High Selectivity and Throughput Carbon Molecular Sieve Hollow Fiber Membrane-Based Modular Air Separation Unit for Producing High Purity $O_2$

FE-1049-18-FY19

Rajinder Singh
Materials Physics and Applications Division
Los Alamos National Laboratory

2021 Gasification Project Review Meeting
DOE – Fossil Energy/NETL
May 4th, 2021
Project Overview

Award Name: High Selectivity and Throughput Carbon Molecular Sieve Hollow Fiber Membrane-Based Modular Air Separation Unit for Producing High Purity O₂

Award Number: FE-1049-18-FY19


Project Manager: Venkat K. Venkataraman

Overall Program Goal: Development of high flux polybenzimidazole-derived carbon molecular sieve hollow fiber membranes having O₂/N₂ selectivity > 20 for high purity O₂ production to meet the needs of a modular 1-5 MWe gasification system
Project Tasks & Team Members

Membrane Design, Fabrication and Evaluation
- JongGeun Seong
- Harshul V. Thakkar
- Jeremy C. Lewis
- Erica P. Craddock
- John A. Matteson
- Kathryn A. Berchtold
- Rajinder P. Singh

Process Modeling and Simulations
- Kamron G. Brinkerhoff
- Brendan J. Gifford
- Alexander J. Josephson
- Christopher S. Russell
- Troy M. Holland

Modular System Design
- Todd A. Jankowski

Materials Physics & Applications Division
Theoretical Division
Earth & Environmental Science Division
Engineering Division
DOE Advanced Energy Systems Program

Gasification systems program

- Coal-based power generation with near-zero emissions
- Reduce the cost and increase efficiency exploiting Radically Engineered Modular Systems (REMS) concepts for gasification system
  - Leverage mass production and learning curve in lieu of traditional scale-up

Advanced technology need:

- Energy efficient air separation technology for high purity O₂ production
- Program Targets:
  - 90-95 vol% purity O₂
  - Low cost and operational efficiency relative to the state-of-the-art technology
Air Separations

- Cryogenic distillation is *the* industrially preferred technique for large-scale, high purity O$_2$ production
  - Cryogenic technology is energy inefficient at small scale
  - Scale dependent estimated specific energy consumption 23 to 63 KJ/mol

- Membrane-based air separation processes have advantages over competing technologies
  - Tailorable output stream conditions (T&P) to match downstream process
  - Improved energy economics

Achieving High $O_2$ Purity With Membranes

- A multi-stage membrane process is necessary to achieve high purity $O_2$ with realistically achievable membranes.
- $O_2$ enriched permeate from 1st membrane stage is further purified using additional membrane stages to achieve target $O_2$ purity of 90-95%.
- A 2-stage design enables high $O_2$ purity, but advantages of additional staging and alternative flow configurations are also be explored.

- Inter-stage compression required for driving force.

Multi-stage Membrane Separation Process to Achieve High Purity

O₂ Selective Membrane Materials

Membrane materials: current state-of-the-art

- O₂/N₂ selectivities approaching 30 for polymer-derived carbon molecular sieve (CMS) membranes achieved

References

Membrane Development Approach

Polybenzimidazole (PBI)-derived carbon molecular sieve membranes for high O₂/N₂ selectivity

- Tightly packed PBI molecular structure resulting from H-bonding and π-π stacking imparts molecular sieving character
  - Base polymer (m-PBI) has high selectivity for gas pairs (e.g. H₂/N₂ ≥ 100; O₂/N₂ = 2)

- Further enhancement of molecular sieving properties via controlled pyrolysis proposed to create ultra-micropores
  - PBI pyrolysis preliminary work: O₂/N₂ selectivity increased from 2 to 30

[Ref: S.S. Hosseini et al. / Separation and Purification Technology 122 (2014) 278–289]

Ref: Rungata et al., Carbon 115 (2017) 237-248
Project Objectives

A membrane-based, modular air separation technology for high purity $O_2$ production

- Develop CMS materials derived from PBI materials (PBI-CMS) to achieve the desired material transport characteristics
- Develop PBI-CMS hollow fiber membranes having the desired membrane performance characteristics
- Conduct process design and analysis and techno-economic analysis based on PBI-CMS hollow fiber membranes for air separation and benchmark against the industry standard cryogenic technology
- Design a modular ASU with integrated peripheral equipment (e.g., blower, vacuum pump, compressor) for high purity $O_2$ production scaled to meet the needs of a 1-5 MWe gasification system
# Project Timeline (BP – 3)

<table>
<thead>
<tr>
<th>Task</th>
<th>Start Date</th>
<th>End Date</th>
<th>BP1</th>
<th>Q1</th>
<th>Q2</th>
<th>Q3</th>
<th>Q4</th>
<th>BP2</th>
<th>Q1</th>
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<th>Q2</th>
<th>Q3</th>
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<td>Task 2.0 - PBI-CMS Hollow Fiber Membrane</td>
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<td>12/15/18</td>
<td>03/30/20</td>
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<td>Task 5.0 - Modular System Design</td>
<td>10/01/22</td>
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# Project Milestones & Success Criteria Point (BP – 3)

