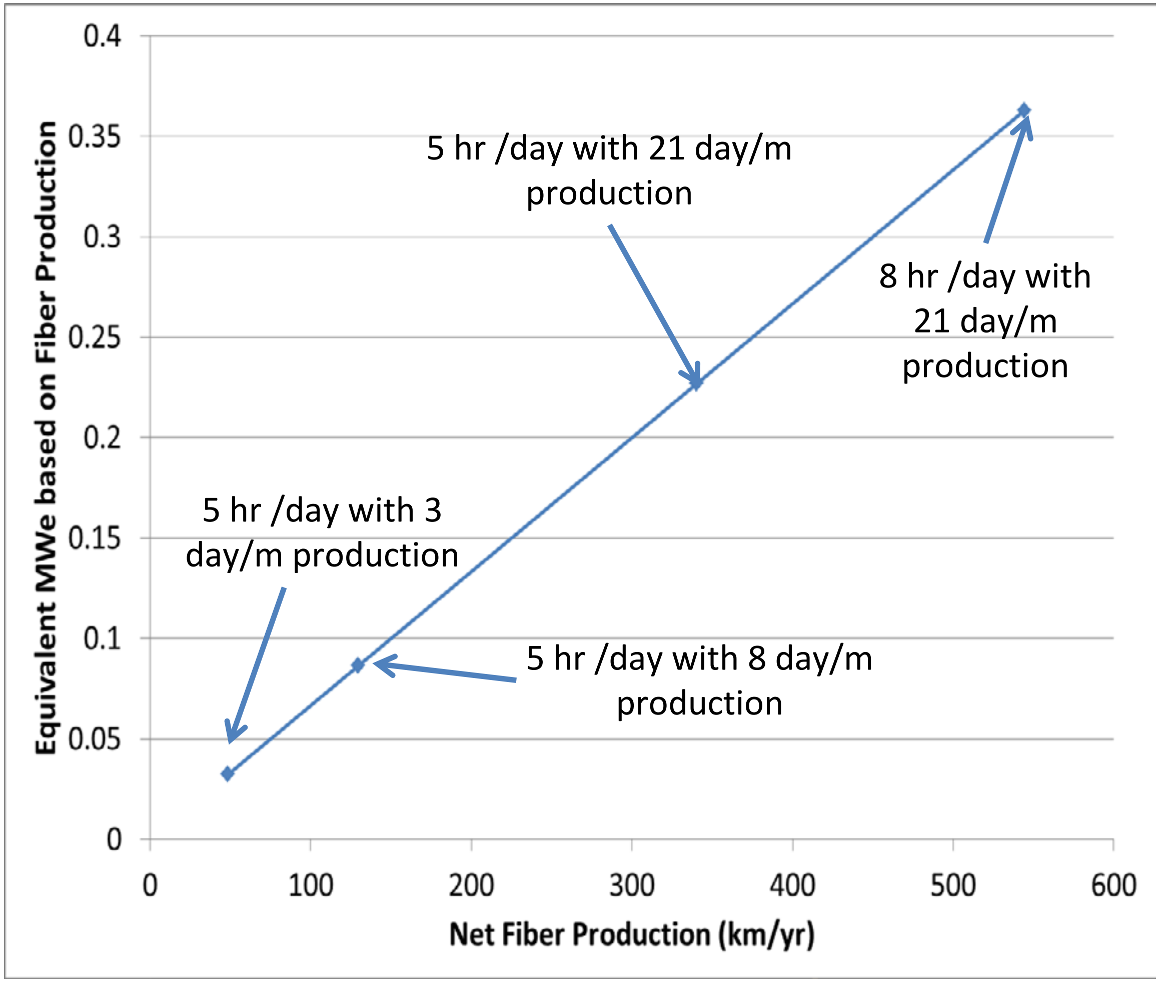
More than 100 km of fiber was fabricated under the current program, and the fibers are tough enough for a "real world" environment. More flexible than ceramic / metallic alternatives



