Novel Polymer Membrane Process For Pre-Combustion CO_2 Capture From Coal-Fired Syngas

DE-FE0001124

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DOE NETL kickoff meeting
November 13, 2009

Outline

- Project timeline and objectives overview
- Membrane technology background
- Project approach
- Results to date
- Project tasks, timeline, success criteria, etc.

Project Overview

Award number #: DE-FE0001124

Project period: 9/15/09 to 9/14/11

Funding: $950k DOE; $150k MTR and $ 90k Tetramer Technologies

DOE program manager: Richard Dunst

Participants: MTR, Tetramer Technologies, Eastman Chemical, Southern Co.

Project scope: The goal of this project is to develop a new polymer membrane and membrane separation process that will provide cost-effective CO_2 management in future coal-based IGCC power plants.

Project plan: Composite membrane development, testing and process design studies in year 1; prototype module testing in the lab in year 2.

- A field test of membrane stamps at Southern starting in Nov 2009
- A module field test at Eastman or Southern in a follow-on project

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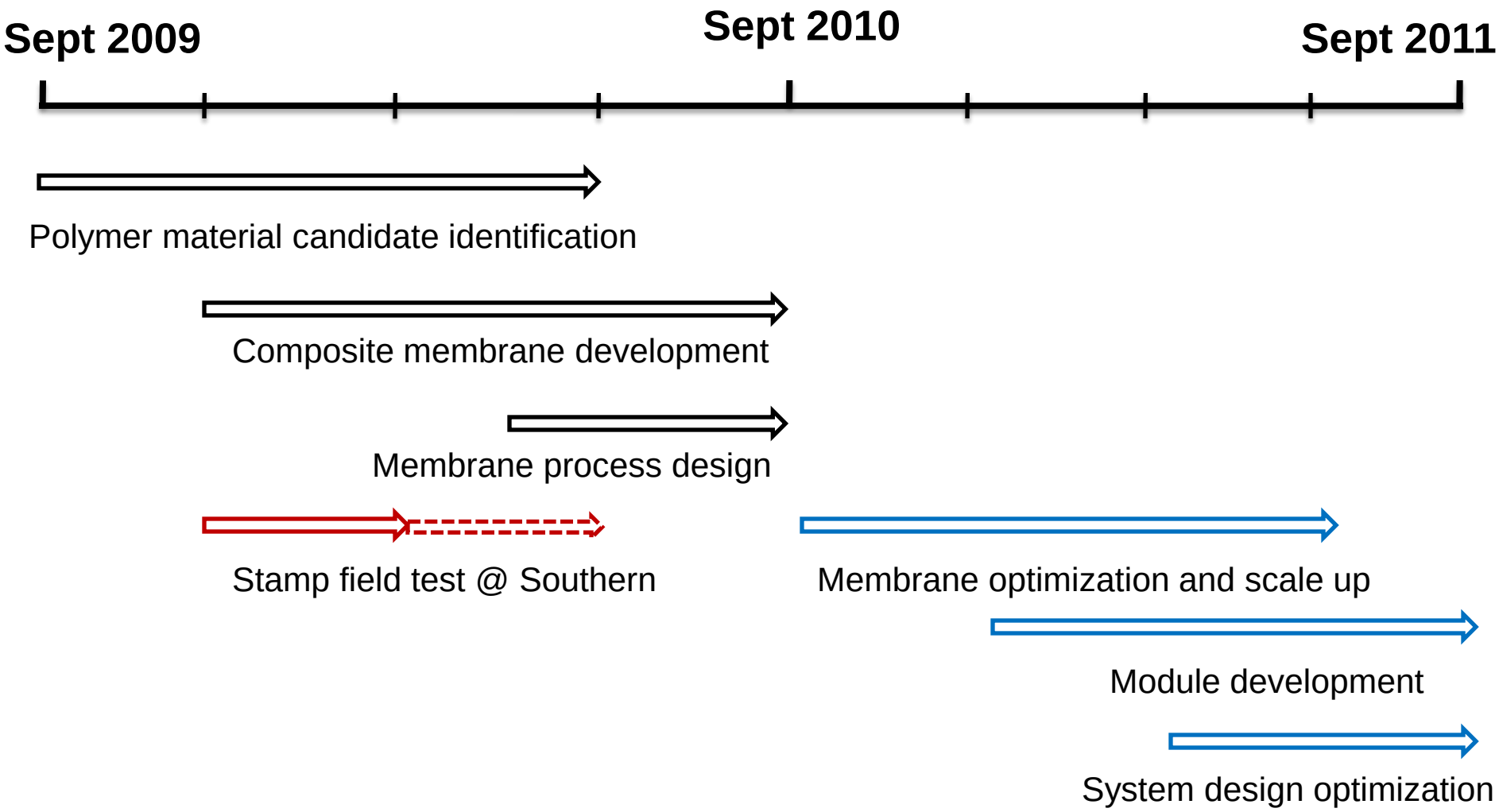
Project Objectives

- Investigate novel, stable high-temperature-stable polymers for use in H_2/CO_2 selective membranes
- Prepare composite polymer membranes and bench-scale modules that have H_2/CO_2 >10 and H_2 permeance > 200 gpu at syngas cleanup temperatures of 100 – 200°C
- Conduct bench-scale testing of optimized membranes and membrane modules with simulated WGS syngas mixtures to evaluate membrane performance and lifetime under expected operating conditions
- Optimize membrane process designs, investigate the sensitivity of different proposed processes to membrane performance, and assess the optimal integration of a membrane system into the syngas cleanup train
- Perform a cost analysis of the polymer membrane-based separation process vs. current cleanup technologies (Rectisol, Selexol, and PSA)

Project Timeline



Introduction to MTR

MTR designs, manufactures, and sells membrane systems for industrial gas separations

Petrochemicals: Propylene/Nitrogen

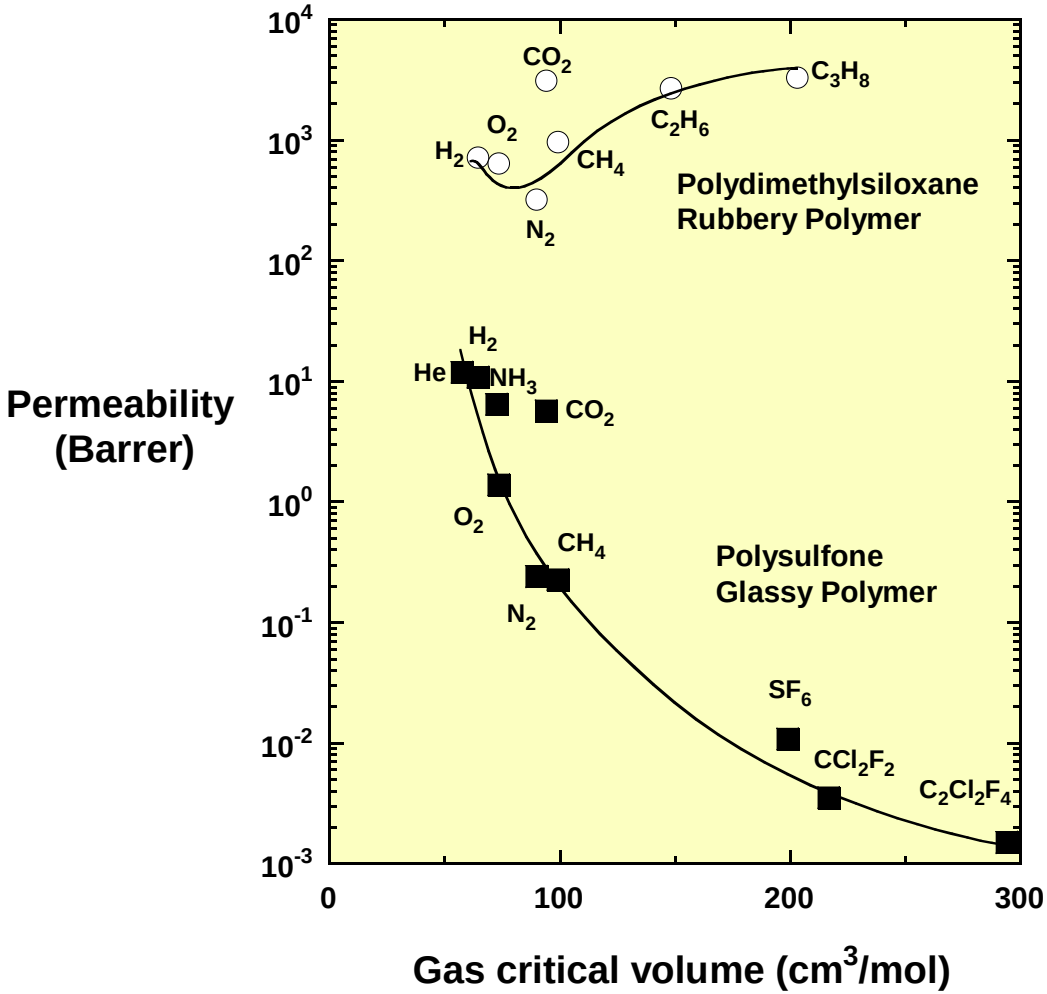
Hydrogen (Refinery): H_2/CH_4, CO, CO_2

Natural Gas:

CO_2/CH_4, CH_4/N_2
NGL/CH_4

Customers include: BP, Chevron, Dominion Exploration, Ercros, ExxonMobil, Formosa Plastics, Innovene, Sabic, Sasol, Sinopec, Solvay, and Statoil.

Membrane Technology Basics



Diffusivity selectivity: favors small molecules

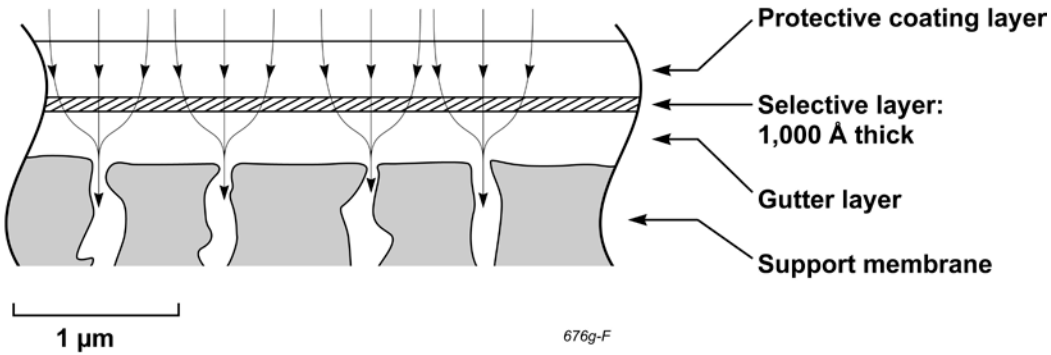
$$\alpha_{A/B} = \frac{P_A}{P_B} = \left(\frac{S_A}{S_B}\right) \times \left(\frac{D_A}{D_B}\right)$$

Solubility selectivity: favors large molecules

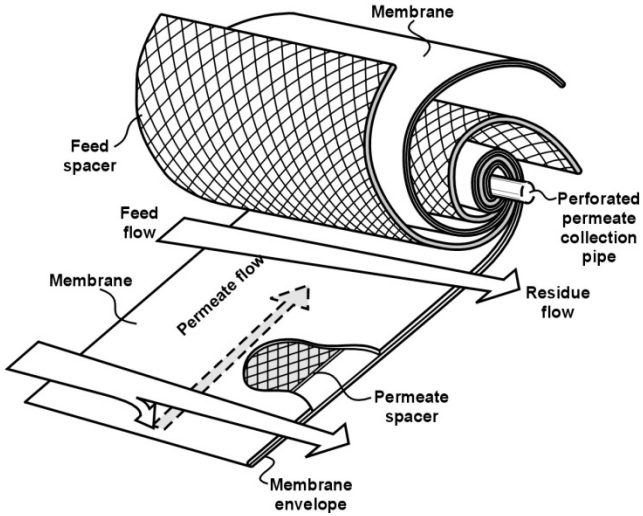
1 Barrer = 10^{-10} cm^3 (STP) cm / (cm^2 s cmHg)

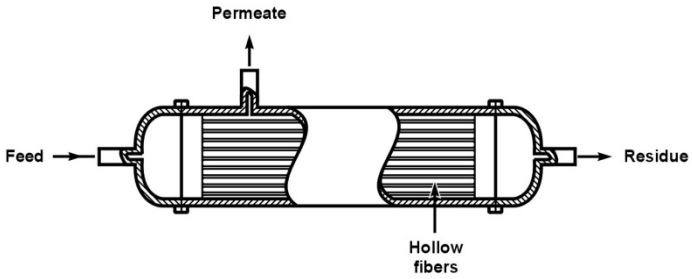
Membrane Technology Basics

- Membranes have to be thin to provide useful fluxes.

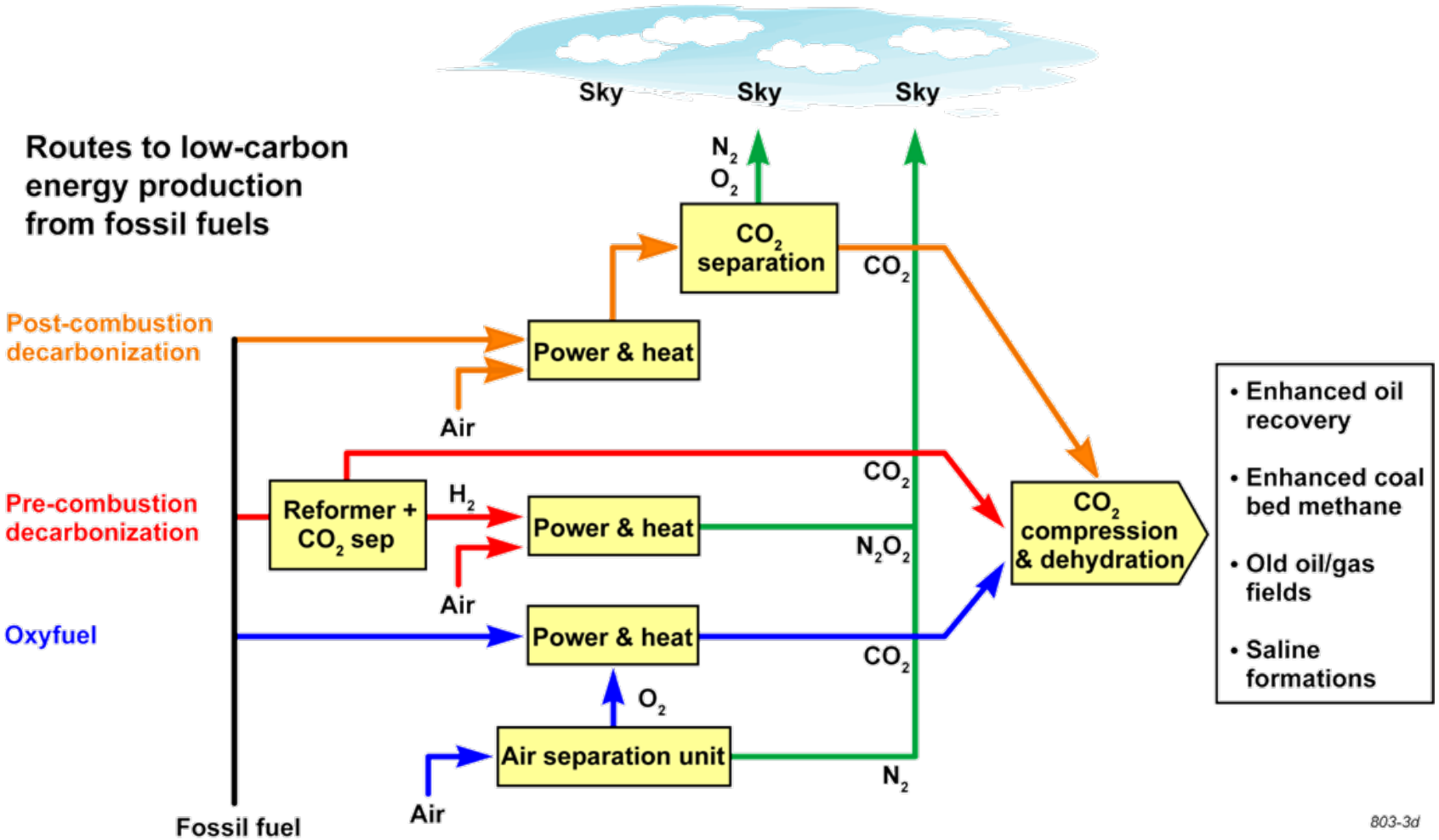


- Spiral-wound and hollow fiber modules are used.

