High Temperature Polymer-Based Membrane Systems for Pre-Combustion Carbon Dioxide Capture

LANL-FE-308-13

Rajinder P. Singh & Kathryn A. Berchtold
Carbon Capture and Separations for Energy Applications (CaSEA) Labs, Material, Physics and Applications Division, Los Alamos National Laboratory

E. David Huckaby
Computational Sciences Division, NETL

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Collaborators Past & Present on our
High T$_g$ Polymer for Carbon Capture Projects

Los Alamos

Kathryn A. Berchtold
Rajinder P. Singh

Mike Gruender
Greg Copeland
Bobby Dawkins

E. David Huckaby
David Alman

C. Elaine Everitt
Lynn Brickett
Michael Matuszewski
Robie Lewis
José D. Figueroa
Jared Ciferno
John Marano

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Project Summary

- **Award Name:**
  - Polymer-Based Carbon Dioxide Capture Membrane Systems

- **Award Number:**
  - FE-308-13

- **Performance Period:**
  - 03/2013-08/2016

- **Current Budget Period:**
  - BP3 of 3 (04/15-08/16)

- **Project Cost (DOE):**
  - $1,972K

- **DOE NETL Project Manager:**
  - David A. Lang
  - C. Elaine Everitt
Overarching Objective

Development and demonstration of an innovative polymer-based membrane separation technology aimed at improving the economics and performance of hydrogen separation and carbon capture from synthesis (syn) gas, enabling more-efficient and cleaner energy production from coal.
Technology Benefits: Pre-combustion Capture

- Carbon capture in integrated gasification combined cycle power (IGCC) systems
  - Economic outcome of H₂/CO₂ separation system is strongly tied to process and separation operating temperatures
  - High temperature membrane system provides process intensification opportunities in the vicinity of water gas shift reactors and/or as membrane reactor

Membrane Advantages for Pre-combustion Carbon Capture:

- CO₂ produced at higher pressure (reduced compression costs)
- Impurity tolerant – Broadly applicable to all syngas feedstocks
- Reduced footprint (Retrofit considerations)
- Lower parasitic load
- Process temperature matching (Warm fuel gas)
- Emission free, i.e. no hazardous chemical use
- Decreased capital costs
- Continuous facile operation (passive process)
- Low maintenance
Technology Challenges & Opportunities

- Commercial polymer membranes and module manufacture/sealing technologies are limited to \( T_{\text{operation}} \approx 150 \, ^\circ \text{C} \).
  - Separation process economics are strongly tied to process/separation temperature.

- Membrane materials and systems capable of withstanding IGCC syngas process conditions are required.
  - Syngas temperatures (>200 \( ^\circ \text{C} \)) and compositions, including \( \text{H}_2\text{S} \) and steam, present a very challenging operating environment for any separation system.

- Large process gas volumes mandate high membrane permeance.
  - High permeance membranes are achieved via appropriate materials design/selection combined with minimization of the membrane selective layer thickness.
  - Thinner selective layers often result in increased defect formation during fabrication.
  - Defect mitigation strategies/sealing materials utilized for current commercial gas separation membranes are not compatible with the thermal and/or chemical environments present in this application.
  - Thermally and chemically robust defect mitigation strategies must be developed to retain the required membrane selectivity characteristics.
Background: PBI Membranes

- PBI-based membranes have commercially attractive $\text{H}_2/\text{CO}_2$ selectivity, exceptional thermal stability ($T_g > 400$ °C), and exhibit tolerance to steam and $\text{H}_2\text{S}$.

- Broad PBI $T_{\text{operation}}$ (150 to 300+ °C) indicates potential for PBI-based membrane module integration at IGCC relevant process conditions.

- The $\text{H}_2$ permeability of the state-of-the-art PBI-based membrane materials mandates ultra-thin selective layers.

- Economic considerations mandate use of a high surface area membrane deployment platform such as hollow fibers (HFs).

