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
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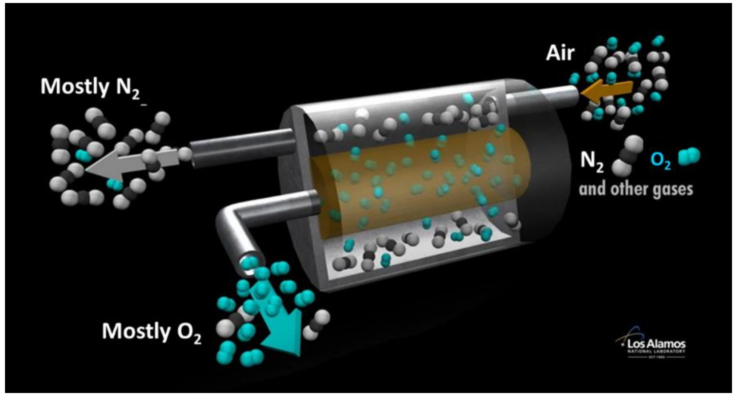
Los Alamos National Laboratory

2020 Gasification Project Review Meeting
DOE – Fossil Energy/NETL
September 2nd, 2020

Project Overview

- **Award Name:** High Selectivity and Throughput Carbon Molecular Sieve Hollow Fiber Membrane-Based Modular Air Separation Unit for Producing High Purity O_2
- **Award Number:** FE-1049-18-FY19
- **Current Project Period:** BP2: 12/2019 – 11/2020
- **Project Manager:** Venkat K. Venkataraman
- **Overall Program Goal:** Development of high flux polybenzimidazole–derived carbon molecular sieve hollow fiber membranes having O_2/N_2 selectivity > 20 for high purity O_2 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

Materials Physics & Applications Division

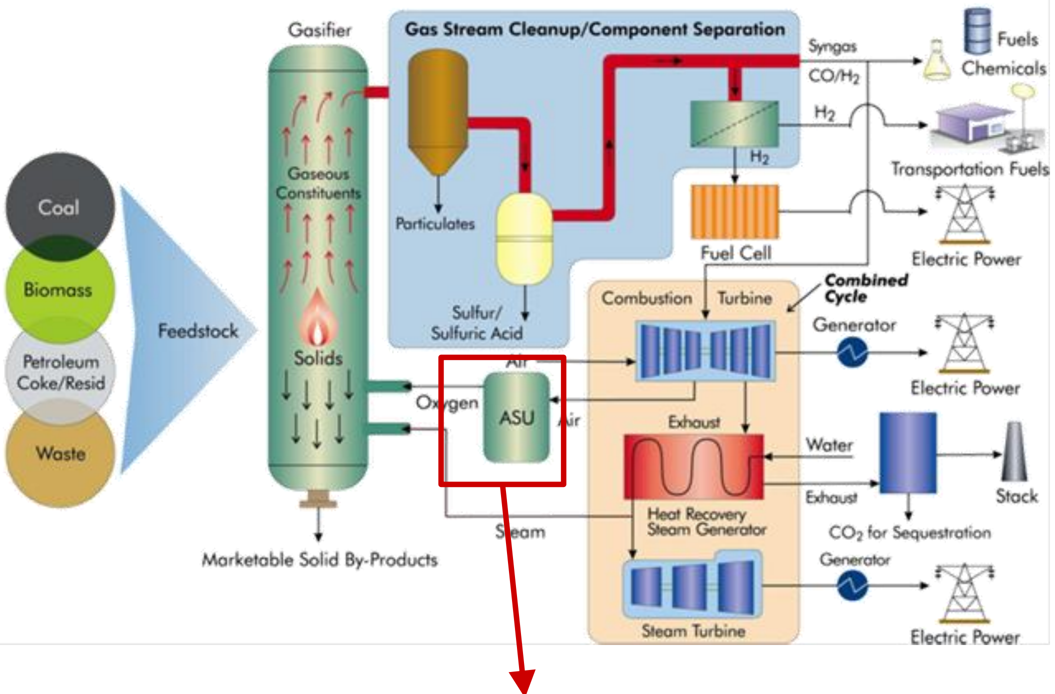
Theoretical Division

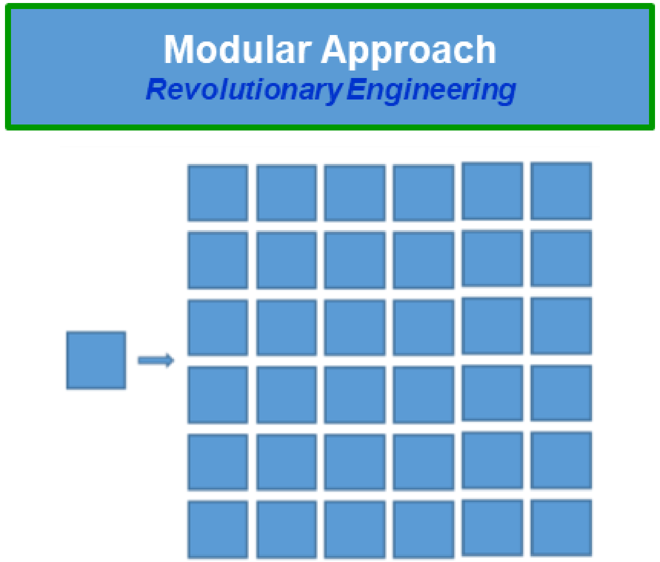
Earth & Environmental Science Division

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



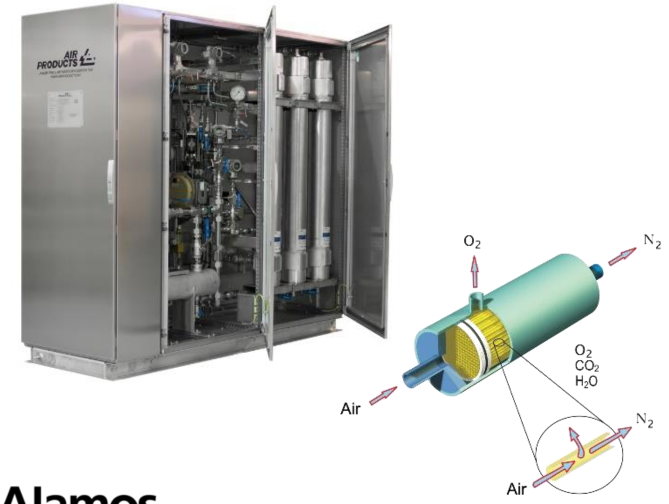


- **Advanced technology need:**
  - Energy efficient air separation technology for high purity O_2 production
  - Program Targets:
    - 90-95 vol% purity O_2
    - Low cost and operational efficiency relative to the state-of-the-art technology

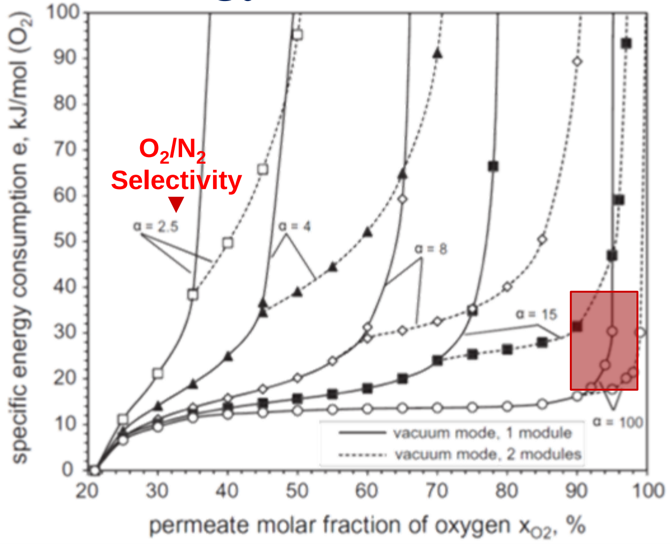
Images: DOE/NETL website

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**
  - Inherent modularity & dramatically reduced footprint
  - Tailorable output stream conditions (T&P) to match downstream process
  - Improved energy economics



Ref: Air Products Inc. & Air Liquide Inc.

