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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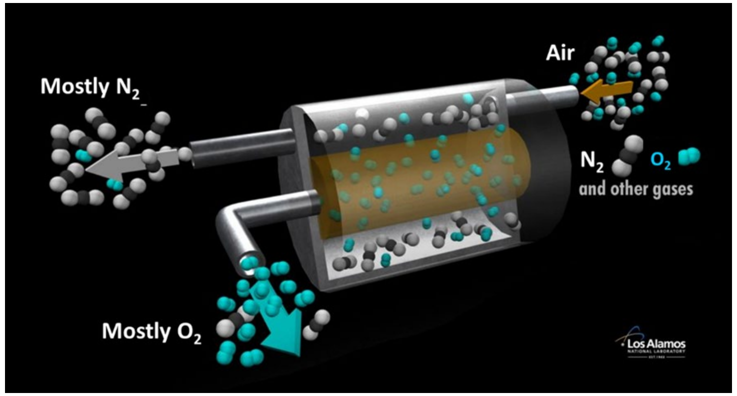
2021 Gasification Project Review Meeting
DOE – Fossil Energy/NETL
May 4th, 2021

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: 12/2020 – 11/2021
- **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 >15 for high purity O_2 production to meet the needs of a modular 1-5 MWe gasification system



Project Tasks & Team Members

Membrane Design, Fabrication and Evaluation

- JongGeun Seong
- Harshul V. Thakkar
- Jeremy C. Lewis
- Erica P. Craddock
- John A. Matteson
- Kathryn A. Berchtold
- Rajinder P. Singh

Process Modeling and Simulations

- Kamron G. Brinkerhoff
- Brendan J. Gifford
- Alexander J. Josephson
- Christopher S. Russell
- Troy M. Holland

Modular System Design

- Todd A. Jankowski

Materials Physics & Applications Division

Theoretical Division

Earth & Environmental Science Division

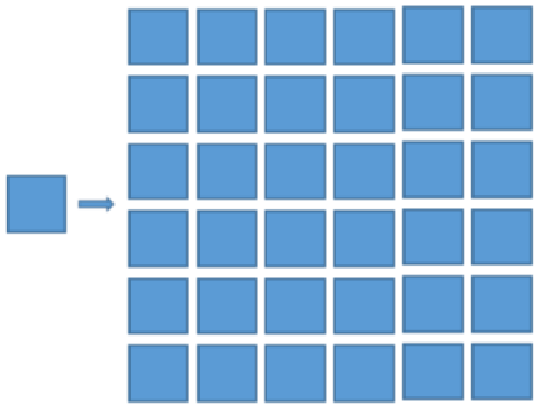
Engineering Division

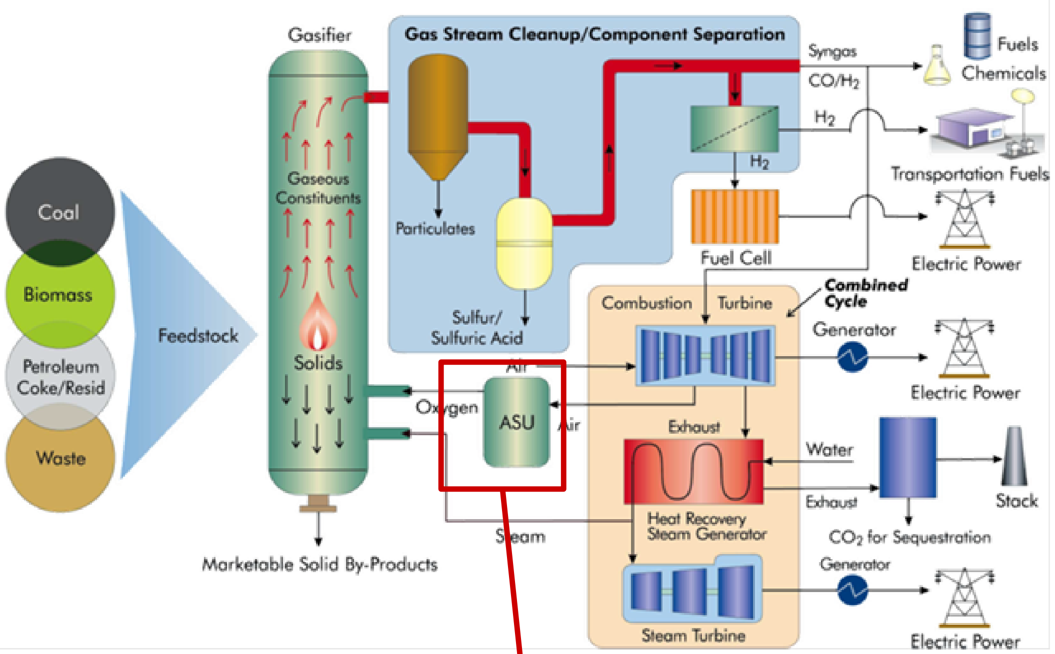
DOE Advanced Energy Systems Program

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

Modular Approach
Revolutionary Engineering





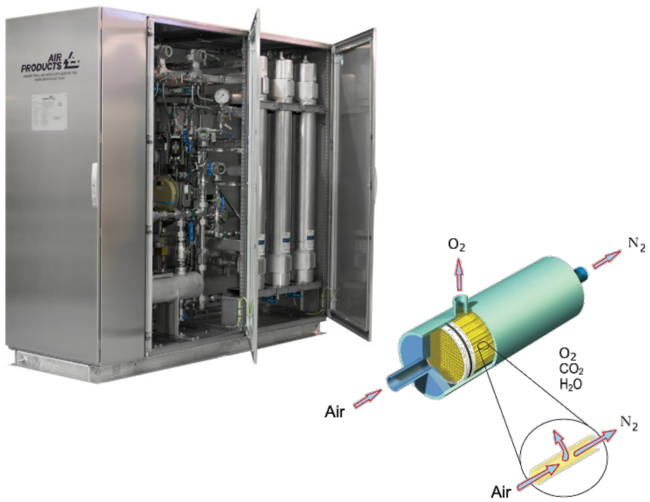
Advanced technology need:

- 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

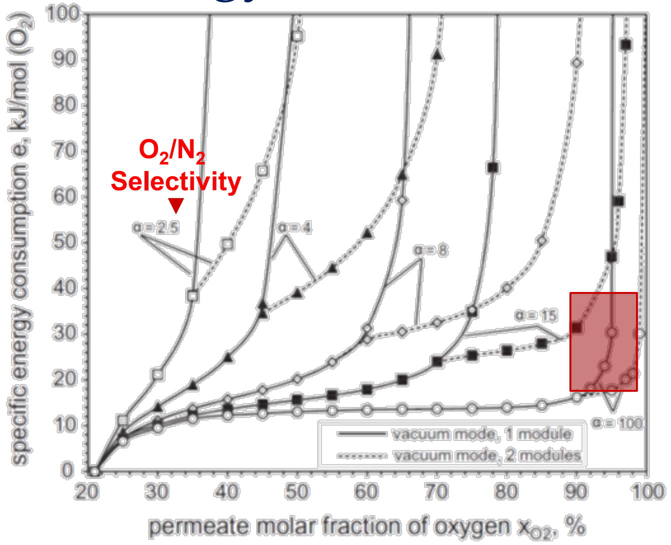
Images: DOE/NETL website

Air Separations

- **Cryogenic distillation is *the* industrially preferred technique for large-scale, high purity O_2 production**
  - State of the art 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.

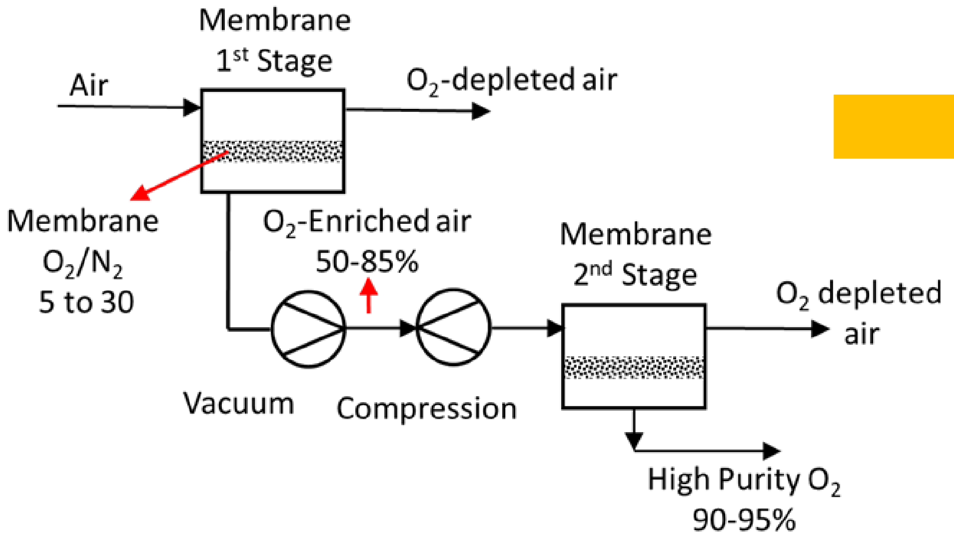


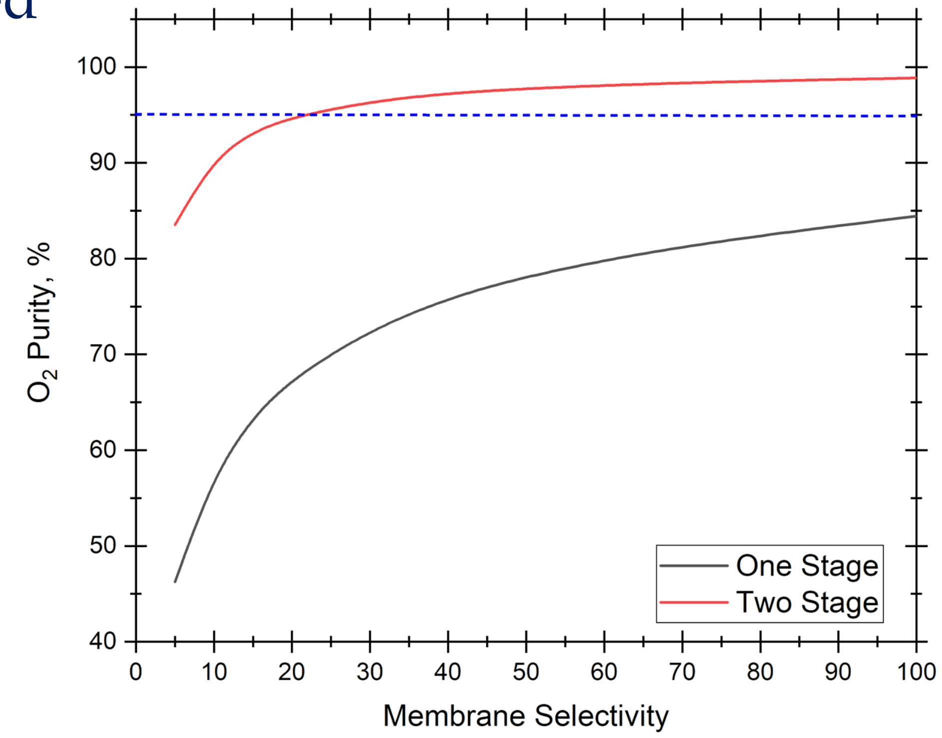
Ref: Meriläinen et al. / Applied Energy, 94 (2012) 285-294

