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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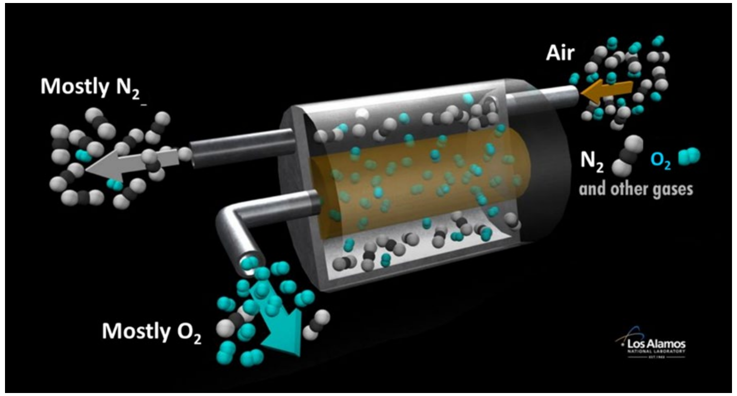
Project Review Meeting
DOE – Fossil Energy/NETL
May 2, 2022

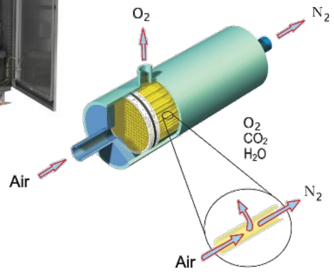
Project Overview

- **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 – 07/2022
- **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

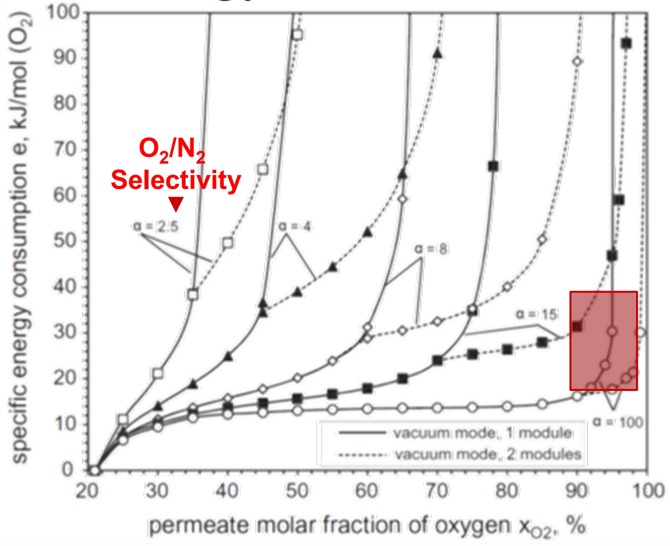


Air Separations

- **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



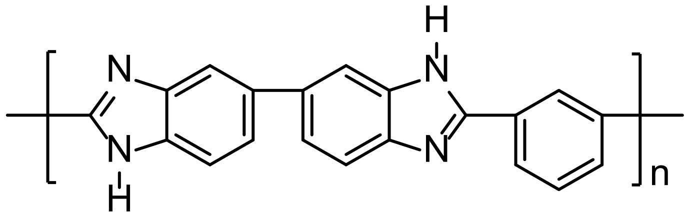
Ref: Air Products Inc. & Air Liquide Inc.



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

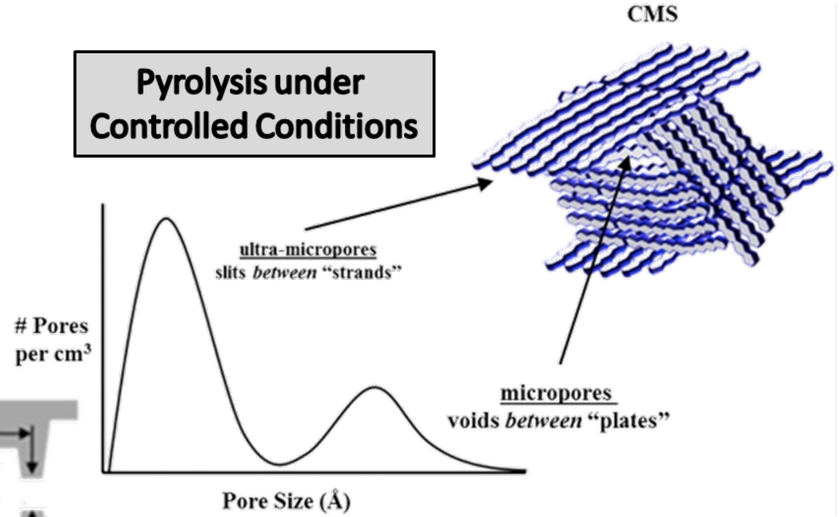
Membrane Development Approach

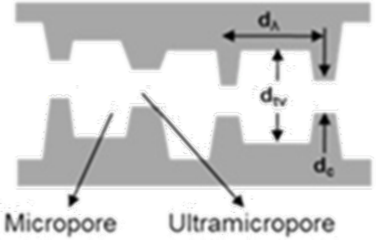
- **Polybenzimidazole (PBI)-derived carbon molecular sieve membranes for high O_2/N_2 selectivity**



  - 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]



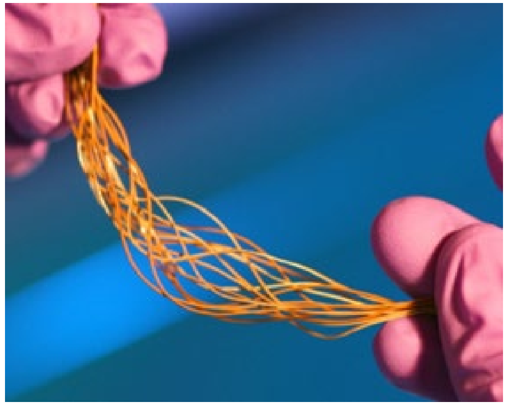


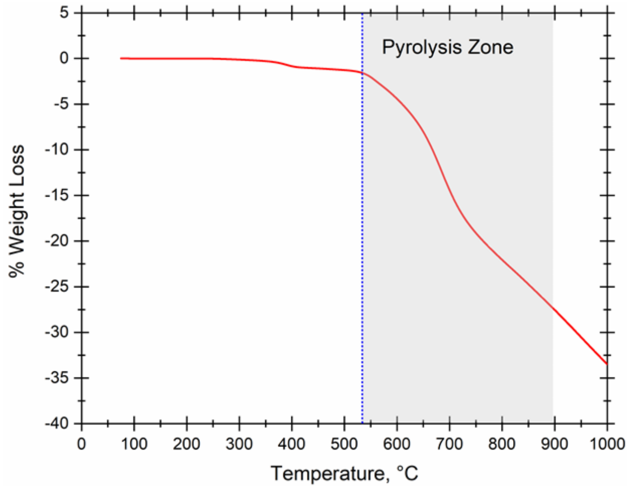
Ref: Rungata et.al., Carbon 115 (2017) 237-248