<table>
<thead>
<tr>
<th>FY</th>
<th>ID</th>
<th>Task #</th>
<th>Description</th>
<th>Planned Completion Date</th>
<th>Status</th>
<th>Verification Method</th>
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<tbody>
<tr>
<td>3</td>
<td>M9</td>
<td>2.0</td>
<td>Set-up a flowing gas pyrolysis system for PBI membrane pyrolysis.</td>
<td>09/30/21</td>
<td>Finished set-up</td>
<td>Membrane performance data</td>
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<td>3</td>
<td>M10</td>
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<td>Develop $O_2$ permeance and $O_2/N_2$ selectivity correlations as a function of selective layer thickness and fabrication process parameters.</td>
<td>11/30/21</td>
<td>In progress</td>
<td>Membrane performance data</td>
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<td>3</td>
<td>M11</td>
<td>3.0</td>
<td>Performance evaluation of PBI-CMS HFMs in realistic air feed mixtures containing $CO_2$, $H_2O$ and $Ar$</td>
<td>11/30/21</td>
<td>In progress</td>
<td>Membrane performance data</td>
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<tr>
<td>3</td>
<td>M12</td>
<td>4.0</td>
<td>Complete the preliminary techno-economic analysis of the 2-stage membrane process and report on the $O_2$ production cost ($/ton)</td>
<td>09/30/21</td>
<td>In process</td>
<td>Report file</td>
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<table>
<thead>
<tr>
<th>No</th>
<th>Decision point</th>
<th>Success Criteria</th>
<th>Date</th>
<th>Outcome</th>
</tr>
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<tbody>
<tr>
<td>4</td>
<td>Go/No-Go for the optimized PBI-CMS hollow fiber membranes</td>
<td>Determine the feasibility of achieving PBI-CMS hollow fiber membranes with high $O_2$ permeance (100 GPU) while maintaining $O_2/N_2$ selectivity of 15 as demonstrated by the membrane fabrication parameter-structure-performance correlations.</td>
<td>11/30/21</td>
<td>In progress; Demonstrated $O_2$ permeance ~72 GPU and $O_2/N_2$ selectivity ~11</td>
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</table>
Membrane Material & Hollow Fiber Development
CMS membrane formation is a multi-step process influenced by numerous membrane formation parameters. Polymer derived CMS membranes are produced through a process that involves PBI polymer, thin-film hollow fibers, base polymer membranes, pyrolysis, and CMS membranes. The characteristics of the polymers include molecular weight, main chain modifications, side chain functionalization, and crosslinking. The morphology of the membranes involves selective layer thickness and porous support morphology. The pyrolysis protocol includes pre-treatment, temperature, time, ramp-rate, and atmosphere.
Base Hollow Fiber Membrane Preparation

Base PBI HFMs having asymmetric morphology fabricated utilizing lab-scale liquid-liquid demixing based fiber spinning capability

Pyrolysis conditions have a tremendous influence on the gas separation performance of the polymer derived CMS membranes

- Efforts focused on the development and optimization of PBI pyrolysis protocols

Pyrolysis Parameters
- Temperature (500 to 900 °C)
- Ramp rate and dwell time
- Environment (e.g., inert, vacuum)

Successfully fabricated mechanically robust PBI-CMS membranes in industrially attractive platform
Achieving High Permeance

Challenge: Mitigate HFM porous support structure collapse during pyrolysis

- Achieving high permeance requires asymmetric morphology: Thin selective layer supported with a porous layer
  - Estimated 1 μm thick selective layer of 2nd Generation (Gen) fibers should enable achievement of project target (100 GPU)

1 GPU = 10⁻⁶ cm³ cm⁻² cmHg⁻¹ s⁻¹
Improving Separation Performance

Material chemistry & processing optimization

Integrally asymmetric and dimensionally stable PBI-CMS HFM

Symmetric PBI-CMS HFM

20 μm

O₂/N₂ Selectivity

O₂ Permeance, GPU

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NNSA
Spatially Controlled Morphology Tailored with Performances

- Achieved dimensional stability changed with fabrication parameters
- Induced thinner skin layer down to >0.5 um
- Tunable O₂/N₂ separation performances
Gas Transport Dependence on Operating Pressure

- ~40-fold improvement in gas permeances with comparable selectivity
- Steady Performance as a function of pressure
Gas Transport Dependence on Operating Temperature

- Arrhenius Eqn. except for 40 °C
- $O_2$ permeance of 66 to 87 GPU and $O_2/N_2$ 11 to 5.6
Membrane Modeling and Process Design
Proposed Process Layout

2-stage membrane air separation process for > 90% O₂ production
Process Modeling Platform Development

- Improved hollow fiber membrane process model and expanded capability to calculate process energy consumption

Membrane Flux Model

\[ J_i = \frac{h_i (p_i^R - p_i^S)}{RT} \]

\[ S_h = 0.68 \cdot Re^{1/2}Sc^{1/3} \]

\[ Sh = \frac{h_i x}{D_i} \]

\[ \mathbf{P}_i = A_i \exp \left( \frac{-E_{A,i}}{R_{gas}T} \right) \]

