Sorption Enhanced Mixed Matrix Membranes for H_2 Purification and CO_2 Capture (DE-FE0026463)

Haiqing Lin and Mark Swihart
Department of Chemical and Biological Engineering
University at Buffalo, State University of New York

Project Kickoff Meeting
DOE NETL, Pittsburgh, PA

10/5/2015

Outline

- Project overview
- Introduction to UB, MTR and NCCC
- Fundamental of gas separation membranes
- Project approach
- Project schedule and milestones
- Summary

Sorption Enhanced Mixed Matrix Membranes for H_2 Purification and CO_2 Capture

Award number:	DE-FE0026463
Project period:	10/1/15 to 9/30/18
Funding:	\$1,470,099 DOE \$ 373,004 UB and MTR contribution
Program manager:	Elaine Everitt
Participants:	University at Buffalo (UB), Membrane Technology and Research, Inc. (MTR), and National Carbon Capture Center (NCCC)
Project Objective:	Develop membranes with a H_2 permeance of 500 gpu and H_2/CO_2 selectivity of 30, enabling membrane-based systems to meet the DOE's target in capturing CO_2 from coal-derived syngas.

Sorption Enhanced Mixed Matrix Membranes for H_2 Purification and CO_2 Capture

Project scope:

- Identify mixed matrix materials with H_2 permeability of 50 Barrers and H_2/CO_2 selectivity of 30 at 150-200°C with simulated syngas;
- Prepare thin film mixed matrix composite membranes with H_2 permeance of 500 gpu and H_2/CO_2 selectivity of 30 at 150-200°C;
- Conduct a 6-week field test of the membranes with real syngas at NCCC.

End Products:

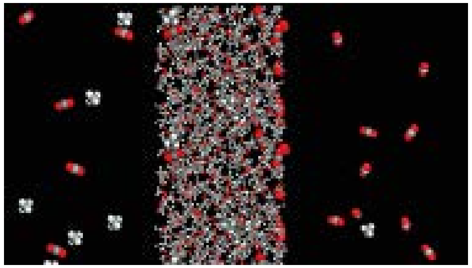
- Robust thin film mixed matrix composite membranes with H_2 permeance of 500 gpu and H_2/CO_2 selectivity of 30 at 150-200°C
- Plan for membrane production scale up and pilot scale testing

SUNY at Buffalo (UB)

- New York State's largest and most comprehensive public university
- Department of Chemical and Biological Engineering
  - Undergrad – 304
  - Graduate – 131 (Masters – 65, PhD – 66)

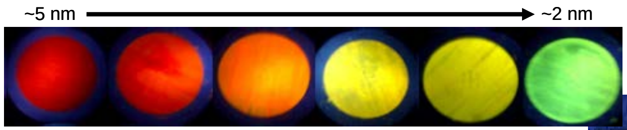
Haiqing Lin

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

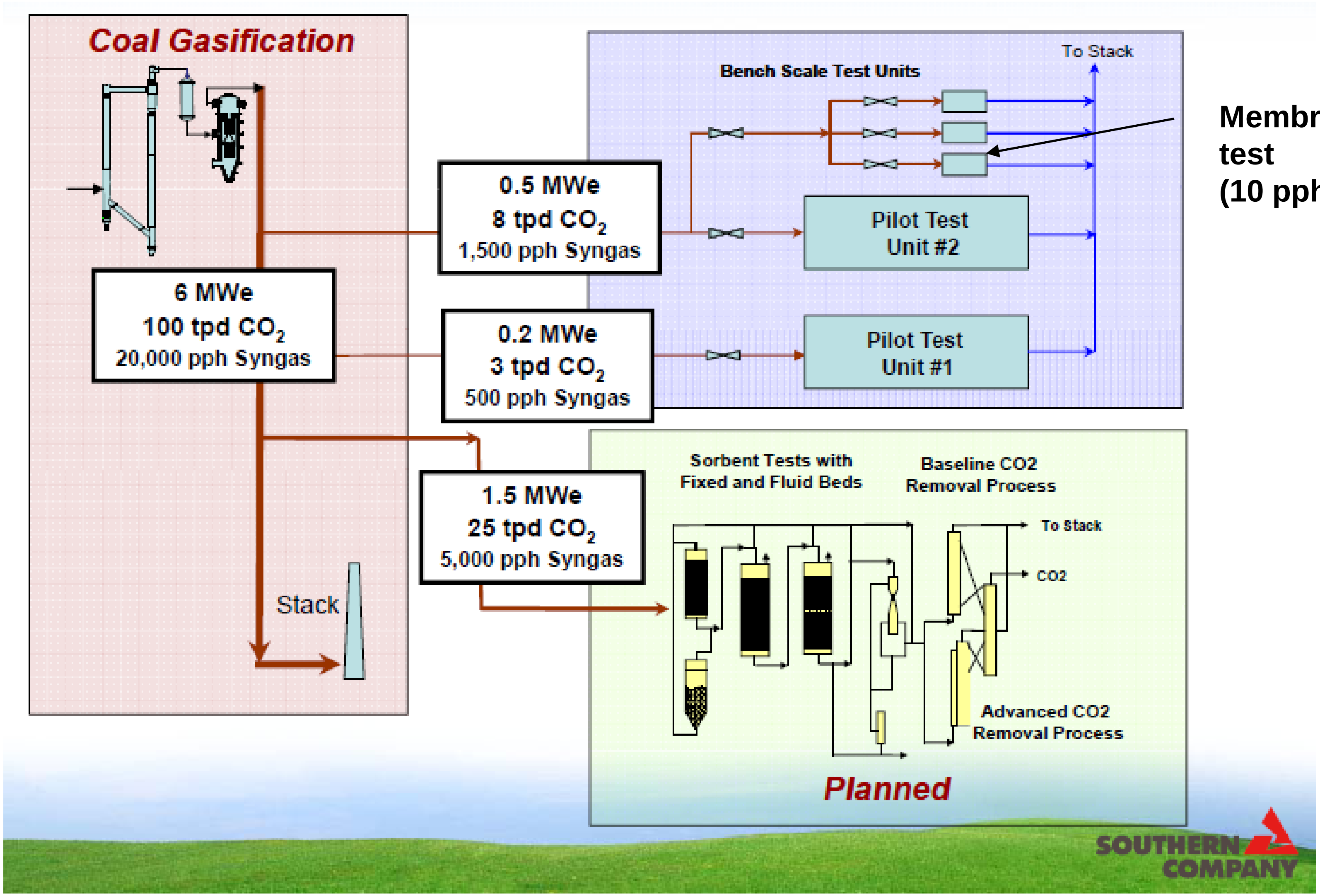


Mark Swihart

- Synthesis and applications of nano-particles and nanostructured materials
- Modeling reacting flows for nanomaterials processing



National Carbon Capture Center (NCCC)



Membrane field test
(10 pph syngas)

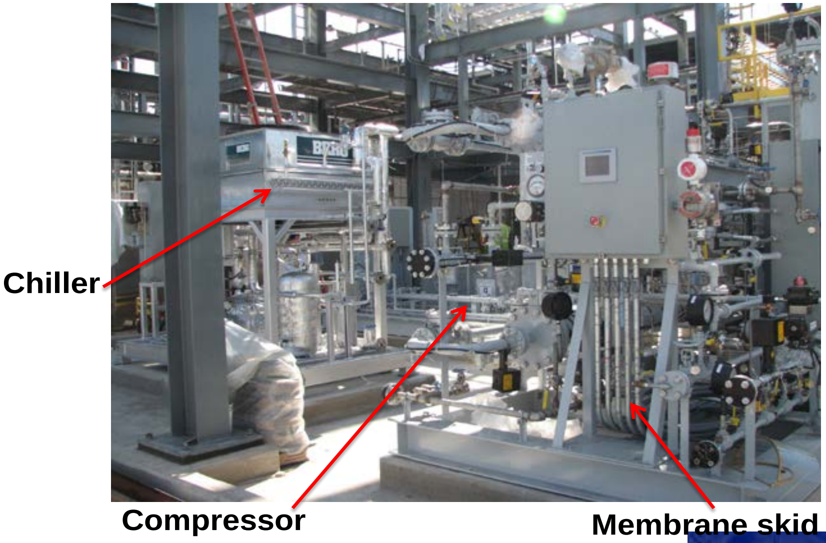
Slide courtesy of Frank Morton, Southern Company

Membrane Technology and Research, Inc. (MTR)

