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Title: Membrane-Based Systems for Carbon Capture and Hydrogen Purification

Author(s): Kathryn A. Berchtold

Intended for: Presentation to Nanyang Technological University and National University of Singapore

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Membrane-Based Systems for Carbon Capture and Hydrogen Purification

This presentation describes the activities being conducted at Los Alamos National Laboratory to develop carbon capture technologies for power systems. This work is aimed at continued development and demonstration of a membrane based pre- and post-combustion carbon capture technology and separation schemes.

Our primary work entails the development and demonstration of an innovative membrane technology for pre-combustion capture of carbon dioxide that operates over a broad range of conditions relevant to the power industry while meeting the US DOE's Carbon Sequestration Program goals of 90% CO_2 capture at less than a 10% increase in the cost of energy services.

Separating and capturing carbon dioxide from mixed gas streams is a first and critical step in carbon sequestration. To be technically and economically viable, a successful separation method must be applicable to industrially relevant gas streams at realistic temperatures and pressures as well as be compatible with large gas volumes. Our project team is developing polymer membranes based on polybenzimidazole (PBI) chemistries that can purify hydrogen and capture CO_2 at industrially relevant temperatures. Our primary objectives are to develop and demonstrate polymer-based membrane chemistries, structures, deployment platforms, and sealing technologies that achieve the critical combination of high selectivity, high permeability, chemical stability, and mechanical stability all at elevated temperatures (>150 °C) and packaged in a scalable, economically viable, high area density system amenable to incorporation into an advanced Integrated Gasification Combined-Cycle (IGCC) plant for pre-combustion CO_2 capture. Stability requirements are focused on tolerance to the primary synthesis gas components and impurities at various locations in the IGCC process. Since the process stream compositions and conditions (temperature and pressure) vary throughout the IGCC process, the project is focused on the optimization of a technology that could be positioned upstream or downstream of one or more of the water-gas-shift reactors (WGSRs) or integrated with a WGSR.

Membrane-Based Systems for Carbon Capture and Hydrogen Purification

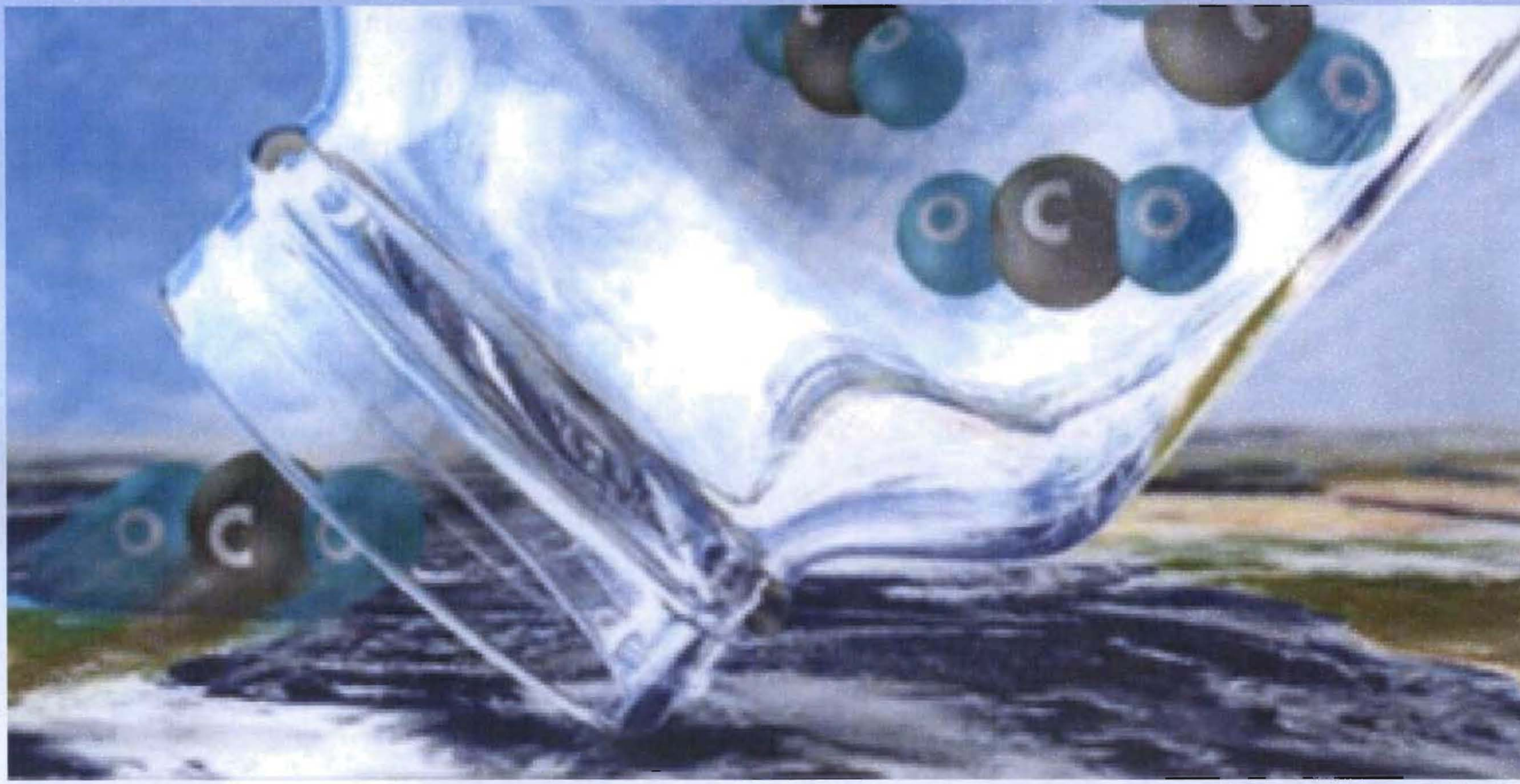

Photo Courtesy of EPRI Journal, Spring 2007

Kathryn A. Berchtold, Ph.D.

Project Leader, Separations, Membranes, CO_2 Capture

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Separation and Capture – A Necessary Step in Sequestration

- Before CO_2 can be sequestered from power plants and other large point sources, it must be captured
  - Post-Combustion Capture
    - Flue gas separations
    - Low driving force (atm pressure, low concentration)
    - Applicable to existing plant fleet
  - Pre-Combustion Capture
    - Synthesis gas separations
    - Higher Driving Force (pressure/concentration)
    - Opportunities for process intensification
      - CO_2 Capture combined with reduction of other pollutant emissions
      - Advanced Shift/Separation Reactors
    - Feasible for new plant designs
  - CO_2 capture is estimated to represent ¾ of the total cost of carbon sequestration (capture, storage, transport, sequestration)

LANL Gas Separations/Carbon Capture R&D

- Membrane-Based Separations
  - Polymeric, ceramic, metallic, facilitated transport, hybrids and processes to take full advantage of those materials
- Membrane Distillation – capillary condensation
- Ionic Liquid-Based CO_2 Sorbents & Membranes
  - Development of engineered systems based on thermally and chemically stable ILs with high CO_2 capacity and selectivity and low regeneration requirements
- Novel Sorbent Development
- Acoustically Driven Gas Separations
- Low Temperature CO_2 Hydrate-Based Process
  - CO_2 removal from shifted-synthesis gas via formation of clathrate-hydrate inclusion compounds
- Hybrid Separation Approaches

Membrane-Based Gas Separations/Carbon Capture R&D

- **High Temperature Polymer-Based Membrane Systems for Pre-Combustion Carbon Dioxide Capture**
  (DOE FE Sequestration, DOE FE Fuels, DOE EERE Industrial Technologies)
  - Rational Design, Synthesis, and Development of Selective Barrier Materials and Processes to Take Full Advantage of Those Materials

PBI PERFORMANCE PRODUCTS, INC
UMKC UNIVERSITY OF MISSOURI-KANSAS CITY
NETL
bp
whitefox
SOUTHERN COMPANY
UNIVERSITY OF SOUTH CAROLINA
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PALL
ENERFEX
SRI International
Visage ENERGY CORP.