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 O_2 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



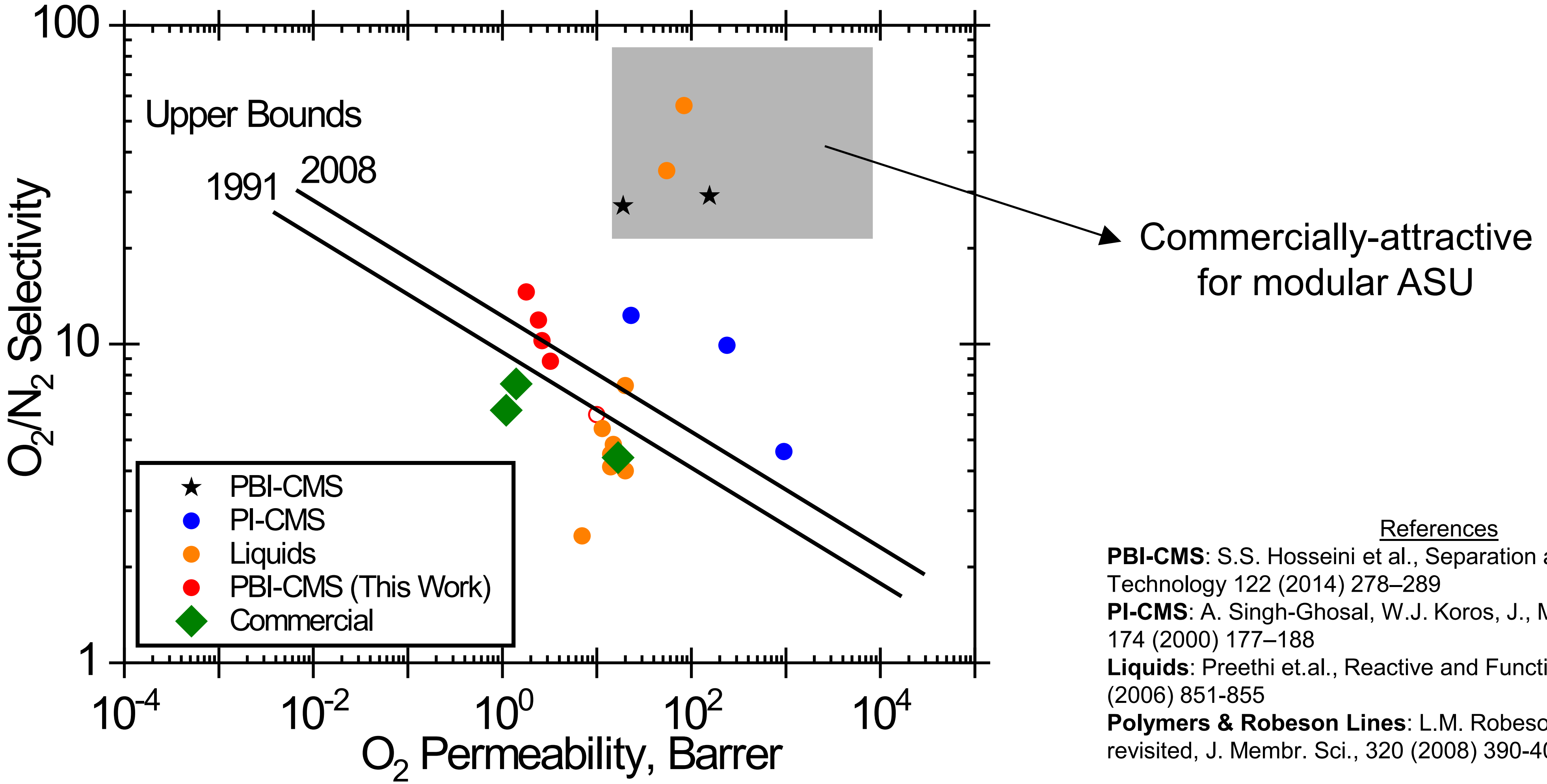


Calculated O_2 Purity. Ref: Ward et.al., J Membrane Sci 1 (1976) 99-108

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

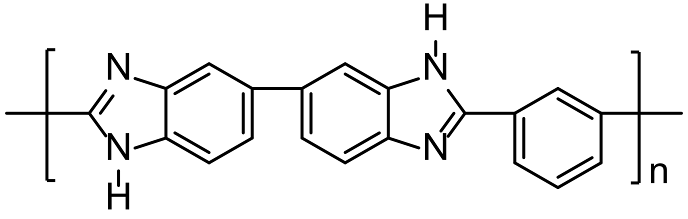
PI-CMS: A. Singh-Ghosal, W.J. Koros, J., Membrane Science 174 (2000) 177–188

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

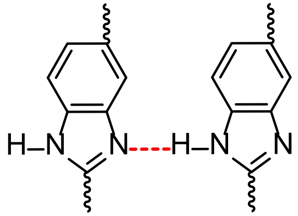
Polymers & Robeson Lines: L.M. Robeson, The upper bound revisited, J. Membr. Sci., 320 (2008) 390-400

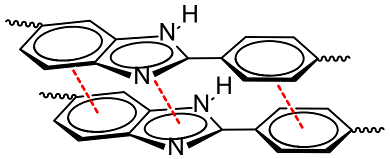
Membrane Development Approach

- **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

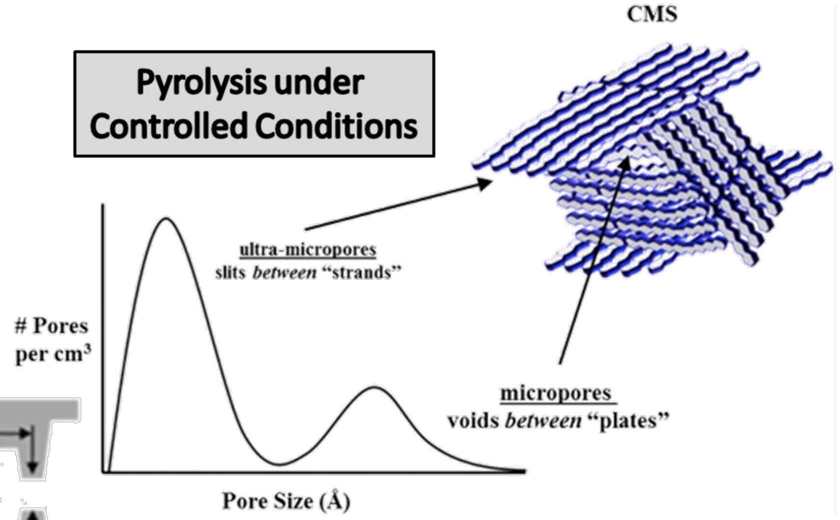


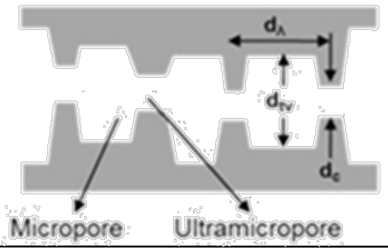


    - Base polymer (*m*-PBI) has high selectivity for gas pairs (e.g. $H_2/N_2 \geq 100$; $O_2/N_2 = 2$)

  - 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

Project Timeline (BP – 3)

			BP1 12/15/18 - 11/30/19				BP2 12/01/19 - 11/30/20				BP3 12/01/20 - 11/30/21				BP4 12/01/21 - 11/30/22				BP5 12/01/22 - 11/30/23			
	Start Date	End Date	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																				
Task 2.0 - PBI- CMS Hollow Fiber Membrane Preparation, Optimization, and Characterization	12/15/18	09/30/22												4								
Subtask 2.1 - Optimize PBI pyrolysis conditions	12/15/18	03/30/20												9								
Subtask 2.2 - CMS hollow fiber membrane preparation	06/01/18	09/30/22												10								
Task 3.0 - Membrane Evaluation and Process Parametric Studies	04/01/19	09/30/23												11								
Task 4.0 - Process Design and Techno-economic Analysis	12/15/18	09/30/22												12								
Task 5.0 - Modular System Design	10/01/22	09/30/23																				

Project Milestones & Success Criteria Point (BP – 3)

FY	ID	Task #	Description	Planned Completion Date	Status	Verification Method
3	M9	2.0	Set-up a flowing gas pyrolysis system for PBI membrane pyrolysis.	09/30/21	**Finished set-up**	Membrane performance data
3	M10	2.0	Develop O_2 permeance and O_2/N_2 selectivity correlations as a function of selective layer thickness and fabrication process parameters.	11/30/21	**In progress**	Membrane performance data
3	M11	3.0	Performance evaluation of PBI-CMS HFMs in realistic air feed mixtures containing CO_2, H_2O and Ar	11/30/21	**In progress**	Membrane performance data
3	M12	4.0	Complete the preliminary techno-economic analysis of the 2-stage membrane process and report on the O_2 production cost ($/ton)	09/30/21	**In process**	Report file
No	**Decision point**		**Success Criteria**	**Date**	**Outcome**	
4	Go/No-Go for the optimized PBI-CMS hollow fiber membranes		Determine the feasibility of achieving PBI-CMS hollow fiber membranes with high O_2 permeance (100 GPU) while maintaining O_2/N_2 selectivity of 15 as demonstrated by the membrane fabrication parameter-structure-performance correlations.	11/30/21	**In progress; Demonstrated O_2 permeance ~72 GPU and O_2/N_2 selectivity ~11**	

Membrane Material & Hollow Fiber Development

Polymer Derived CMS Membranes

- CMS membrane formation is multi-step process

PBI Polymer → (Thin-Film Hollow Fibers) → Base Polymer Membrane → (Pyrolysis) → CMS Membranes

- Numerous membrane formation parameters influence the separation performance of the polymer derived CMS membranes

Polymer Characteristics

- Molecular weight
- Main chain modifications
- Side chain functionalization
- Crosslinking