Li, J Membrane Sci 461 (2014)
Berchtold, J Membrane Sci 415 (2012)

- $\sim 250 \text{ m}^2/\text{m}^3$ @ 75% packing density
- $2K–20K+ \text{ m}^2/\text{m}^3$ @ $\leq 75$% packing density
Project Overview

Objectives

- Realize high performance PBI-based HF membranes for pre-combustion hydrogen separation/carbon capture
  - Minimize membrane support costs, maximize membrane flux, retain thermo-mechanical & thermo-chemical stability characteristics, and increase the area density achievable in a commercial module design
  - Produce an asymmetric PBI HF comprised of a thin, dense defect-minimized PBI selective layer and an open, porous underlying support structure with morphology characteristics tailored to optimize transport and mechanical property requirements (use and lifetime).
  - Develop materials and methods to further mitigate defects in ultra-thin selective layers for use under process relevant conditions.
  - Reduce perceived technical risks of utilizing a polymeric membrane based technology in challenging (thermal, chemical, mechanical) syngas environments
Project Focus Areas: Tasks

Hollow Fiber Fabrication
- PBI-based high area density, high permeance membrane development

Sealing Layer Development & Integration
- Membrane defect mitigation materials and methods development

Module Fabrication
- Single and multi-fiber membrane module fabrication
- CFD utilization to aid in membrane and module performance validation and guide module design (with NETL)

Demonstration and Validation of Developed Materials and Methods
<table>
<thead>
<tr>
<th>Milestones/Decision Points M/D</th>
<th>Project Milestones/Deliverables</th>
<th>Planned/Actual Completion Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-1</td>
<td>Demonstrate feasibility of coating sealing layer on hollow fibers</td>
<td>COMPLETE BP1Q1</td>
</tr>
<tr>
<td>M-2</td>
<td>Initiate mixed gas hollow fiber testing under realistic syngas conditions</td>
<td>COMPLETE BP1Q1</td>
</tr>
<tr>
<td>D-1</td>
<td>Demonstrate hollow fiber membrane with pure gas H₂ permeance of at least 150 GPU and H₂/CO₂ selectivity of at least 20 under realistic process conditions</td>
<td>COMPLETE BP1Q3</td>
</tr>
<tr>
<td>M-3</td>
<td>Demonstrate ability to control the selective layer thickness</td>
<td>COMPLETE BP2Q1</td>
</tr>
<tr>
<td>M-4</td>
<td>Demonstrate sealing layer efficacy and composite structure tolerance to syngas operating environments</td>
<td>COMPLETE BP2Q3</td>
</tr>
<tr>
<td>D-2</td>
<td>Demonstrate single hollow fiber membrane with mixed gas H₂ permeance ≥ 250 GPU and H₂/CO₂ selectivity ≥ 25 in simulated syngas environments</td>
<td>COMPLETE BP2Q4</td>
</tr>
<tr>
<td>M-5</td>
<td>Report on stage cut influences on membrane performance and module design optimization and fabrication (with NETL).</td>
<td>COMPLETE BP2Q4</td>
</tr>
<tr>
<td>M-6</td>
<td>Report on multi-fiber membrane module performance in simulated syngas environments</td>
<td>45%</td>
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Hollow Fiber Fabrication & Evaluation
Key Accomplishments: Hollow Fiber Fabrication

- Developed novel methods for PBI hollow fiber membrane
  - **Industrially attractive fabrication process:** Continuous spinning using commercially available polymer and environmentally benign coagulant

- Exceptional fiber characteristics
  - **Macro-void Free:** Interconnected porous support morphology with porous inner surface layer
  - **Selective Layer:** Nearly defect-free selective layer with thickness controllable between 100 and 3000 nm
  - **Robust Manufacturing process:** Repeatability demonstrated by fabricating multiple batch of fiber under same conditions

Provisional Patent filed: June 2015
Non-provisional Patent filed: June 2016
DOE Docket S133262/L2015020
PBI Hollow Fiber: SL Thickness Variation

SEM micrographs - HF shell side – all taken at the same magnification (25kX)
Robust Spinning Process Demonstration

