High Selectivity and Throughput Carbon Molecular Sieve Hollow Fiber Membrane-Based Modular Air Separation Unit for Producing High Purity O_2

FE-1049-21-FY21

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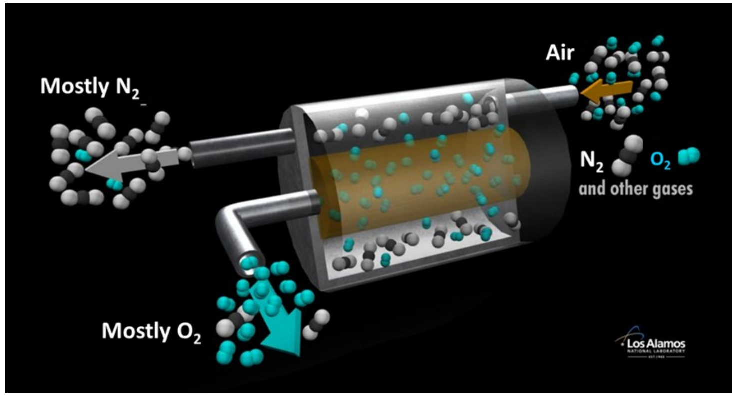
Los Alamos National Laboratory

Project Review Meeting
DOE – Fossil Energy/NETL
April 25th, 2024

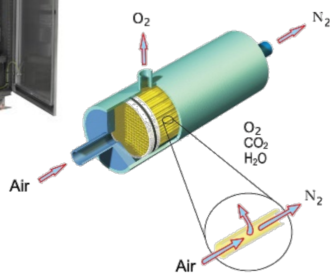
Project Overview

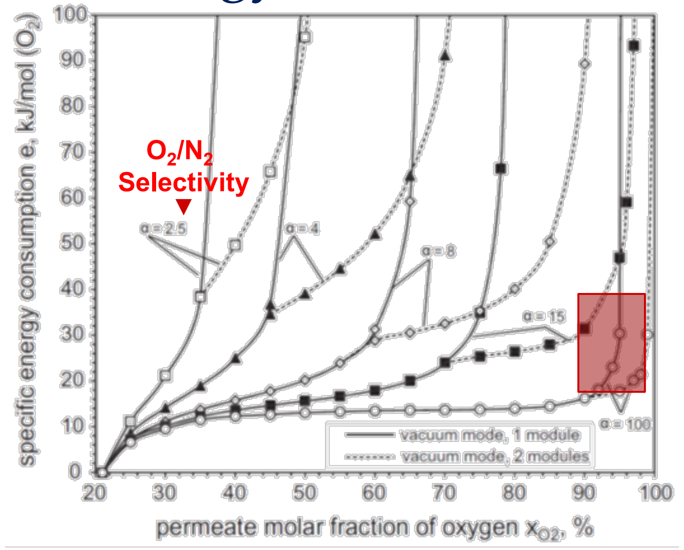
- **Award Name:** High Selectivity and Throughput Carbon Molecular Sieve Hollow Fiber Membrane-Based Modular Air Separation Unit for Producing High Purity O_2
- **Award Number:** FE-1049-21-FY21
- **Current Project Period:** BP4: 06/2023 – 12/2024
- **Project Manager:** Katelyn Ballard
- **Overall Program 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





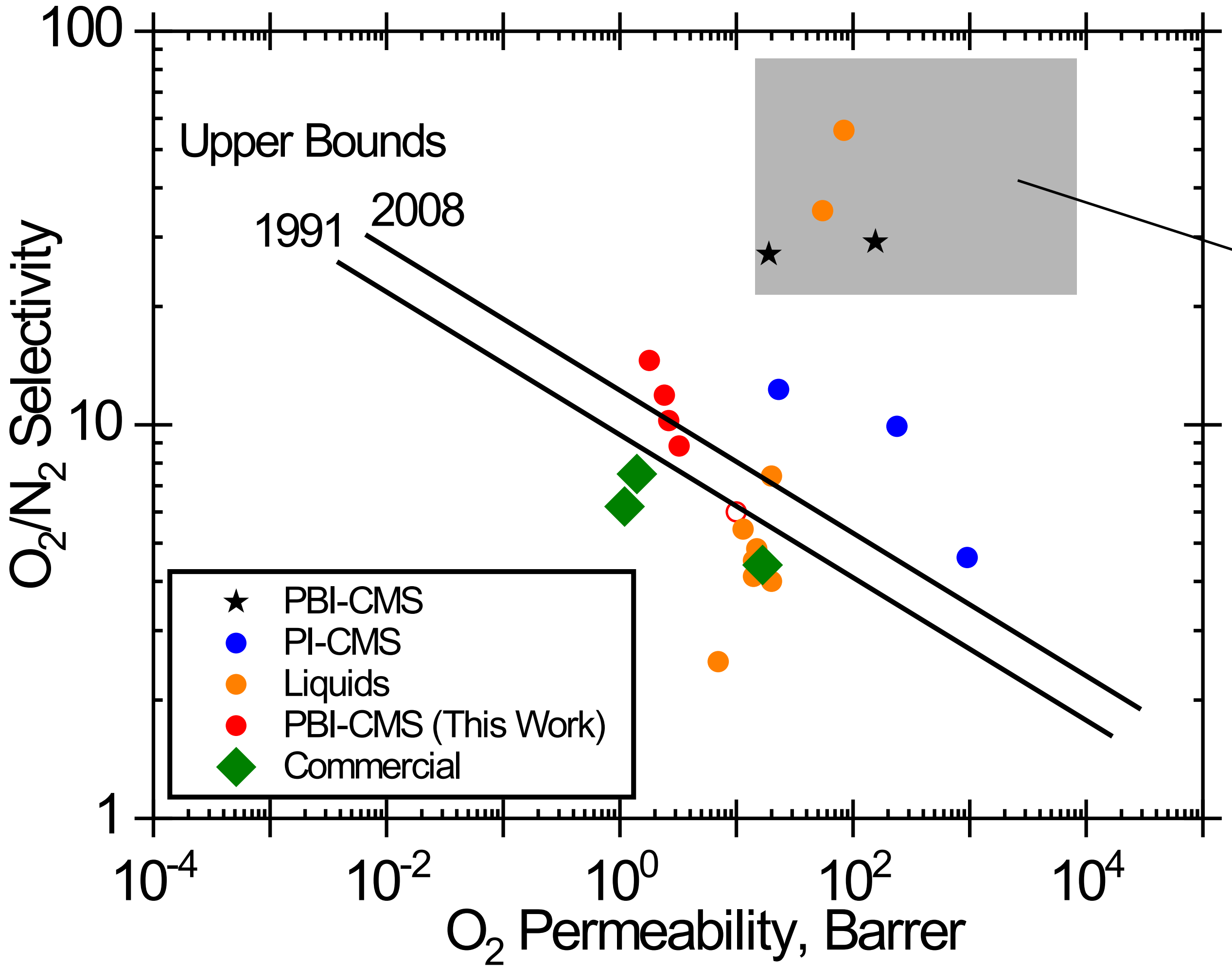
Ref: Air Products Inc. & Air Liquide Inc.

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 achieved



References

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

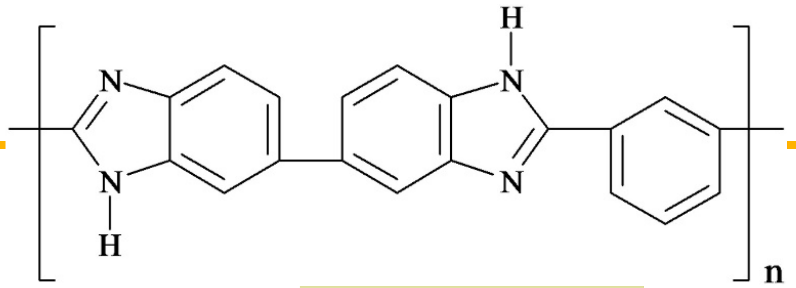
PI-CMS: A. Singh-Ghosal, W.J. Koros, J., Membrane Science 174 (2000) 177–188

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

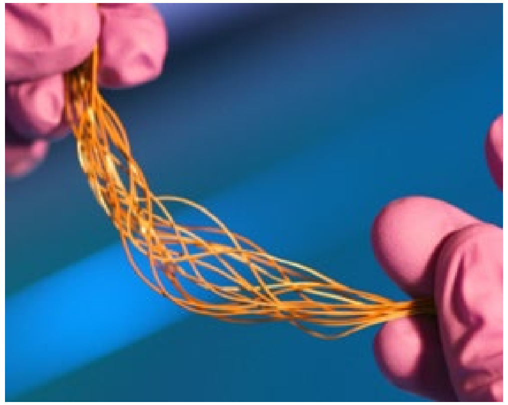
Membrane Material and Industrial Platform Development