Polymer Derived CMS Membranes

- CMS membrane formation is multi-step process

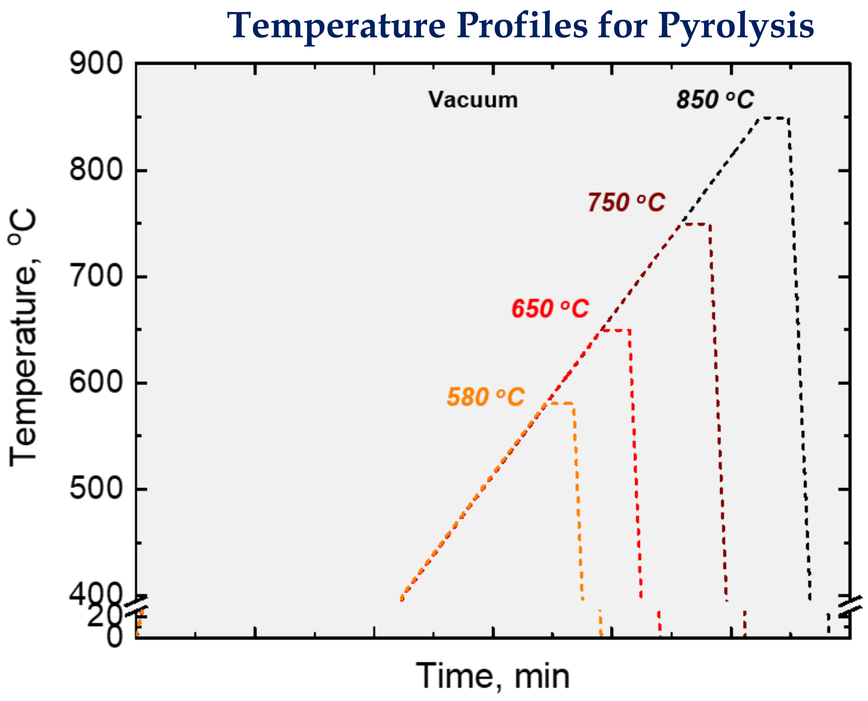
Commercial PBI Polymer → Hollow Fibers → Base Polymer Membrane → Pyrolysis → CMS Membranes

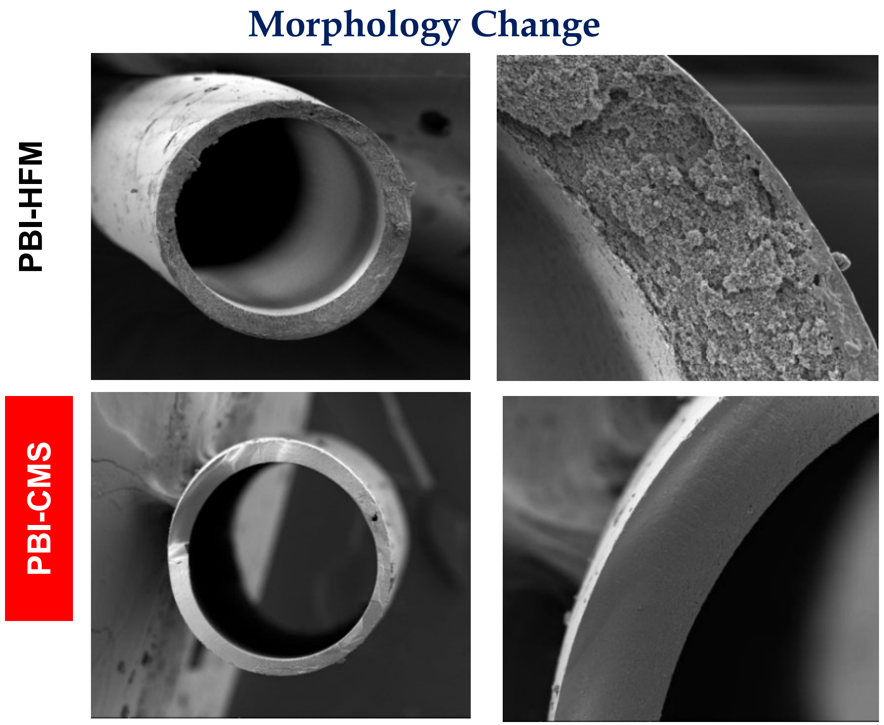




Ref. *Berchtold & Singh, et.al. 2018 US Patent 10071345*

Tailoring Separation Performance: Pyrolysis Temperature



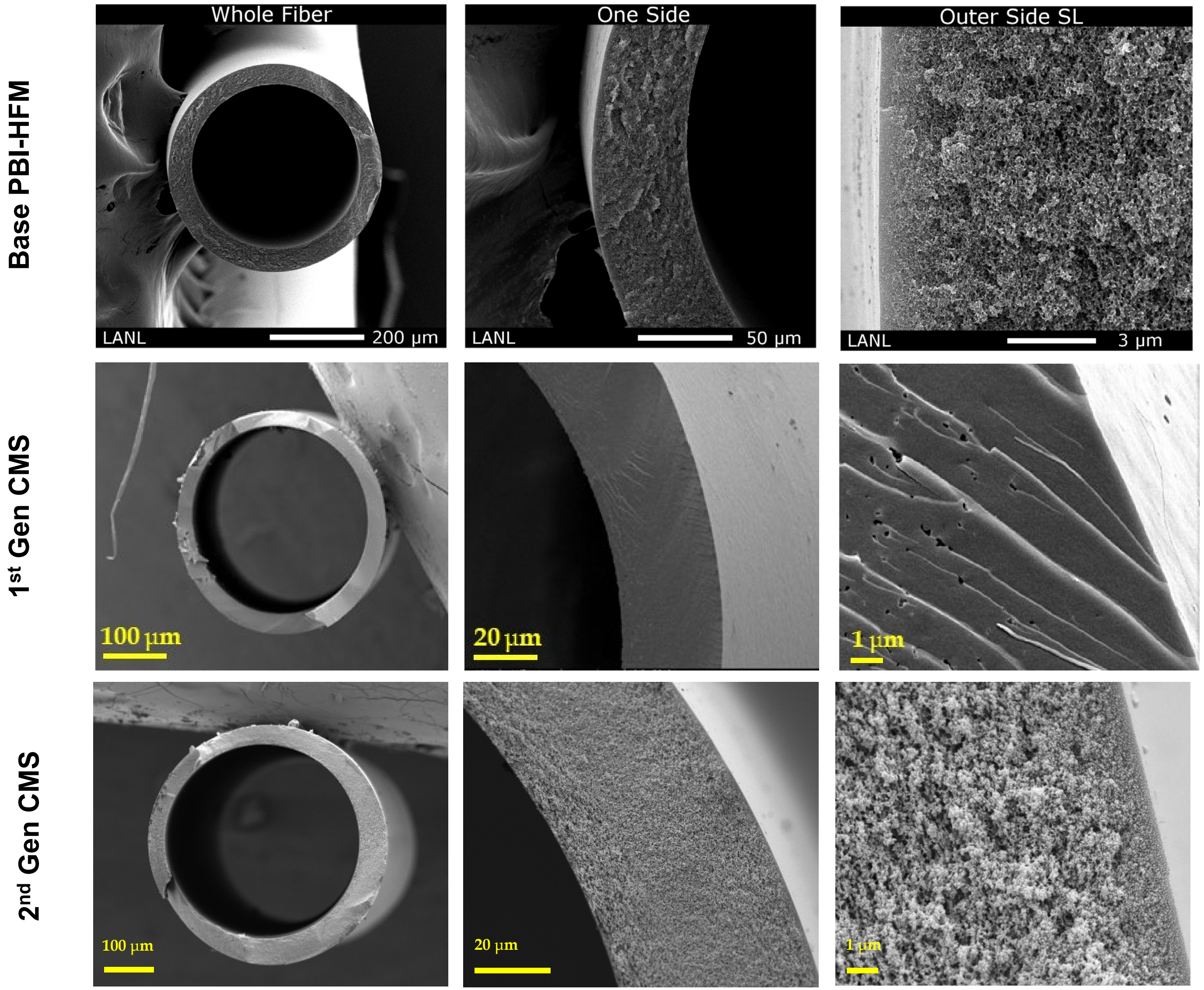


Sample	Ideal Separation Performance		Estimated O_2 permeability [Barrer]
	O_2 permeance, GPU	O_2/N_2	
PBI	0.204	1.02	0.06
CMS-580	0.303	8.44	8.48
CMS-650	3.964	8.47	99
CMS-750	0.782	13.7	16.4
CMS-850	42.3	0.90	550

