Development of Carbon Molecular Sieves Hollow Fiber Membranes based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties

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NETL CO_2 Capture Technology Project Review Meeting
Pittsburgh, PA

8/26/2019

Project Overview

Award number: DE-FE0031636

Project period: 10/1/18 to 9/30/21

Program manager: Andrew O′Palko

Project Objective: Develop CMS hollow fiber membranes with H_2 permeance of 1000 GPU and H_2/CO_2 selectivity of 40 at 200-300 ^oC, enabling membrane-based systems capturing 90% CO_2 from coal-derived syngas with 95% CO_2 purity at a cost of electricity 30% less than baseline capture approaches.

Team Members	Federal Share	Cost-share	Total	Roles
UB	$534,999	$202,225	$737,224	Materials development
LANL	$200,000	$0	$200,000	Membrane development
Trimeric	$ 65,000	$0	$ 65,000	Techno-economic analysis
Total:	$799,999	$202,225	$1,002,224	

Project Scope in Each Budget Period

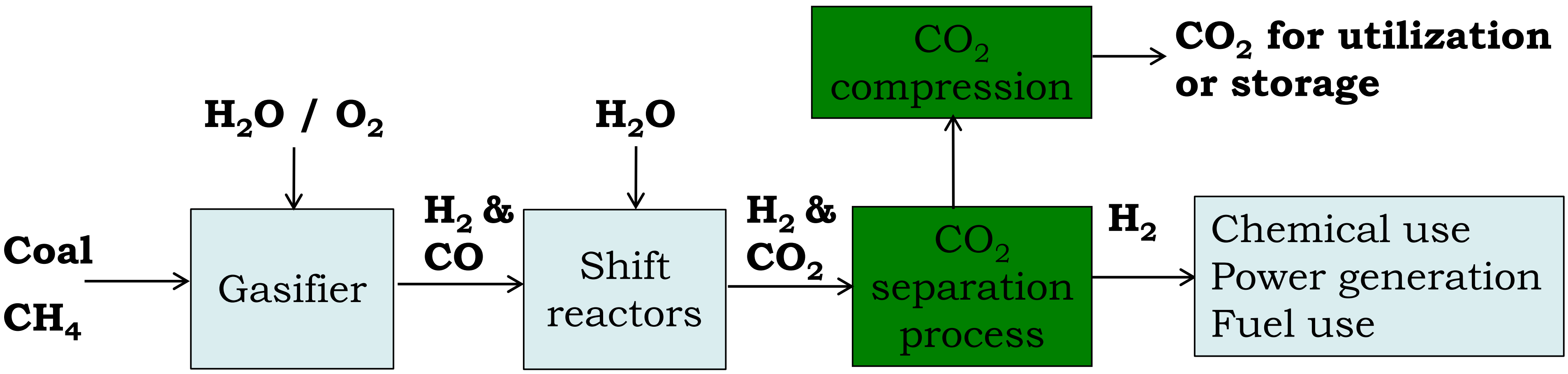
BP 1 Materials development (10/1/18 – 3/31/20; 18 months)

- Optimize CMS materials with an H_2 permeability of 200 Barrers and H_2/CO_2 selectivity of 40 with simulated syngas; and
- Optimize the hollow fiber membranes based on PBI doped with polyprotic acids.

BP 2 Membrane development (4/1/20 – 9/30/21; 18 months)

- Optimize membranes achieving the targeted H_2/CO_2 separation performance;
- Test membranes using simulated syngas containing H_2S, CO and water vapor;
- Determine the efficiency of the membrane reactors for the WGS reaction; and
- Conduct the techno-economic analysis.

CO_2 separation is energy-intensive and expensive

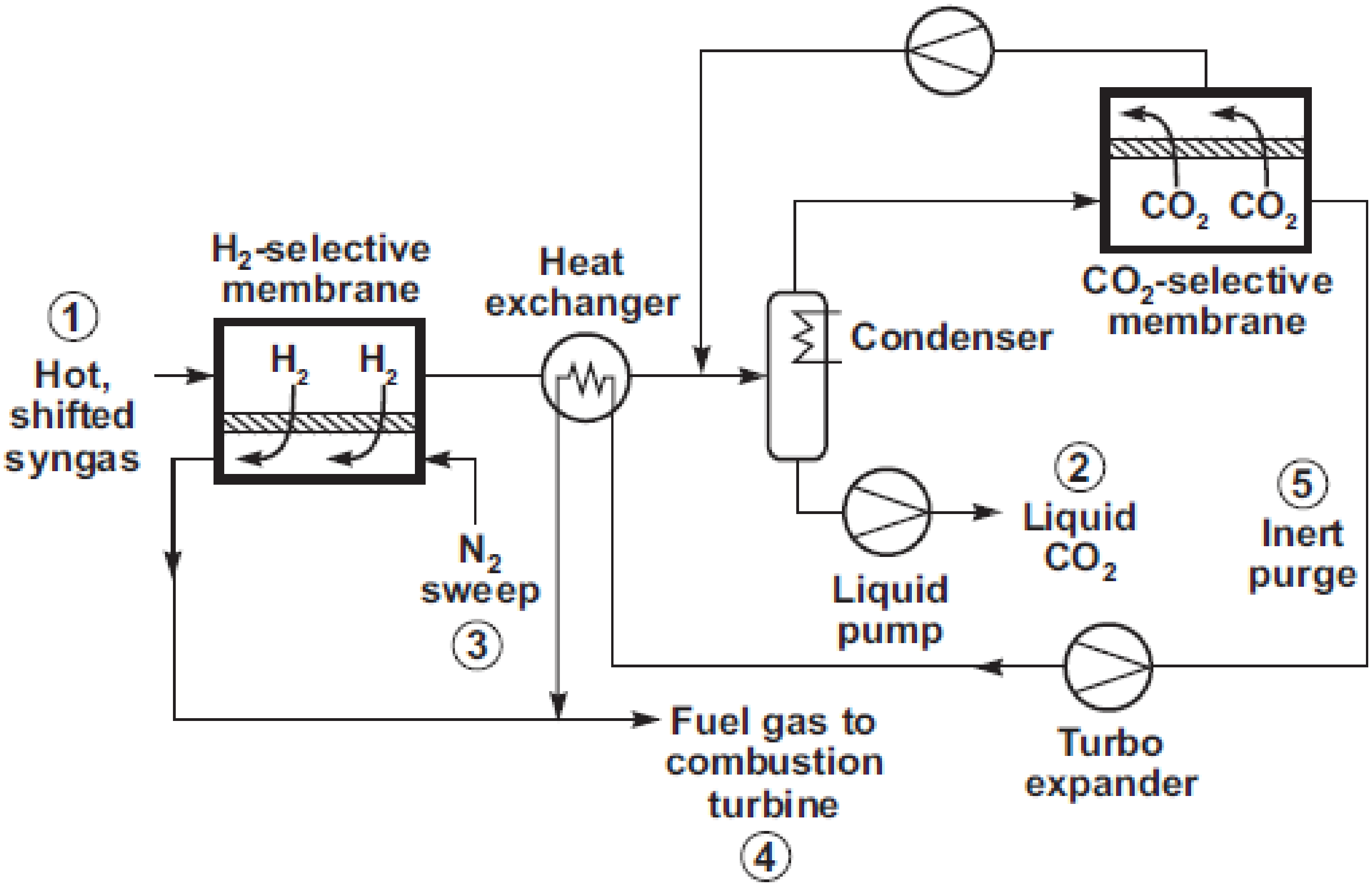


GEE IGCC/Selexol 543 MWe plant (Case 2)

