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

Los Alamos National Laboratory

Rajinder P. Singh

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Gasification and Transformative Power Generation
Pittsburgh, PA

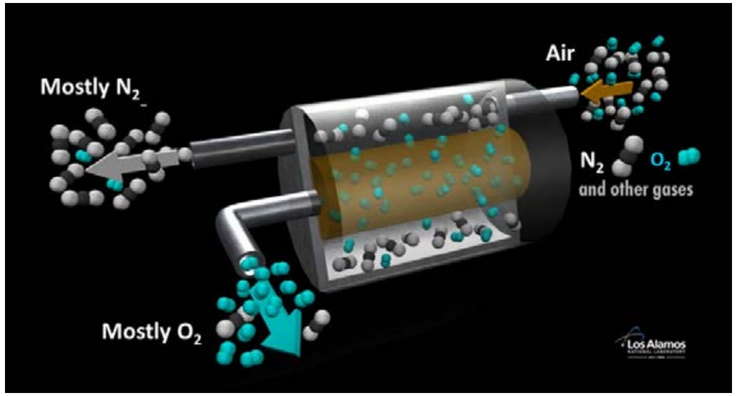
DOE – Fossil Energy/NETL

Outline

- Project Overview
- Membranes for Air Separation
- Technical Approach
- Experiments and Results
- Next Steps
- Summary

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:** BP1: 12/2018 – 11/2019
- **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

- **Materials Physics and Applications Division (MPA)**
  - Rajinder P. Singh
  - Kathryn A. Berchtold
  - John A. Matteson
  - Jong Geun Seong

Membrane Design, Synthesis & Characterization
Evaluation and Parametric Studies

- **Theoretical Division (T)**
  - Joel D. Kress
  - Christopher S. Russell
  - Troy M. Holland
  - Alexander J. Josephson
  - John M. Baca

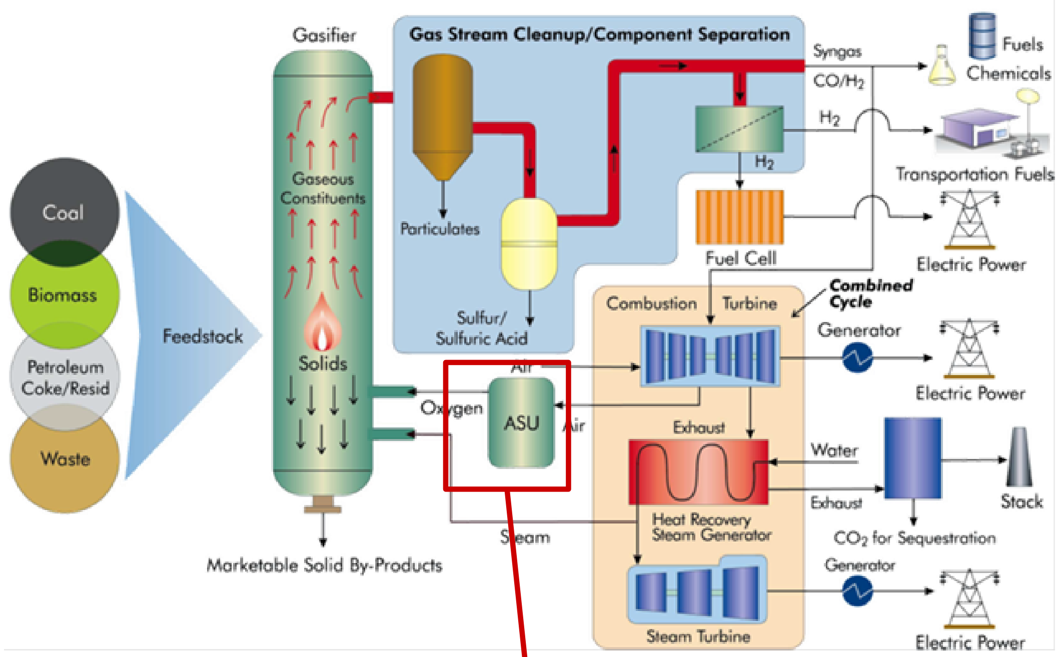
Process Modeling and Simulations

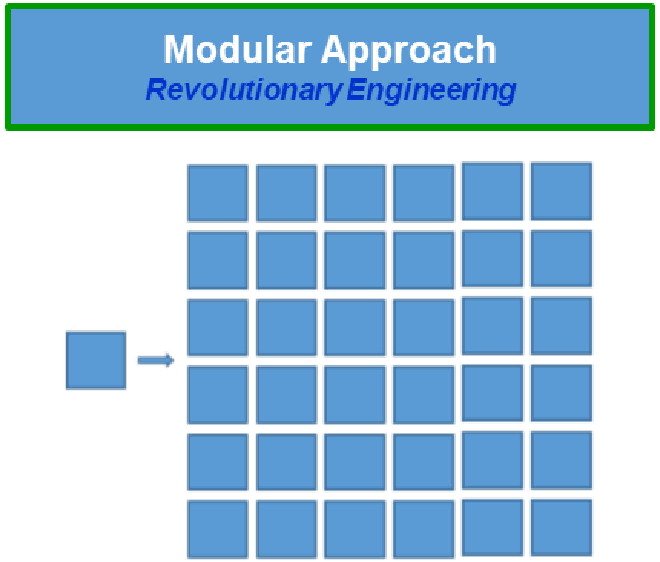
- **Engineering Technology and Design Division (E)**
  - Todd A. Jankowski

Modular Systems Design

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



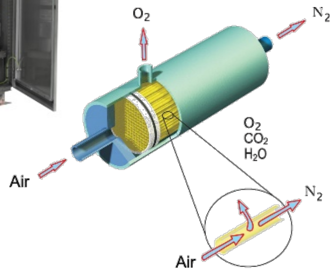


- **Advanced technology need:**
  - Energy efficient air separation technology for high purity O_2 production
  - Program Targets:
    - 90-95 vol% purity O_2
    - Low cost and operational efficiency relative to the state-of-the-art technology

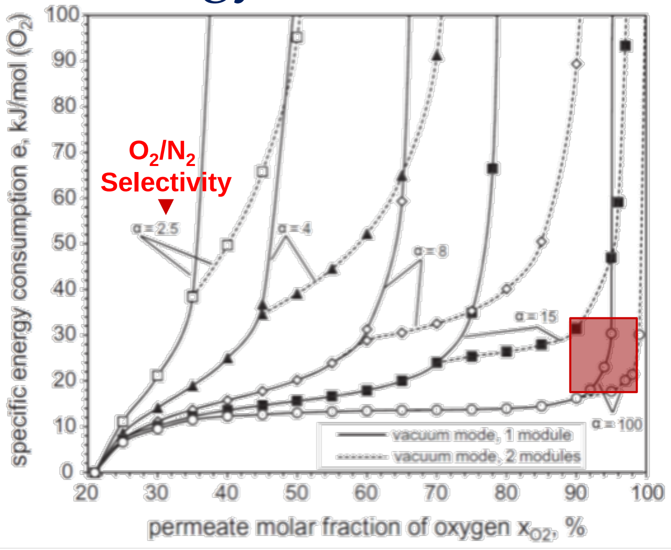
Images: DOE/NETL website

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.

