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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[2]Los Alamos National Laboratory;
[3]Trimeric Corporation

Project Kickoff Meeting (WebEx)
DOE NETL, Pittsburgh, PA

11/16/2018

Outline

- Project overview
- Introduction to UB, LANL and Trimeric
- Fundamental of gas separation membranes
- Project approach and preliminary data
- Project schedule and milestones
- Summary

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

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
University at Buffalo (UB)	$534,999	$202,225	$737,224
Los Alamos National Laboratory (LANL)	$200,000	$0	$200,000
Trimeric Corporation (Trimeric)	$ 65,000	$0	$ 65,000
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)

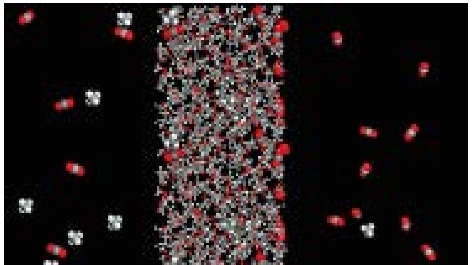
- Optimize membranes achieving the targeted H_2/CO_2 separation performance;
- Test membranes using simulated syngas containing H_2S, CO and water vapor;
- Determine the efficiency of the membrane reactors for the WGS reaction; and
- Conduct the techno-economic analysis.

SUNY at Buffalo (UB)

- New York State’s largest and most comprehensive public university - more than 300 high-quality programs
- Dept. of Chemical and Biological Engineering
  - Undergraduate: ~ 300
  - Graduate: ~ 140 (Masters – 70, PhD – 70)

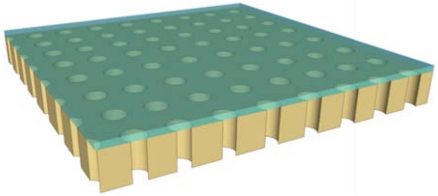
Haiqing Lin

- Novel membrane materials for CO_2 capture from flue gas and syngas
- Understanding polymer structure/property correlations in thin films



Los Alamos National Laboratory (LANL)

- **LANL, located in Los Alamos, New Mexico is a DOE/NNSA research and development center with programs in national security, science, energy, and environmental management.**
- **Carbon Capture and Separations for Energy Applications (CaSEA) Laboratory**
  - Membrane and separation science
  - Material processing for industrial deployment
  - Performance property characterizations



Thin film composite
Ultrasonic Spray Coating

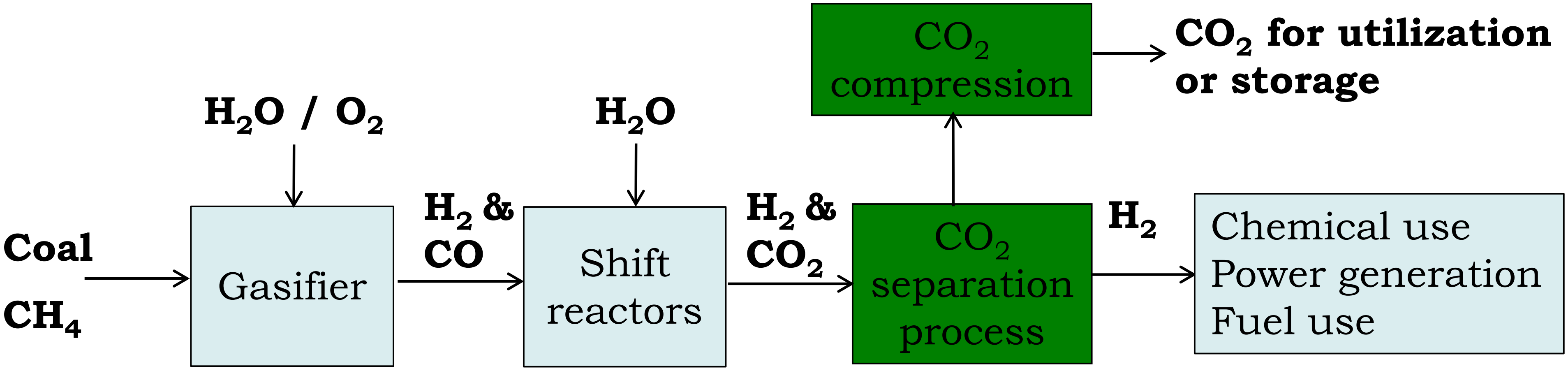
Tubular Composite
Membranes

Hollow Fibers

Trimeric Corporation (Trimeric)

- Privately-owned consulting firm located in Buda (Austin), Texas
- Provides technical services (i.e., expertise in the form of labor hours) to private industry and government-funded clients
- Specializes in process chemical engineering and R&D
  - 18 process chemical engineers, plus access to very experienced experts
- Is independent of licensed technologies or chemicals – an unbiased advocate for our clients with a technology-neutral position
- CO_2 Project Experience – Capture, Purification, Dehydration/Compression, Pipelines, Liquefaction

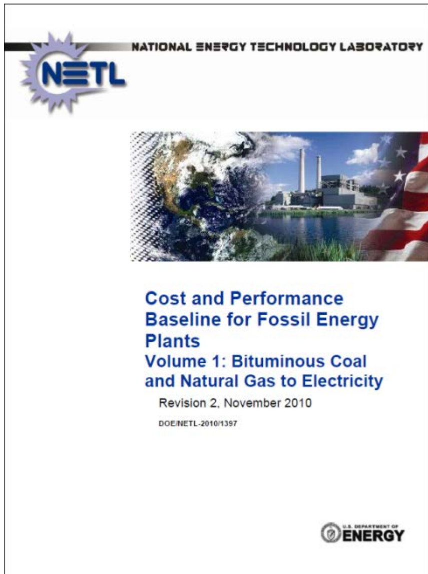
CO_2 separation is energy-intensive and expensive


Coal
CH_4
H_2O / O_2
Gasifier
H_2 & CO
H_2O
Shift reactors
H_2 & CO_2
CO_2 separation process
CO_2 compression
CO_2 for utilization or storage
H_2
Chemical use
Power generation
Fuel use

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.


NATIONAL ENERGY TECHNOLOGY LABORATORY

NETL

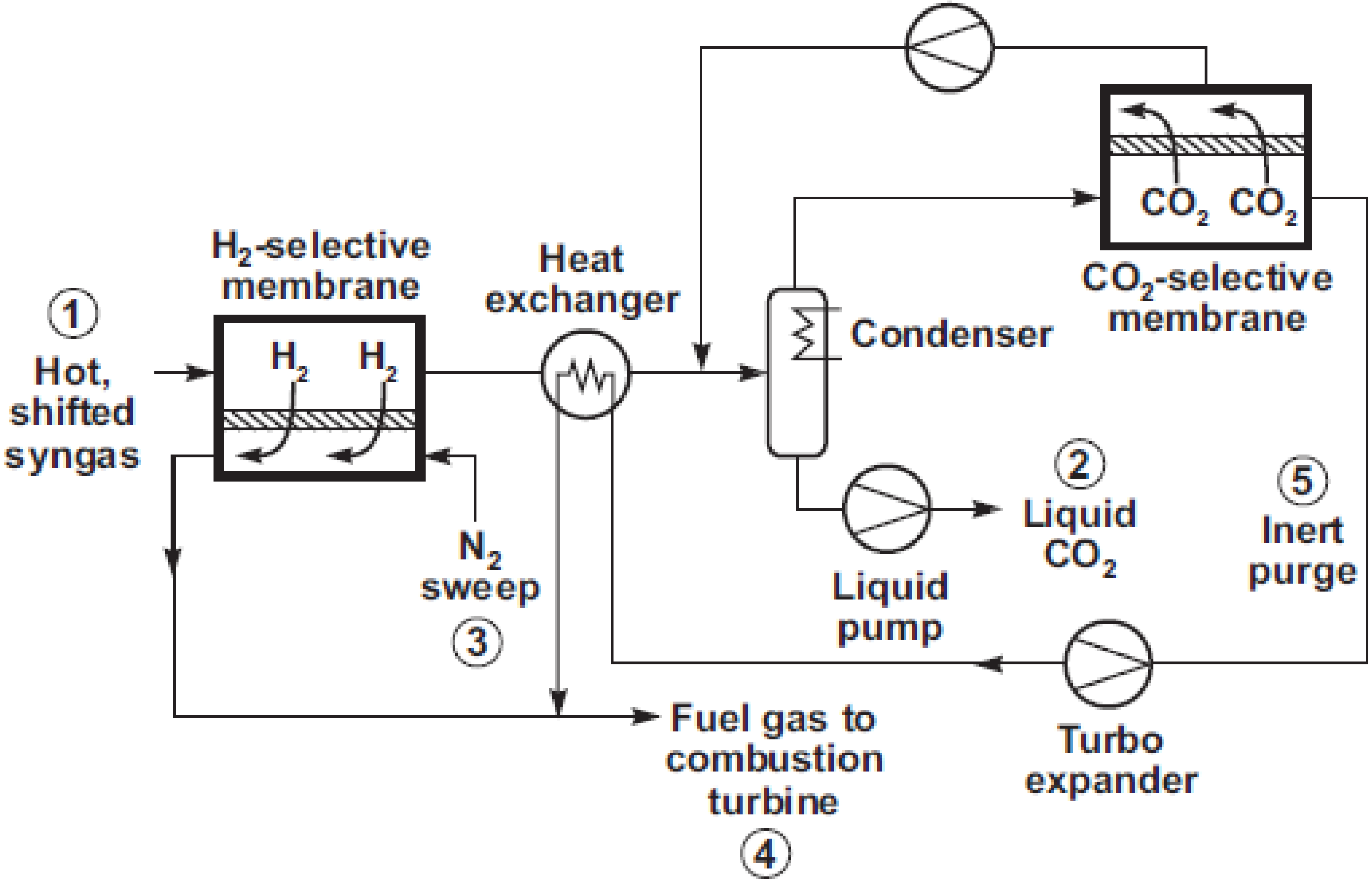
Cost and Performance Baseline for Fossil Energy Plants
Volume 1: Bituminous Coal and Natural Gas to Electricity