	CO_2 capture
Power consumption	50 MWe
Capital cost	$252 MM

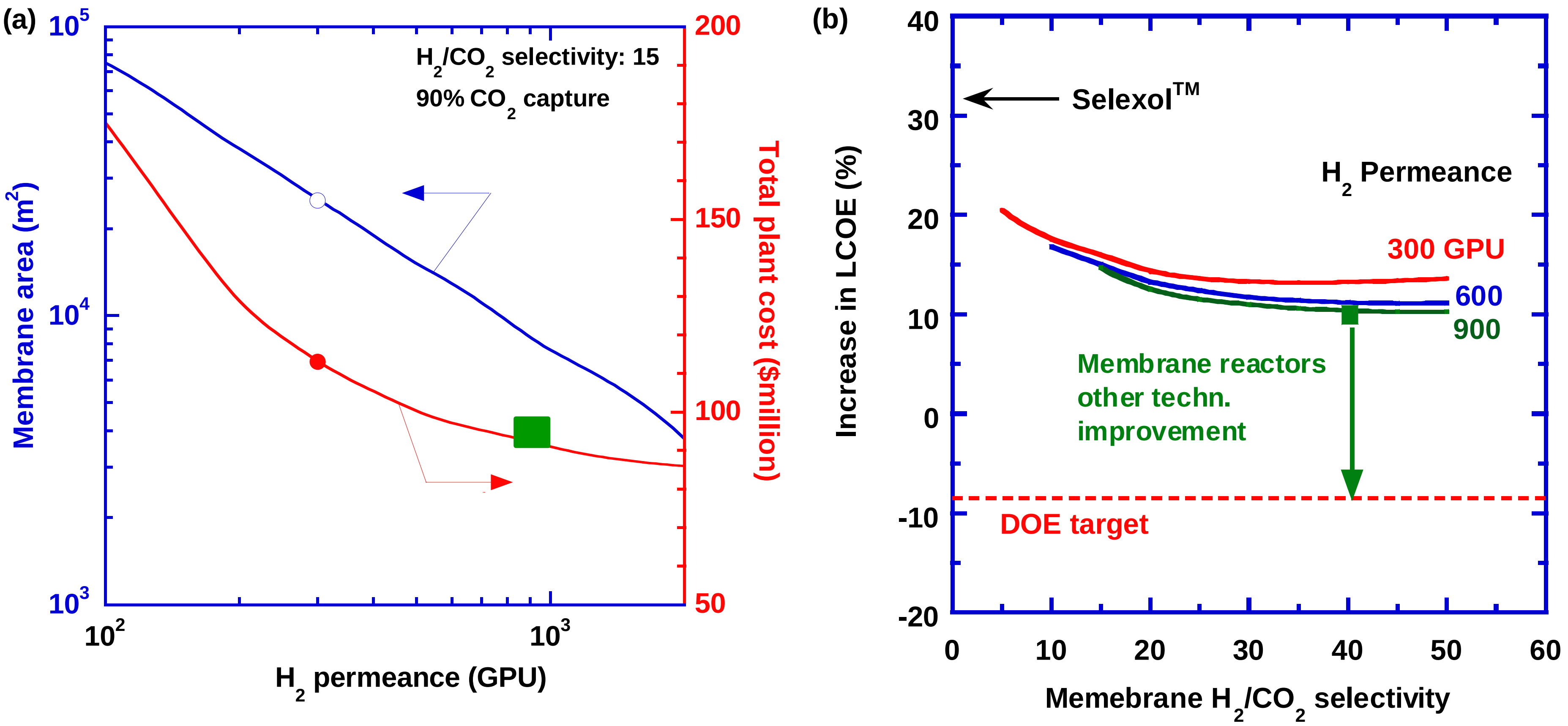
Lower cost and more energy efficient separation technology is needed.

MTR's Membrane Process Design



Merkel, Zhou and Baker, *J. Membr. Sci.*, 389, 442 (2012)
Merkel, et al., *NETL CO_2 Capture Technology Meeting*, 2011.

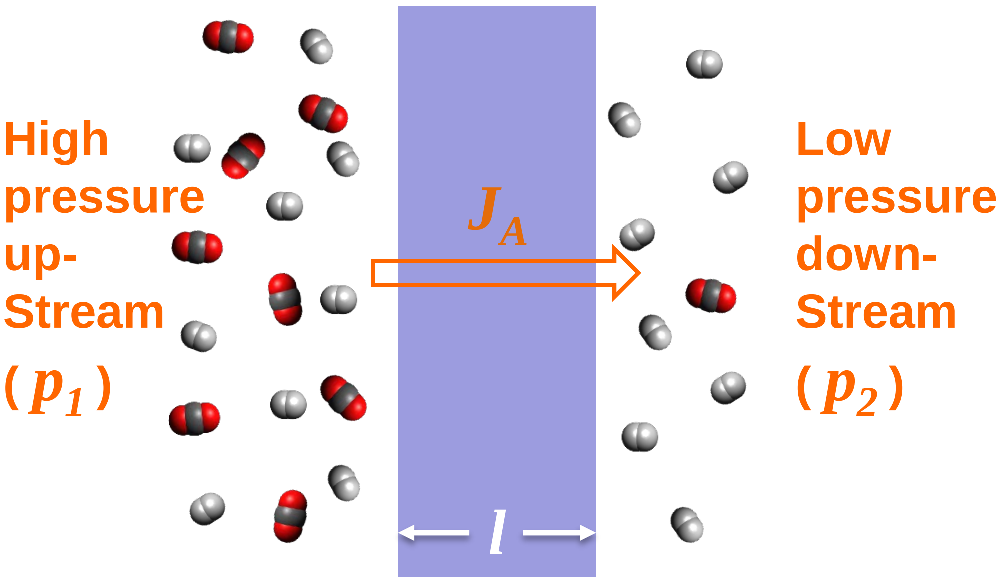
MTR's Techno-Economic Analysis



Merkel, Zhou and Baker, J. Membr. Sci., 389, 442 (2012)
Merkel, et al., NETL CO_2 Capture Technology Meeting, 2011.

Membrane: Energy-efficient Separation

Solution-diffusion model



Productivity - Permeability

$$P_A = S_A \times D_A$$

Purity - Gas selectivity

solubility selectivity

$$\alpha_{H_2/CO_2} = \frac{P_{H_2}}{P_{CO_2}} = \left(\frac{S_{H_2}}{S_{CO_2}}\right) \times \left(\frac{D_{H_2}}{D_{CO_2}}\right)$$

diffusivity selectivity

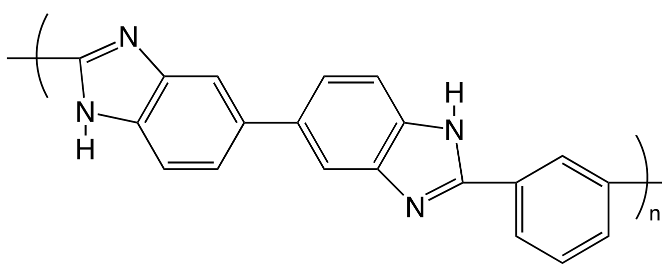
(1) Sorption on upstream side
(2) Diffusion down partial pressure gradient
(3) Desorption on downstream side

Wijmans and Baker, *J. Membr. Sci.* **107**, 1 (1995)