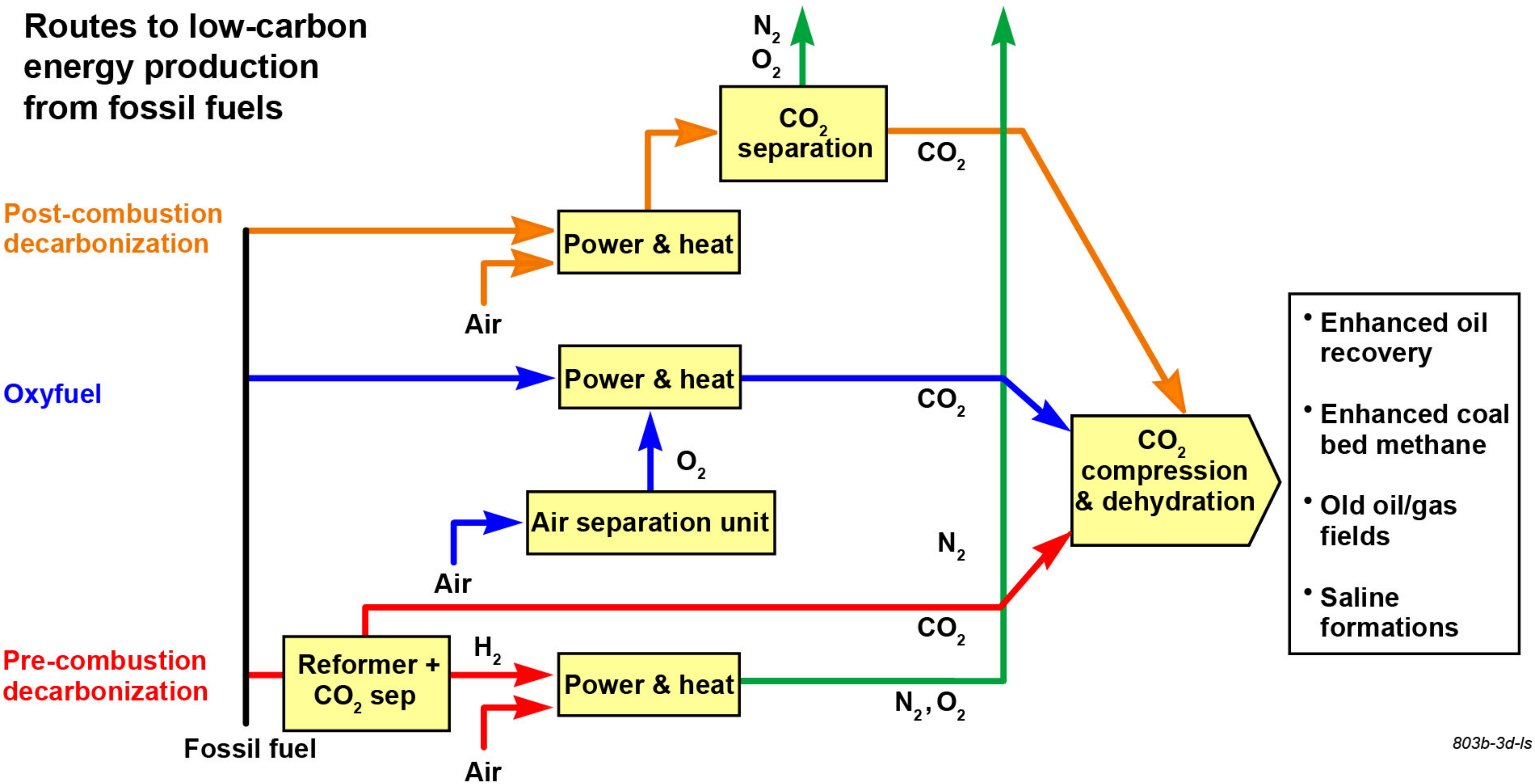
Dedicated to development and commercialization of membrane-based separation technologies

Commercial system for hydrogen purification

Field test system for H_2/CO_2 separation at NCCC



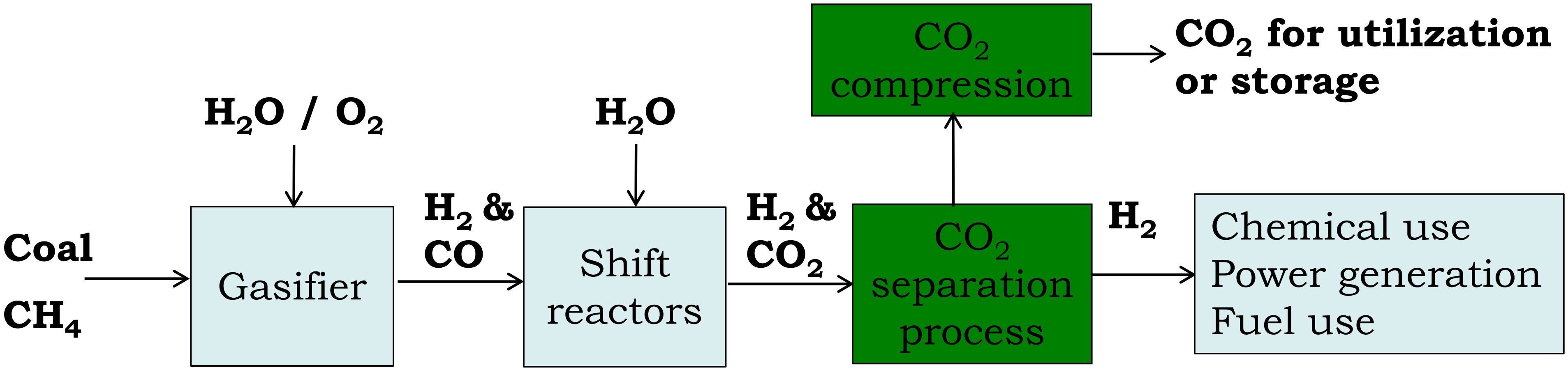
CO_2 Capture from Power Plants: 30% Reduction in CO_2 Emissions



(Coal & natural gas)

