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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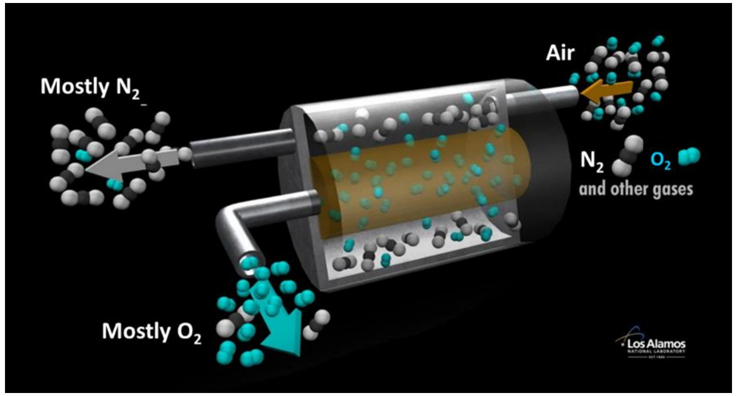
FY 23 FECM/NETL Spring R&D Project Review Meeting
DOE – Fossil Energy/NETL
April 18, 2023

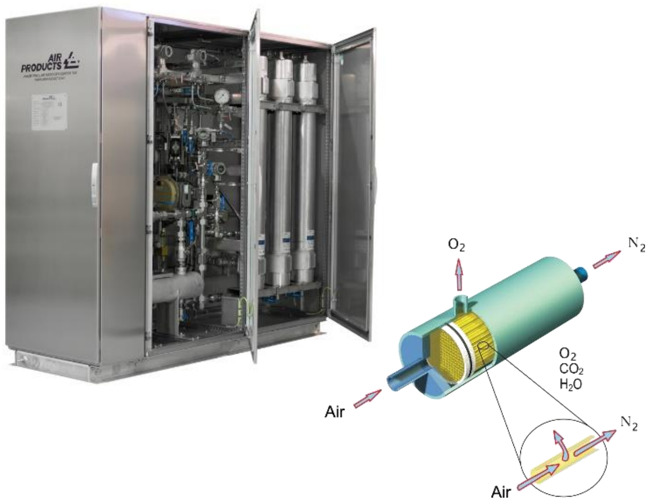
Project Overview

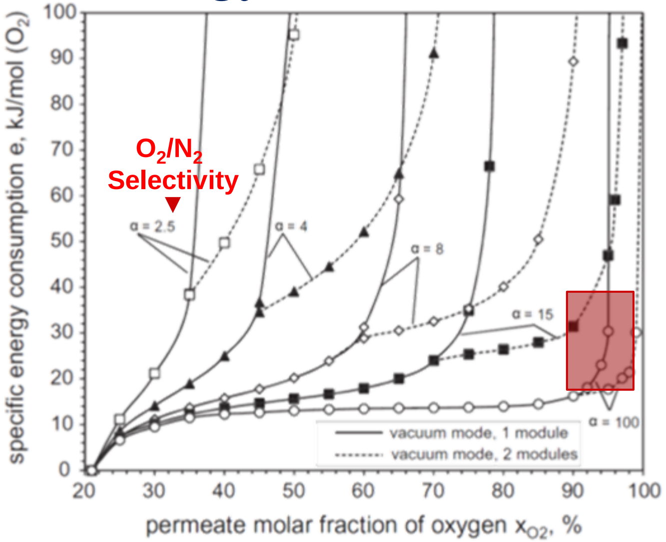
- **Award Name:** High Selectivity and Throughput Carbon Molecular Sieve Hollow Fiber Membrane-Based Modular Air Separation Unit for Producing High Purity O_2
- **Award Number:** FE-1049-18-FY19
- **Current Project Period:** BP3: 08/2021 – 03/2023
- **Project Manager:** Evelyn Lopez
- **Overall Program Goal:** Development of high flux polybenzimidazole–derived carbon molecular sieve hollow fiber membranes having O_2/N_2 selectivity > 15 for high purity O_2 production to meet the needs of a modular 1-5 MWe gasification system



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





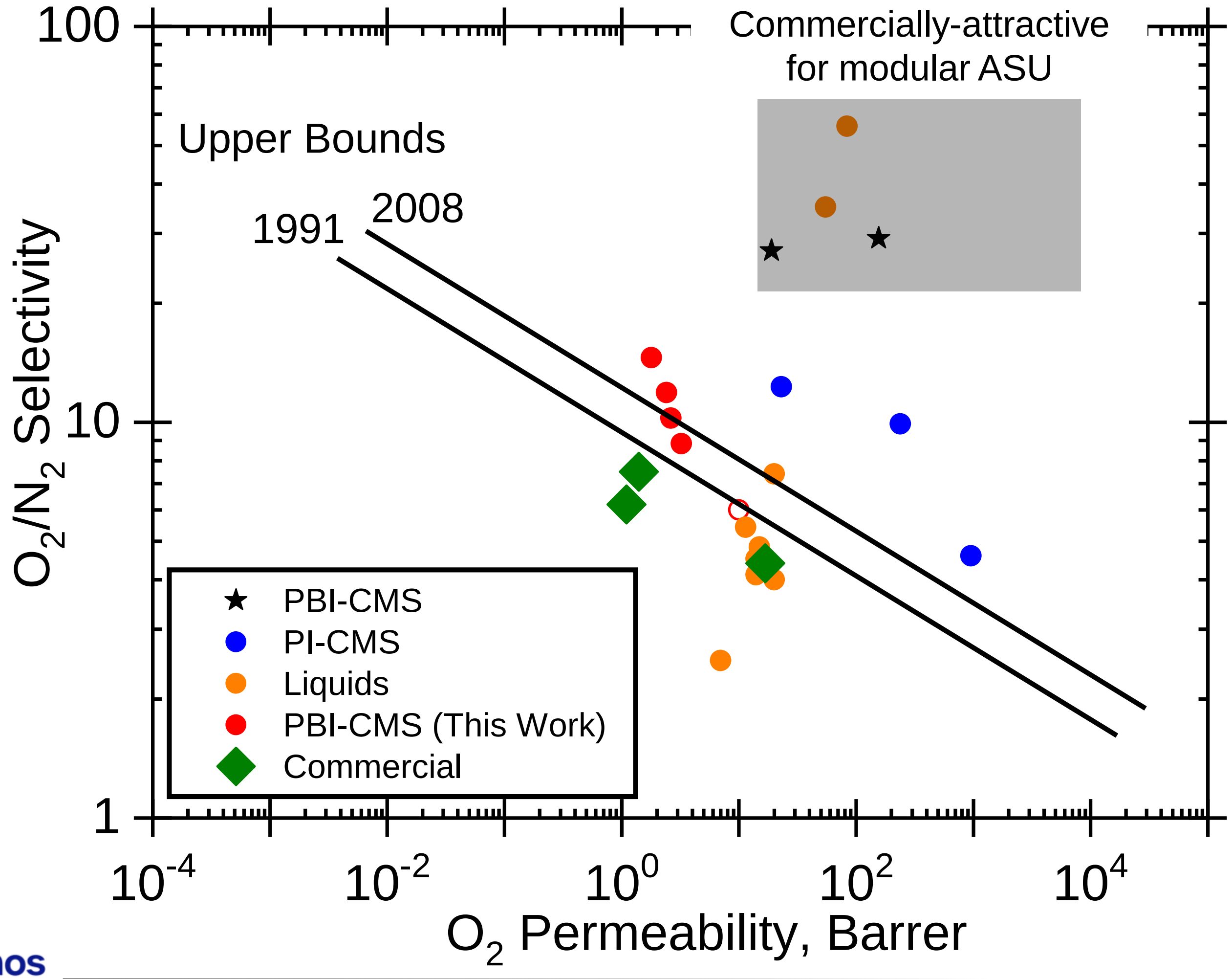
Ref: Air Products Inc. & Air Liquide Inc.

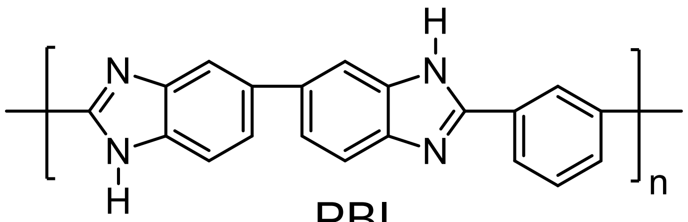
Ref: Meriläinen et al. / Applied Energy, 94 (2012) 285-294

O_2 Selective Membrane Material Needs

Membrane materials: current state-of-the-art

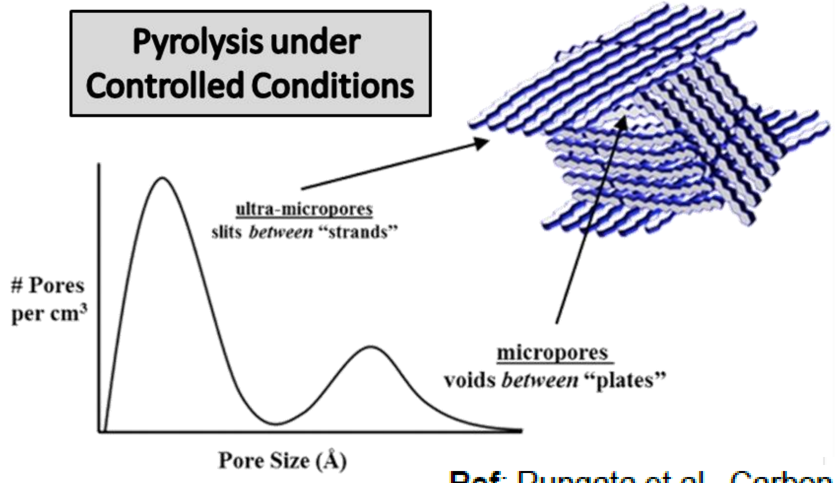
- O_2/N_2 selectivities approaching 30 for polymer-derived carbon molecular sieve (CMS) membranes





PBI

CMS



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

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

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 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 modular gasification system