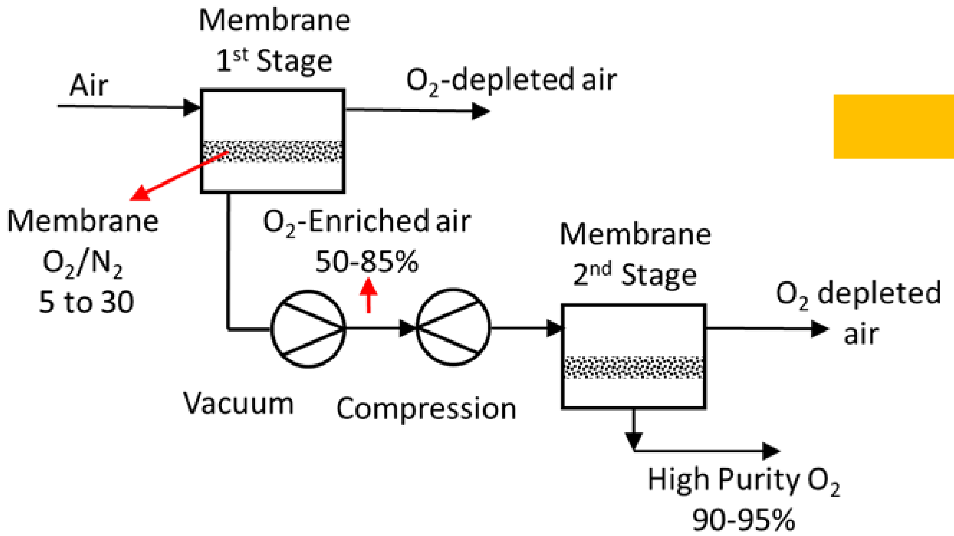


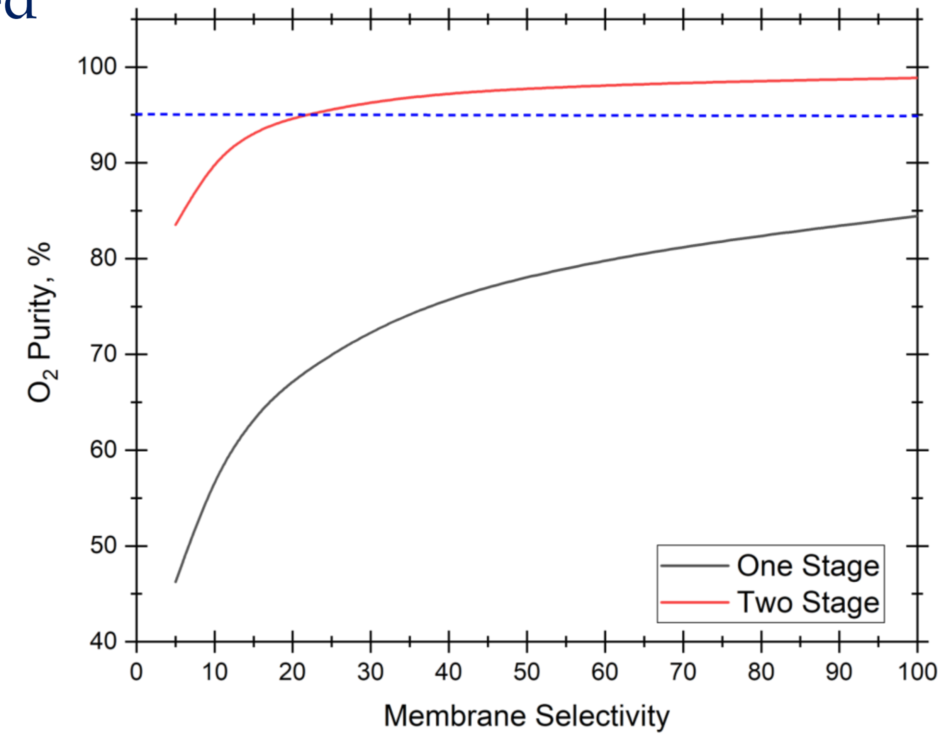
Ref: Meriläinen et al. / Applied Energy, 94 (2012) 285-294

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 O2 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





Calculated O_2 Purity. Ref: Ward et.al., J Membrane Sci 1 (1976) 99-108

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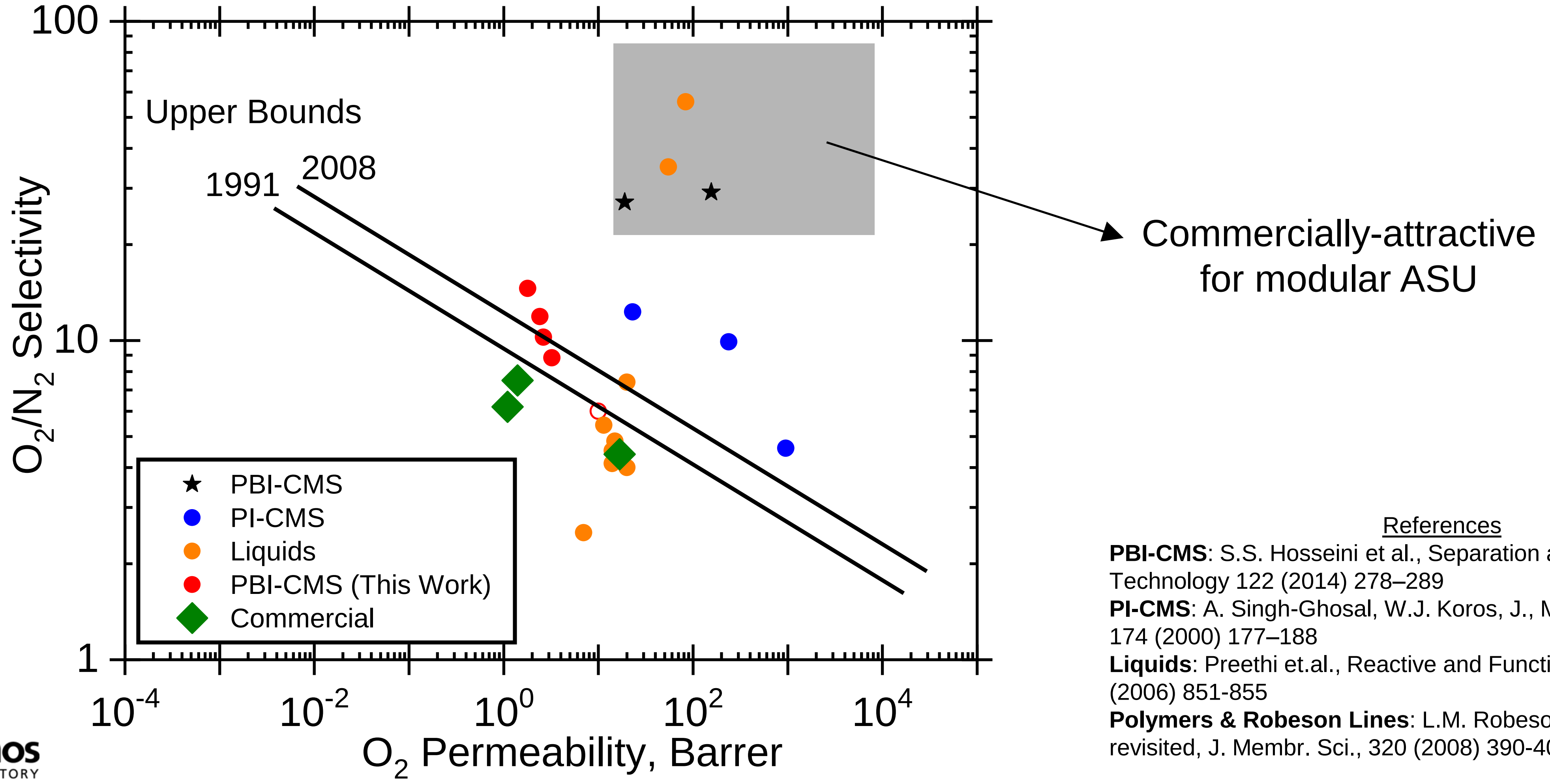
O_2 Selective Membrane Materials