- **Immobilized Ionic Liquid-Based CO_2 Membranes for Post-Combustion Carbon Dioxide Capture** (DOE-ARPA-E)
  - Development of engineered memebrane systems based on thermally and chemically stable gelled-RTIL and RTIL/poly(RTIL) composites with unprecedented CO_2 permeance

arpa·e
Colorado University of Colorado at Boulder
EPRI ELECTRIC POWER RESEARCH INSTITUTE
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- **Membrane Inclusive Hybrid Separation Approaches for Pre- & Post- Combustion CO_2 Capture**
  (DOE U.S. China Clean Energy Research Center)

US–China Advanced Coal Technologies Consortium:
Clean-Coal Technologies

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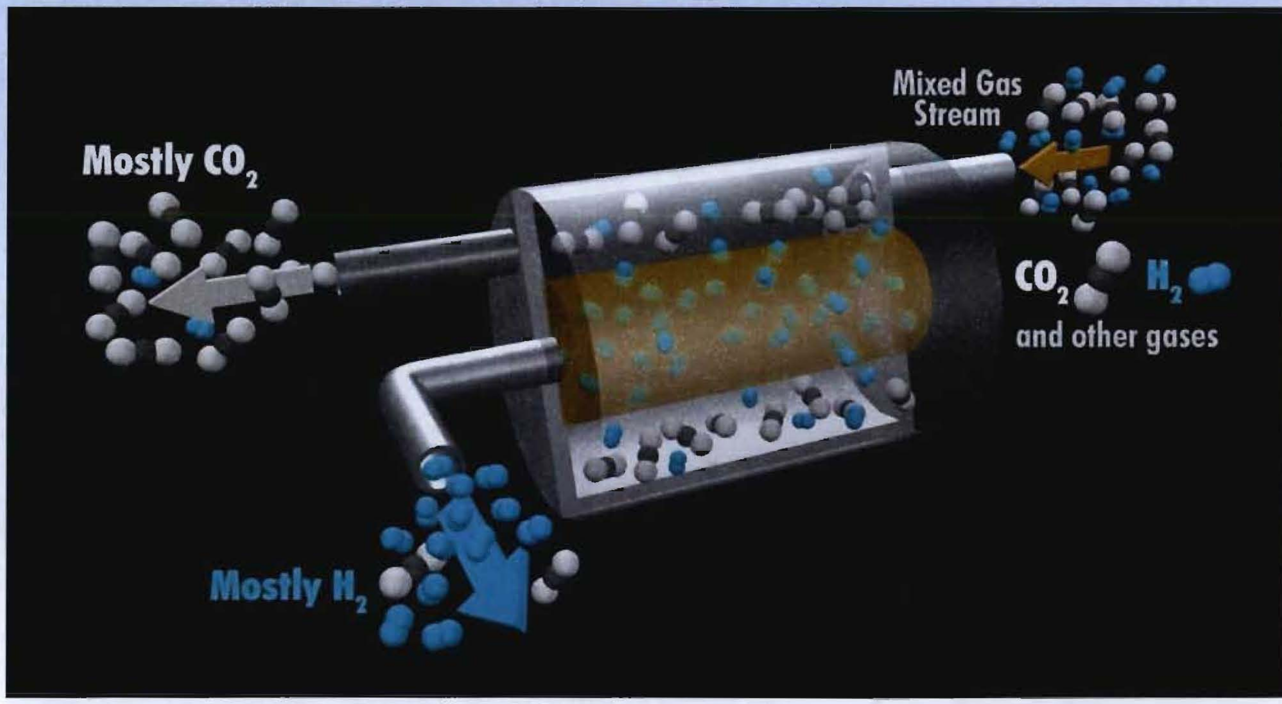
Challenges/Opportunities

- Design, control, prediction, and synthesis of tailored material morphologies, free volume architectures, & chemistries
- Understanding and utilization of structure-property relationships over multiple length scales
- Overcoming temperature, selectivity, productivity, chemical resistance, durability, and economic limitations of the state-of-the-art

Molecule	Kinetic Diameter (Å)	Diameter Ratio (X/H_2)
He	2.60	0.90
H_2O	2.65	0.92
H_2	2.89	1.00
NO	3.17	1.10
CO_2	3.30	1.14
Ar	3.40	1.18
O_2	3.46	1.20
H_2S	3.52	1.22
N_2	3.64	1.26
CO	3.76	1.30
CH_4	3.80	1.31

- Understanding and optimization of mass transfer coupled with heat transfer and mechanical response
- Scale-up from laboratory measurements to field behavior (including changes in impurities, operating conditions, and time scales)
- Systems integration and optimization

Polymer-Based Membrane Systems for Pre-Combustion CO_2 Capture at Elevated Temperatures



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Separation and Capture – National Needs/Membrane Opportunities

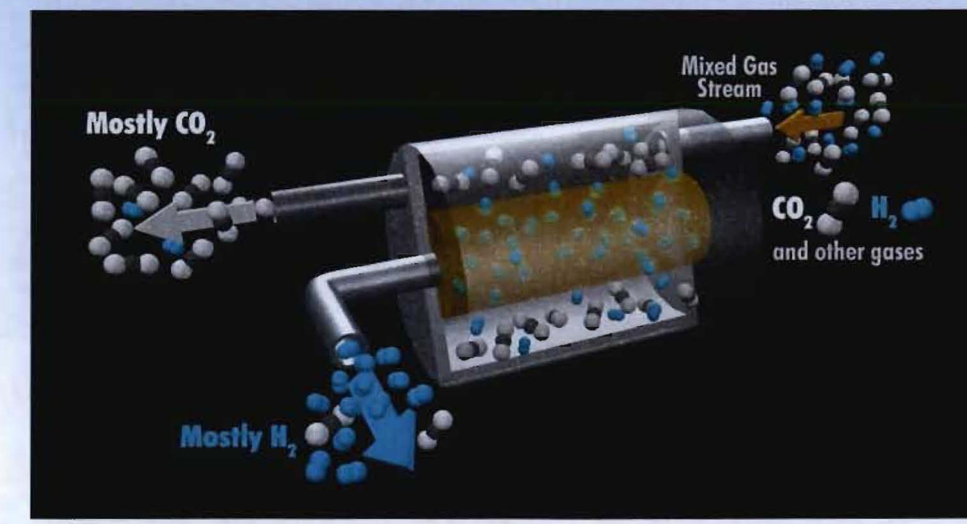
- High Temperature Membranes are in Great Demand…
  - Membrane reactors, Synthesis gas separations (Power systems, IGCC, Gas-To-Liquids, Hydrogen production, Fuels & chemicals processing and Production), Fuel cells (Reforming – Centralized, Distributed)
    - Gasification derived syn-gas:
      H_2-based fuel gas for power, fuels, or chemicals production
      Captured CO_2 for sequestration or EOR
  - Alternative technologies (PSA, TSA, adsorption, absorption, cryogenic separation) have drawbacks (Selexol-benchmark design for IGCC)
    - Energy intensive
    - Produce CO_2 at atmospheric pressure
    - Low temperature processes
    - Can be high maintenance and cost (capital and operating) compared to membrane technology
- But are in Short Supply – Materials
  - Existing membrane materials have limiting temperatures, selectivity, productivity, chemical resistance, material properties

Overarching Objectives

Produce a high temperature membranes, modules, and processes for *synthesis gas separations.*

Develop a comprehensive understanding of how to manipulate and control permselectivity and processability in high T_g polymers.