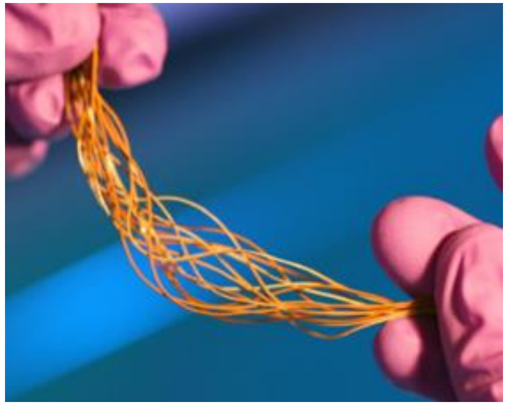
Membrane Material and Industrial Platform Development

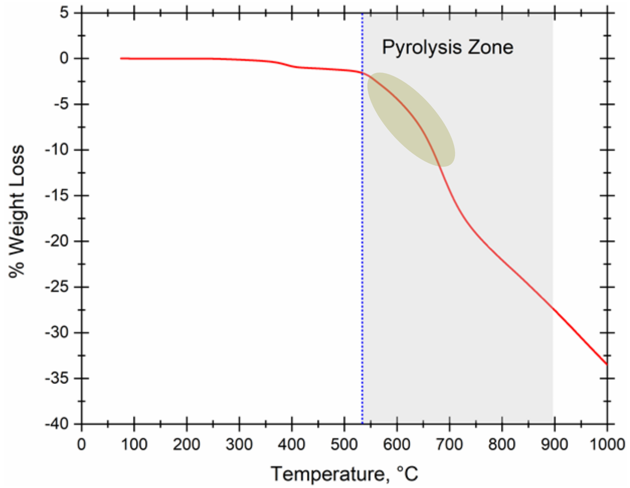
Polymer Derived CMS Membranes

- CMS membrane formation is multi-step process

Commercial PBI Polymer → Hollow Fibers → Base Polymer Membrane → Pyrolysis → CMS Membranes

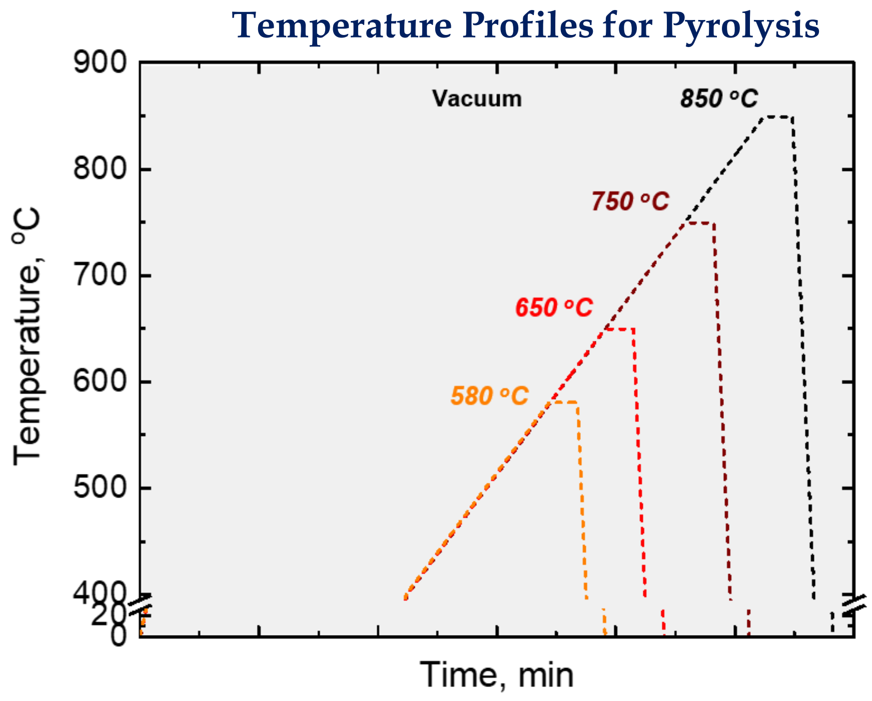
PBI Performance Products, Inc.

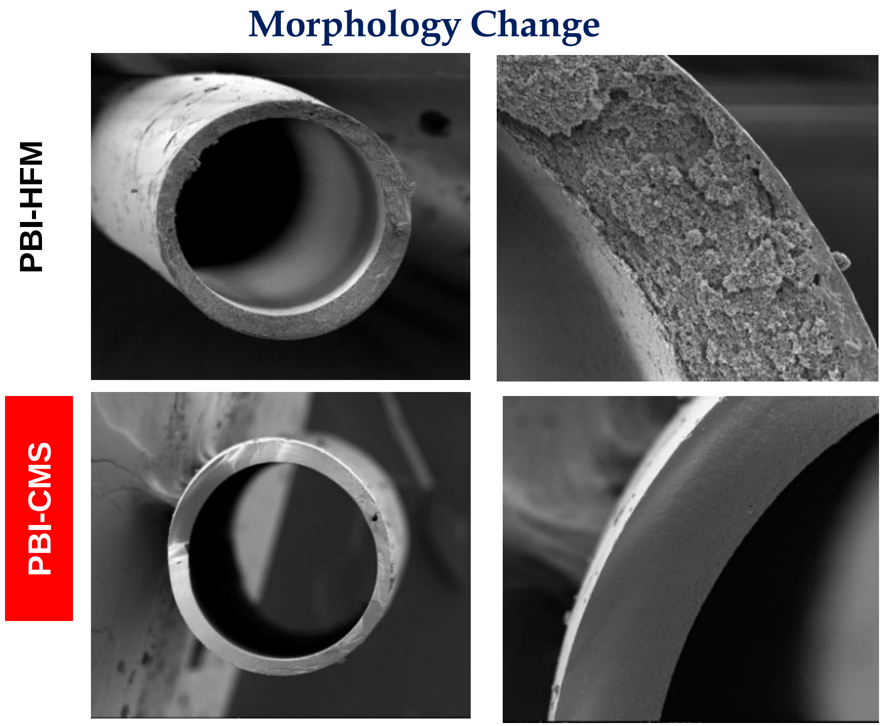




Ref. *Berchtold & Singh, et.al. 2018 US Patent 10071345*

Tailoring Separation Performance: Pyrolysis Temperature



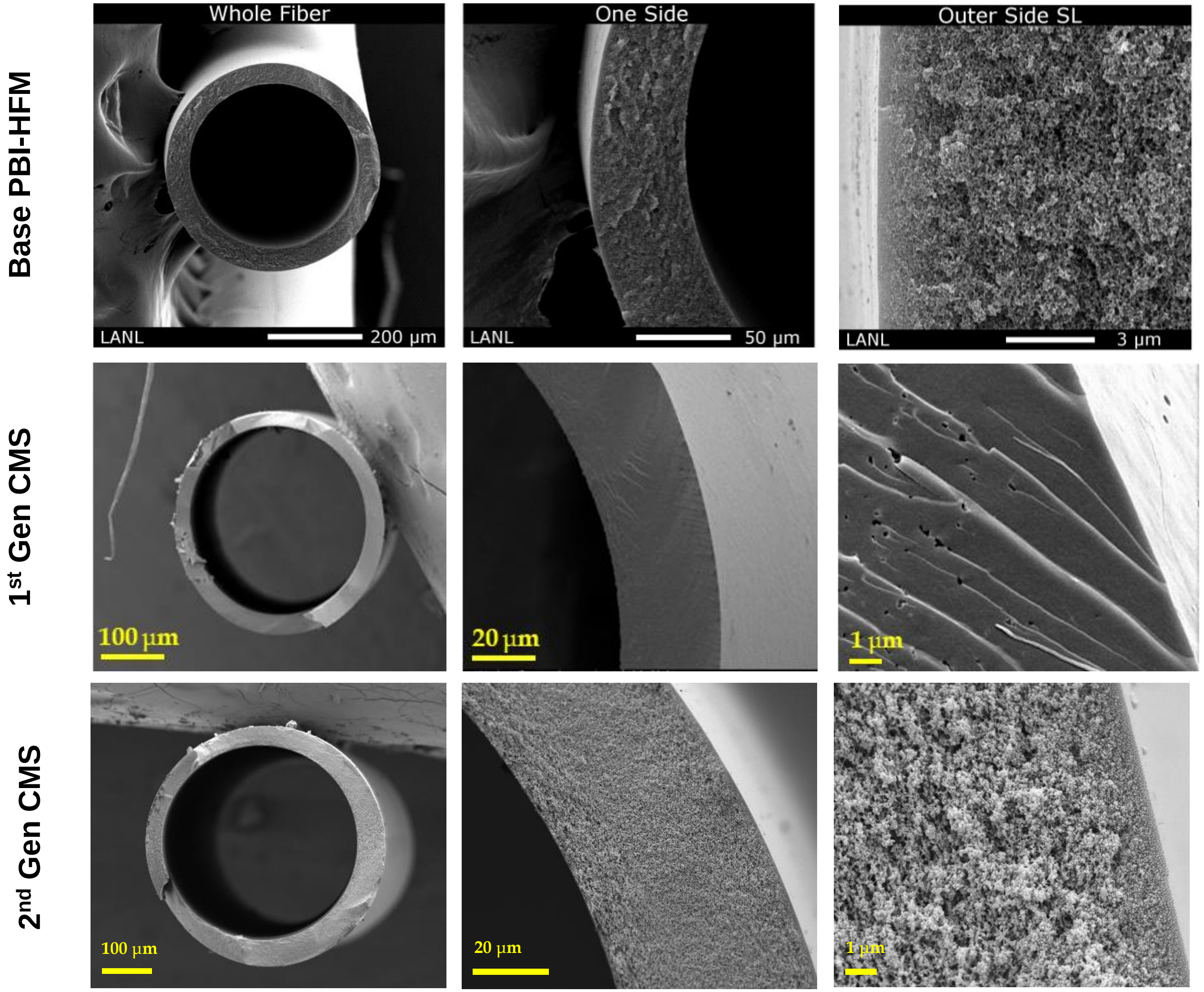


Sample	Ideal Separation Performance		Estimated O_2 permeability [Barrer]
	O_2 permeance, GPU	O_2/N_2	
PBI	0.204	1.02	0.06
CMS-580	0.303	8.44	8.48
CMS-650	3.964	8.47	99
CMS-750	0.782	13.7	16.4
CMS-850	42.3	0.90	550