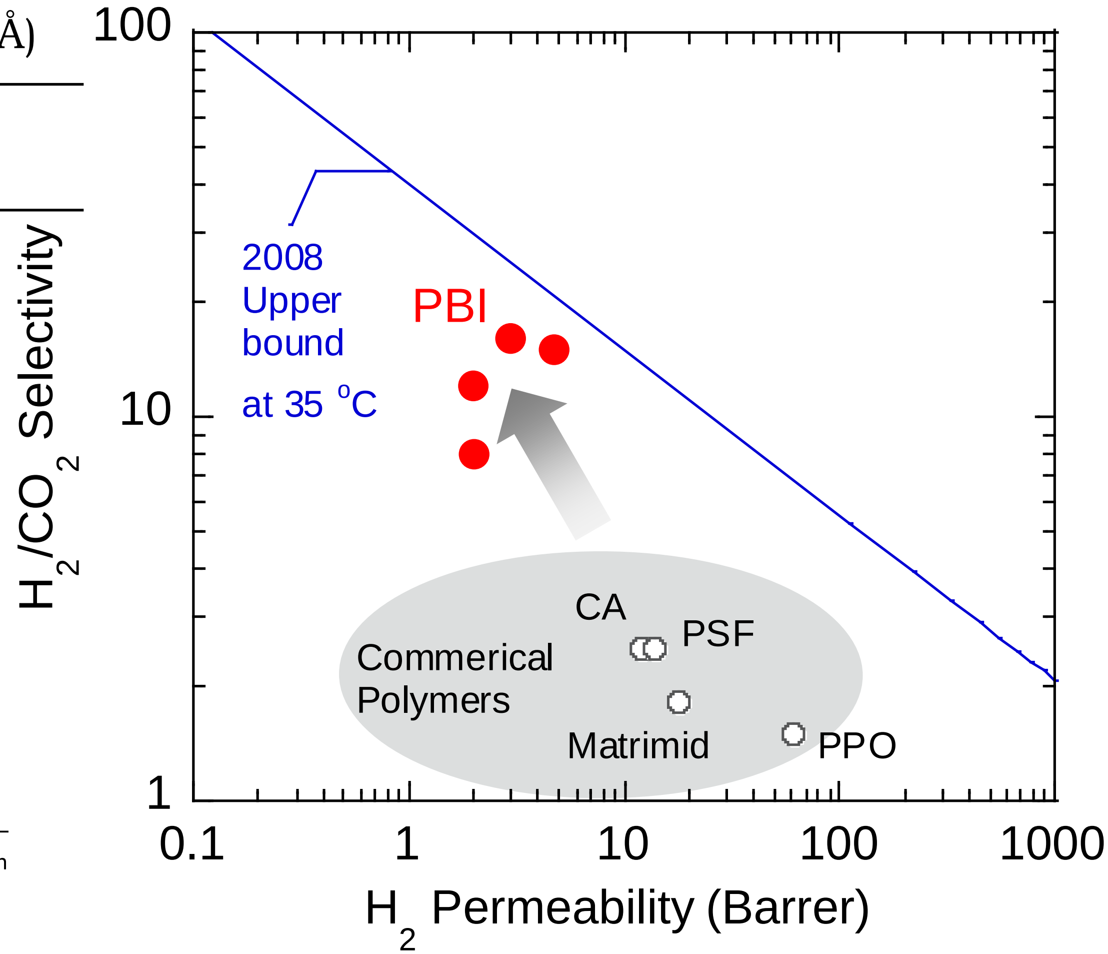
Permeability/Selectivity Tradeoff

	Critical temperature (K)	Kinetic diameter (Å)
H_2	33	2.89
CO_2	304	3.3

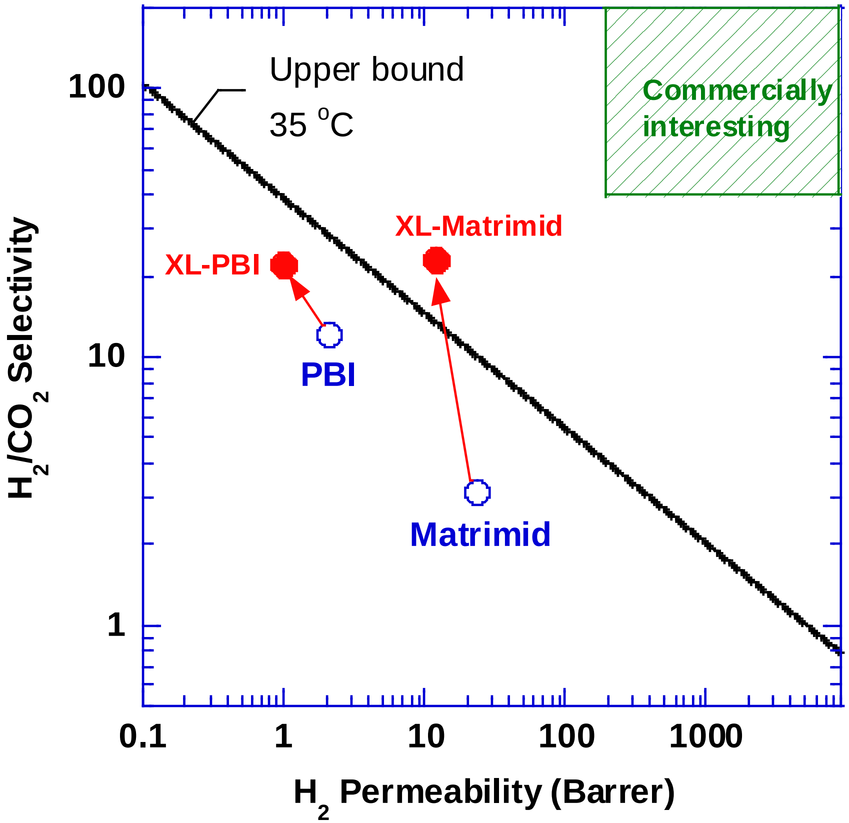
$$\frac{S_{H_2}}{S_{CO_2}} << 1 \quad \text{and} \quad \frac{D_{H_2}}{D_{CO_2}} >> 1$$

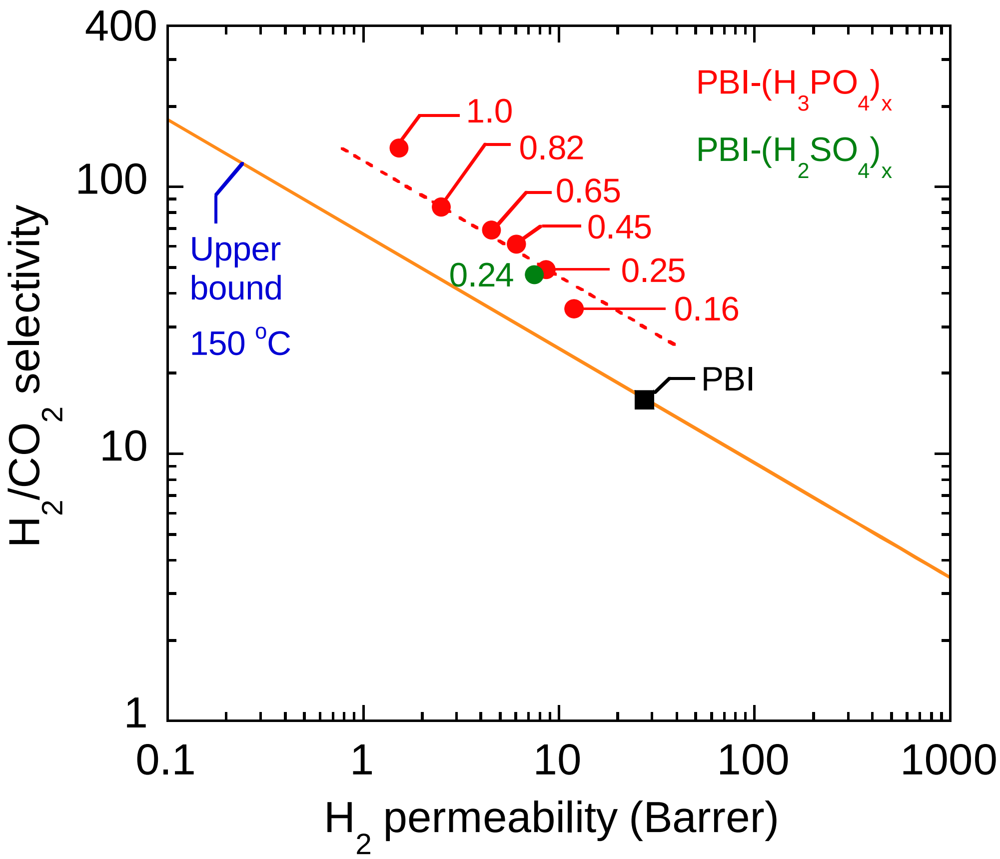


Polybenzimidazole (PBI)
(Celazole®)



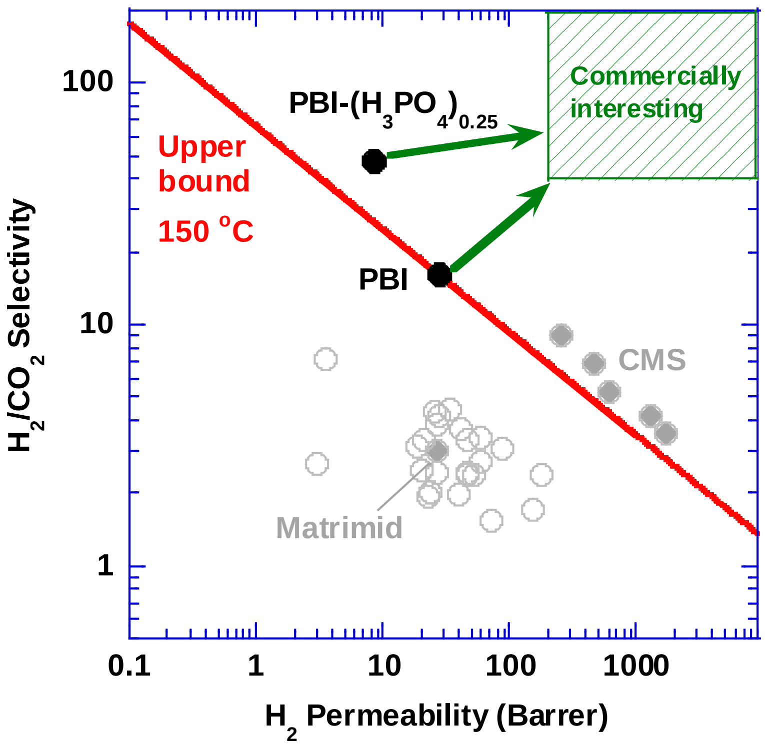
Polymeric Membranes for H_2/CO_2 Separation