Revision 2, November 2010

DOE/NETL-2010/1397

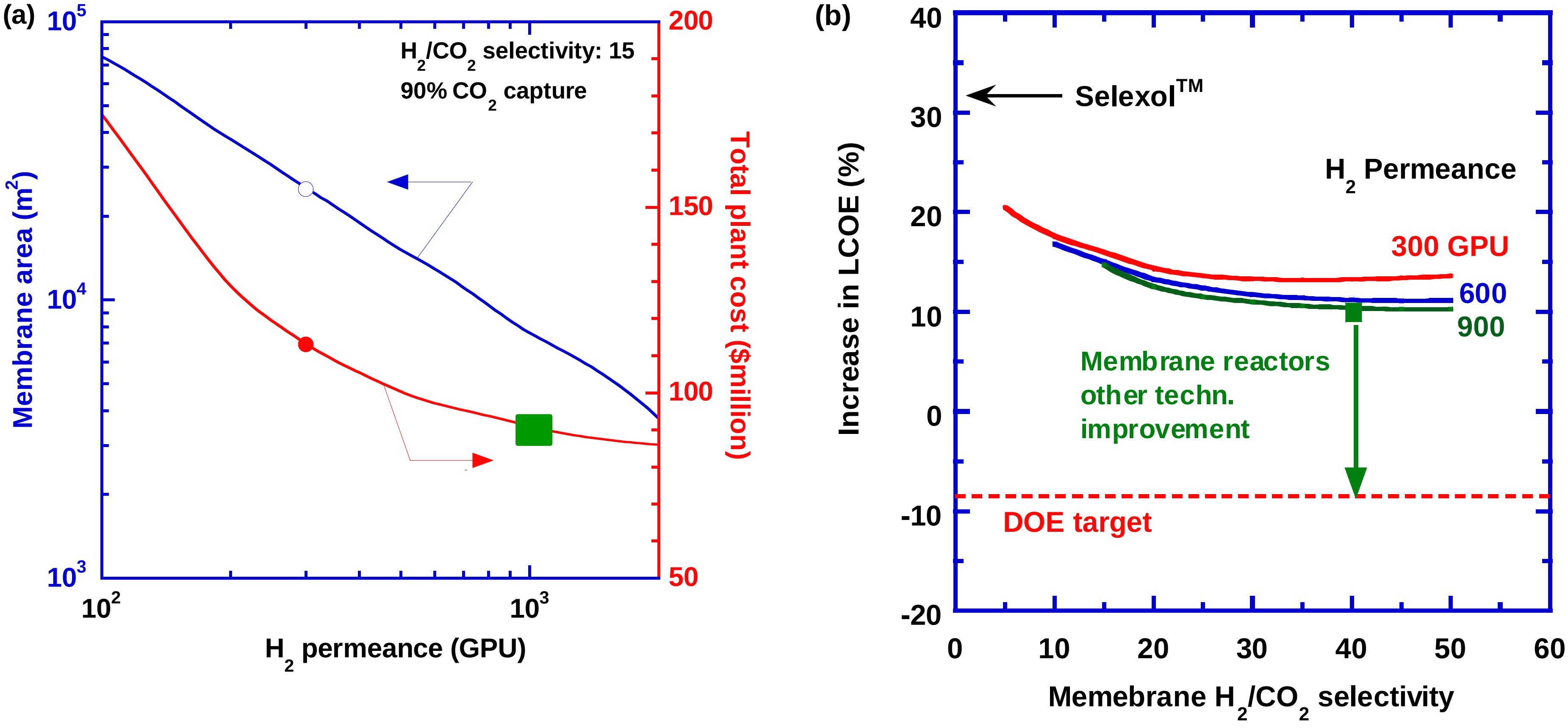
U.S. DEPARTMENT OF ENERGY

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)
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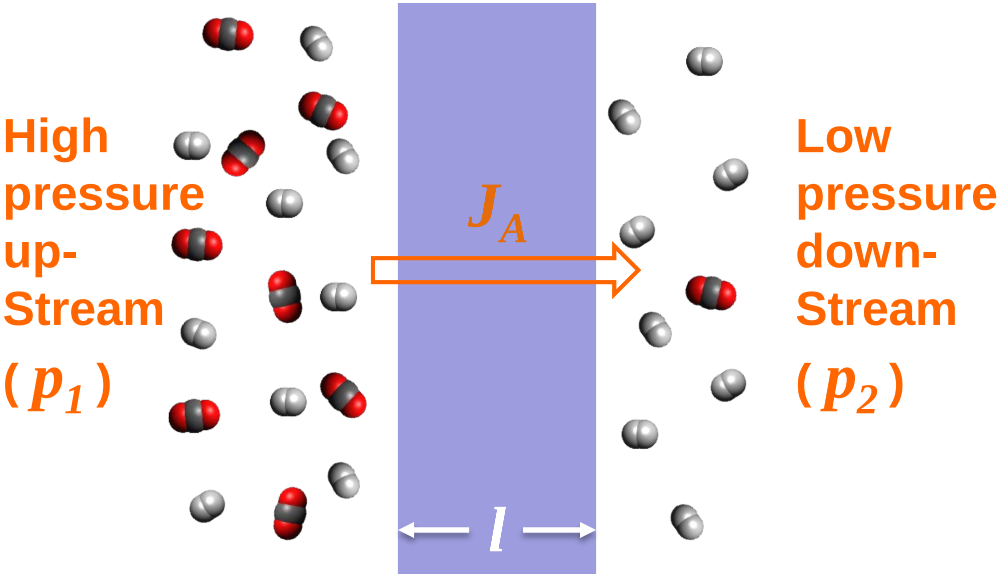
Membrane: Energy-efficient Separation