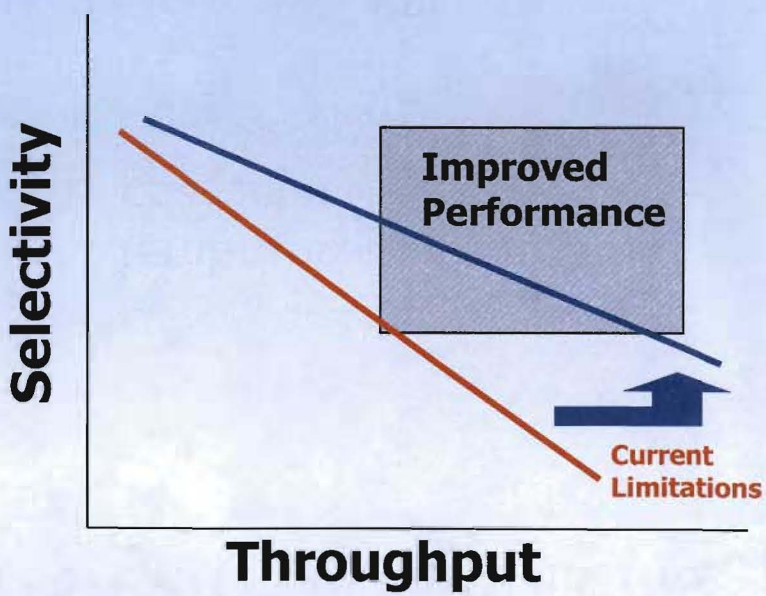
- Temperature Stability
- Chemical Stability
- Mechanical Stability



- Industrially Attractive Separation Characteristics

High T_g Polymeric Membranes

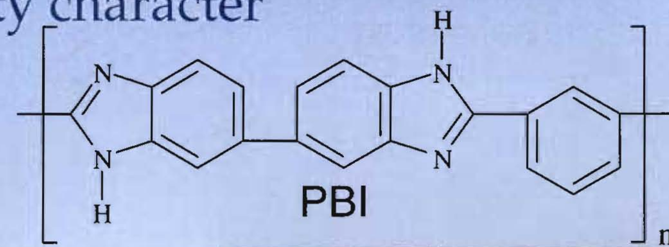
- **Commercially available polymer membranes are limited to 150 °C operating temperature**
  - Economic advantages of membrane separations are strongly tied to process/separation temperature
- **Tradeoff between selectivity and productivity has proven difficult to overcome**
  - Key U.S. DOE Program Goals
    - >90% CO_2 Capture
    - <10% increase in COE
- **Chemical & mechanical stability and durability are often elusive**
  - **Commercial Viability Driven by Combination**

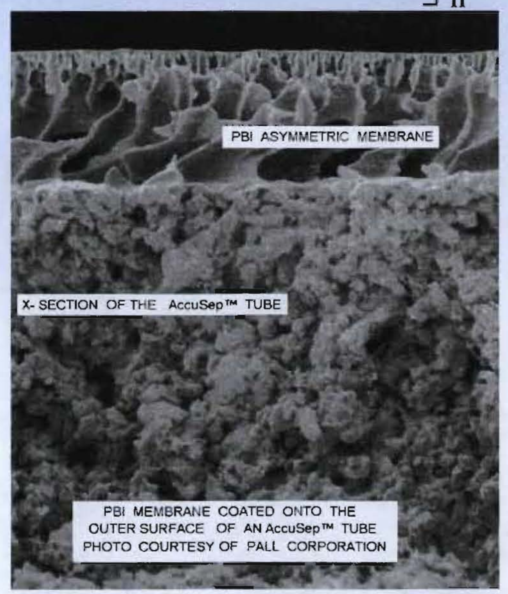


Overview

➤ Efforts Focused on Gasification-Derived Syn-Gas

- H_2 Purification & Pre-combustion CO_2 Capture
  - Higher Driving Force (Pressure/Concentration)
  - Opportunities for Process Intensification
- Focused on Development of High T_g (Polybenzimidazole (PBI)-based Polymeric Membranes with tailored chemistry, morphology, and permselectivity character
  - Thermally stable (T_g ~ 450-500 °C)
    - Facilitates process integration $T_{operation}$ up to ~400 °C
  - Mechanically Stable
  - Chemically resistant
    - Sulfur tolerant at operation temperatures
  - Processable



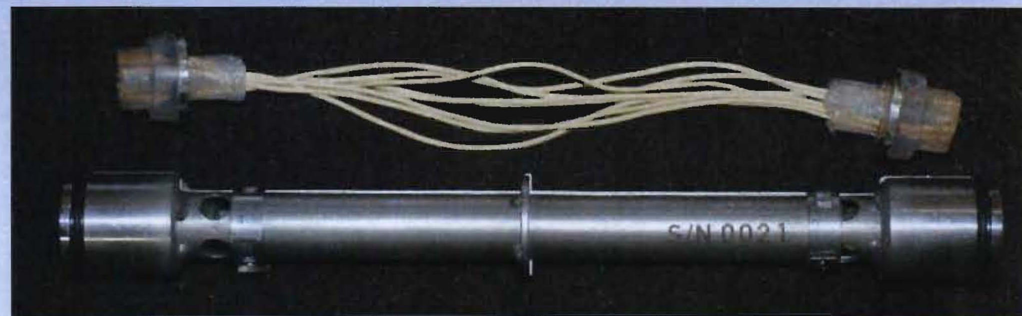


- Development of a fundamental understanding of how to manipulate and control the free-volume architecture of the selective layer
- Critical Evaluation of Developed Materials at Industrially Relevant Process Conditions
- Systems Integration Efforts to Optimize % CO_2 Capture and Minimize Cost

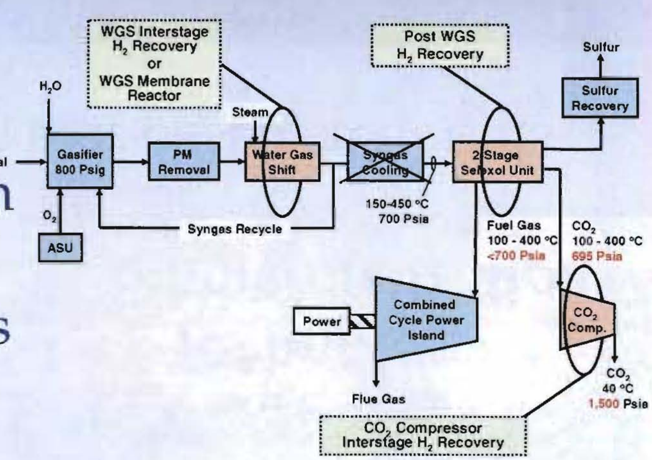
Development Pathways

I. ↕ II. → **Technically and Economically Viable Separation Technology** → **Technology Commercialization**

I. Draw from our existing work on High T_g polymer based-materials and polymer-composite module design



- Membrane Productivity Optimization
  - Selective layer deposition
  - Hollow fiber spinning
- Membrane & Module Design
  - Potting materials & methods
  - Membrane cartridge design
- In-Lab Testing/Demonstration/Validation
- Out-of-Lab Testing/Demonstration/Validation
- Strategic Selection of Partnerships/ Collaborations to Facilitate Continued Progress
- Systems Integration / Economic Analysis
  - Optimize %CO_2 Capture and Minimize Cost



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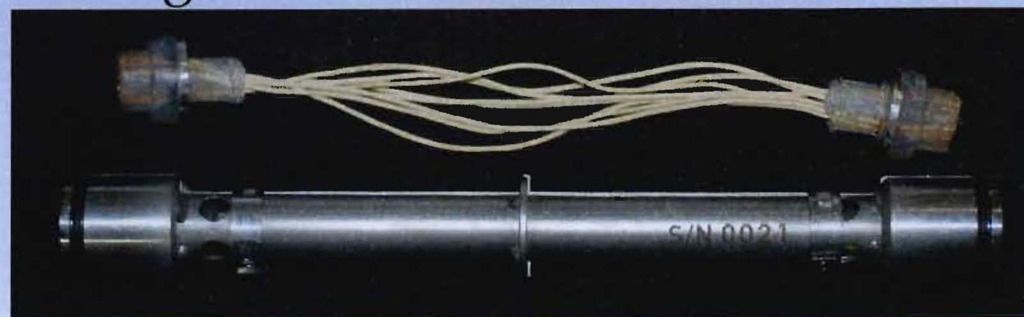