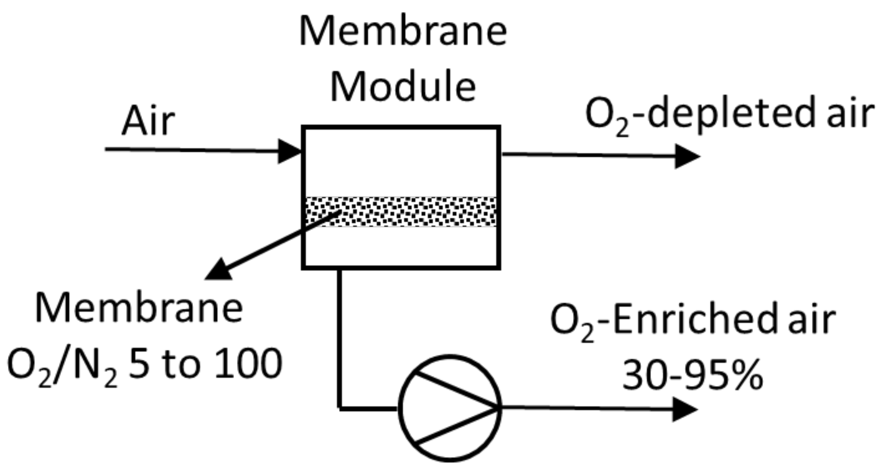


Ref: Meriläinen et al. / Applied Energy, 94 (2012) 285-294

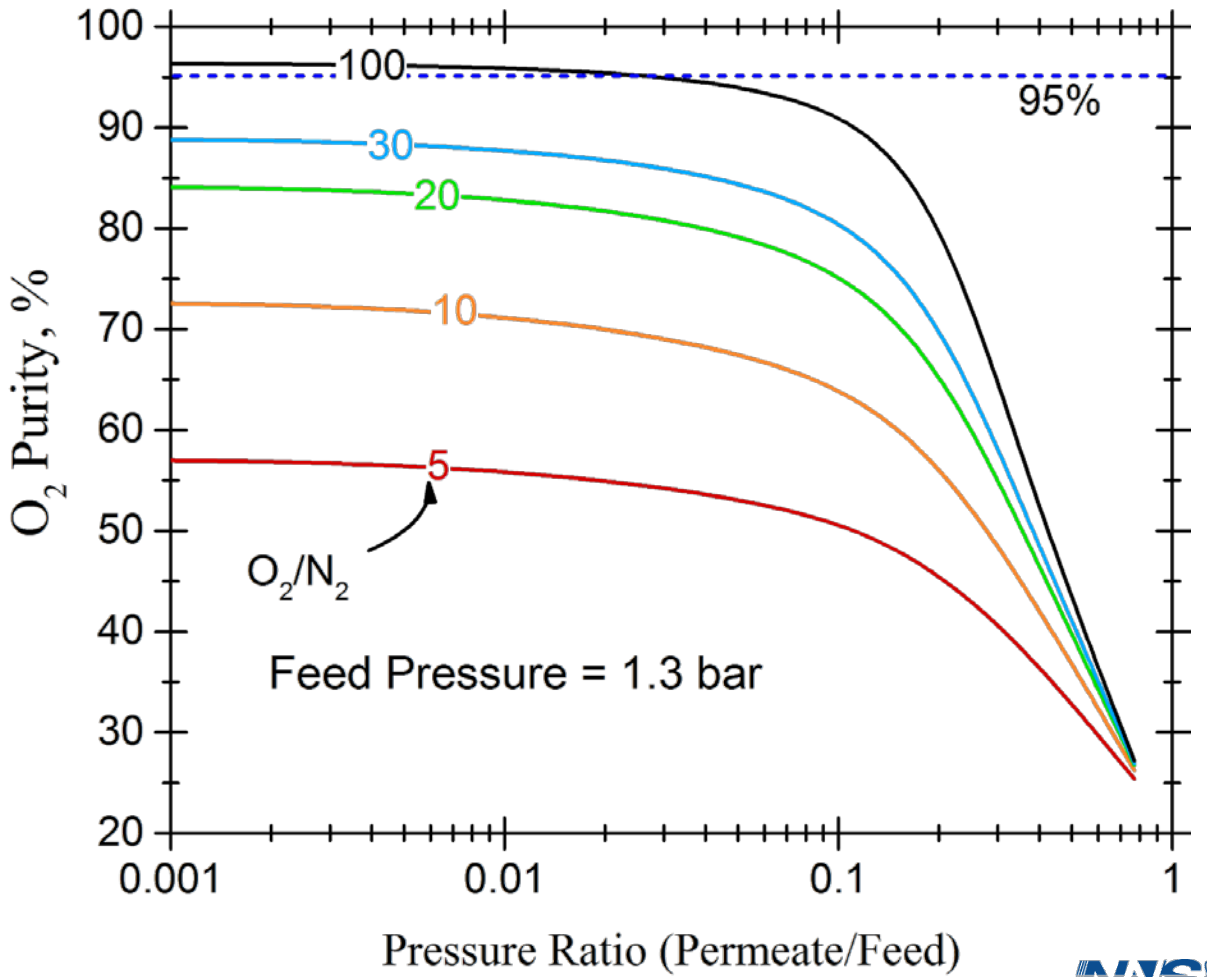
Membranes for Air Separations

- **Membrane selectivity has a pronounced influence on the achievable O_2 purity**
  - O_2/N_2 selectivity ~100 required to achieve > 95% O_2 purity in a single stage membrane separation process
    - Current commercial membranes have low O_2/N_2 selectivity (~5)