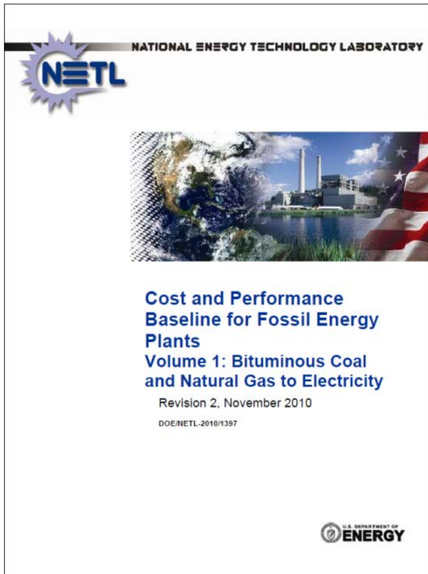
The U.S. DOE NETL

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


NATIONAL ENERGY TECHNOLOGY LABORATORY

NETL

Cost and Performance Baseline for Fossil Energy Plants

Volume 1: Bituminous Coal and Natural Gas to Electricity

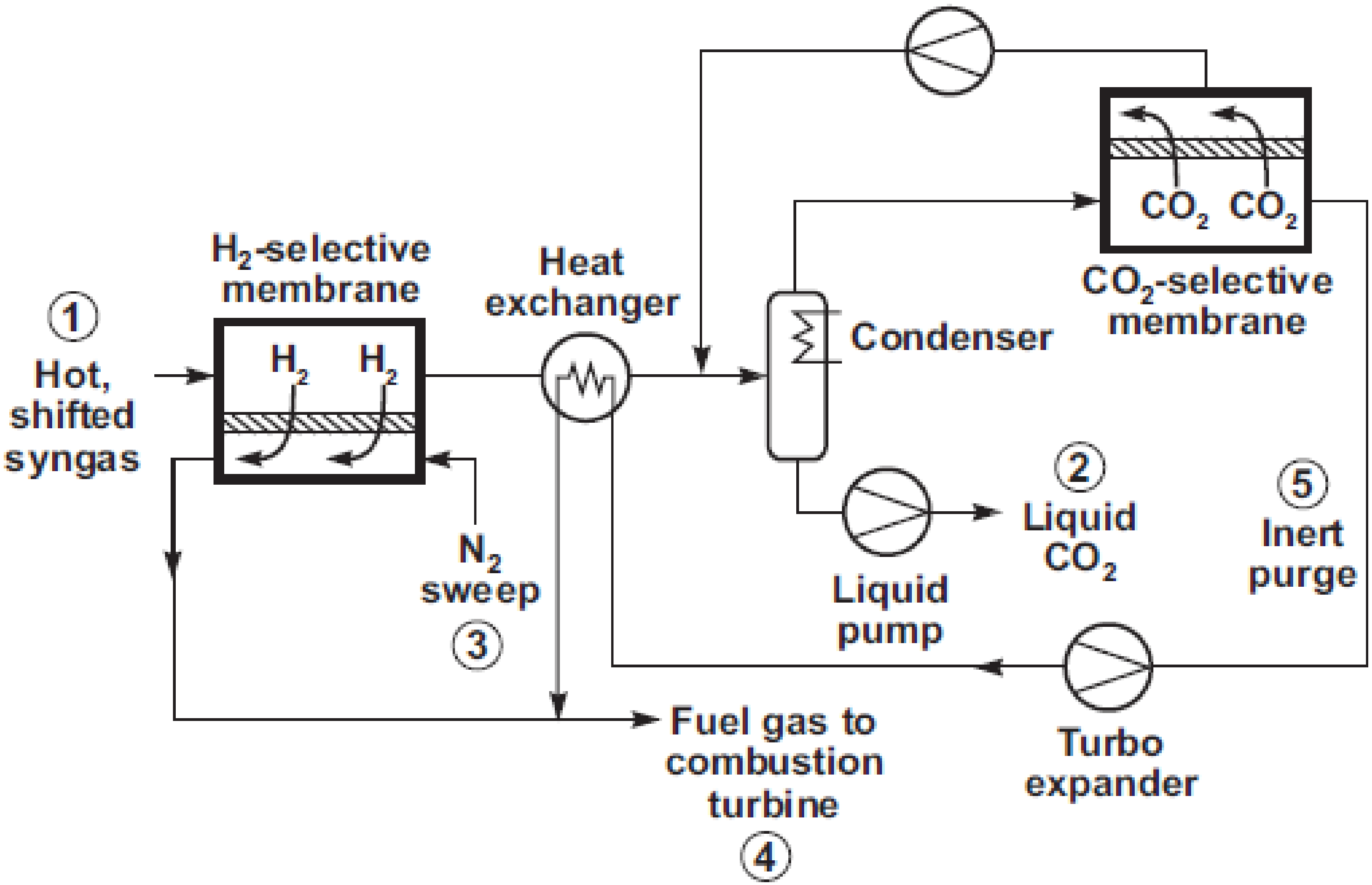
Revision 2, November 2010

DOE/NETL-2010/1397

ENERGY

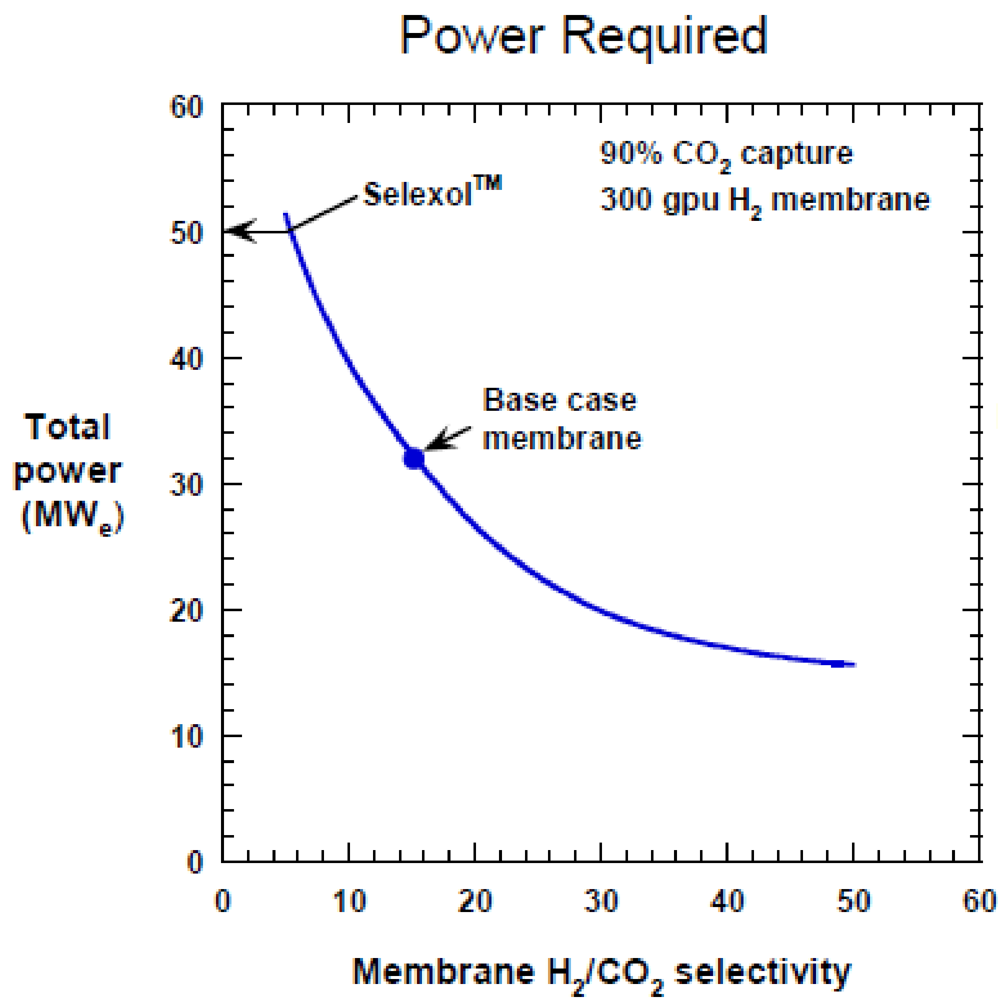
Lower cost and more energy efficient separation technology is needed.

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

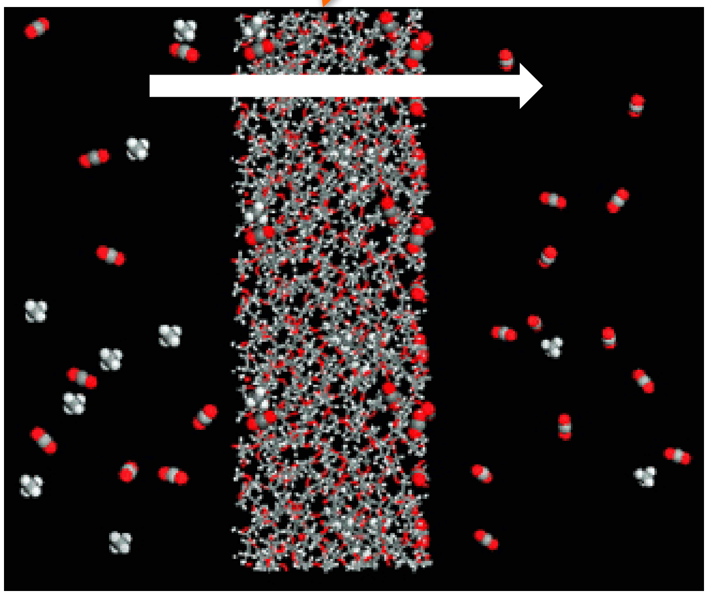


Merkel, Zhou and Baker, J. Membr. Sci., 389, 442 (2012)
Merkel, et al., NETL CO_2 Capture Technology Meeting, 2011.

Membrane: Energy Efficient Separation

Membrane

High pressure up-stream



Low pressure down-stream

$$P_A = \frac{N_A}{A_m(\Delta p_A / l)}$$

$$P_A = S_A \times D_A$$

solubility selectivity

$$\alpha_{A/B} = \frac{P_A}{P_B} = \left(\frac{S_A}{S_B}\right) \times \left(\frac{D_A}{D_B}\right)$$

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)
Simulation prepared by Dr. Xiaoyan Wang

Membrane Permeation Unit

Permeability: material intrinsic property

$$P_A = \frac{N_A}{A_m(\Delta p_A / l)}$$

1 Barrer = 10^{-10} cm^3(STP) cm/cm^2 s cmHg

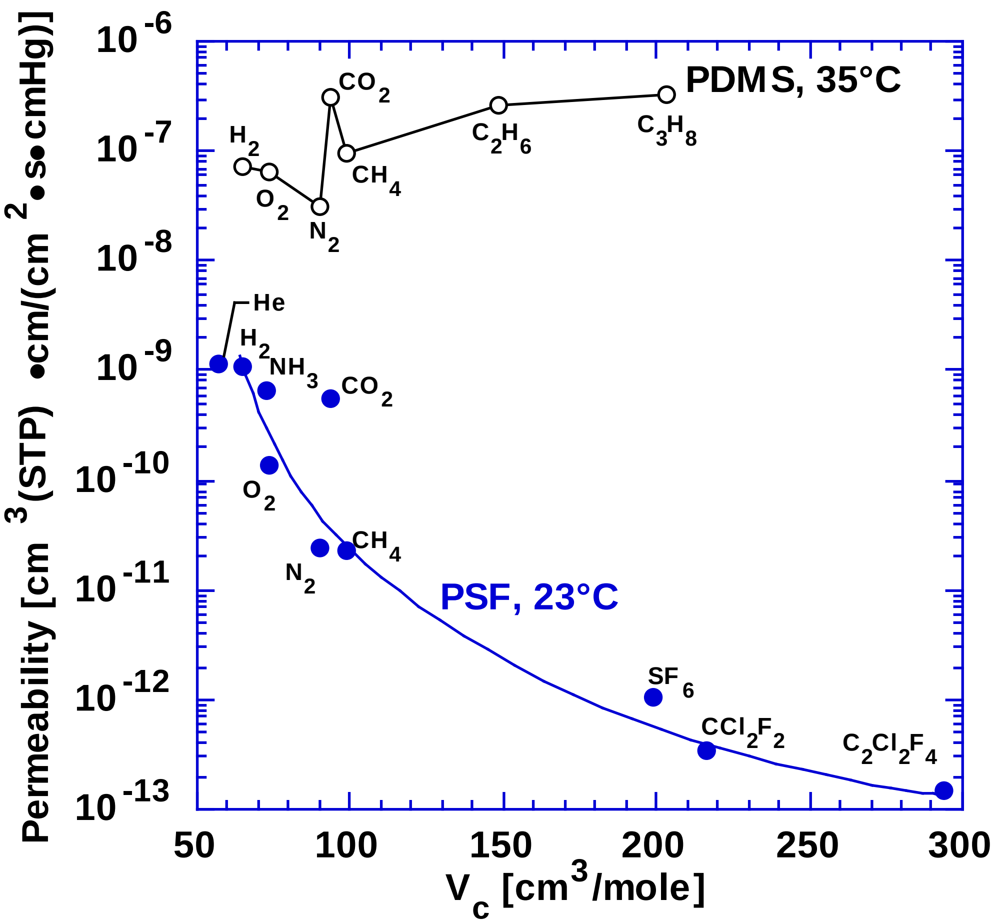
Permeance: thin film property

$$\frac{P_A}{l} = \frac{N_A}{A_m \Delta p_A}$$

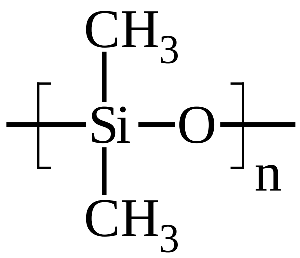
1 gpu = 10^{-6} cm^3(STP)/cm^2 s cmHg

50 Barrers
0.1 μm → **500 gpu**

Tailoring Polymer Structure for Targeted Separation Properties



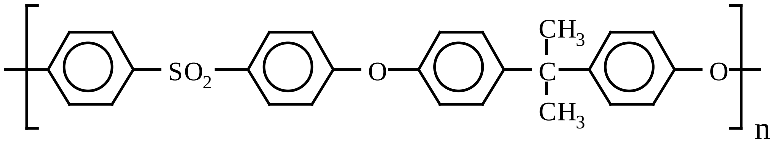
PDMS:



flexible, rubbery polymer

T_g= - 123°C

PSF:



rigid, glassy polymer

T_g= + 186°C

H_2/CO_2 Separation: Opposed Solubility Selectivity and Diffusivity Selectivity

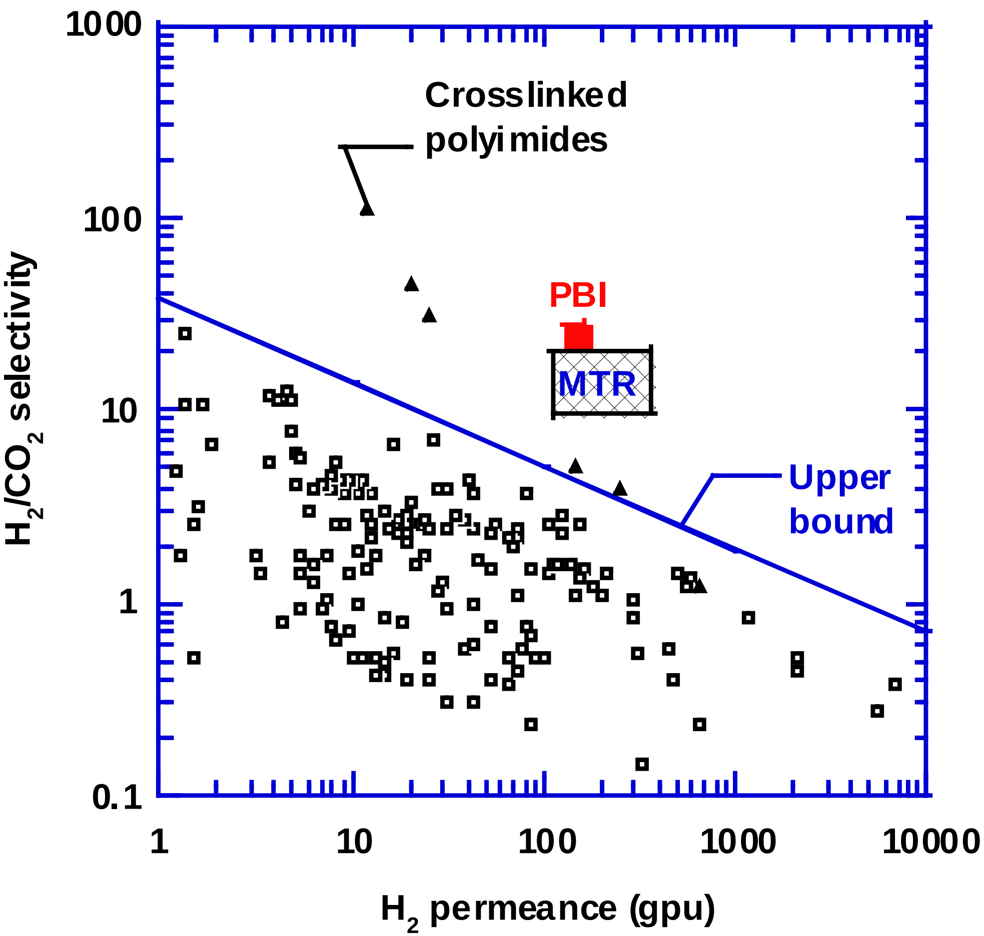
$$\alpha = \frac{P_{H_2}}{P_{CO_2}} = \frac{S_{H_2}}{S_{CO_2}} \times \frac{D_{H_2}}{D_{CO_2}}$$

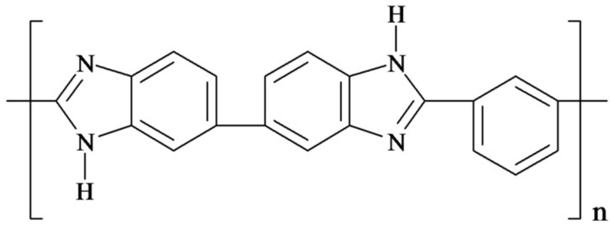
$$\frac{S_{H_2}}{S_{CO_2}} << 1 \quad \text{and} \quad \frac{D_{H_2}}{D_{CO_2}} >> 1$$

Penetrant	Condensability	Size
	Critical Temperature, K	Kinetic Diameter, Å
H_2	33	2.89
CO_2	304	3.3

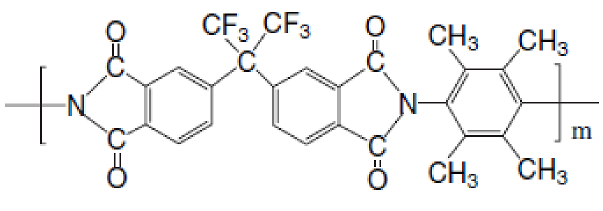
Polymer		P_{H_2} (Ba)	α_{H_2/CO_2}
Glassy	Polysulfone	14	2.5
	Poly(2,6-dimethyl phenylene oxide)	98	1.6
	Cellulose acetate	14	2.5
Rubbery	Cis-polyisoprene	54	0.4
	Poly(dimethylsiloxane)	800	0.2

State-of-Art Membrane Materials





Berchtold, et al., NETL CO_2 Capture Technology Meeting, 2015.
Jayaweera, et al., NETL CO_2 Capture Technology Meeting, 2015.



L. Shao,et al., J. Membr. Sci., 256 (2005) 46-56.

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

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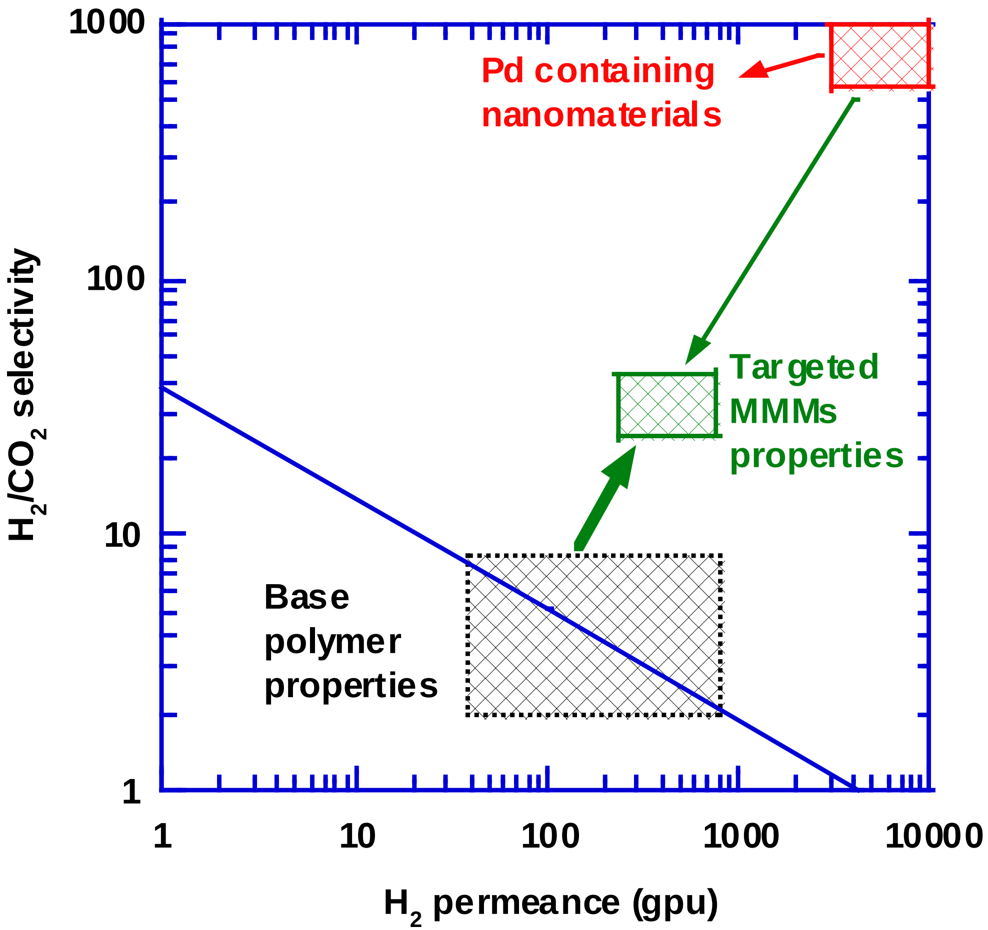
H_2/CO_2 Solubility Selectivity

$$\alpha = \frac{P_{H_2}}{P_{CO_2}} = \frac{S_{H_2}}{S_{CO_2}} \times \frac{D_{H_2}}{D_{CO_2}}$$