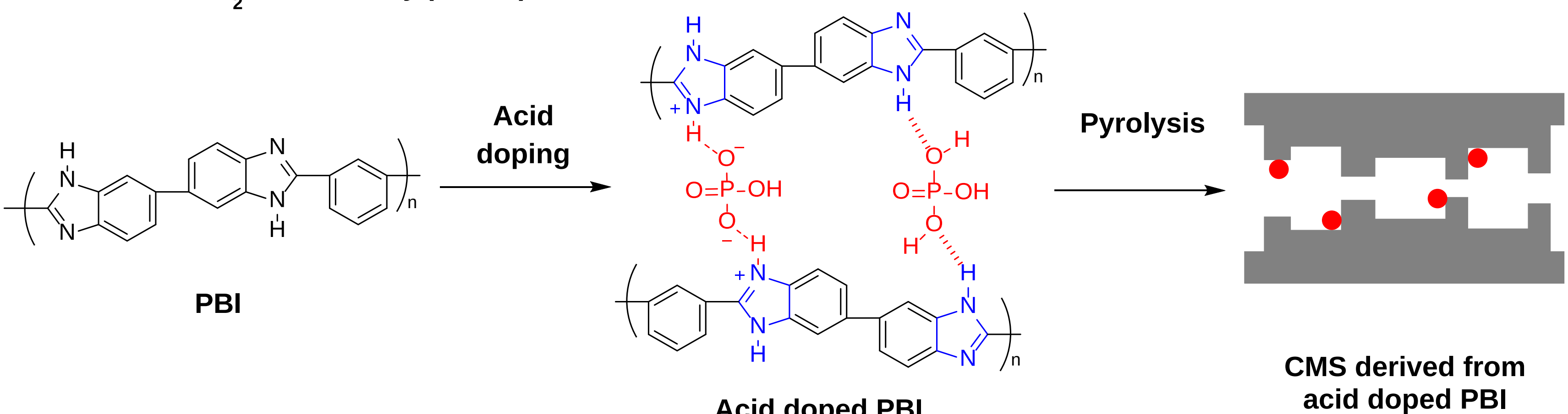
Shao, Low, Chung, and Greenberg *J. Membr. Sci.* 2009, 327, 18-31.
Zhu, Swihart, and Lin *J. Mater. Chem. A* 2017, 5 (37), 19914-19923.
Zhu, Swihart and Lin, *Energy Environ. Sci.* 2018, 11 (1), 94-100.

Our Approach: Carbonizing PBI/acid to Enhance H_2/CO_2 Separation Performance

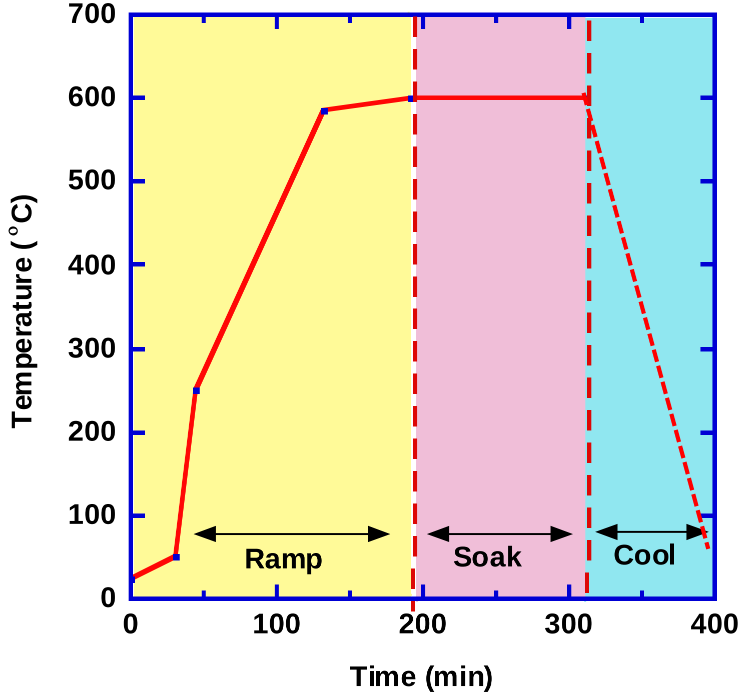


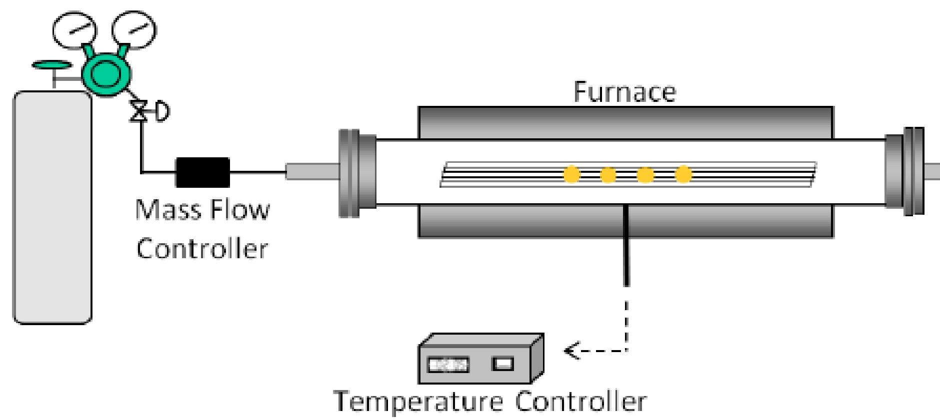
Poly(benzimidazole) (PBI)