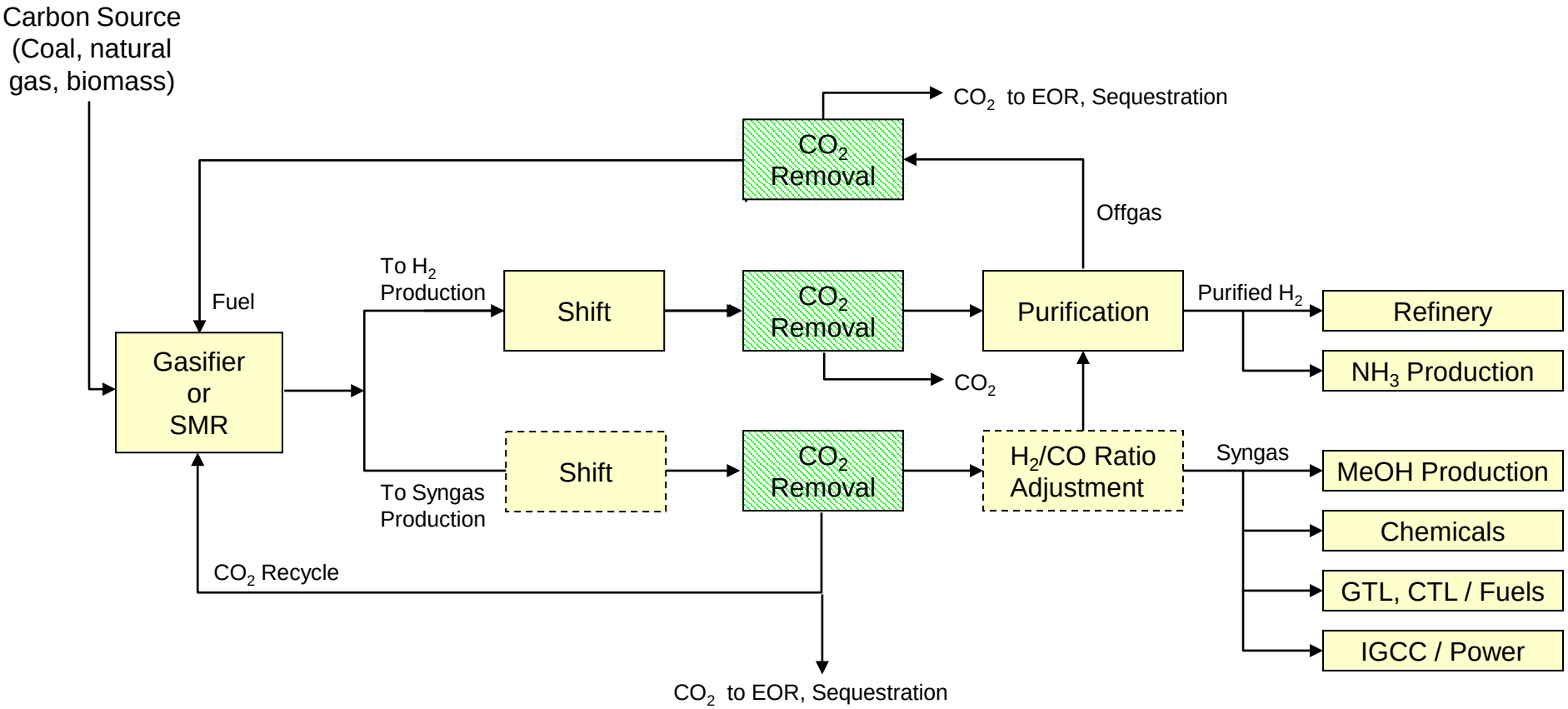




Fossil Fuel Energy with CO_2 Capture Options

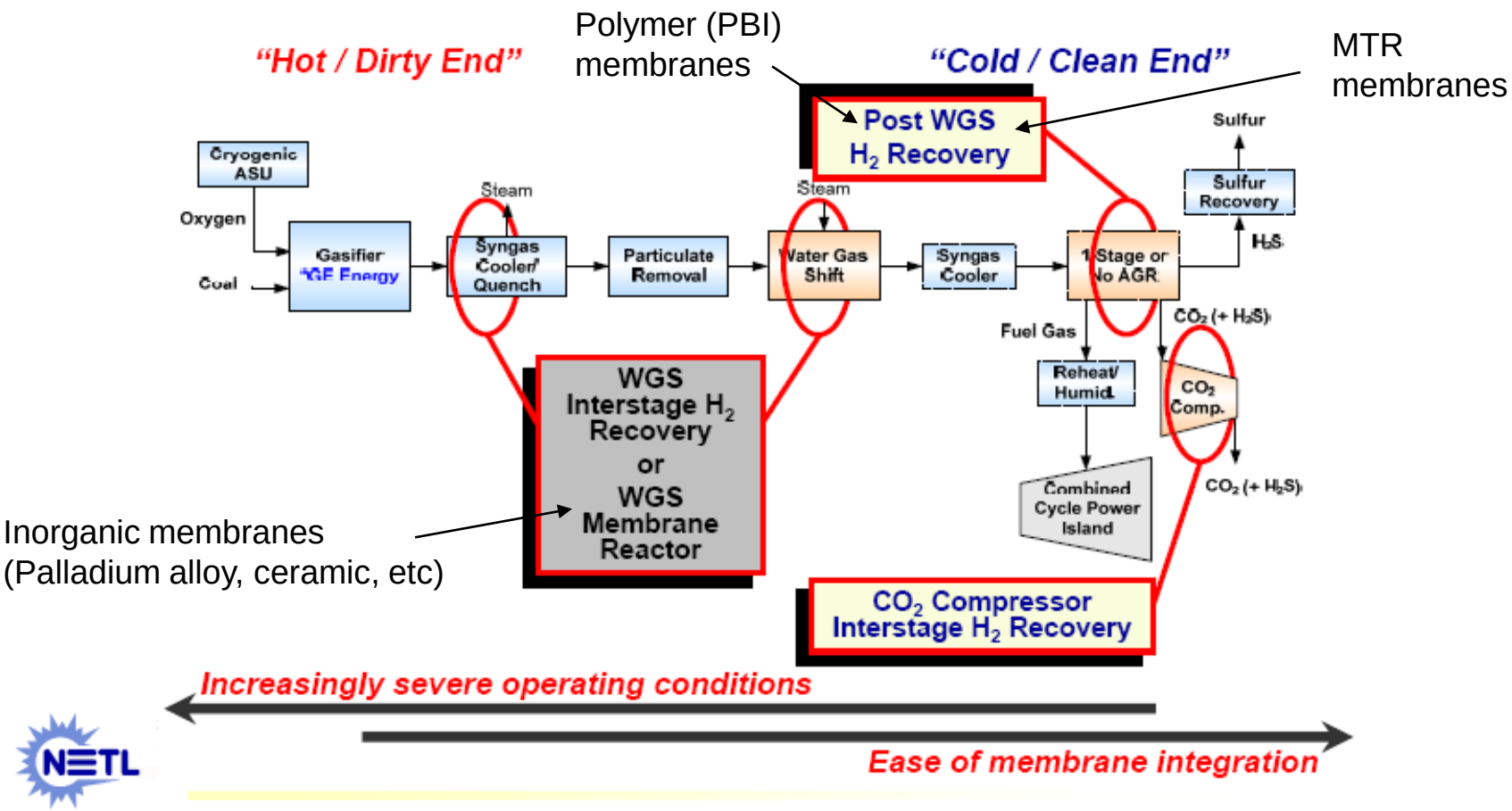


Polymer Membranes Are Being Used to Treat Syngas Today



- In all commercial systems, the membranes operate below 60°C
- Most membrane systems recover H_2 from syngas; a few remove CO_2