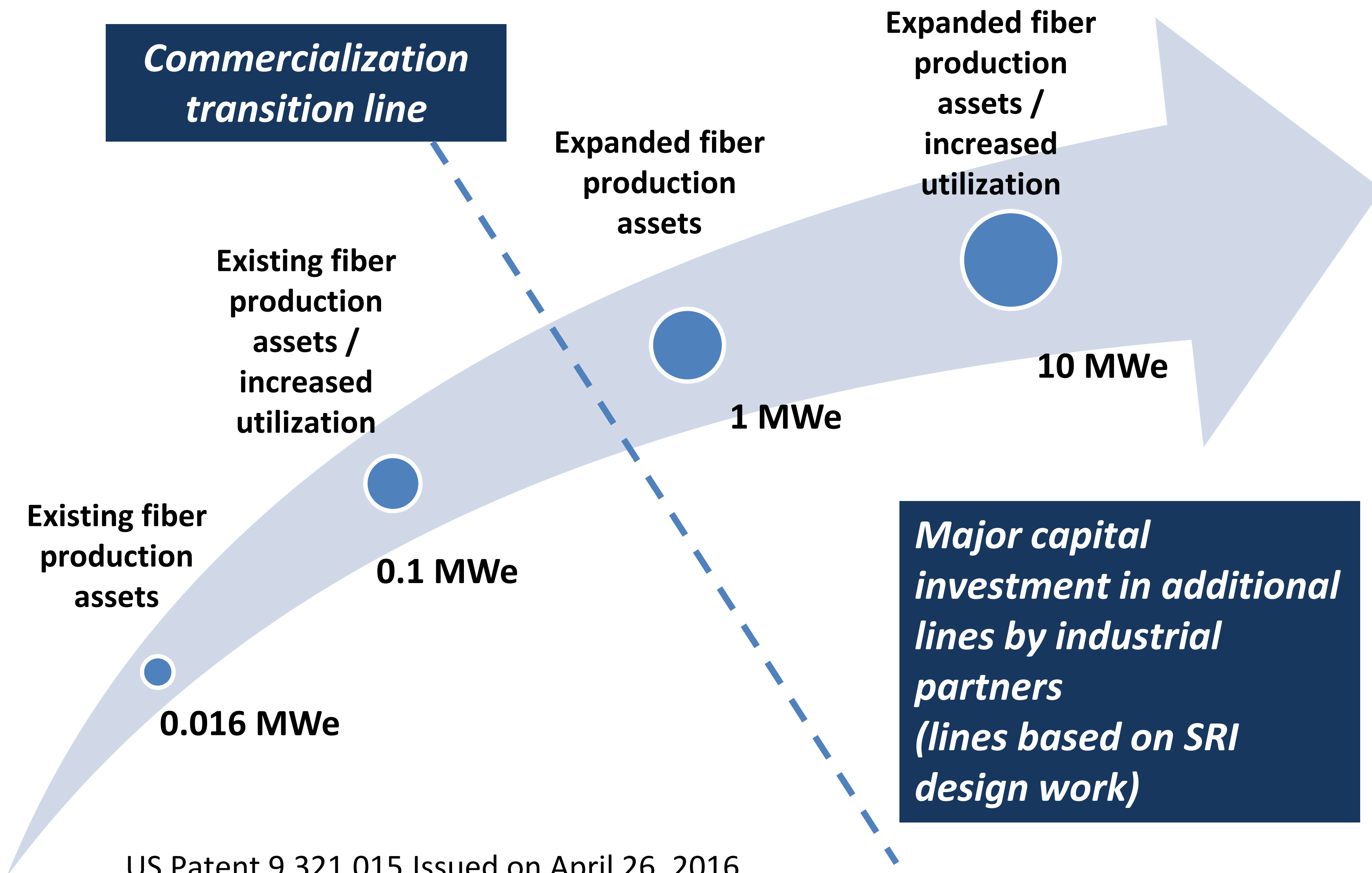
Fiber withstanding ¼-in Mandrel Test

Beyond 50 kW_{th} (0.016 MW_e) - Existing Fiber Production Capacity Analysis

- Fiber production capacity analysis based on two (2) existing fiber production lines
- Run rates of 3-5 m/min
- Yield assumed to be 75%
- Look to increase run hours /day
- Look to increase production days /month
- Maintain one shift



The Road to Small and Large Pilots



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

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- 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)
- Staff at NCCC

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