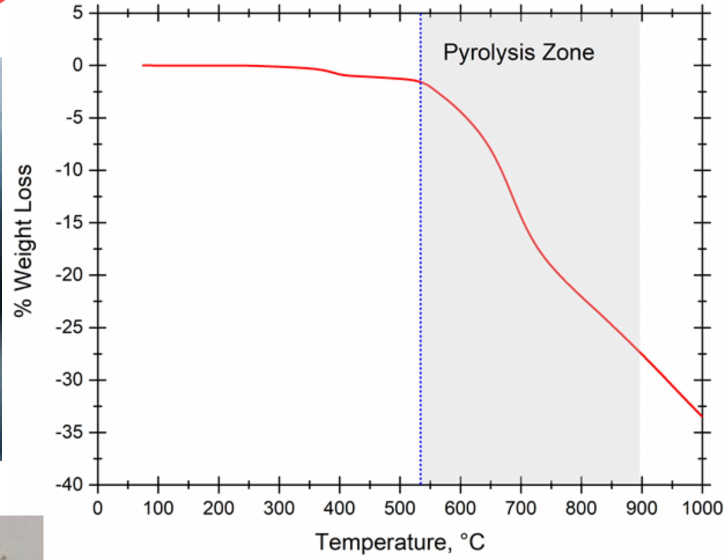
Polymer Derived CMS Membranes



- CMS membrane formation is multi-step process

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

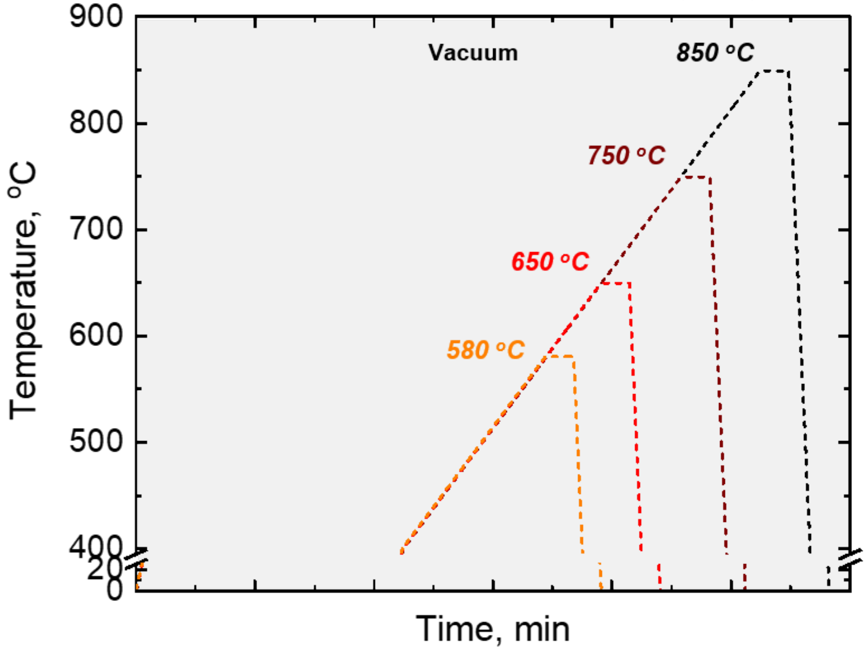




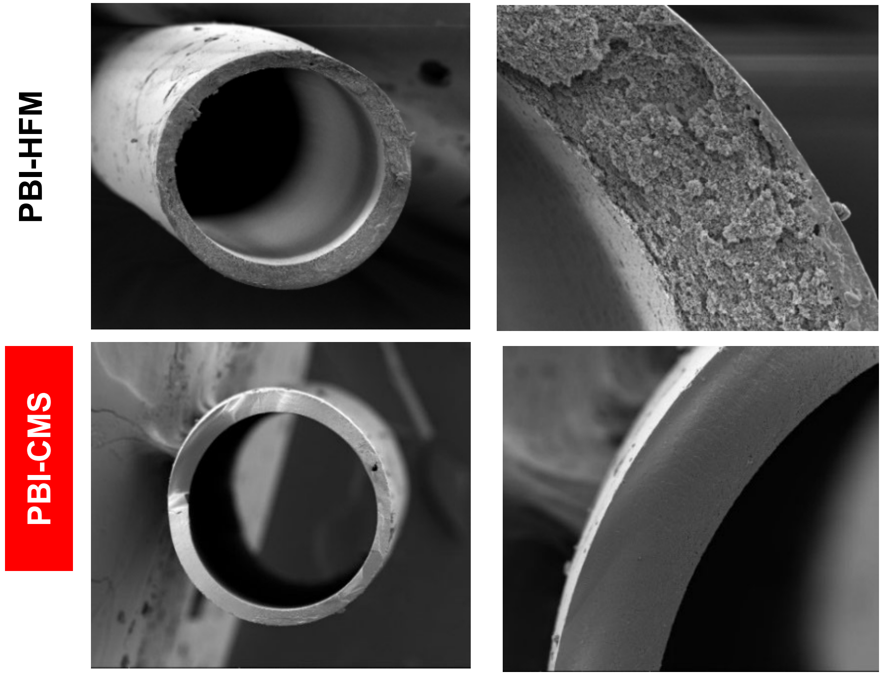
Ref. *Berchtold & Singh, et.al. 2018 US Patent 10071345*

Tailoring Separation Performance: Pyrolysis Temperature

Temperature Profiles for Pyrolysis



Morphology Change

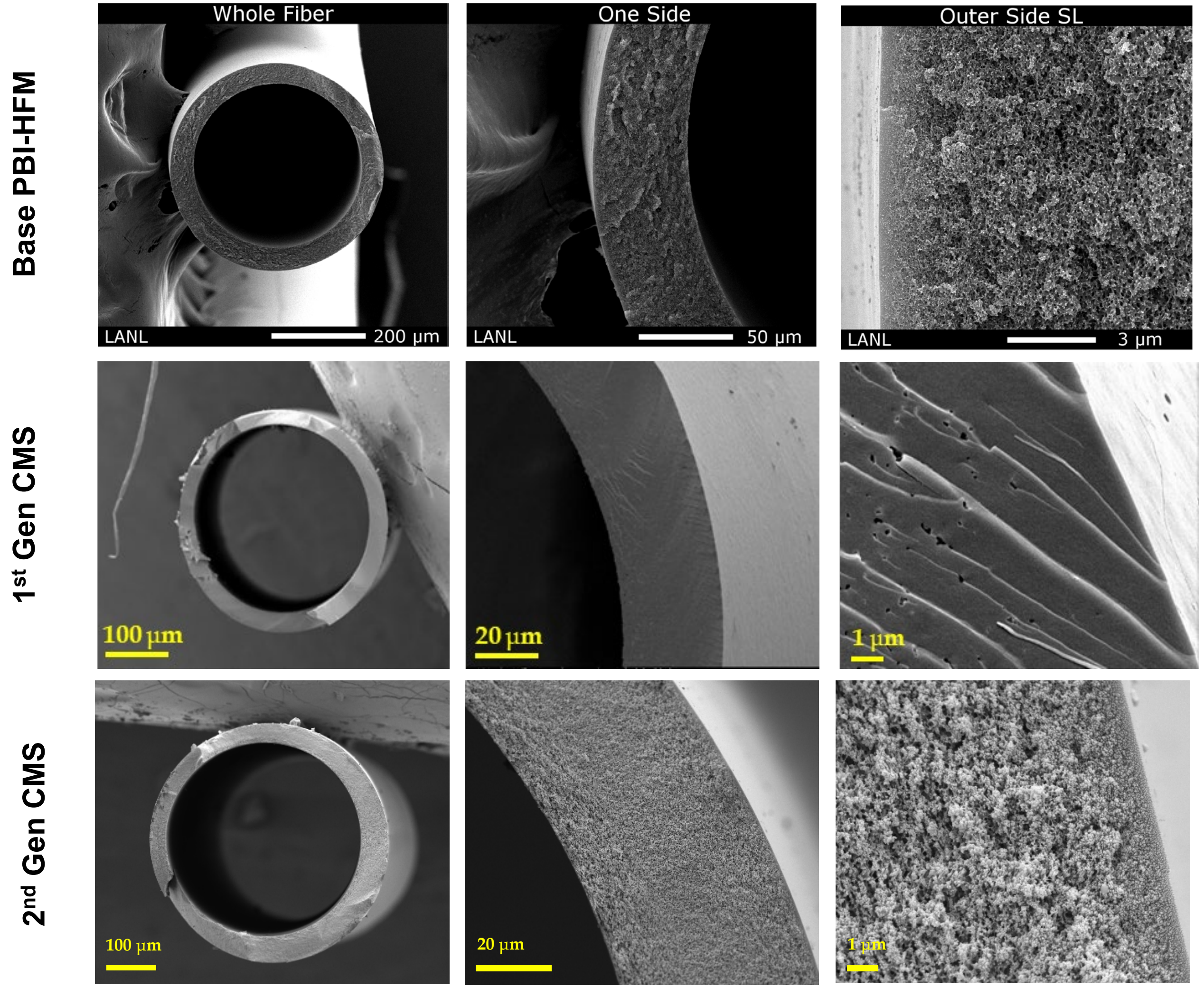


Sample	Ideal Separation Performance		Estimated O_2 permeability [Barrer]
	O_2 permeance, GPU	O_2/N_2	
PBI	0.204	1.02	0.06
CMS-580	0.303	8.44	8.48
CMS-650	3.964	8.47	99
CMS-750	0.782	13.7	16.4
CMS-850	42.3	0.90	550

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

Achieving High Permeance

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

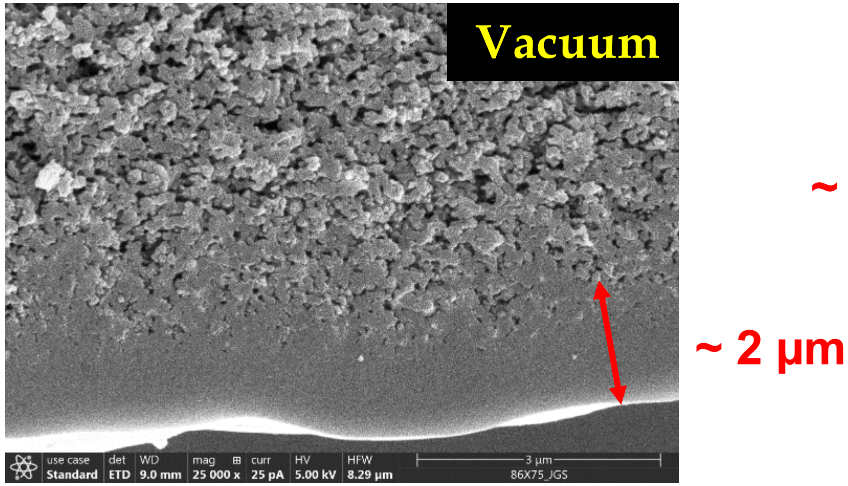


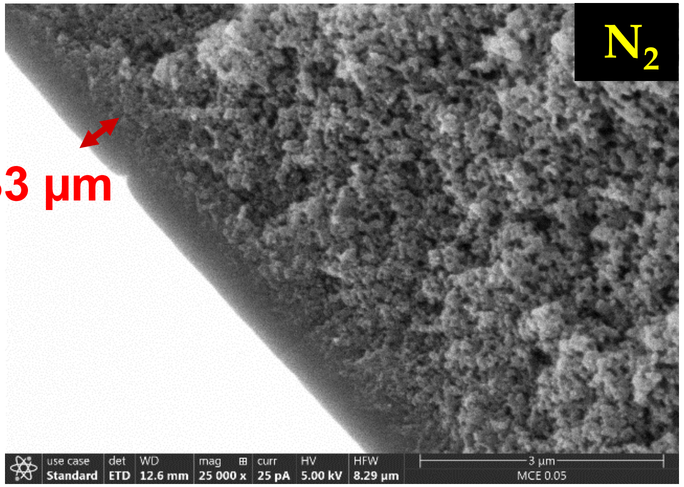
US Patent Application 18/170,722

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	Ideal Permeance, GPU					Ideal 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