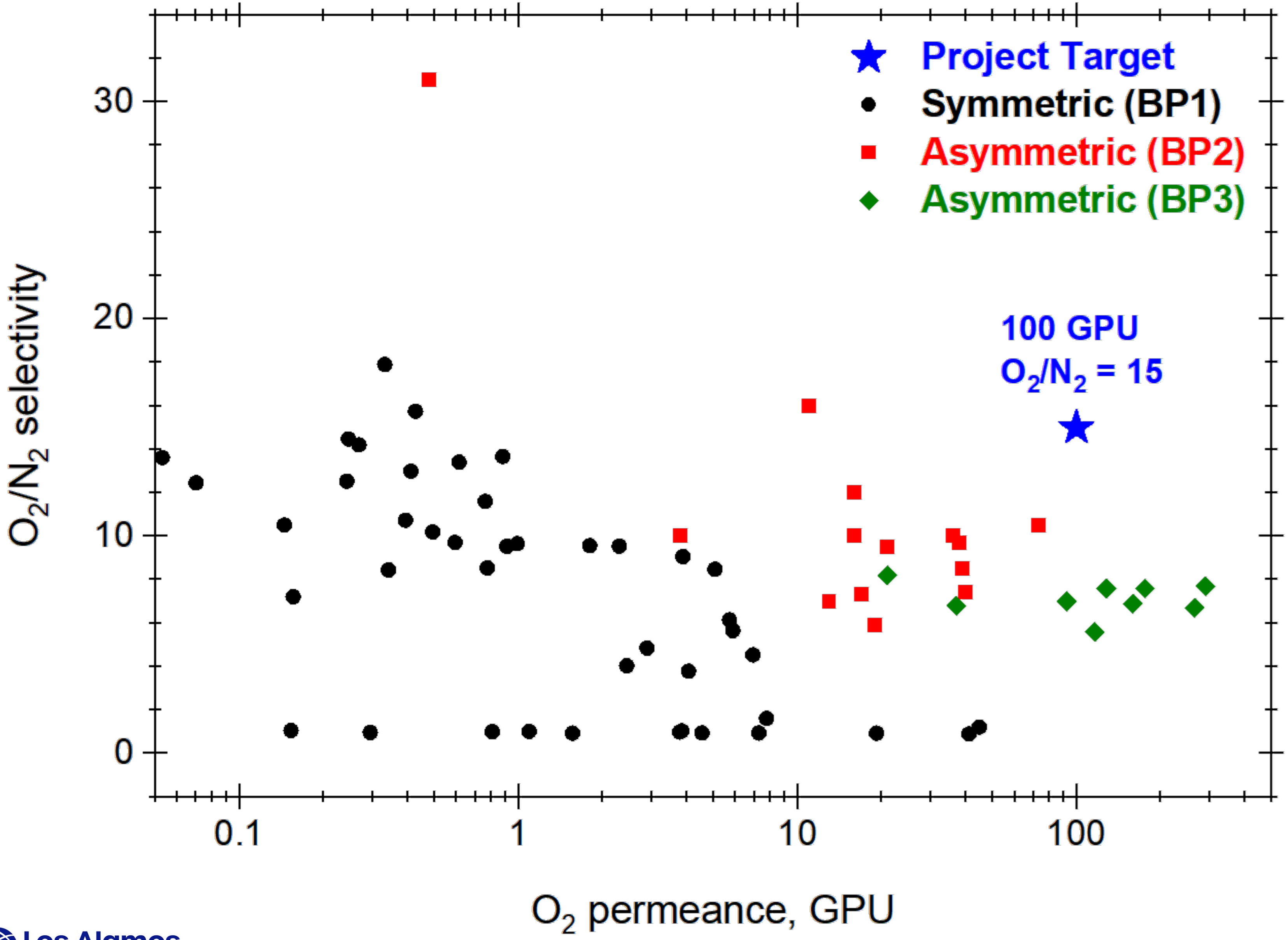
Seong & Singh et.al., Carbon 192, 71-83, 2022

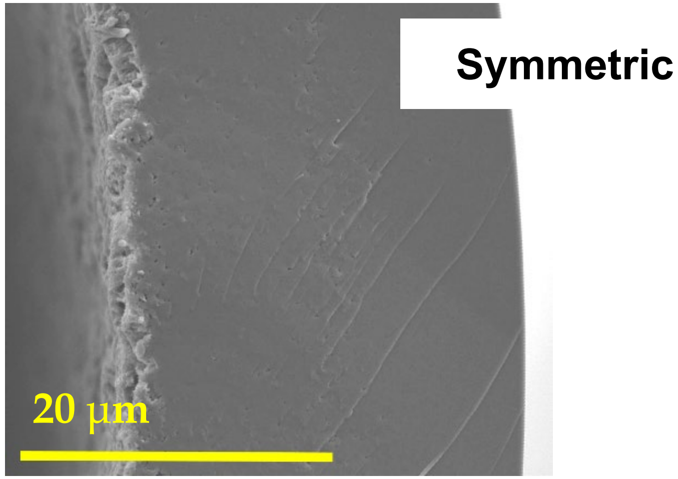
Achieving High Permeance

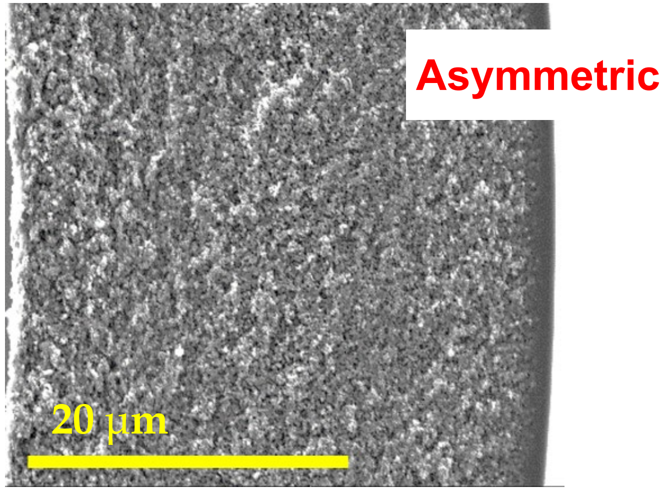
- **Challenge: Mitigate HFM porous support structure collapse during pyrolysis**