Seong & Singh et.al., Carbon 192, 71-83, 2022

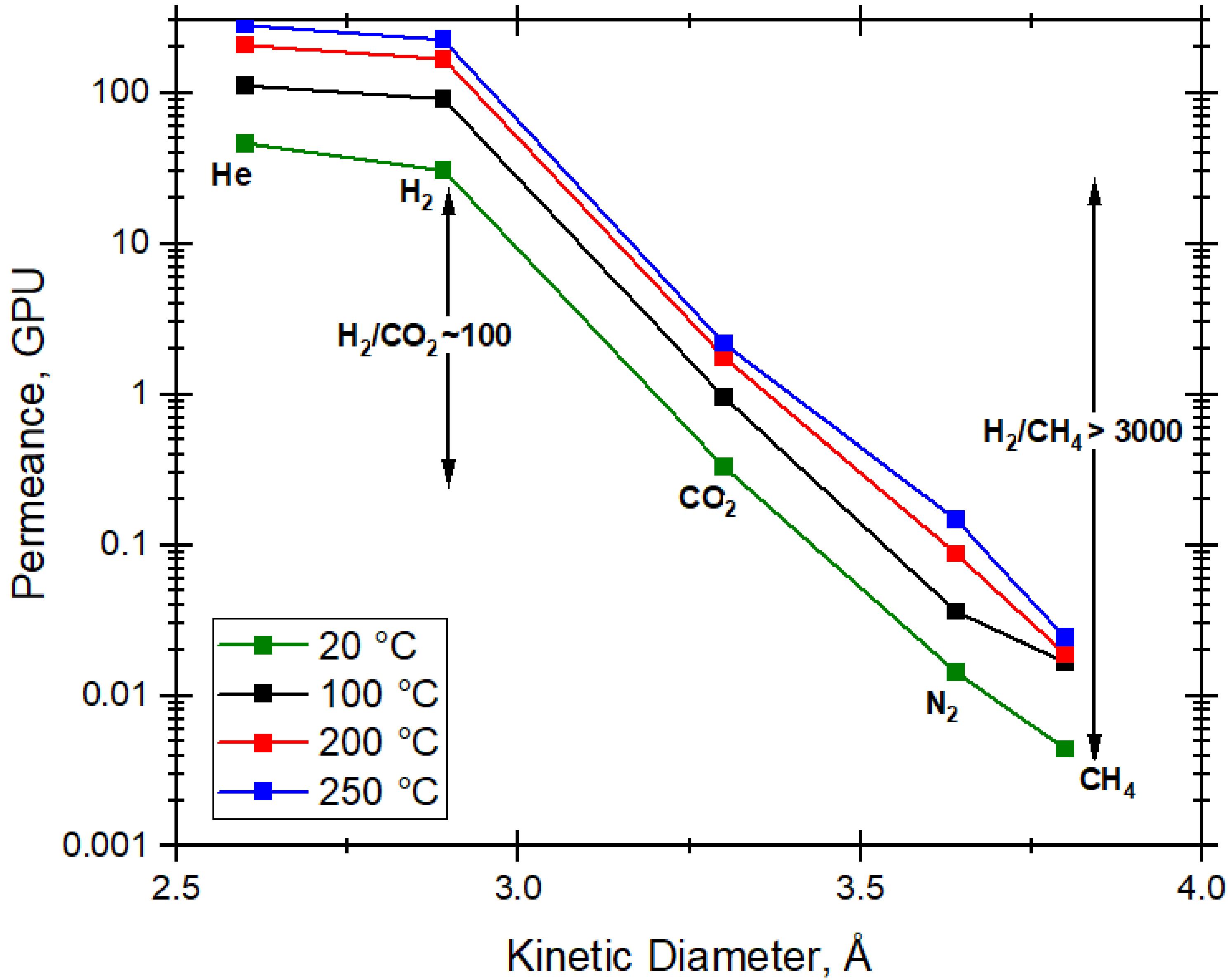
Achieving High Permeance

- Challenge: Mitigate HFM porous support structure collapse during pyrolysis



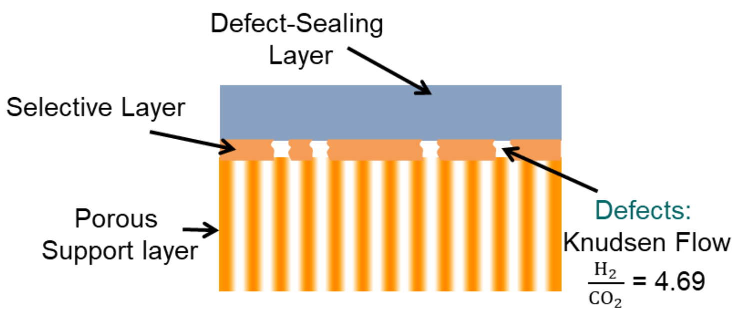
US Patent Application - 18/170,722

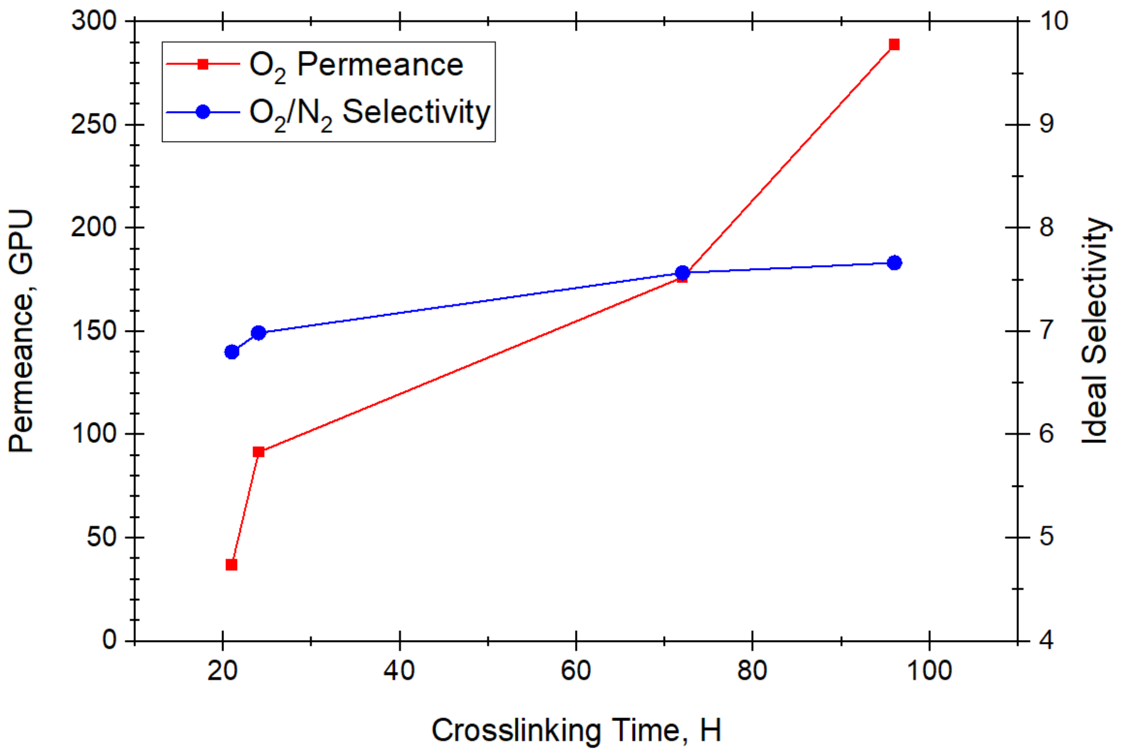
PBI-CMS Membranes – Exceptional Molecular Sieving