Solution-diffusion model



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

Productivity - Permeability

$$P_A = S_A \times D_A$$

Purity - Gas selectivity

solubility selectivity

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

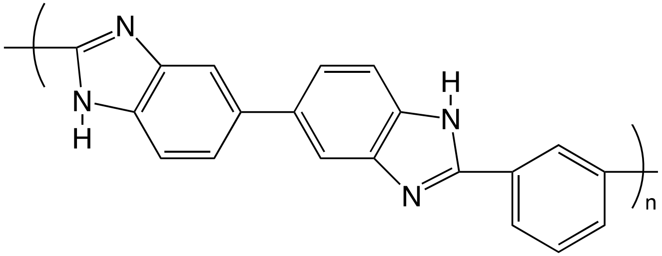
diffusivity selectivity

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

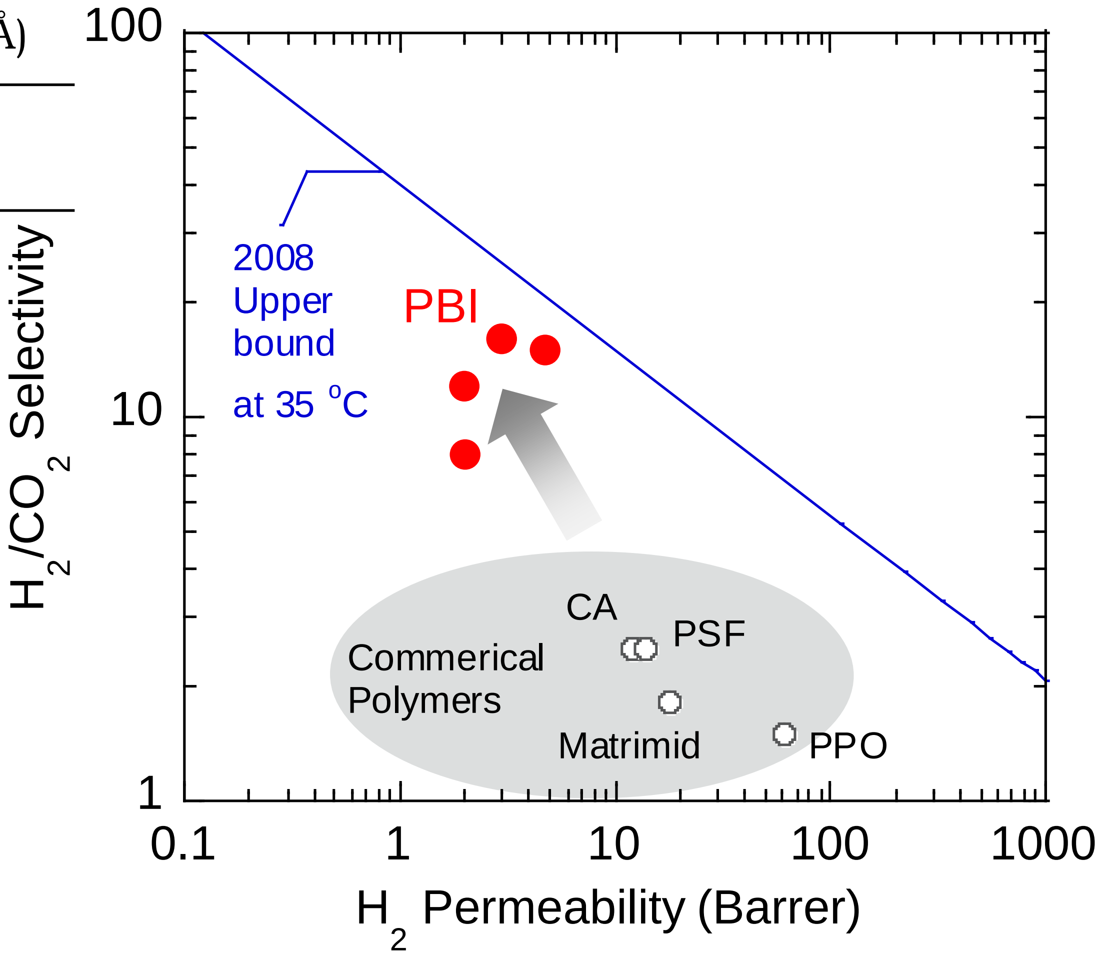
Permeability/Selectivity Tradeoff

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

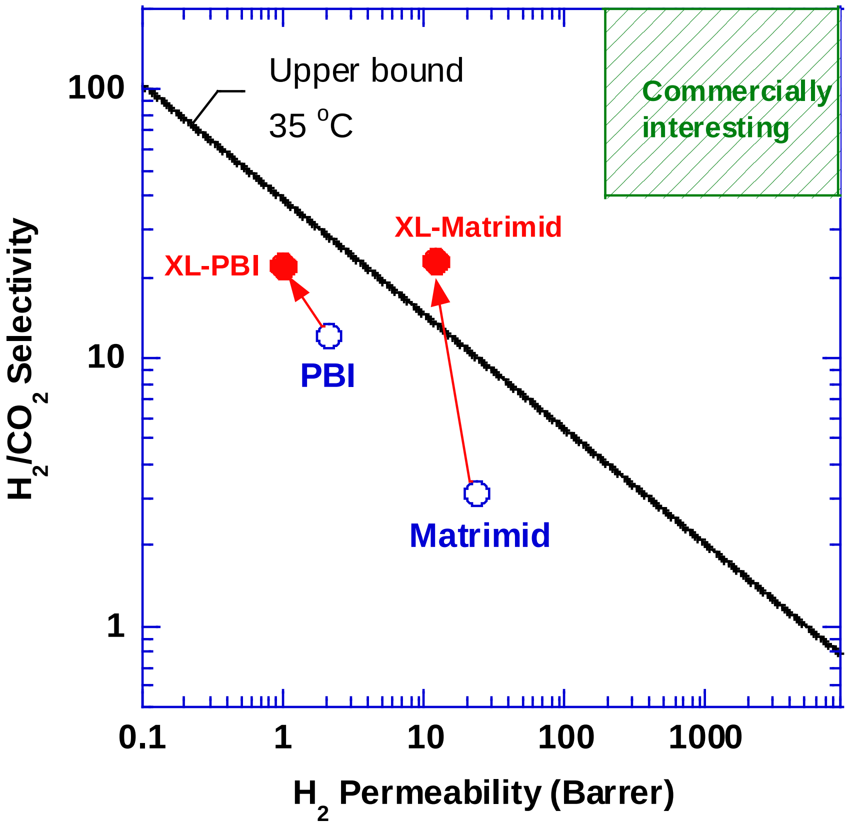
$$\frac{S_{H_2}}{S_{CO_2}} << 1 \quad \text{and} \quad \frac{D_{H_2}}{D_{CO_2}} >> 1$$

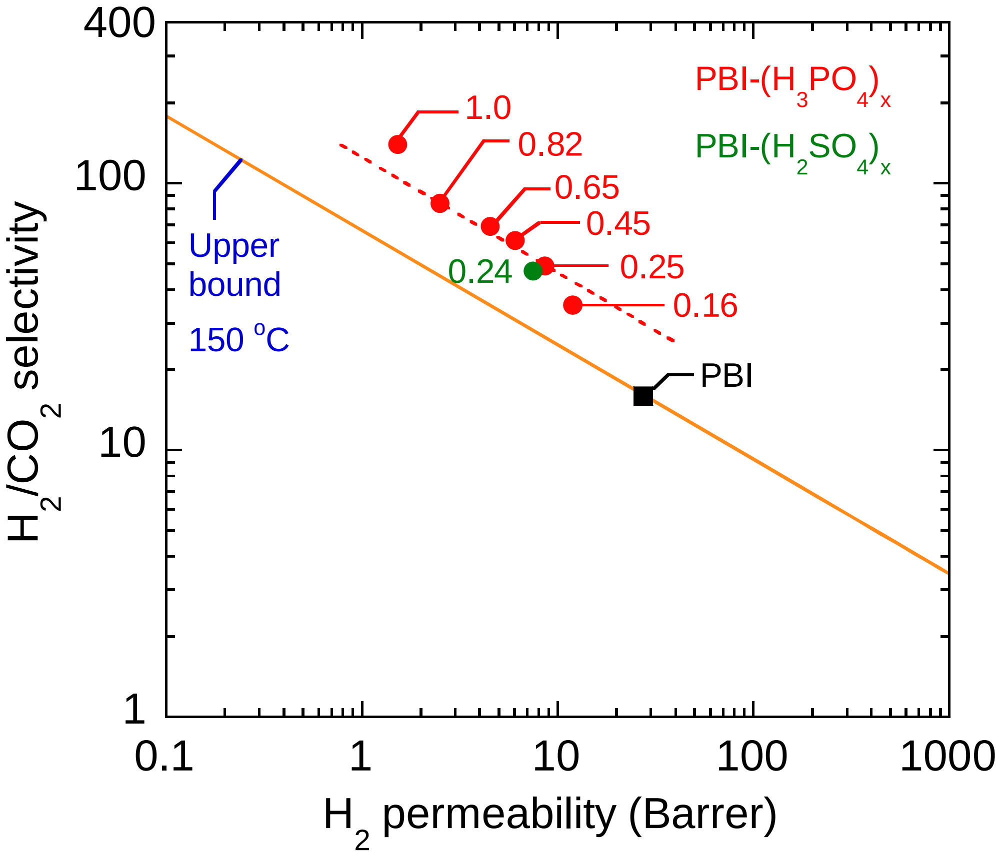


Polybenzimidazole (PBI)
(Celazole®)