- **Membrane materials: current state-of-the-art**
  - O_2/N_2 selectivities approaching 30 for polymer-derived carbon molecular sieve (CMS) membranes achieved



References

PBI-CMS: S.S. Hosseini et al., Separation and Purification Technology 122 (2014) 278–289

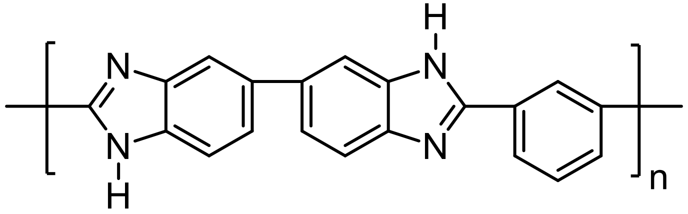
PI-CMS: A. Singh-Ghosal, W.J. Koros, J., Membrane Science 174 (2000) 177–188

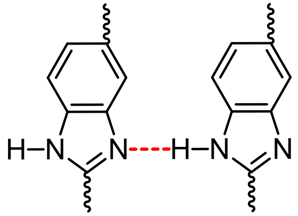
Liquids: Preethi et.al., Reactive and Functional Polymers, 66 (2006) 851-855

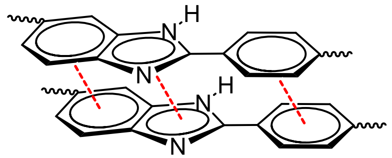
Polymers & Robeson Lines: L.M. Robeson, The upper bound revisited, J. Membr. Sci., 320 (2008) 390-400

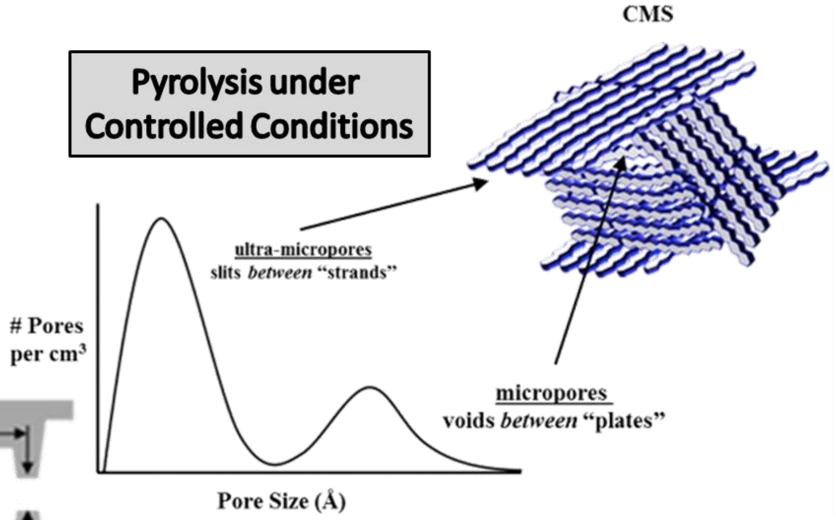
Membrane Development Approach

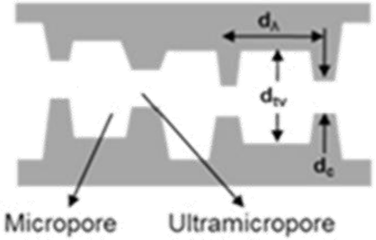
- **Polybenzimidazole (PBI)-derived carbon molecular sieve membranes for high O_2/N_2 selectivity**
  - Tightly packed PBI molecular structure resulting from H-bonding and π-π stacking imparts molecular sieving character
    - Base polymer (*m*-PBI) has high selectivity for gas pairs (e.g. $H_2/N_2 \geq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