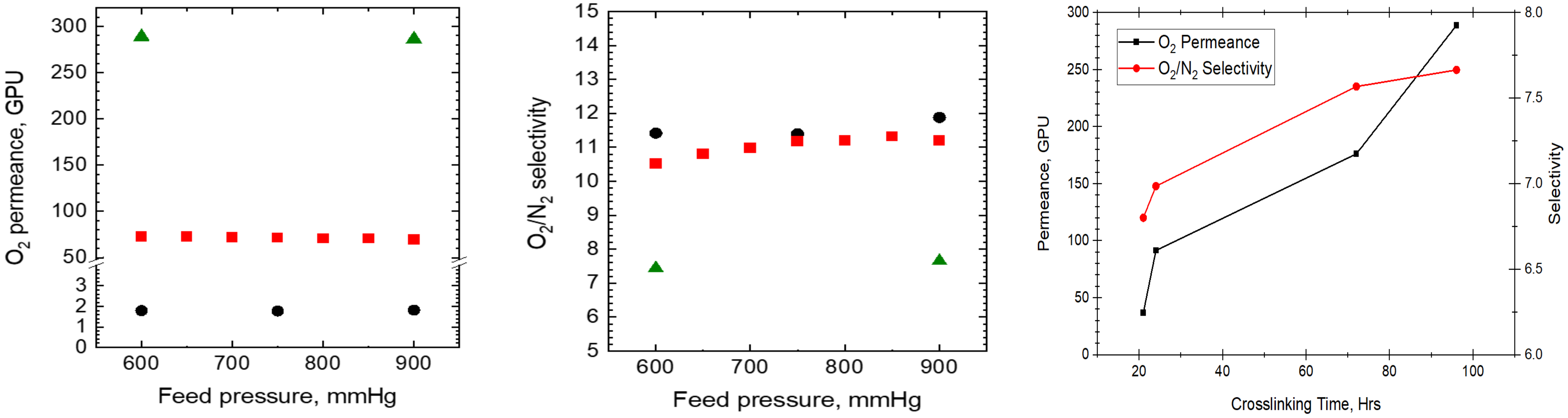




- CMS-PBI HFM fabricated under vacuum had thicker selective layer as compared to membrane fabricated in inert flowing gas resulting in higher O_2 permeance

PBI-CMS HFM: Pressure Independent Separation Performance

- **Pressure independent separation performance indicate defect-free HFMs**



- Symmetric (BP1)
- Asymmetric (BP2)
- Asymmetric (BP3)

- Understand the influence of fabrication process parameters and develop performance-fabrication parameter-property correlations

Scale-up – Demonstrating Industrial Feasibility

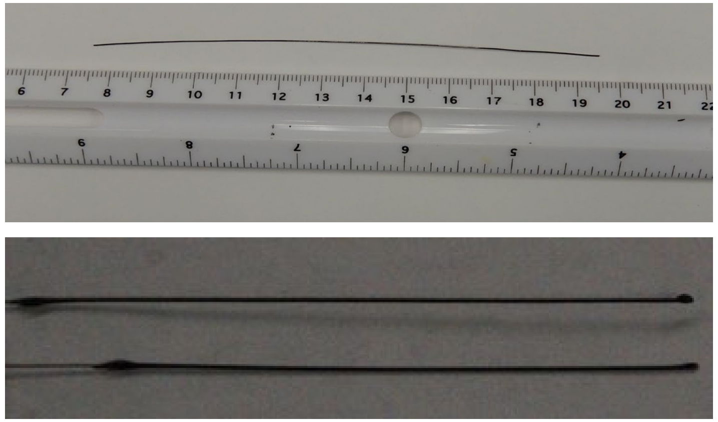
- **Efforts focused on the translational of fabrication methods (post-spinning crosslinking and pyrolysis) for fabrication of PBI-CMS multi-fiber modules**

Batch Process

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

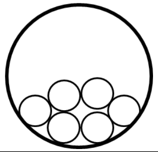
Pyrolysis

Single fiber

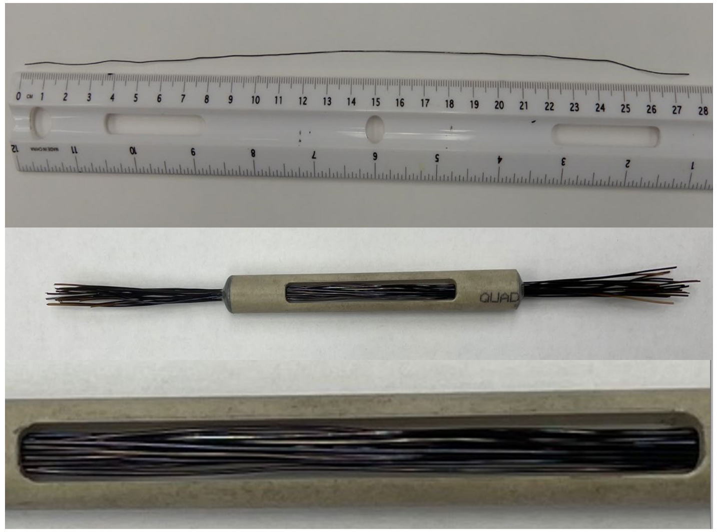


Flow-Through Process

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



Multi-fiber pyrolysis under industry relevant inert gas flow

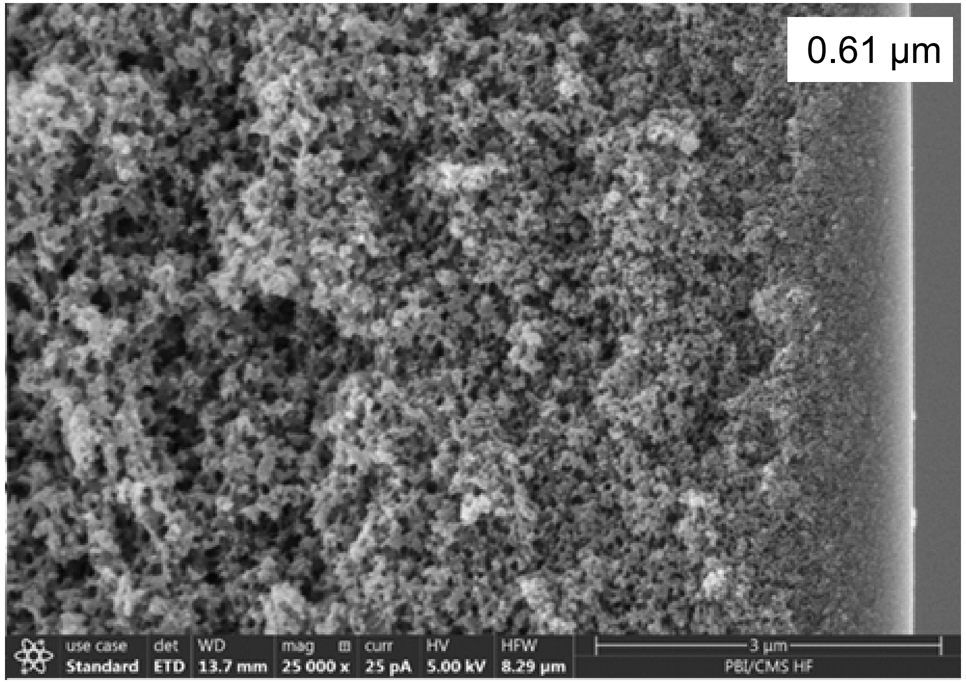


Strong PBI-CMS HFMs – Improved Selectivity

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

Sample	Pyrolysis Atmosphere	Permeance, GPU			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

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

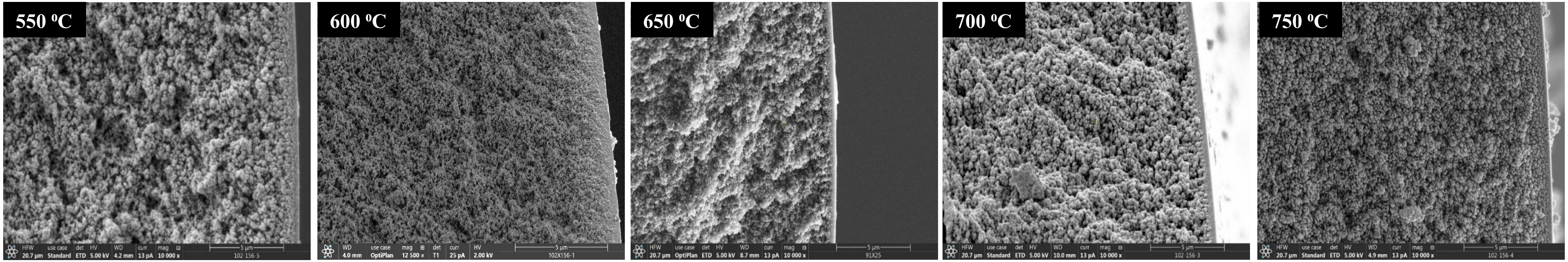


- Fiber spinning process slightly changed to increase SL thickness of the base PBI HFMs
- PBI-CMS HFMs having ~ 0.6 µm SL were produced as compared to ~ 0.3 µm in previous PBI-CMS HFMs.

Disclosure under review

Unique Morphology of PBI CMS HFM w.r.t Pyrolysis Temperature

Impact of pyrolysis temperature (550-750 ^{0}C)on PBI HFM morphology



Pore tightening with increase in temperature

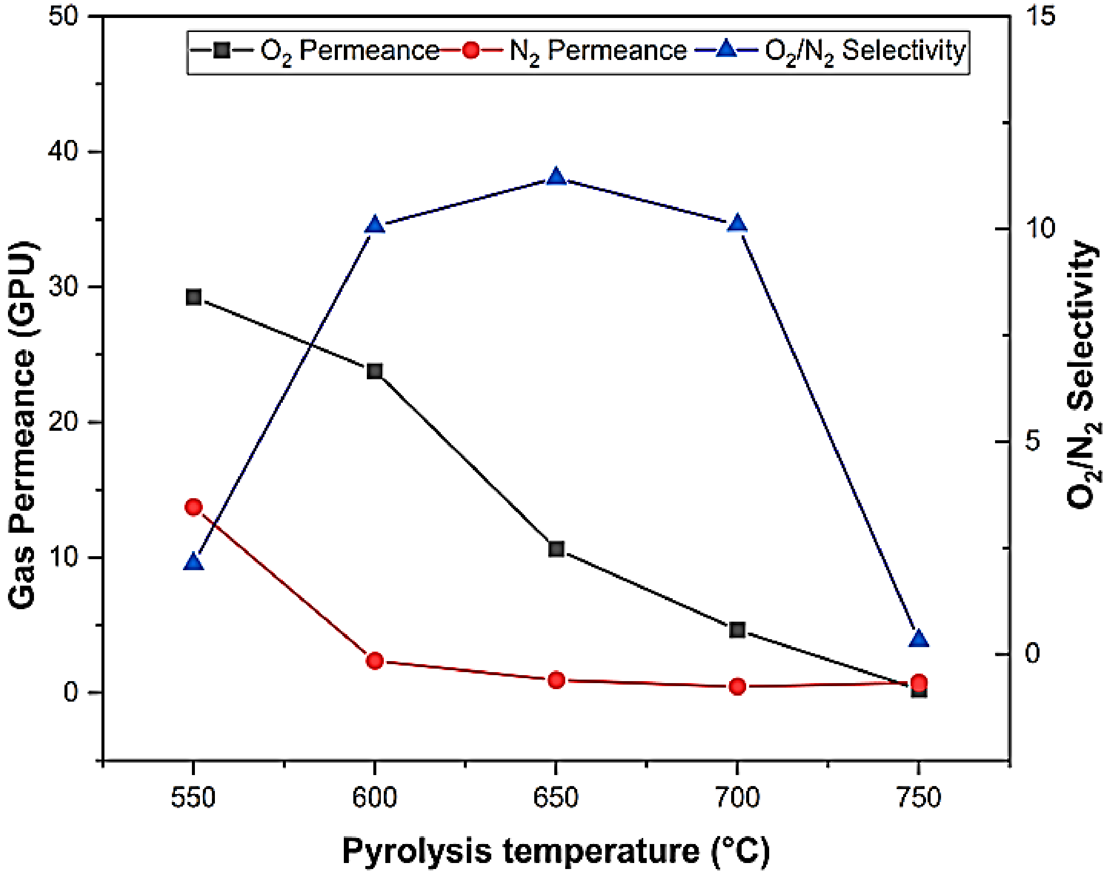
Pyrolysis Temperature (^{0}C)	Selective layer thickness (nm)
550	142.0 ± 17
600	211.8 ± 70
650	310.7 ± 10
700	434.0 ± 29
750	539.8 ± 28