Membrane Morphology

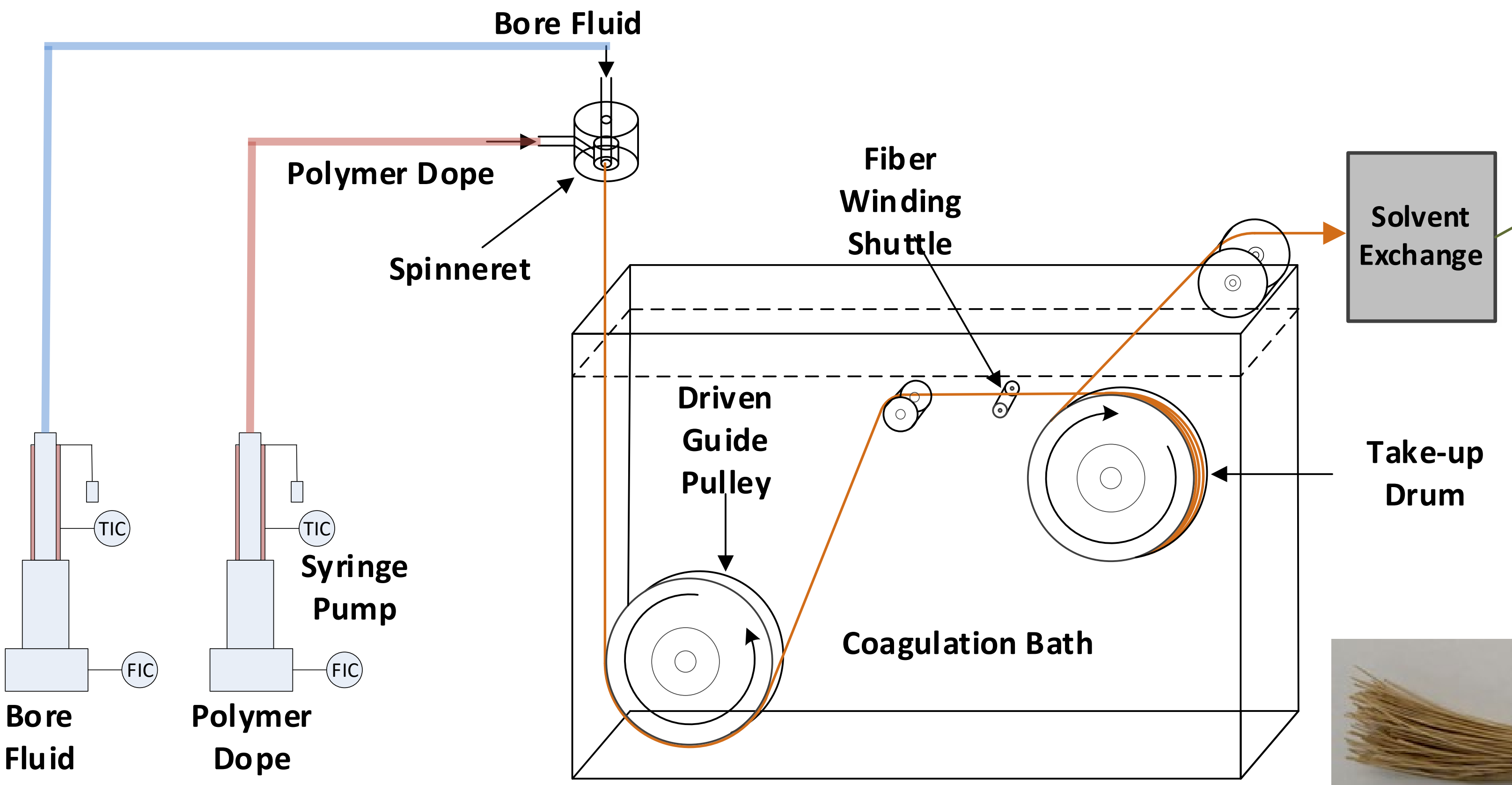
- Selective layer thickness
- Porous support morphology

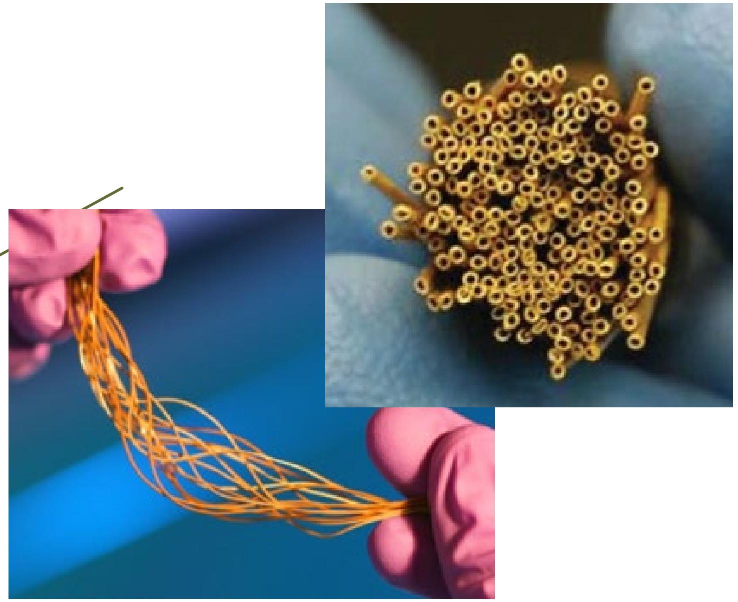
Pyrolysis Protocol

- Pre-treatment
- Temperature
- Time
- Ramp-rate
- Atmosphere

Base Hollow Fiber Membrane Preparation

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

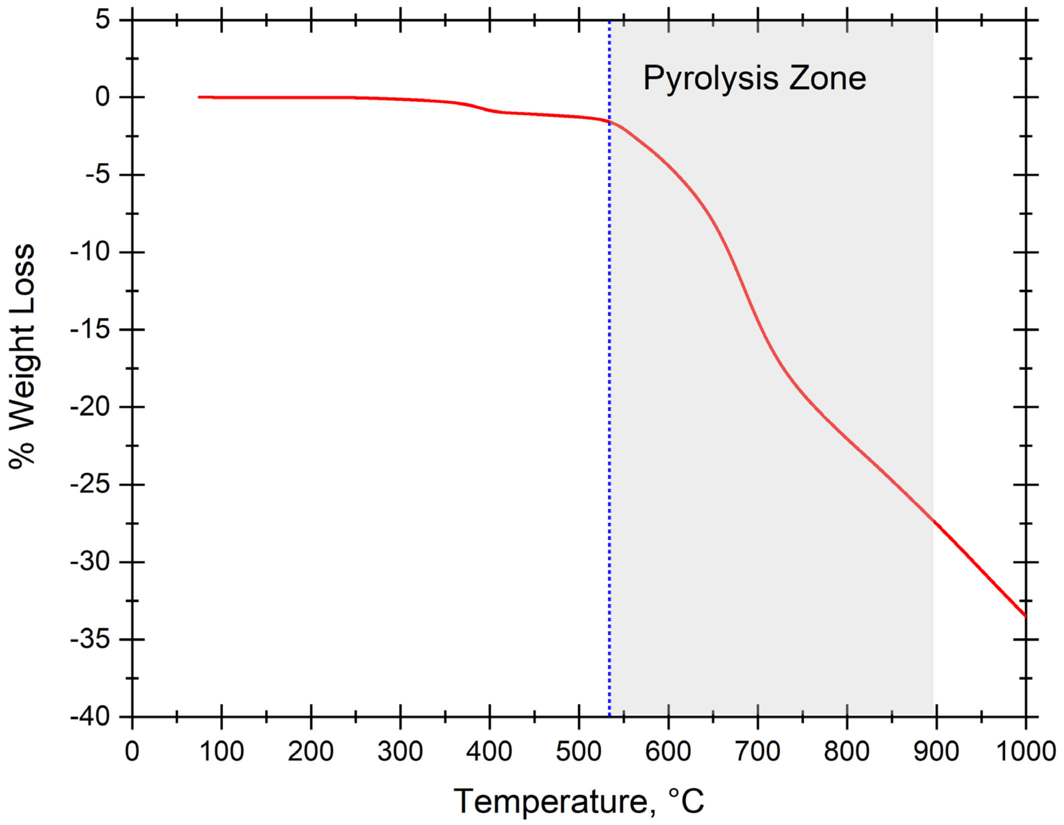




Ref. *Berchtold & Singh, et.al. 2018 US Patent 10071345*

PBI Membrane Pyrolysis

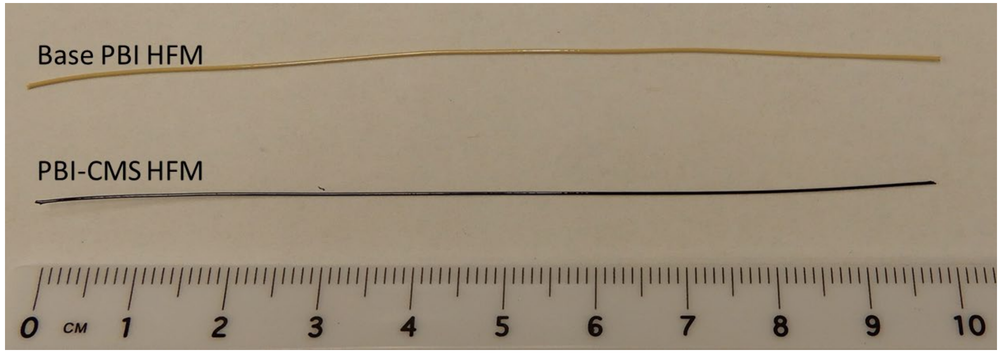
- **Pyrolysis conditions have a tremendous influence on the gas separation performance of the polymer derived CMS membranes**
  - Efforts focused on the development and optimization of PBI pyrolysis protocols



