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

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Outline

- Project overview
- Membrane technology background
- Project progress as of 07/31/2011
- Future plans

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Project Overview

- Project Schedule
  - 9/17/2009 to 9/16/2011
  - Project tasks are complete; we are now working on the final report
- Project Cost
  - Funding: $950k DOE; $150k MTR and $ 90k Tetramer Technologies
  - Actual costs through 5/31/11: $1,129,362
- Project Manager – Rick Dunst
- Project Milestones
  - Confirm that composite membranes meet target performance – hydrogen permeance of 200 gpu and H_2/CO_2 selectivity of 10 with mixtures.
  - Using actual membrane performance data, complete design studies that show the membrane process has the potential to meet DOE program targets.
  - Complete fabrication of bench-scale membrane modules and demonstrate module performance/lifetime during simulated water gas shift (WGS) mixture testing.
  - Finish data analysis, process optimization studies, and comparative economic evaluation.

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Project Overview:
Objectives and Scope of Work

- Membrane development
  - High-temperature stable polymers for use in H_2/CO_2
  - Composite membranes that have H_2/CO_2 >10 and H_2 permeance >200 gpu at syngas cleanup temperatures (100-200°C)

- Membrane performance evaluation
  - Evaluate membrane and lab-scale membrane module performance using pure gases in the lab
  - Evaluate membrane stamps using simulated syngas lab mixtures

- Process design analysis
  - Optimize membrane process designs and assess the optimal integration of a membrane system
  - Perform a cost analysis of the polymer membrane process vs. current cleanup technologies, e.g., Selexol

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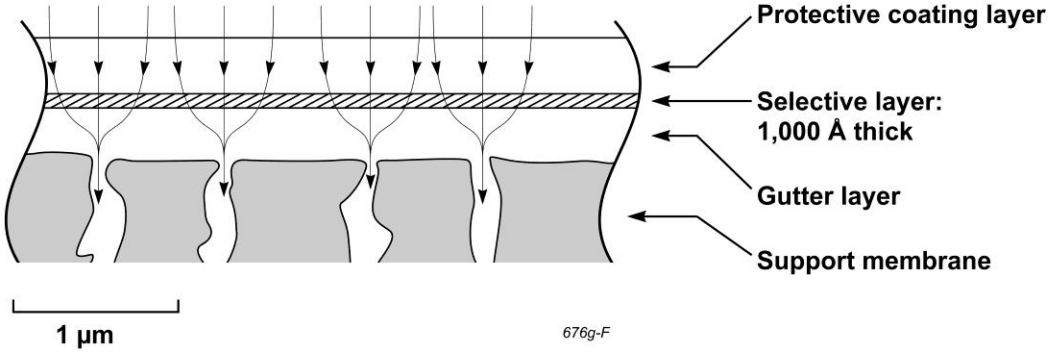
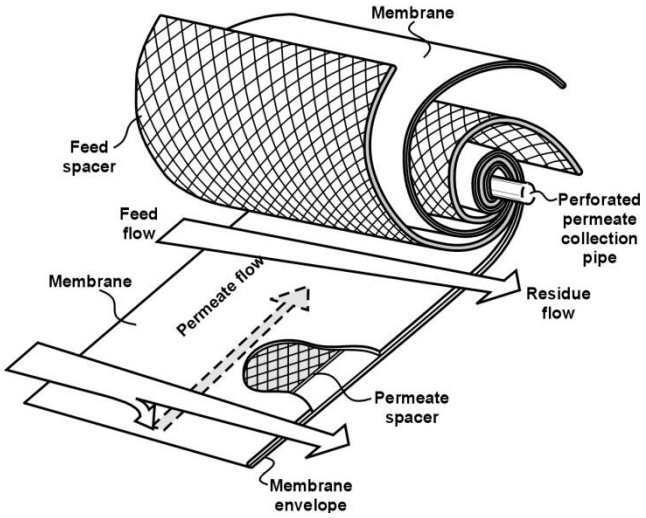
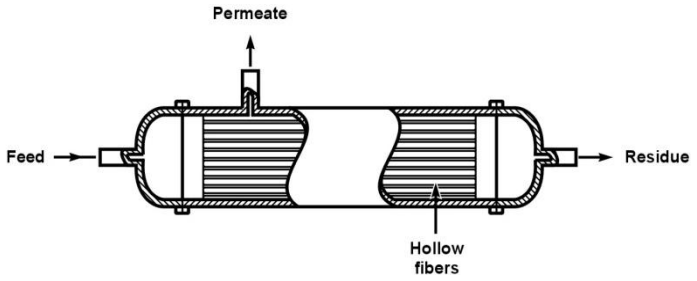
Membrane Technology Basics