- Commercially available
- High T_g (417 °C), T_d : 550 °C



Protocol to Prepare Carbon Molecular Sieve (CMS) Materials





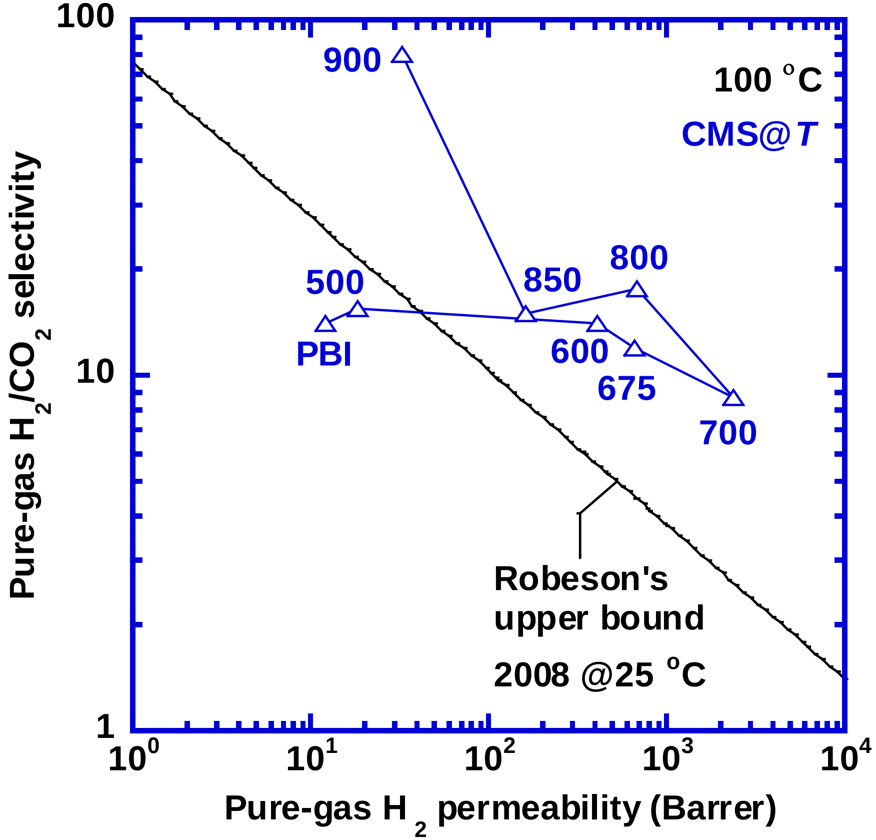
Pyrolysis Protocols: 200 cc N_2/min

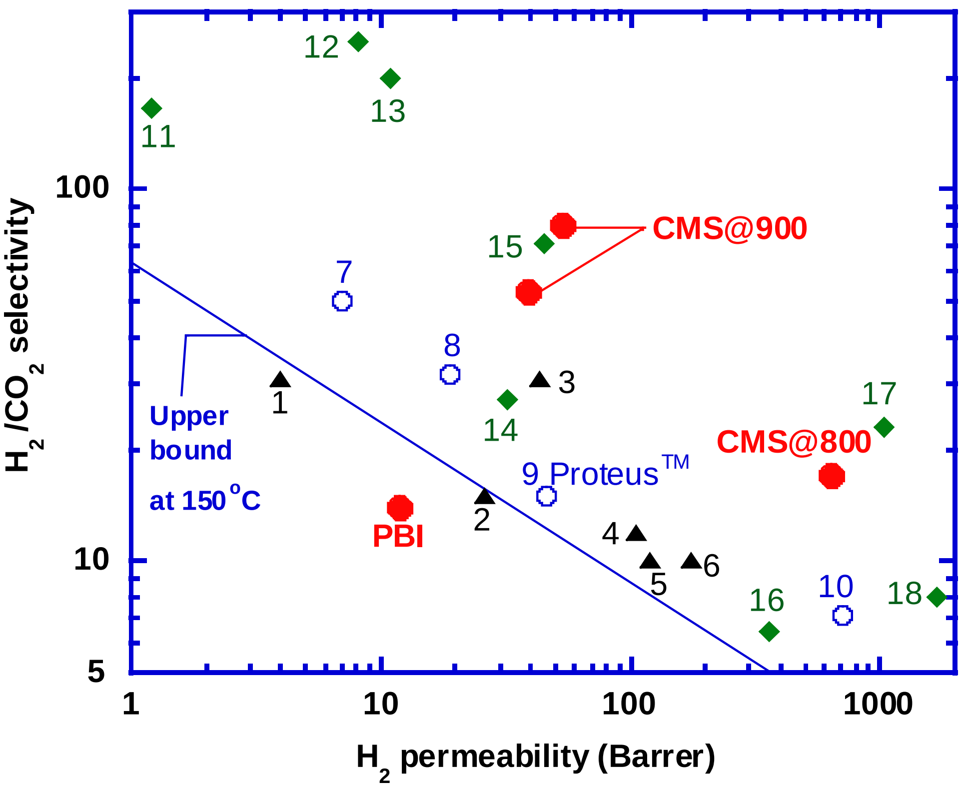
- Ishothermal at 25 ˚C for 30 min
- 25 ˚C to 50 ˚C with ramp rate of 0.83 ˚C/min
- 50 ˚C to 250 ˚C with ramp rate of 13.3 ˚C/min
- 250 ˚C to (T_{max} -15 ˚C) with ramp rate of 3.85 ˚C/min
- (T_{max} -15 ˚C) to T_{max} with ramp rate of 0.25 ˚C/min
- Stay at T_{max} for 2 hours and cool down under N_2 flow

T_{max}: 600-900 ºC

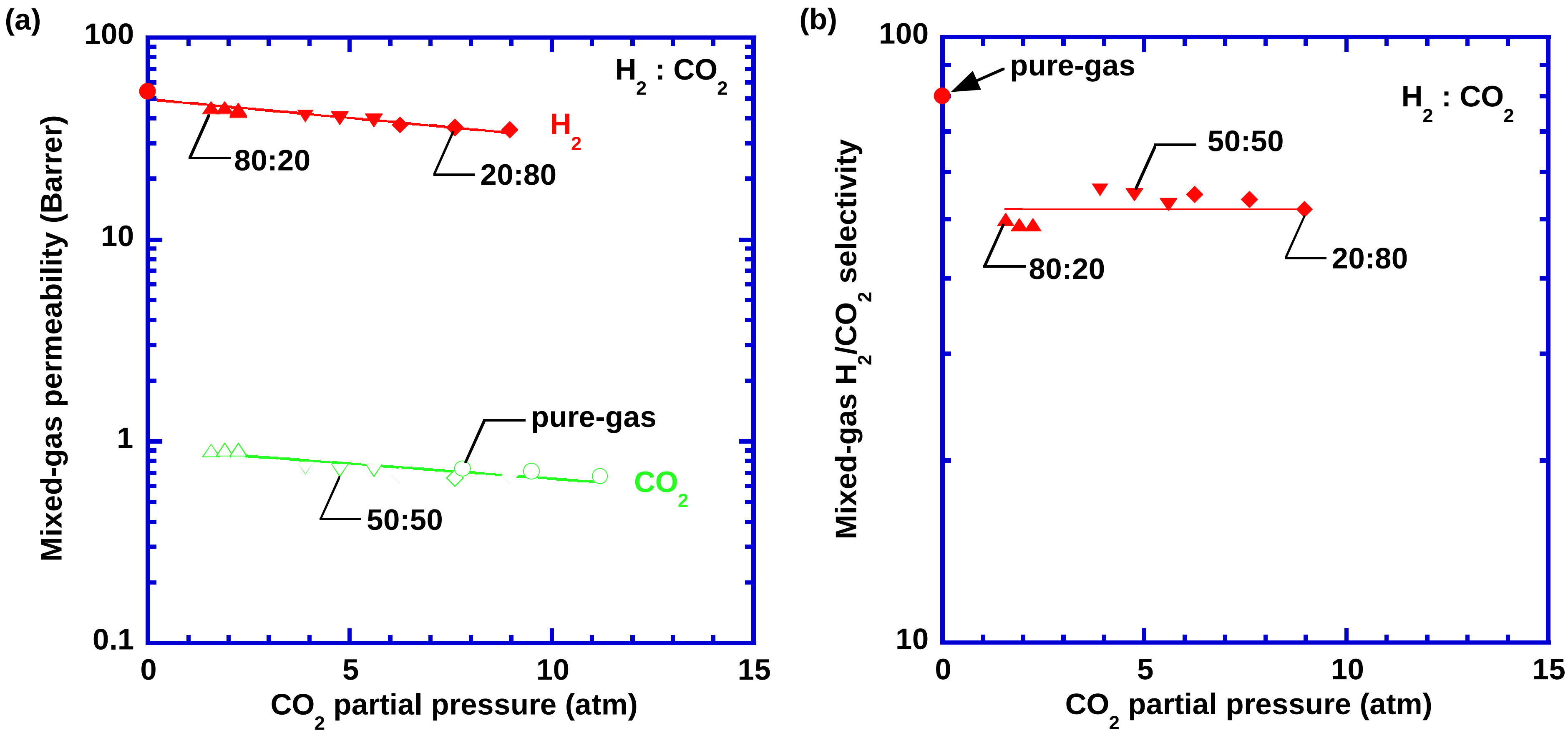
Rungta, Koros, et al.; *Carbon*, 115, 237-248 (2017)