DOE is Funding Membrane Research for Syngas Cleanup



- *Hot or warm syngas cleanup offers the potential for improved thermal efficiency*
- *H_2 selective membranes reduce CO_2 compression costs*

Pros and Cons of Membranes for Syngas Cleanup

Advantages:

- Simple design; small footprint
- Energy efficient compared to sorption processes
- No water used; no leakage or disposal of chemical solvents
- Potential for process intensification – high temperature membrane reactors

Challenges:

- Difficult operating conditions especially for hot/warm gas cleanup; stability in presence of contaminants
- Lack of reproducible, low-cost module fabrication technology for inorganic membranes
- Lack of references

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MTR Approach

- Use new polymers that can easily be adapted to existing low-cost membrane system components used in natural gas and RO industries
- Operate membranes at ~150°C; a near-term bridging technology between current cold AGR processes and future hot gas cleanup strategies (membrane reactors, etc.)
- Investigate process designs using H_2 and CO_2-selective membranes in tandem
- Focus on process design and tailor membrane properties to “fit” the process operating conditions

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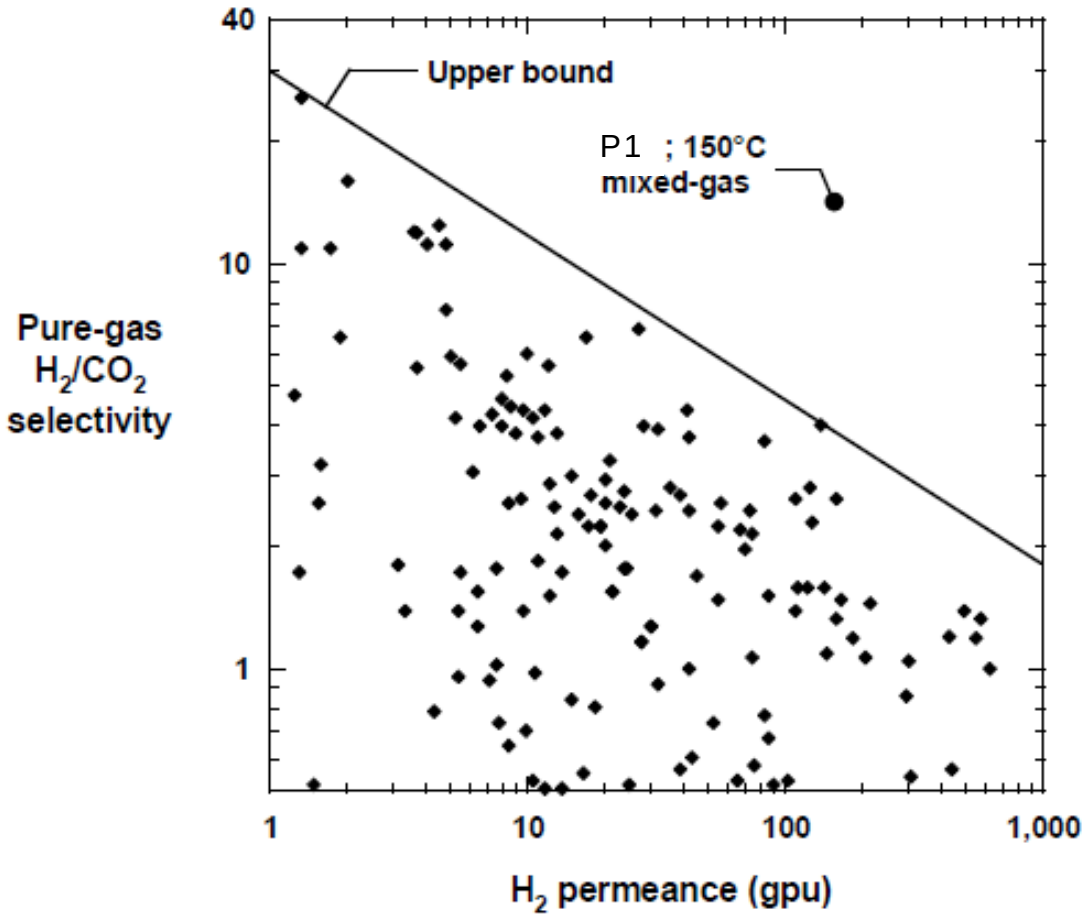
MTR Proteus Membrane Shows Promising Performance



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

1 ft^3(STP)/(h ft^2 psi) = 1,600 gpu

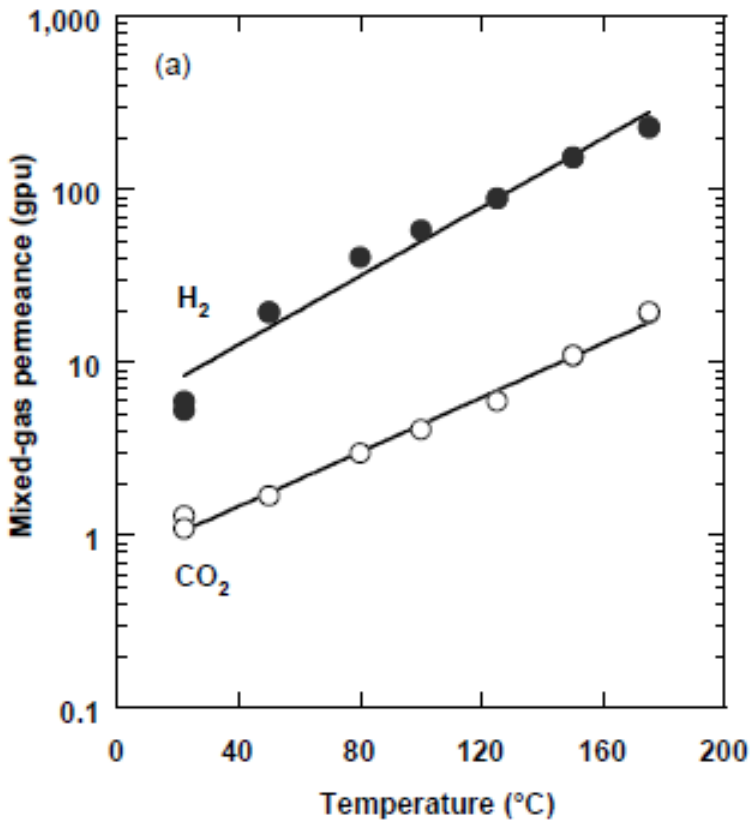
10^{-6} mol/(m^2 s Pa) = 3,000 gpu

10^{-2} mol/(m^2 s bar) = 300 gpu

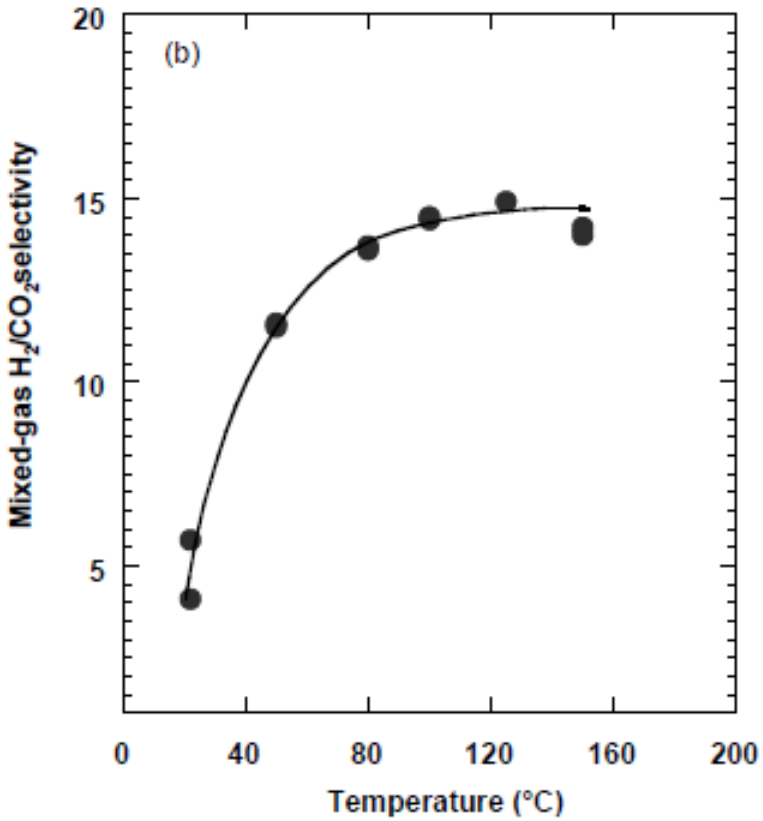
Polymer data from Robeson are mostly pure-gas permeability measurements in the vicinity of room temperature. P1 data is a 50/50 H_2/CO_2 feed mixture at 50 psig.