O_2/N_2 Performance Summary



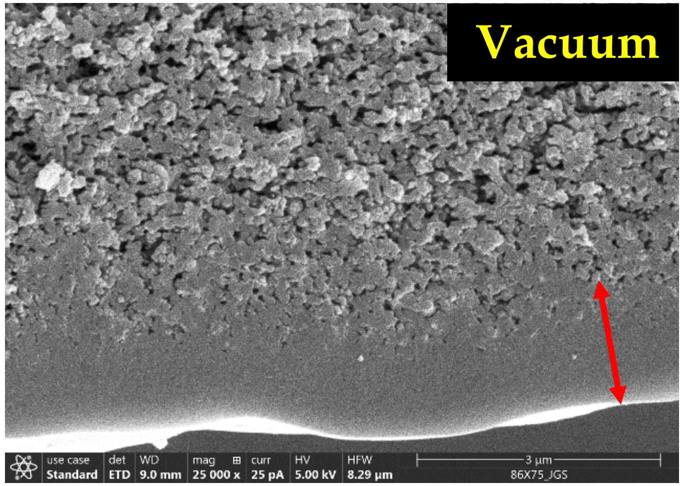




Tailoring Separation Performance: Pyrolysis Atmosphere

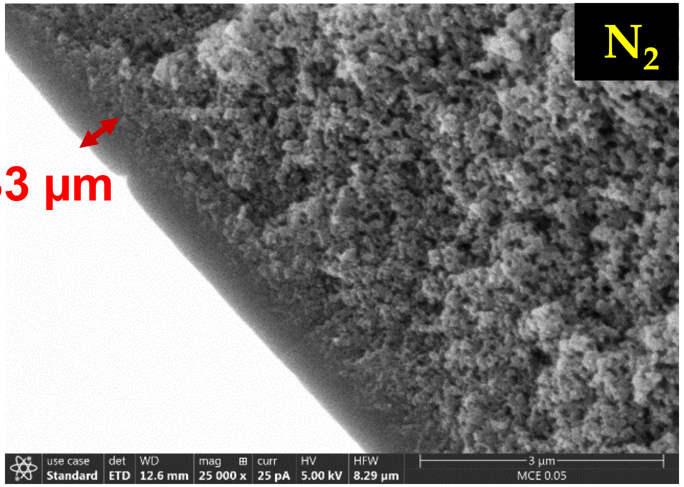
- **Pyrolysis under inert flowing gas is more practical for industrial deployment**
  - Inert gas pyrolysis produced PBI-CMS HFMs having higher O_2 permeance with similar selectivity as compared to vacuum pyrolysis

Sample	Pyrolysis Atmosphere	Permeance, GPU					Selectivity			
		He	O_2	CO_2	Ar	N_2	He/N_2	O_2/N_2	O_2/Ar	CO_2/N_2
Membrane 1	Vacuum	179	87		14	13	14	6.7	6.2	
Membrane 2	Inert (N_2) Gas Flow	517	159	835	27	23	22	6.9	5.9	36
Membrane 3	Inert (N_2) Gas Flow	648	265	1350	41	40	16	6.7	6.5	34