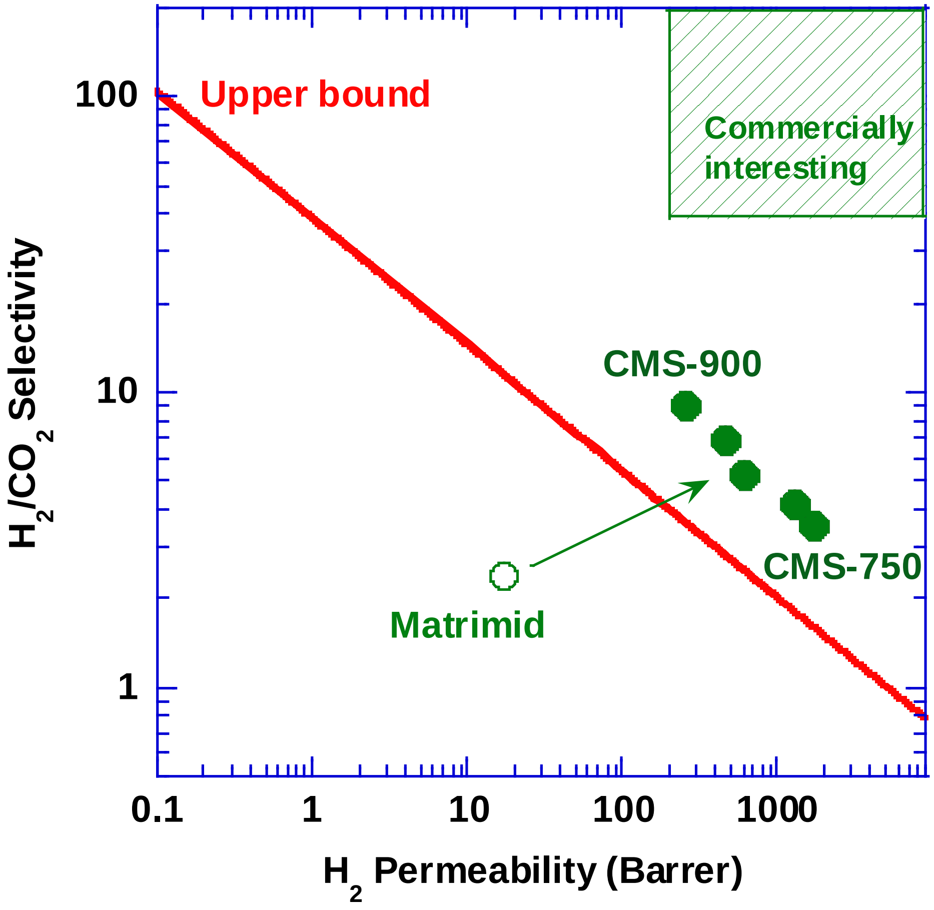
Polymeric Membranes for H_2/CO_2 Separation

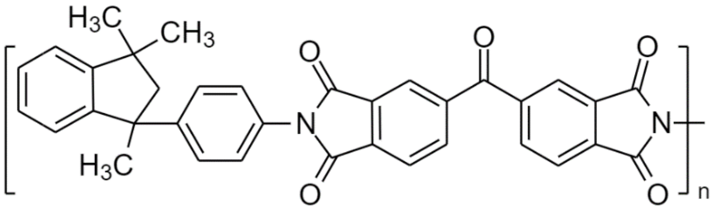




Shao, Low, Chung, and Greenberg *J. Membr. Sci.* 2009, 327, 18-31.
Zhu, Swihart, and Lin *J. Mater. Chem. A* 2017, 5 (37), 19914-19923.
Zhu, Swihart and Lin, *Energy Environ. Sci.* 2008, 11 (1), 94-100.

CMS Membranes

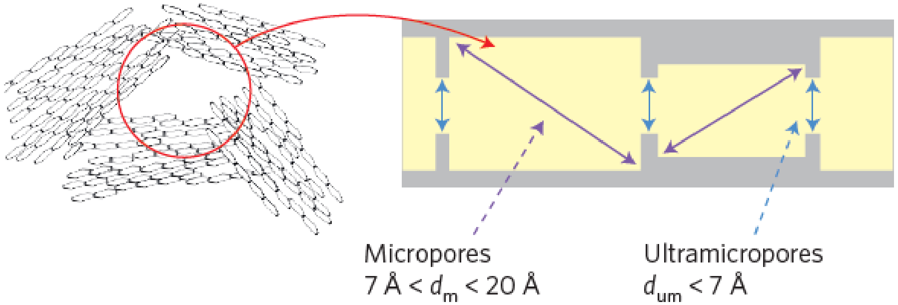




Matrimid® T_d : 500 °C

Pyrolysis
(500-800 °C)

CMS has 'turbostratic' sp^2
hybridized graphene-like sheets



Koros and Chang; *Nat. Mat.*, 16, 289-197 (2017)
Ning and Koros; *Carbon*, 66, 511-522 (2014)
Rungta, Koros, et al.; *Carbon*, 115, 237-248 (2017)

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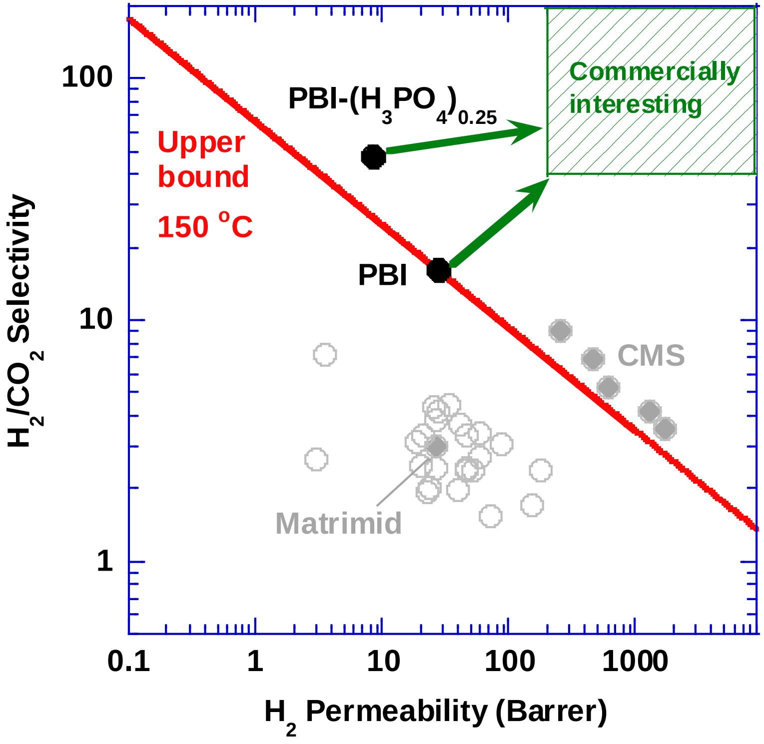
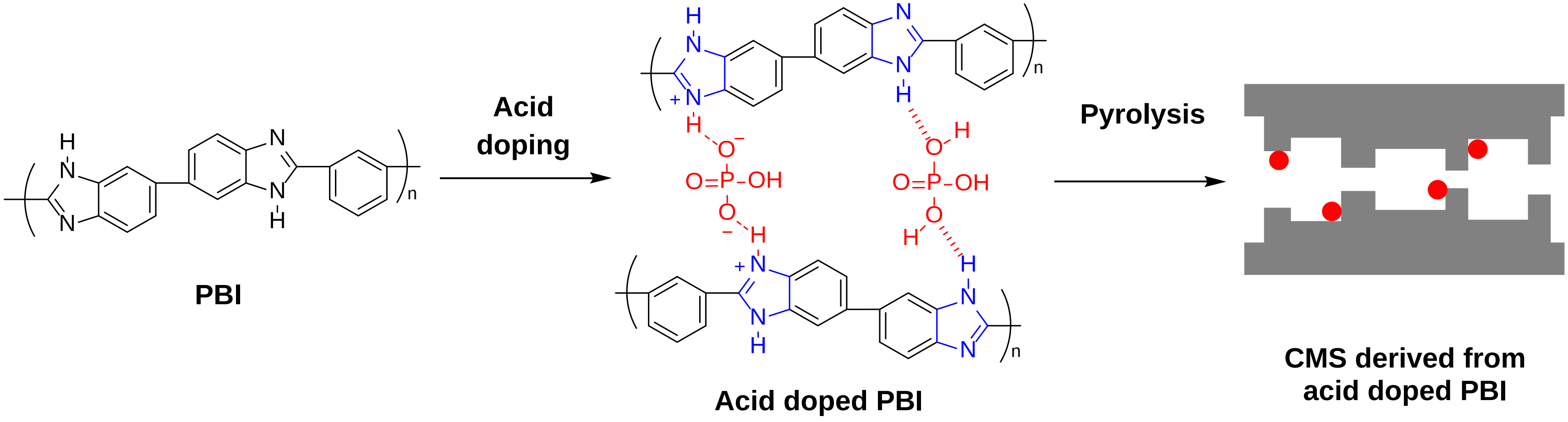
Our Approach: Carbonizing PBI/acid to Enhance H_2/CO_2 Separation Performance