Materials	Temp. (ºC)	H_2 solubility $cm^3(STP)/(cm^3 atm)$	H_2/CO_2 solubility selectivity
Poly(dimethyl siloxane)	35	0.10	0.078
Polysulfone	35	0.075	0.036
Matrimid®	35	0.12	0.035
Teflon AF2400	35	0.21	0.13
Poly(1-(trimethyl-silyl) propine) (PTMSP)	35	0.40	0.11
Pd metal*	**25**	**38,000**	**> 1,000**

1 $cm^3(STP)/(cm^3$ atm) = 0.009 wt.% for H_2 at 1 atm

Our Approach: Mixed Matrix Materials



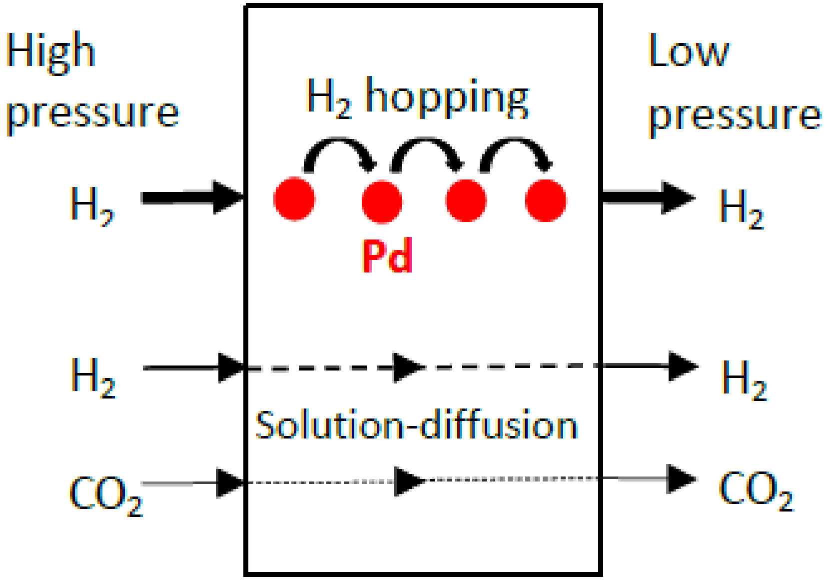
Crosslinked polymers:

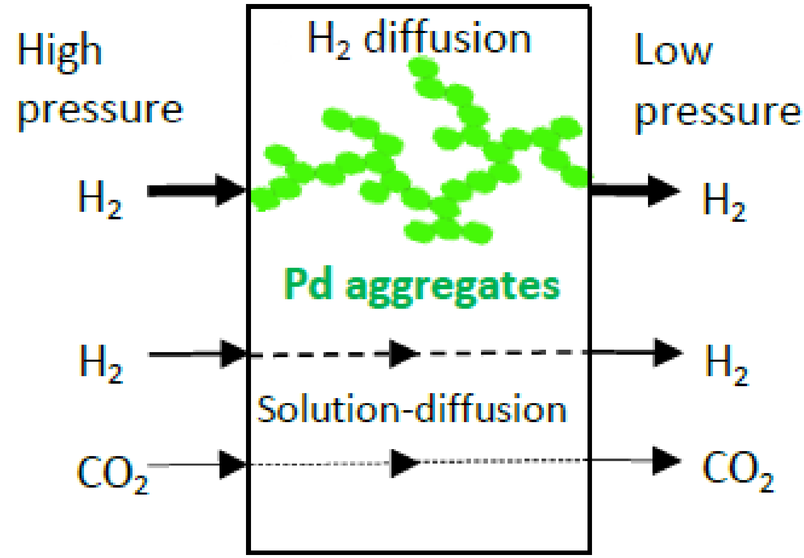
- Thermally stable
- Size sieving

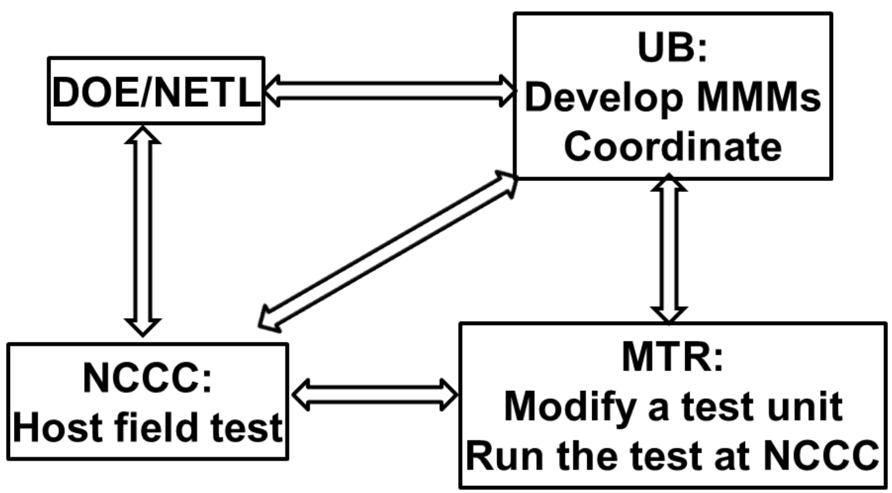
Pd-based nanoparticles:

- Dispersible
- Stable against sulfur components

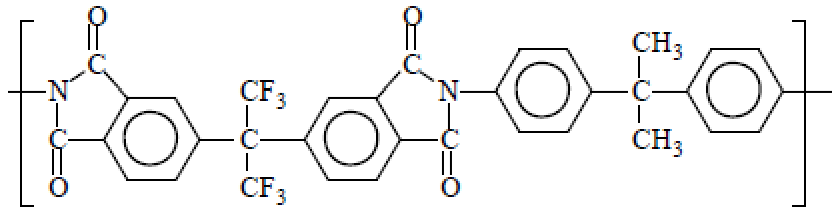
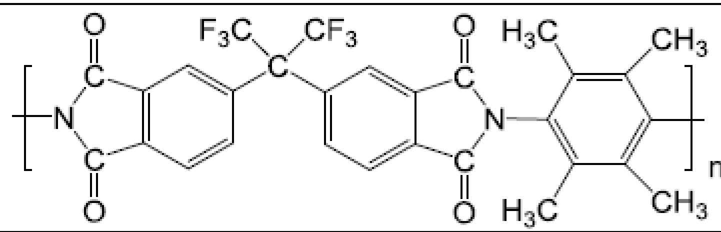
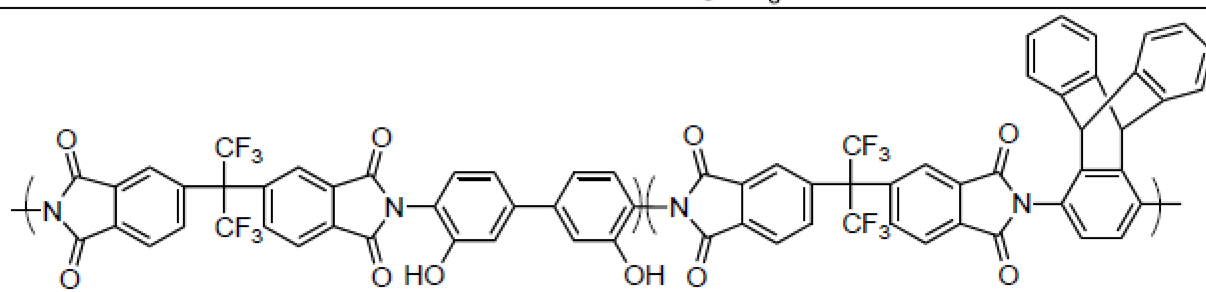
Facilitated Transport



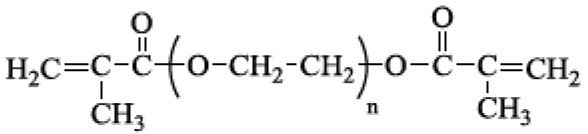
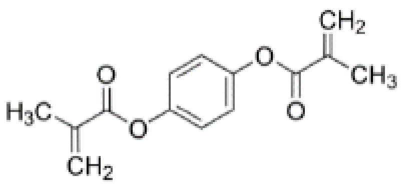
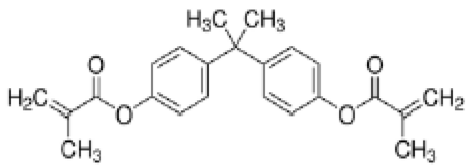
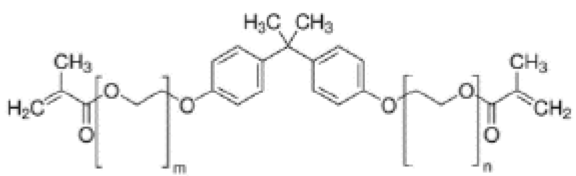
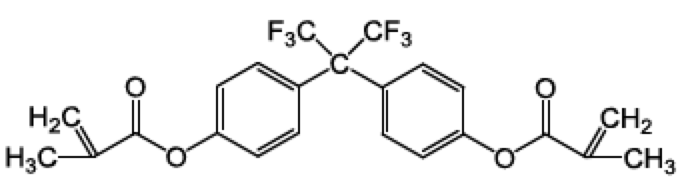