Super H_2/CO_2 Separation Performance of PBI-CMS

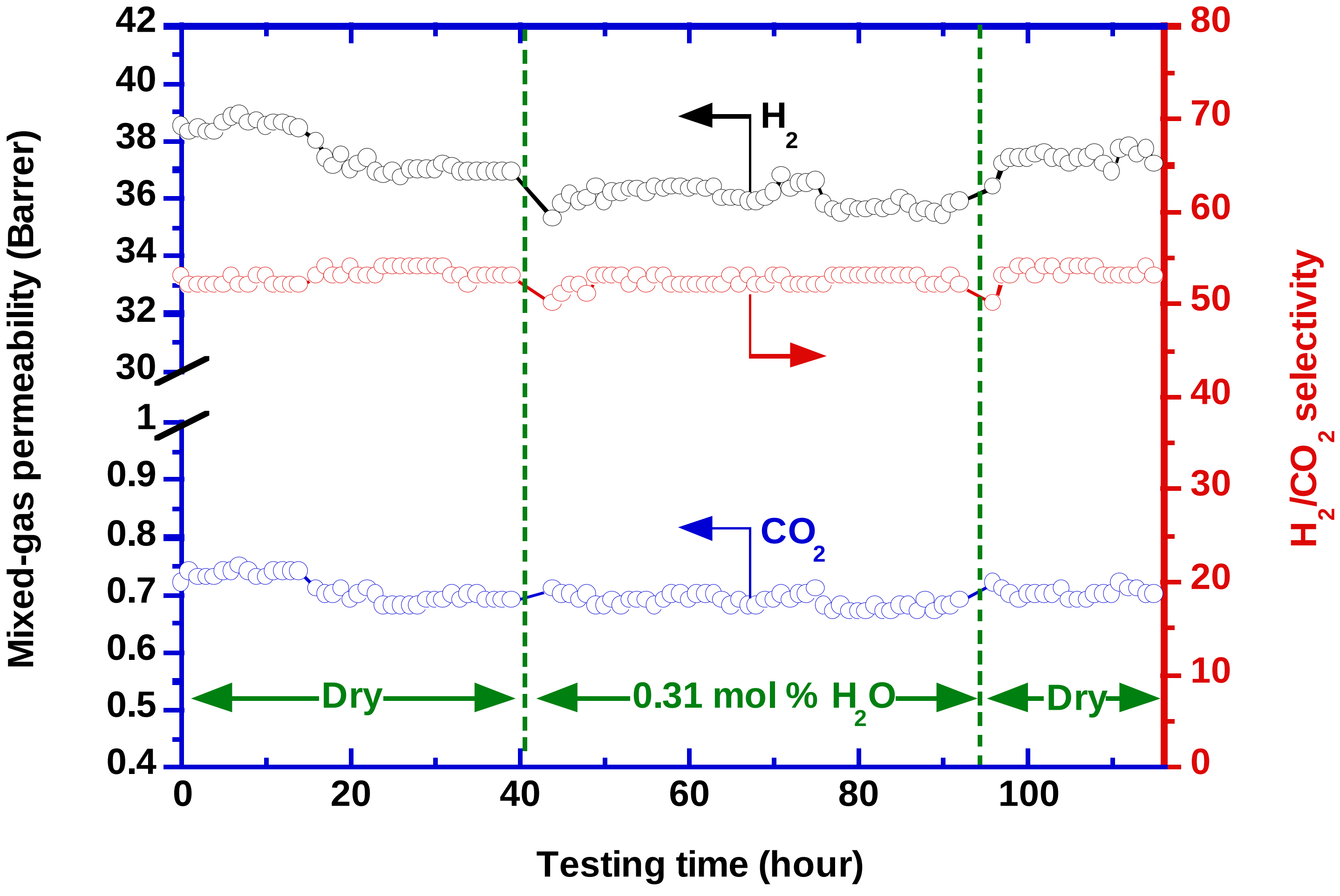




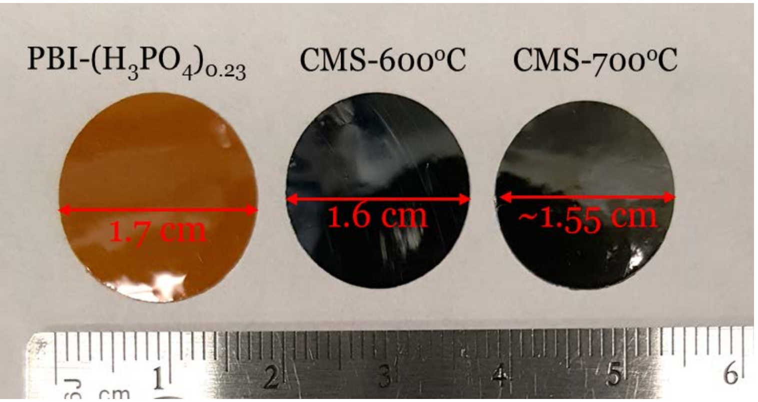
Mixed-gas H_2/CO_2 Separation Performance of PBI-CMS@900 at 100 ºC

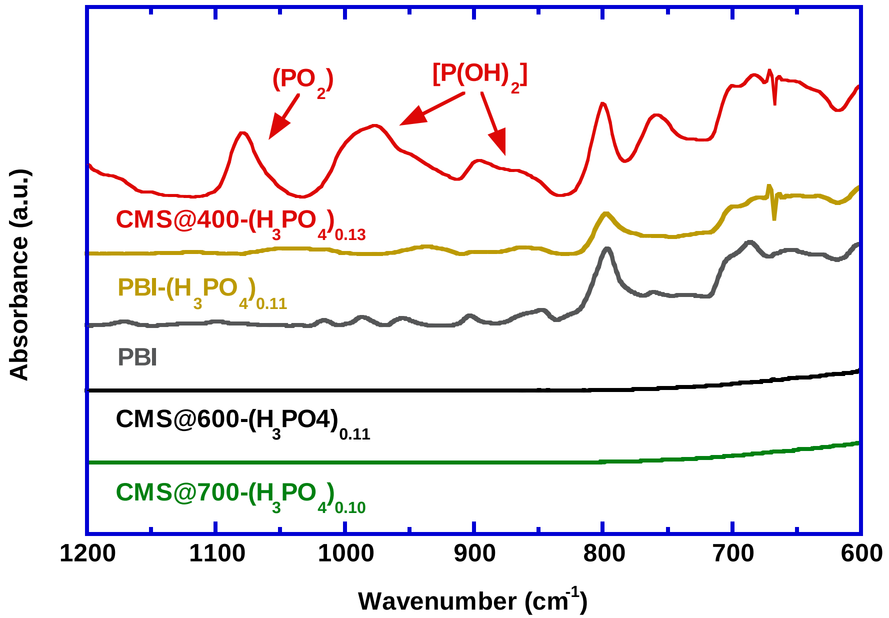


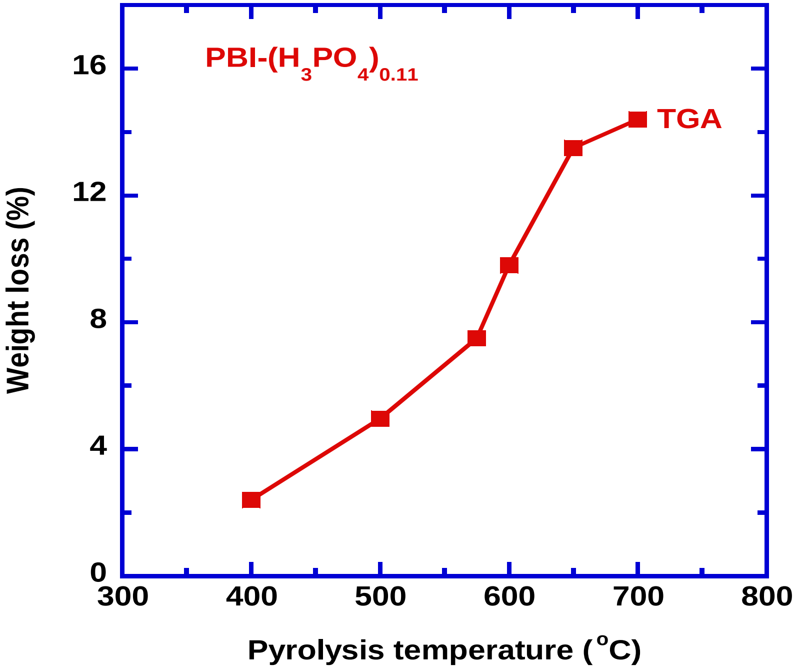
Stable H_2/CO_2 Separation Performance of PBI-CMS@900 at 100 °C