Mixed-Gas Performance of MTR Proteus Membrane

Permeance

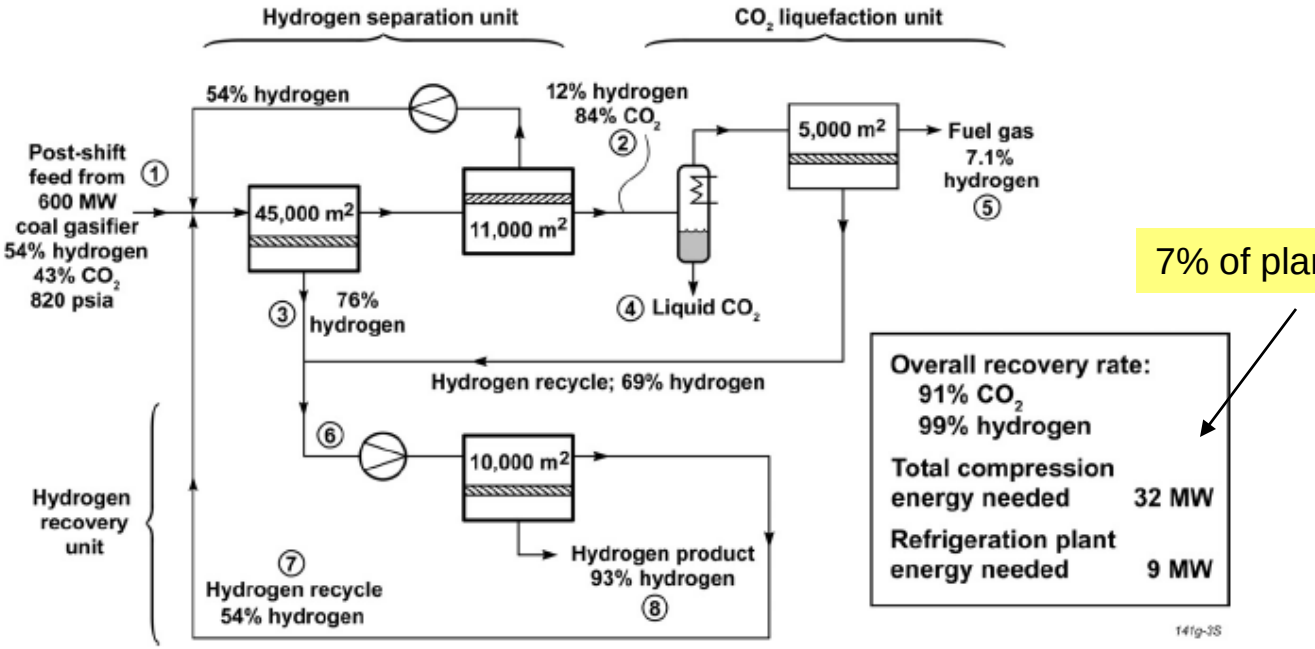


Selectivity



H_2/CO_2 selectivity increases with increasing temperature presumably because CO_2 selectivity decreases rapidly at elevated temperature.

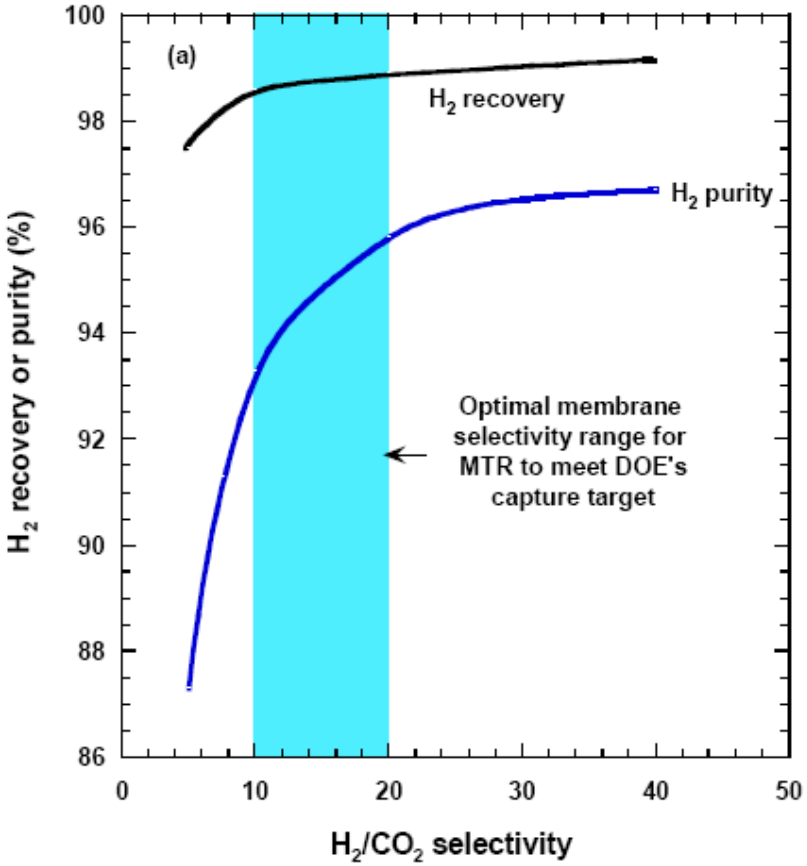
A Possible Membrane Process Design

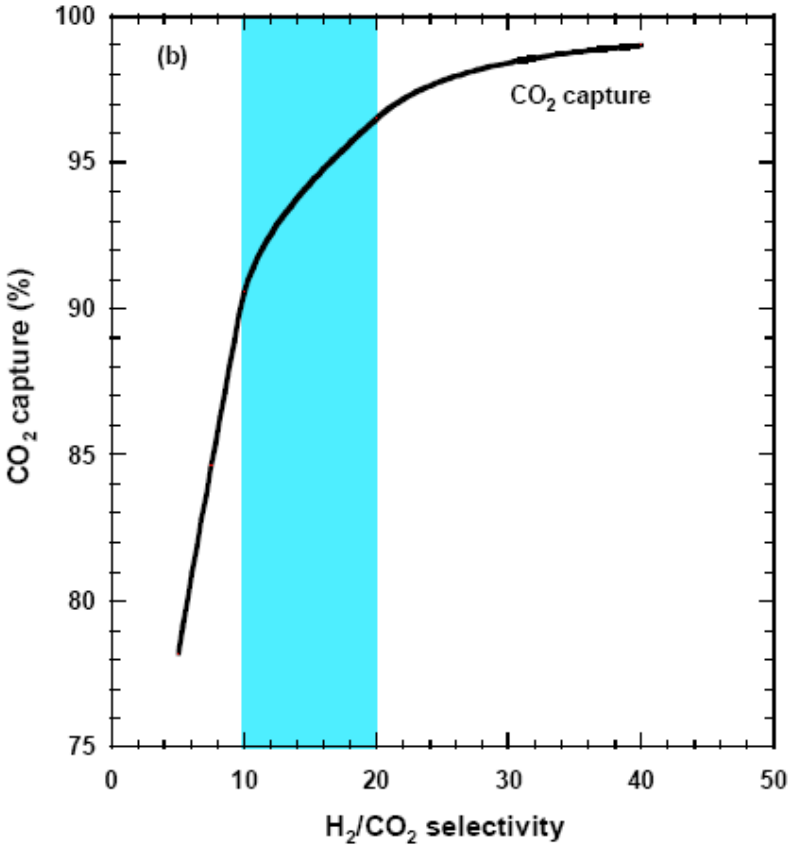


7% of plant power

Stream[a]	① Feed Gas	② CO_2 Condenser Feed	③ First Permeate	④ Liquid CO_2	⑤ Fuel Gas Vent	⑧ H_2 Product
Components (%)						
Hydrogen	54.0	11.9	76.3	0.0	7.1	93.3
Carbon dioxide	43.0	83.6	21.2	96.2	54.7	4.7
Other and inerts	3.0	4.5	2.5	3.80	38.2	2.0
Flow (m^3/s)	100	50.6	95.4	40.4	2.5	57.1
Pressure (psia)	840	825	200	815	815	65