~ 2 µm

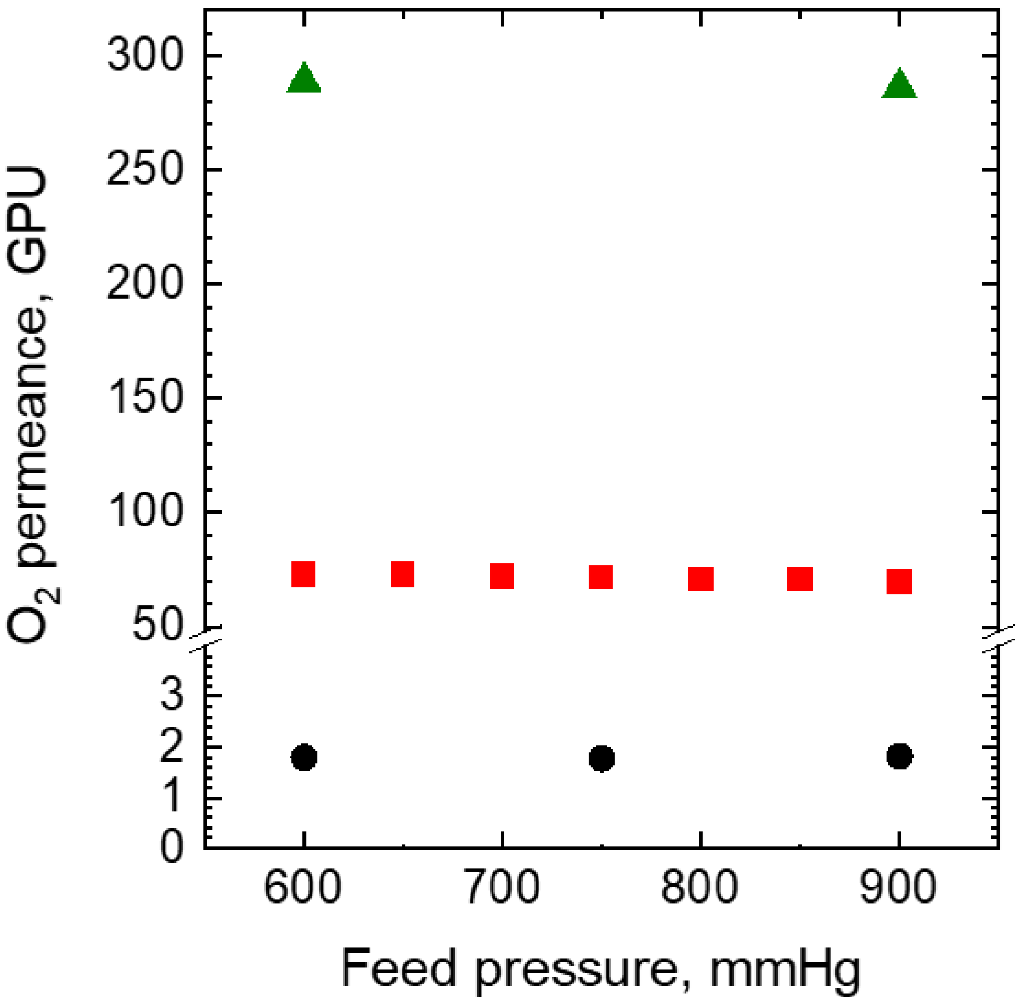
~ 0.33 µm

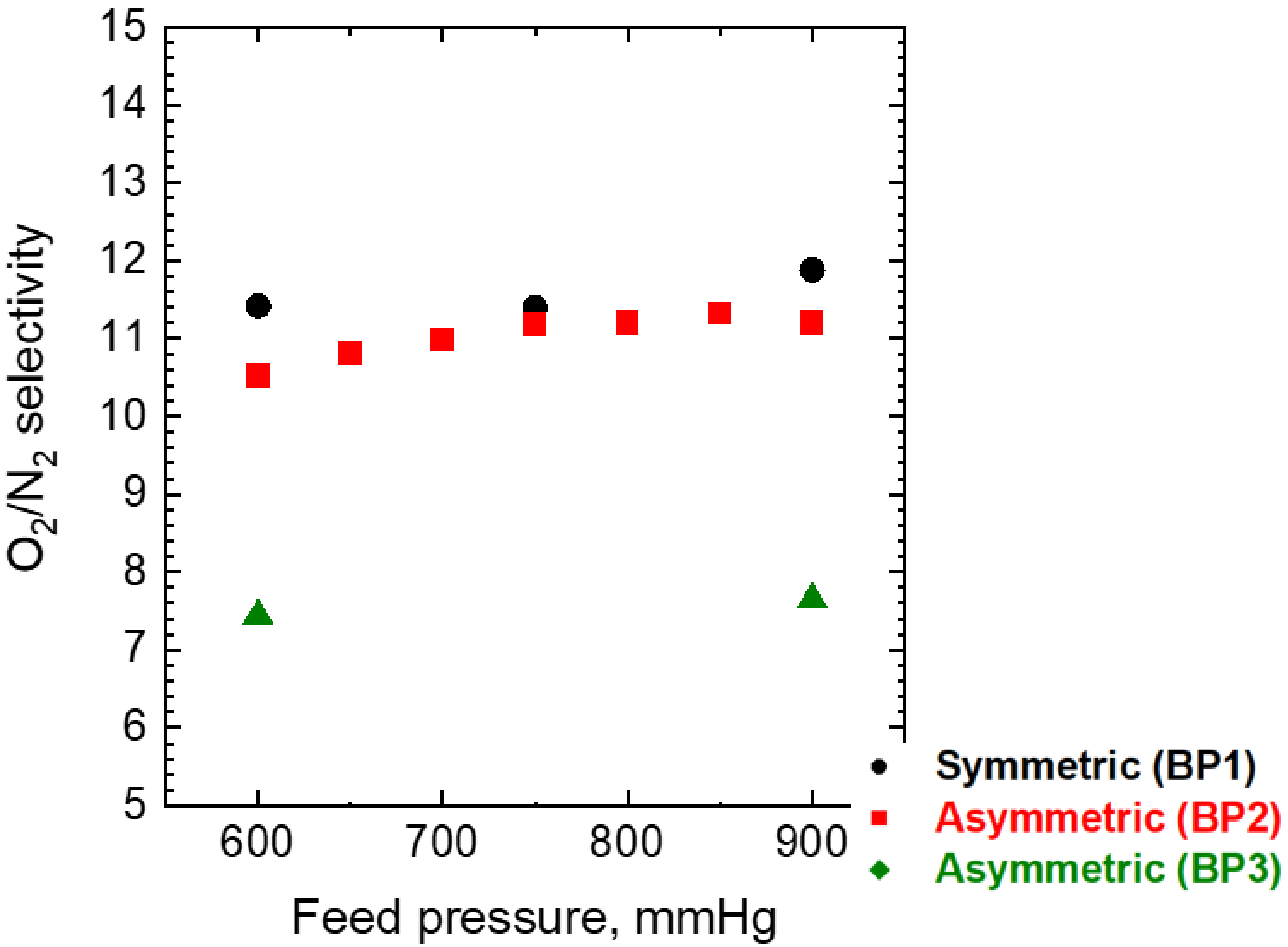


- CMS-PBI HFM fabricated under vacuum had thicker selective layer as compared to membrane fabricated in inert flowing gas resulting in higher O_2 permeance

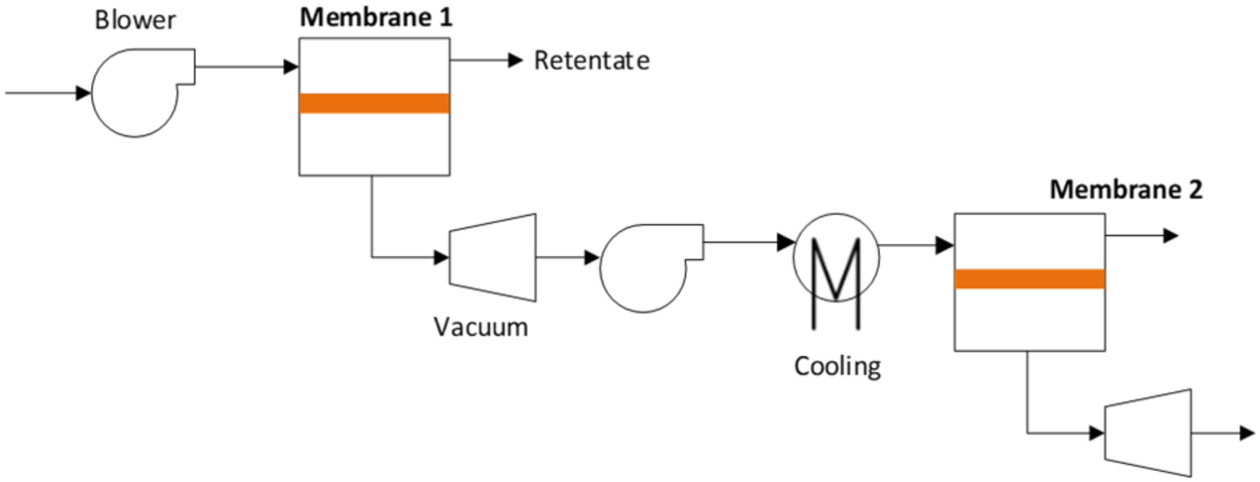
PBI-CMS HFM: Pressure Independent Separation Performance