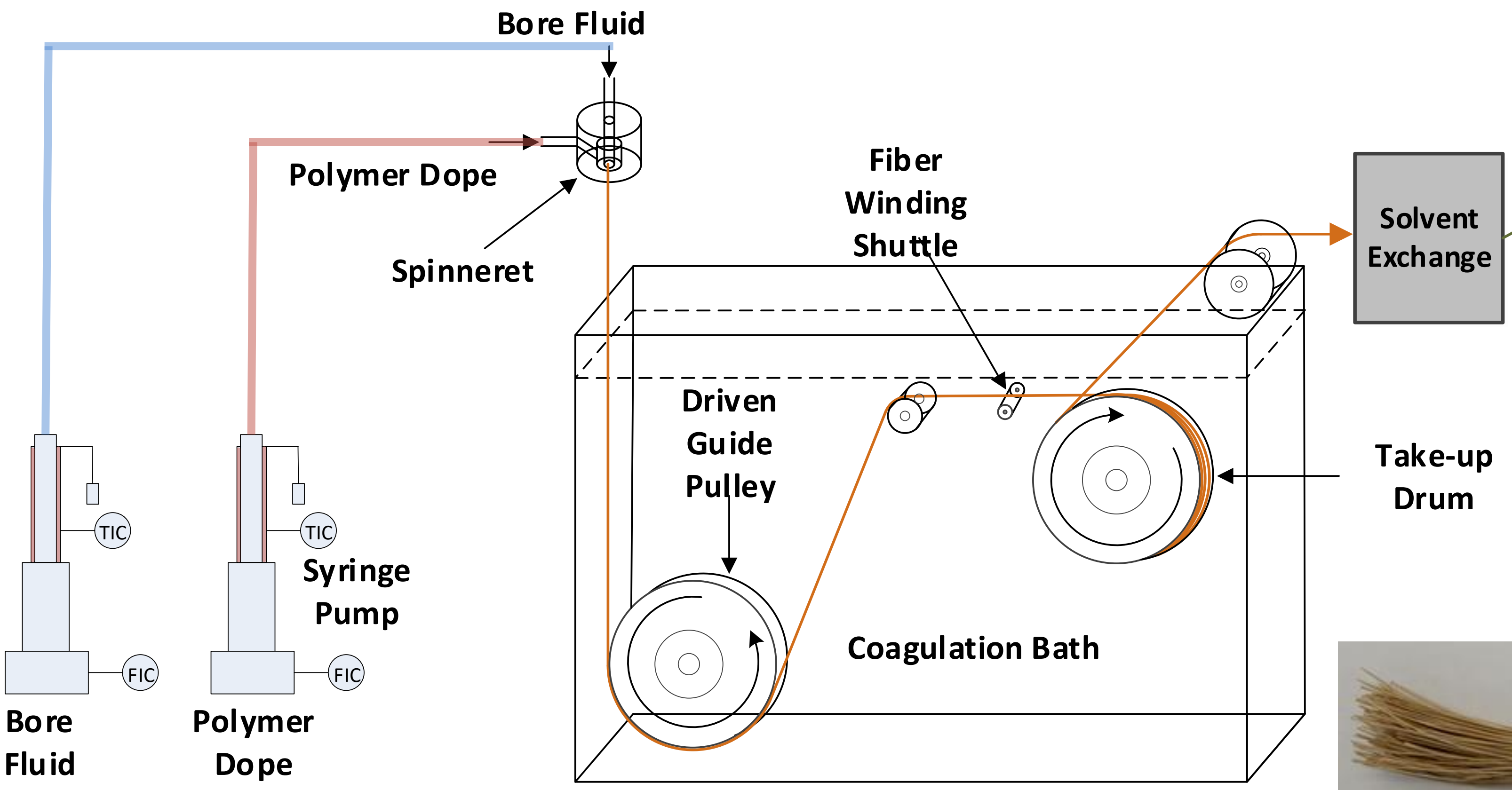
Project Objectives

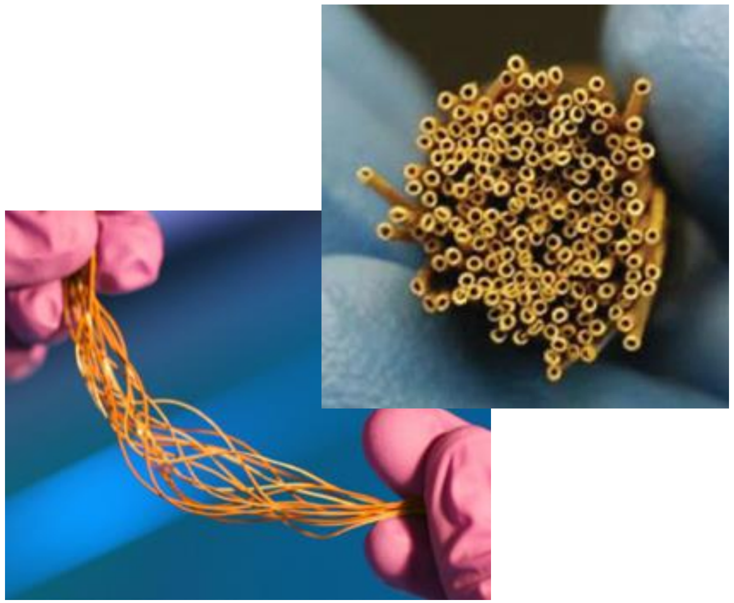
- **A membrane-based, modular air separation technology for high purity O_2 production**
  - Develop CMS materials derived from PBI materials (PBI-CMS) to achieve the desired material transport characteristics
  - Develop PBI-CMS hollow fiber membranes having the desired membrane performance characteristics
  - 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

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**





Ref. *Berchtold & Singh, et.al. 2018 US Patent 10071345*

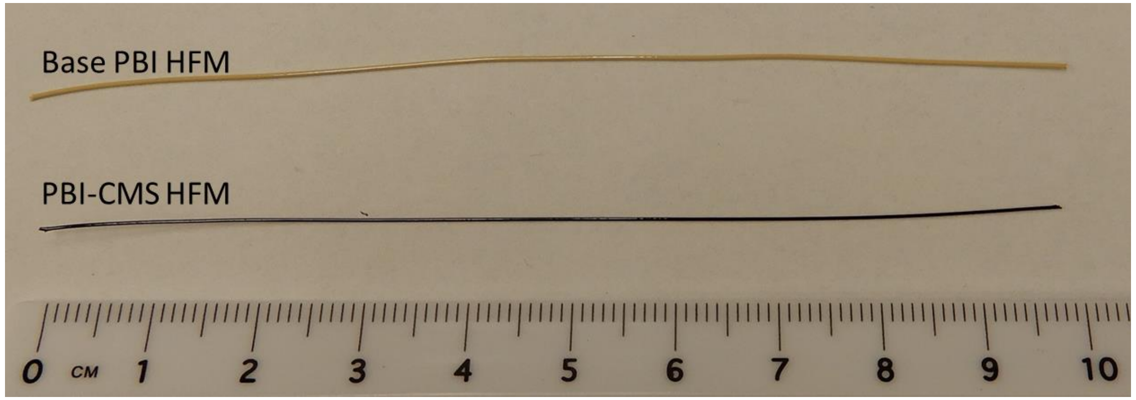
PBI Membrane Pyrolysis

- **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

Pyrolysis Parameters

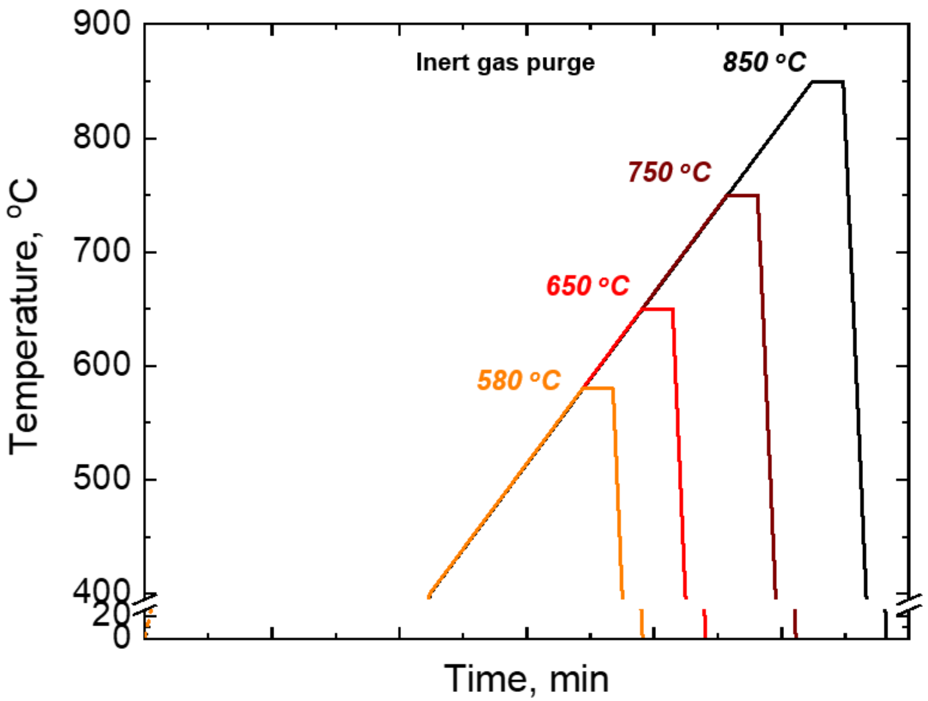
- Temperature (500 to 900 °C)
- Ramp rate and dwell time
- Environment (e.g. inert, vacuum).