Pyrolysis Parameters

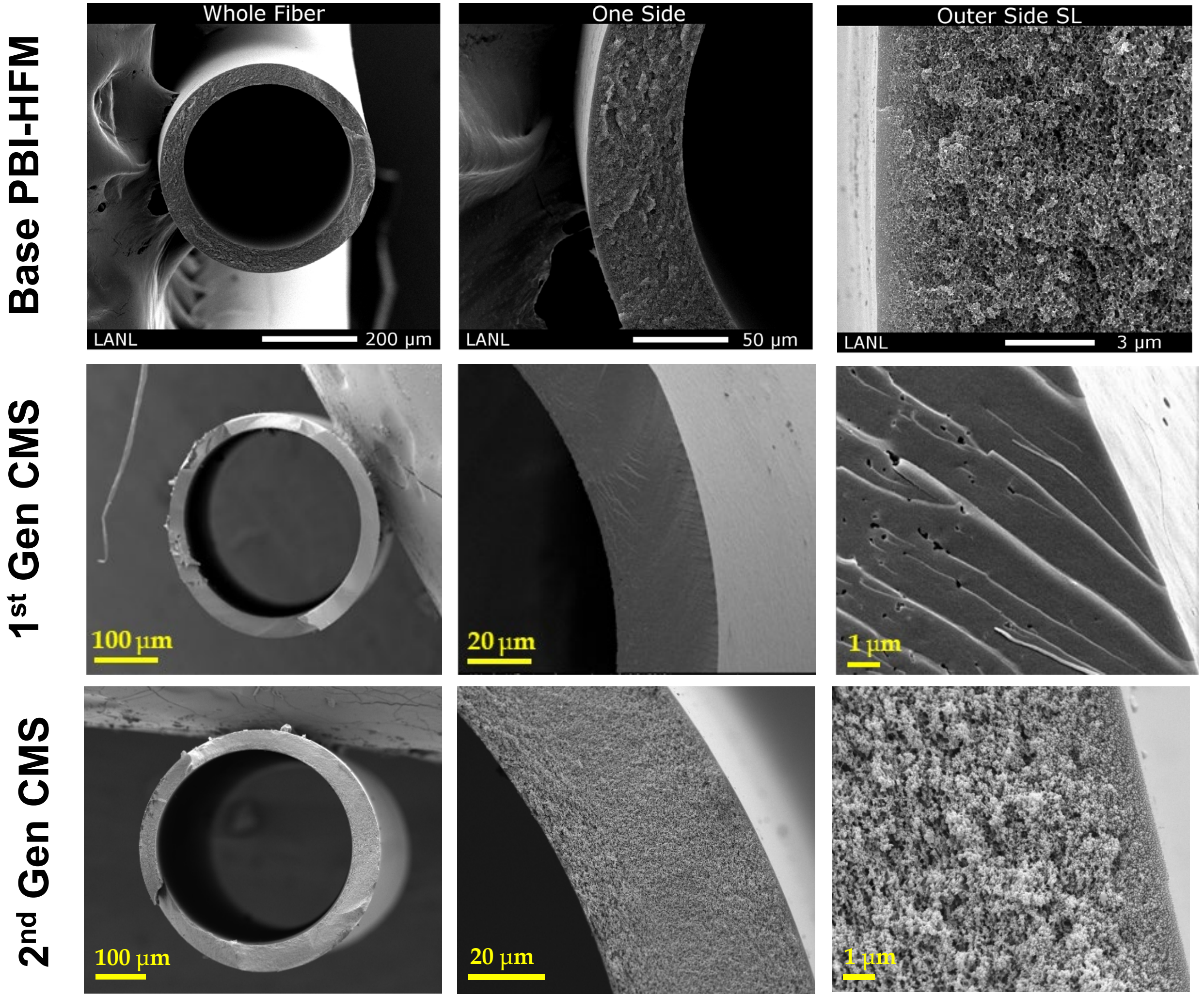
- Temperature (500 to 900 °C)
- Ramp rate and dwell time
- Environment (e.g. inert, vacuum)

Successfully fabricated mechanically robust PBI-CMS membranes in industrially attractive platform



Achieving High Permeance

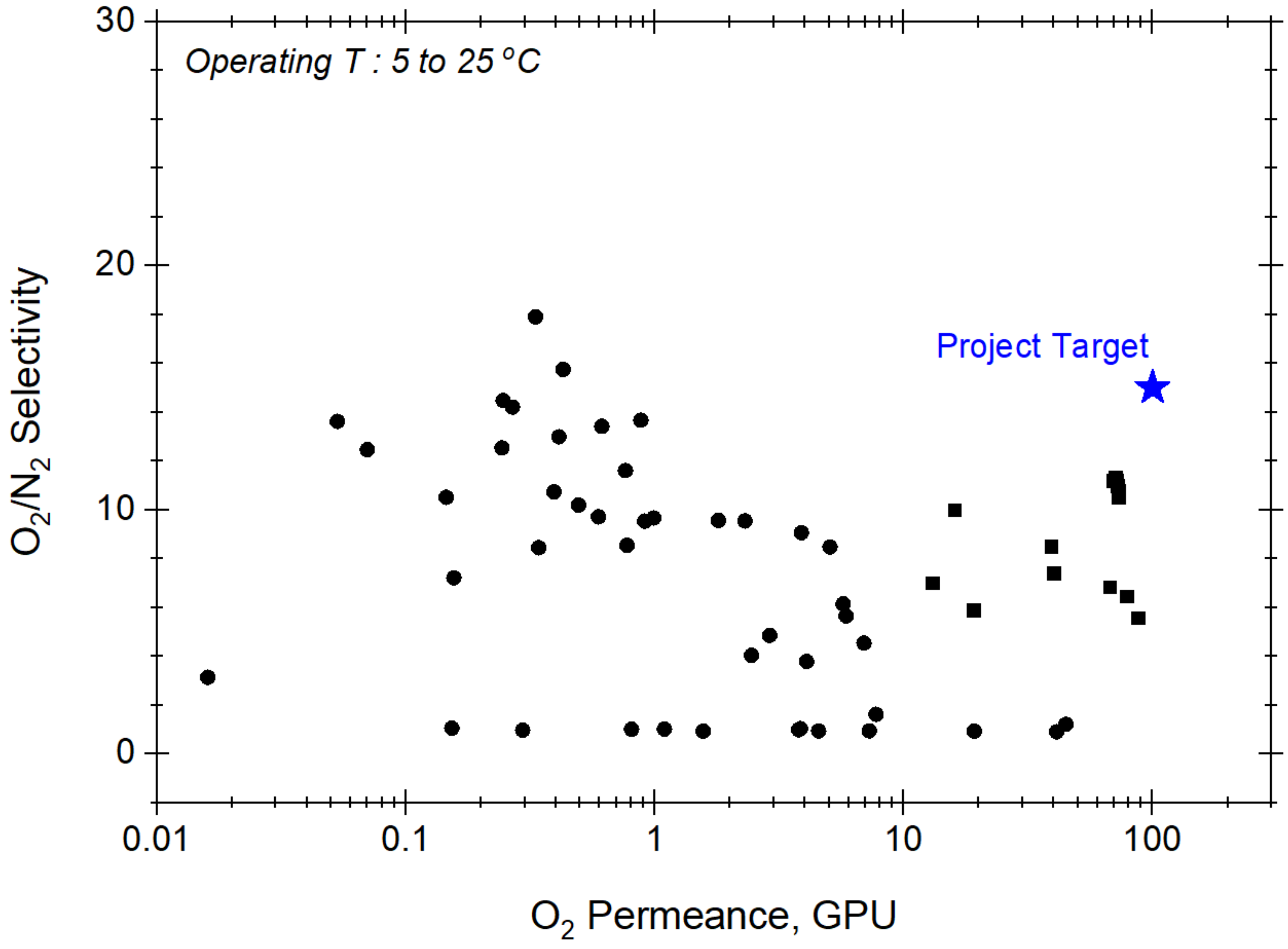
Challenge: Mitigate HFM porous support structure collapse during pyrolysis

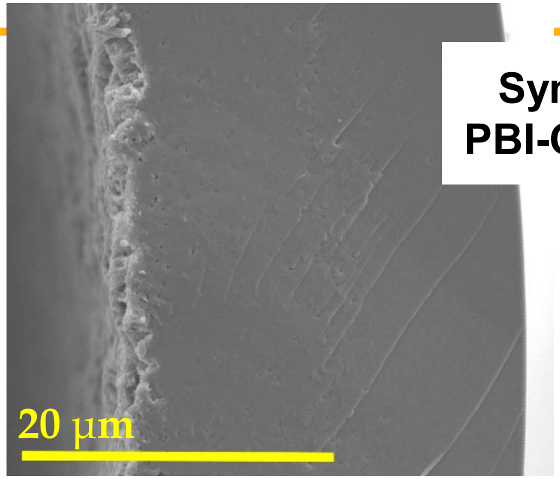


- Achieving high permeance requires asymmetric morphology: Thin selective layer supported with a porous layer
  - Estimated 1 µm thick selective layer of 2nd Generation (Gen) fibers should enable achieve-ment of project permeance target of 100 GPU

1 GPU = 10^{-6} cm^3 cm^{-2} $cmHg^{-1}$ s^{-1}

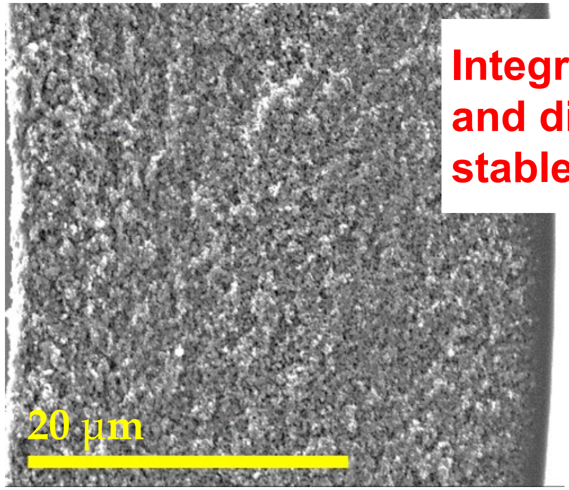
Improving Separation Performance





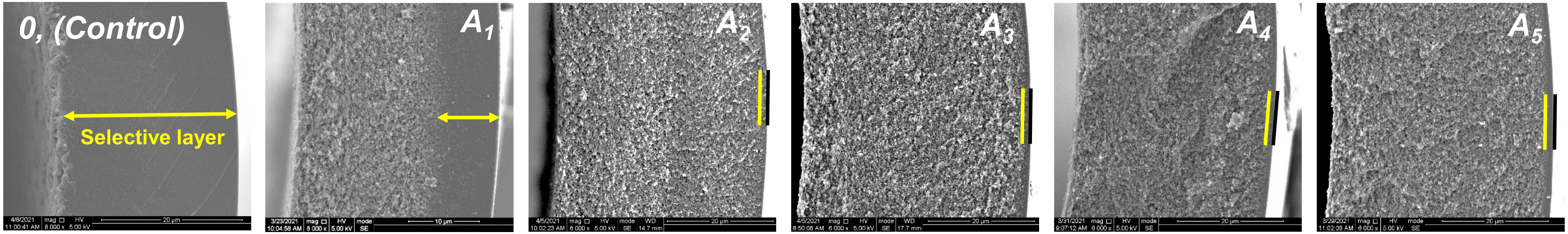
Symmetric PBI-CMS HFM

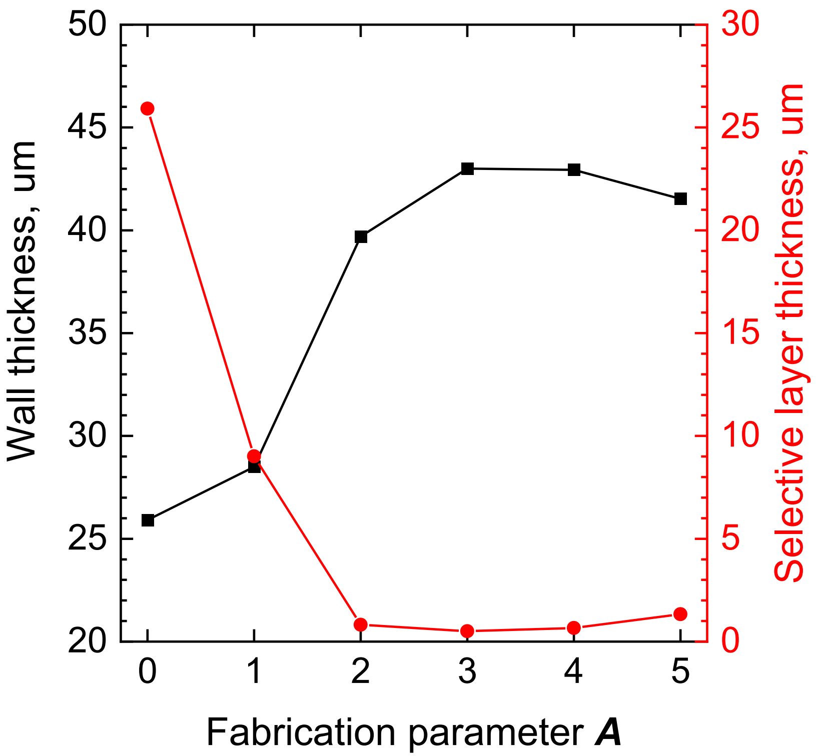
Material chemistry & processing optimization