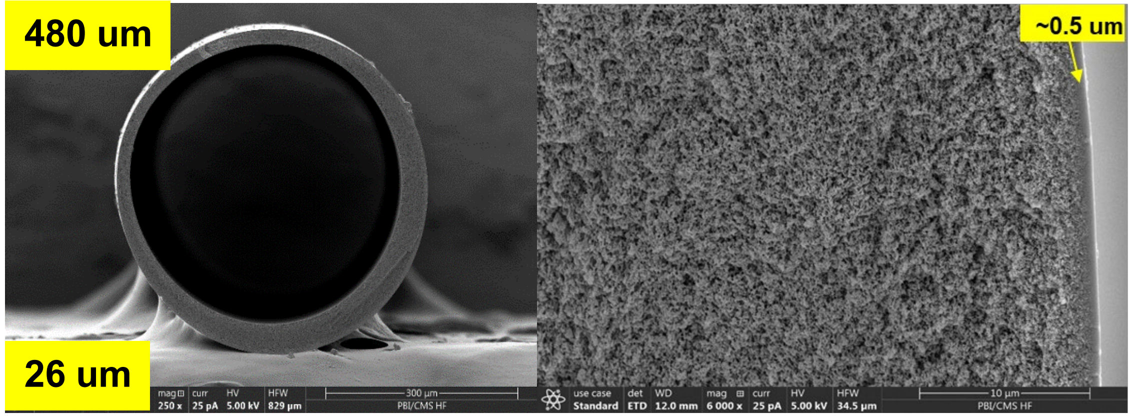
- An extraordinarily thinner selective layer in the CMSMs was achieved, ranging from 0.14- 0.54 µm
- The bottleneck of regulating selective layer thickness below 1µm, facilitated by DBX crosslinking of PBI HFM followed by controlled pyrolysis procedure, was demonstrated

Ideal O_2/N_2 Performance Summary

- **Impact of pyrolysis temperature (550-750 ºC)on O_2/N_2 separation performance was evaluated.**

Degassed under **vacuum** at 180 º C

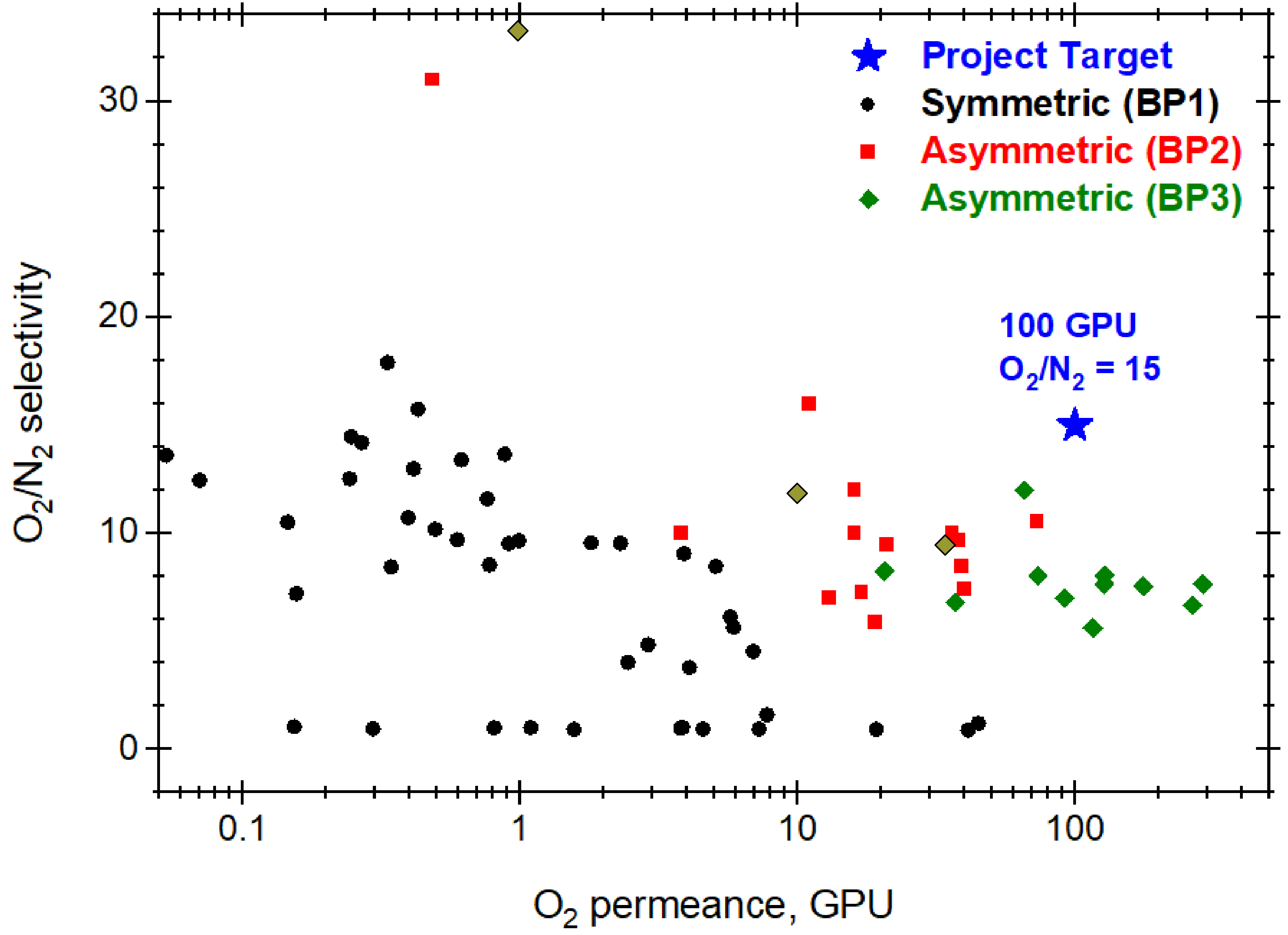


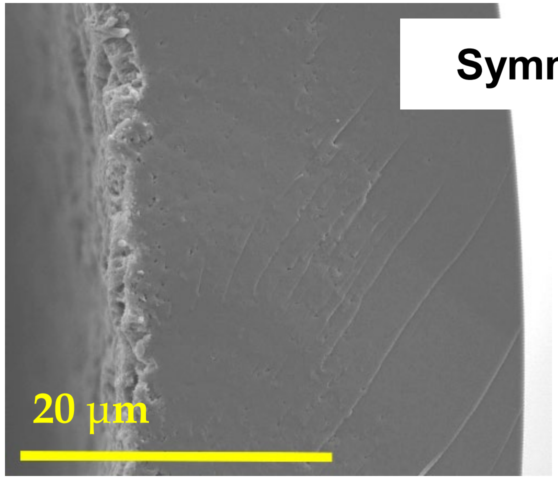


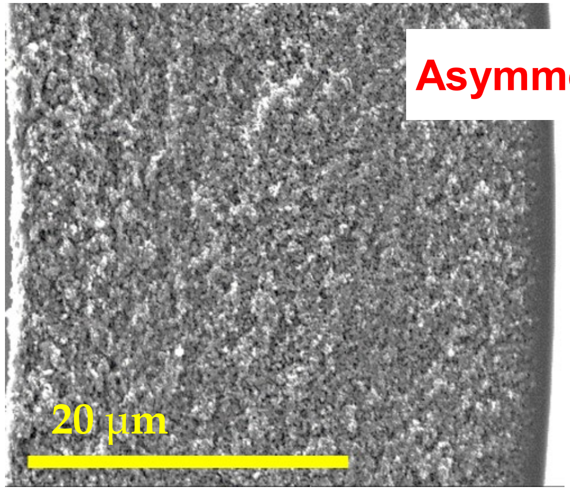
- Selectivity improved significantly (~4.5x) with increase in pyrolysis temperature from 550 to 650 º C while a sudden drop (~90%) in selectivity was observed at 750 ºC when compared to 700 ºC.

- Optimum pyrolysis temperature was found to be 600-650 º C to achieve high O_2/N_2 separation.

Ideal O_2/N_2 Performance Summary

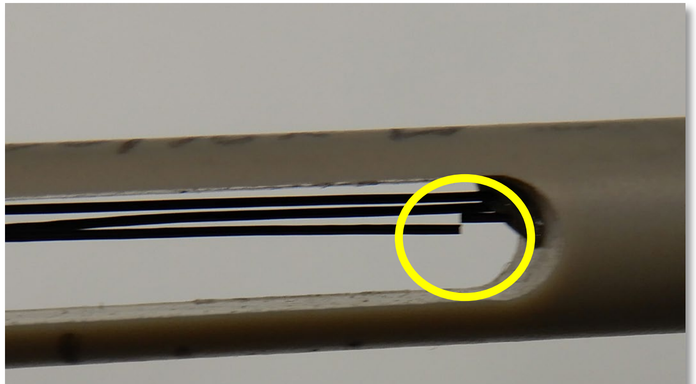






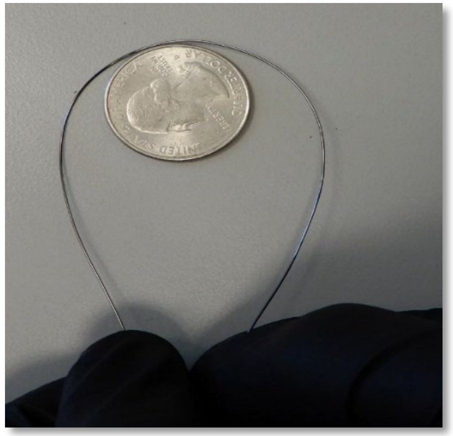
Improved Mechanical Robustness

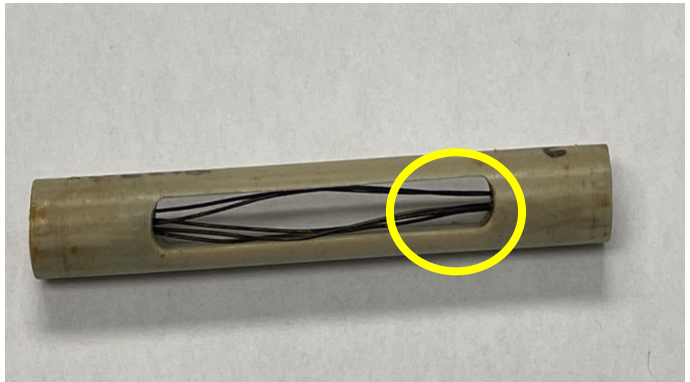
- **While PBI derived HFMs demonstrated improved mechanical robustness, but multi-fiber module fabrication presented challenges**
  - High temperature epoxies are rigid which caused significant stress at epoxy-fiber causing breakage.