One-stage Membrane Separation Process



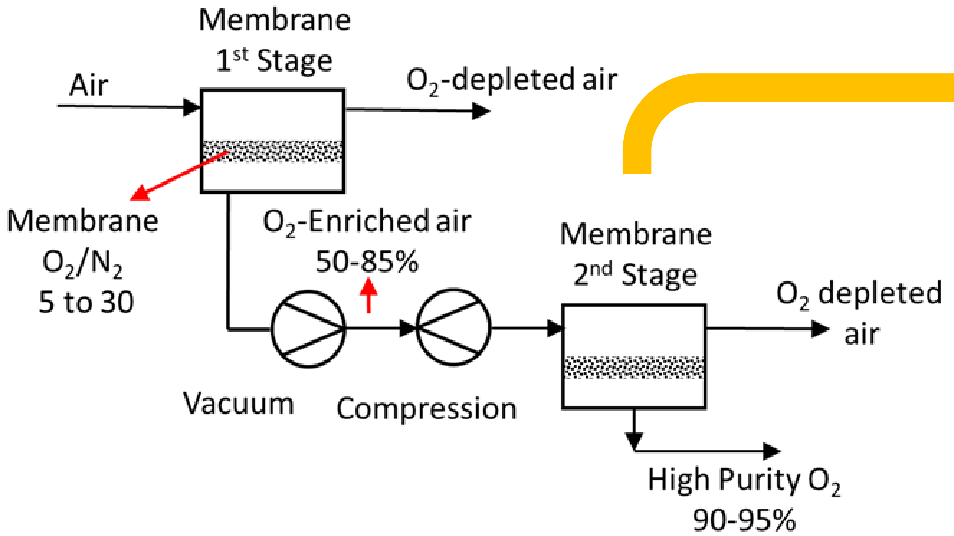
Calculated O_2 Purity.
Ref: Ward et.al., J Membrane Sci 1 (1976) 99-108



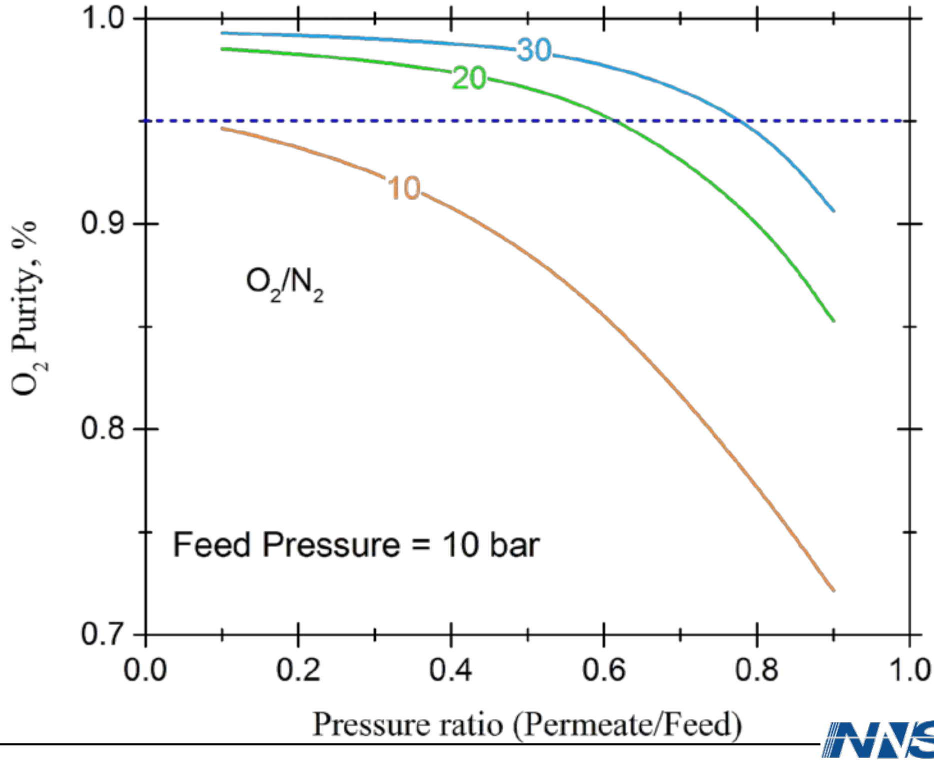
Achieving High O_2 Purity With Membranes

- **A multi-stage membrane process is proposed 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 having an O_2/N_2 selectivity between 20 to 30
  - 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



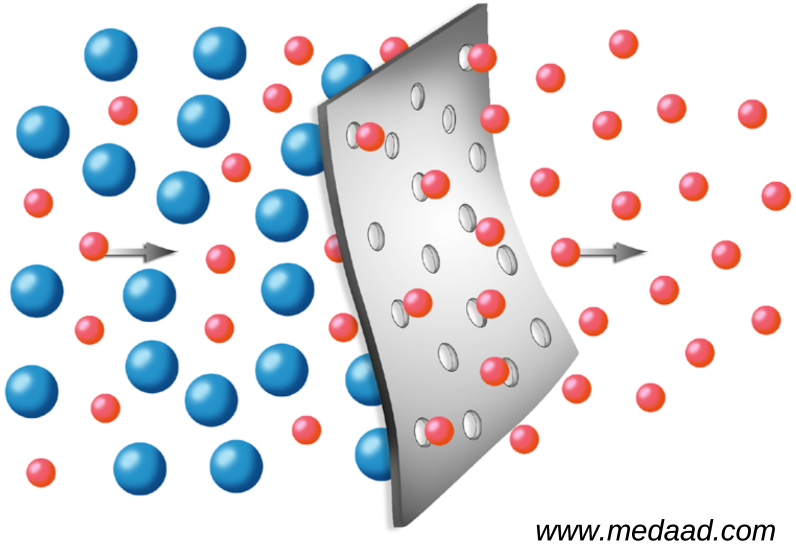
Calculated O_2 Purity two-stage operation.
Ref: Ward et.al., J Membrane Sci 1 (1976) 99-108



Membrane Fundamentals

- **Membrane performance is a function of a material's permeabity and selectivity**
  - Solution-diffusion transport mechanism

Molecular sieving membrane materials



www.medaad.com

<u>*Productivity*</u> → *Permeability*

$$P = D * S$$

<u>*Product Purity*</u> → *Selectivity*

$$\alpha_{O_2/N_2} = \frac{D_{O_2}}{D_{N_2}} * \frac{S_{O_2}}{S_{N_2}}$$

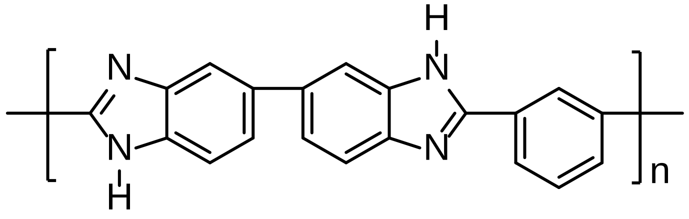
Size Dependent

Penetrant-Material interactions

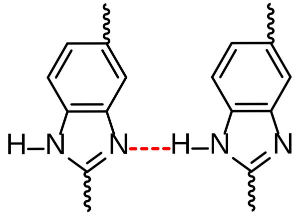
Gas	Kinetic Diameter, nm	Critical Temperature, K
O_2	0.346	154.6
N_2	0.364	126.2