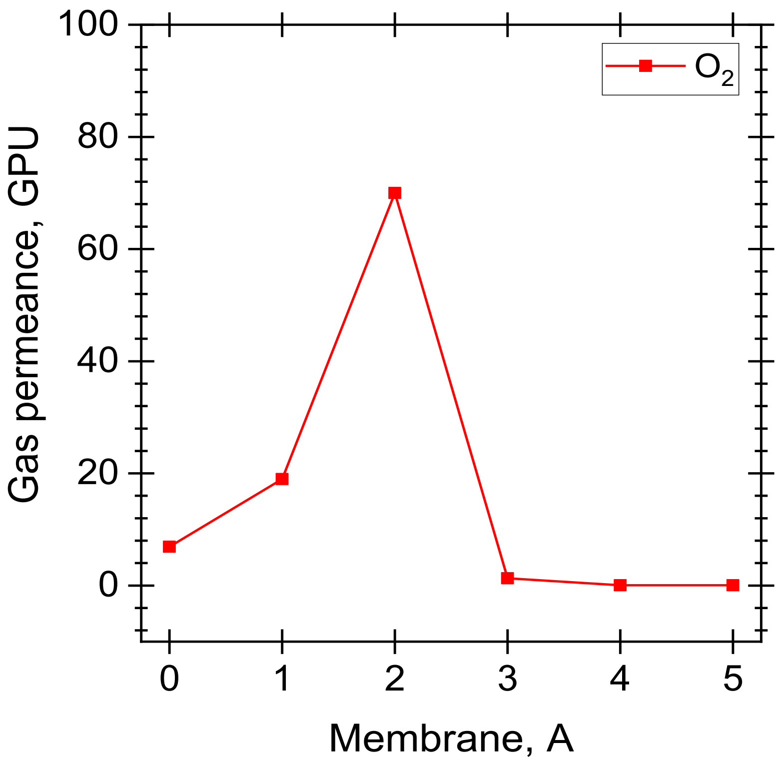


Integrally asymmetric and dimensionally stable PBI-CMS HFM

Controlled Morphology and Selective Layer Thickness



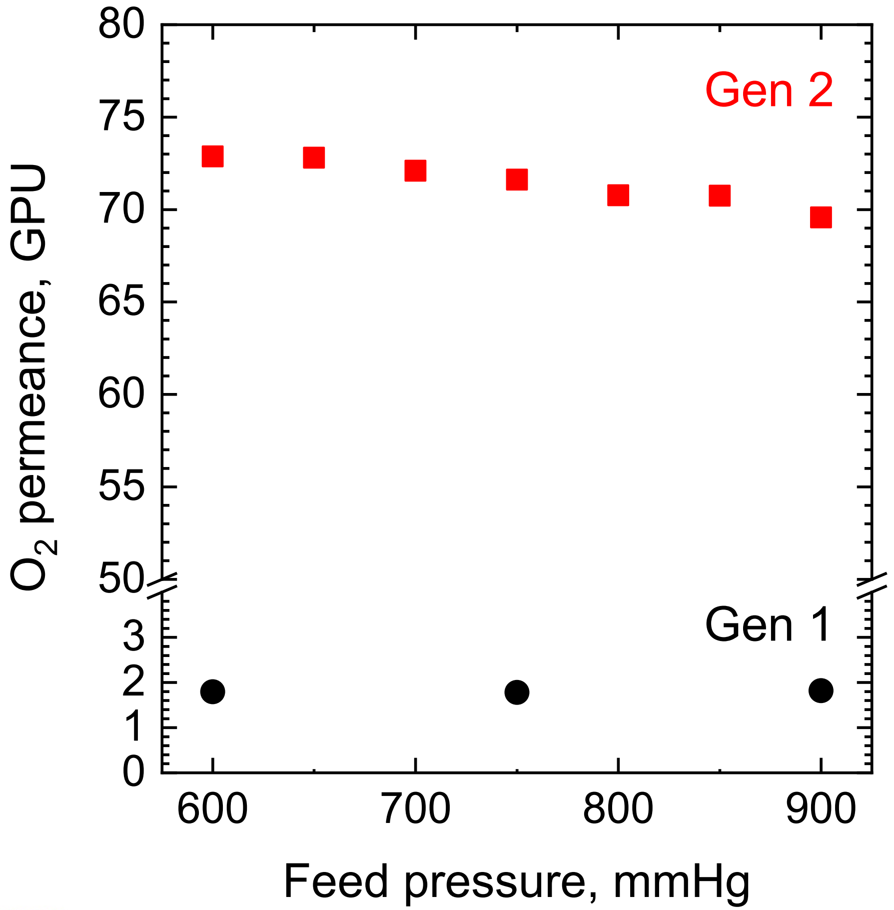


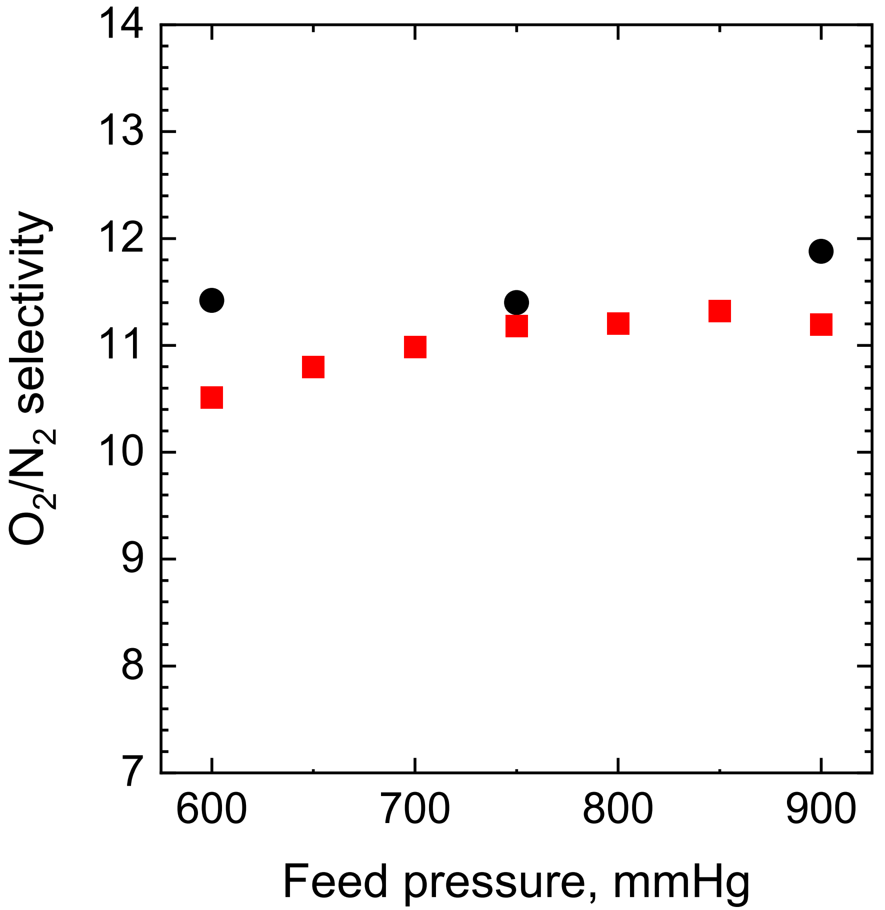


- Modified PBI-HFM fabrication protocol leads to
  - smaller pyrolysis induced dimensional change in HFMs
  - better selective layer thickness control
  - higher O_2 permeance

Influence of Feed Pressure on Perm-Selectivity

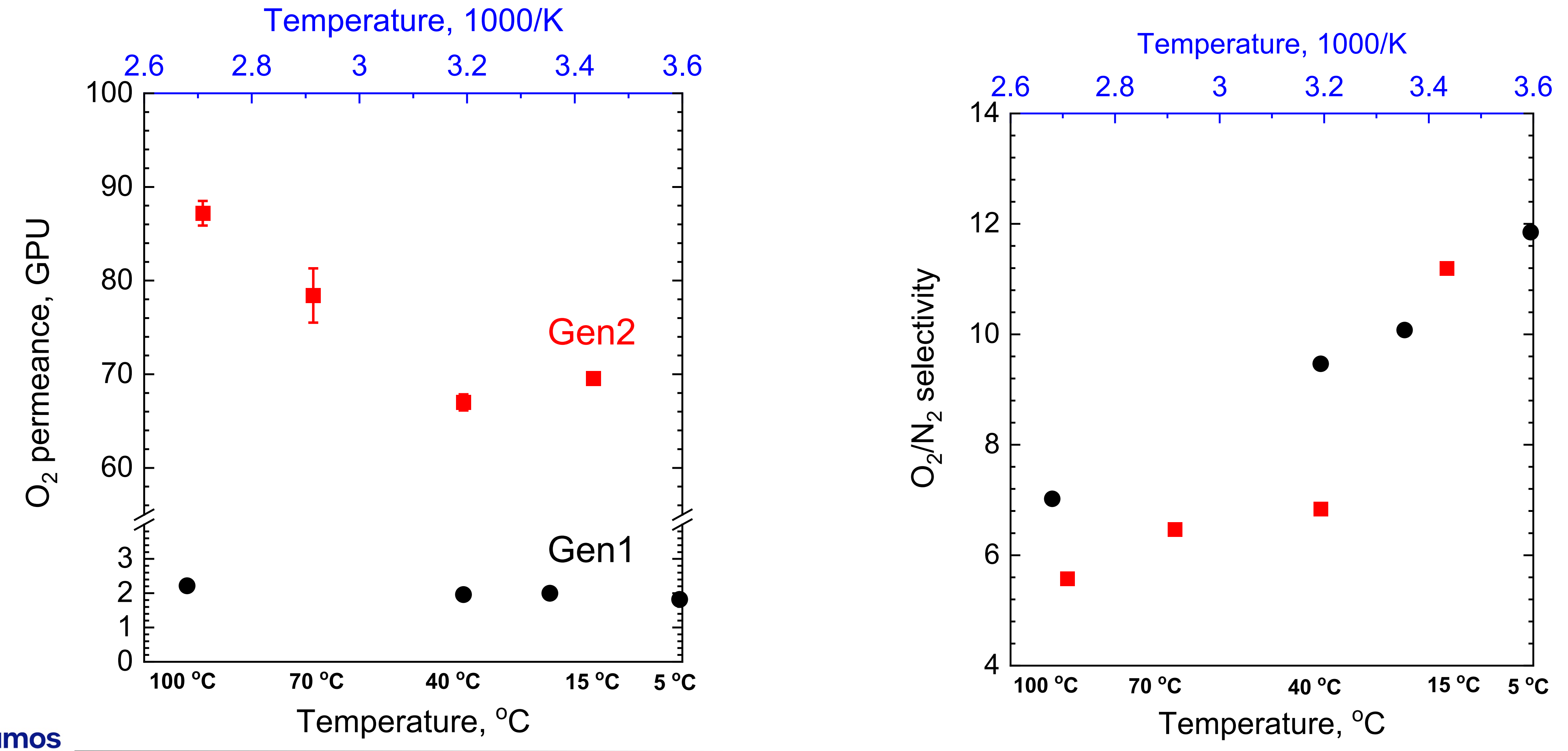
- **Steady performance as a function of pressure**
- **Modified fabrication process led to ca. 40-fold improvement in O_2 permeance with comparable selectivity**