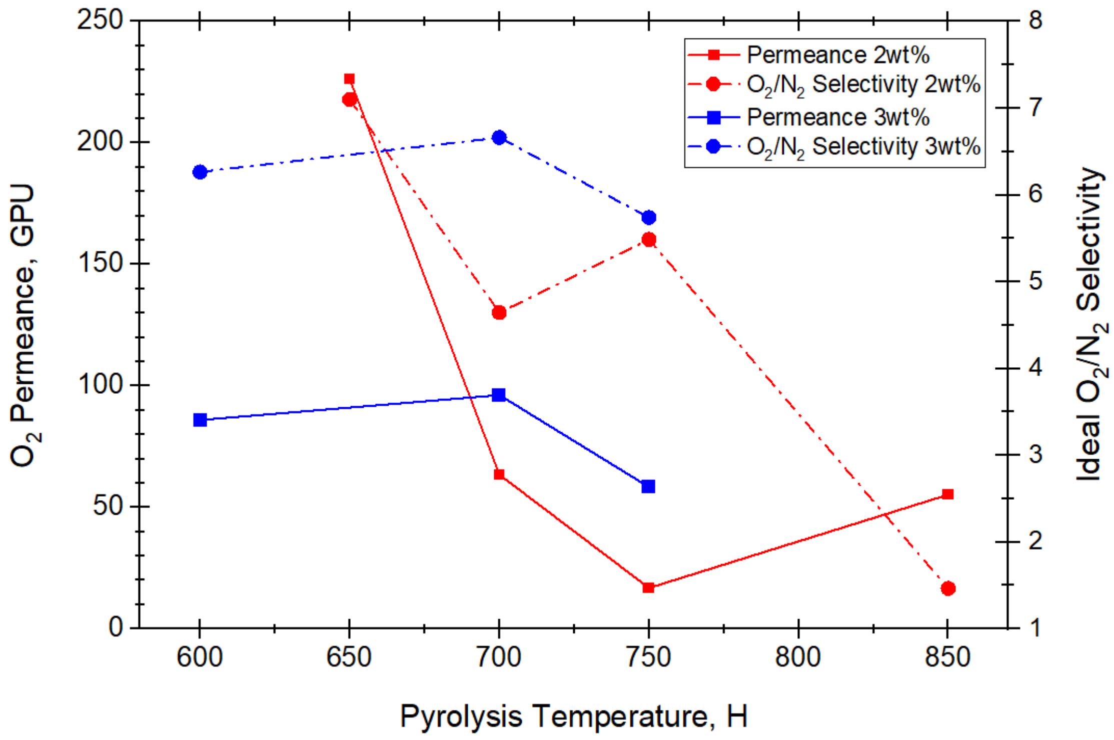


Tuning PBI-CMS HFM Fabrication Process

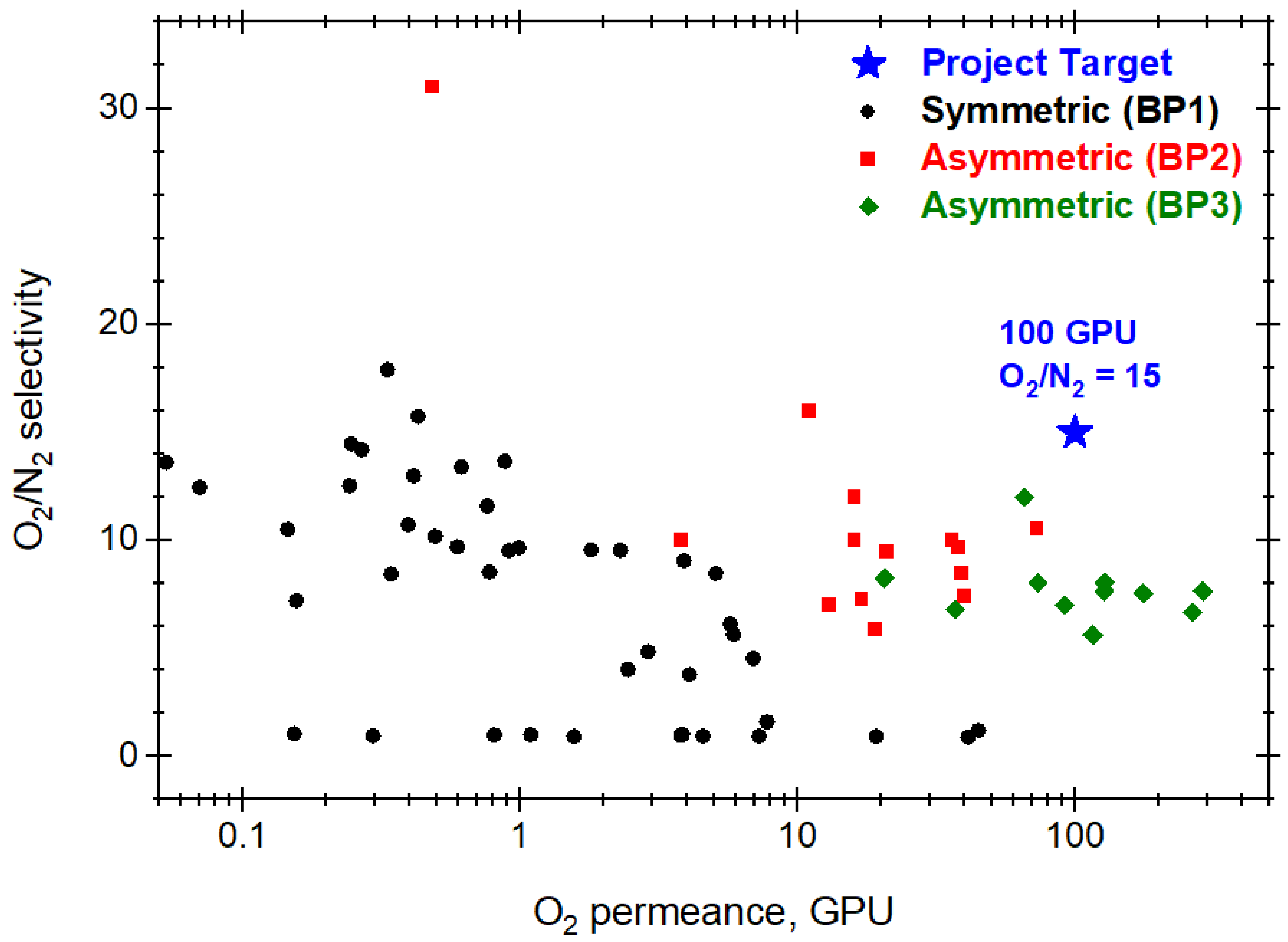
- **Several parameters to tailor separation performance**
  - Base HFM selective layer (SL) thickness, X-linking density and molecule, pyrolysis temperature, and defect sealing layer (PDMS)
    - Balancing SL intrinsic perm-selectivity and thickness

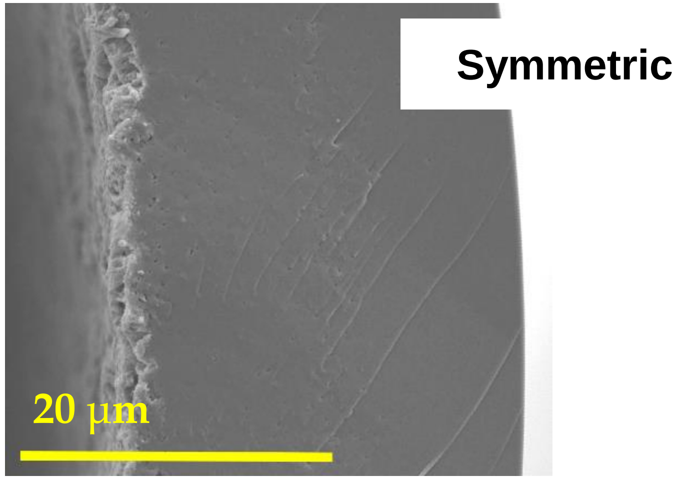


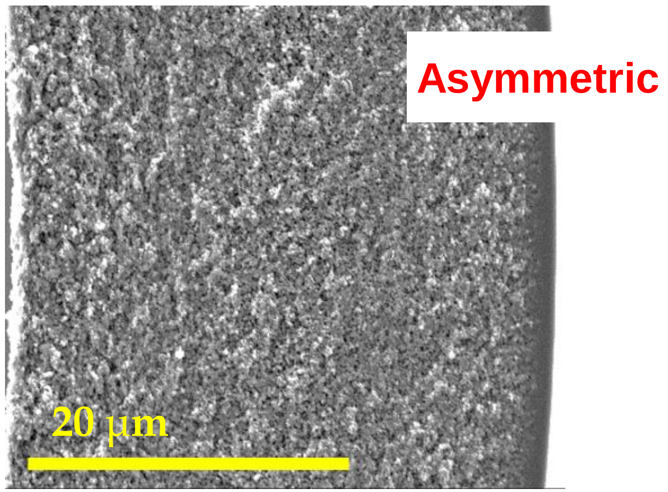




Ideal O_2/N_2 Performance Summary



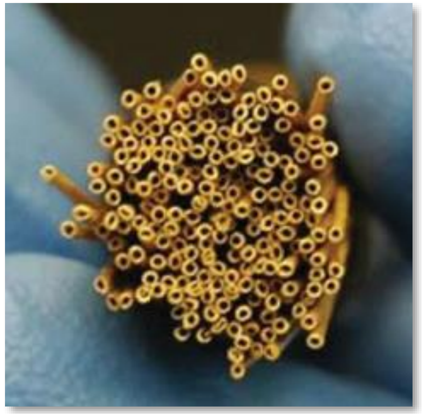




Lab-Scale Demonstration

Step-up in PBI-CMS Hollow Fiber Fabrication Capability

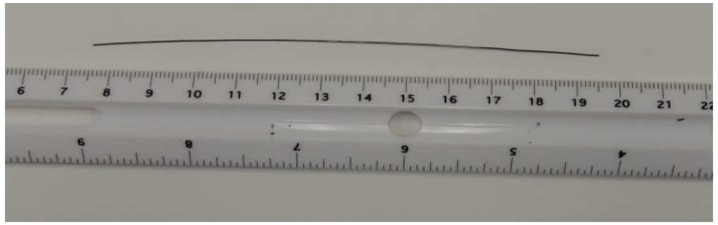
- **Efforts focused on the translational of fabrication methods (post-spinning crosslinking and pyrolysis) for fabrication of PBI-CMS multi-fiber modules**



Batch Process

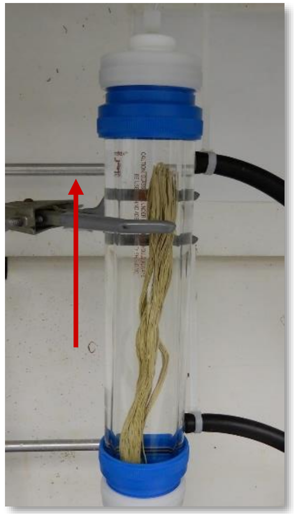
- *Few fiber strand X-linked in vial under slow agitation*

Single fiber Pyrolysis

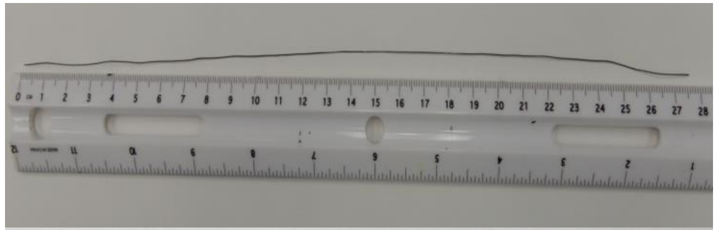


Flow-Through Process

- *Simultaneous processing of fiber bundle*
- *X-linking performed as part of solvent exchange process*



Multi-fiber pyrolysis under industry relevant inert gas flow



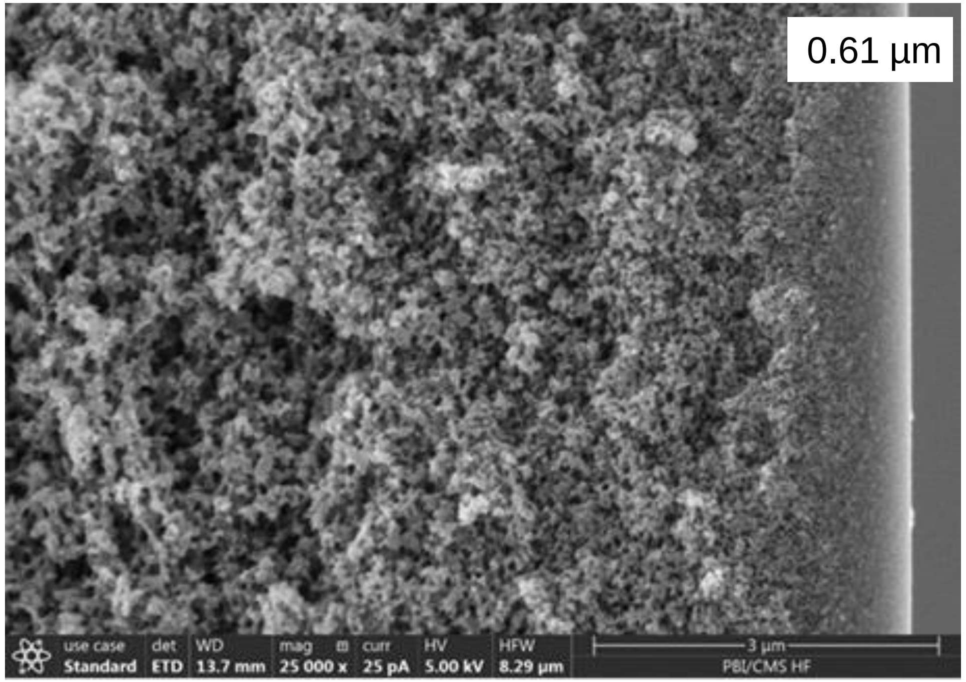
PBI-CMS HFMs – Improved Selectivity

- **Successfully fabricated PBI-CMS HFMs with high pure gas O_2/N_2 selectivity**