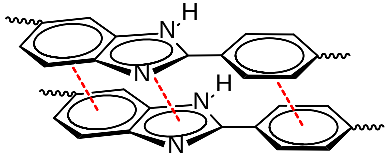
Membrane Development Approach

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

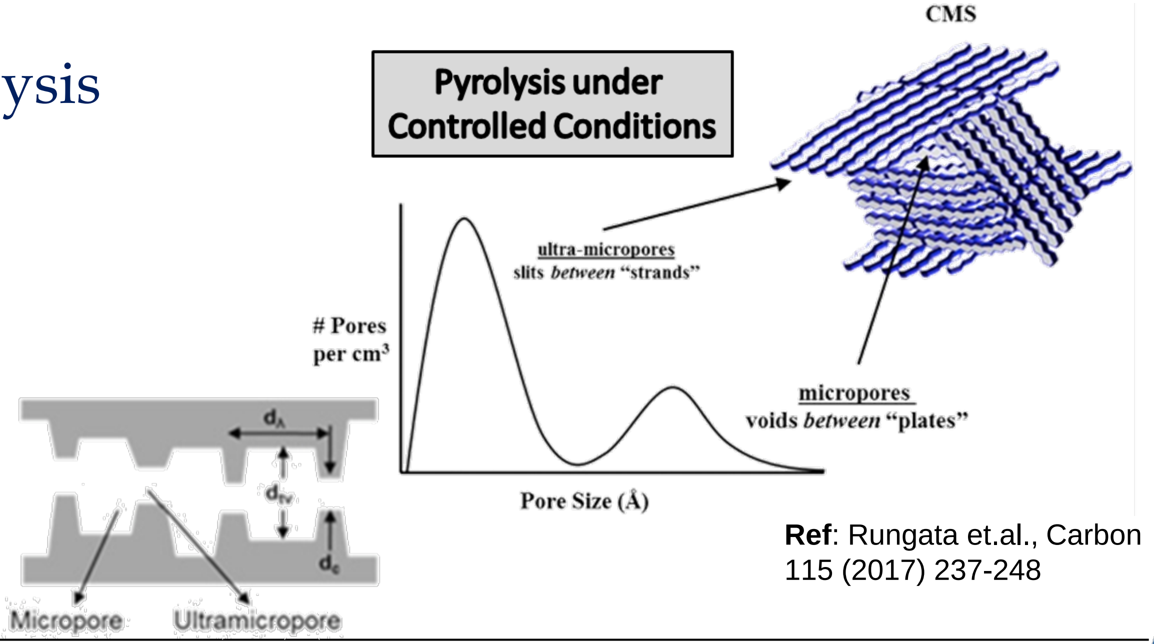


  - Tightly packed PBI molecular structure resulting from H-bonding and π-π stacking imparts molecular sieving character





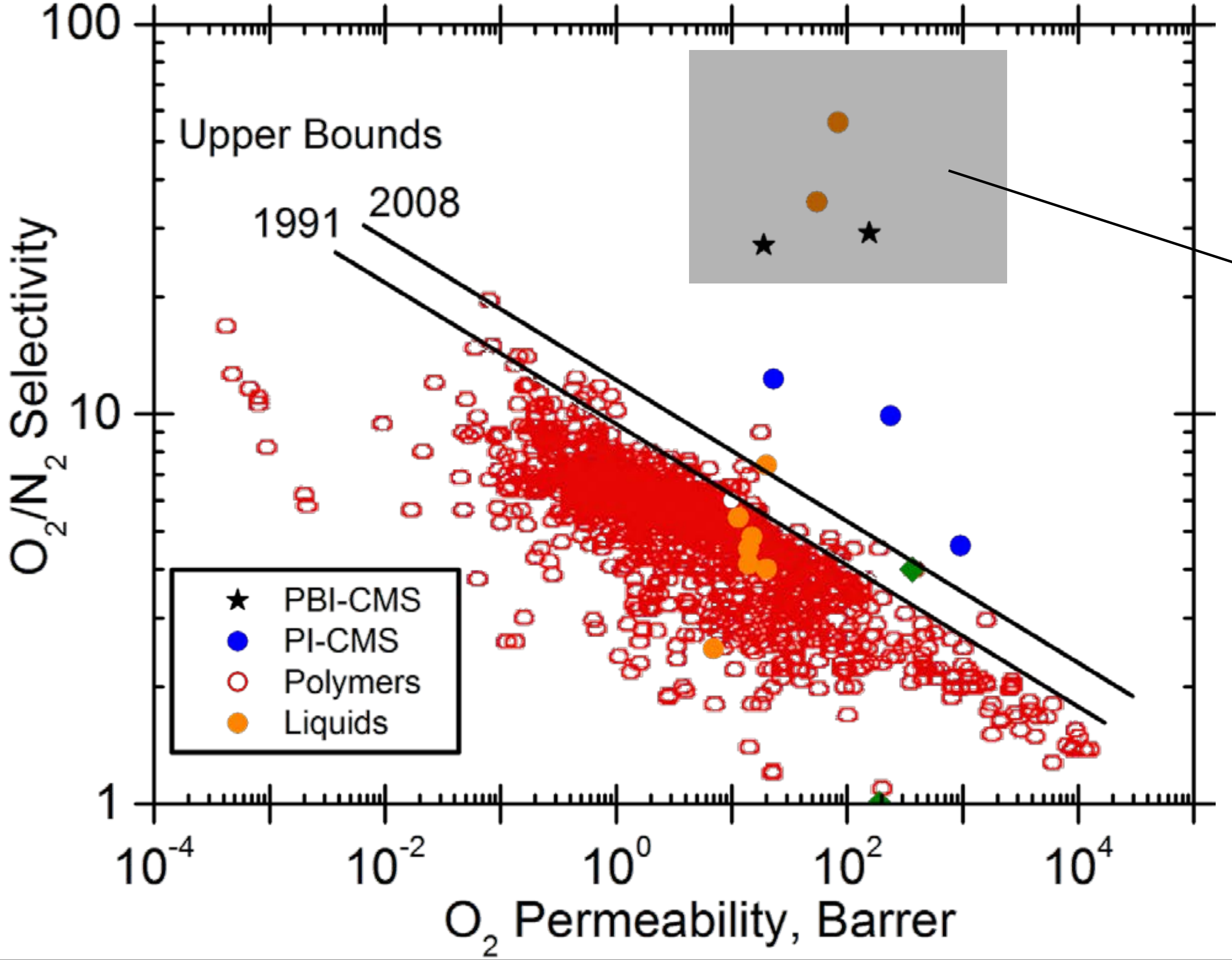
    - Base polymer (*m*-PBI) has high selectivity for gas pairs (e.g. $H_2/N_2 \geq 100$; $O_2/N_2 = 2$)
  - Further enhancement of molecular sieving properties via controlled pyrolysis proposed to create ultra-micropores
    - PBI pyrolysis preliminary work: O_2/N_2 selectivity increased from 2 to 30
      [Ref: S.S. Hosseini et al. / Separation and Purification Technology 122 (2014) 278–289]