Influence of Temperature on Perm-Selectivity

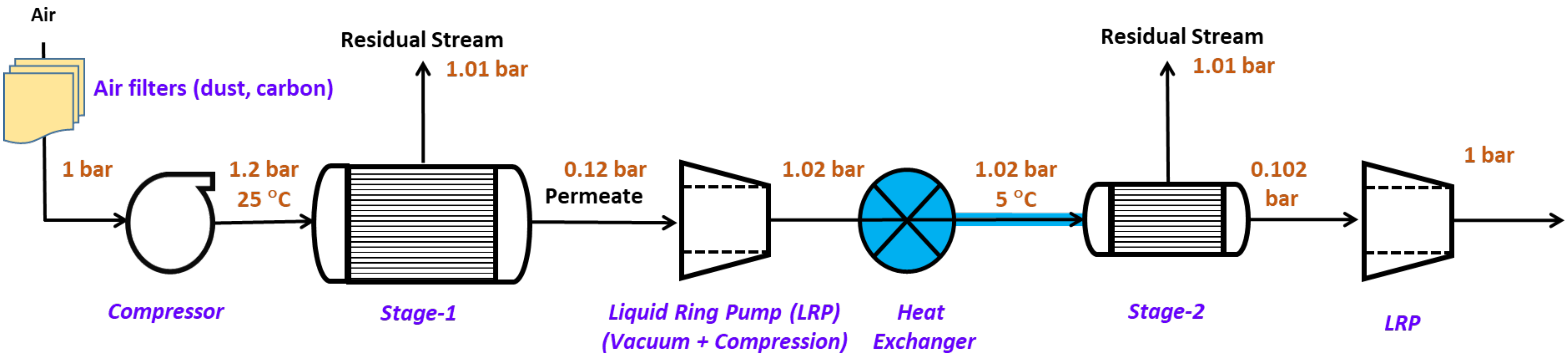
- Overall O_2 and N_2 permeances follow Arrhenius expression
- Gen2: O_2 permeance and O_2/N_2 ranged from of 66 to 87 GPU and 11 to 5.6, resp.



Membrane Modeling and Process Design

Proposed Process Layout

- 2-stage PBI-CMD HFMs-based air separation process for > 90% O_2 production

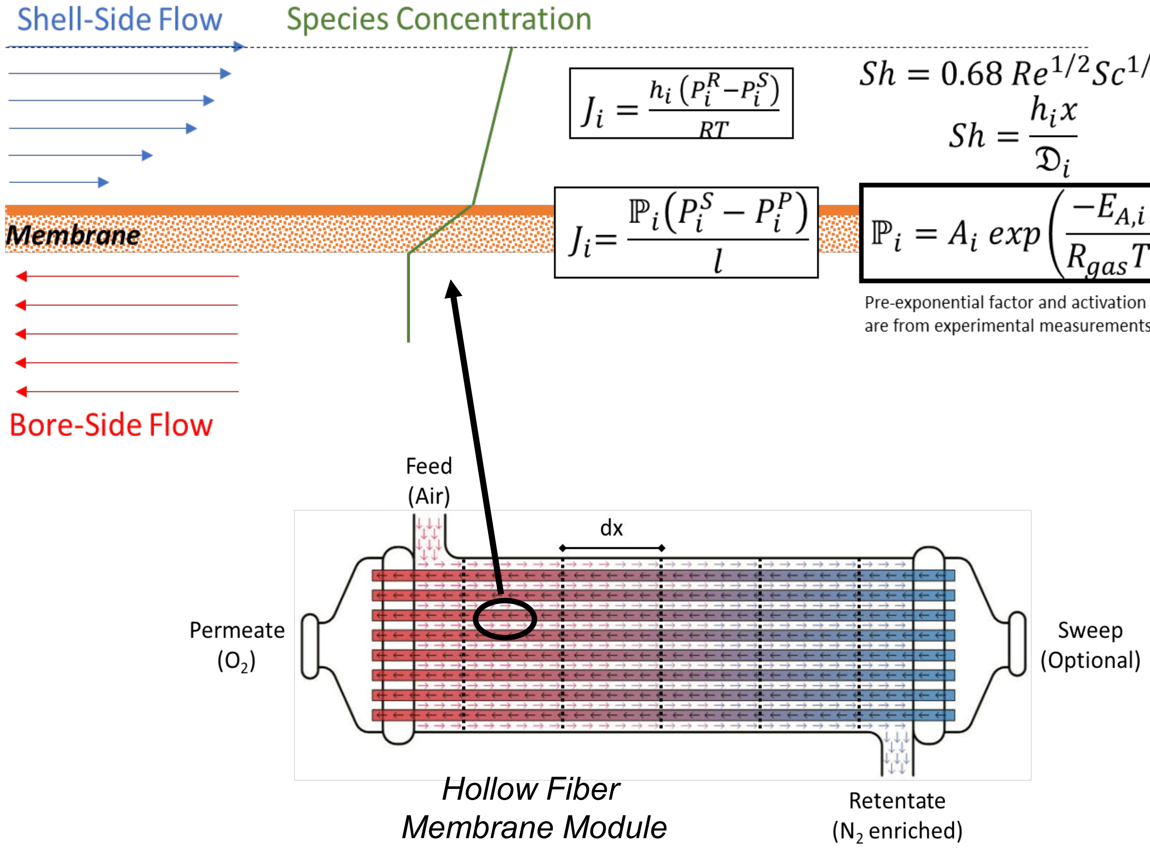


Process Modeling Platform Development

- **Improved HFM process model and expanded capability to calculate process energy consumption**