- Pressure independent separation performance indicate defect-free HFMs





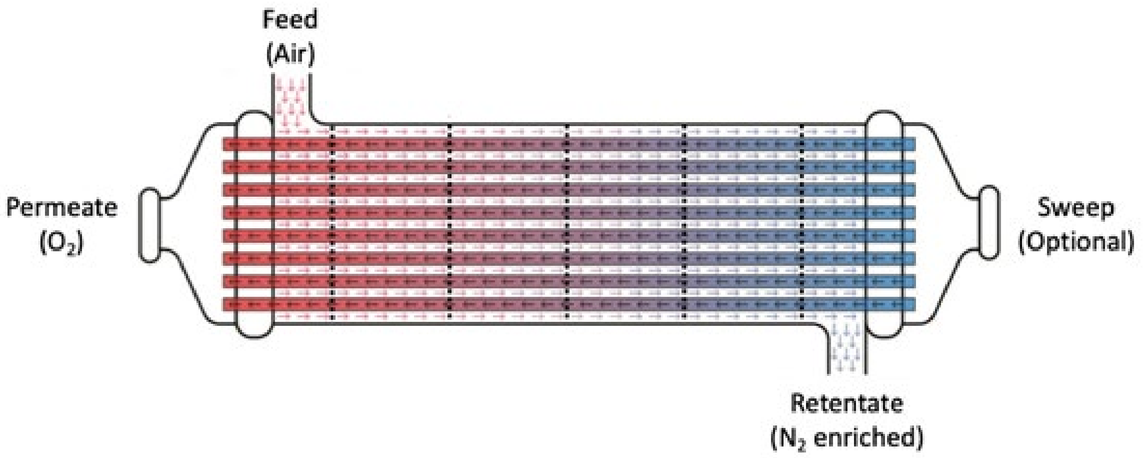
Techno-economic Analysis – Design Basis



Multi-stage Membrane Process

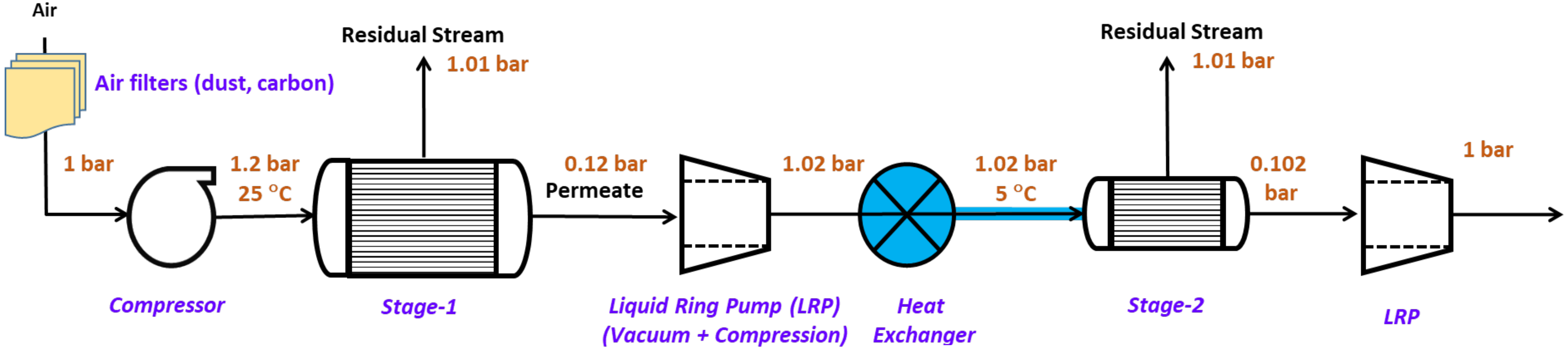
Membrane module	Input values
HF Diameter, µm	300-500
Wall Thickness, µm	30
Selective Layer Thickness, µm	0.1 to 1.0
O_2 permeance, GPU	100-300
O_2/N_2 selectivity of the membrane	10-30
Module Diameter, m	0.25
Module Length, m	0.4-1
Surface Area Density, m^2/m^3	3000
Membrane cost, $\$/m^2$	50-125

Process Parameters	Input values
O_2 Production Rate, TPD	15
Hours of operation per year	7884
Pressure ratio	10
Electricity cost, $/MWh	80
Membrane installation factor	0.3

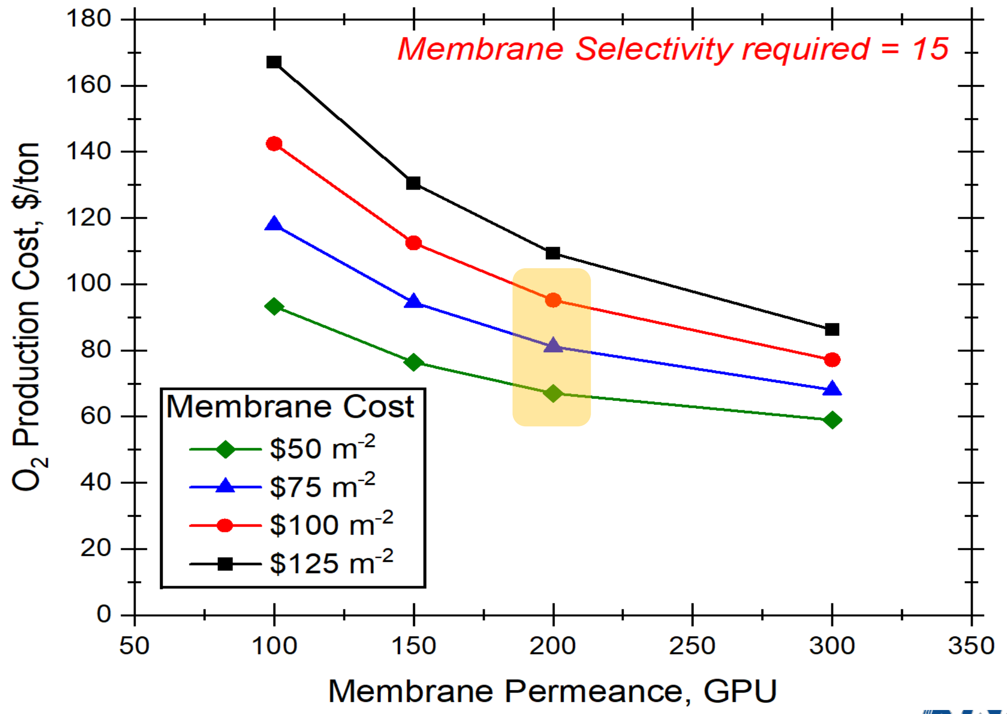


Permeate Evacuation Process Scheme

- Preliminary TEA: 2-stage process for > 90% O_2 production

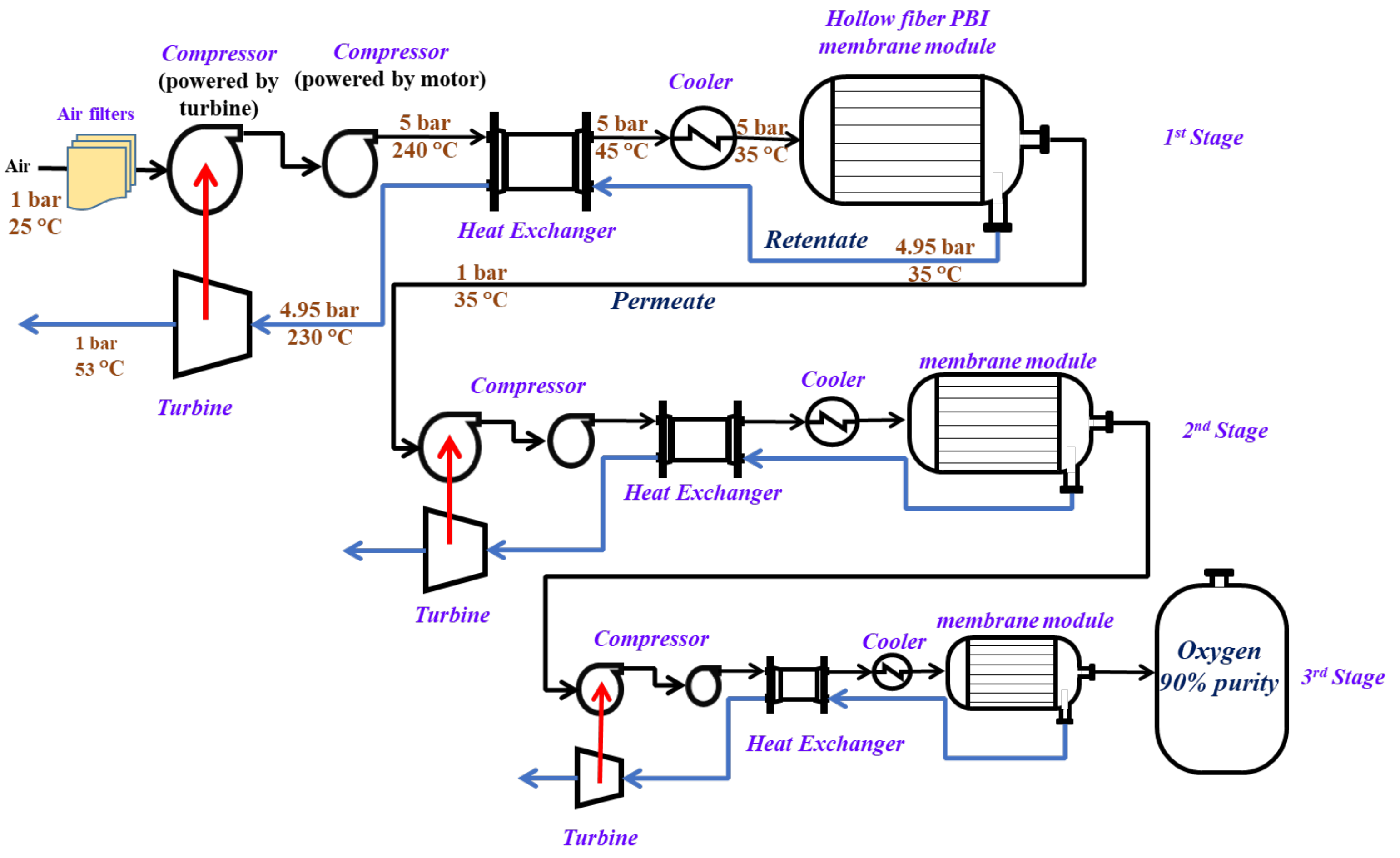


Permeate evacuation process	Input values
O_2 Production Rate, TPD	15
Number of Membrane Stages	2
Inlet volume of air, Kg/s	1.5
Pressure of inlet air, bar	1.01 to 1.20
Temperature Stage-1 and stage-2, °C	25 & 5
O_2 purity (%) at Stage-1 and Stage-2	57-62, 90-95
Pump efficiency, % and temperature, °C	40-64, 15
Membrane installation factor	0.3-0.4