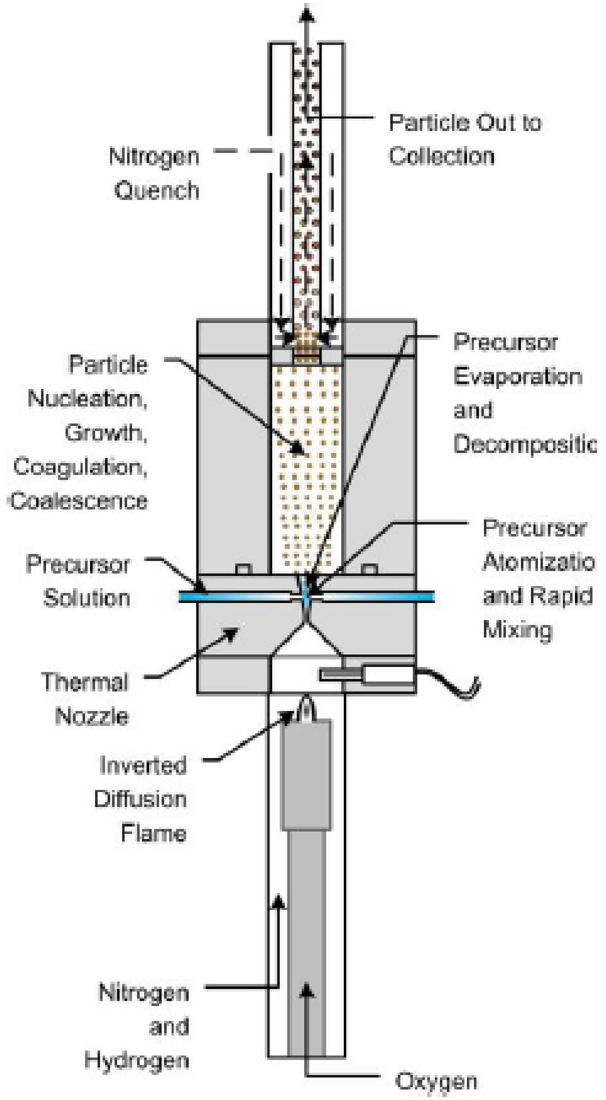
Polymers to Be Crosslinked

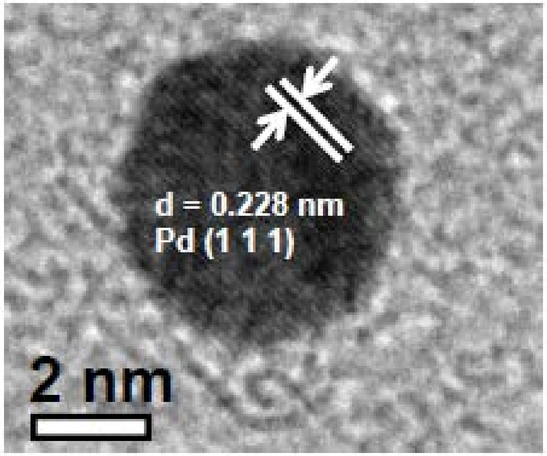
Polymer	Structure	Comments
6FDA-IPDA		Base polyimide showing good H_2/CO_2 selectivity after crosslinking
6FDA-Durene		More open structure achieving high H_2 permeability
6FDA-HAB-Triptycene copolyimide		More open structure achieving high H_2 permeability

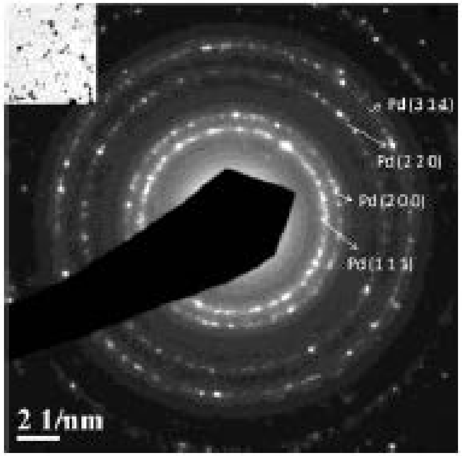
Crosslinkers

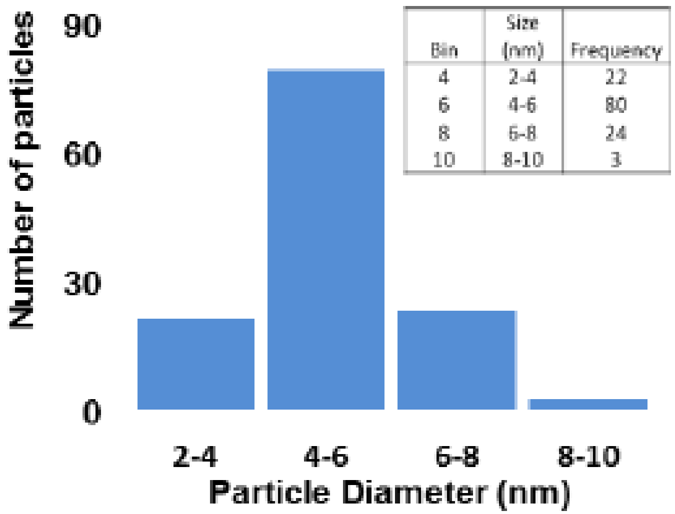
Abbreviation	Monomer	Structure	Comments
A1	poly(ethylene glycol) dimethacrylate		n = 1, 2, 3, 4, 5, 6, 10
B1	1,4-phenylene dimethacrylate		
B2	bisphenol A dimethacrylate		
B3	bisphenol A ethoxylate dimethacrylate		m, n = 2
B4	4,4-(hexafluoroisopropylidene) diphenylene methacrylate		