Membrane Flux Model

python™



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

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

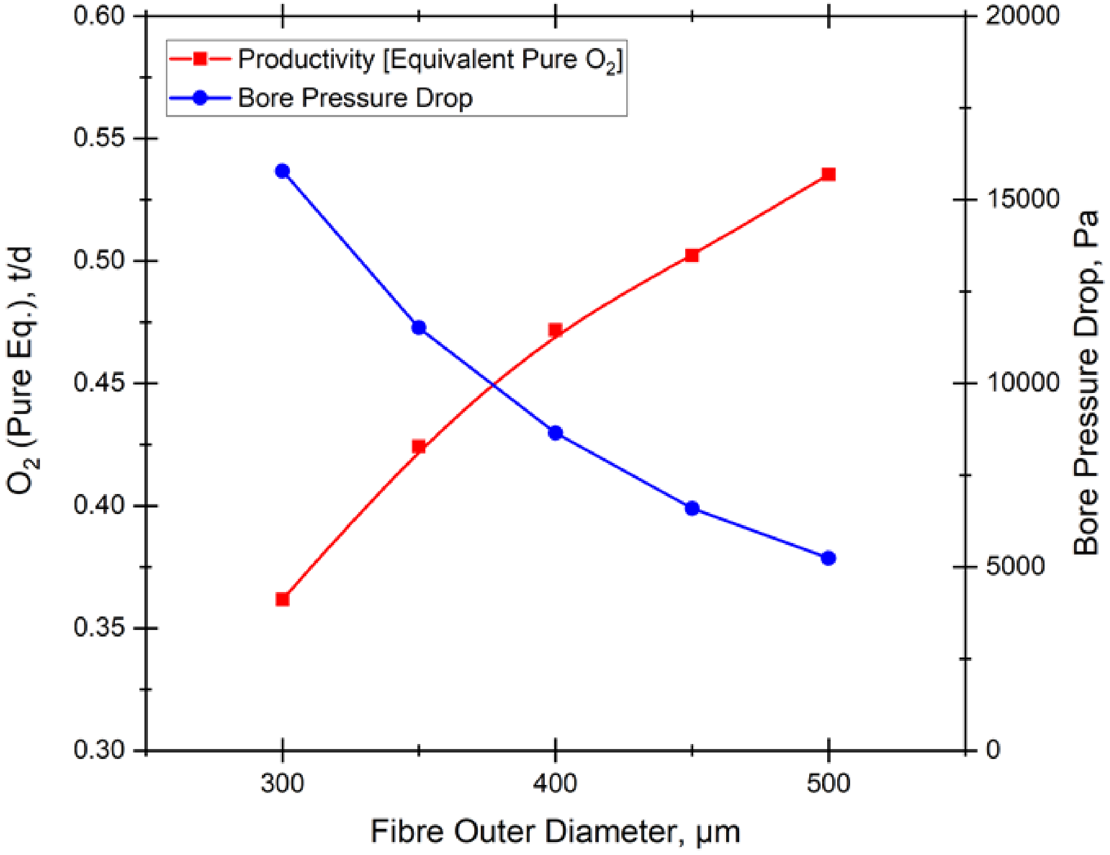
$$Sh = \frac{h_i x}{\mathfrak{D}_i}$$

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

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

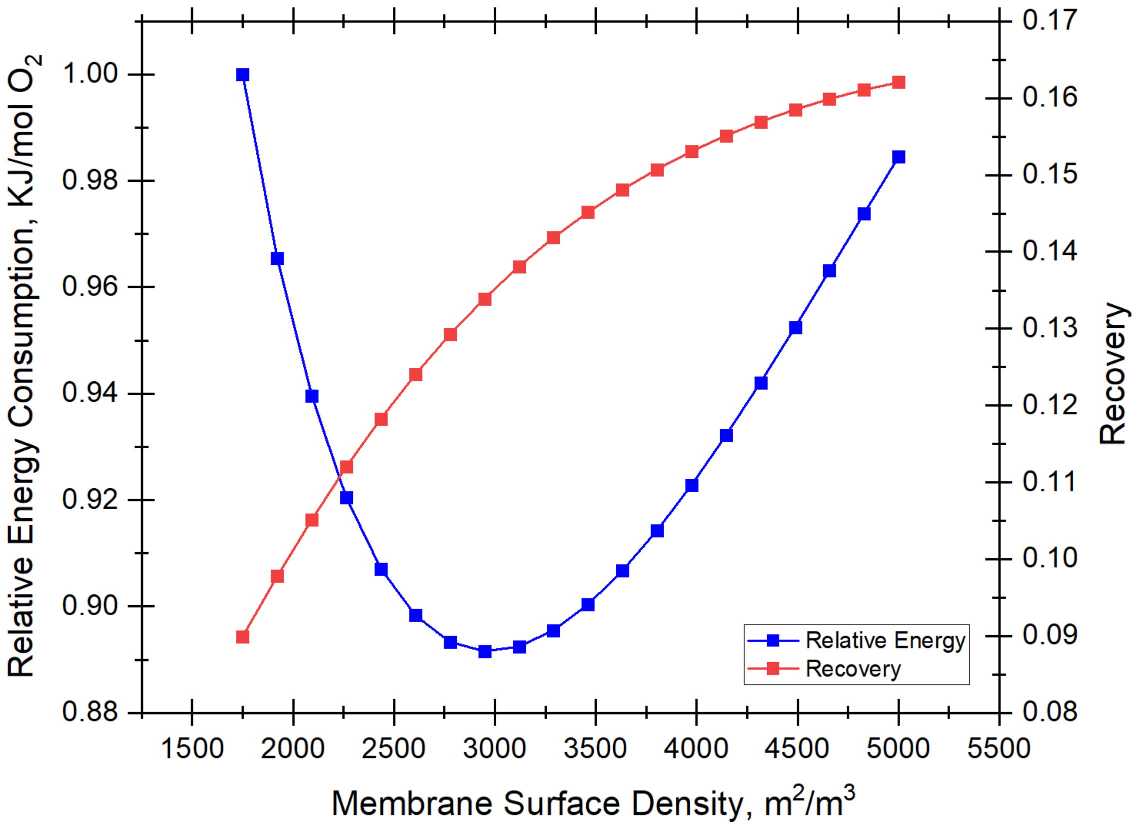
Pre-exponential factor and activation energy are from experimental measurements

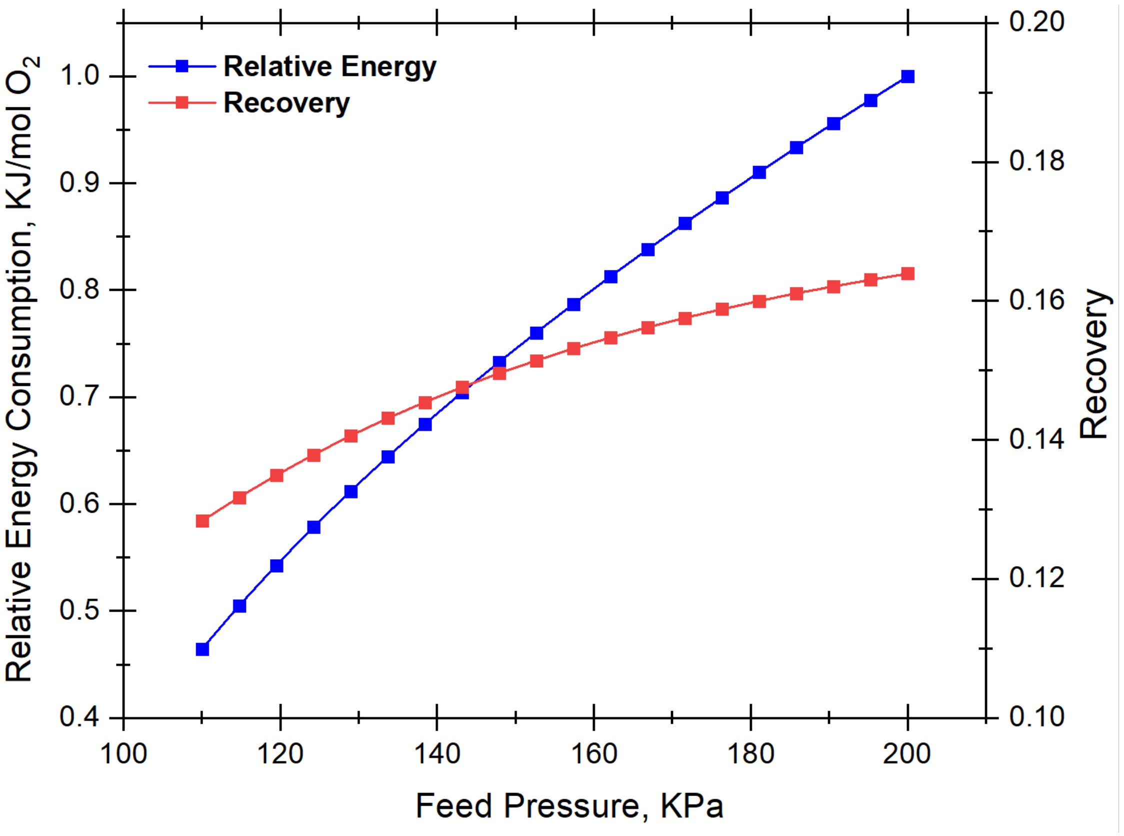
- Membrane module optimization to minimize parasitic energy losses



Process Energy Consumption Optimization

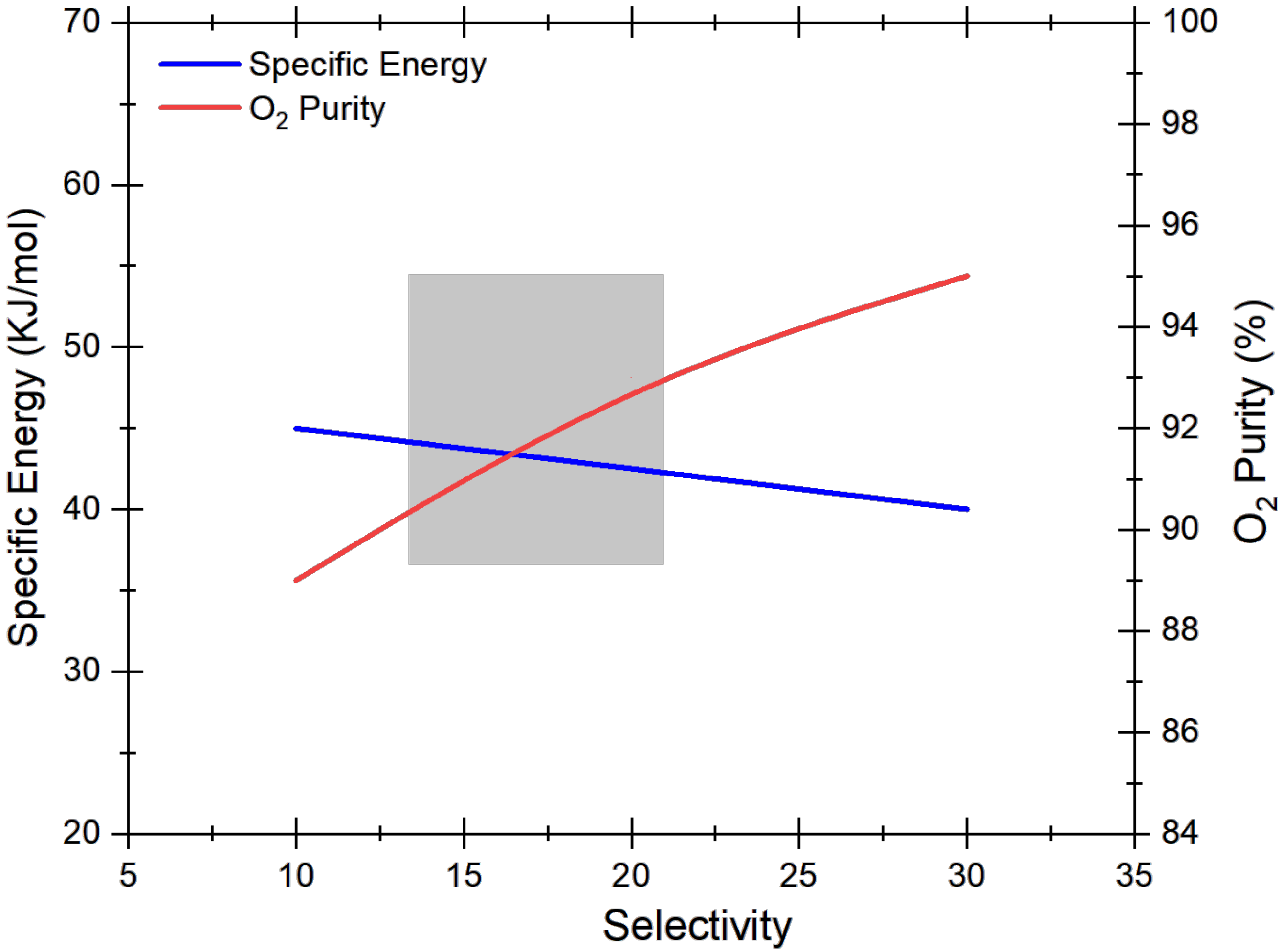
- Rigorous analysis of process parameters and membrane module design to minimize process energy consumption



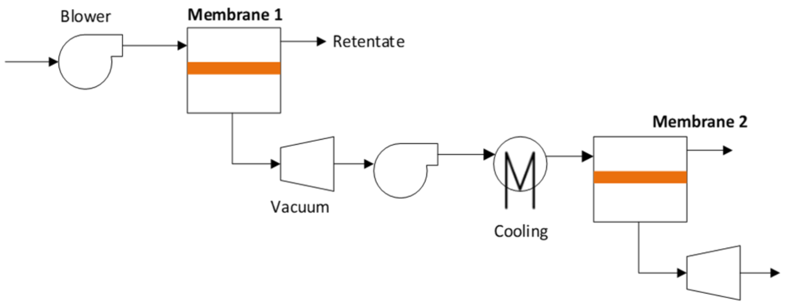


Energy Consumption

- **Revised specific energy consumption calculation**
  - 40 to 45 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 20



Techno-economic Analysis – Design Basis Developed



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	50-300
O_2/N_2 selectivity of the membrane	10-30
Module Diameter, m	0.25
Module Length, m	1-3
Surface Area Density, m^2/m^3	3000
Area Ratio Stage 1/Stage 2	~ 5/1
Membrane cost, $\$/m^2$	30-100

Process parameters	Input values
O_2 Production Rate, TPD	10
Number of Membrane Stages	2
Inlet volume of air, Kg/s	1-3
Pressure of inlet air, bar	1.01 to 1.20
Temperature Stage-1 and stage-2, ˚C	25 & 5
Hours of operation per year	7884
Pressure ratio	10
Membrane effective thickness, µm	0.3 to 1
O_2 purity (%) at Stage-1 and Stage-2	60-65, 90-95
Pump efficiency, % and temperature, ˚C	40-64, 15
Membrane installation factor	0.35-0.45
Electricity cost, $/MWh	50 - 60