- Successfully fabricated PBI-CMS membranes in industrially attractive platform

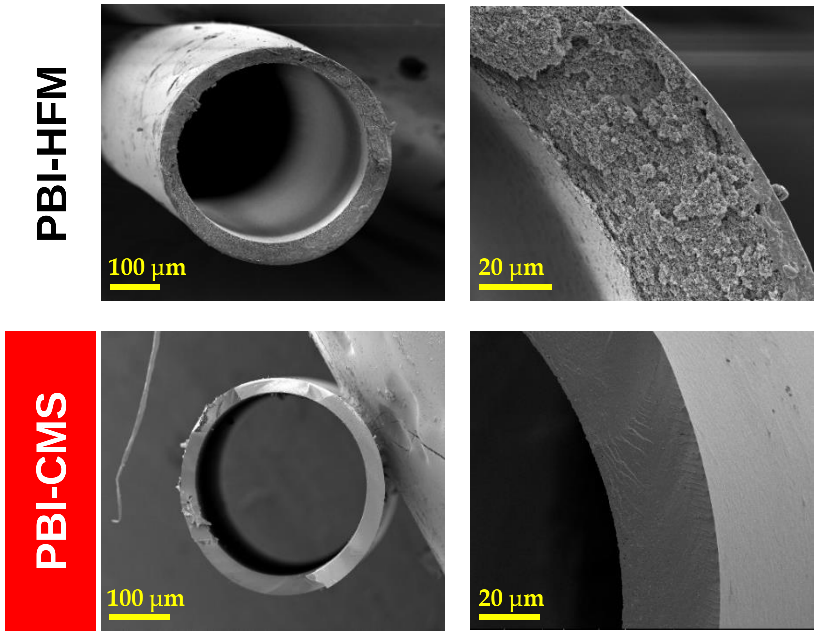


Tailoring Separation Performance: Pyrolysis Temperature

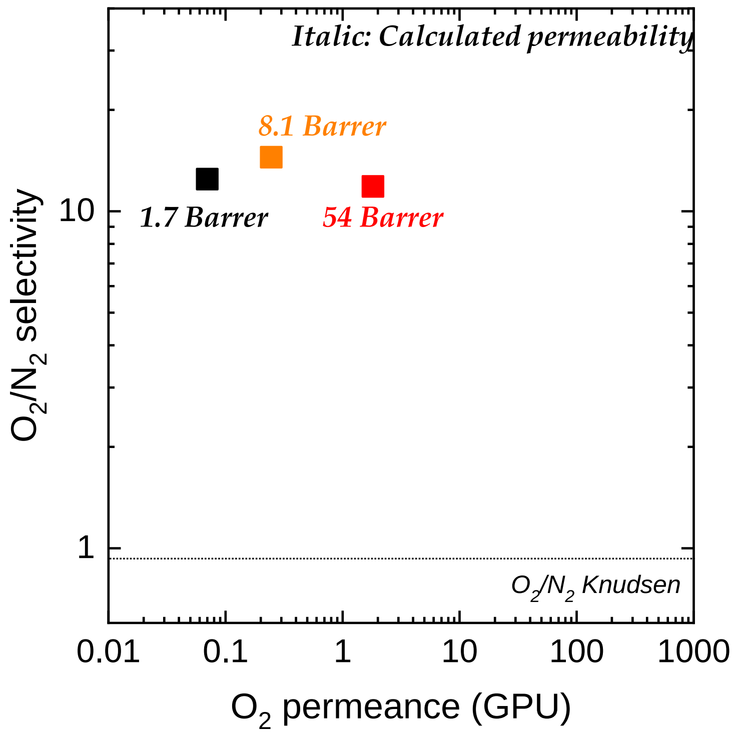
Temperature profiles for pyrolysis



Morphology change



O_2 separation performance change



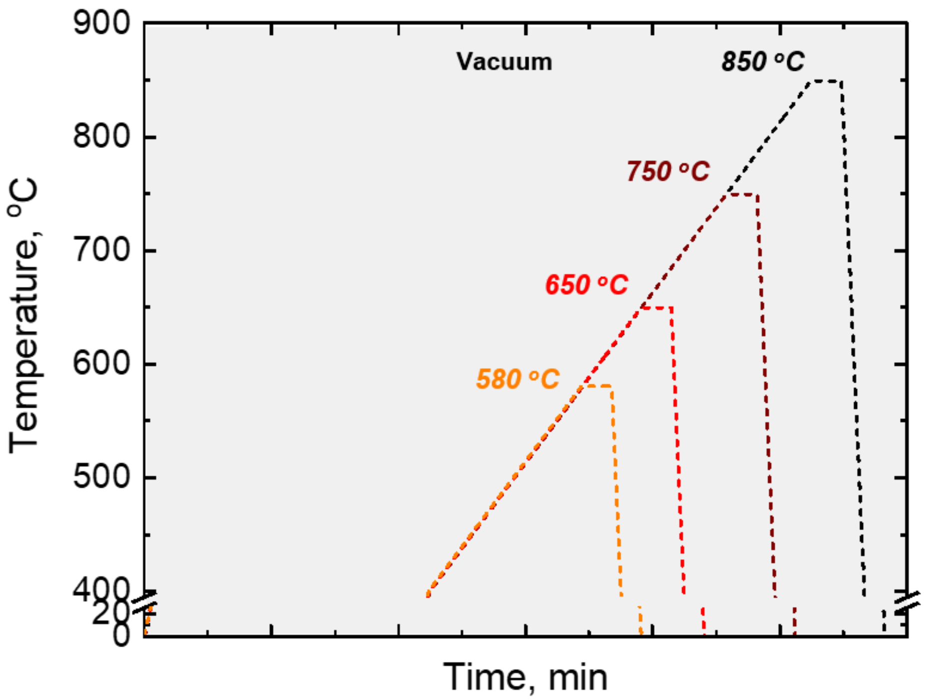
Dimensional changes

Dimen.	580 °C	650 °C	750 °C	850 °C
OD (µm)	357	343	324	318
ID (µm)	303	289	272	273
WT (µm)	27	26	26	23

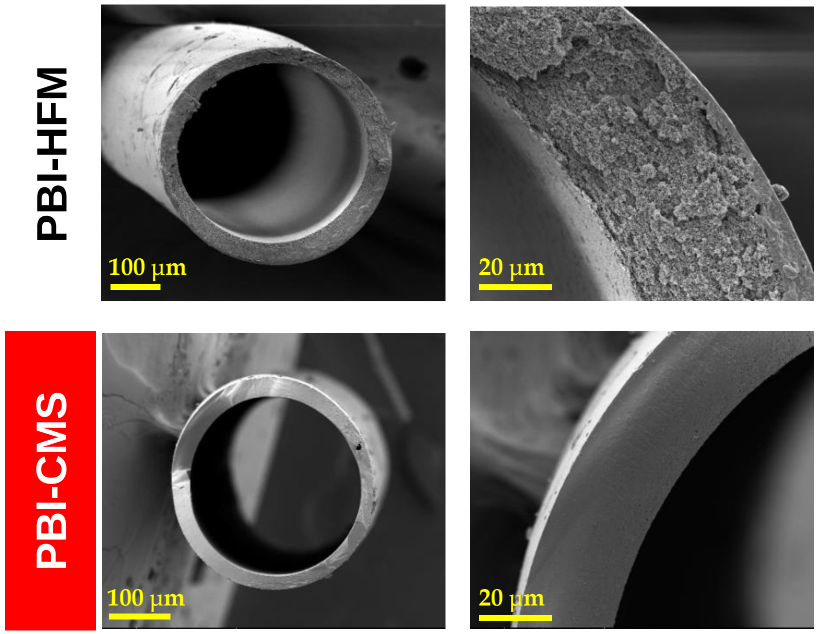
- **Support porous morphology collapse observed during pyrolysis**
- **Dimensional shrinkage by 30%**
- **Permeance changes with retained O_2/N_2 selectivity**