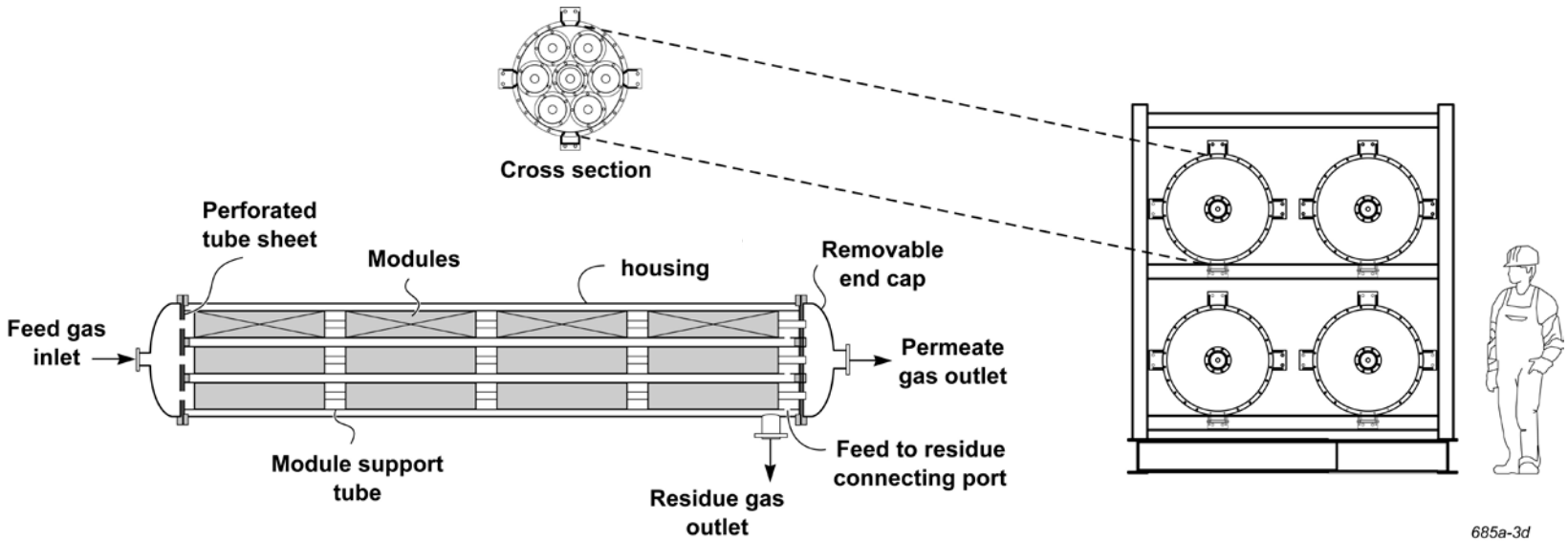
Current Selectivity is Sufficient to Meet DOE Performance Targets





Membrane selectivity requirements depend on the process design. Operating condition constraints often limit the useful selectivity.

Higher Permeance Helps Cost and Footprint



A 600 MW plant would require about 70,000 m^2 for 90% capture at 200 gpu H_2 permeance. This amounts to 14 module skids with an installed cost of about $11 MM

If H_2 permeance is doubled to 400 gpu, only 7 skids are required with a capital cost of ~ $6 MM

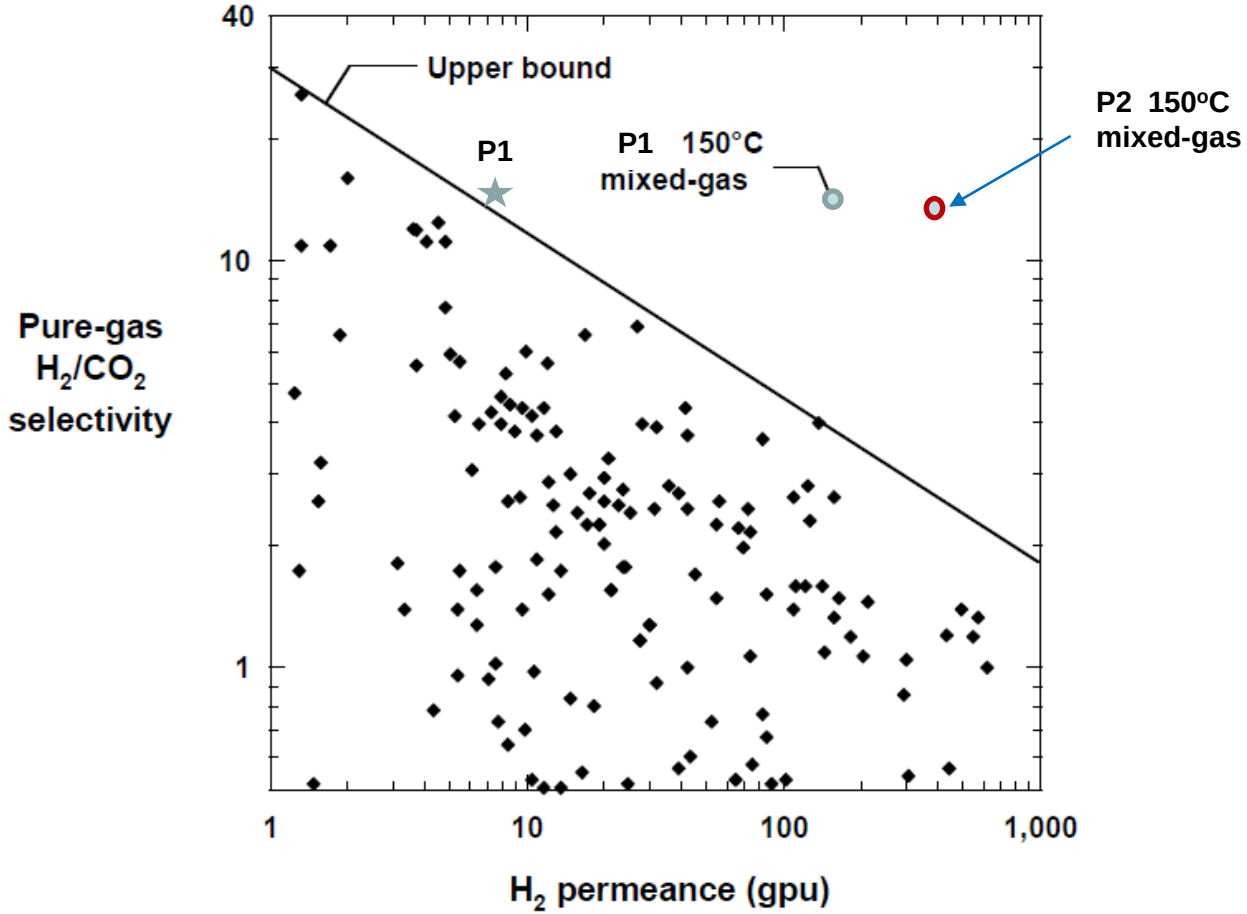
Very Big Membrane Plants Exist Today

Ashkelon desalination plant

- 40,000 spiral-wound RO membrane modules (Dow Filmtec®)
- 1.5 million m^2 membrane area