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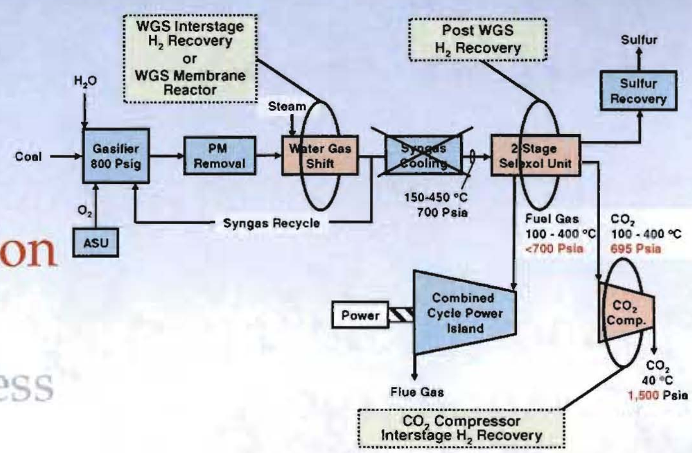


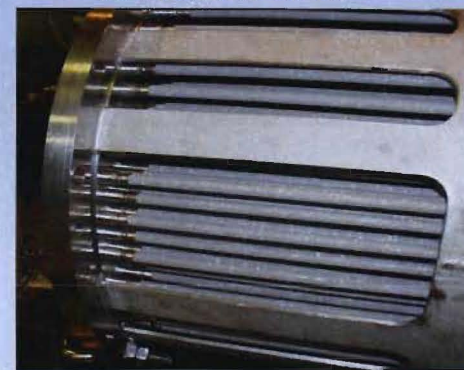
Scale-Up and Optimization: Transition to Hollow Fiber Platform

~0.5 cm²

~30-80 cm²

Hundreds of cm²

Hundreds of m²



- Design similar to heat exchanger
- ½″ OD x 96″ long tubes

~250 m²/m³ @
75% packing density

High Area Density Hollow Fiber Platform

Hundreds of cm²

2000 – 30,000+ m²/m³ @
75% or even lower packing densities

Gas Permeation Testing Capability

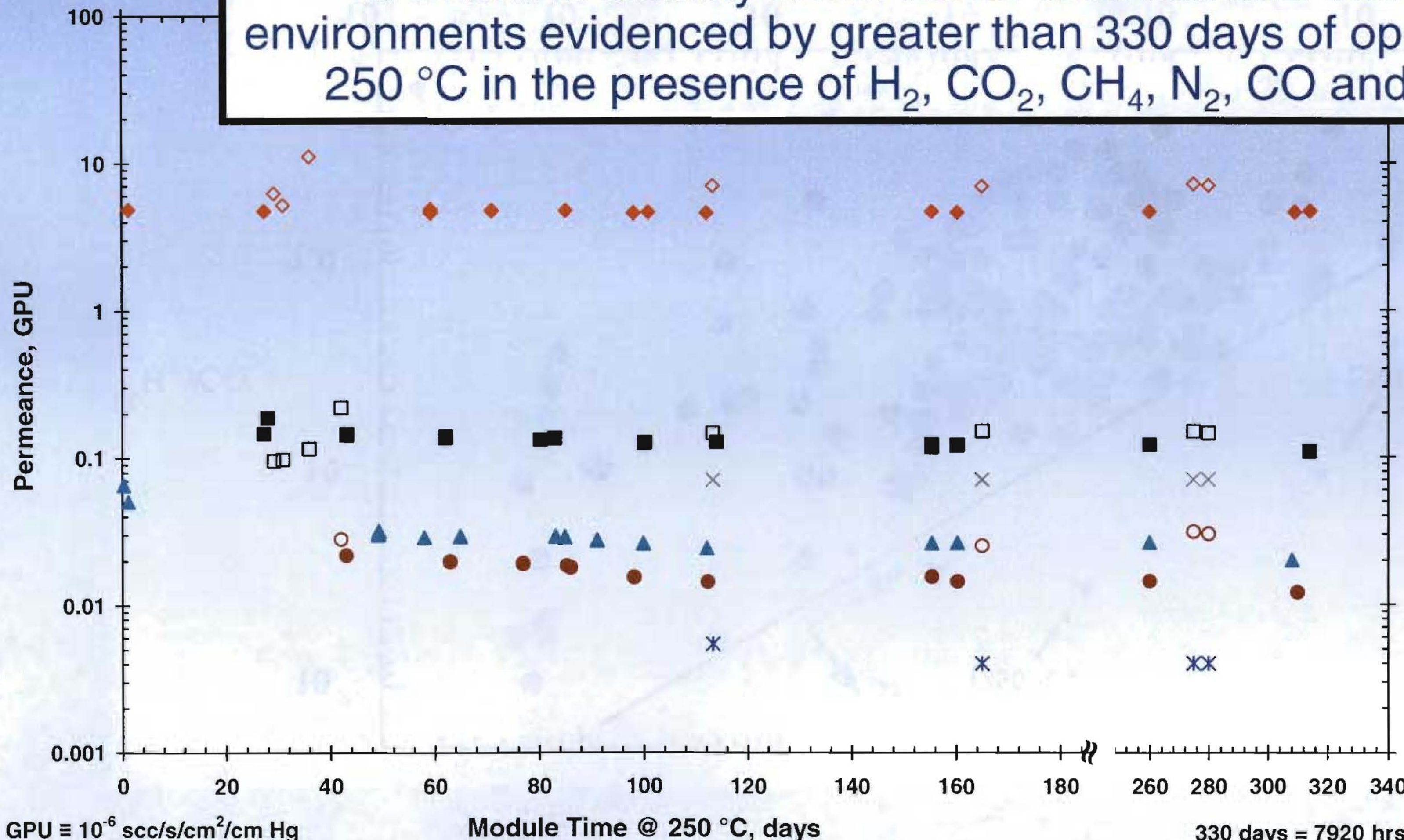
- Membrane Evaluation with Industrially Relevant Feedstocks at Industrially Relevant Temperatures
  - Membrane Testing Capabilities Over a Broad Temperature Range (ambient – 1000 °C)
  - Single Gas Testing (pressure rise and pressure decay)
  - Multi/Mixed Gas (flow through system)
  - Experimental testing on various size thin film disk and tubular membrane modules
  - Testing of Industrially Relevant Feed Streams (Inert, Flammable and Toxic gas capability – e.g., H_2, CO_2, CH_4, N_2, NO_x, SO_x, CO, H_2O and H_2S)
  - Fixturing and sealing for broad range of membrane materials (e.g., polymers, metals, ceramics) over a wide temperature range

Durability

Single Gas Experiments: ◆ H_2, ■ CO_2, ● CH_4, ▲ N_2

Mixed Gas Experiments: ◇ H_2, □ CO_2, ○ CH_4, △ N_2, × CO, ✳ H_2S

Membrane stability under harsh chemical and thermal environments evidenced by greater than 330 days of operation at 250 °C in the presence of H_2, CO_2, CH_4, N_2, CO and H_2S.



GPU ≡ 10^{-6} scc/s/cm^2/cm Hg

330 days = 7920 hrs

H_2S is at detection limit of our analytical equipment.
Thus, permeance is between the reported value and zero.