Tailoring Separation Performance: Pyrolysis Atmosphere

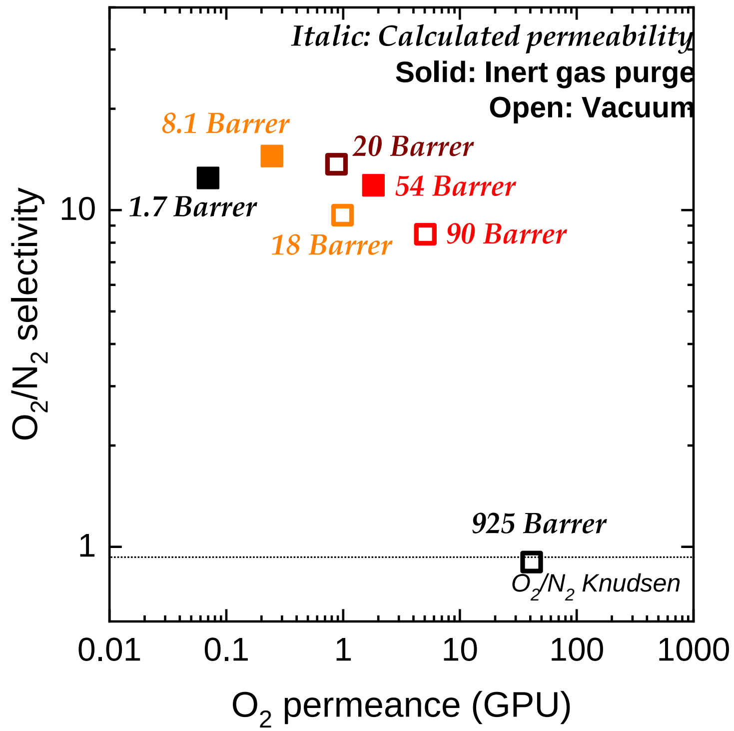
Temperature profiles for pyrolysis



Morphology change



O_2 separation performance change

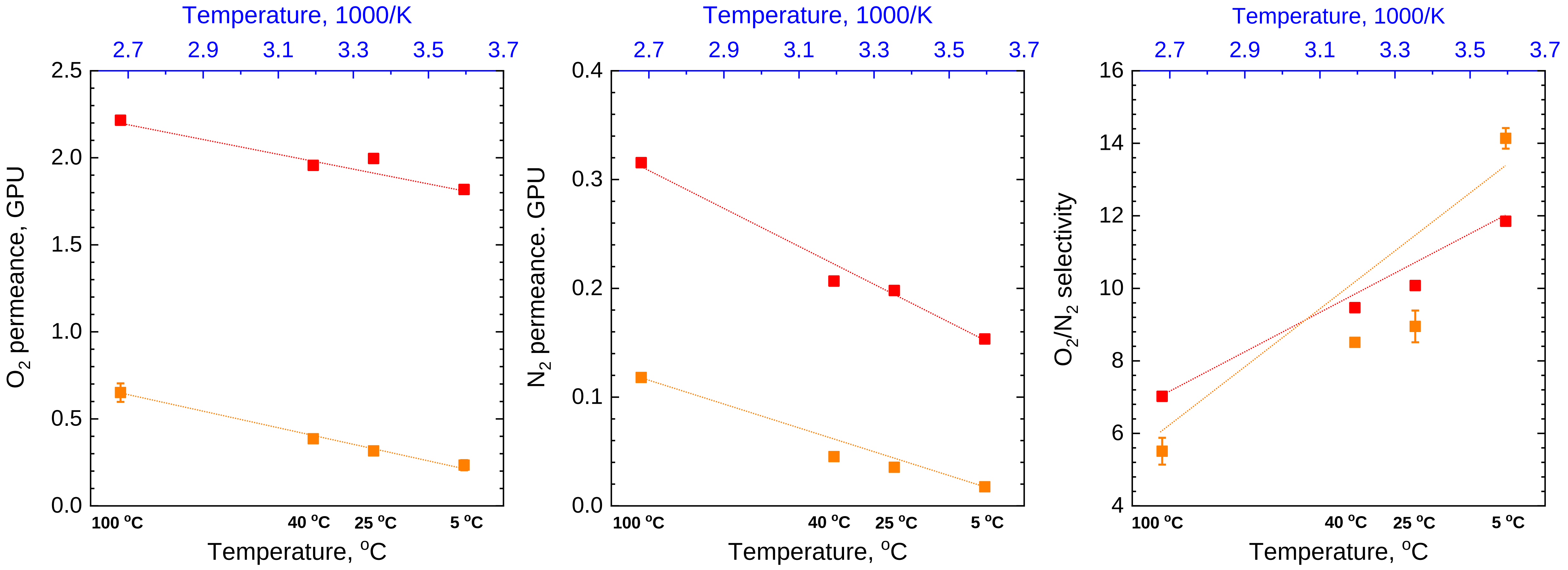


Dimensional changes

Dimen.	*580 °C*	*650 °C*	*750 °C*	*850 °C*
OD (µm)	340	340	304	333
ID (µm)	290	288	268	286
WT (µm)	23	27	18	21

- **Vacuum applied during pyrolysis**
- **Relative to inert gas purging, additional shrinkage by 33% was observed under vacuum**
- **Higher O_2 permeance achieved**

PBI-CMS HFM Performance: Temperature Influence



- **PBI-CMS HFMs exhibit similar Arrhenius behavior with temperature**
- **Higher $E_{p,oxygen}$ (~9.2kJ/mol) in comparison to CA (~3.4) and PI (~5.6)**

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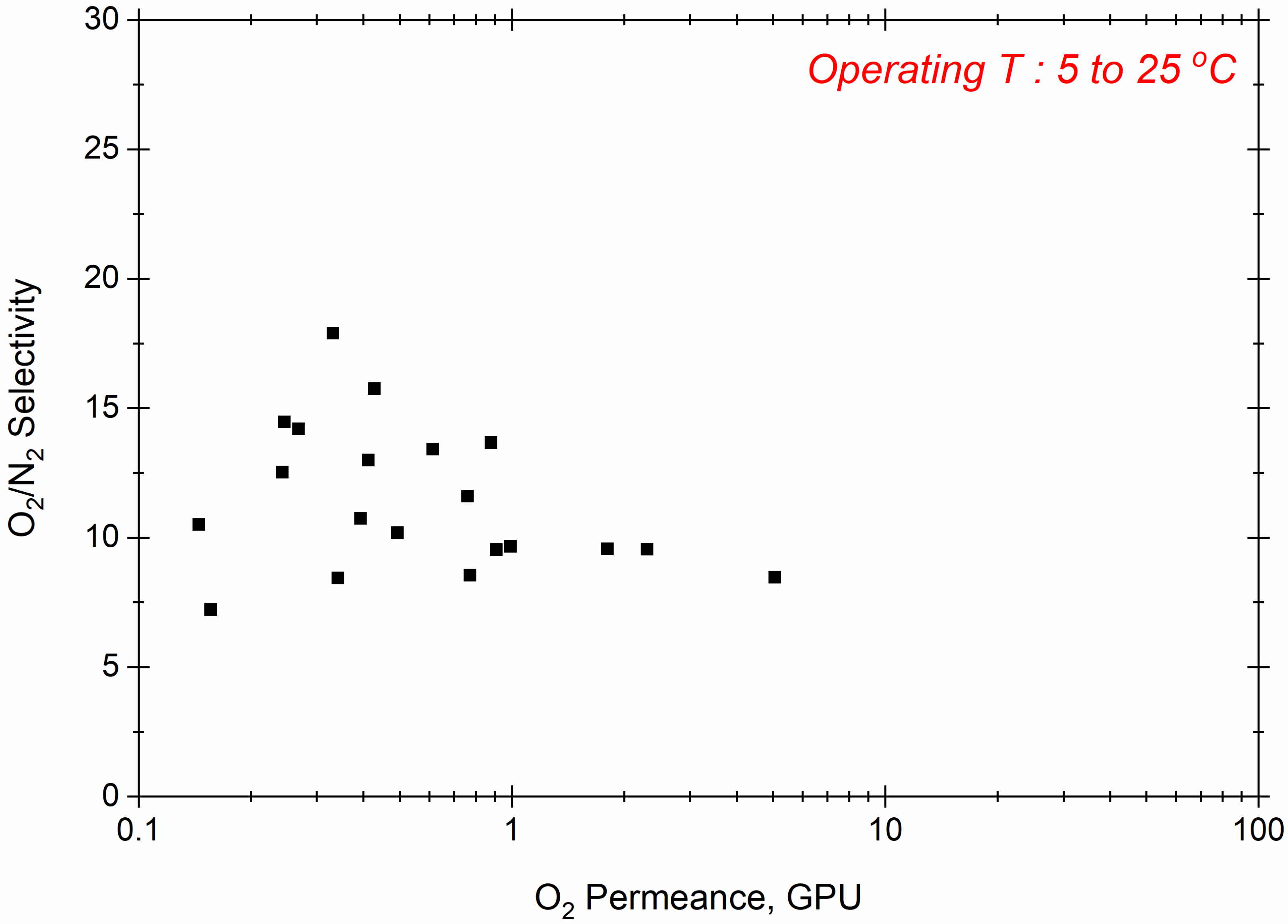
Ideal Permeation Performance Summary



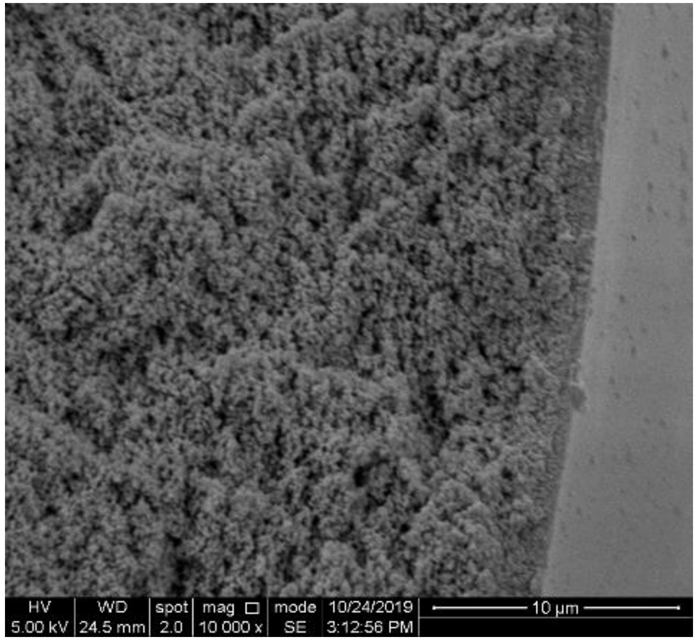
- Large span in the measured O_2/N_2 separation performance of PBI-CMS membranes as a function of pyrolysis conditions and operating temperature
  - O_2/N_2 selectivity and O_2 permeance ranged from 7 to 18 & 0.2 to 5 GPU, respectively
  - Provides opportunities for energy efficient membrane process design