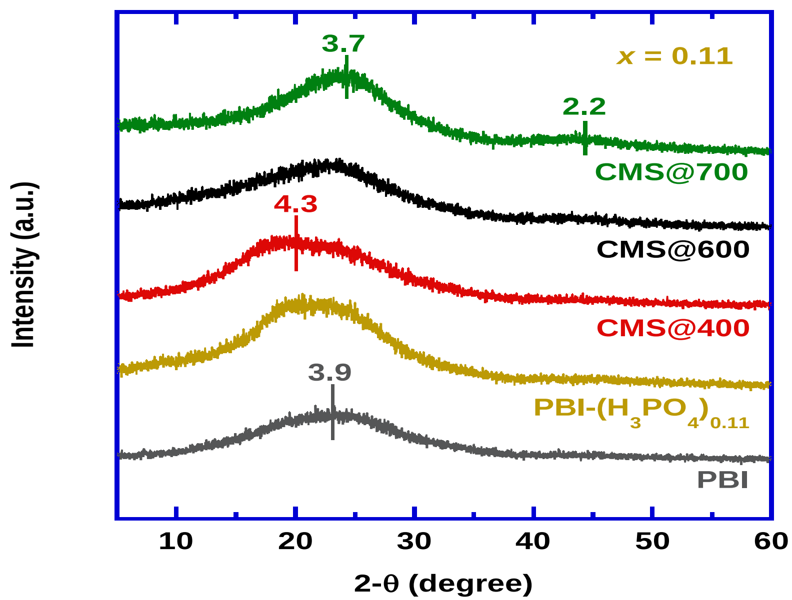


Carbonization of H_3PO_4 Doped PBI

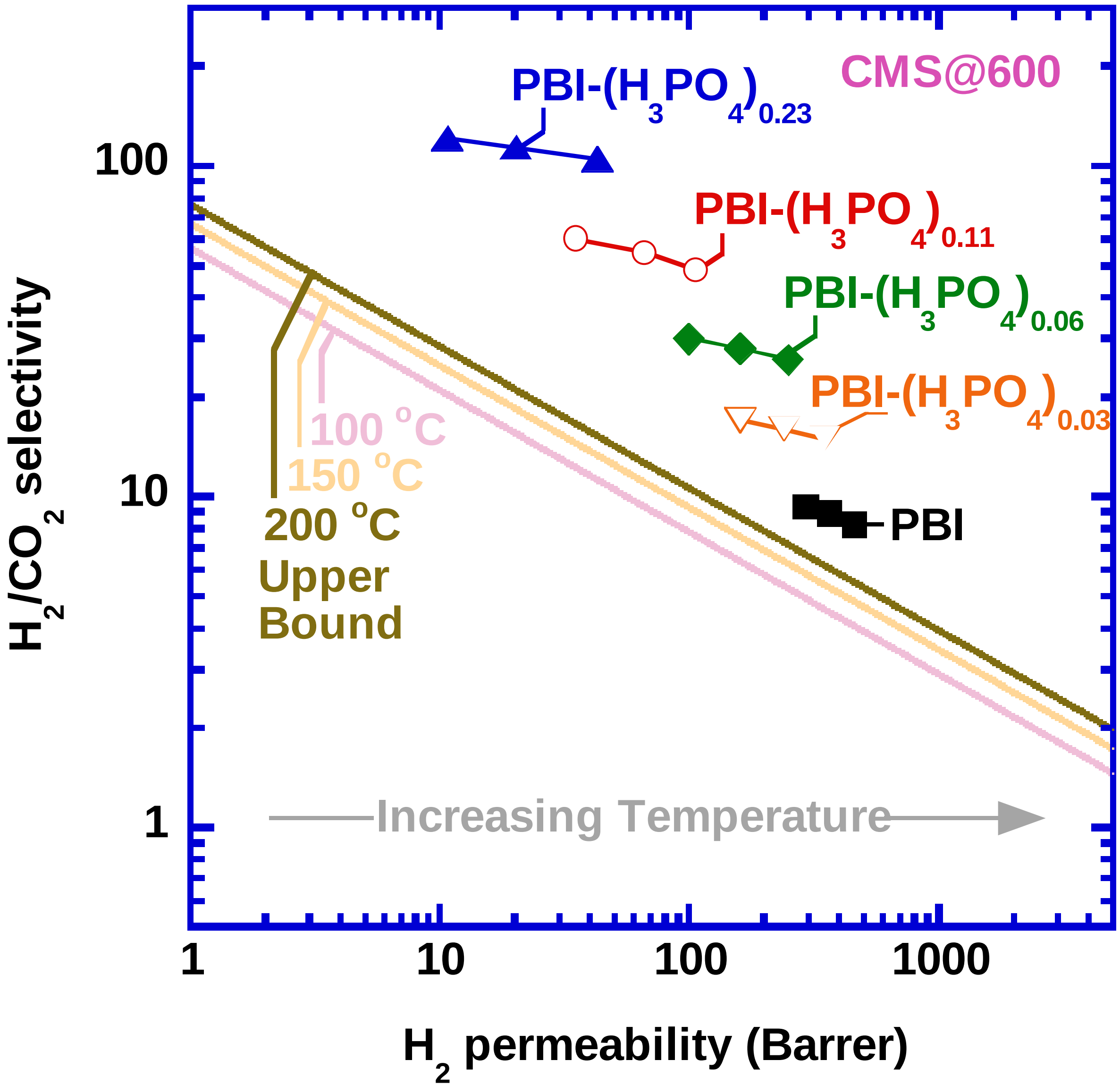






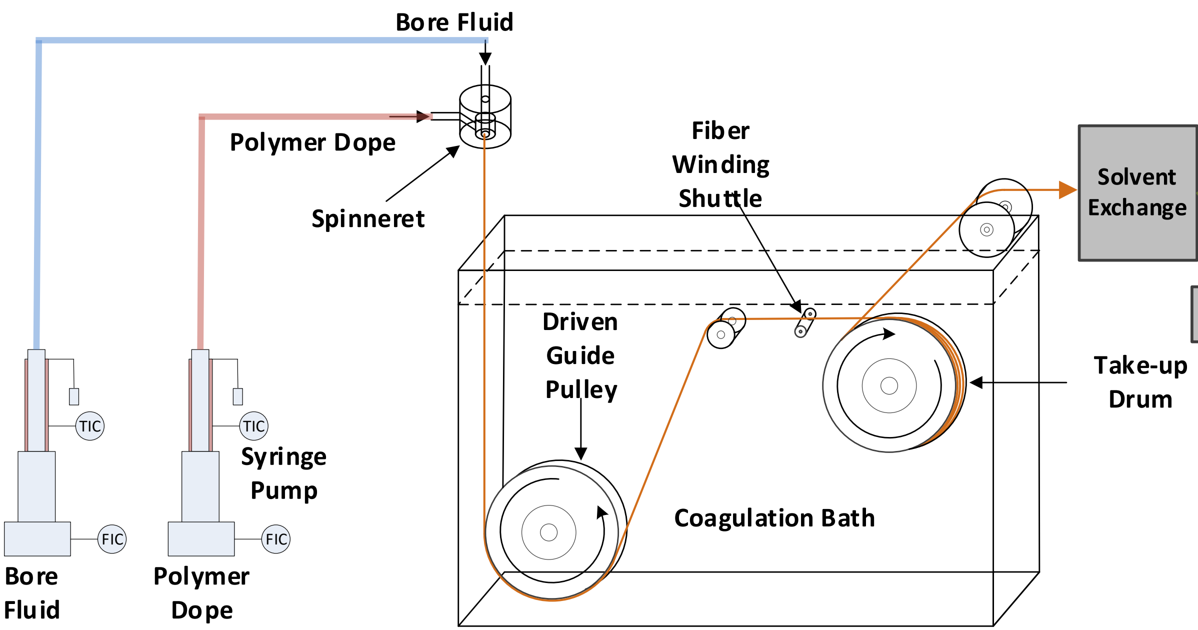


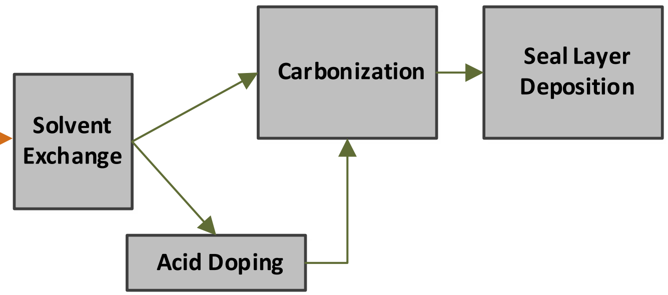
Effect of H_3PO_4 Doping and Pyrolysis Temperature on H_2/CO_2 Separation at 100 °C



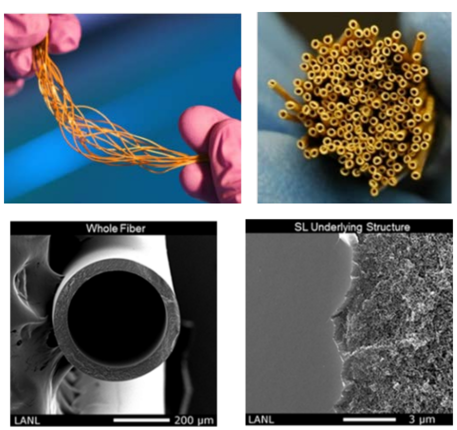
Hollow Fiber (HF) Membrane

- High membrane surface area platform
  - The H_2 permeability of the PBI-based CMS membrane materials mandates ultra-thin selective layers and high surface area membrane deployment platforms
- Approach: PBI HF membranes carbonization to obtain PBI-CMS HF membranes
  - Liquid-liquid demixing based spinning process developed to obtain high performance base PBI HF membranes with thin selective layer