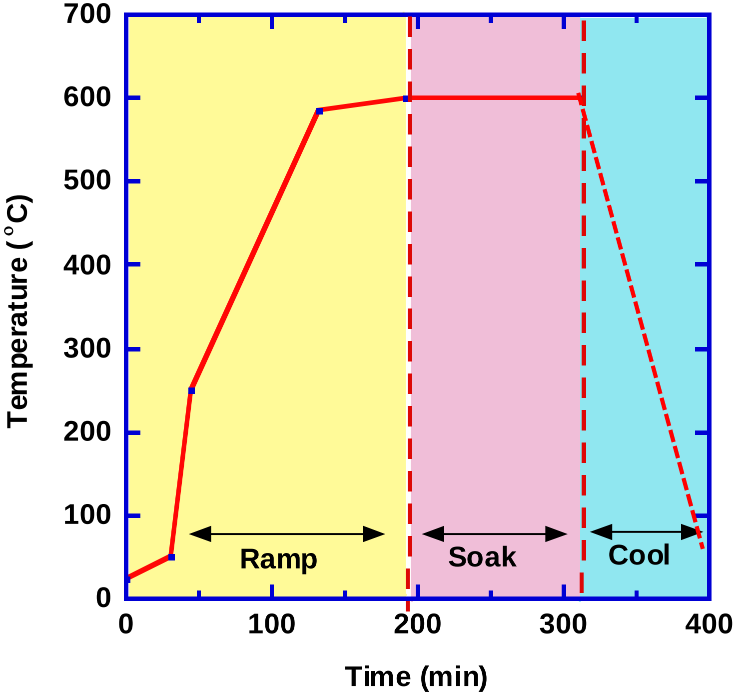


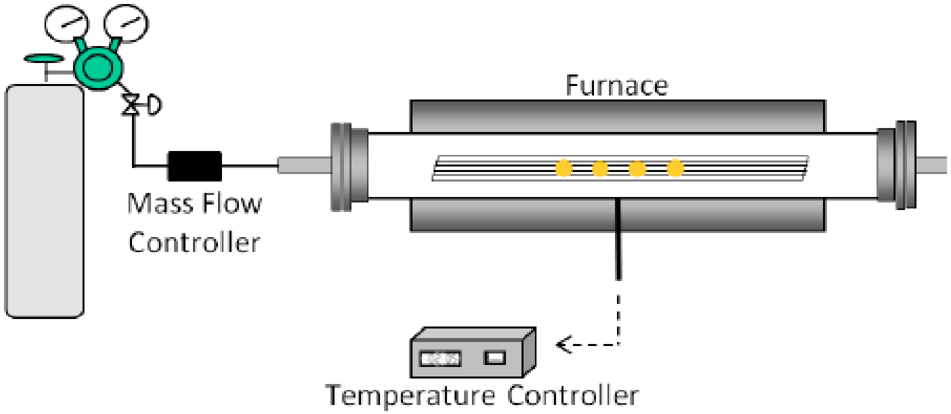
Poly(benzimidazole) (PBI)