Improving Separation Performance

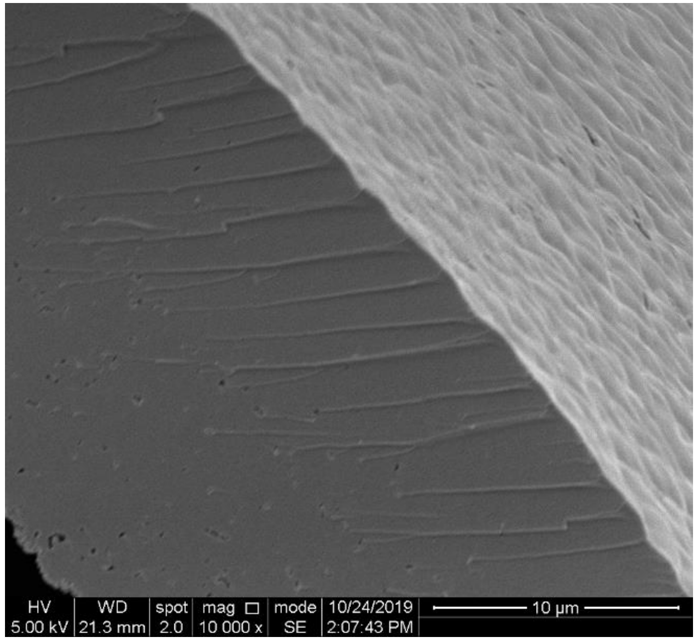
Material chemistry and processing optimization

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

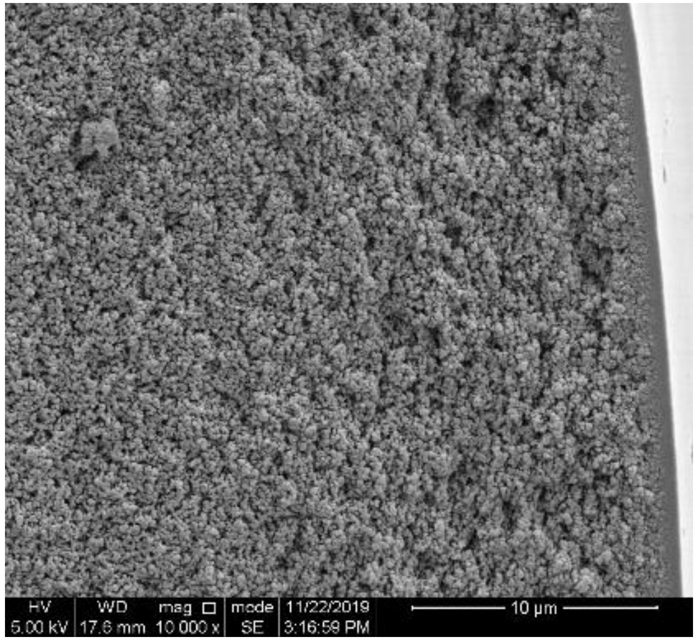
Base PBI
Polymer Membrane



1st Gen: Thick Symmetric
PBI-CMS Membrane



2nd Gen: Asymmetric
PBI-CMS Membrane



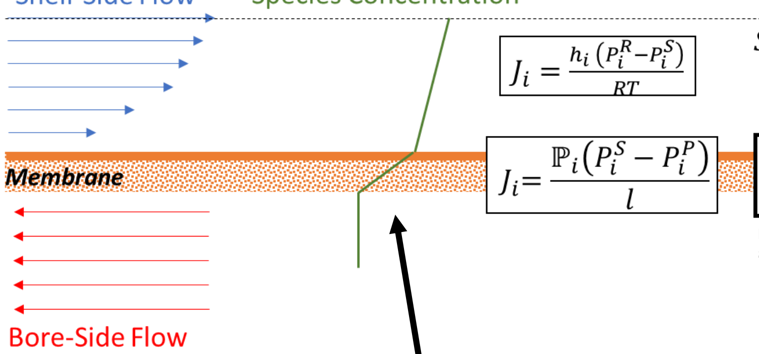
Membrane Modeling and Process Design

Process Modeling Platform Development

- **Developed hollow fiber membrane model and integrated with Aspen Plus process simulation software for air separation process development**

Membrane Flux Model

python™



$$J_i = \frac{h_i \left(P_i^R - P_i^S\right)}{RT}$$

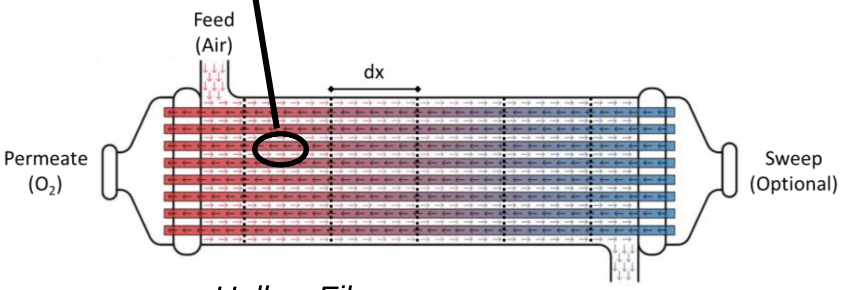
$$Sh = 0.68\, Re^{1/2} Sc^{1/3}$$

$$Sh = \frac{h_i x}{\mathfrak{D}_i}$$

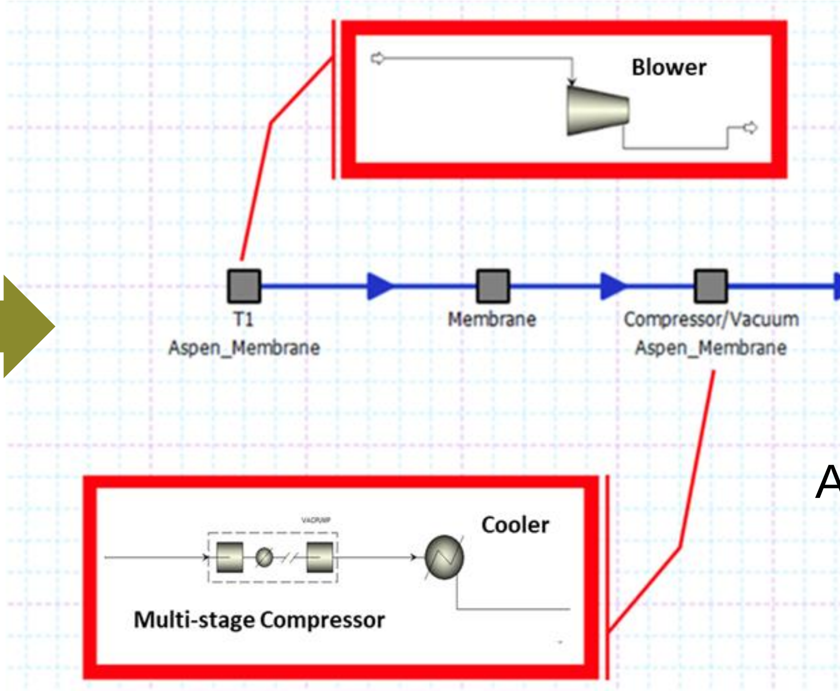
$$J_i = \frac{\mathbb{P}_i \left(P_i^S - P_i^P\right)}{l}$$