LANL Lab-scale continuous HF spinning system using a custom micro-machined spinneret

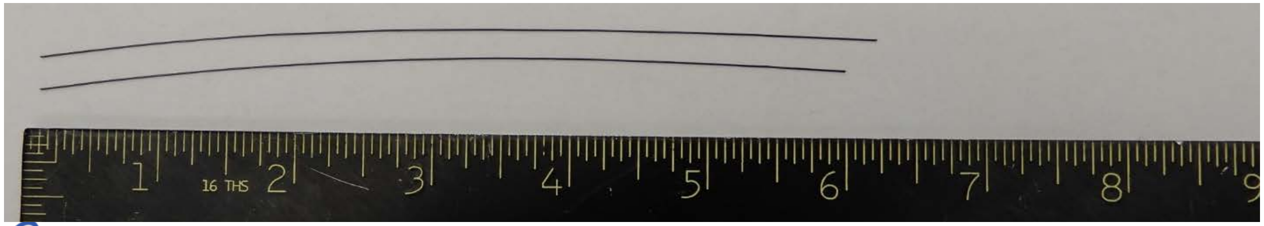


Fiber Diameter: 200 to 500 µm
SL Thickness: 150 to 500 nm

PBI-CMS HF Membrane Fabrication

- Goal: Development of base PBI HF membranes having variety of morphologies including selective layer thickness and support layer structure
  - *In-situ* formation of an integrally skinned HF using commercially available PBI material leveraging LANL PBI spinning capability and process understanding
- Initiated base PBI HF membrane fabrication and pyrolysis to obtain PBI-CMS HF membranes
  - Utilized spinning conditions known to produce PBI HF membranes with thin selective layer and porous support structure
  - Pyrolyzed at 580 °C for 1 hour in inert atmosphere

Base PBI HFM



Carbonized PBI HFM

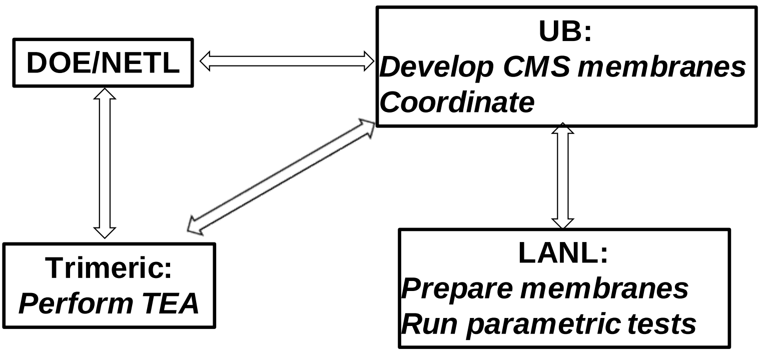
Path Forward

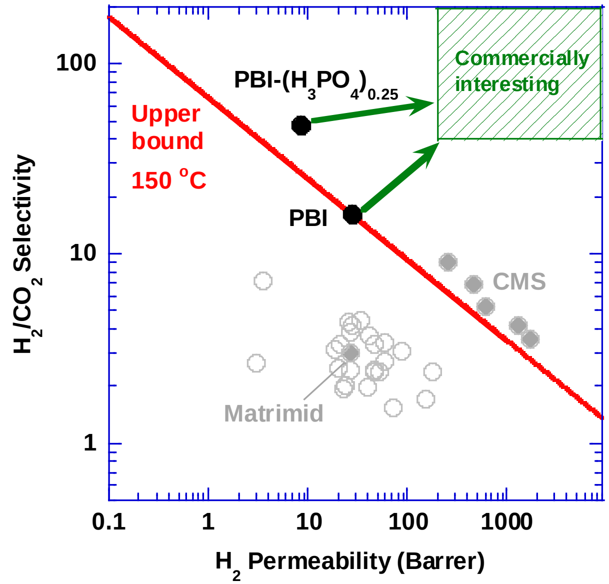
- HF fabrication, acid doping and carbonization
  - Fabrication optimization of PBI and acid doped PBI HF membranes to achieve defect minimized thin selective layer membranes
    - Milestone BP1 Q2FY20: Acid doped PBI HF membranes exhibiting $H_2/CO_2 \approx 40$.
  - Pyrolysis condition optimization to achieve high performance PBI-CMS HF membranes with minimized porous support structure collapse during carbonization
  - Demonstrate fabrication consistency via performance demonstration of fibers from multiple, replicate spinning campaigns
- Sealing Layer Development & Integration
  - Develop and optimize post-carbonization defect seal layer deposition process for PBI-CMS HF membranes
- Demonstration and Validation of Developed Materials and Methods
  - Evaluate PBI, acid doped PBI and PBI-CMS HF membranes for H_2/CO_2 separation properties at syngas relevant process conditions
  - Conduct parametric tests of PBI-CMS HF membranes in CO and H2S containing simulated syngas at process relevant conditions

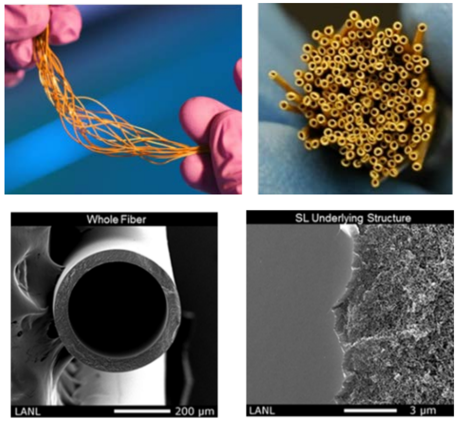
BP1 Techno-Economic Analysis (TEA)

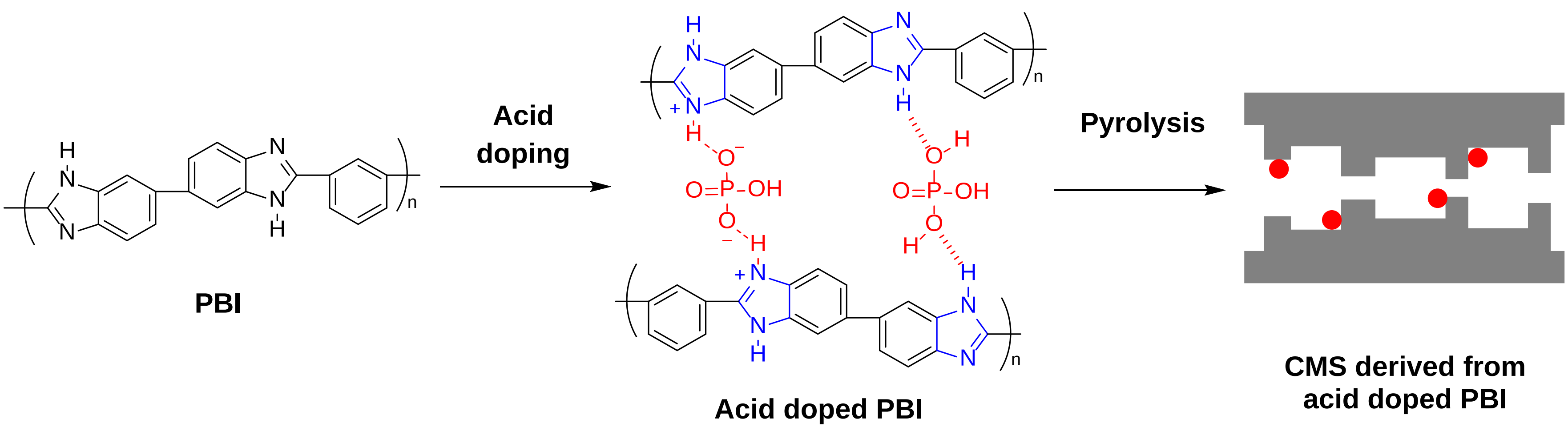
- Cursory analysis during BP1
  - Identify key cost drivers, sensitivities for key variables
  - Identify opportunities for process optimization
  - Bottom-up analysis during BP2
- UB to provide
  - Conceptual design, process simulation and material/energy balances
  - Data on membrane permeance and selectivity
- Key data
  - Inlet pressure, membrane pressure drop
  - Compositions of product streams from membrane
  - Fate of contaminants (CO, H_2S, H_2O)
  - Membrane costs
- Develop preliminary CAPEX, OPEX and energy analysis
- Due 3/31/20

Summary









LANL approval for public release (LA-UR-18-30903)