Mechanically Weak Interface

- **Novel Approach:**
  - Development of novel HFM with extremely high mechanical strength allows to carry air separation at high temperature and flow.



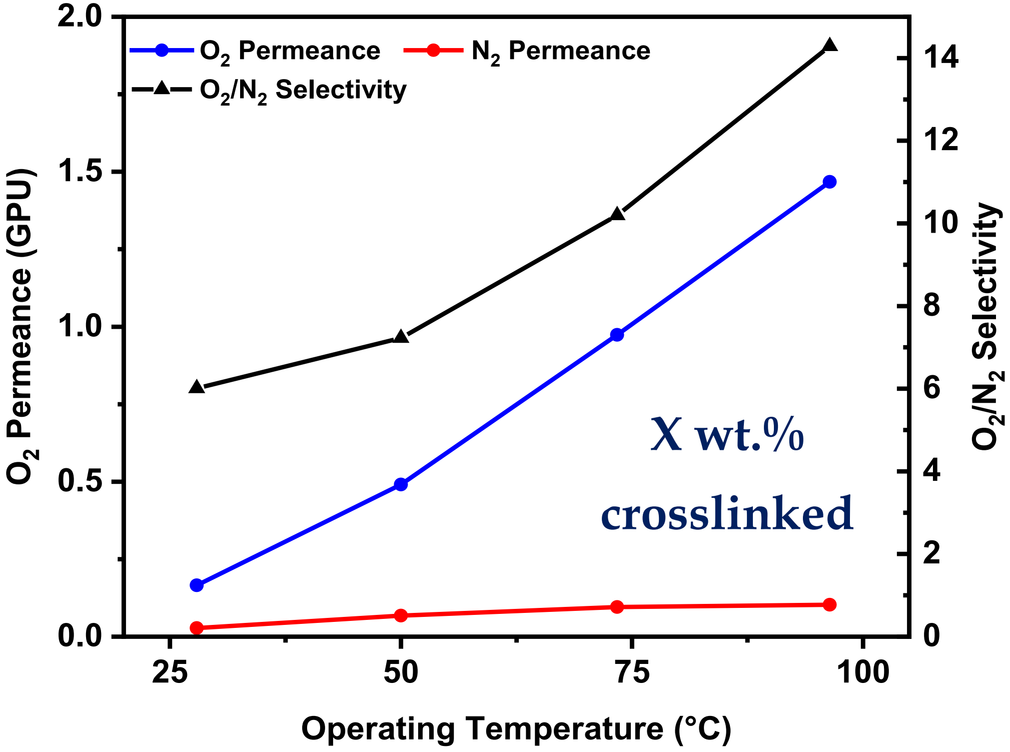


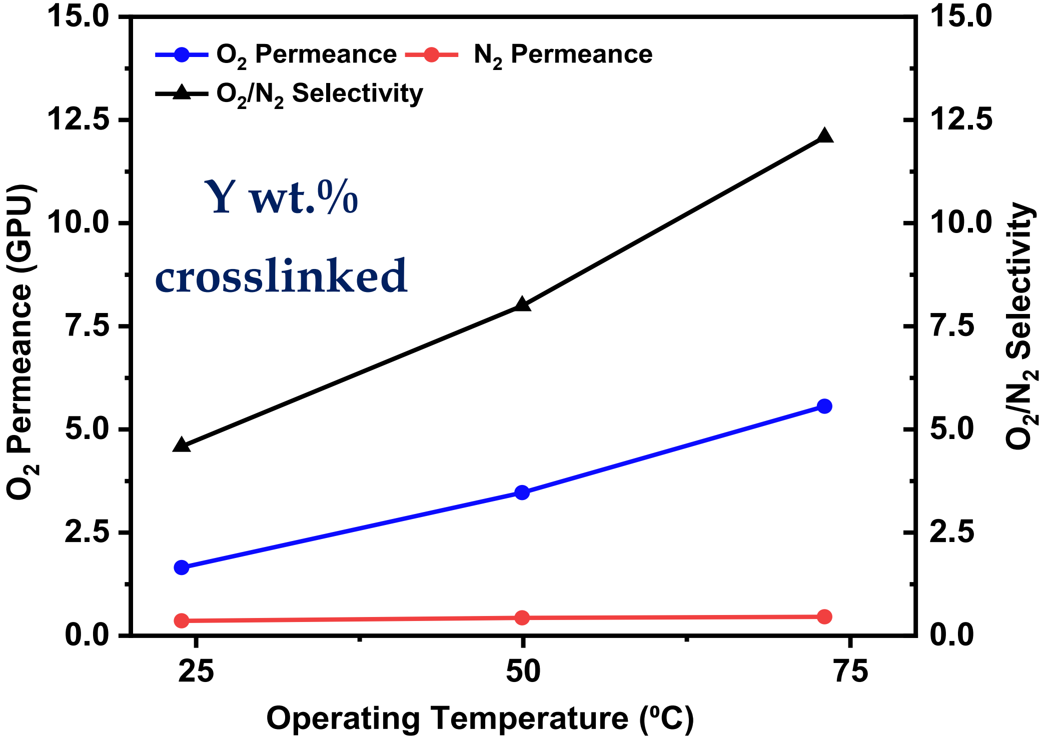
Mechanically Strong Interface

Disclosure under review

Mixed O_2/N_2 Performance Summary

- **High O_2/ N_2 selectivity (~15) demonstrated for industry representative multi-fiber module**

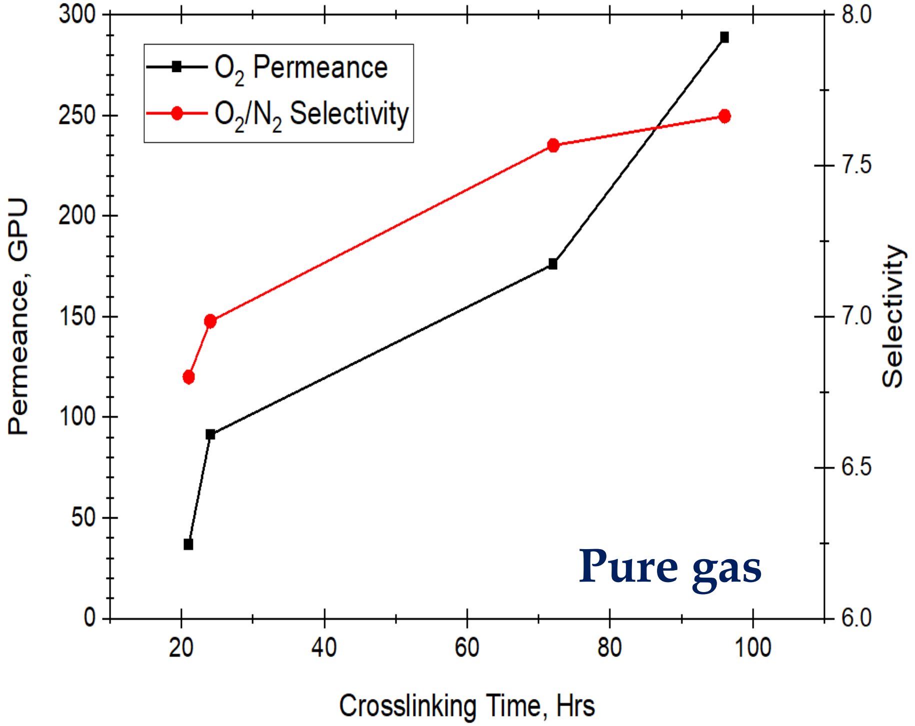


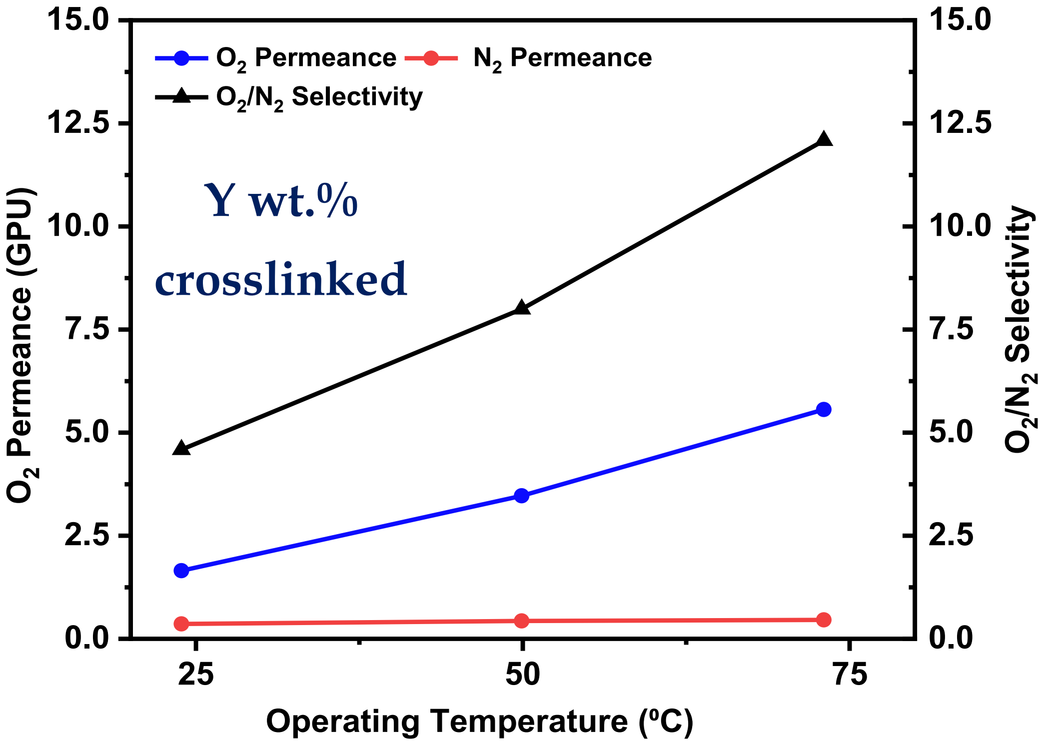


- The O_2/N_2 separation performance improved at higher temperature
- Based on pure gas data HFMs with thinner selective layer and optimized crosslinking will lead to higher O_2 permeances.