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



PBI Pyrolysis Protocol





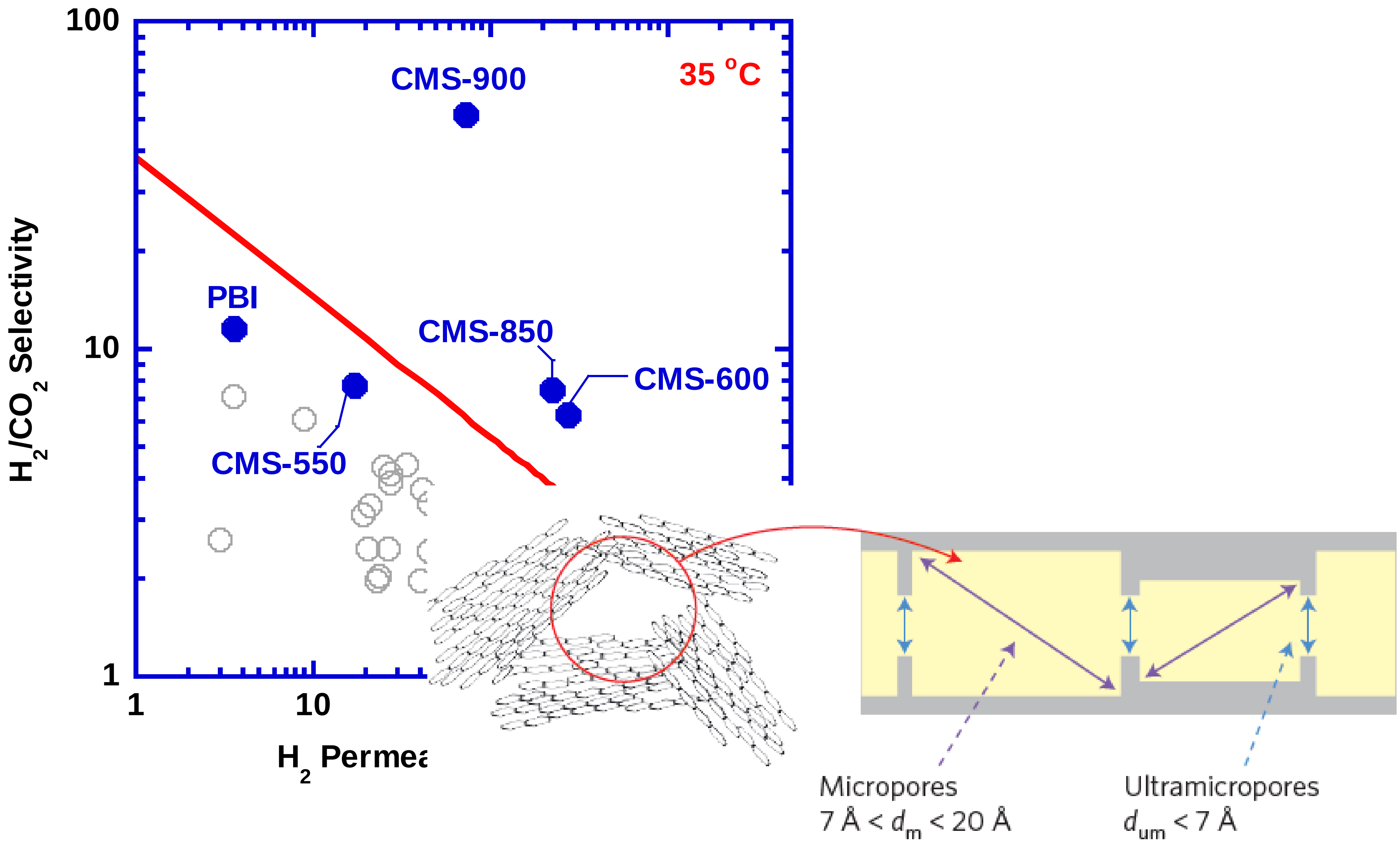
Pyrolysis Protocols: 200 cc N_2/min

- 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

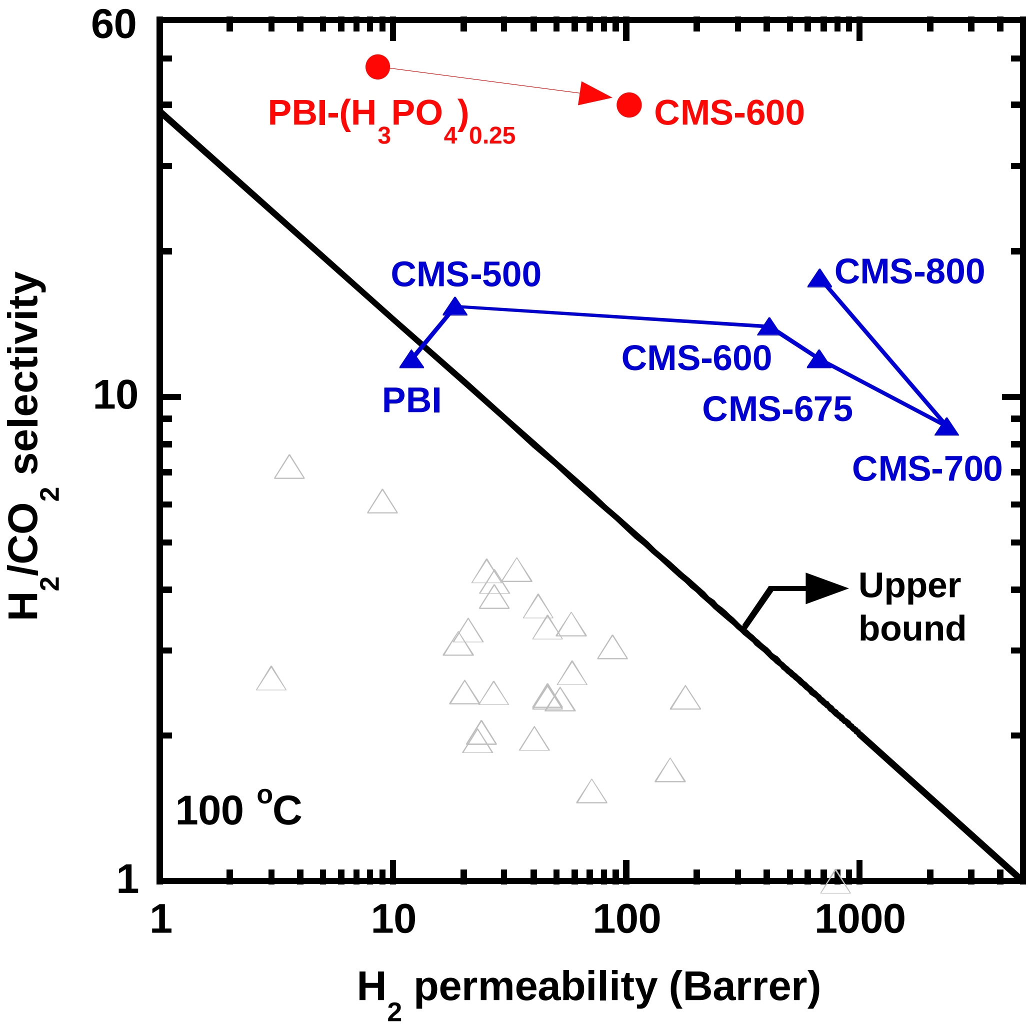
T_{max}: 600-900 °C

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

Effect of Pyrolysis Temperature on H_2/CO_2 Separation at 35 ˚C

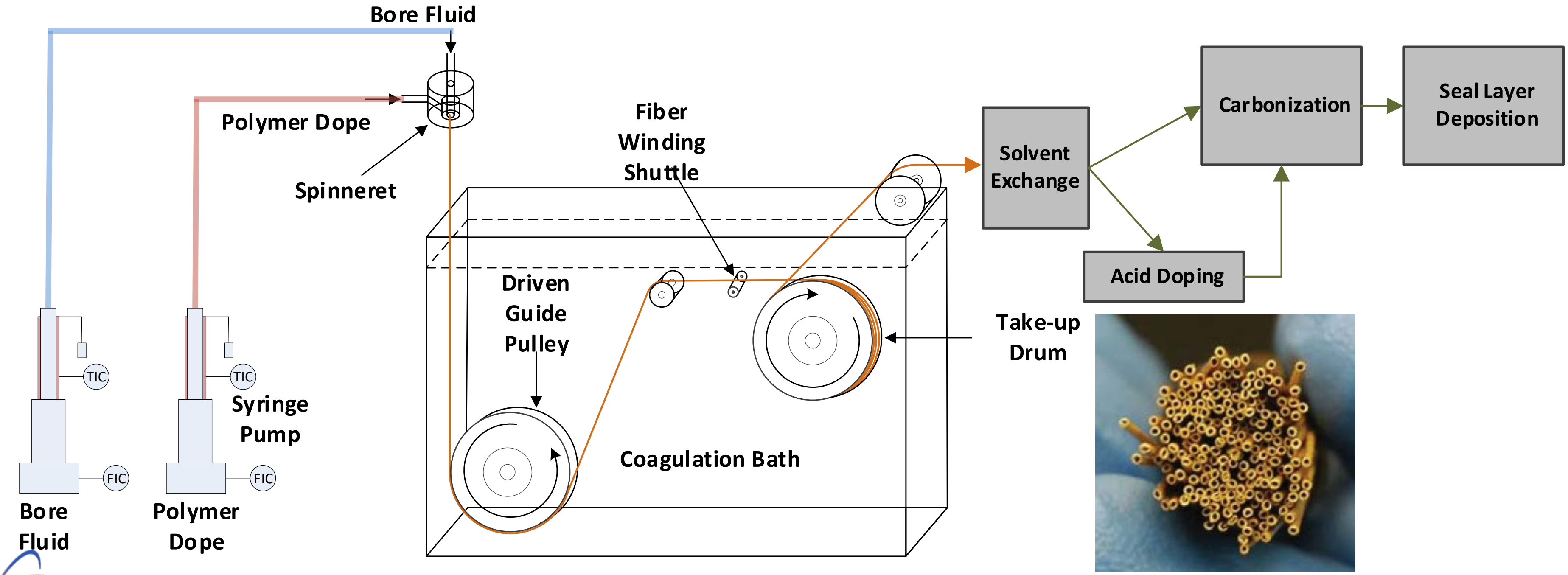


Effect of H_3PO_4 Doping and Pyrolysis Temperature on H_2/CO_2 Separation at 100 ˚C



Hollow Fiber Membrane Fabrication

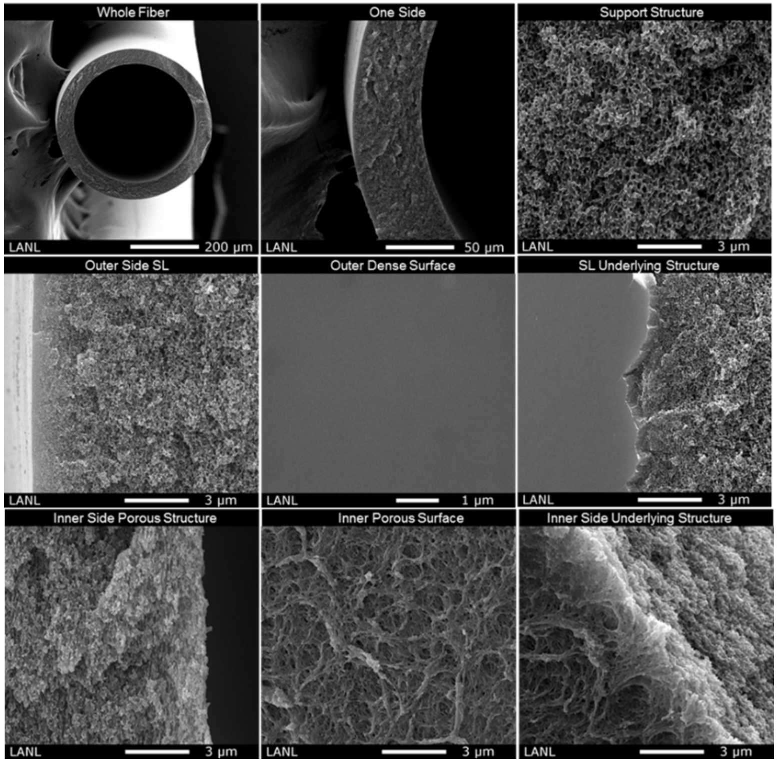
- PBI hollow fiber membrane carbonization in controlled atmosphere to fabricate CMS hollow fiber membrane
  - Fabricate base PBI hollow fiber membranes having a variety of morphologies including the support layer porous structure and dense layer thickness
  - Incorporate and optimize the post-fabrication acid doping and carbonization steps to obtain CMS hollow fiber membranes
  - Incorporate already demonstrated defect minimizing PBI-based seal layer having thermo-chemical properties to withstand syngas operating conditions & environments