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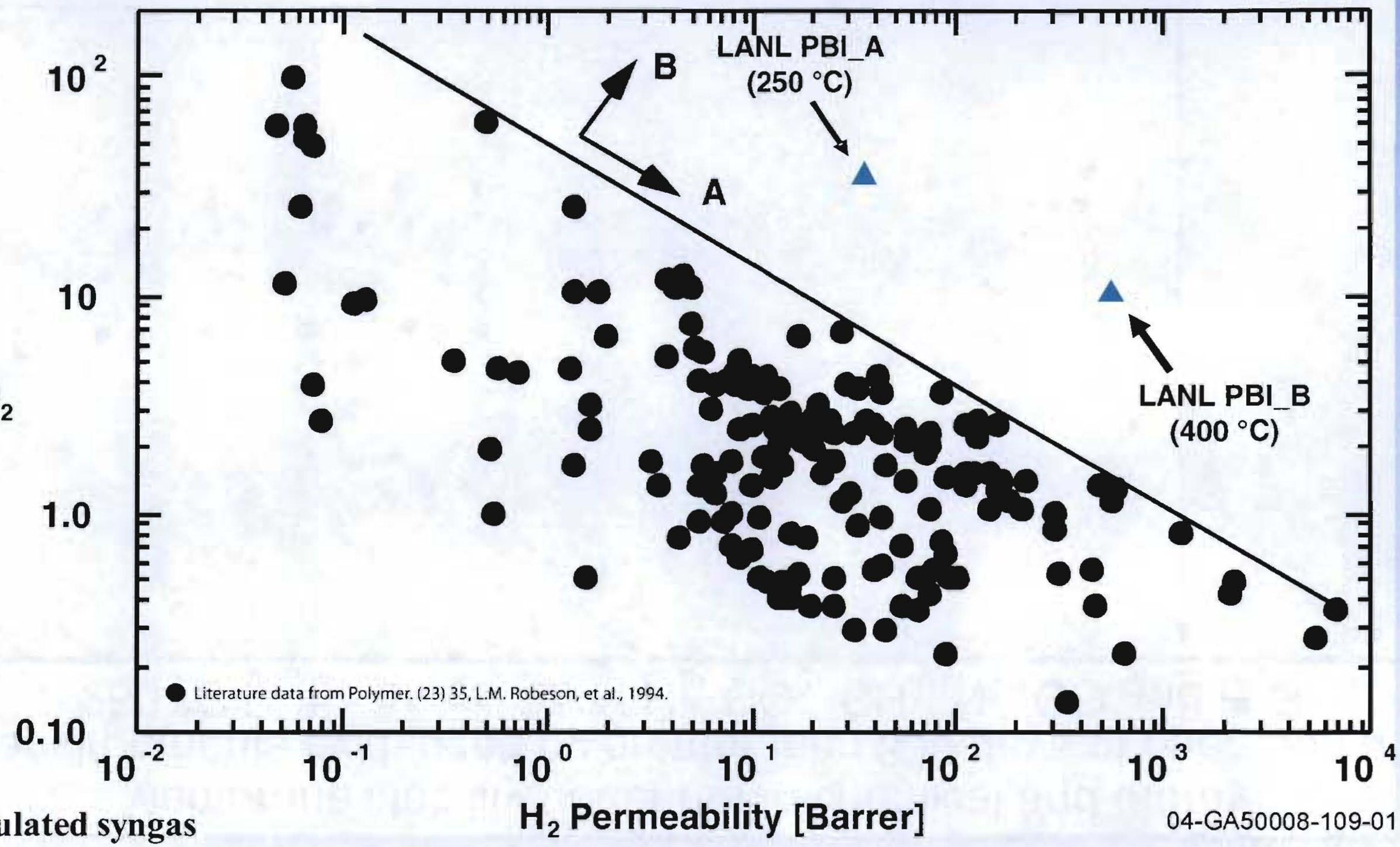
Selectivity vs. Permeability: H_2/CO_2



▲ = "wet" simulated syngas

We have demonstrated improved selectivity over the state-of-the-art while operating at industrially attractive conditions

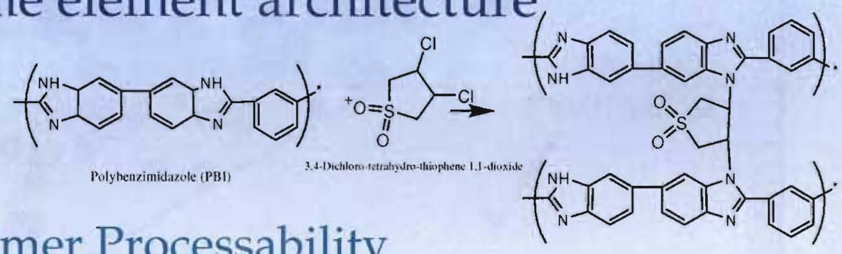
1 barrer = 10^{-10} cm^3-cm/s-cm^2-cmHg

Development Pathways

I. ↕ II. → **Technically and Economically Viable Separation Technology** → **Technology Commercialization**

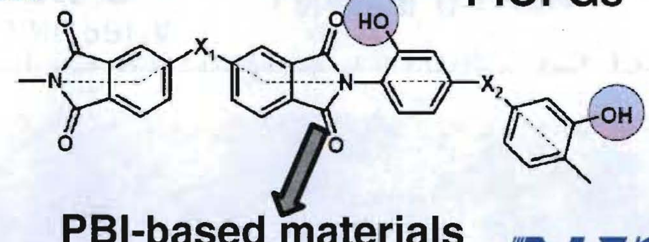
II. Rational Design, Synthesis, & Development of New (*and Improved*) PBI-based Selective Barrier Materials

- PBI-based Compounds
- Utilize chemical/physical/thermal manipulations to selectively tailor the molecular morphology and free volume element architecture
  - Enhanced Gas Separation Properties (H_2/CO_2 Selectivity, H_2 Flux)
  - Maintain or Improve Upon Chemical, Thermal, Mechanical Stability and Polymer Processability



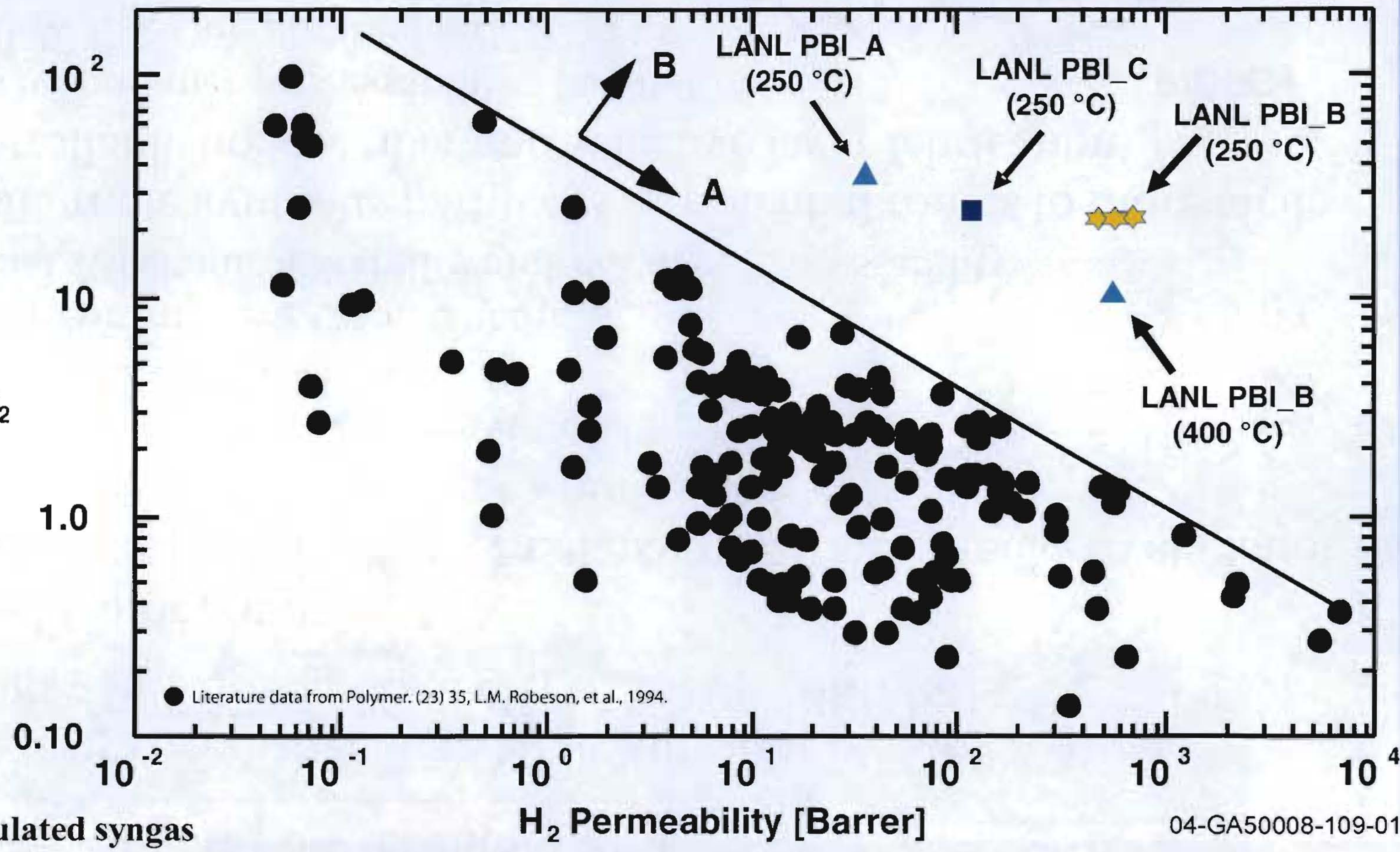
- Utilize alternate synthetic pathways as potential routes to more facile and controllable hollow fiber and selective layer fabrication
  - Focus on polymer processability; facilitation of hollow fiber membrane fabrication
  - Maintenance/Minimal degradation of Chemical, Thermal, Mechanical Stability