Mixed O_2/N_2 Performance Summary

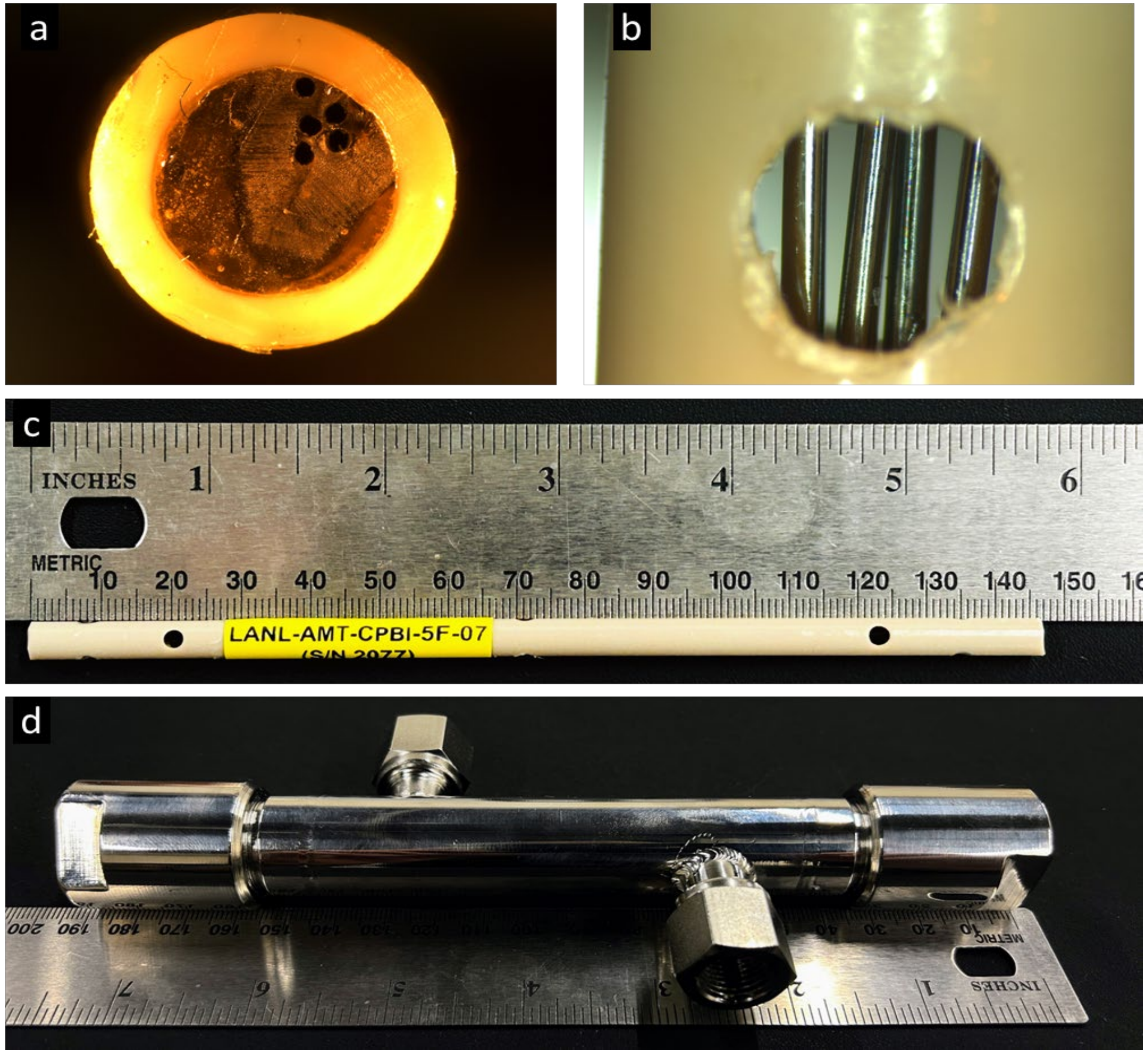
- High O_2/N_2 selectivity (~15) demonstrated for industry representative multi-fiber module





- The O_2/N_2 separation performance improved at higher temperature
- Based on pure gas data HFMs with thinner selective layer and optimized crosslinking will lead to higher O_2 permeances.

Collaboration with Applied Membrane Technology (AMT)



- Collaboration with AMT was established.
- Three modules (two polymer and one CMS) with 5-10 fibers each were prepared by AMT
- The module dimensions: 0.375" D X 5.75" L
- The initial batches were test and optimize the **epoxy**, fiber length and evaluation.
- High temperature epoxy (~230 º C) seems promising
- New batch is on its way to AMT.

EP42HT-2 Product Information

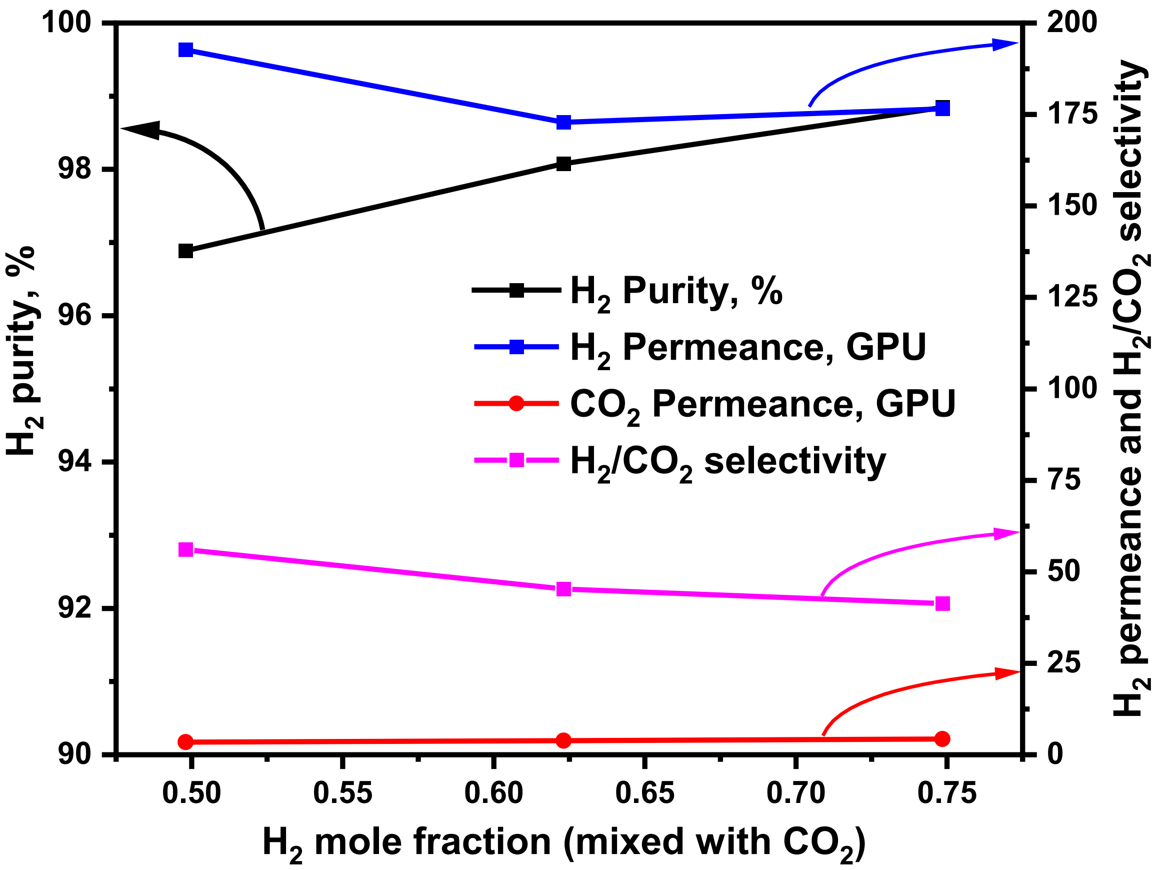
Two component, room temperature curing epoxy compound

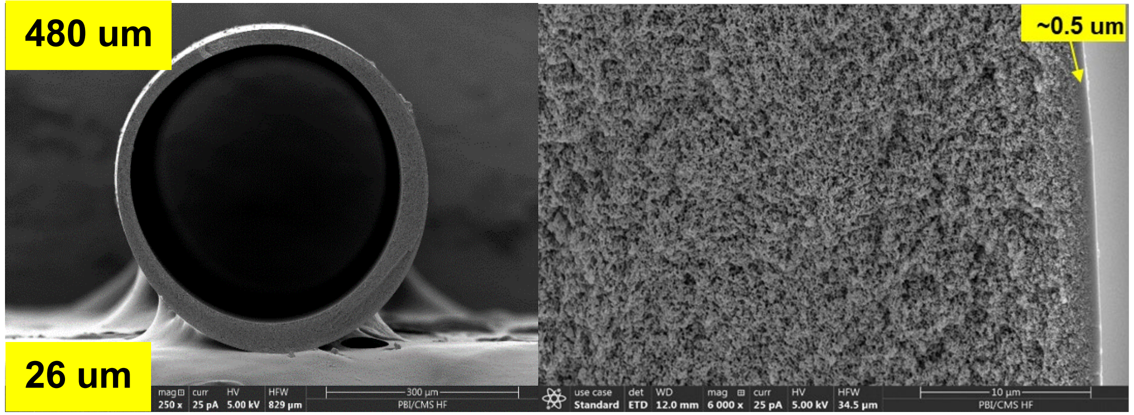
Key Features

- Heat, chemical and steam resistance
- Cures at ambient or elevated temperatures
- Can be used for bonding, sealing, coating, casting & potting applications
- Serviceable from -60°F to +450°F

Overall Gas Separation Performance

- PBI CMS HFM was evaluated for H_2/ CO_2 separation at 180 ⁰C and 50 psi for different H_2 (50-75%) mole fraction.