Sample	Pyrolysis Atmosphere	Pure Gas Permeance, GPU			Ideal Selectivity	
		He	O_2	N_2	He/N_2	O_2/N_2
Membrane 1	Inert (N_2) Gas Flow	722	65.5	23	132	12.0

Flow Through X-linking

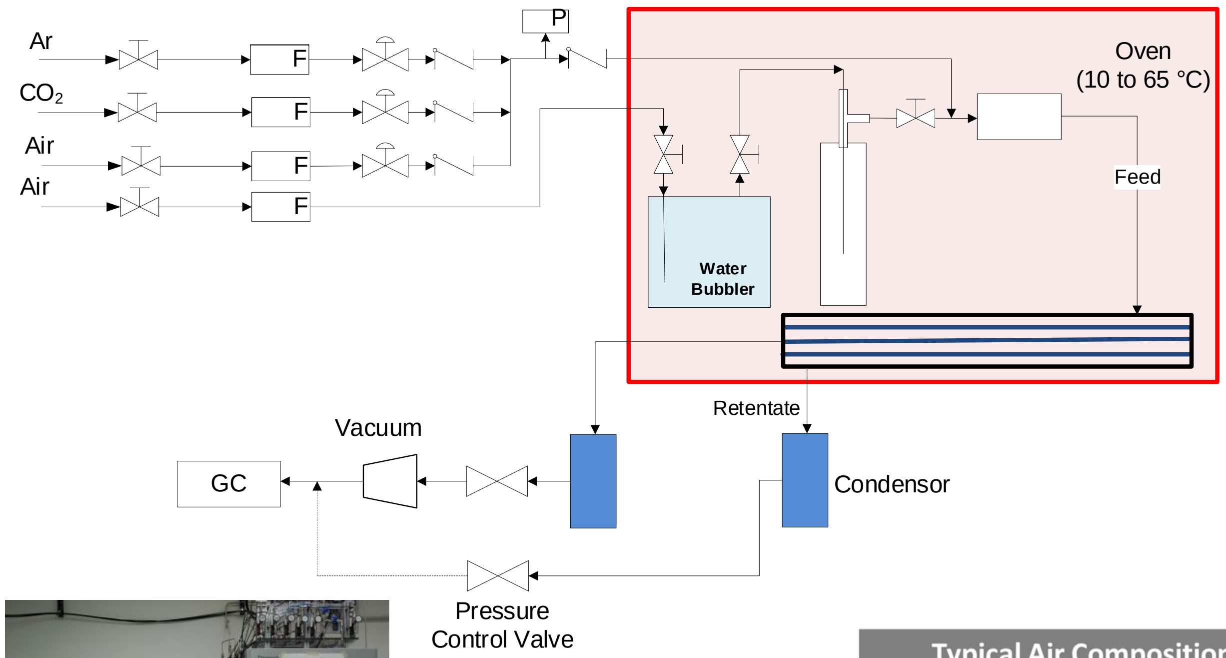
- Combination of slightly thicker selective layer (SL), and optimized and scalable x-linking method results in further reducing defects and improved selectivity



- Fiber spinning process slightly changed to increase SL thickness of the base PBI HFMs
- PBI-CMS HFMs having ~ 0.6 µm SL were produced as compared to ~ 0.3 µm in previous PBI-CMS HFMs.

Separation Performance Evaluation Under Relevant Process Conditions

- **Perform multi-fiber module testing under simulated conditions including in presence of trace components (e.g water vapor, CO_2)**

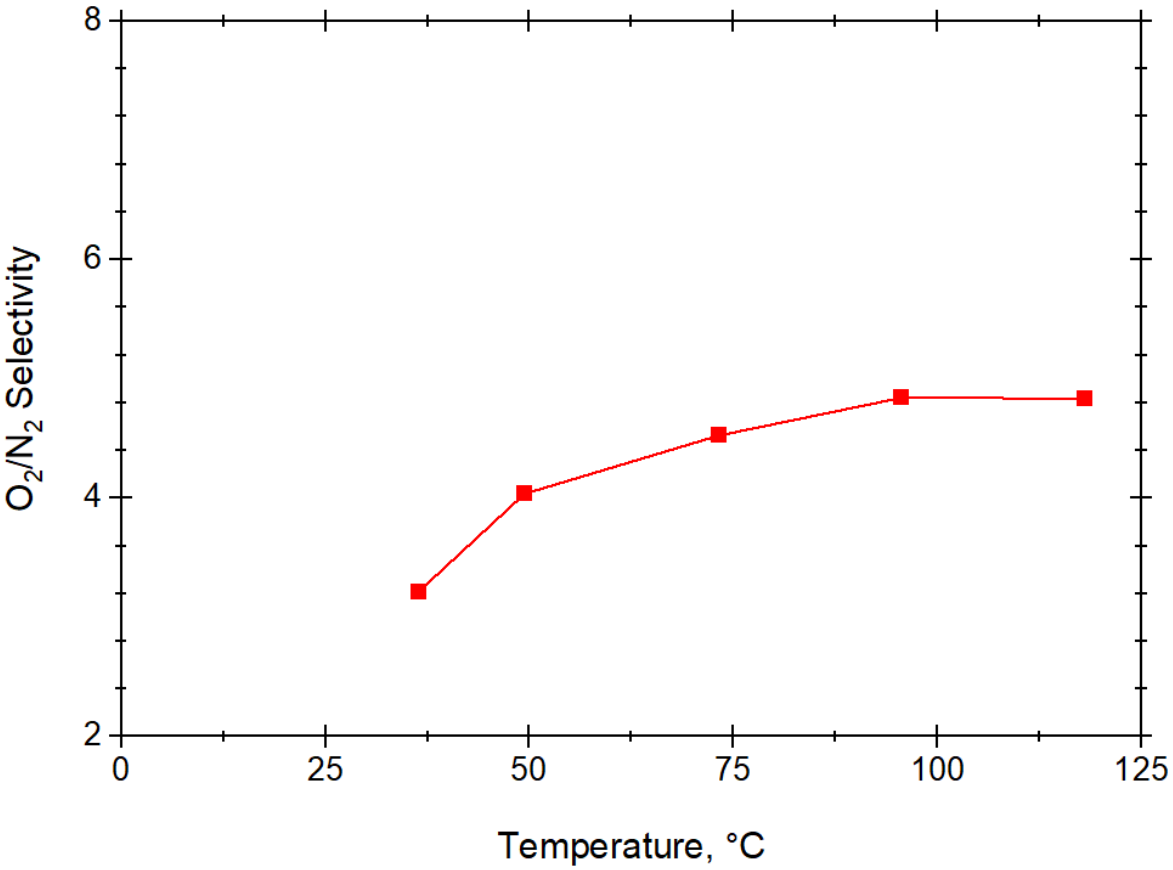


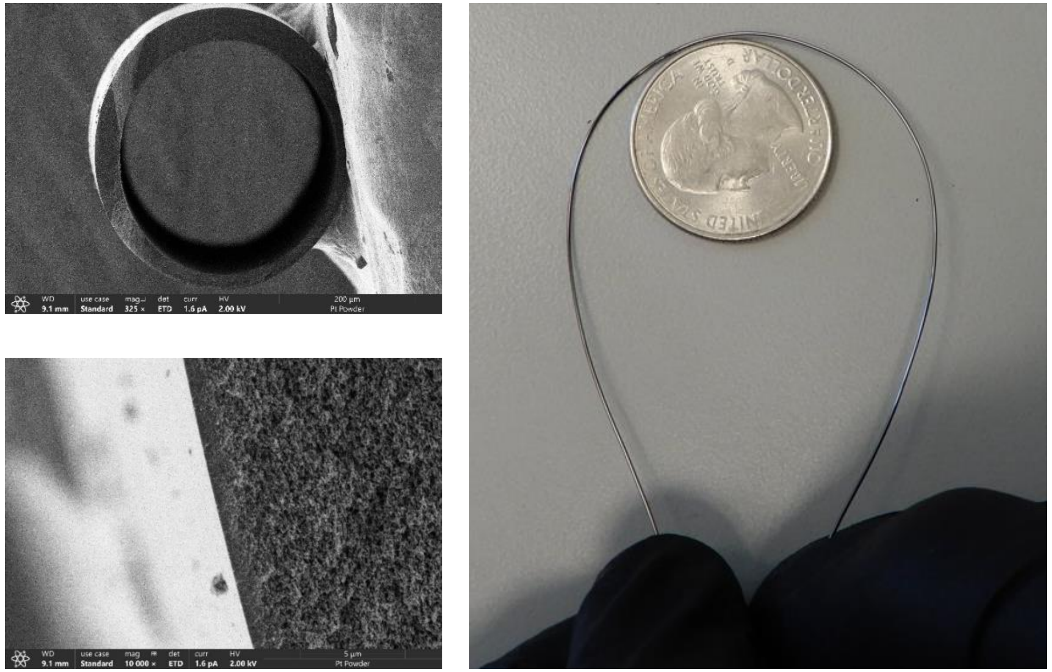
Typical Air Composition	
N_2	78% (vol. Dry Basis)
O_2	21%
Ar	0 to 0.93
CO_2	0 to 400 ppm
Relative Humidity	10 to 90%

Lab-scale multi-fiber (20) membrane module

Multi-fiber Membrane Module Evaluation

- **Promising preliminary air separation performance measured for multi-fiber membrane module**
  - Pre-conditioning protocol to be incorporated in multi-fiber module evaluation





