Session: Pre-Combustion Capture Projects

Development of Pre-Combustion CO$_2$ Capture Process Using High-Temperature PBI Hollow-Fiber Membranes

Indira S. Jayaweera
Sr. Staff Scientist and CO$_2$ Program Leader
SRI International

June 23-June 26, 2015 • Sheraton Station Square • Pittsburgh, Pennsylvania
Project Overview and Technology Background
Why the High-Temperature Membrane Separation of CO₂?

Advantages of Membrane-Based Separation
- No need to cool syngas
- Reduced CO₂ compression costs
- Emission free, i.e., no solvents
- Decreased capital costs
- Low maintenance

Characteristics of PBI Membranes
- PBI has 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

Note: PBI hollow fiber membrane (HFM) is a H₂O and H₂ transporting membrane
Project Overview

- Cooperative agreement grant with U.S. DOE-NETL
- 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:
  - Ms. Elaine Everitt
Objectives

Program Objective:
To develop polybenzimidazole (PBI) membrane-based H₂/CO₂ 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% CO₂ capture rate at a cost of $40/tonne of CO₂ captured by 2025.

Project Objectives:
Obtain sufficient *bench-scale data* for high-temperature PBI polymer membrane separation of pre-combustion syngas to H₂-rich and CO₂-rich components. Utilize the data to evaluate the technical and economic viability of PBI-based membrane separation system to achieve NETL’s Capture Program Performance Goals.
### Approach

<table>
<thead>
<tr>
<th>Task #</th>
<th>BP</th>
<th>Task</th>
<th>Status</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 &amp; 2</td>
<td>Project management</td>
<td>On-Going</td>
<td>On-track</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>- Advanced development of asymmetric hollow fiber spinning</td>
<td>On-Going</td>
<td>On-track</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Spinning defect-minimized fibers at km lengths</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Assembling of multi-fiber modules 1-in, 2-in, 4-in modules</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Installation of sub-scale fiber module test unit in laboratory</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Conduct laboratory tests to generate parametric performance test database</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Modeling of membrane performance</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Technology transfer to initiate industrial scale fiber spinning</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Design modification of the 50-kWth skid design to house commercial membrane modules</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>Modification of the 50-kWth test unit and installation at NCCC for the field tests</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>Test the skid in a field setting using 50-lb/hr syngas stream from the gasifier at the NCCC and measure membrane performance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 &amp; 6</td>
<td>2</td>
<td>- Process technoeconomic analysis (TEA) for ~550 MWe Plant;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Environmental health and safety (EH&amp;S) analysis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>Decommission the system</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Critical Challenge:**

*Adapting spinning procedures used for fabricating standard polymeric hollow-fiber membranes to this high-temperature polymer*
Required membrane architecture for gas separation

- Thin dense layer for gas separation
- Porous support for structural strength to stand high pressures

**Composite membrane**
- Membrane dense layer and porous layer are two different materials (e.g., polymer on porous metal)
  - **Benefits**
    - Ideal for proof of concept
  - **Limitations**
    - High cost of materials
    - Large footprint
    - Limited permeation

**Asymmetric integral structure**
- Fiber is made of one material
  - **Benefits**
    - Low cost
    - Small footprint
    - Easy system scale up
  - **Challenges**
    - Longer fiber-development time
- Development of PBI polymer membrane to replace the original concept that used the PBI-coated porous stainless steel tubes.

- Development of new PBI formulation, installation of a spinning line, and defect free fiber spinning with ~1 μm dense layer (process patent pending).

**Fibers Developed Under Previous DOE Program**

**Shell side**

**Lumen side**

**Porous support**

**Porous lumen surface**

**Dense layer**

**Shell surface**

- Membrane stability over 1000 hr was demonstrated.

- H₂/CO₂ selectivities and their permanence data established for 1-μm dense layer.

**Measured H₂/CO₂ selectivity and H₂ permeance at 225°C for over 1000 hr.**

**High-temperature/high-pressure PBI membrane performance for H₂ separation from syngas**

- **Selectivity** = 40

A significant achievement in fiber development was made under DE-FC26-07NE43090
Progress and Current Status
Installation of the second spinning line ~ 1 km/day capacity

Original Spinning System

SRI-formulated dope made from commercial PBI (available from PBI Performance Products, Inc.)