Preliminary Estimates (Best Case Scenarios)

Energy Consumption, KJ/mol	33-55
Production Cost, $\$/tonne\ O_2$	30-80

Performance Benchmarking

Performance Benchmarking

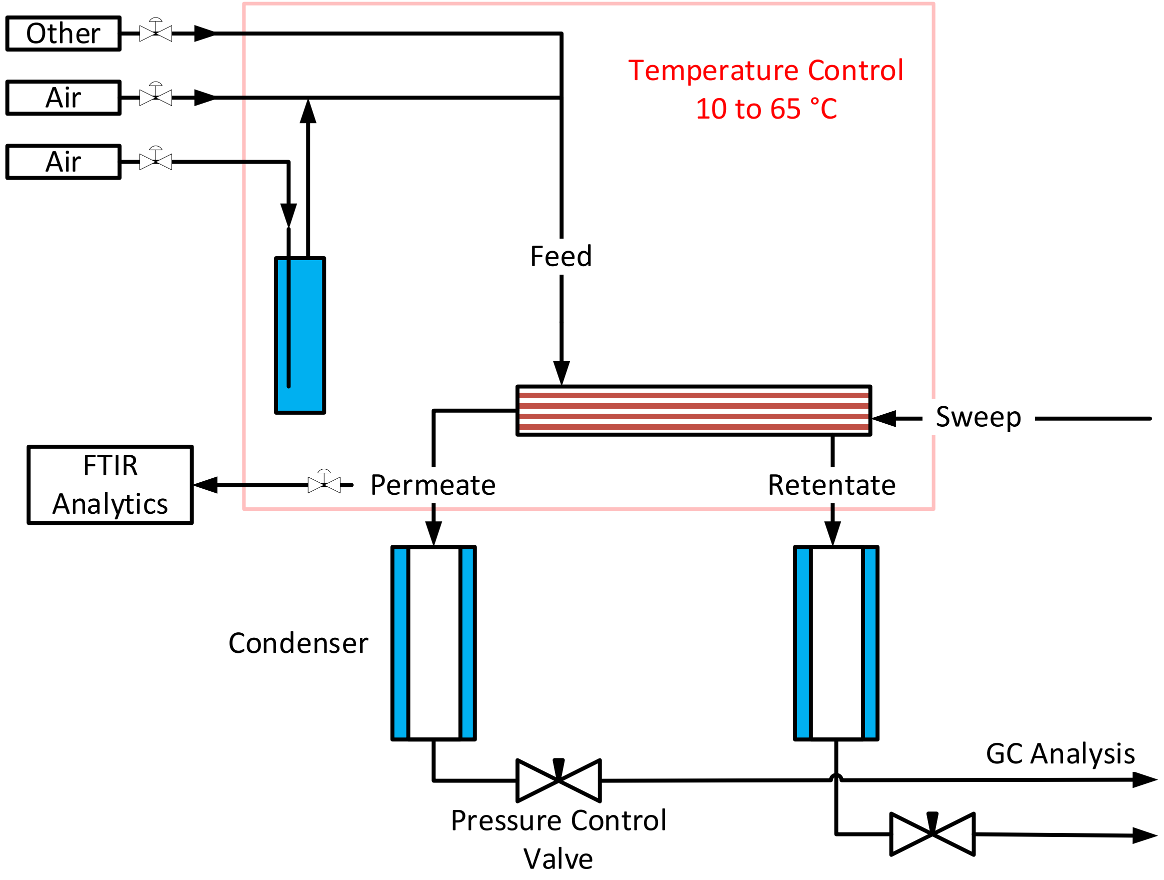
- **Evaluation of PBI-CMS HFMs in air feed stream**
  - Influence of water vapor and CO_2 on the membrane separation performance

- Lab-scale membrane module
- O_2 permeance and selectivity data collection at process relevant operating conditions
  - Feed Pressure: 1-3 bar
  - Temperature: 10 to 100 °C
  - RH: 5 to 90%
- Real-time detection of H_2O and CO_2
- Benchmark performance data for model validation
- Initiated system and analytical equipment calibration

Addendum

Air Separation Performance Evaluation

- **Mixed gas permeation system schematic for evaluation of PBI-CMS HFMs at process relevant operating conditions**

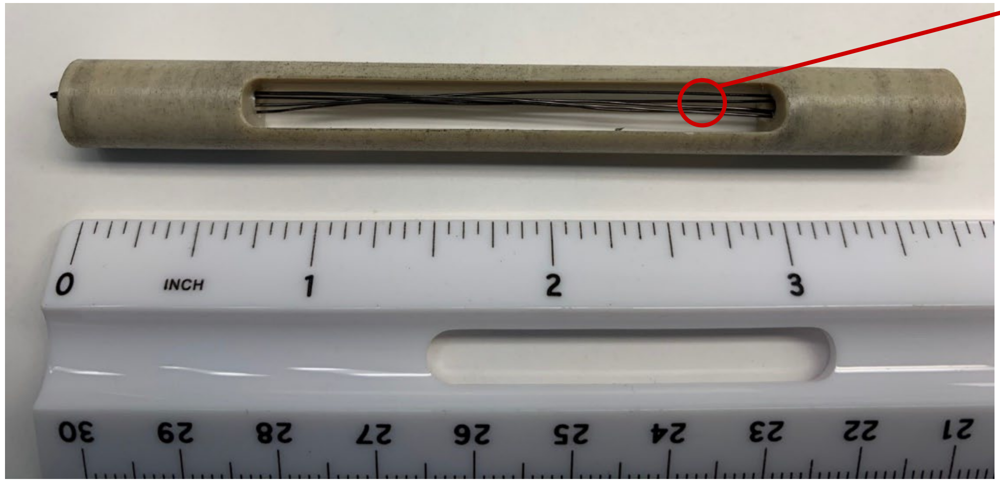


Typical Air Composition	
N_2	78% (vol. Dry Basis)
O_2	21%
Ar	0 to 0.93
CO_2	0 to 400 ppm
Relative Humidity	10 to 90%

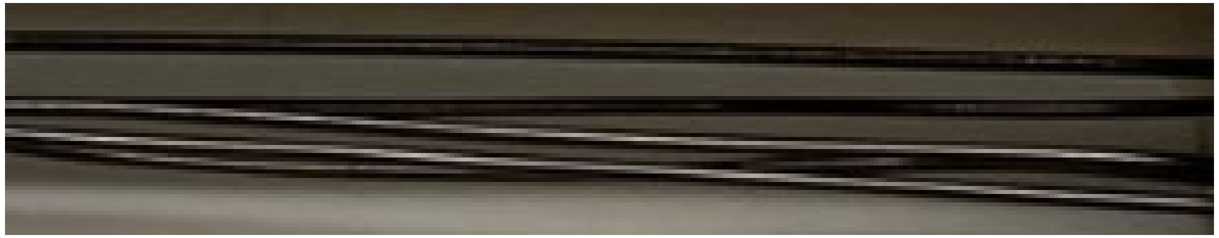
Multi-Fiber Membrane Module

Addendum

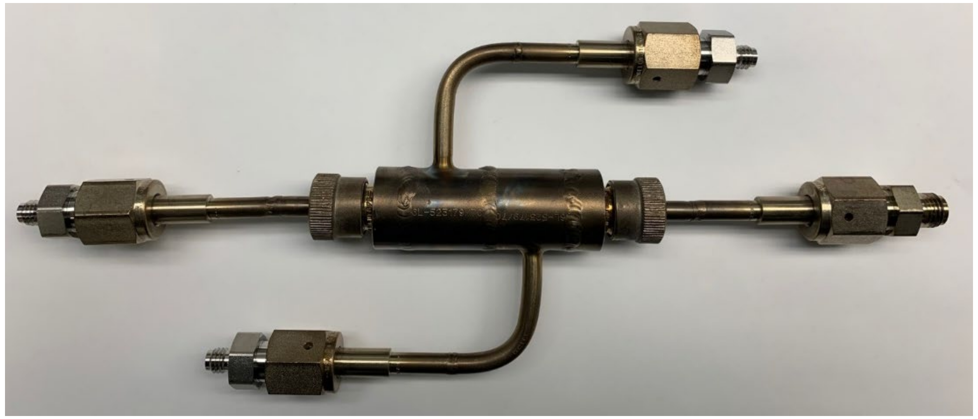
- **Laboratory scale PBI-CMS multi-fiber membrane module for air separation performance evaluations at process relevant conditions**



Multi-fiber cartridge



5 PBI-CMS HFMs



Membrane module shell with flow-through on feed and permeate sides

Future Work

Membrane Design and Fabrication

- Compare performance of the PBI-CMS HFMs fabricated under flowing inert gas (N_2) and vacuum.
- Develop O_2 permeance and O_2/N_2 selectivity correlations as a function of the selective layer thickness and fabrication process parameters.

Membrane Evaluation and Performance Benchmarking

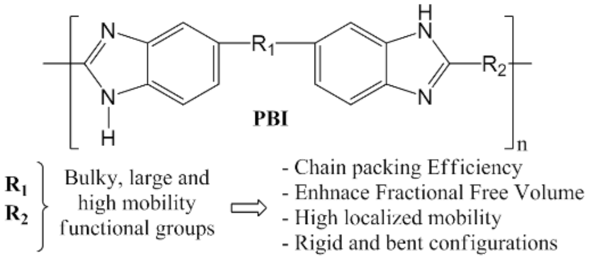
- Performance evaluation of PBI-CMS HFMs in realistic air feed mixtures containing CO_2, H_2O and Ar

Techno-economic Analysis

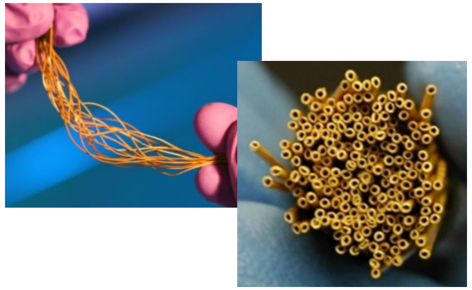
- Complete the preliminary techno-economic analysis of the 2-stage membrane process and report on the O_2 production cost ($/ton)

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



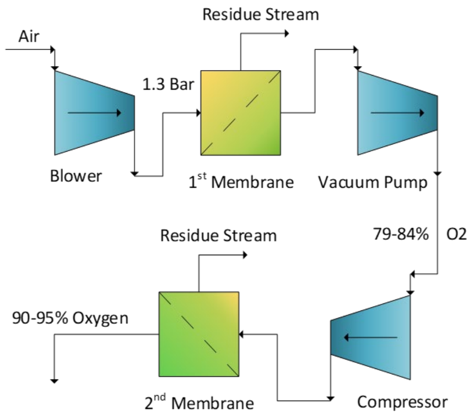
Material Design & Synthesis



Processing & Membrane Synthesis

CMS Membranes

Lab-scale Demonstration & Evaluation



Process Modeling

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