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

O_2 Selective Membrane Materials

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



Commercially-attractive for modular ASU

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

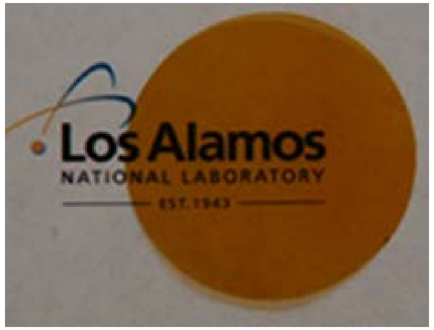
- **A membrane-based, modular air separation technology for high purity O_2 production**
  - Develop CMS materials derived from PBI materials (PBI-CMS) to achieve the desired material transport characteristics
    (O_2 permeability of 100 Barrer and O_2/N_2 selectivity of 20 to 30)
  - Develop PBI-CMS hollow fiber membranes having the desired membrane performance characteristics
    (O_2 permeance of 100 GPU and O_2/N_2 selectivity of 20 to 30)
  - 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

1 Barrer = 1 GPU @ 1μm film

Membrane Material & Hollow Fiber Development

Pyrolysis Protocols Optimization

- **Pyrolysis conditions have a tremendous influence on the gas separation properties of polymer derived CMS membranes**
- **Efforts targeting development and optimization of PBI pyrolysis protocols have been initiated with the goals of:**
  - Obtaining highly O_2 selective CMS materials (i.e., with O_2 / N_2 selectivity)
  - Understanding the influence of critical pyrolysis conditions on separation performance
  - Characterizing the impact of PBI macro-molecular characteristics on the resultant CMS membranes



Cast 10 to 50 µm PBI in inert atmosphere

Pyrolysis →

Parameters

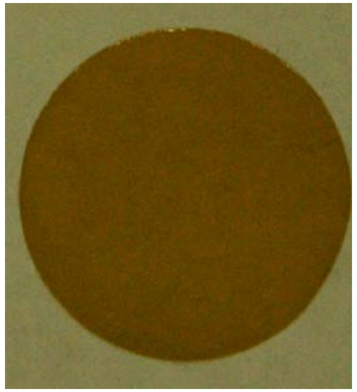
- Temperature (500 to 900 °C)
- Ramp rate and dwell time
- Environment (e.g. inert, reactive/templating (e.g. O_2, H_2, NH_3), vacuum).

36” quartz tube furnace

Pyrolysis Protocols Optimization (cont.)

- 1^{st} generation PBI-CMS thin films successfully fabricated

Neat PBI



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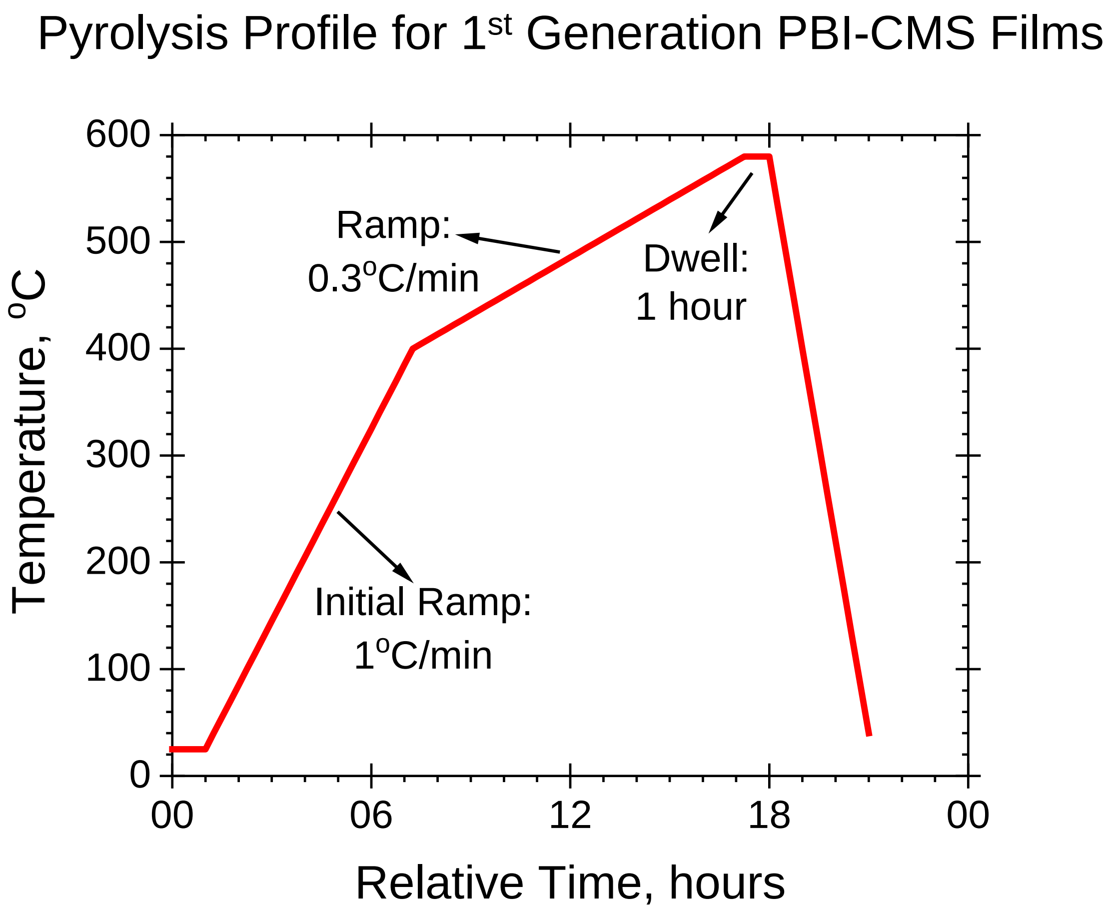
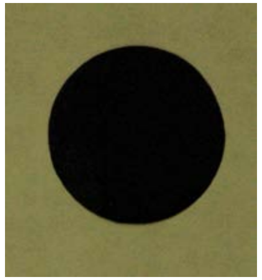


Pyrolysis Protocols Optimization (cont.)