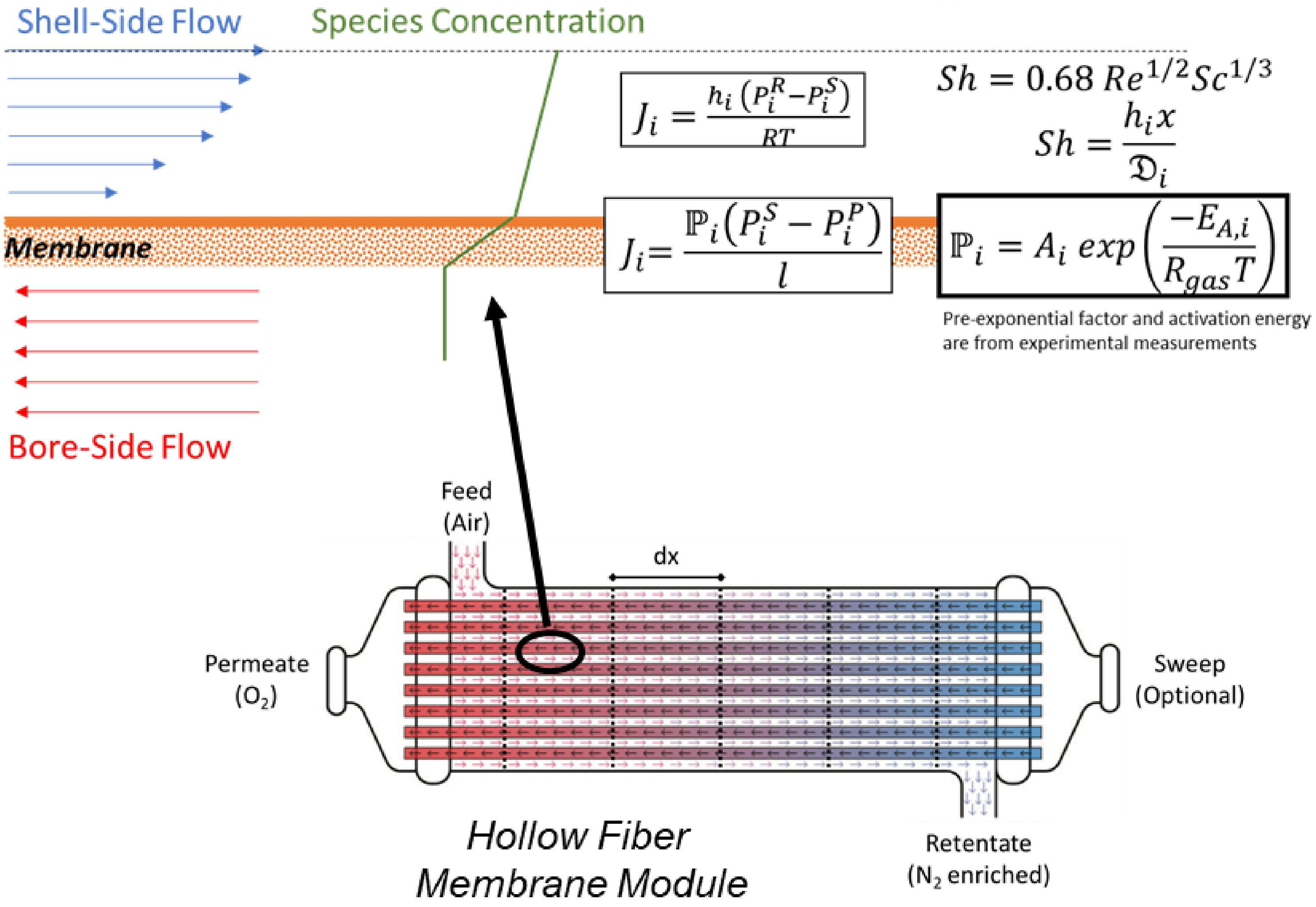


- Superior H_2/ CO_2 separation performance with ~50 selectivity and >175 GPU was achieved, resulting in high H_2 purity (~99%)
- Membrane can be further fine tuned to further enhance the purity and meet industrial standards (99.99%).

Process Design and Techno-Economic Analysis

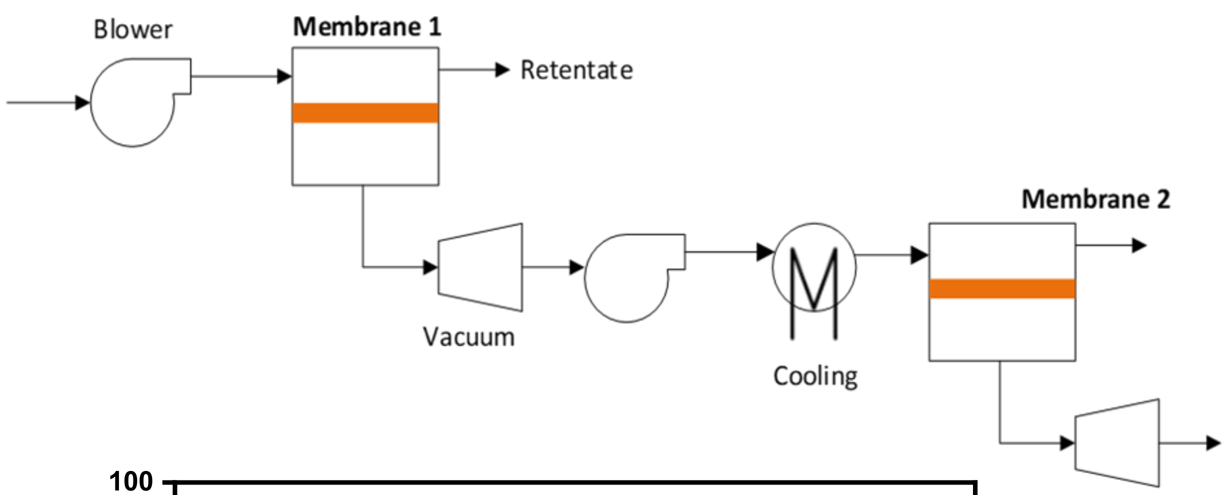
Process Modeling Platform Development

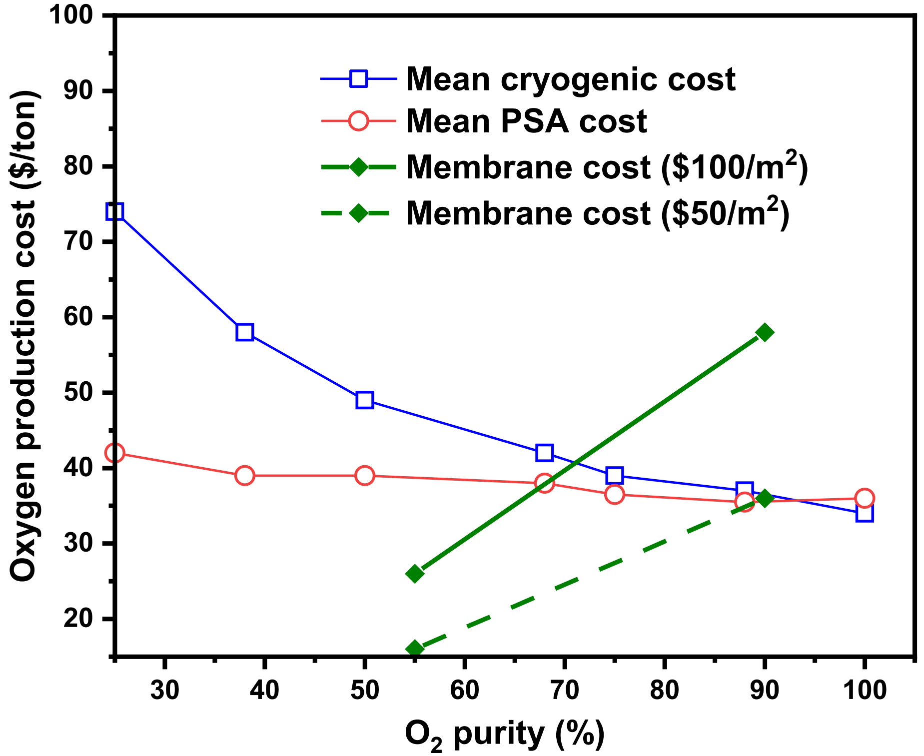
- **Developed hollow fiber membrane model and integrated with Aspen Plus process simulation software for air separation process development**



Techno-economic Analysis –2-Stage Membrane Process (Vacuum)

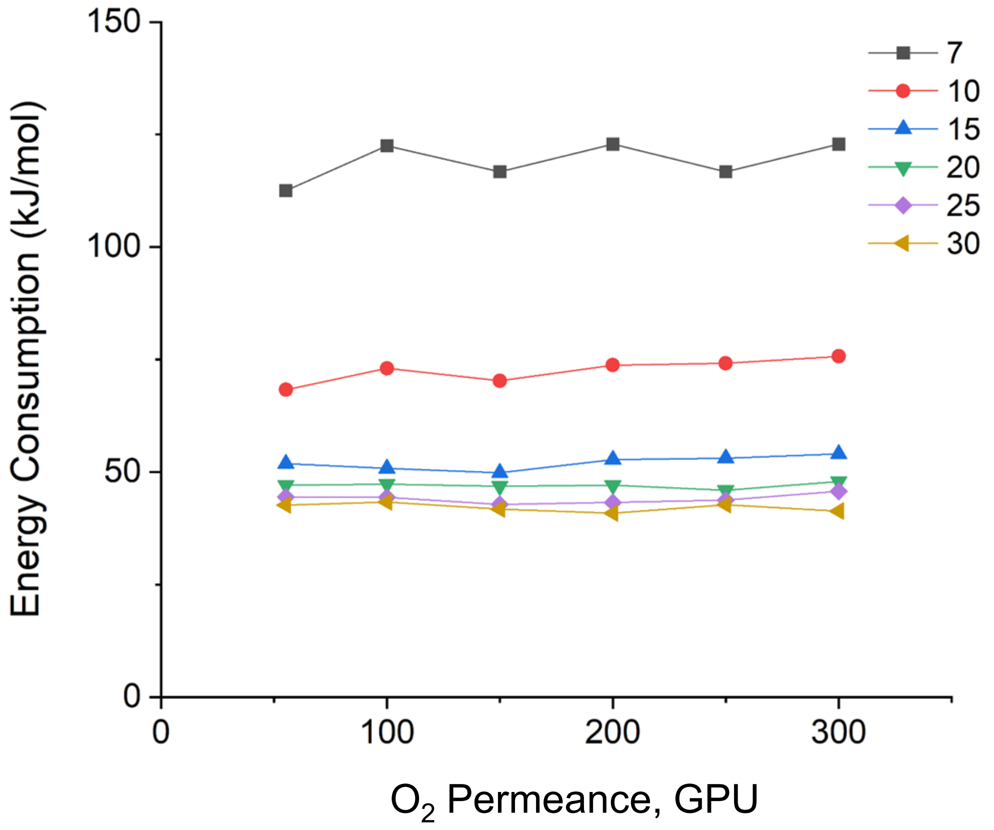
Membrane module	Input values
HF Diameter, μm	400
Wall Thickness, μm	30
Selective Layer Thickness, μm	1.0
O_2 permeance, GPU	55-**300**
O_2/N_2 selectivity of the membrane	10-**30**
Module Diameter, m	0.25
Module Length, m	0.4-1
Surface Area Density, m^2/m^3	3000
Membrane cost, $\$/m^2$	50-100
Electricity cost, $/kWh	0.06-0.1
Process Parameters	**Input values**
O_2 Production Rate, TPD (1-5 MW)	10
Annual capacity factor	90%
Indirect cost factor	53%
Aromatization factor (FCR)	7%
Life of equipment, y	10