- Membrane module optimization to minimize parastatic energy losses

Graph showing the relationship between bore pressure drop and fibre outer diameter, with productivity (equivalent pure O₂) and oxygen concentration over fibre outer diameter.
Process Energy Consumption Optimization

- Rigorous analysis of process parameters and membrane module design to minimize process energy consumption

![Graphs showing energy consumption and recovery vs. membrane surface density and feed pressure](image-url)
Energy Consumption

Revised specific energy consumption calculation

- 40 to 45 KJ/mol O$_2$ for 90 to 95% purity O$_2$ achievable with demonstrated PBI-CMS HFMs having O$_2$/N$_2$ selectivity of 10 to 20
Techno-economic Analysis – Design Basis Developed

**Process parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Input values</th>
</tr>
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<tbody>
<tr>
<td>O₂ Production Rate, TPD</td>
<td>10</td>
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<tr>
<td>Number of Membrane Stages</td>
<td>2</td>
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<tr>
<td>Inlet volume of air, Kg/s</td>
<td>1-3</td>
</tr>
<tr>
<td>Pressure of inlet air, bar</td>
<td>1.01 to 1.20</td>
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<tr>
<td>Temperature Stage-1 and stage-2, °C</td>
<td>25 &amp; 5</td>
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<td>Hours of operation per year</td>
<td>7884</td>
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<td>Pressure ratio</td>
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<td>Membrane effective thickness, µm</td>
<td>0.3 to 1</td>
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<td>O₂ purity (%) at Stage-1 and Stage-2</td>
<td>60-65, 90-95</td>
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<td>Pump efficiency, % and temperature, °C</td>
<td>40-64, 15</td>
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<td>Membrane installation factor</td>
<td>0.35-0.45</td>
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<td>Electricity cost, $/MWh</td>
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**Membrane module**

<table>
<thead>
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<td>HF Diameter, µm</td>
<td>300-500</td>
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<tr>
<td>Wall Thickness, µm</td>
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<tr>
<td>Selective Layer Thickness, µm</td>
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<td>O₂ permeance, GPU</td>
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<td>O₂/N₂ selectivity of the membrane</td>
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<td>Module Diameter, m</td>
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<td>Module Length, m</td>
<td>1-3</td>
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<td>Surface Area Density, m²/m³</td>
<td>3000</td>
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<td>Area Ratio Stage 1/Stage 2</td>
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<td>Membrane cost, $/m²</td>
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**Preliminary Estimates (Best Case Scenarios)**

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<td>Energy Consumption, KJ/mol</td>
<td>33-55</td>
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<td>Production Cost, $/tonne O₂</td>
<td>30-80</td>
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</table>
Performance Benchmarking
Performance Benchmarking

Evaluation of PBI-CMS HFMs in air feed stream

- Influence of water vapor and CO$_2$ on the membrane separation performance

- Lab-scale membrane module
- O$_2$ permeance and selectivity data collection at process relevant operating conditions
  - Feed Pressure: 1-3 bar
  - Temperature: 10 to 100 °C
  - RH: 5 to 90%
- Real-time detection of H$_2$O and CO$_2$
- Benchmark performance data for model validation
- Initiated system and analytical equipment calibration
Mixed gas permeation system schematic for evaluation of PBI-CMS HFMs at process relevant operating conditions

Typical Air Composition

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<tr>
<th>Gas</th>
<th>Concentration</th>
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<td>N\textsubscript{2}</td>
<td>78% (vol. Dry Basis)</td>
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<tr>
<td>O\textsubscript{2}</td>
<td>21%</td>
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<td>Ar</td>
<td>0 to 0.93</td>
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<tr>
<td>CO\textsubscript{2}</td>
<td>0 to 400 ppm</td>
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<tr>
<td>Relative Humidity</td>
<td>10 to 90%</td>
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</table>
**Multi-Fiber Membrane Module**

Laboratory scale PBI-CMS multi-fiber membrane module for air separation performance evaluations at process relevant conditions.

- Multi-fiber cartridge
- 5 PBI-CMS HFM
- Membrane module shell with flow-through on feed and permeate sides
Future Work

.timeline

Membrane Design and Fabrication

- Compare performance of PBI-CMS HFMs fabricated under flowing inert gas (N₂) and vacuum.
- Develop O₂ permeance and O₂/N₂ selectivity correlations as a function of selective layer thickness and fabrication process parameters.

Membrane Evaluation and Performance Benchmarking

- Performance evaluation of PBI-CMS HFMs in realistic air feed mixtures containing CO₂, H₂O and Ar

Techno-economic Analysis

- Complete the preliminary techno-economic analysis of the 2-stage membrane process and report on the O₂ production cost ($/ton)
The outcome of this work will be a next generation membrane platform with processability and scalability characteristics amenable to industrial deployment at a modular scale while enabling low-cost and energy efficient high purity O$_2$ production for advanced gasification power systems.
Acknowledgements

DOE - NETL Gasification Program

- Venkat Venkataraman
- David Lyons

Los Alamos National Laboratory

- MPA, T, EES and E Divisions

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