- **1st generation PBI-CMS thin films show promising gas separation characteristics**
  - Preliminary pyrolysis conditions optimized to obtain mechanically robust PBI-CMS thin films for gas permeation evaluation

PBI - CMS



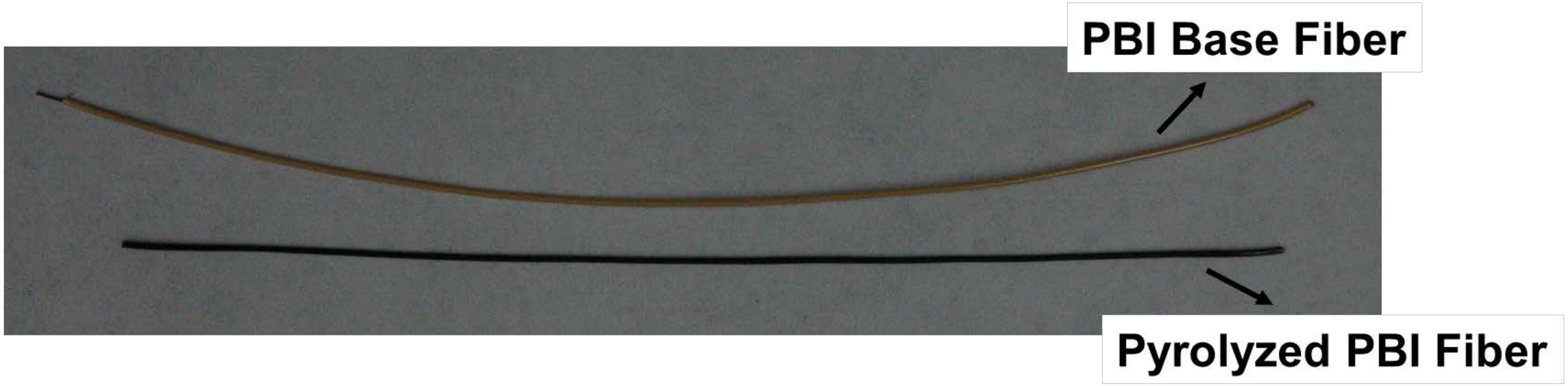
  - Pure gas permeation properties indicate that PBI-CMS thin films are defect-free

Gas Pair	Ideal Selectivity
He/N_2	227
CO_2/N_2	58

*O_2 permeation evaluation will be initiated this quarter

PBI-CMS Hollow Fiber Membrane Development

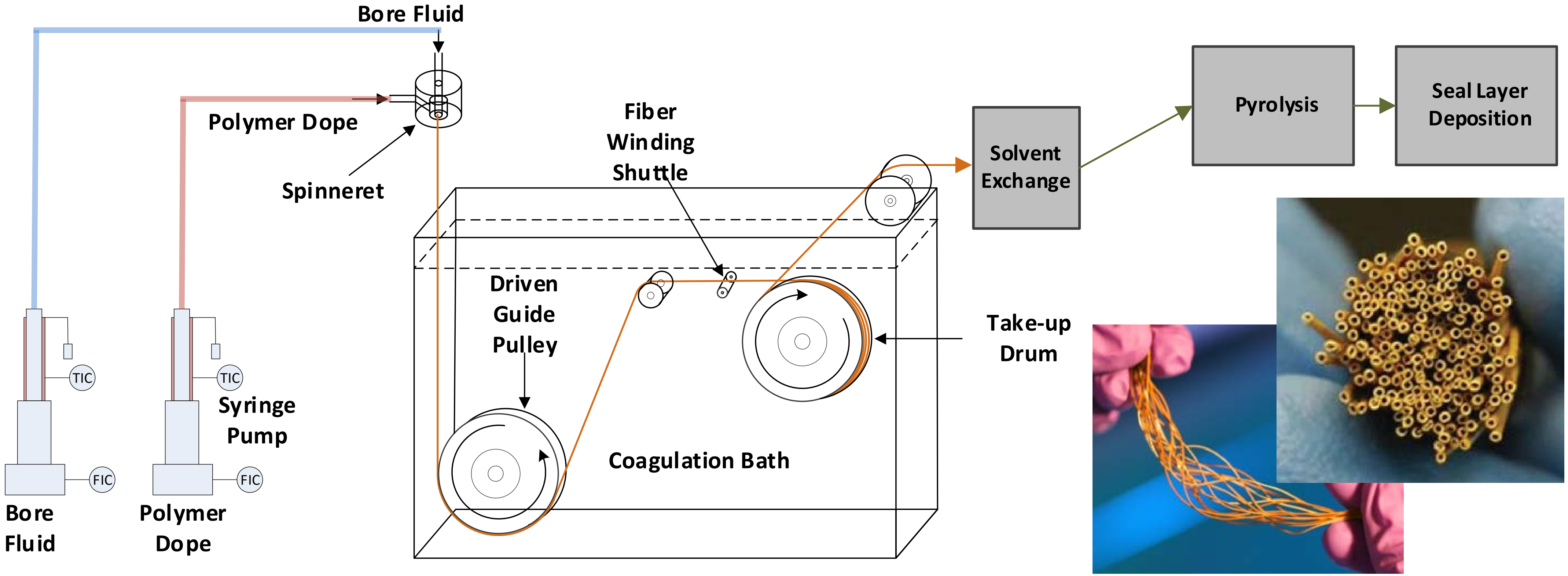
- **Economic considerations mandate the use of a high surface area to volume membrane deployment platform**
  - Hollow fiber membrane platform enables high surface area density membrane deployment (2K to 20K+ m^2/m^3)
  - Large membrane surface areas are required to process the large gas volumes envisioned for this air separation challenge
- **Pyrolysis of PBI hollow fiber membranes is utilized to fabricate PBI-derived CMS hollow fiber membranes**



Hollow Fiber Membrane Platform

Base PBI hollow fiber membrane fabrication

- Established PBI hollow fiber membranes fabrication capability is utilized
- Hollow fiber membranes having a variety of morphologies including the support layer porous structure and dense layer thickness are fabricated