Second Spinning System

Main Focus: Quality Control
Fiber Spinning

Installation of the second spinning line ~ 1 km/day capacity

Scratch on the fiber surface showing the dense layer and the open porous support structure underneath

SRI-formulated dope made from commercial PBI (available from PBI Performance Products, Inc.)

Main Focus: Quality Control
We have developed protocols for spinning < 0.3 μm micron dense layer hollow fiber membranes with membrane OD 450 to 650 μm. Pictures shown are for ~ 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 very good reproducibility

Testing of over 30 1-in fiber bundles for fiber spinning optimization

Spinning (>30 km) and shipping of ~ 10 km of fiber to Generon to fabricating a 2-in module for initial testing of the prototype skid
Fiber Performance Testing

Prototype test unit setup at SRI site
~ 1 kW_{th} capacity (~ 0.16 m^2 fiber surface area)

- Single gases tested: CO_2, H_2, CO and N_2
- Gas mixtures tested: 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

Data acquisition

Feed gas

Potted fiber bundles with 14-in length, 100 fibers, and high packing density
Gas Permeation Results from Single Gas Testing: Effect of Temperature and Pressure

Measured permeance of H₂ and CO₂ through a <0.3 µm dense layer fiber bundle as a function of temperature and differential pressure.

Measured permeance of H₂ and CO₂ through a <0.3 µm dense layer fiber bundle as a function of temperature and differential pressure.
Single-Gas Testing: Effect of Temperature and Pressure

Measured permeance of $\text{H}_2$ and $\text{CO}_2$ through a < 0.3 µm dense layer fiber bundle as a function of temperature and differential pressure. Permeate side at 1 bar

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

Performance monitored over a three-month period with the HFM exposed to pressure swing at 1 to 15 atm; and temperature swing at 20 °C to 225 °C.

H$_2$/CO$_2$ selectivity = 40
H$_2$/N$_2$ selectivity = 98
H$_2$/CO selectivity = 103
H$_2$/H$_2$S selectivity > 200*

H$_2$/CO$_2$ selectivity = 22 ±2
H$_2$ permeance = 120 GPU
$E_{\text{H}_2} = 16.1 \text{ kJ/mol}$

Dense layer ~ 2 µm

Dense layer ≤ 0.3 µm

* Previous work
Mixed-Gas Testing: Effect of CO$_2$ concentration

H$_2$ and CO$_2$

H$_2$ recovery and CO$_2$ capture at varying CO$_2$/H$_2$ compositions at 225°C and at a ΔP of 200 psi (H$_2$/CO$_2$ selectivity = ~40)

Observation: >95% H$_2$ recovery is possible without a cascade
Mixed-Gas Testing: Effect of Selectivity

H₂/CO₂/N₂ Mixture

H₂ recovery and CO₂ capture at 225°C and at a ΔP value of 200 psi (stage cut > 0.5)

Observation:
It is challenging to capture >90% CO₂ at high H₂ recoveries (>95%) with a single element.
Fabrication of Large Modules: 2-in Module

A protocol was developed for potting PBI HFM without dry spots

The method was tested using SRI fibers (1 m²)

SRI plan to evaluate the performance with H₂O/N₂ mixtures

Prototype 2-in module

SRI spun fibers (~ 5 km shown)

2-in module cross-section

Actual 2-in module
Accomplishments in fiber spinning at SRI have revealed:
- Ways to produce defect-free fibers
- Best use of analytical techniques to determine the trace levels of solvent left in the fibers
- New coagulant for industrial setting

Accomplishments in fiber spinning at Generon:
- Fabricated 150-200 micron OD, 75-100 micron ID, and macro-void free fibers
  - Currently improving the fiber porosity

Accomplishments in fiber module fabrication at Generon:
- Fabricated a 2-in module using SRI fibers
- Completed 4-in module design

Accomplishments in fiber spinning at PBI Performance:
- Produced new formulations for SRI specification in support of Generon and SRI fiber spinning

Lesson learned: Implementation of the spinning technology in an industrial setting requires considerable time.
PBI HFMs can be produced at km lengths with minimum defects.

Upper limit for $\text{H}_2/\text{CO}_2$ selectivity is $\sim 40$.

Practical $\text{H}_2/\text{CO}_2$ selectivity for laboratory-scale spun fibers is 20-25 with shell-side dense layer.

