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 P. Singh
Materials Physics and Applications Division
Los Alamos National Laboratory

2021 Gasification Project Review Meeting
DOE – Fossil Energy/NETL
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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 >15 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

**Division Assignments**
- 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 O₂ production
  - State of the art 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

Ref: Air Products Inc. & Air Liquide Inc.
Achieving High O₂ Purity With Membranes

A multi-stage membrane process is necessary to achieve high purity O₂ with realistically achievable membranes

- O₂ enriched permeate from 1st membrane stage is further purified using additional membrane stages to achieve target O₂ purity of 90-95%
- A 2-stage design enables high O₂ 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 $O_2/N_2$ selectivity

- Tightly packed PBI molecular structure resulting from H-bonding and $\pi-\pi$ stacking imparts molecular sieving character
  - Base polymer ($m$-PBI) has high selectivity for gas pairs (e.g. $H_2/N_2 \geq 100$; $O_2/N_2 = 2$)

- Further enhancement of molecular sieving properties via controlled pyrolysis proposed to create ultra-micropores
  - PBI pyrolysis preliminary work: $O_2/N_2$ 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 O₂ 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 O₂ production scaled to meet the needs of a 1-5 MWe gasification system
## Project Timeline (BP – 3)

<table>
<thead>
<tr>
<th>Task Description</th>
<th>Start Date</th>
<th>End Date</th>
<th>Q1</th>
<th>Q2</th>
<th>Q3</th>
<th>Q4</th>
<th>BP1 (12/15/18 - 11/30/19)</th>
<th>BP2 (12/01/19 - 11/30/20)</th>
<th>BP3 (12/01/20 - 11/30/21)</th>
<th>BP4 (12/01/21 - 11/30/22)</th>
<th>BP5 (12/01/22 - 11/30/23)</th>
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<tbody>
<tr>
<td><strong>Task 1.0 - Project Management &amp; Planning</strong></td>
<td>12/15/18</td>
<td>09/30/23</td>
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<tr>
<td><strong>Task 2.0 - PBI-CMS Hollow Fiber Membrane Preparation, Optimization, and Characterization</strong></td>
<td>12/15/18</td>
<td>09/30/22</td>
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<td><strong>Subtask 2.1 - Optimize PBI pyrolysis conditions</strong></td>
<td>12/15/18</td>
<td>03/30/20</td>
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<td><strong>Subtask 2.2 - CMS hollow fiber membrane preparation</strong></td>
<td>06/01/18</td>
<td>09/30/22</td>
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<td><strong>Task 3.0 - Membrane Evaluation and Process Parametric Studies</strong></td>
<td>04/01/19</td>
<td>09/30/23</td>
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<td><strong>Task 4.0 - Process Design and Techno-economic Analysis</strong></td>
<td>12/15/18</td>
<td>09/30/22</td>
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<td><strong>Task 5.0 - Modular System Design</strong></td>
<td>10/01/22</td>
<td>09/30/23</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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<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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<tr>
<td>3</td>
<td>M10</td>
<td>2.0</td>
<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>
</tr>
<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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<tr>
<th>No</th>
<th>Decision point</th>
<th>Success Criteria</th>
<th>Date</th>
<th>Outcome</th>
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<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. Numerous membrane formation parameters influence the separation performance of the polymer derived CMS membranes.

### Polymer Characteristics
- Molecular weight
- Main chain modifications
  - Side chain functionalization
- Crosslinking

### Membrane Morphology
- Selective layer thickness
- Porous support morphology

### Pyrolysis Protocol
- Pre-treatment
- Temperature
- Time
- Ramp-rate
- Atmosphere
Base Hollow Fiber Membrane Preparation

Base PBI HFMs having asymmetric morphology are 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 permeance target of 100 GPU.

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

Symmetric PBI-CMS HFM

Material chemistry & processing optimization

Integrally asymmetric and dimensionally stable PBI-CMS HFM

$20 \, \mu m$

$20 \, \mu m$

Operating $T$: 5 to 25 °C

$O_2/N_2$ Selectivity vs. $O_2$ Permeance, GPU

Project Target

Los Alamos National Laboratory
Controlled Morphology and Selective Layer Thickness

Modified PBI-HFM fabrication protocol leads to

- smaller pyrolysis induced dimensional change in HFM
- better selective layer thickness control
- higher $O_2$ permeance
Influence of Feed Pressure on Perm-Selectivity

- Steady performance as a function of pressure
- Modified fabrication process led to ca. 40-fold improvement in O$_2$ permeance with comparable selectivity

![Graphs showing the influence of feed pressure on O$_2$ permeance and O$_2$/N$_2$ selectivity for Gen 1 and Gen 2.](image-url)
Influence of Temperature on Perm-Selectivity

- Overall $O_2$ and $N_2$ permeances follow Arrhenius expression

- Gen2: $O_2$ permeance and $O_2/N_2$ ranged from 66 to 87 GPU and 11 to 5.6, resp.
Membrane Modeling and Process Design
Proposed Process Layout