Mechanically Robust Asymmetric PBI-CMS HFMs with < 1 µm selective layer

Invention Disclosure Pending

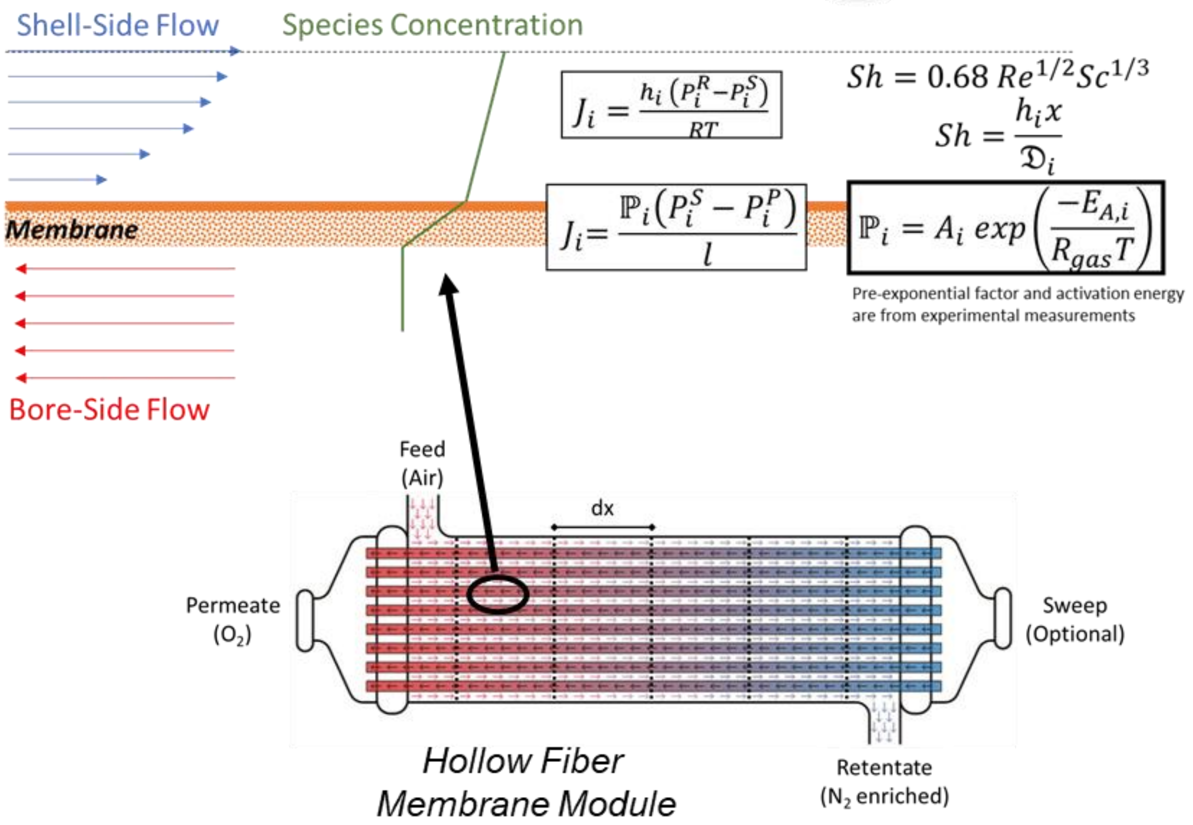
Process Design and Techno-Economic Analysis

Process Modeling Platform Development

- **Developed hollow fiber membrane model and integrated with energy and cost model tool for envisioned air separation process design**

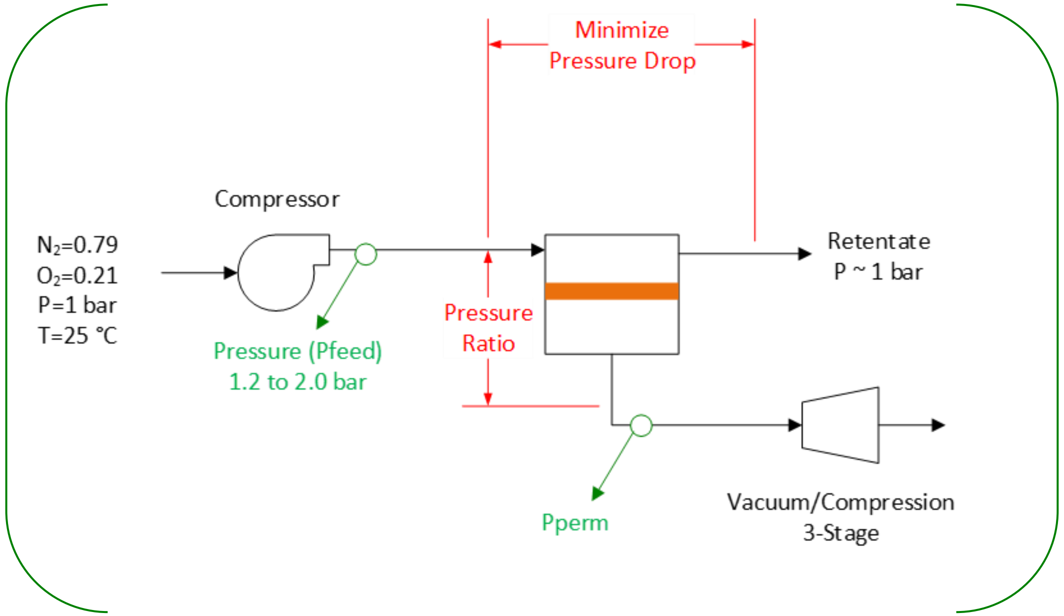
Membrane Flux Model

python™



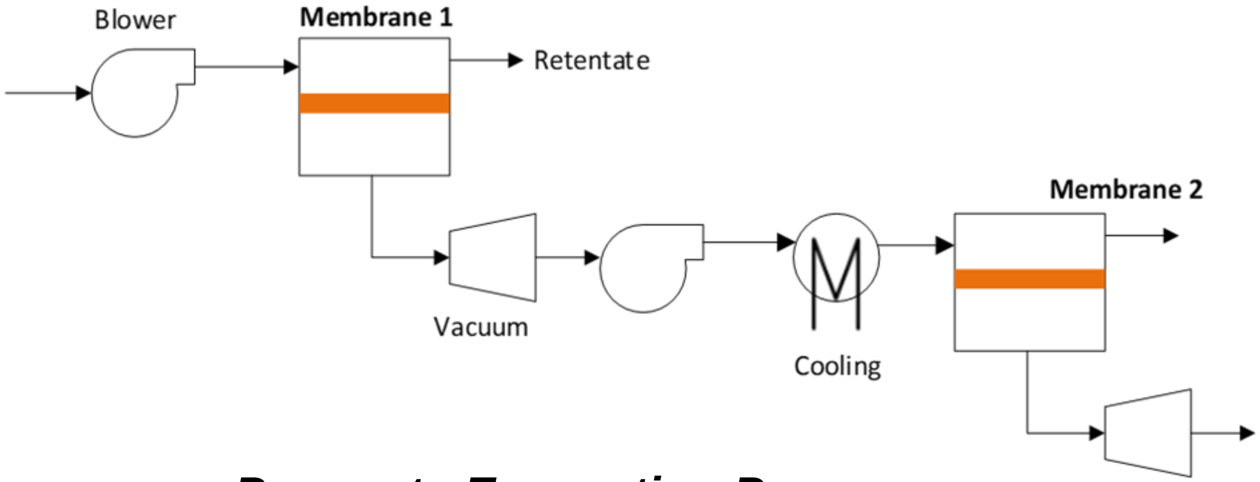
Multi-Stage Process Model

python™



Stage n=1,2,3…..

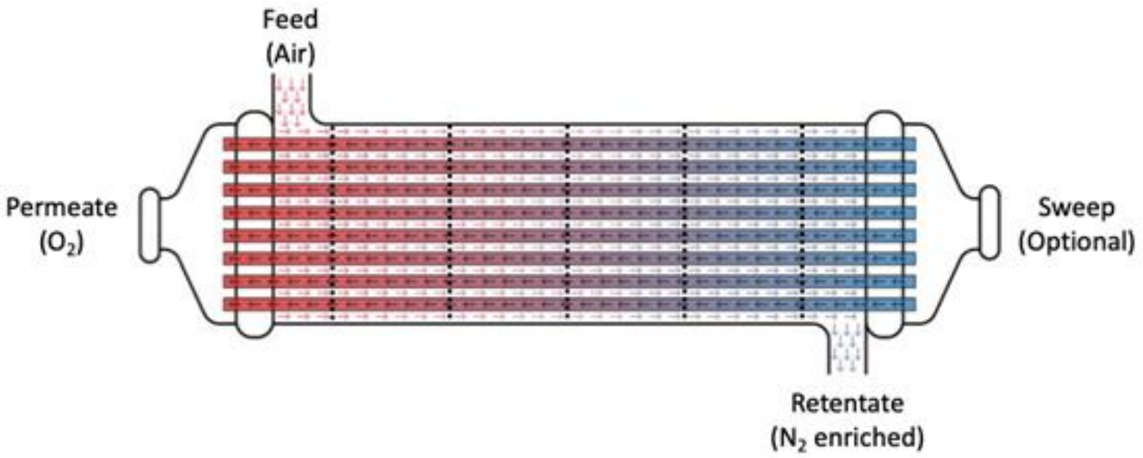
Techno-economic Analysis – Design Basis



Permeate Evacuation Process
Simplest Process Design

Process Parameters	Input values
O_2 Production Rate, TPD	10
Annual capacity factor	90%
Indirect cost factor	53%
Fixed Charge Rate (FCR)	7%
Life of equipment, y	25