Membrane test systems reach steady-state operation very rapidly (within few minutes).

50 kW$_{\text{th}}$ skid design completed and fabrication contracted
  - Fabrication will be completed in BP2

SRI PBI HFM: ¼-in Mandrel Test
Transition from smaller-module to larger-module testing

### BP1 / BP2

<table>
<thead>
<tr>
<th>Module Size</th>
<th>Budget Period</th>
<th>Fiber Supplier/ Module Supplier</th>
<th>Test Site</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-in x 12-in</td>
<td>BP1 and BP2</td>
<td>SRI/Generon</td>
<td>SRI</td>
</tr>
<tr>
<td>4-in x 20-in*</td>
<td>BP2</td>
<td>SRI/Generon</td>
<td>NCCC (50 MWth)</td>
</tr>
<tr>
<td>6-in x 40-in</td>
<td>BP2</td>
<td>Generon/Generon</td>
<td>NCCC (50 MWth)</td>
</tr>
</tbody>
</table>

#: Module design in BP1, Skid design and fabrication in BP1, Skid update in BP2

PBI Dope Supplier: PBI Performance Products
Future Work

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

- Process safety review and Hazard/Operability (HazOp) Study
- Installation of the test unit at NCCC
- Short term and longer duration testing (225 °C, ~ 200 psi)
Membrane Performance Simulation for Field Testing

N2 sweep (N2SWP) at 15.1 psia
- %: 100.00
- slpm: 384.74

Feed (WGSGAS) at 214.7 psia
- CO₂: 7.33%, 44.69 slpm
- CO: 0.87%, 5.30 slpm
- CH₄: 0.49%, 2.99 slpm
- N₂: 35.62%, 217.19 slpm
- H₂: 55.48%, 338.28 slpm
- H₂O: 0.21%, 1.28 slpm
- Total: 100.00%, 609.73 slpm

Permeate (H2FL) at 15.0 psia
- CO₂: 0.69%, 4.96 slpm
- CO: 0.03%, 0.19 slpm
- CH₄: 0.01%, 0.05 slpm
- N₂: 0.37%, 2.63 slpm
- H₂: 44.95%, 321.73 slpm
- H₂O: 0.17%, 1.23 slpm
- N2 SWP: 53.78%, 384.74 slpm
- Total: 100.00%, 715.53 slpm

Retentate (CO2CAP) at 210.9 psia
- CO₂: 14.25%, 39.73 slpm
- CO: 1.83%, 5.12 slpm
- CH₄: 1.05%, 2.93 slpm
- N₂: 76.92%, 214.56 slpm
- H₂: 5.93%, 16.55 slpm
- H₂O: 0.02%, 0.05 slpm
- Total: 100.00%, 278.94 slpm

Membrane parameters
- H₂ Permeance = 120 GPU
- H₂/CO₂ Selectivity = 25
- Dense layer thickness = 0.3
- Membrane area = 14.6 m²

89% CO₂ Capture
95% H₂ Recovery
Future Work (continued)

**Process design and engineering study:**

- Determine how the high temperature hollow-fiber PBI membrane process concept would be incorporated into a nominal 550-MWe gasification-based power plant with CCUS.
- Use an IGCC process based on a GE-oxygen-blown gasifier and Selexol-based CO₂ removal as the base case.
- Perform the work in collaboration with EPRI.

The preliminary estimations show that the CO₂ capture cost for combined process would be ~ $39/tonne of CO₂ captured compared to $52/tonne of CO₂ captured for IGCC with the baseline technology, Selexol.

**Benchmarked against NETL simulations**

**Aspen Process Simulation & GT Pro Simulation**

**Economic Analysis**

- < 20% increase in COE

**Develop Membrane Performance Targets**

- New data from current study
- Updated COE
Acknowledgements

- Elaine Everitt (NETL)
- SRI Team
- Richard Callahan (Enerfex, Inc.)
- Kevin O’Brien (Energy Commercialization, LLC)
- Greg Copeland (PBI Performance Products)
- Mike Gruende (PBI Performance Products)
- John Jensvold and his team (Generon IGS)
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.
Technical Contact:
Dr. Indira Jayaweera
Sr. Staff Scientist
CO₂ Program Leader
Indira.jayaweera@sri.com
1-650-859-4042

Thank You