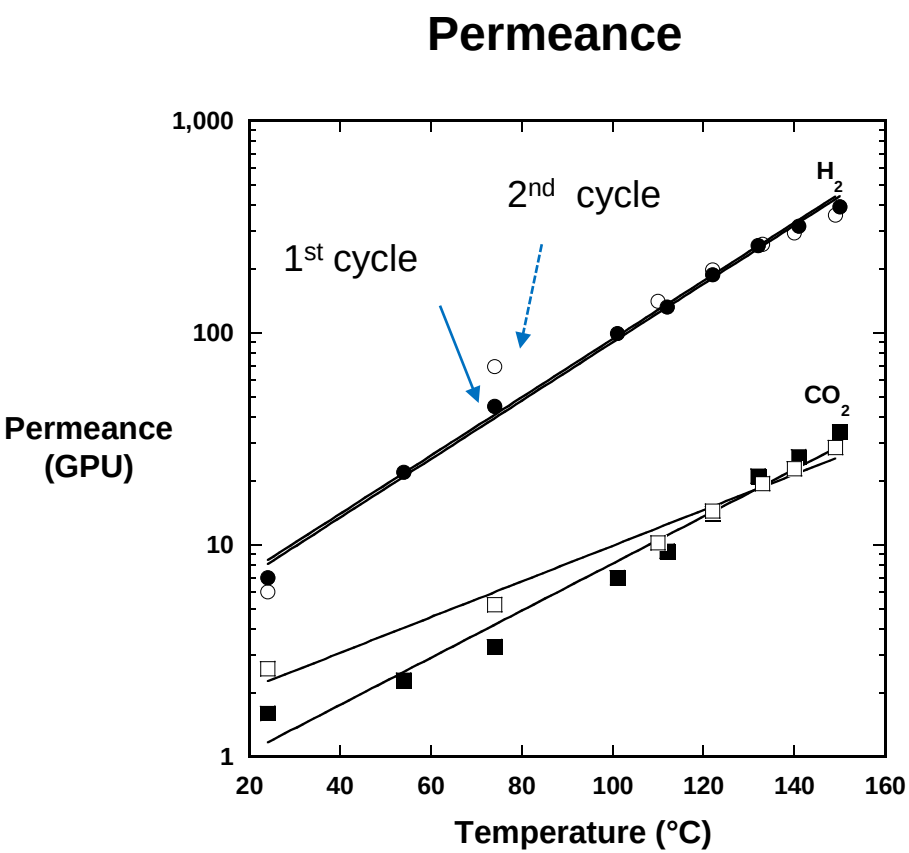
- Installed membrane skid cost is <$50/$m^2$
- Plant produces 100 million m^3/yr of fresh water

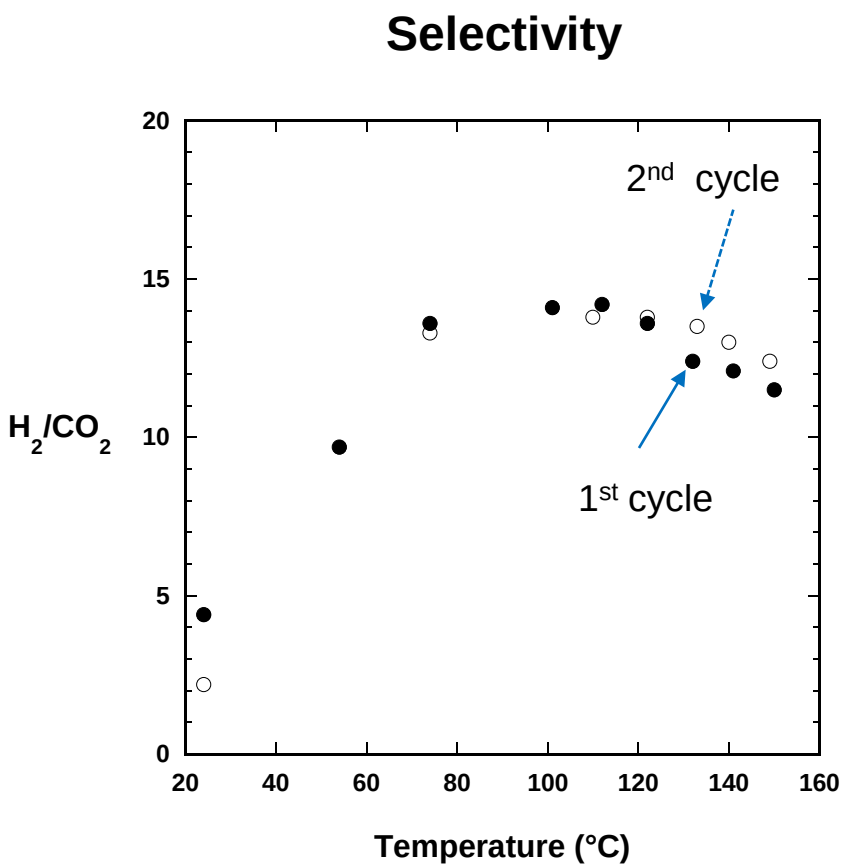
Improved Membrane Performance



The current membrane gives mixed-gas H_2 permeance > 300 gpu with a H_2/CO_2 selectivity > 10 at 150°C. Further optimization is possible.