Pd-Based Nanoparticles

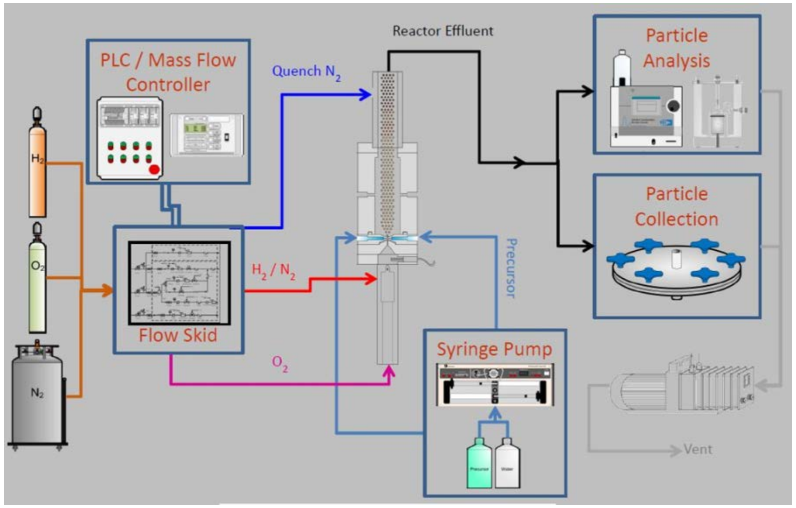


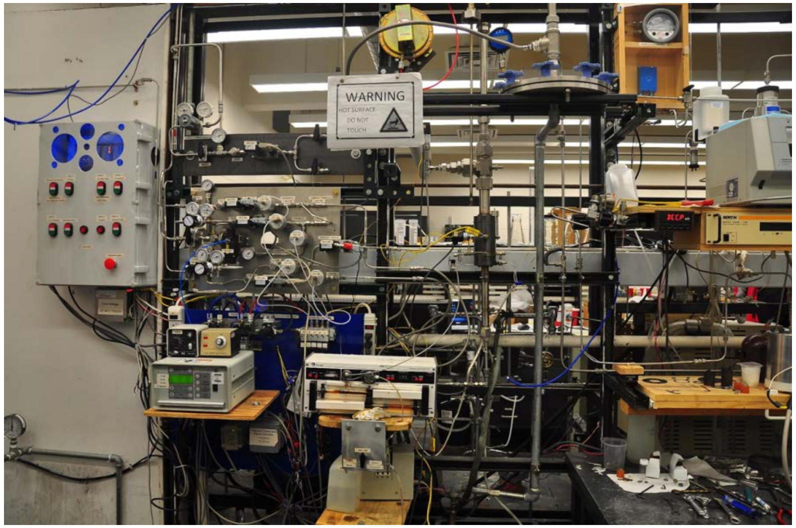


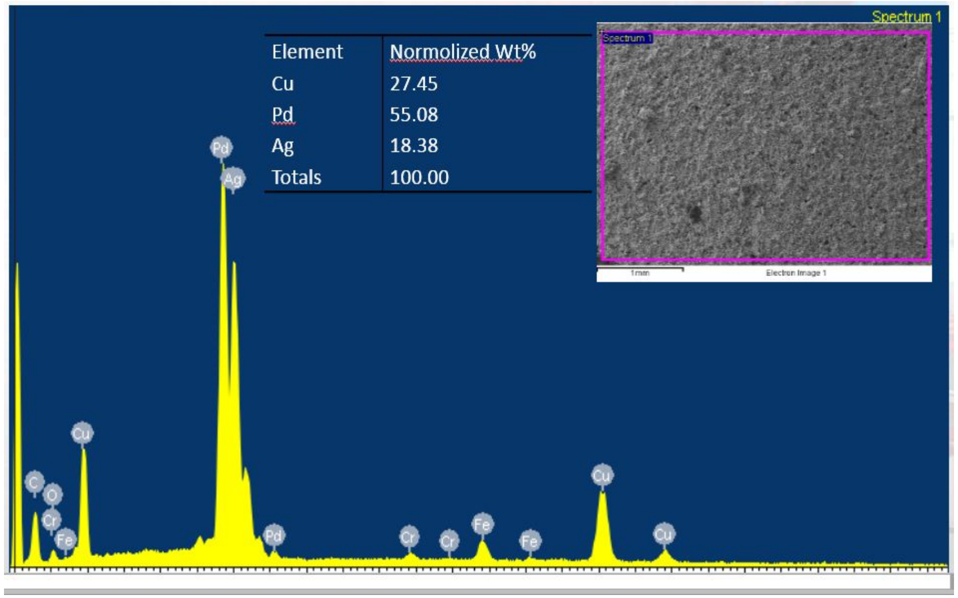




Pd Alloy Nanoparticles and Production Scale up

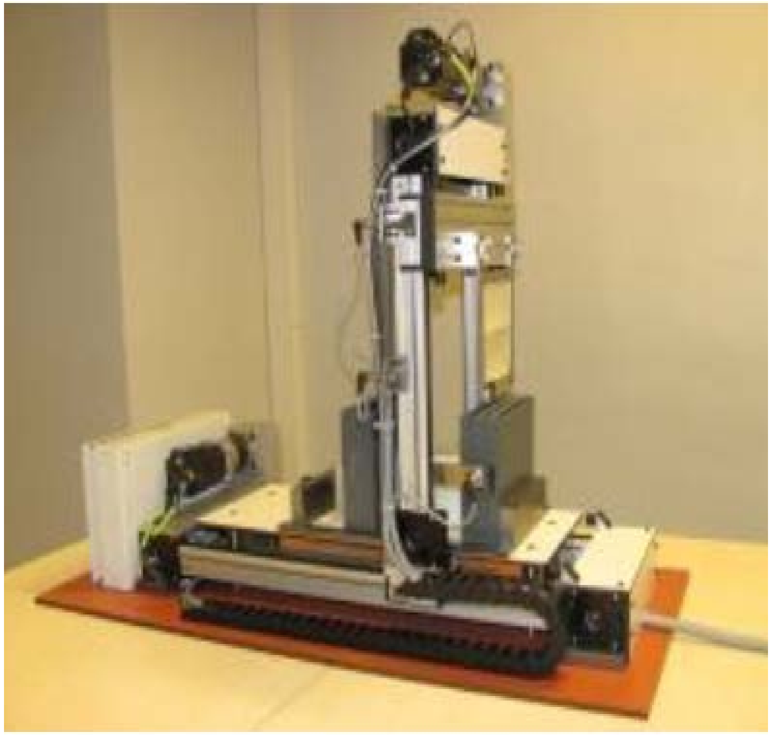




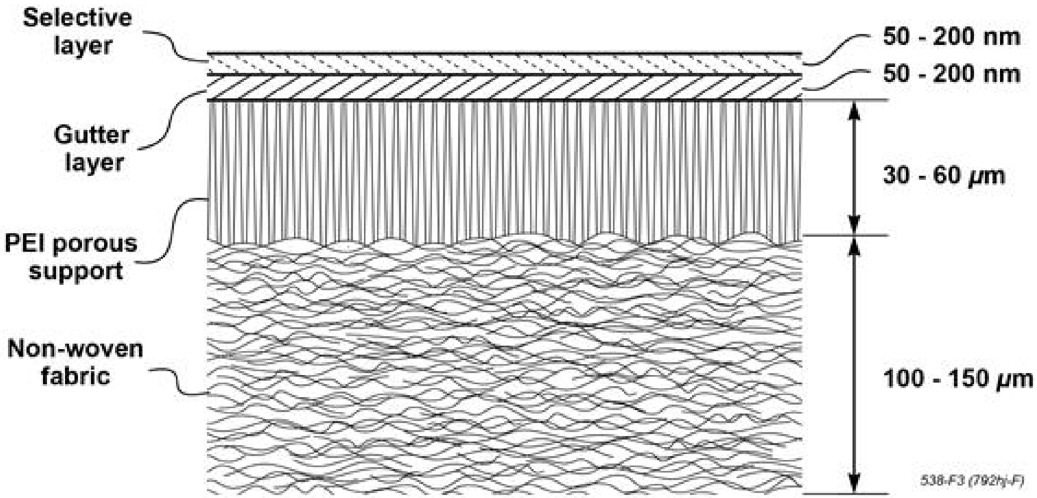


$Pd_{0.5}Ag_{0.2}Cu_{0.3}$ nanoparticles

Mixed Matrix Membranes



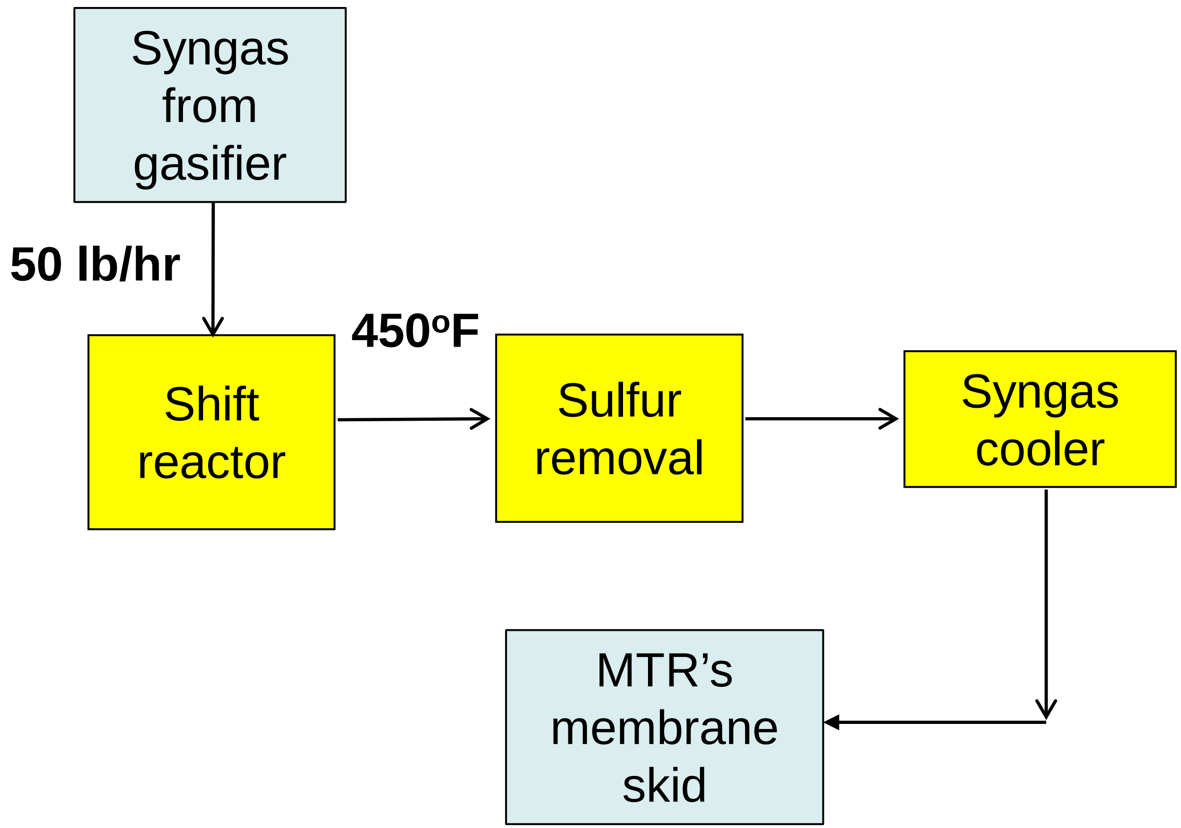
Automatic dip coater



Thin film composite membranes

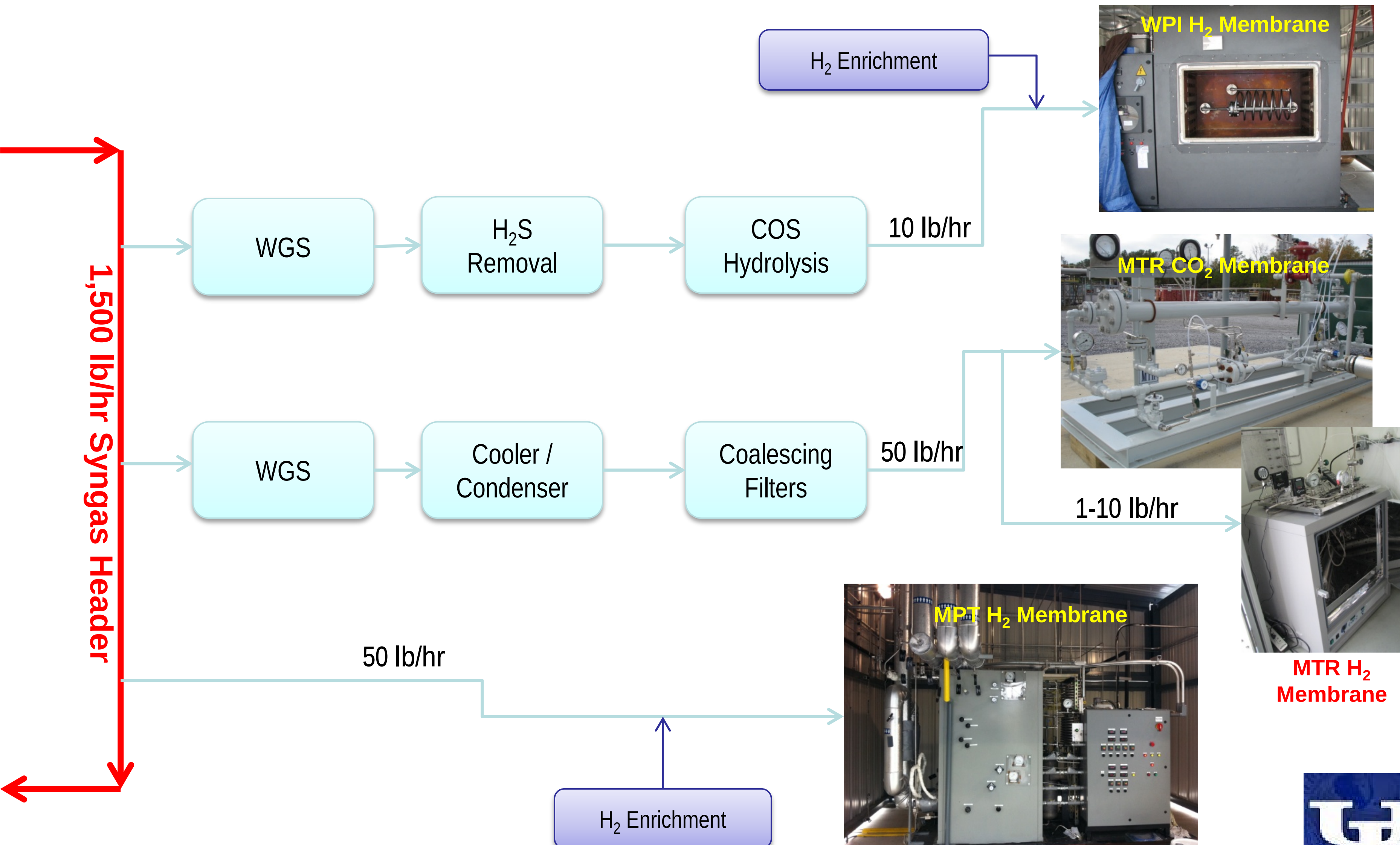
H. Lin *et al.*, *J. Membr. Sci.* 457, 149-161 (2014).

NCCC Syngas Pretreatment



Feed is coal-derived syngas at 150-200 psia, shifted or unshifted, with or without sulfur compounds

Membrane Test Configuration at NCCC



 Provided by Tony Wu at NCCC

Project Schedule and Milestones

Tasks	Start date	End date
Task 1. Project Management and Planning	10/1/15	9/30/18
Milestones a,b,c: SOPO finalized; kickoff meeting held; Final report submitted		
Task 2. Design and Synthesize High Temperature Polymers for H_2/CO_2 Separation	10/1/2015	6/30/2016
Task 3. Design, Synthesize, Functionalize, and Characterize Pd-based Nanomaterials	10/1/2015	6/30/2016
Task 4. Prepare and Characterize Mixed Matrix Materials	1/1/2016	9/30/2016
Task 5. Characterize H_2/CO_2 Separation Properties	1/1/2016	9/30/2016
Milestones d,e: Mixed matrix materials with superior H_2/CO_2 separation properties prepared		

Tasks	Start date	End date
Task 7 Scale up Polymer Synthesis	10/1/2016	3/31/2017
Task 8. Scale up Synthesis of Pd-based Nanomaterials	10/1/2016	3/31/2017
Task 9. Prepare Thin Film Composite Membranes	1/1/2017	9/30/2017
Task 10. Conduct Parametric Tests of Membranes for H_2/CO_2 Separation	1/1/2017	12/31/2017
Task 11. Design and Modify Membrane Stamp Test Unit for NCCC Field Test	6/1/2017	12/31/2017