PIOFGs



PBI-based materials

Rational Design of New PBI-based Materials



▲ = "wet" simulated syngas

■ ★ = **PBI free-volume architecture manipulation leads to increased flux with minimal impact on selectivity**

We have demonstrated improved selectivity over the state-of-the-art while operating at industrially attractive conditions

1 barrer = 10^{-10} cm^3-cm/s-cm^2-cmHg

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Development Pathways

I. ↕ II. → **Technically and Economically Viable Separation Technology** → **Technology Commercialization**

I. Draw from our existing work on High T_g polymer based-materials and polymer-composite module design

- Membrane Productivity Optimization
  - Selective layer deposition
- Membrane & Module Design
  - Potting materials & methods
  - Membrane cartridge design
- In-Lab Testing/Demonstration/Validation
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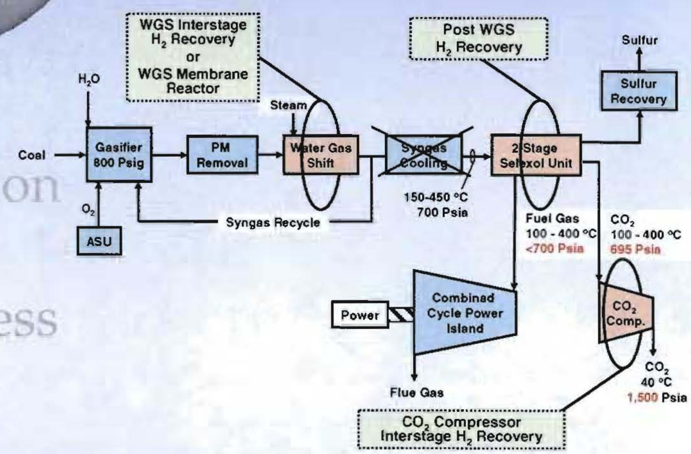
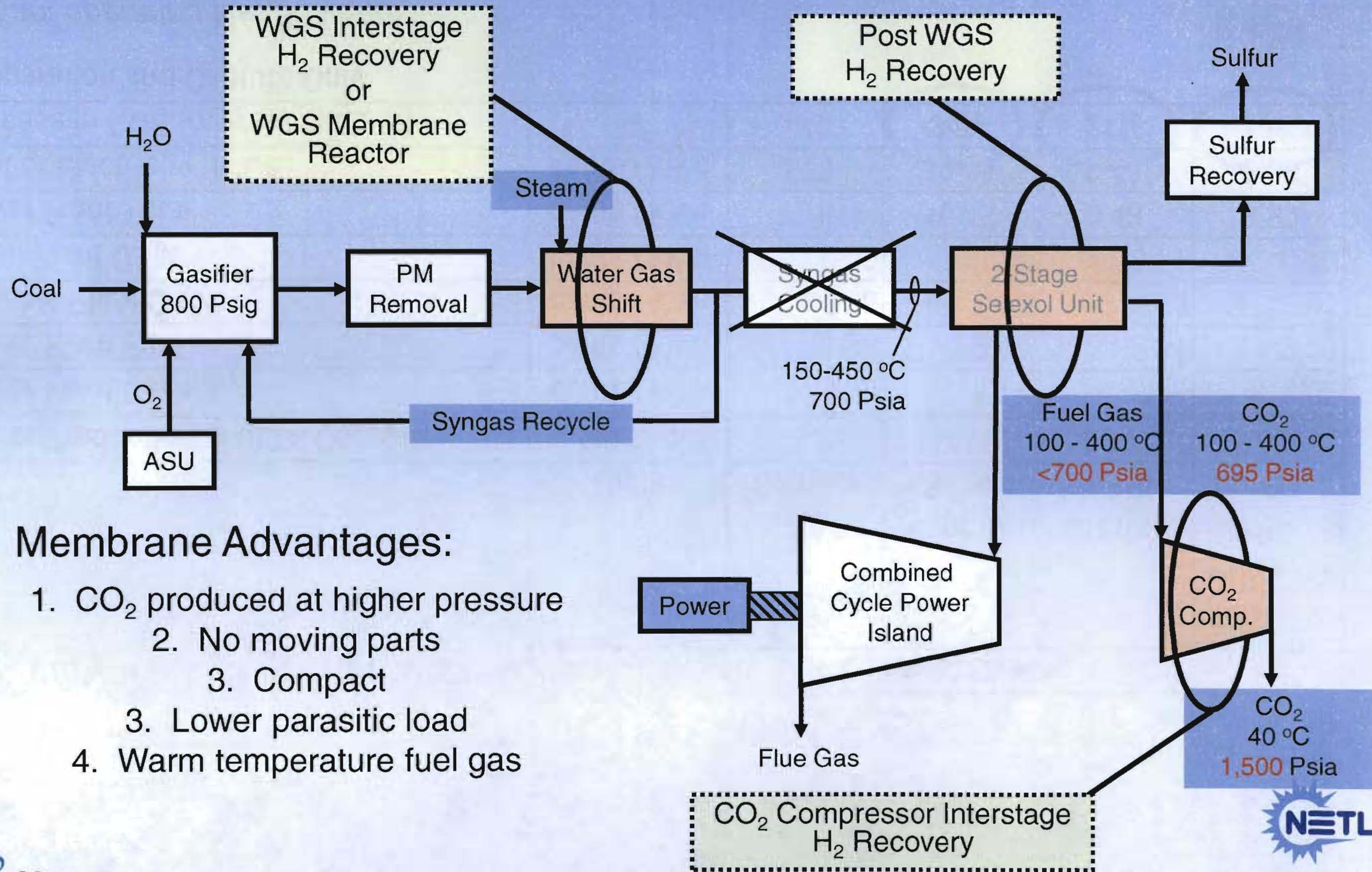
- Strategic Selection of Partnerships/ Collaborations to Facilitate Continued Progress
- Systems Integration / Economic Analysis
  - Optimize %CO_2 Capture and Minimize Cost



System Design Technical Approach

1. Develop membrane unit model for predicting performance and cost (spreadsheet based)
2. Develop Aspen-based process system model for simulating IGCC with carbon capture
3. Conduct techno-economic analysis of membrane technologies
   - Establish benchmark design - baseline
   - Optimize membrane parameters
   - Modify IGCC process flowsheet as required
4. Establish performance targets required to achieve successful technology commercialization

Areas of IGCC Process Targeted for Membrane Separations



Membrane Advantages:

1. CO_2 produced at higher pressure
2. No moving parts
3. Compact
3. Lower parasitic load
4. Warm temperature fuel gas

Economic Analysis: PBI Membrane Base Capture System Approaches the U.S. DOE Goals

CO_2 capture: 3.3 Million tonnes/yr.