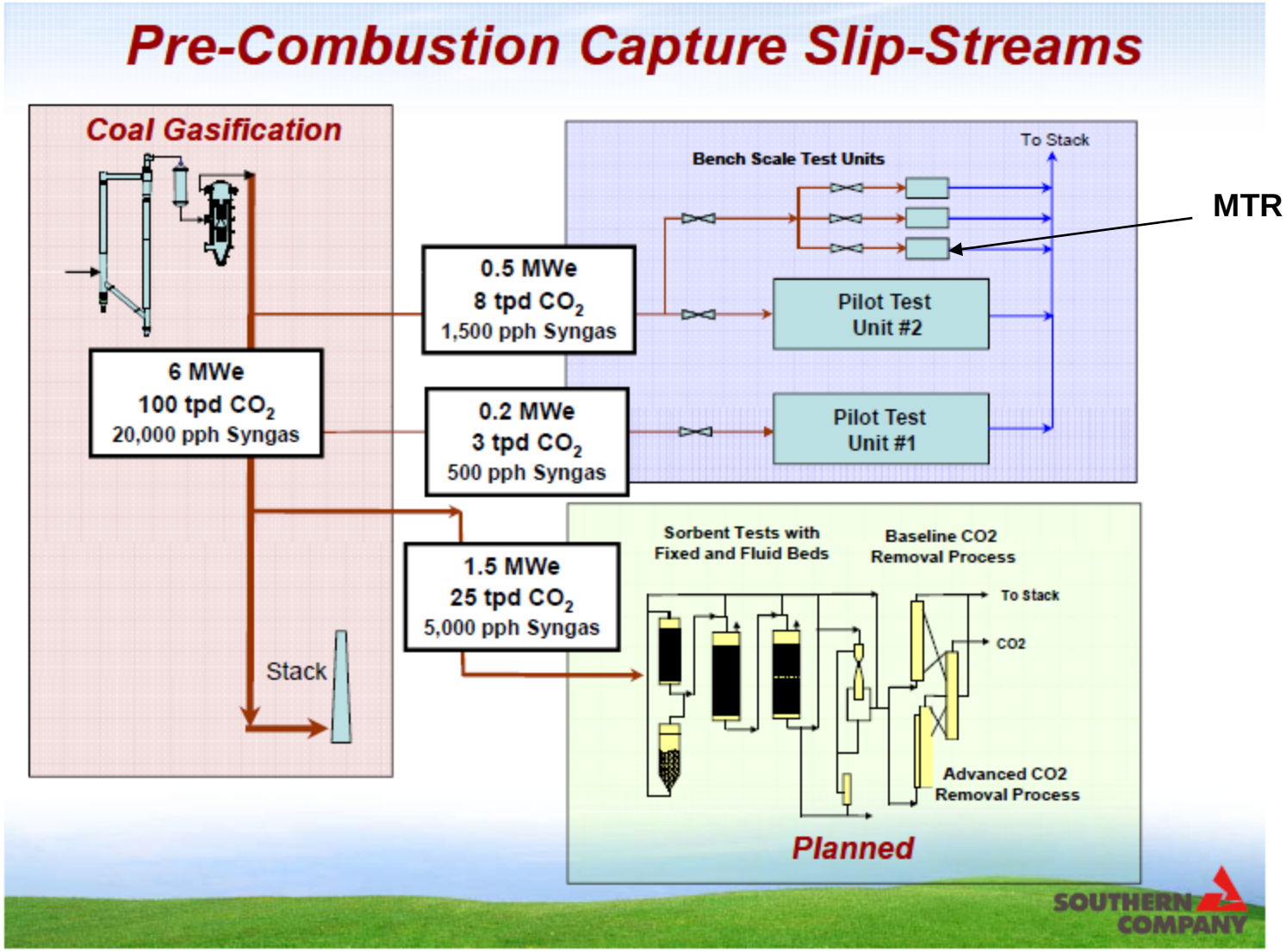
Performance is Stable So Far





Tests were conducted on membrane stamps (area = 13 cm^2) with a 50/50 H_2/CO_2 feed gas mixture at 50 psig. Each temperature cycle takes 1 day to complete.

Field Test at Southern Company's PSDF



Slide courtesy of Frank Morton, Southern Company

MTR's Membrane Field Test Unit

PERMEATE GAS

RESIDUE GAS

FEED GAS Inlet

Southern Field Test Details

- CO_2-selective Polaris modules and H_2-selective Proteus membranes will be tested
- Gas is unshifted, air-blown syngas supplied at ~200 psia and 40°C (Polaris) or 150°C (Proteus)
- Samples will run continuously for ~3 weeks with coal-derived syngas
- Key objectives are to
  - examine membrane performance with real syngas, including gases difficult to study in the lab (CO, H_2S)
  - Investigate the membrane performance stability and, if degradation occurs, try to identify mechanisms
- Performance data from the field test will be used to update process designs

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Project Partners/Roles

- MTR – Composite membrane fabrication and testing, membrane scale-up, module manufacture, run field tests, process design studies, economic analysis
- Tetramer Technologies – specialized polymer synthesis, characterization and scale-up
- Eastman Chemical – membrane process integration evaluation, possible field demo
- Southern Company – Host field test at the NCCC

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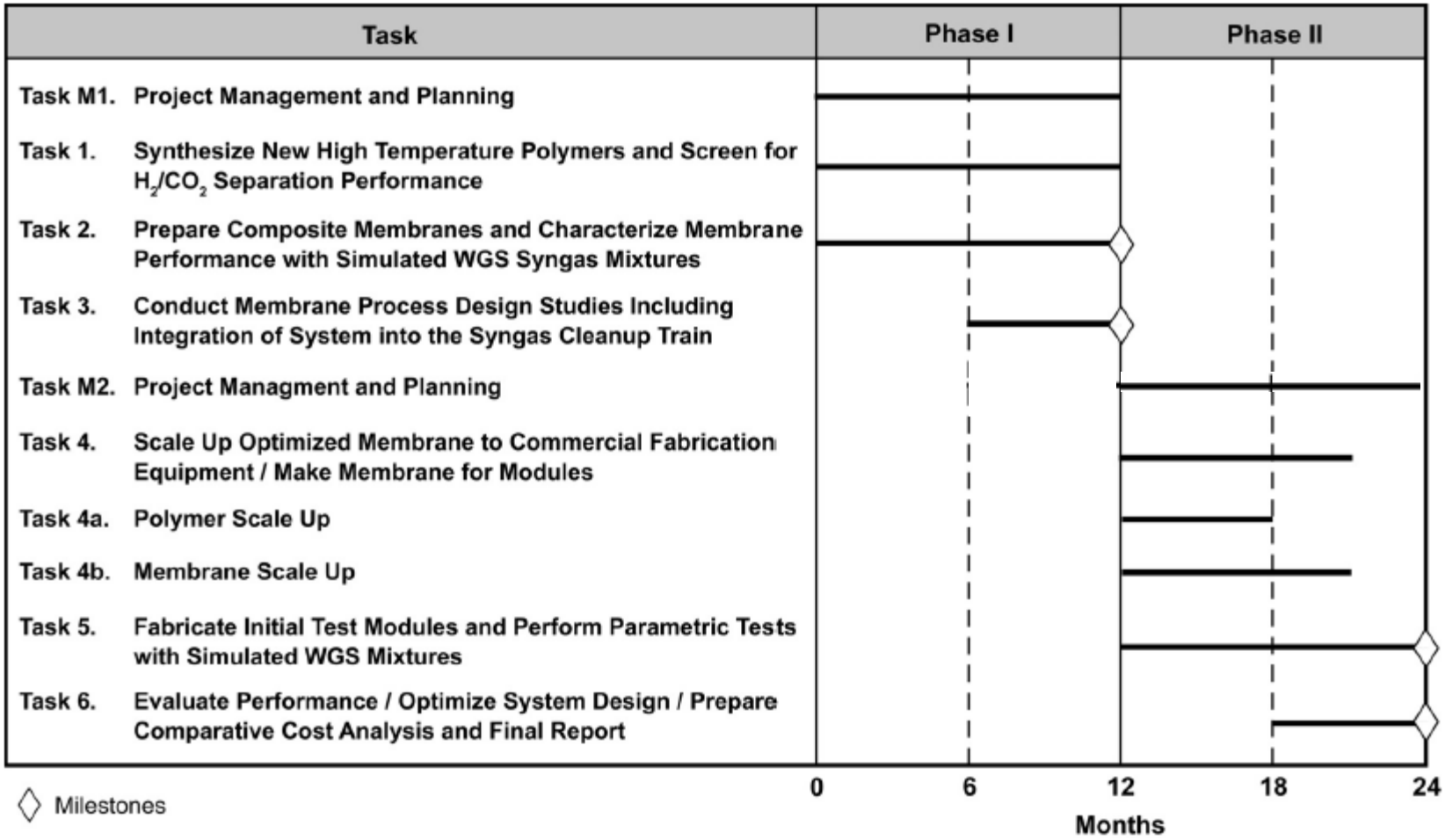
Project Tasks



Success Criteria

Phase 1

1. Confirm that composite membranes made from novel membrane selective layers give hydrogen permeances of at least 200 gpu and H_2/CO_2 selectivities of greater than 10 in bench-scale tests to separate model syngas mixtures.

2. Using these actual membrane performance data, demonstrate that a membrane process has the potential to meet DOE pre-combustion CO_2 capture program targets.

Phase 2

1. Complete scale up of optimized membrane polymer, prepare composite membranes, and fabricate these membranes into bench-scale modules.

2. In tests of membrane modules with simulated WGS mixtures, demonstrate module performance and lifetime consistent with small-scale membrane stamp studies.

3. Evaluate membrane process performance and conduct data analysis and optimization studies. Determine the overall technical and economic competitiveness of the proposed process as compared to alternative technologies and the DOE program targets. If the analysis is promising, design a field test unit for future demonstration at Eastman.

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Risk Management

Risk

- Membrane or module stability at elevated temperature in a challenging chemical environment is not sufficient

Approach

- Conduct early screening of membranes with real syngas to determine lifetime and potential degradation mechanisms
- Work with Tetramer to modify polymer chemistry as necessary
- Apply high temperature module know-how from bioethanol treatment

Risk

- Cost and energy savings compared to Selexol are not compelling

Approach

- Work with Eastman and Southern to compare membrane process costs with standard technology

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Summary

- Polymer membranes have potential for pre-combustion CO_2 capture
- There may be benefits to using both CO_2-selective (cold gas cleanup) and H_2-selective (warm gas cleanup) membranes
- Preliminary results show mixed-gas H_2/CO_2 selectivity of 10 – 15 and H_2 permeance of >300 gpu at 150°C
- Low-cost module fabrication techniques can be used
- Field tests will be key to determine membrane lifetime in a challenging chemical environment

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