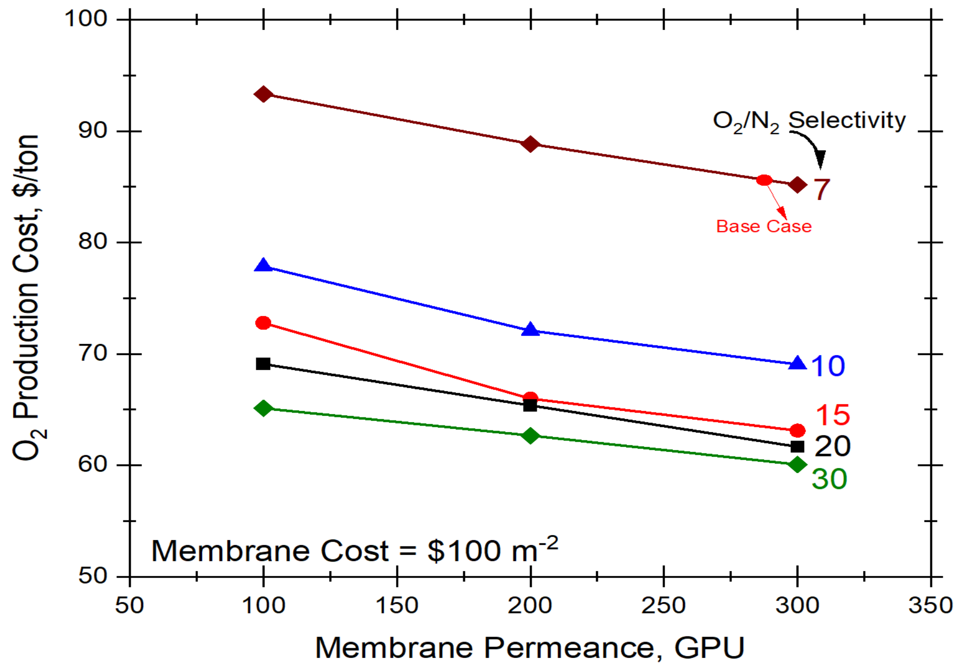


Feed Compression Process Scheme

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



Feed compression process	Input values
O_2 Production Rate, TPD	15
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



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.	07/31/2022	in-progress
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.	07/31/2022	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

Project Timeline (BP – 3)

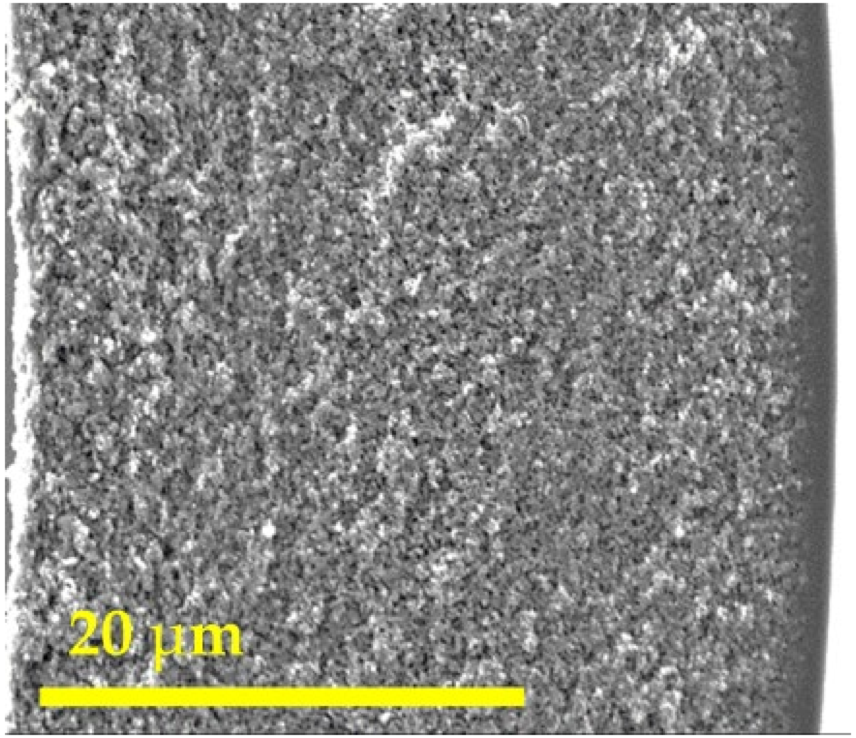
			BP1				BP2								BP3				BP4			BP5				
			12/15/18 - 11/30/19				12/01/19 - 07/31/21								08/01/21 - 07/31/22				08/01/22-07/31/23			08/01/23-07/31/24				
	Start Date	End Date	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Task 1.0 - Project Management & Planning	12/15/18	09/30/23																R1								
Task 2.0 - PBI- CMS Hollow Fiber Membrane Preparation, Optimization, and Characterization	12/15/18	09/30/22															R4	1 R2								
Subtask 2.1 - Optimize PBI pyrolysis conditions	12/15/18	03/30/20																								
Subtask 2.2 - CMS hollow fiber membrane preparation	06/01/18	09/30/22																								
Task 3.0 - Membrane Evaluation and Process Parametric Studies	04/01/19	09/30/23															R6									
Task 4.0 - Process Design and Techno-economic Analysis	12/15/18	09/30/22															R3									
Task 5.0 - Modular System Design	10/01/22	09/30/23																								

PBI-CMS HFM Performance Improvement

- **Goal (R1 & R2): Report a plan to fabricate asymmetric PBI-CMS HFMs with 1 μm selective layer to achieve O_2 permeance of 100 GPU and O_2/N_2 selectivity of 15**