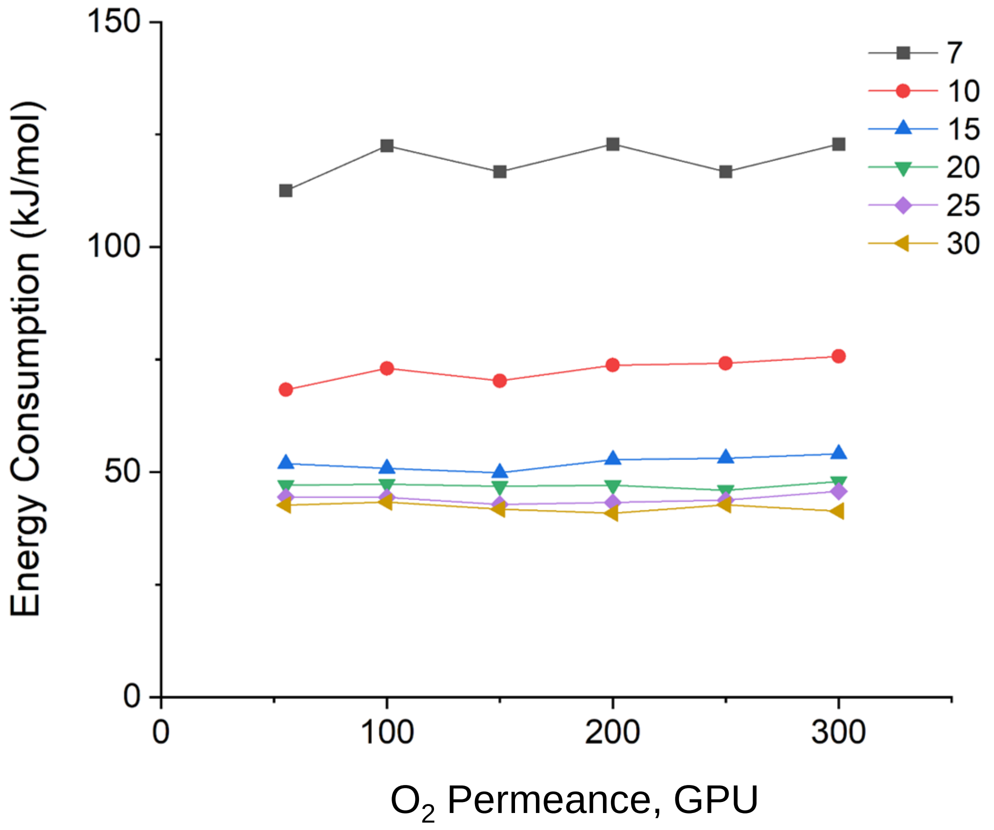
Membrane module	Input values
HF Diameter, μm	400
Wall Thickness, μm	30
O_2 permeance, GPU	55-300
O_2/N_2 selectivity of the membrane	10-30
Module Diameter, m	0.25
Module Length, m	0.4-1
Surface Area Density, m^2/m^3	3000
Membrane cost, $\$/m^2$	50-125
Electricity cost, $/kWh	0.06-0.1

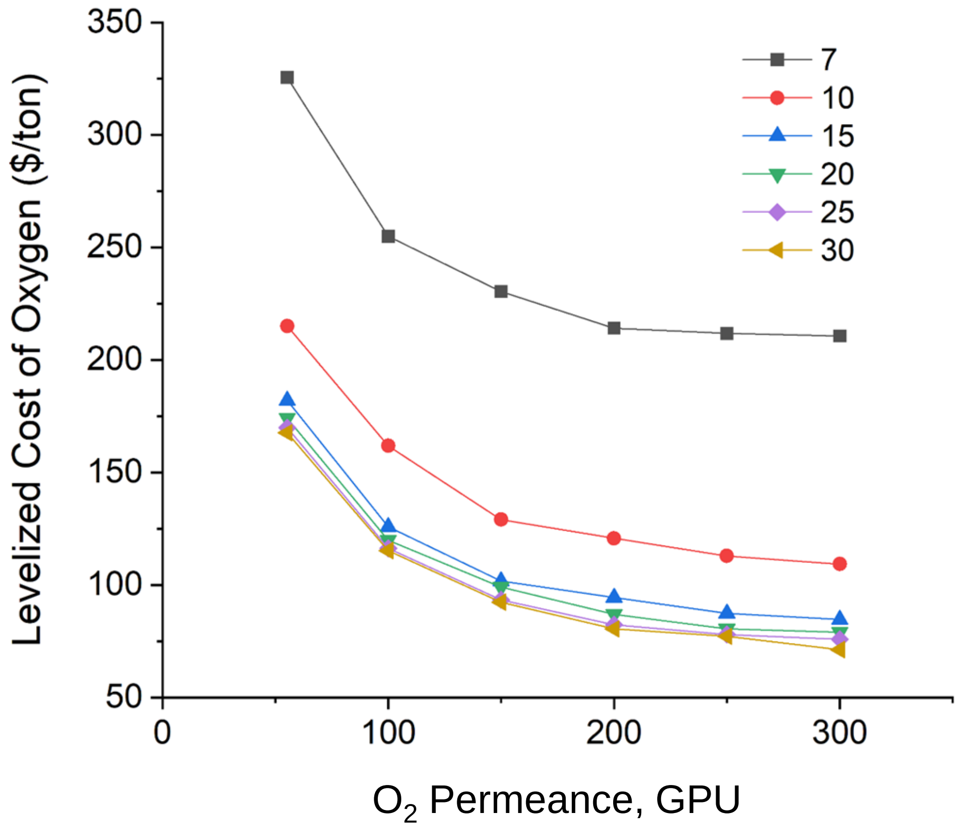


Ref:

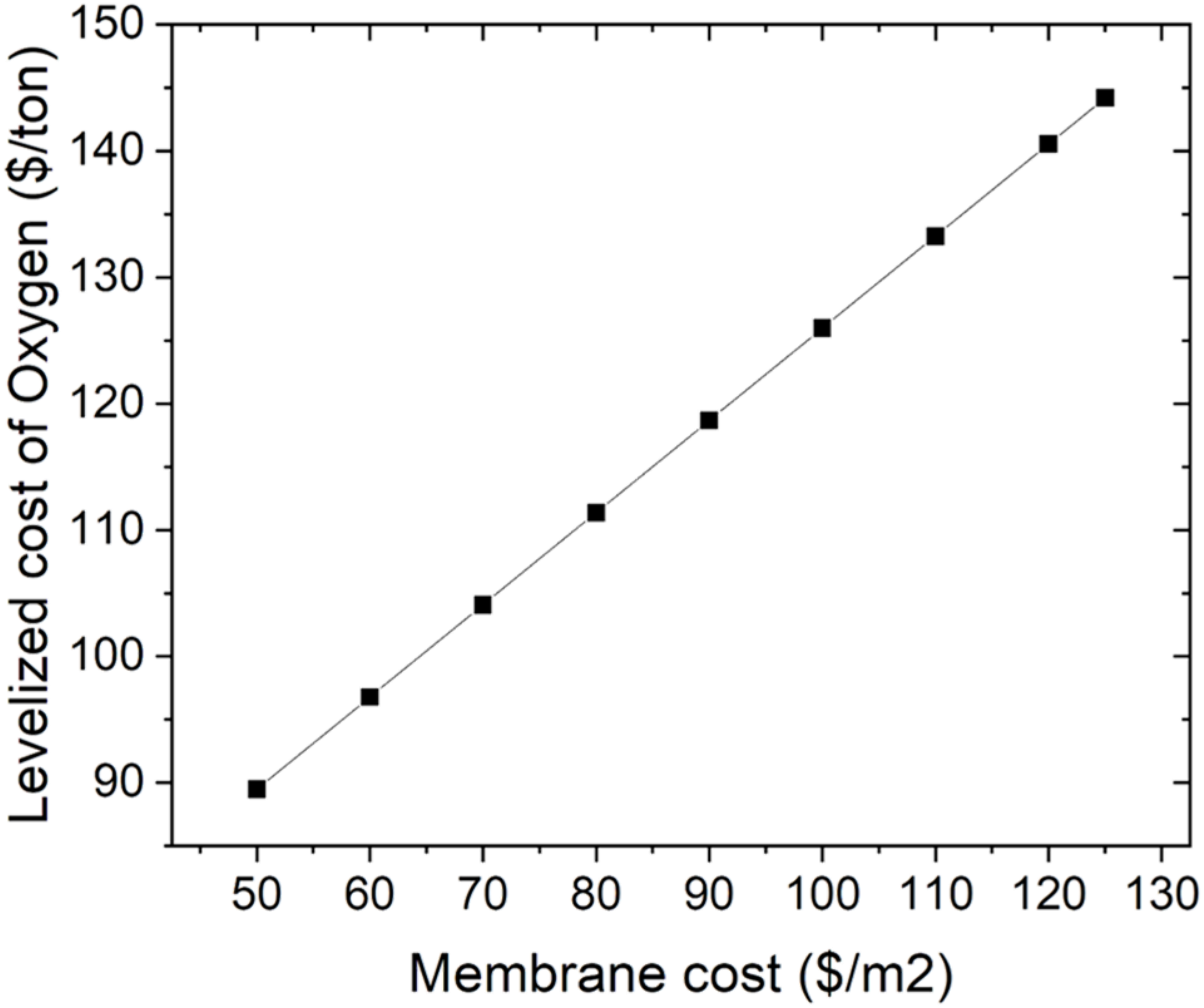
Membrane Performance Controls O_2 Production Cost

- **Energy consumption and cost of O_2 production calculated for membrane process as a function of O_2 permeance and O_2/N_2 selectivity**
  - Modelled fluid flow dynamics and operating conditions to achieve minimize O_2 production cost for each permeance-selectivity combination