		Project Cases			
	Units	No Capture	Capture w/Selexol	Capture w/PBI	Capture w/PBI no H_2S removal
Power Production @100% Capacity	**GWh/yr**	5,455	4,461	4,943	5,035
Power Plant Capacity	**cents / kWh**	4.50	6.19	5.49	5.02
Power Plant Fuel	**cents / kWh**	1.90	2.47	2.31	2.26
Variable Plant O&M	**cents / kWh**	0.78	1.00	0.92	0.91
Fixed Plant O&M	**cents / kWh**	0.60	0.79	0.71	0.70
Power Plant Total	**cents / kWh**	7.78	10.45	9.43	8.89
Cost of Electricity* (COE)	**cents / kWh**	**7.78**	**10.45**	**9.43**	**8.89**
Increase in COE (over no capture)	**%**	***n/a***	***34%***	***21%***	***14%***

*** Separation and Capture Only**

Plant operating life: 30 years;
Capacity Factor: 80%;
Capital charge factor: 17.5%

Summary

The PBI-based hollow fiber platform offers a means to produce an economically viable, high area density membrane systems amenable to and tailorable for incorporation into syn-gas based chemicals, fuels, and power production processes for pre-combustion CO_2 capture.

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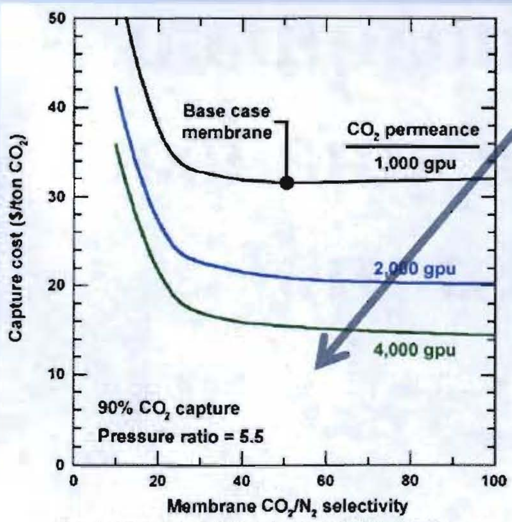
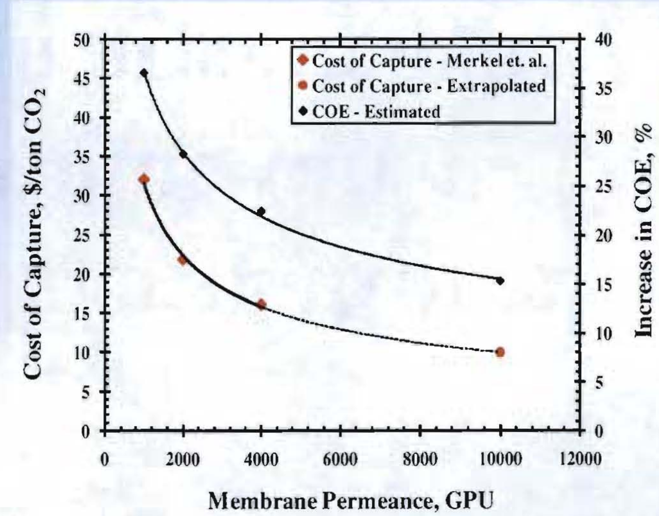
Immobilized Ionic Liquid-Based CO_2 Membranes for Post-Combustion Carbon Capture

10,000 GPU

< $10/ton of CO_2 captured



Merkel T.C. *et al*, J. Membr. Sci. 359(1-2) 2010.



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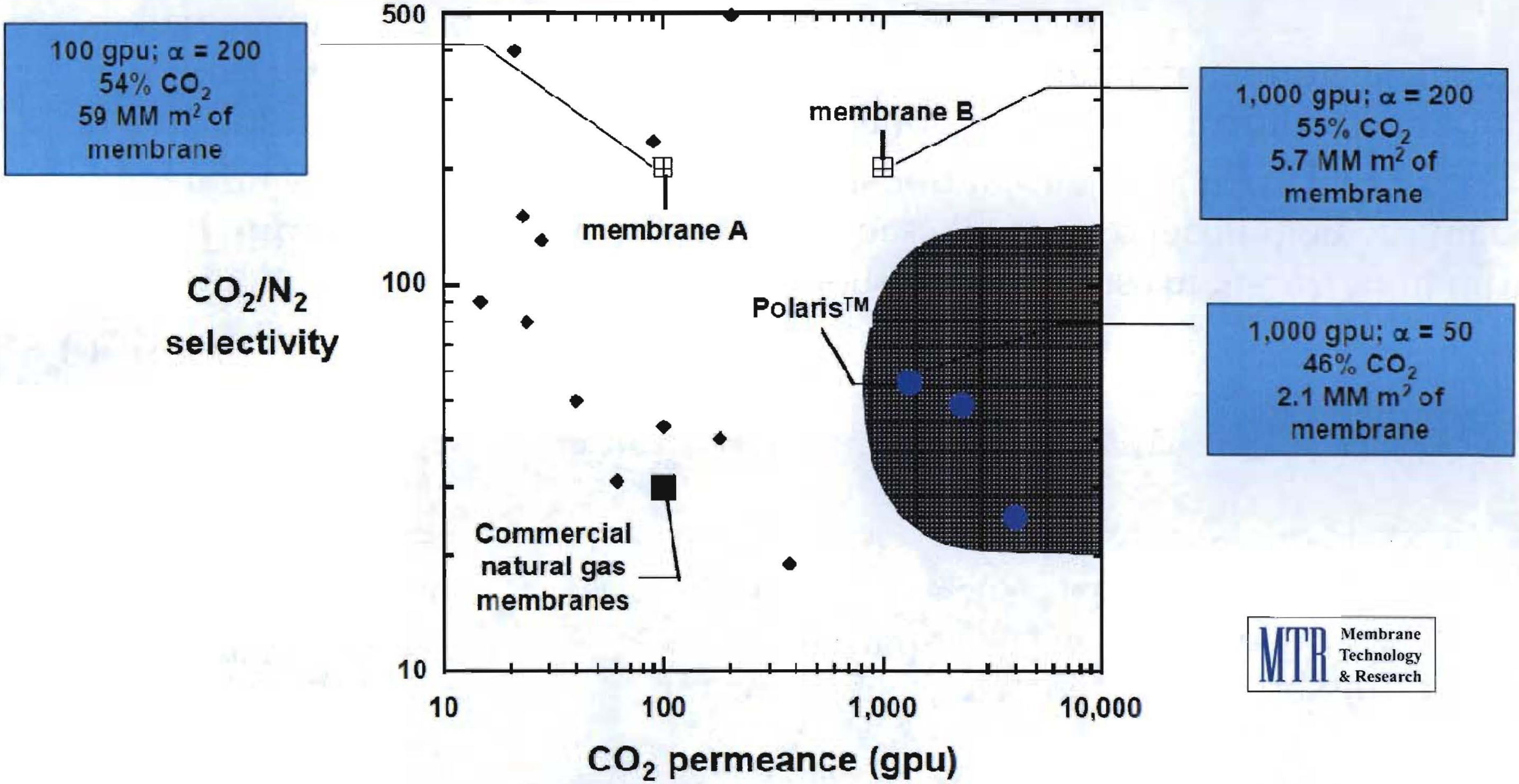
High Membrane Permeance is Critical



Membrane Technology & Research

Amo, K., Baker, R. et al. North American Membrane Society (NAMS) 2009
Calculations assume a pressure ratio of 10 with 13% CO_2 in the feed and 90% capture.