Permeance = Permeability / thickness

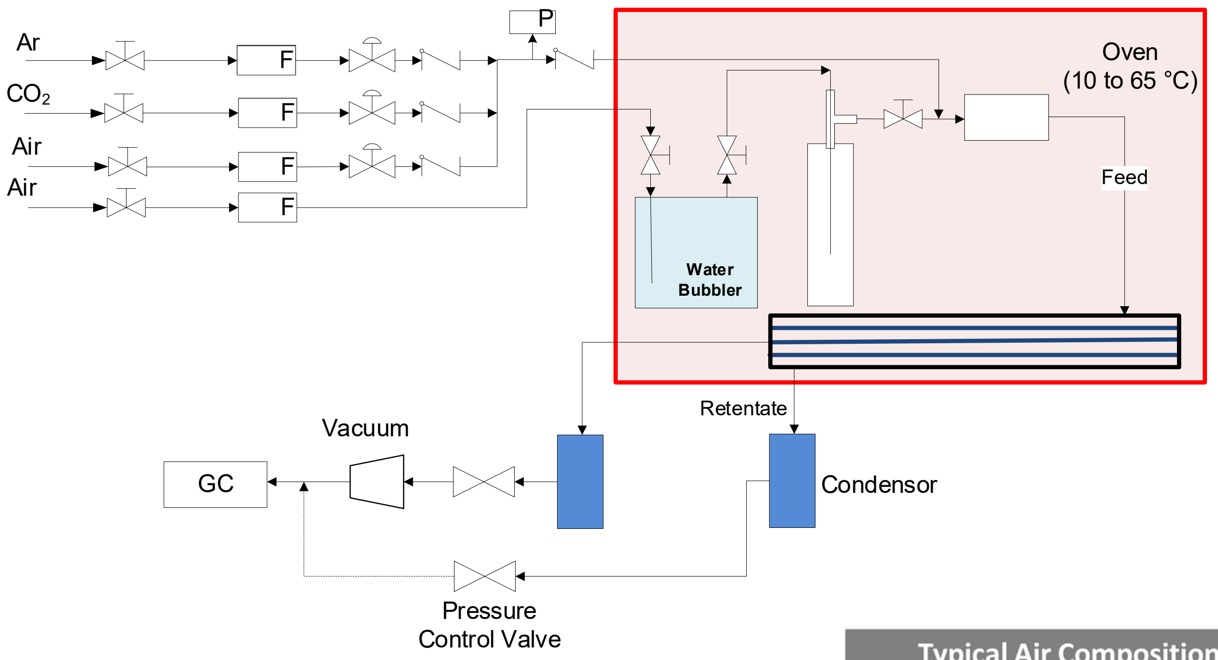
100 GPU = 150 Barrer / 1.5 μm



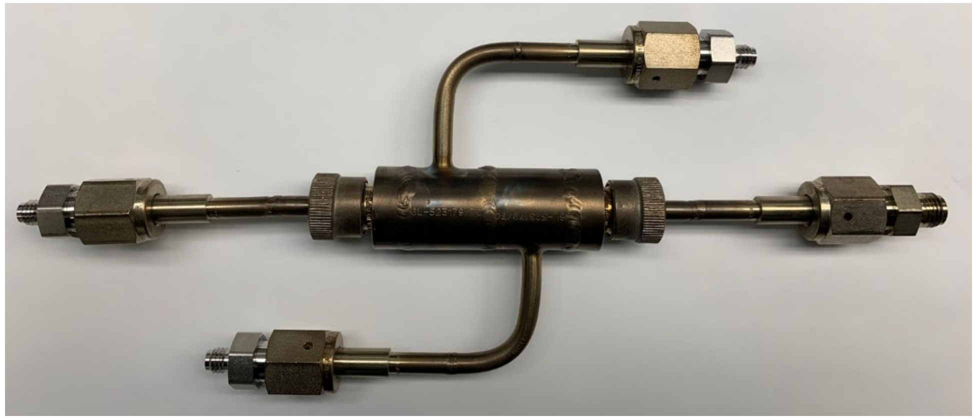
- **Method developed to mitigate asymmetric morphology collapse during pyrolysis**
  - Achieved PBI-CMS HFMs with selective layer thickness 1-2 μm
  - Demonstrated O_2 permeance > 200 GPU and O_2/N_2 selectivity of ca. 7
- **Refine novel fabrication methods to improve selectivity**
  - Understand the influence of fabrication process parameters and develop performance-fabrication parameter-property correlations

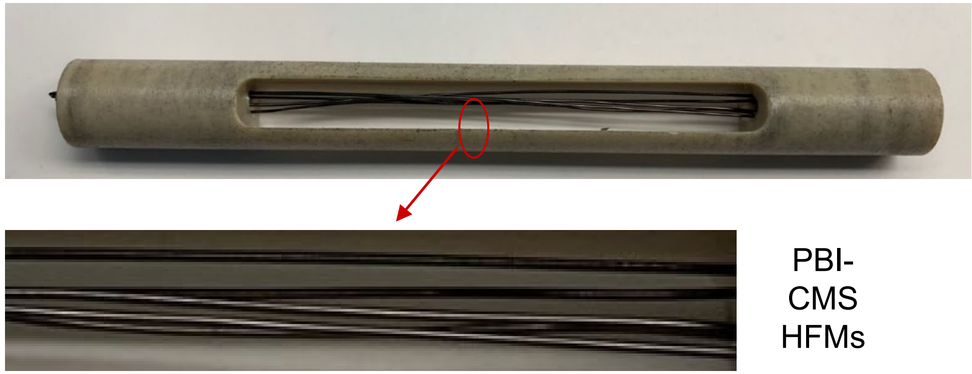
Membrane Evaluation Under Realistic Conditions

- **Perform single and multi-fiber testing under realistic 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%



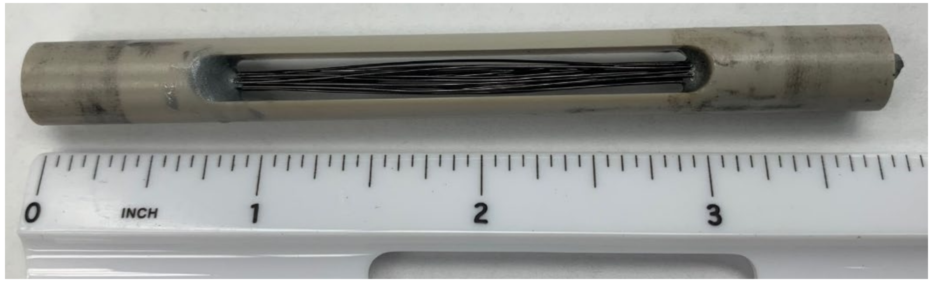


PBI-CMS HFMs

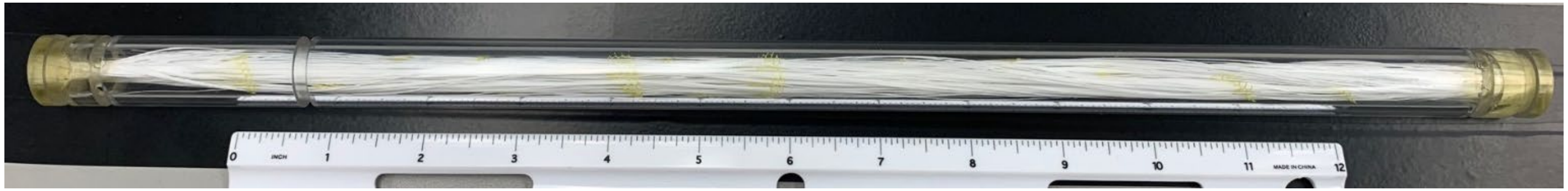
Lab-scale multi-scale membrane module

Modular ASU Design and Prototype Development

- **Design Plan (FY23): Development of process design package**
  - O_2 (90 to 95%) for a modular 1-5 MWe gasification system
  - Engage with membrane manufacturer for module design specifications
  - OEM configuration and vendor quotations for components e.g. blower, vacuum pumps
  - Detailed TEA
- **Lab-scale prototype (FY23)**
  - Long term laboratory validation
- **Future development: Pilot Testing (FY23+)**
  - 1-10 kg/day O_2 system design and construction



50 to 200 fibers in 4” module



1000-2000 fibers in 12” x 1” module: Example module

With industry collaboration

Acknowledgements

- **DOE – NETL Gasification Program**
  - Evelyn Lopez
  - David Lyons
- **Los Alamos National Laboratory**
  - JongGeun Seong (*PD – Materials*)
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