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 (Raj) Singh
Los Alamos National Laboratory

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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 > 20 for high purity O₂ production to meet the needs of a modular 1-5 MWe gasification system
Team Members

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

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

Modular System Design
- Todd A. Jankowski
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 O\(_2\) production
- Program Targets:
  - 90-95 vol% purity O\(_2\)
  - Low cost and operational efficiency relative to the state-of-the-art technology

Images: DOE/NETL website
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


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

![Graph showing O₂/N₂ selectivity and permeability across different materials and years.]

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
Membrane Material & Hollow Fiber Development
Base Hollow Fiber Membrane Preparation

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

PBI Membrane Pyrolysis

- Pyrolysis conditions have a tremendous influence on the gas separation performance of the polymer derived CMS membranes
  - Focused efforts on development and optimization of PBI pyrolysis protocols

- Successfully fabricated PBI-CMS membranes in industrially attractive platform

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

Support porous morphology collapse observed during pyrolysis
- Dimensional shrinkage by 30%
- Permeance changes with retained $O_2/N_2$ selectivity

Temperature profiles for pyrolysis

Morphology change

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<th>650 °C</th>
<th>750 °C</th>
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<td>WT (μm)</td>
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Tailoring Separation Performance: Pyrolysis Atmosphere

Vacuum applied during pyrolysis

Relative to inert gas purging, additional shrinkage by 33% was observed under vacuum

Higher O₂ permeance achieved

Temperature profiles for pyrolysis

Morphology change

Dimensional changes

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<td>WT (μm)</td>
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</table>
**PBI-CMS HFM Performance: Temperature Influence**

- **PBI-CMS HFM**s exhibit similar Arrhenius behavior with temperature.
- Higher $E_{p,\text{oxygen}}$ (~9.2 kJ/mol) in comparison to CA (~3.4) and PI (~5.6).
Ideal Permeation Performance Summary

- Large span in the measured O$_2$/N$_2$ separation performance of PBI-CMS membranes as a function of pyrolysis conditions and operating temperature.
- O$_2$/N$_2$ selectivity and O$_2$ permeance ranged from 7 to 18 & 0.2 to 5 GPU, respectively.
- Provides opportunities for energy efficient membrane process design.

Operating $T$: 5 to 25°C
Improving Separation Performance

Material chemistry and processing optimization

- Targeted towards retention of asymmetric morphology of base PBI membrane during pyrolysis to obtain asymmetric PBI-CMS hollow fiber membranes

Base PBI Polymer Membrane

1st Gen: Thick Symmetric PBI-CMS Membrane

2nd Gen: Asymmetric PBI-CMS Membrane
Membrane Modeling and Process Design
Developed hollow fiber membrane model and integrated with Aspen Plus process simulation software for air separation process development.
Preliminary Process Design

Simulated 2-stage membrane process for high purity O₂ production from air

- Estimated specific energy consumption ranged from 40 to 60 KJ/mol O₂ for 90 to 95% purity O₂ achievable with demonstrated PBI-CMS HFMs having O₂/N₂ selectivity of 10 to 18
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.
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