- Demonstrated successful manufacture of multiple batches of our high performance fiber

  - Evaluated fiber manufacturing process reproducibility using the optimized fiber spinning process parameters anticipated for multi-fiber module production
  - Demonstrated consistency of dope preparation and dope stability over extended periods of time (multiple batches of polymer dope produced and used over a 12 month period)
  - Demonstrated manufacturing process robustness
    - Batches produced by multiple operators yielding the same resultant fibers
    - Multiple batches produced yielding nearly identical wall thickness, overarching geometry, and morphology
Key Accomplishment: Defect Sealing Layer

- Developed novel defect-sealing layer materials
- Demonstrated readily scalable methods for deposition of a thin (ca. 200 nm) seal layer on PBI hollow fibers
**Key Accomplishment: Separation Performance**

- Industrially attractive performance with high H$_2$ permeance (50 to 500 GPU) and H$_2$/CO$_2$ (19 to 30) at 250 to 350 °C

- Demonstrated exceptional thermo-chemical robustness
  - Tolerance to CO, steam and H$_2$S at realistic process conditions

![Graph showing H$_2$ Permeance, H$_2$/CO$_2$ Selectivity, H$_2$/N$_2$ Selectivity over time and temperature](image)

- Exceptional thermo-mechanical robustness
  - Fibers tested in simulated syngas at high differential pressure (200 PSI) and 200 to 350 °C

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Multi-Fiber Module Fabrication & Evaluation
Goal: Develop laboratory scale multi-fiber module to enable module design and potting materials & methods assessment at realistic pre-combustion carbon capture conditions

Potting material is a significant challenge for industrial deployment of PBI membrane technology for pre-combustion carbon capture

- Long term hydrothermal stability at process conditions of commercial potting materials (e.g. silicones, epoxies) unknown
- Lab scale modules enables down-selection of a suitable high temperature potting material for long-term evaluation under realistic conditions

Small scale module fabrication has additional challenges including the need for minimization of potting material wicking and defects in the seal ends

- High viscosity potting material desirable to minimize wicking but creates fiber ends encapsulation issues
- High temperature potting materials require extensive heat treatment to minimize shrinkage and mechanical failure due to evolving gases during curing and use
Fabricated laboratory scale PBI multi-fiber modules

- Identified commercial potting material to enable evaluation at elevated temperature
- Optimized fabrication protocol to minimize capillary wicking while achieving defect-free interface between potting material and fibers
- < 0.1%/24 hr weight loss measured for the down-selected potting material at 250 °C in inert conditions.
- Optimized curing and heat-treatment protocols

Good adhesion between fiber and potting material

Pure Gas Evaluation
He/CO₂ ≈ 8.5
Fibers w/o seal Layer
Membrane Simulations
Performance Assessment

- Influence of stage cut on PBI membrane performance simulated using Computation Fluid Dynamic (CFD) model based on single fiber data
  - Stage cut reduces the effective $\text{H}_2$ permeance
  - Difficult to achieve 90% $\text{H}_2$ recovery and 90% carbon capture using single stage membrane operation
  - Additional downstream purification step or improved $\text{H}_2/\text{CO}_2$ selectivity required to meet CCS targets

  * Multi-stage membrane operation further improves performance*
Conclusions & Path Forward

Project Accomplishments:
- Novel methods to spin high permeance, H₂ selective continuous PBI hollow fibers developed
- Membrane defect mitigation materials and methods developed
- Long-term stability of developed PBI hollow fibers demonstrated in simulated syngas environments
- Lab-scale multi-fiber modules developed
- Developed intellectual property protected

Technology Path Forward and Next Phase Efforts:
- Development & Demonstration
  - Demonstration of multi-fiber modules in real syngas at National Carbon Capture Center
  - Need to further improve H₂/CO₂ separation performance to minimize the need for downstream processing
- Scale-up & Commercialization
  - Discussions with industry on-going: next-phase PBI membrane technology development and demonstration planning
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