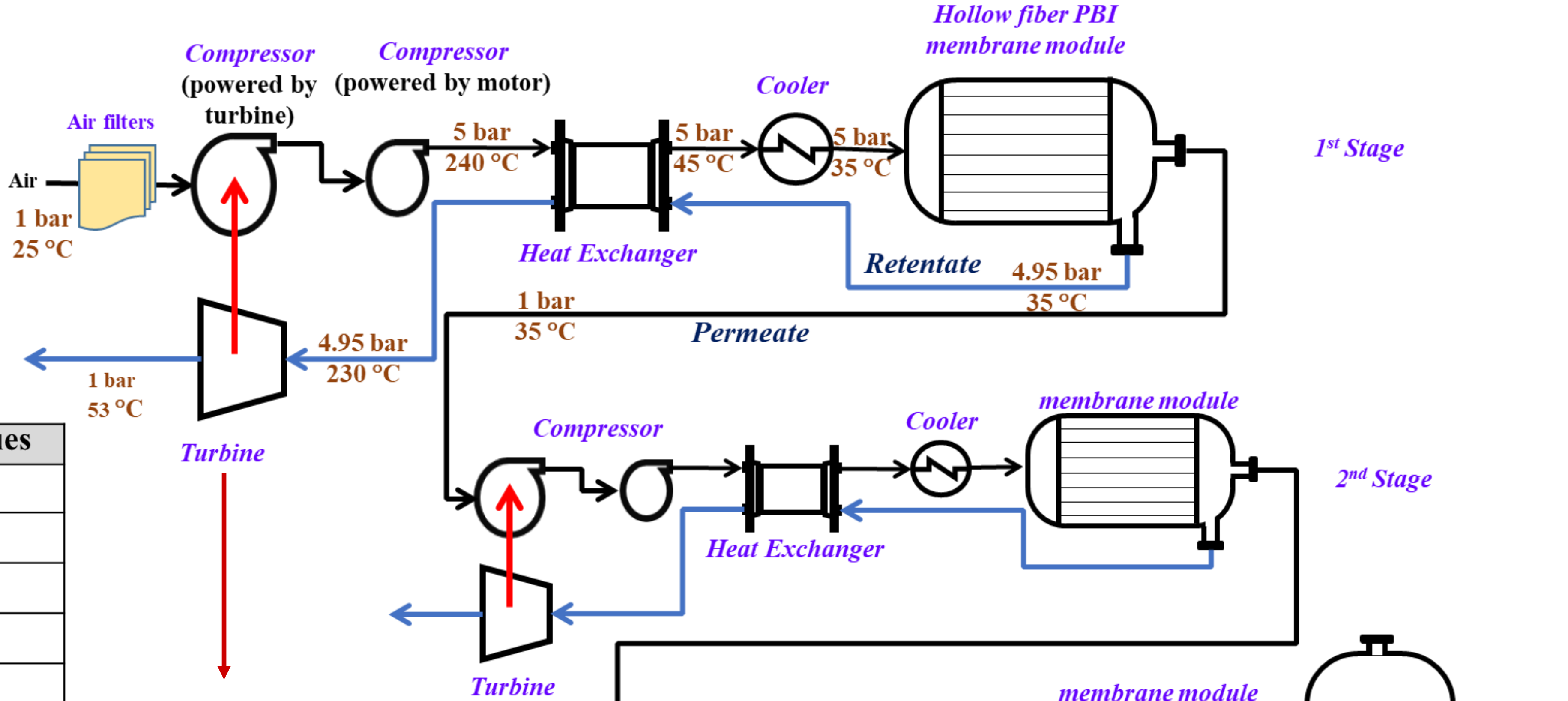


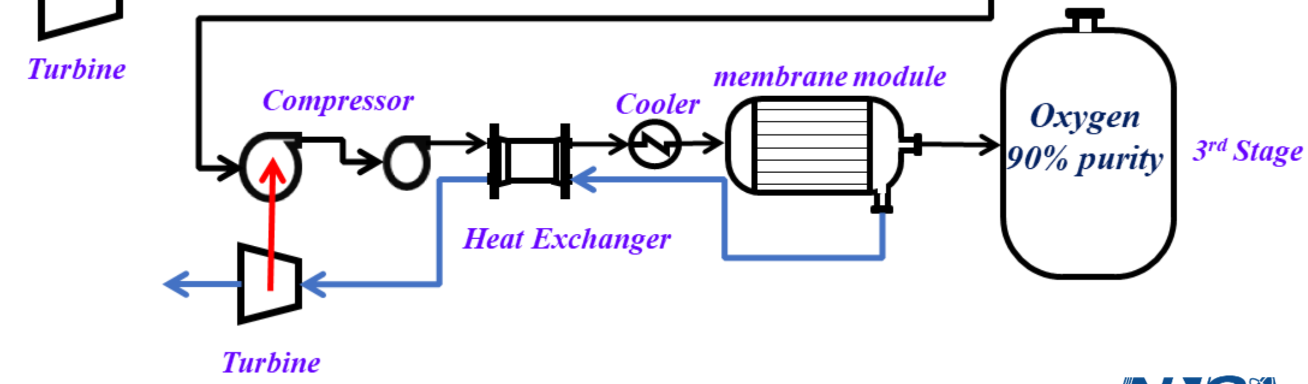
Membrane Cost Deciding Factor



Alternate Process – Feed Compression and Energy Recovery

- **Preliminary TEA: 3-stage process for > 90% O_2 production**



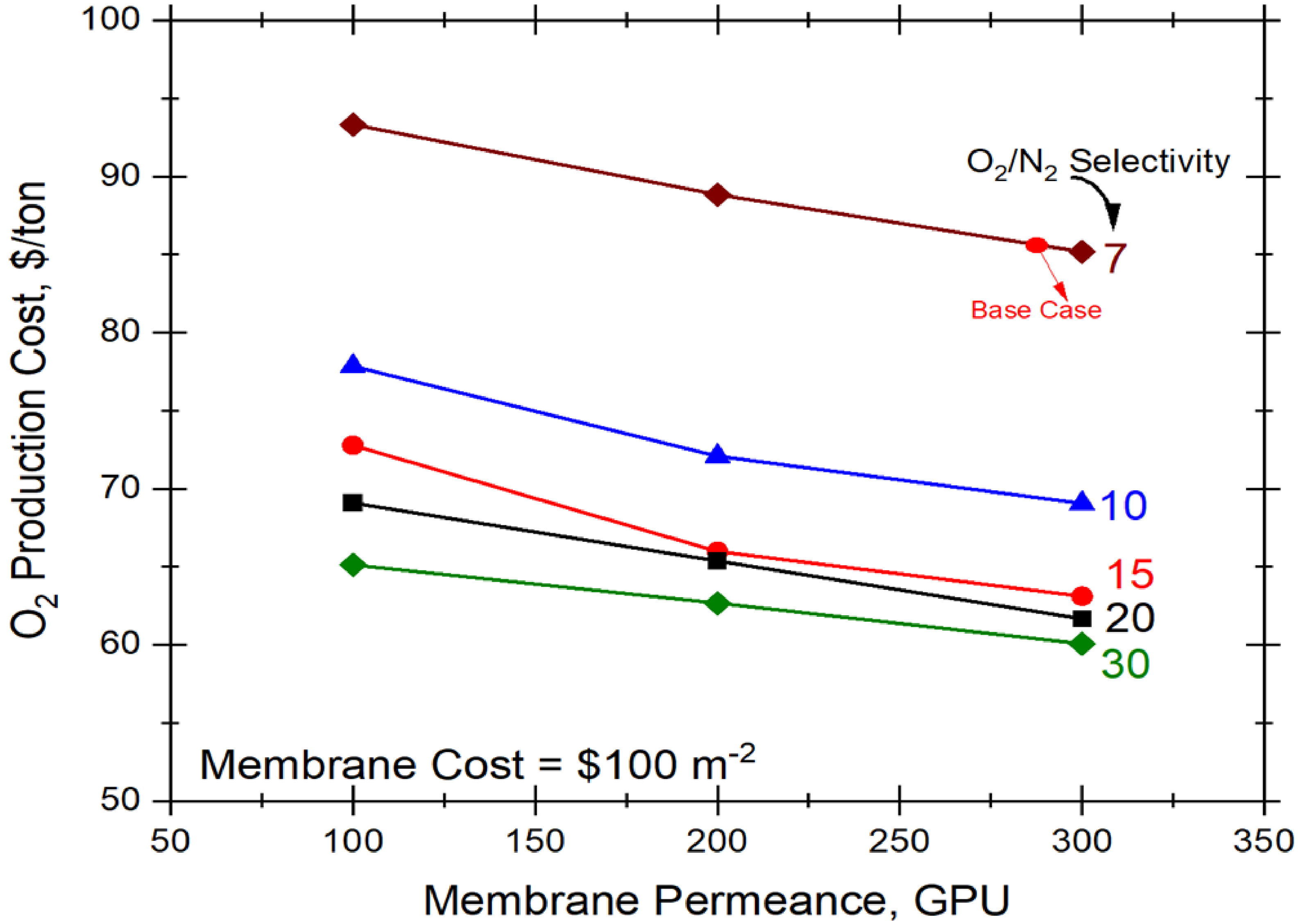


Feed compression process	Input values
O_2 Production Rate, TPD	10
Number of Membrane Stages	2-3
Inlet volume of air, Kg/s	1-1.1
Pressure of inlet air, bar	5-9
Stage Temperature, ˚C	35

First grid-scale compressed air battery now operational

1.5 Mwe SustainX
Seabrook, New Hampshire

Lower O_2 Production Cost Possible



Project Milestones (BP – 3)

BP	ID	Task #	Description	Planned Completion Date	Status
3	R1	1.0	Perform a stage-gate review to determine the progress and potential to reach the project goals and achieve competitive energy consumption.	03/31/2023	Complete
3	R2	2.0	Report a plan to DOE to reach a 1-micron thick selective layer and demonstrate that the permeance can reach 100 gas permeation units (GPU) while maintaining selectivity of at least 15.	06/31/2023 (Extension)	in-progress
3	R3	4.0	Determine goals for cost, permeability, and selectivity that can be reached by looking at what can be practically achieved for the material and process. Use these practical goals to evaluate the system performance in terms of energy and purity.	03/31/2022	Complete
3	R4	2.0	Set up a laboratory system with controlled pyrolysis conditions under flowing gas, which could be a practical way of simulating industrial conditions.	03/31/2022	Complete
3	R6	3.0	Perform argon testing to determine the maximum possible O_2 purity.	03/31/2022	Complete

Future Plan (TRL advancement from 3 to 5)

- **Continue materials development efforts to improve selectivity at high O_2 permeance (≥ 100 GPU)**
- **Membrane module evaluation under laboratory conditions**
  - Successfully developed methods to fabricate multi-fiber modules (> 20 fibers) to validate separation performance in simulated laboratory conditions
  - Compressed gas feed and permeate side at process relevant operating conditions for both permeate evacuation and feed compression cases

  TRL 4

  - Laboratory scale validation under relevant conditions
    - Prototype multi-fiber module fabricated using lab-scale potting machine
    - Performance assessment of multi-fiber module in ambient air under process relevant operating conditions

  TRL 5

- **Gather application relevant data for facilitating industrial interest for commercialization**
  - Engage with commercialization partners to develop plan for engineering design and pilot-scale evaluations

Acknowledgements

- **DOE/FECM**
  - Evelyn Lopez
  - Dave Lyons
- **Los Alamos National Laboratory**
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  - Prashant Sharan (*Lead - TEA*)
  - Michael Dugas (*GRA*)
  - Ibtida Sultana (*Postdoc*)
- **Previous Team Members**
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  - Jeremy Lewis (*Plug Power*)
  - Kamron Brinkerhoff (*LANL Staff*)

Thank you!!