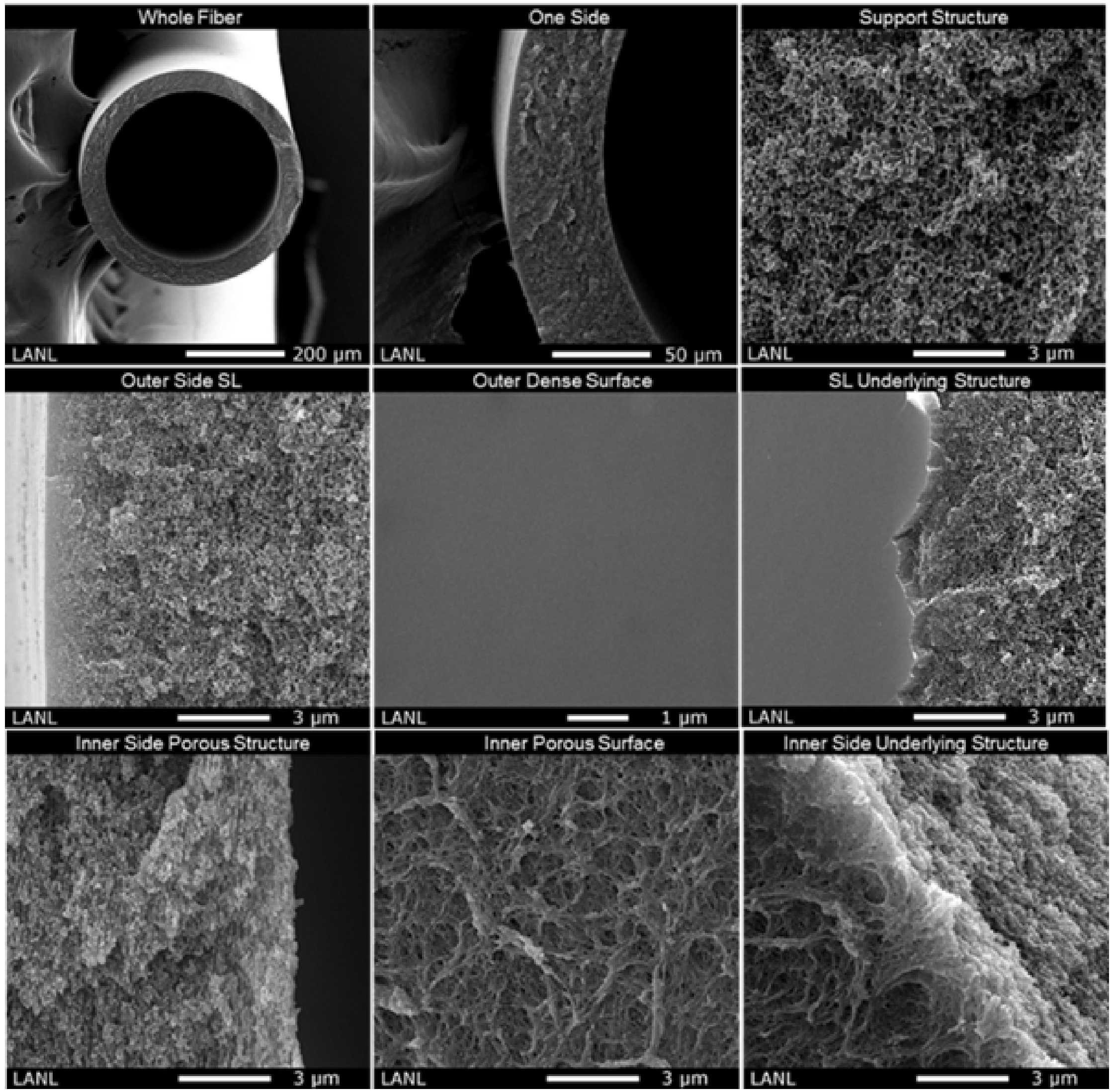


LANL Lab-scale continuous hollow fiber spinning system comprising a custom micro-machined spinneret

OD: 300 to 500 µm
Thickness: 50-100 µm

High Performance Base PBI Fibers

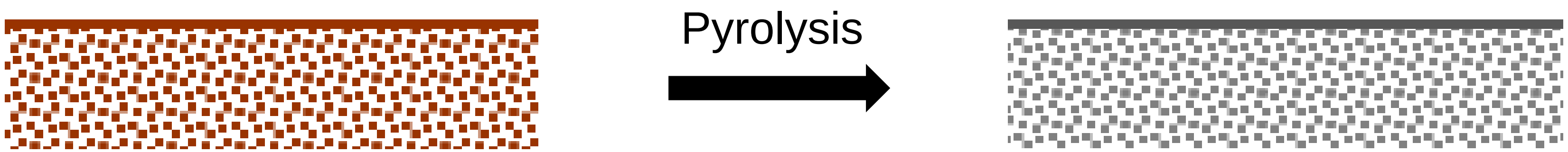
- **PBI spinning protocols developed to obtain high performance PBI hollow fiber membranes**
  - Nearly defect-free dense layer production (H_2/N_2 Selectivity ≥ 200)
  - Selective layer thickness control (ca. 200 to 2000 nm) demonstrated
  - Macro-void free morphologies achieved
  - Porous support layer and inner surface produced
  - Industrially attractive fabrication process developed and demonstrated: flammable & toxic solvent use minimized/mitigated



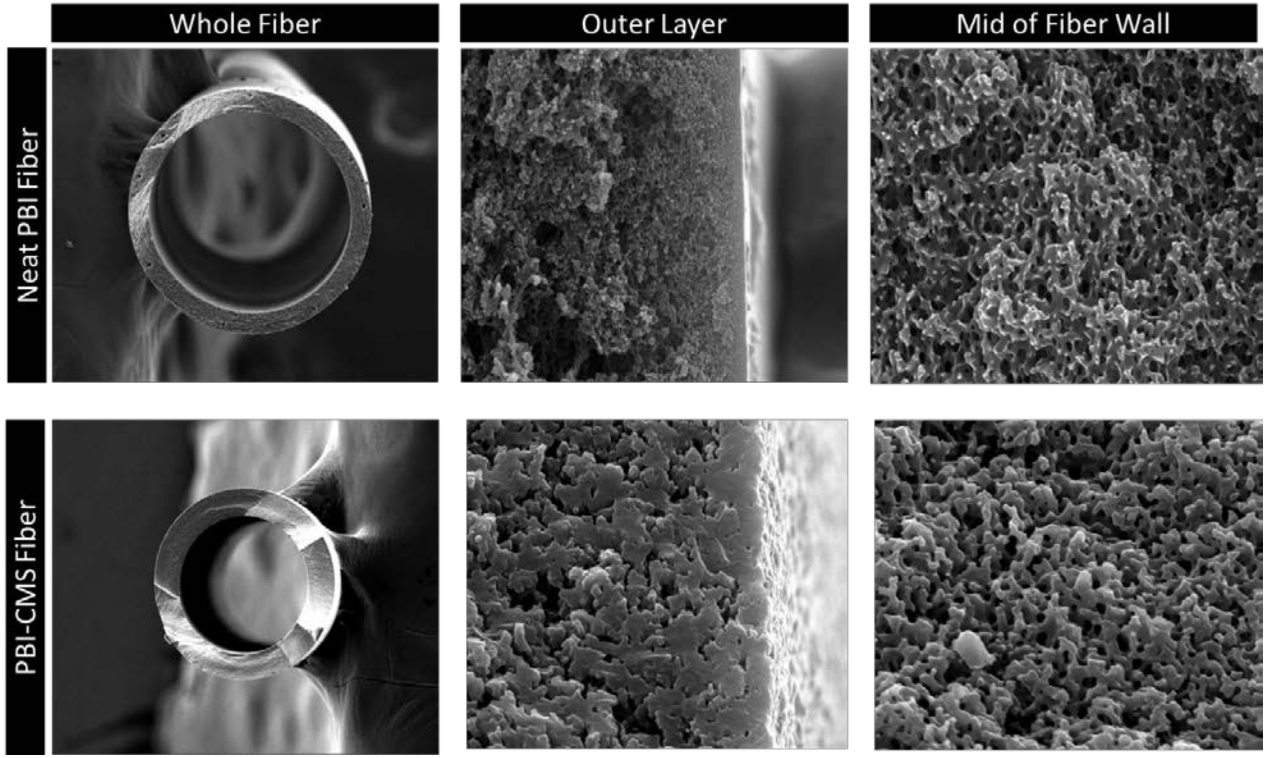
Berchtold & Singh, et.al. 2018 US Patent 10071345