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

Pre-exponential factor and activation energy are from experimental measurements



Hollow Fiber Membrane Module

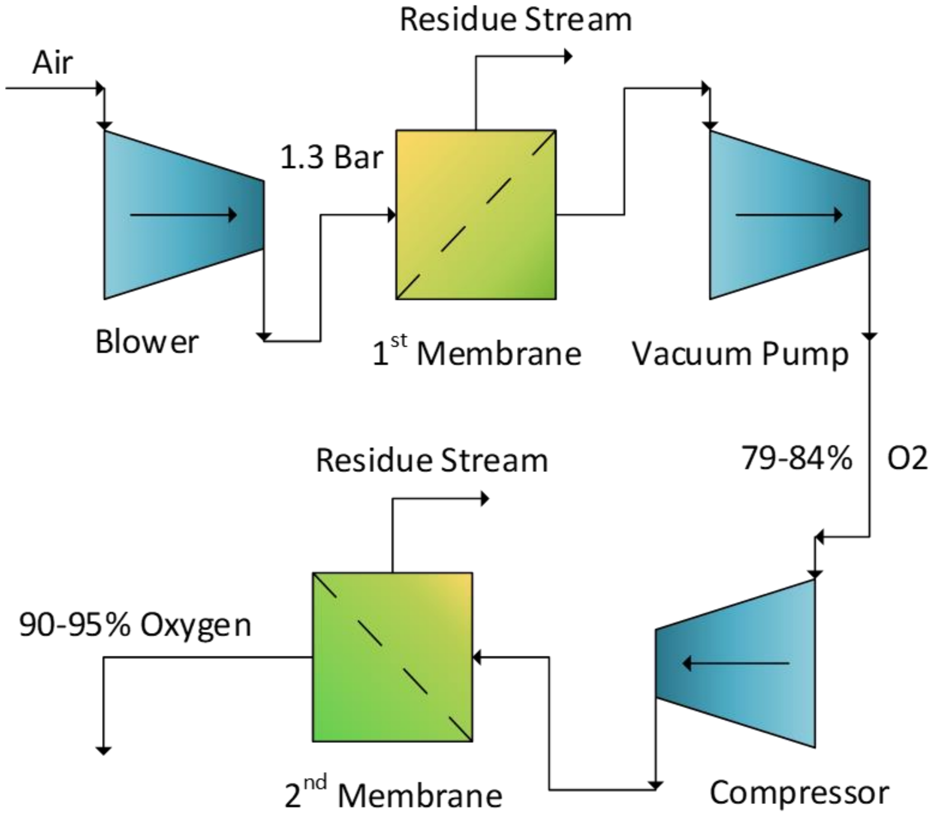


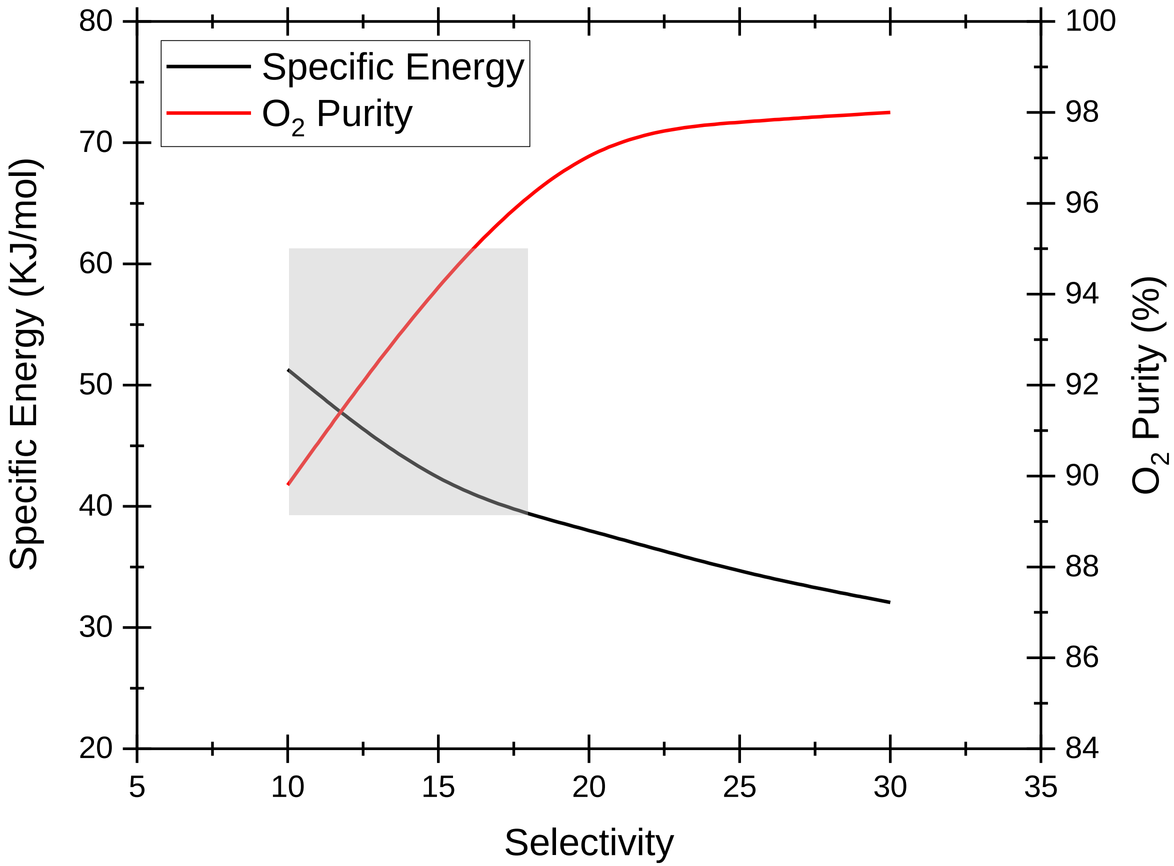
Aspen Plus

CCSI[2]
Carbon Capture Simulation for Industry Impact

Preliminary Process Design

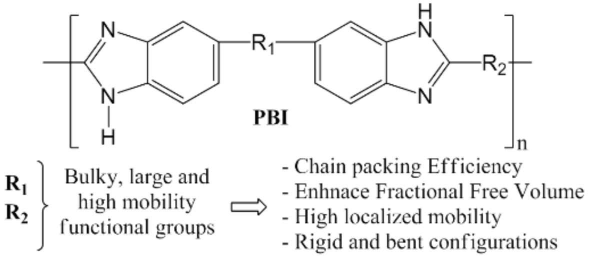
- **Simulated 2-stage membrane process for high purity O_2 production from air**
  - Estimated specific energy consumption ranged from 40 to 60 KJ/mol O_2 for 90 to 95% purity O_2 achievable with demonstrated PBI-CMS HFMs having O_2/N_2 selectivity of 10 to 18



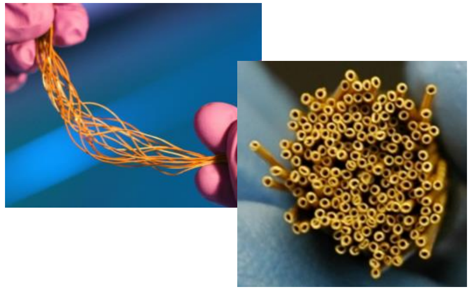


Summary

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



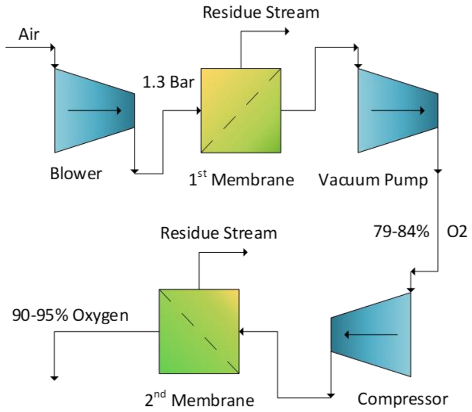
Material Design & Synthesis



Processing & Membrane Synthesis

CMS Membranes

Lab-scale Demonstration & Evaluation



Process Modeling

Thank you