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

Developing CMS Hollow Fiber Membranes with Ideal Morphology

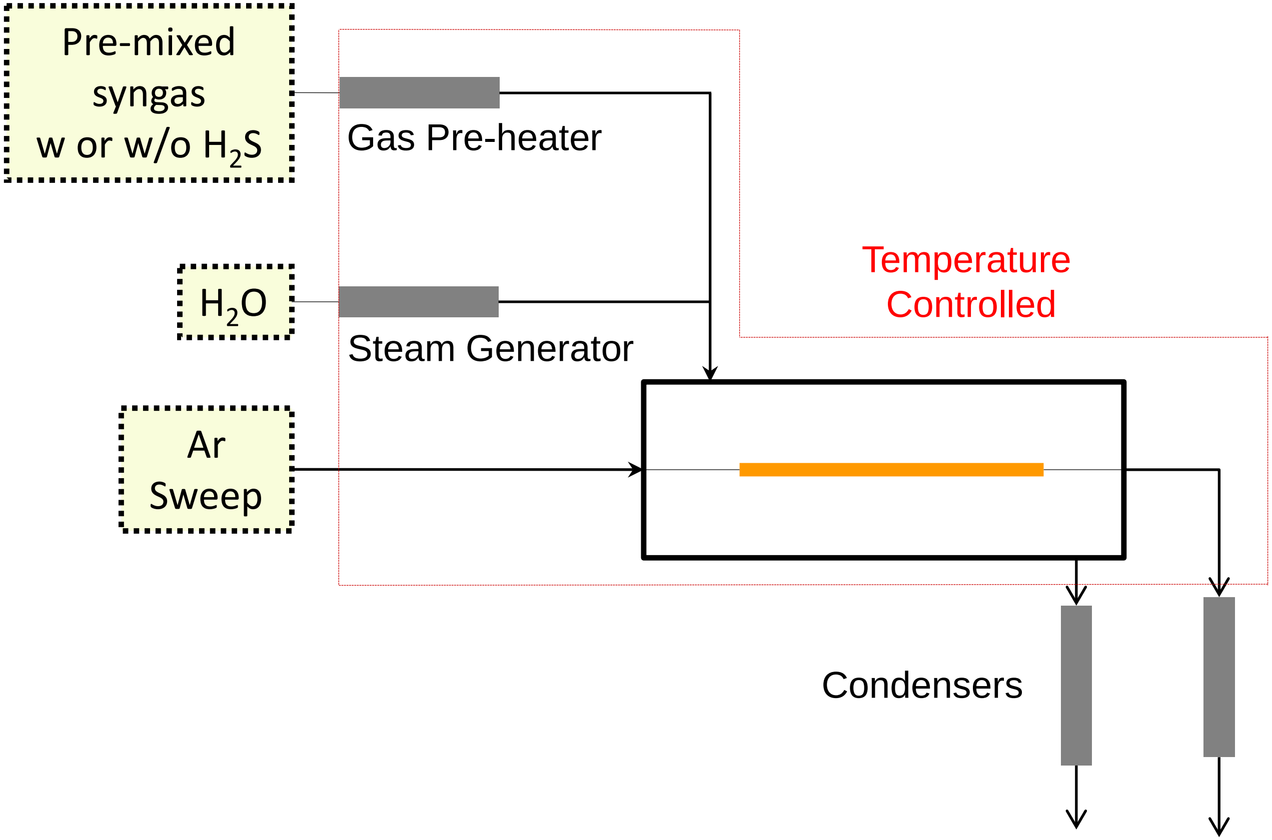
- Base PBI hollow fiber membrane structure will have strong influence on the morphology, separation performance and mechanical strength of the resulting CMS hollow fiber membranes
  - Project goal is to optimize the PBI HFM porous support structure to minimize porous support layer collapse and densification during carbonization
  - Controlled pre-carbonization acid doping of the PBI hollow fiber membranes will be leveraged to improve the CMS hollow fiber membranes permeation and mechanical properties
- Leverage recently developed spinning protocols to obtain high performance PBI hollow fiber membranes
  - Thin nearly defect-free dense layer
  - Macro-void free for high strength
  - Selective layer thickness control (demonstrated ability to control selective layer thickness from ca. 200 to 2000 nm)
  - Porous inner surface layer
  - Industrially attractive fabrication process: Minimized flammable & toxic solvent use



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

Synthesis Gas Evaluations

- CMS hollow fiber membranes will be tested in wet simulated syngas mimicking NETL hydrogen membrane testing guidelines
  - Typical syngas composition and temperature in the vicinity of water gas shift reactors



Pre-mixed syngas w or w/o H_2S

H_2O

Ar Sweep

Gas Pre-heater

Steam Generator

Temperature Controlled

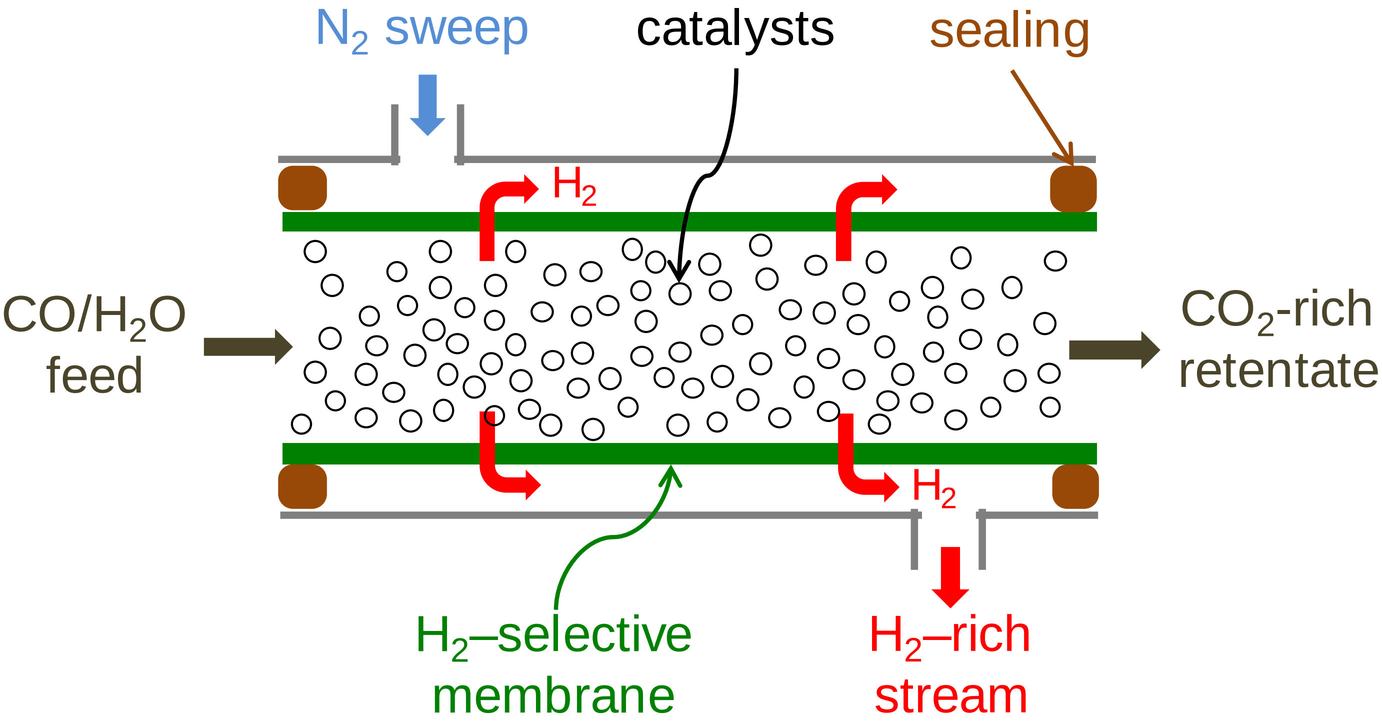
Condensers

To pressure controller, flow & composition measurement

Feed composition	Test 1	Test 2
H_2 (%)	50	50
CO_2 (%)	30	30
H_2O (%)	19	19
CO (%)	1	1
H_2S (ppm)	0	20
Total Feed Pressure (psia)	200	200
Temp (°C)	200-350	

Ref: NETL Test protocol – Testing of hydrogen separation membranes, 2008.

Membrane Reactors



Process intensification to further reduce the CO_2 capture cost.

Introduction to Techno-Economic Analysis (TEA)

- Objective: Provide broad overview of technology development and TEA
  - Evaluate technical feasibility of technology
  - Estimate process economics
- Discussion topics include:
  - Process engineering tasks
  - Economic analysis tasks
  - Economic analysis challenges

Typical Process Engineering Tasks

- Develop conceptual design and material/energy balances
- Develop process simulation
- Identify data gaps / missing data for technology developer
- Size major equipment and develop equipment list
- Perform preliminary economic analysis

Economic Analysis: Bottom-Up Approach (1 of 3)

- Clearly establish goals and outcomes for TEA, and define cases to be evaluated
- Estimate energy performance
  - Electric and thermal requirements (primarily electric for membrane processes)
- Select and size equipment
  - Establish design T/P, materials of construction
  - Important to understand physical/mechanical limitations for equipment size
- Estimate purchased equipment costs
  - Vendor quotations, in-house databases, software

Economic Analysis: Bottom-Up Approach (2 of 3)

- Estimate total plant costs (CAPEX)
  - Materials, engineering, process/project contingencies, etc.
  - Use of single Lang factor may be more appropriate
- Estimate operating and maintenance costs (OPEX)
  - Labor, utilities, fuel, consumables, membrane replacement cost and frequency, waste disposal, etc.
- Calculate economic metrics and compare to reference case/baseline technology
  - Cost and Performance Baseline for Fossil Energy Plants Volume 1b: Bituminous Coal (IGCC) to Electricity (Revision 2b – Year Dollar Update, July 2015) – Case B5B

Economic Analysis: Bottom-Up Approach (3 of 3)

- Identify opportunities for process optimization – energy recovery, reduce water makeup, etc.
- Identify key equipment size and cost drivers, and evaluate tradeoffs between technical feasibility, energy performance, and costs

Economic Analysis Challenges

- Is there sufficient information to conduct a bottom-up analysis?
  - Is a factored approach more appropriate?
- Identify key equipment size and cost drivers
  - Perform sensitivity analyses for key variables
- Identify risks/unknowns and estimate potential impact on economic viability
- Report cost estimate as a function of level of accuracy
- Are there constraints from surrounding environment – host site water availability, thermal energy temperature limitations, footprint, etc.