2-stage PBI-CMD HFMs-based air separation process for > 90% O₂ production
Process Modeling Platform Development

- Improved HFM process model and expanded capability to calculate process energy consumption

Membrane Flux Model

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

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

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

\[ i = \frac{\Delta p_i (p_i^S - p_i^F)}{l} \]

- Membrane module optimization to minimize parasitic energy losses

![Diagram of Hollow Fiber Membrane Module](image)

- Output parameters and graph data from experimental measurements

![Graph](image)

- Oxygen productivity and bore pressure drop vs. fiber outer diameter
Process Energy Consumption Optimization

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

Revised specific energy consumption calculation

- 40 to 45 kJ/mol O₂ for 90 to 95% purity O₂ achievable with demonstrated PBI-CMS HFMs having O₂/N₂ selectivity of 10 to 20
## Techno-economic Analysis – Design Basis Developed

### Process parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Input values</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ Production Rate, TPD</td>
<td>10</td>
</tr>
<tr>
<td>Number of Membrane Stages</td>
<td>2</td>
</tr>
<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>
</tr>
<tr>
<td>Temperature Stage-1 and stage-2, °C</td>
<td>25 &amp; 5</td>
</tr>
<tr>
<td>Hours of operation per year</td>
<td>7884</td>
</tr>
<tr>
<td>Pressure ratio</td>
<td>10</td>
</tr>
<tr>
<td>Membrane effective thickness, µm</td>
<td>0.3 to 1</td>
</tr>
<tr>
<td>O₂ purity (%) at Stage-1 and Stage-2</td>
<td>60-65, 90-95</td>
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<tr>
<td>Pump efficiency, % and temperature, °C</td>
<td>40-64, 15</td>
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<tr>
<td>Membrane installation factor</td>
<td>0.35-0.45</td>
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<tr>
<td>Electricity cost, $/MWh</td>
<td>50 - 60</td>
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</tbody>
</table>

### Membrane module

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Input values</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF Diameter, µm</td>
<td>300-500</td>
</tr>
<tr>
<td>Wall Thickness, µm</td>
<td>30</td>
</tr>
<tr>
<td>Selective Layer Thickness, µm</td>
<td>0.1 to 1.0</td>
</tr>
<tr>
<td>O₂ permeance, GPU</td>
<td>50-300</td>
</tr>
<tr>
<td>O₂/N₂ selectivity of the membrane</td>
<td>10-30</td>
</tr>
<tr>
<td>Module Diameter, m</td>
<td>0.25</td>
</tr>
<tr>
<td>Module Length, m</td>
<td>1-3</td>
</tr>
<tr>
<td>Surface Area Density, m²/m³</td>
<td>3000</td>
</tr>
<tr>
<td>Area Ratio Stage 1/Stage 2</td>
<td>~ 5/1</td>
</tr>
<tr>
<td>Membrane cost, $/m²</td>
<td>30-100</td>
</tr>
</tbody>
</table>

### Preliminary Estimates (Best Case Scenarios)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy Consumption, KJ/mol</td>
<td>33-55</td>
</tr>
<tr>
<td>Production Cost, $/tonne O₂</td>
<td>30-80</td>
</tr>
</tbody>
</table>
Performance Benchmarking

Evaluation of PBI-CMS HFMIs in air feed stream

- Influence of water vapor and CO₂ on the membrane separation performance

- Lab-scale membrane module
- O₂ 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 H₂O and CO₂
- Benchmark performance data for model validation
- Initiated system and analytical equipment calibration
Air Separation Performance Evaluation

* Mixed gas permeation system schematic for evaluation of PBI-CMS HFMs at process relevant operating conditions

### Typical Air Composition

<table>
<thead>
<tr>
<th>Gas</th>
<th>Composition</th>
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<tbody>
<tr>
<td>N₂</td>
<td>78% (vol. Dry Basis)</td>
</tr>
<tr>
<td>O₂</td>
<td>21%</td>
</tr>
<tr>
<td>Ar</td>
<td>0 to 0.93</td>
</tr>
<tr>
<td>CO₂</td>
<td>0 to 400 ppm</td>
</tr>
<tr>
<td>Relative Humidity</td>
<td>10 to 90%</td>
</tr>
</tbody>
</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's

Membrane module shell with flow-through on feed and permeate sides
Future Work

MEMBRANE DESIGN AND FABRICATION

- Compare performance of the PBI-CMS HFMs fabricated under flowing inert gas (N₂) and vacuum.
- Develop O₂ permeance and O₂/N₂ selectivity correlations as a function of the 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)
Summary

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.

**Material Design & Synthesis**
- Bulky, large and high mobility functional groups
- Chain packing Efficiency
- Enhance Fractional Free Volume
- High localized mobility
- Rigid and bent configurations

**Process Modelung**

**CMS Membranes**

**Lab-scale Demonstration & Evaluation**
Acknowledgements

ــ DOE – NETL Gasification Program

 Evelyn Lopez
 Venkat Venkataraman
 David Lyons

髫 Los Alamos National Laboratory
 MPA, T, EES and E Divisions

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