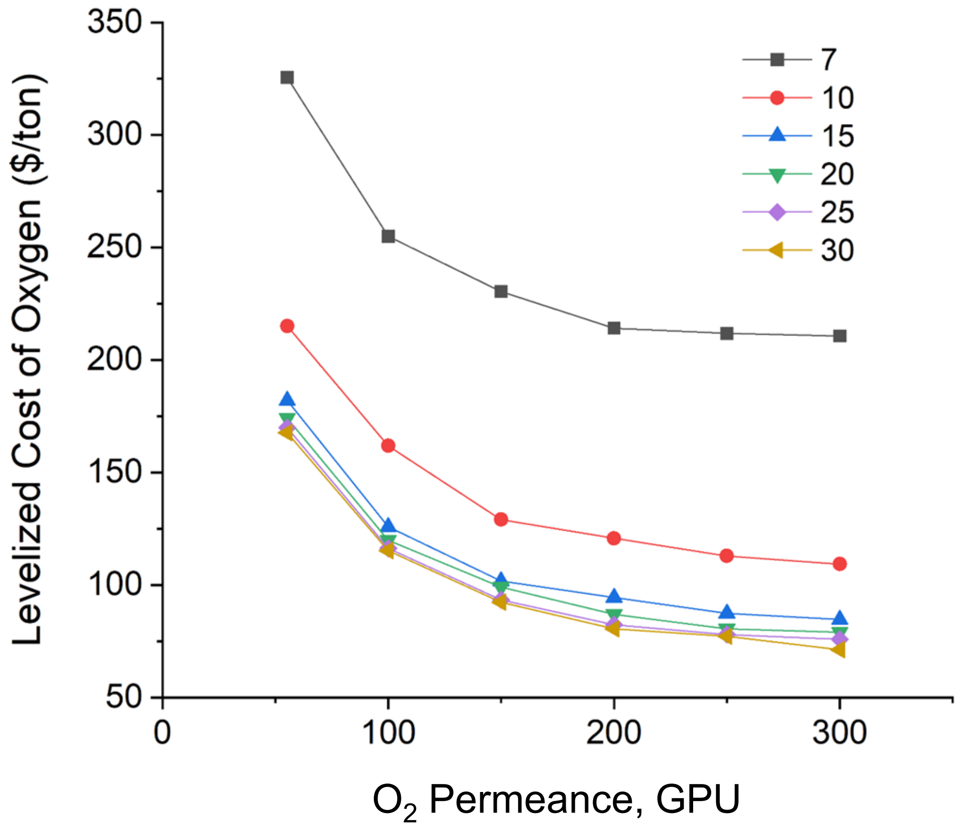




Membrane Performance Controls O_2 Production Cost

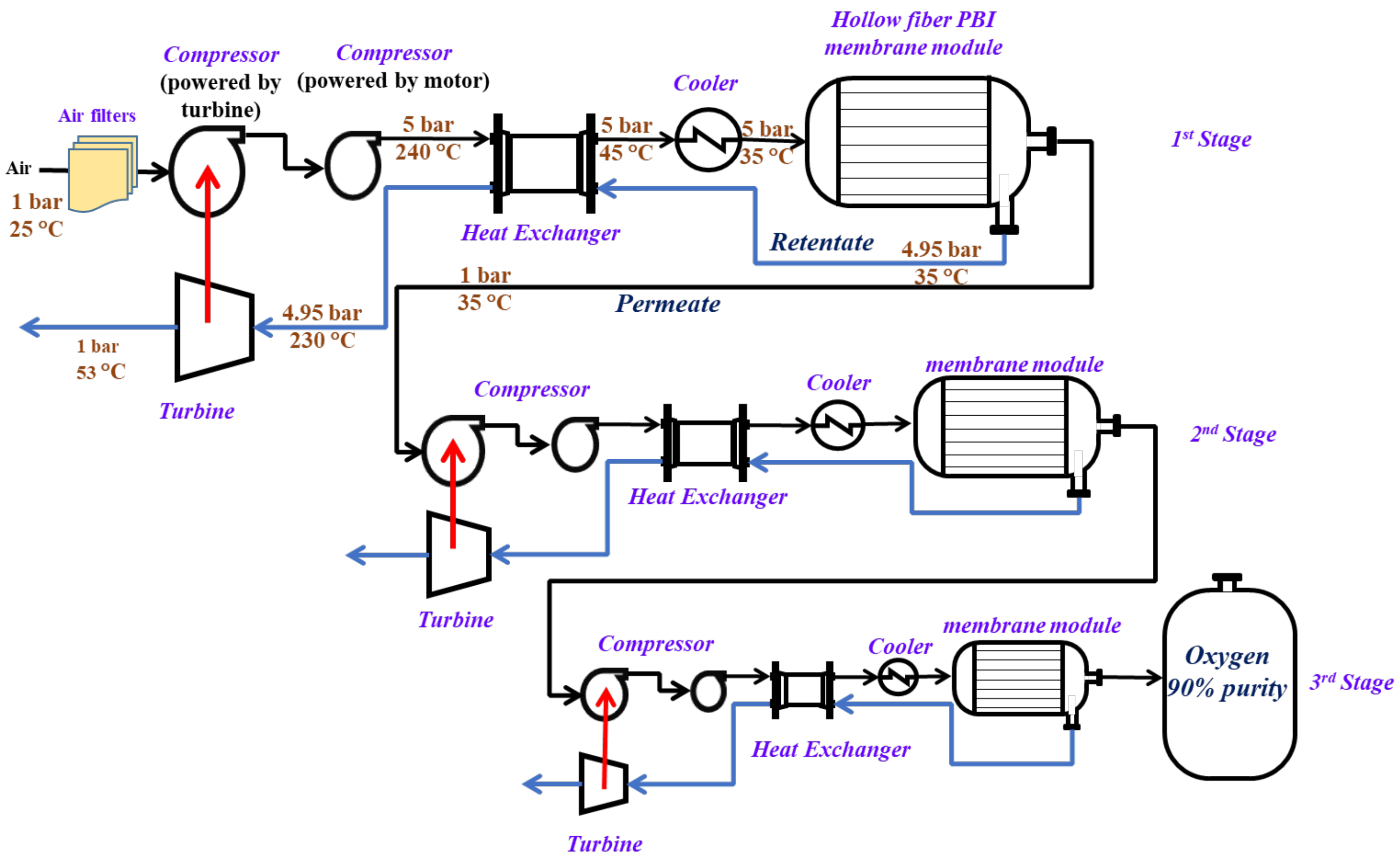
- **Energy consumption and cost of O_2 production calculated for membrane process as a function of O_2 permeance and O_2/N_2 selectivity**
  - Modelled fluid flow dynamics and operating conditions to achieve minimize O_2 production cost for each permeance-selectivity combination



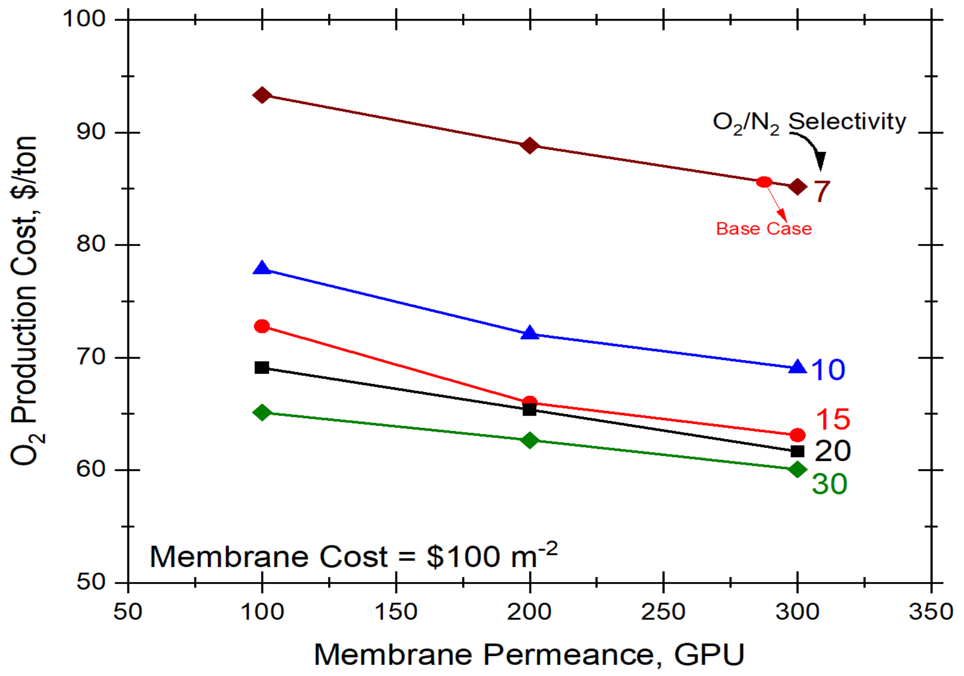


TEA–3-Stage Membrane Process (Compression)

- 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



Achievements

- ✓ **Mitigation of structural collapse during pyrolysis process**
- ✓ **Thinner selective layer (< 1 μm) was achieved**
- ✓ **Project goal of high O_2/N_2 selectivity (~15) was achieved**
- ✓ **Demonstrated scaled-up process to commercialize CMS HFMs**
- ✓ **Developed CMS HFMs with extremely high mechanical strength**
- ✓ **High temperature epoxy was found**

Project Milestones (BP – 4)

BP	ID	Task #	Description	Due Date	Status
4	M1	3.0	Develop industry representative multi-fiber module and measure O_2 permeance and selectivity	12/31/2024	in-progress
4	M2	2.0	Demonstrate achievement of project goal of high purity (≥ 90%) O_2 production in simulated multistage membrane process.	12/31/2024	in-progress
4	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.	12/31/2024	in-progress
4	R7	3.0	Perform organics testing to determine the long-term adverse impacts on membrane stability and performance.	12/31/2024	in-progress

Project Team

Project Manager: Katelyn Ballard (current) and Evelyn Lopez (former)

- **Los Alamos National Laboratory**
  - Rajinder P. Singh (*Project Lead*)
  - Harshul V. Thakkar (*Lead – Evaluations*)
  - Prashant Sharan (*Lead - TEA*)
  - Michael Dugas (*GRA*)
  - Sarah Davis (*Postbach – Membrane Characterization*)
  - Shraavya Rao (*Postdoc - start date: 3rd June*)
- **Previous Team Members**
  - Ibtida Sultana (*Intel*)
  - JongGeun Seong (*Samsung*)
  - Jeremy Lewis (*Plug Power*)
  - Kamron Brinkerhoff (*LANL*)

Thank you!!