Milestone f: Mixed matrix membranes with superior H_2/CO_2 separation properties prepared		
Task 13. Run One-Month Field Test at NCCC	1/1/2018	6/30/2018
Task 14. Analyze Field Test Results / Membrane Post-analysis	4/1/2018	9/30/2018
Milestone h: Successful field test completed		

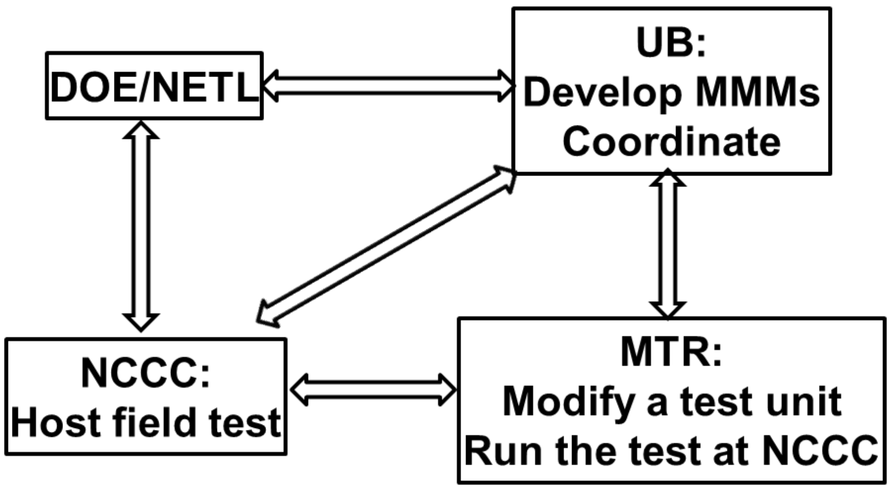
Project Milestones

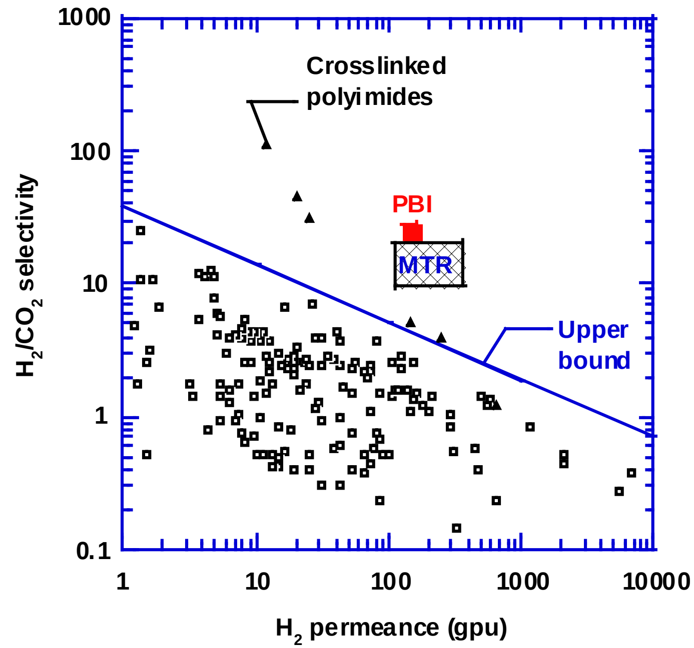
Budget Period	**ID**	**Description**	**Planned Completion Date**
1	**a**	**Updated Project Management Plan**	**11/30/15**
1	**b**	**Kickoff Meeting**	**12/31/15**
3	c	Final report	9/30/18
1	d	Polymers and nanomaterials with promising H_2/CO_2 separation properties identified and prepared	6/30/16
1	e	Mixed matrix materials with superior H_2/CO_2 separation properties prepared	9/30/16
2	f	Mixed matrix membranes with superior H_2/CO_2 separation properties	12/31/17
2	g	Field test unit modified	12/31/17
3	h	Successful field test	6/30/18

Risk Management

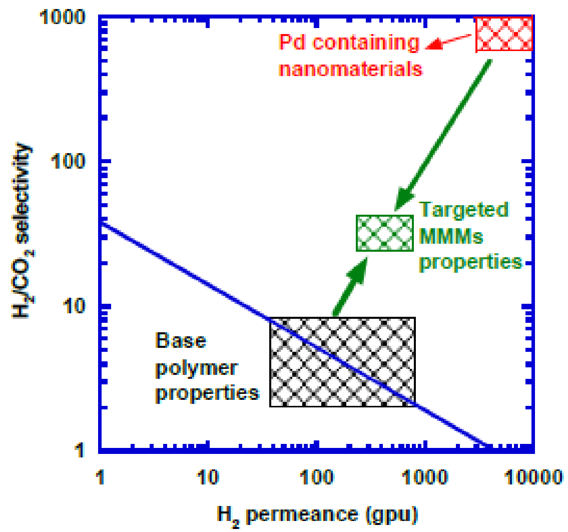
Description of Risk	Probability	Impact	Risk Management Mitigation and Response Strategies
Technical Risks:			
Membrane stability	Moderate	Moderate	Field test at NCCC to verify; process designs with pretreatment
Fabrication of thin film composite membranes	Low	Moderate	Acquire an advanced membrane dip coater; Support from MTR
Resource Risks:			
Recruit four PhD students	**Low**	**Moderate**	**Promote the project to new students; Promote existing MS students to PhD; Shift senior students to this project**
Management Risks:			
Capability to coordinate multi-organization effort	Low	Low	Regular meetings and phone conferences; Internal monthly reports

Summary





(a) Extraodinary separation property in Pd



(b) Tailoring Pd-based nanomaterials for H_2 sorption and diffusion