Conclusions

- Proper technology evaluation requires careful and detailed process engineering work
    - Important to document all engineering and economic assumptions for transparency
- A proper evaluation must address the following items / requirements:
    - Collection of fundamental data
    - Proper material and energy balances
    - Impact of thermodynamic constraints
    - Impact of end user requirements

Project Schedule and Milestones

Tasks	Start date	End date
Task 1. Project Management and Planning	10/1/18	9/30/21
Milestones a,b,c,d,e,f: SOPO finalized; kickoff meeting held; Final report submitted; State point data table, TMP, Environmental Assessment		
Task 2. Prepare, Optimize and Characterize PBI Doped with Polyprotic Acids	10/1/18	6/30/19
Task 3. Prepare, Optimize and Characterize CMS Materials	1/1/19	12/31/19
Task 4. Prepare and Optimize Hollow Fiber Membranes Based on PBI and PBI Doped with Polyprotic Acids	7/1/19	3/31/20
Task 5. Characterize H_2/CO_2 Separation Properties	1/1/19	3/31/20
Task 6. Perform Process Technical Analysis	7/1/19	3/31/20
Milestone g: CMS films with H_2 permeability of 200 Barrers and H_2/CO_2 selectivity of 40		
Milestone h: Hollow fiber membranes based on PBI doped with polyprotic acids exhibiting H_2/CO_2 selectivity of 40		

Tasks	Start date	End date
Task 7. Prepare CMS Hollow Fiber Membranes Based on PBI	4/1/20	9/30/20
Task 8. Prepare CMS Hollow Fiber Membranes Based on PBI Doped with Polyprotic Acids	7/1/20	3/31/21
Task 9. Conduct Parametric Tests of Membranes for H_2/CO_2 Separation	10/1/20	9/30/21
Task 10. Evaluate the CMS Membranes for WGS Reactors	1/1/21	9/30/21
Task 11. Evaluate Economic Potential of Membrane Process Compared to Other Capture Technologies	1/1/21	9/30/21
Milestone i: CMS hollow fiber membranes with H_2 permeance of 1,000 GPU and H_2/CO_2 selectivity of 40		
Milestone j. Database of H_2/CO_2 separation properties in the CMS hollow fiber membranes at various pressures, temperatures and feed gas compositions		
Milestone k: Performance data of membrane reactors for the WGS reaction		

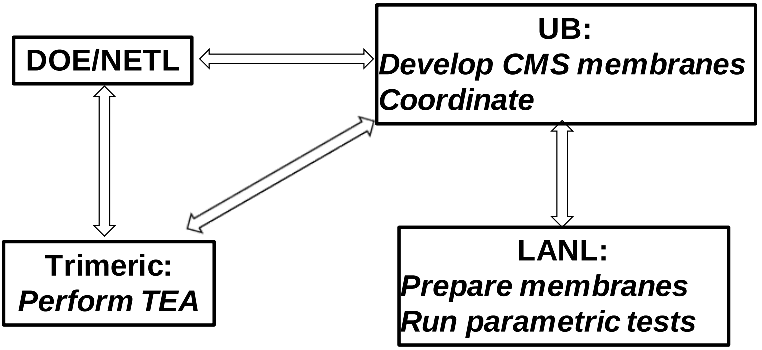
Project Milestones

Budget Period	ID	Description	Completion Date
1	**a**	**PMP finalized**	**10/30/18**
1	**b**	**Project kick-off meeting**	**11/30/18**
2	c	Final techno-economic analysis submitted	9/30/2021
2	d	State Point Data Table	9/30/2021
2	e	Technology Maturation Plan	9/30/2021
2	f	Environmental Health and Safety Risk Assessment	9/30/2021
1	g	CMS films with H_2 permeability of 200 Barrers and H_2/CO_2 selectivity of 40	12/31/2019
1	h	Hollow fiber membranes based on PBI doped with polyprotic acids exhibiting H_2/CO_2 selectivity of 40	3/31/2020
2	i	CMS hollow fiber membranes with H_2 permeance of 1,000 GPU and H_2/CO_2 selectivity of 40	9/30/2021
2	J	Database of H_2/CO_2 separation properties in the CMS hollow fiber membranes at various pressures, temperatures, and feed gas compositions	9/30/2021
2	k	Performance data of membrane reactors for the WGS reaction	9/30/2021

Risk Management

Description of Risk	**Probability**	**Impact**	**Risk Management**
Technical Risks:			
Fabrication of CMS membranes with a thin selective layer	Moderate	Moderate	Control the pyrolysis conditions; draw support from Dr. Raj Singh's group at LANL
Long-term stability of CMS membranes	Moderate	Moderate	Long-term test with simulated syngas at LANL
Integrity of CMS membrane modules	Low	Moderate	Optimize components; draw support from Dr. Raj Singh's group at LANL
Resource Risks:			
Recruit two PhD students	**Low**	**Moderate**	**Promote existing MS students to PhD; Shift senior students to this project**
Management Risks:			
Capability to coordinate multi-organization effort	Low	Moderate	Regular meetings and phone conferences; Internal monthly reports

Summary

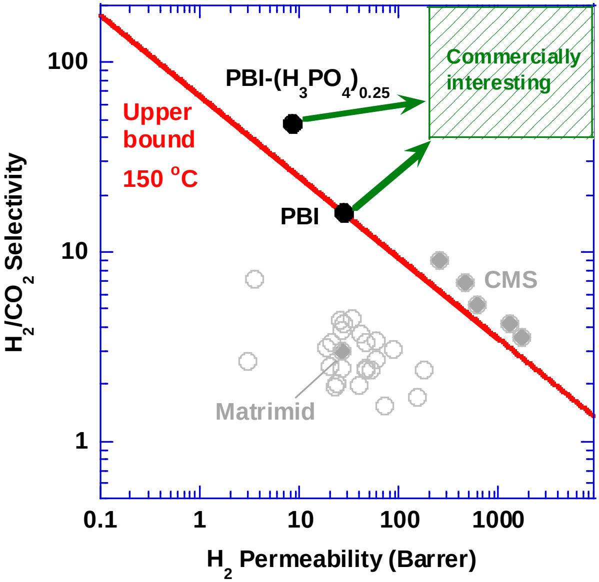


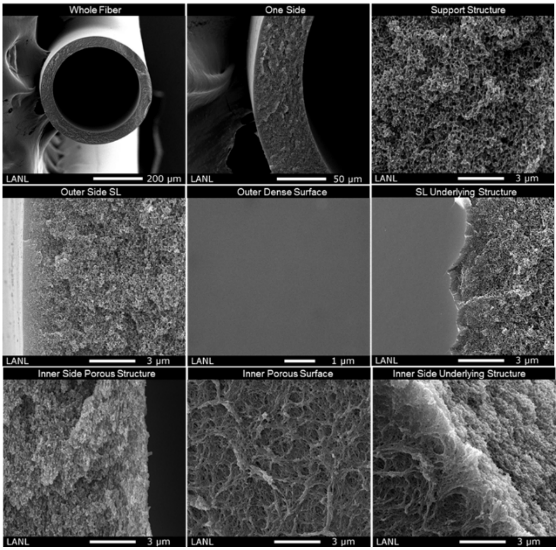
DOE/NETL

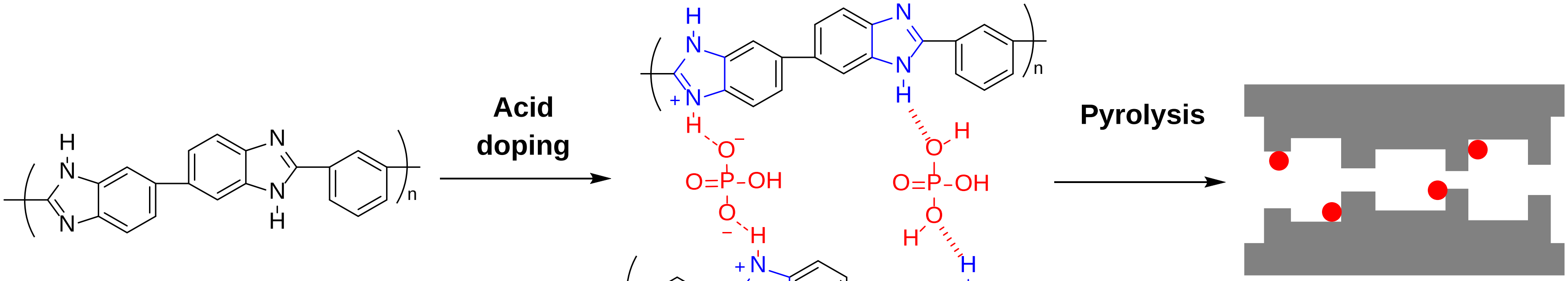
UB:
Develop CMS membranes
Coordinate

Trimeric:
Perform TEA

LANL:
Prepare membranes
Run parametric tests







PBI

Acid doped PBI

CMS derived from acid doped PBI