How to Achieve a Membrane with Very High Permeance & Adequate Selectivity??

- Challenge
  - Design, control, prediction, and synthesis of material chemistries and morphologies (support & selective layer) that enable enhanced CO_2 transport. Can we achieve >>5,000 GPU? >>10,000GPU??
    - Thermal, mechanical, and chemical resistance and durability in the target process environment
    - Incorporation into a high area density module design ⇒ maximized impact on process economics
- Opportunities
  - Development of new materials directions that comprise high CO_2 solubility, high diffusivity, and mechanical robustness (w or w/o facilitation or other manipulations of the dominant gas transport mechanism(s))
  - Development of a fundamental understanding of how to manipulate and control the selective layer molecular morphology and free-volume element architecture
  - Membrane platform and fabrication method development for selective layer thickness minimization without performance compromise
    - Understanding and optimizing the support/selective layer interface - especially in composite structures

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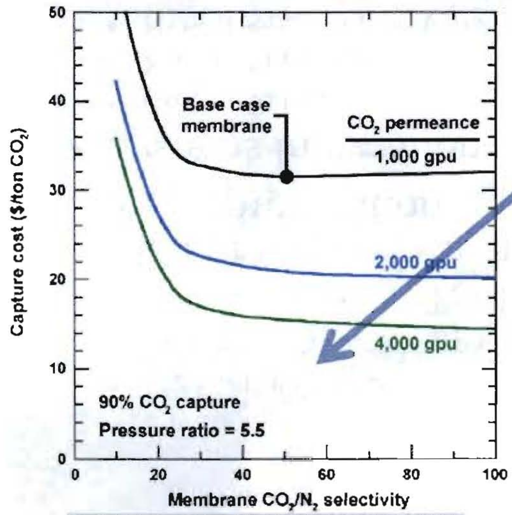
Achieving a 10,000 GPU Permeance for Post-Combustion Carbon Capture with Gelled Ionic Liquid-Based Membranes



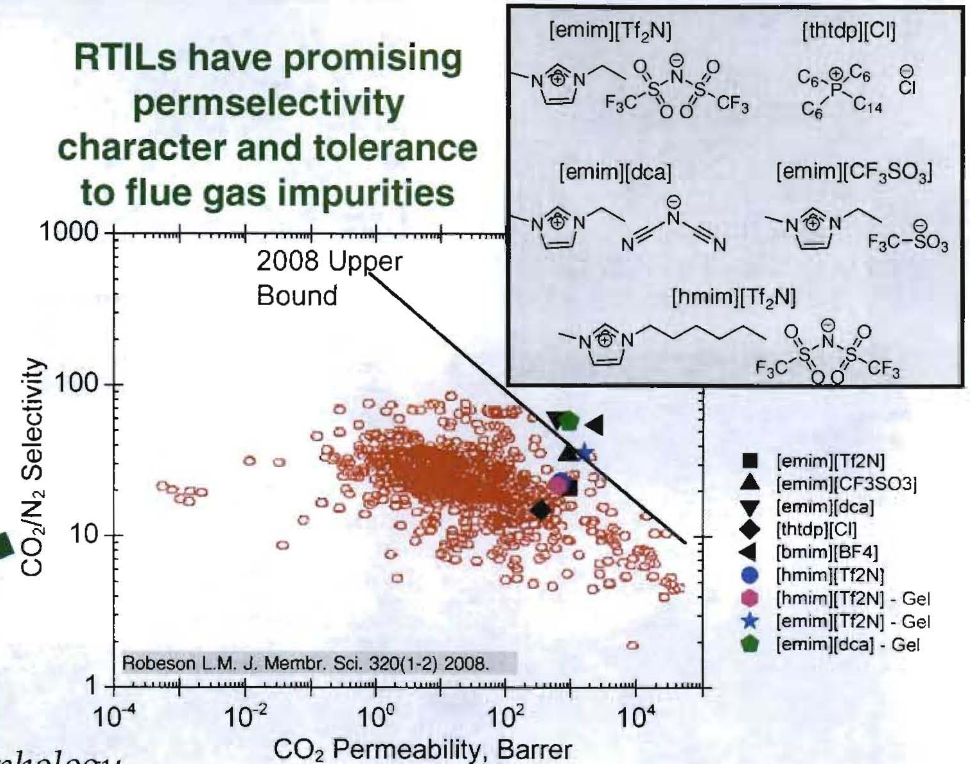
Merkel T.C. *et al*, J. Membr. Sci. 359(1-2) 2010.

10,000 GPU

↓

< \$10/ton of CO_2 captured

RTILs have promising permselectivity character and tolerance to flue gas impurities



Challenge:

Material stability: SLM format limitations

Enhancing permeability thru chemistry & molecular morphology

Approach:

Tailored gel-ILs, RTIL/poly(RTIL) composites, incorporation of task specific complexation chemistries

Challenge:

Enhancing permeance through selective layer thickness (SL) minimization

Permeability = 1000 barrer → **Permeance (100 nm thick SL) = 10,000 GPU**

Approach:

Commercially viable fabrication technique development using ultrasonic spray coating technology (USCT) -- enabling controlled ultra-thin SL deposition on commercially attractive support platforms

Membrane Permeance 10,000 GPU & Selectivity > 20

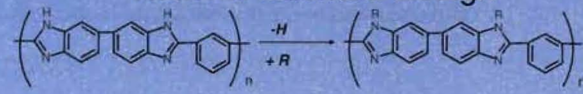
arpa·e

Materials for Separations S & T

Technically and Economically Viable Technology Development Through:

- **Rational Design, Synthesis, and Development of New (*and improved*) Selective Barrier Materials**
  - Long-term stability in harsh operating environments, high selectivity, high throughput (flux, loading capacity, etc.)
  - Utilization of LANL Expertise in polymers, high-temperature polymers, ionic liquids, porous ceramics, metals, metal alloys, dense ceramics, facilitated transport materials, membrane distillation materials, & hybrids
- **Membrane and Module Development**
  - Membrane Morphology Design & Optimization
  - High Temperature (>150 °C) Operation
  - Stability in Chemically Challenging Separations Environments
  - Mechanically Stable
  - Industrially Attractive Separation Characteristics
- **Development of Tools for Long-Term Membrane Performance Prediction and Optimization**
- **Systems Integration**
  - Greenfield Plants
  - Retrofit Applications
  - Hybrid Separation Systems
- **Strategic Selection of Future Partnerships/Collaborations**

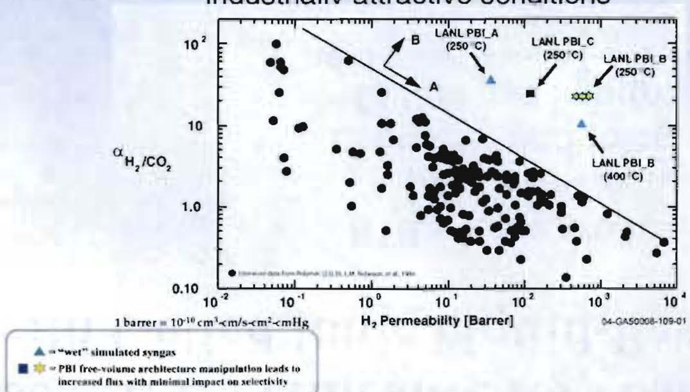
Rational Materials Design



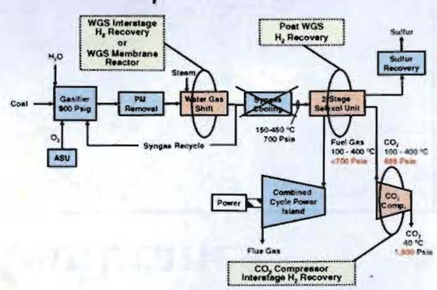
Morphology Optimization

Membrane and Module Design, Evaluation, & Scale-Up

Demonstrate improvements over the state-of-the-art while operating at industrially attractive conditions



Systems Integration and Optimization



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