High Performance CMS Membranes

- Develop PBI-CMS hollow fiber membranes with a thin defect-free dense selective layer



- Mitigating porous support structure collapse is critical to achieving high flux (productivity) membranes
  - Promising preliminary results at LANL showing production of PBI-CMS fibers without porous support collapse
- Gas transport property characterization of PBI-CMS HFMs in progress



Membrane Modeling and Process Design

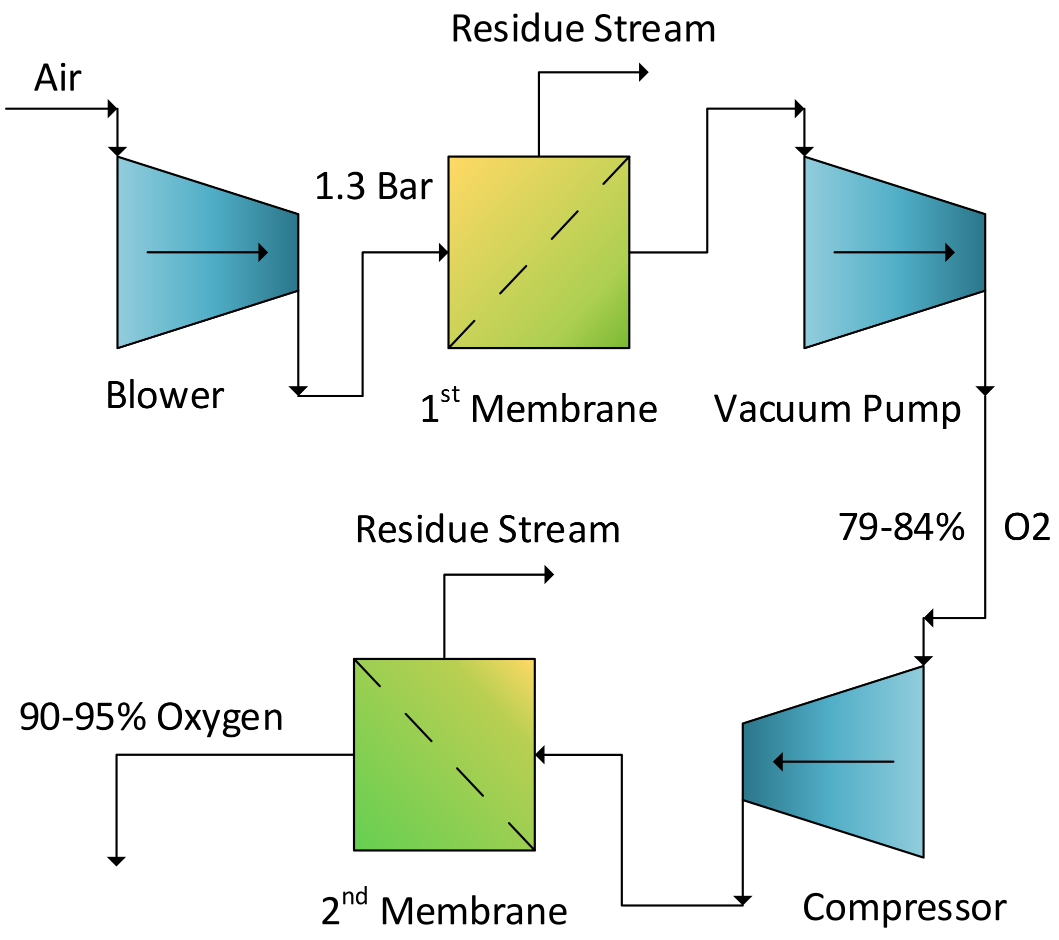
Process Design and Simulations

- **Develop a conceptual process design and perform process simulations for multi-stage membrane operation**
  - Demonstrate energy and cost improvements as compared to the state-of-the-art industrial air separation method

Membrane Modeling	Process Modeling
▫ Develop a membrane model for multi-component feeds to evaluate membrane process parameter influences ▫ Calculate membrane area and separation efficiency as a function of process operating conditions and membrane properties ▫ **Status**: Coding completed in Python, model validation and testing in progress	▫ Develop an overall process model and perform preliminary techno-economic analysis ▫ Estimate energy required for multi-stage membrane process for high purity O_2 production from air and compare to that estimated for competing technologies ▫ **Status**: Membrane model integration with Aspen ongoing. Using CCSI^2 toolset for easy transition between Aspen and Python Scripts

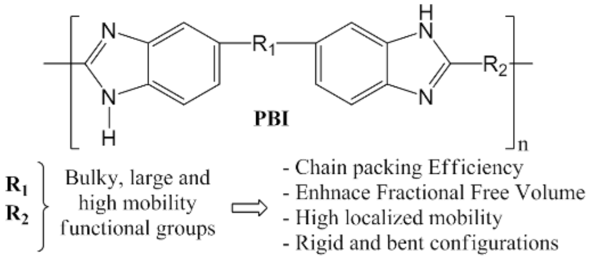
Preliminary Process Design

- **A preliminary 2-stage membrane process envisioned to provide high purity O_2**
  - Vacuum on permeate side of 1st stage to provide driving force
  - Permeate from 1st stage is compressed to create driving force for the 2nd stage
  - Preliminary calculations indicate achievement of 98% O_2 purity for membranes in both stages having an O_2/N_2 selectivity of 20
    - Initial simulations indicate 17% O_2 recovery achieved at these conditions
  - Extensive model testing and validation will be conducted using known datasets

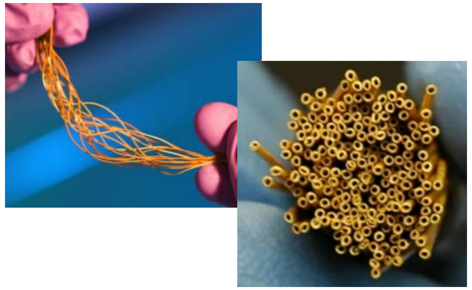


Summary

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

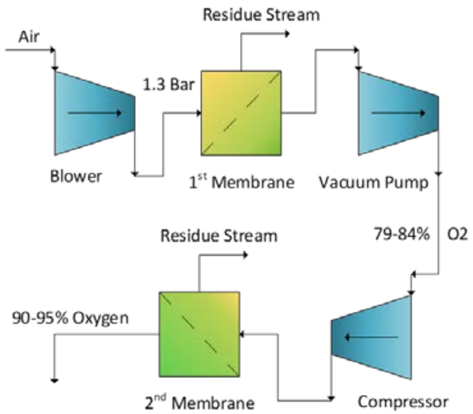


Processing & Membrane Synthesis

CMS Membranes

Lab-scale Demonstration & Evaluation

Process Modeling



Thank you