- Membranes have to be thin to provide useful fluxes.



- Spiral-wound and hollow fiber modules are used.





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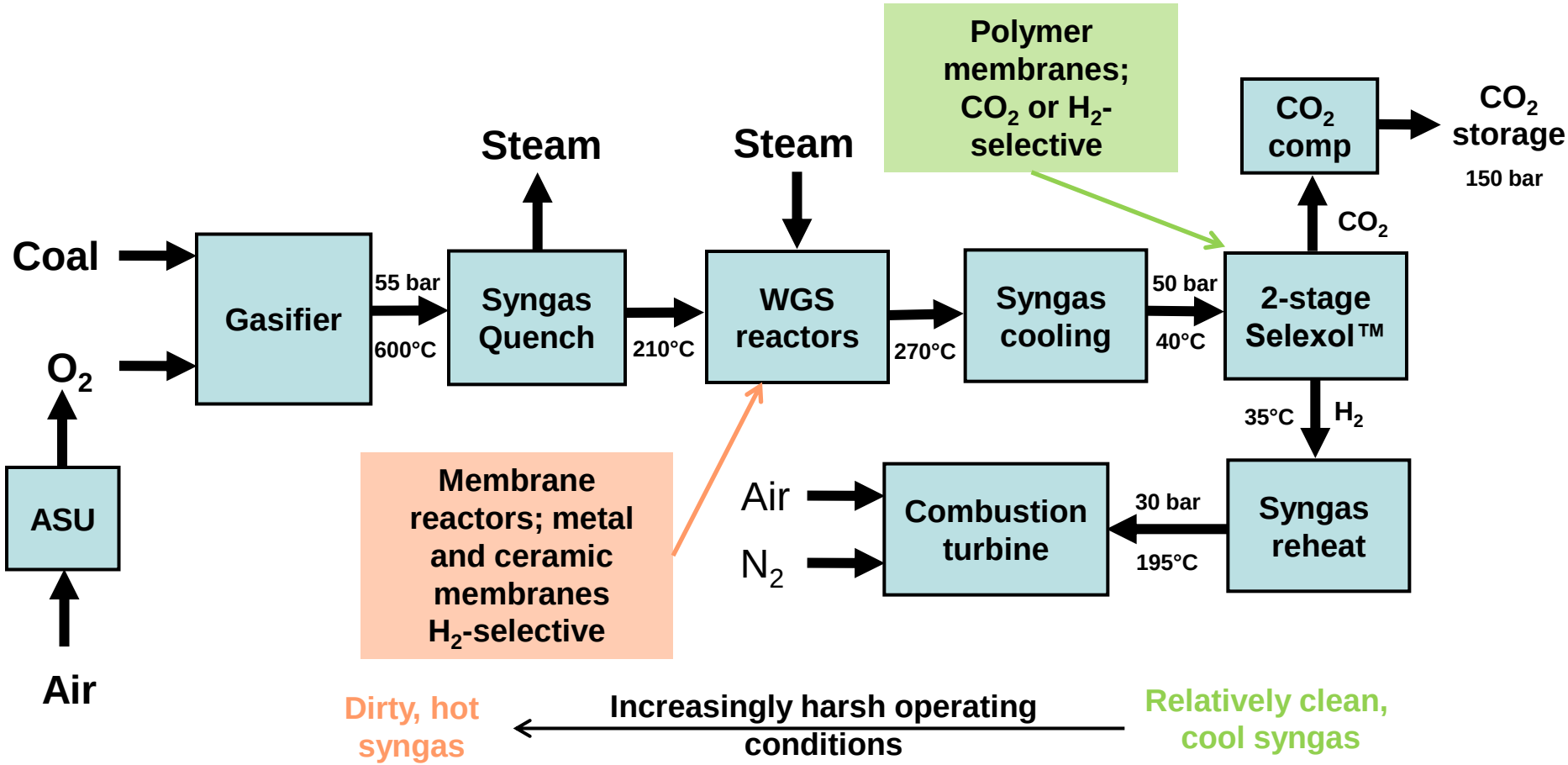
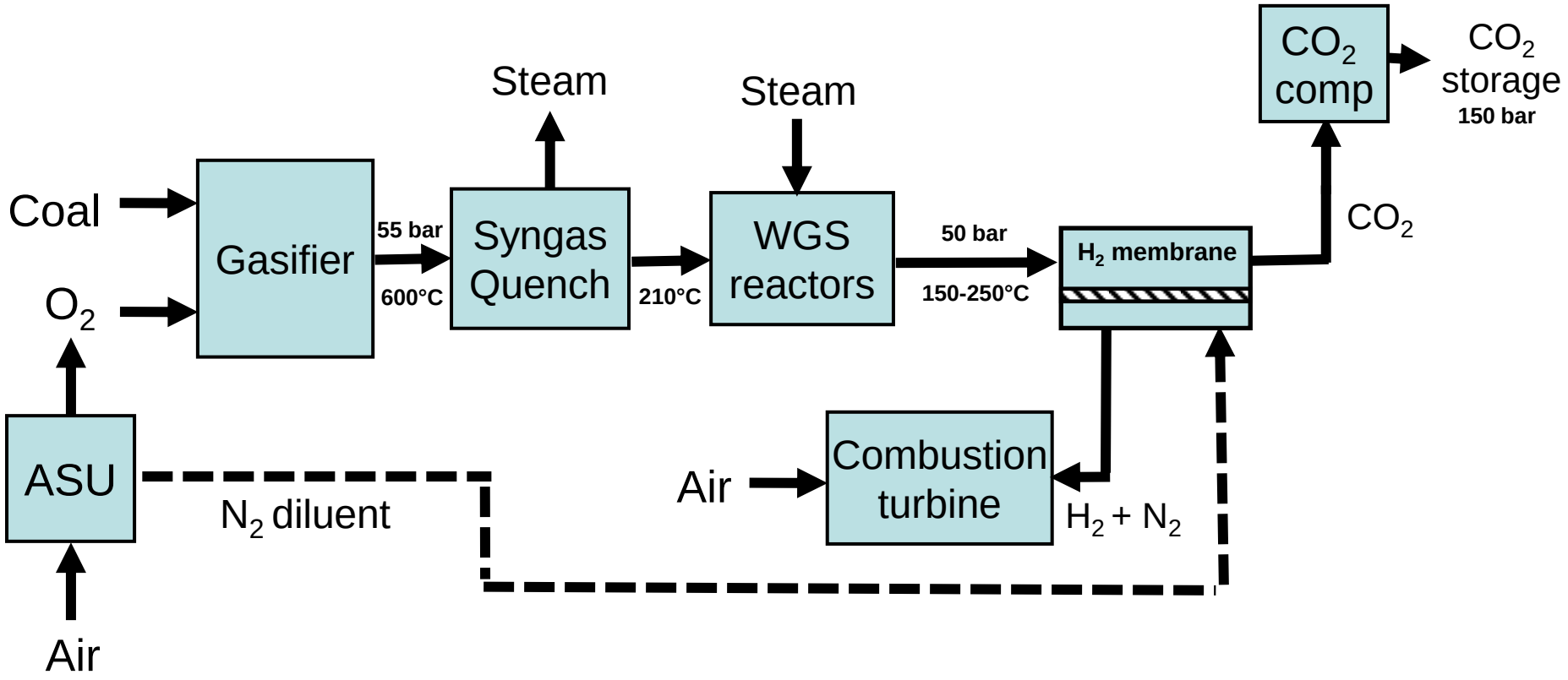
Syngas Cleanup Options



- Hot syngas cleanup membranes offer the potential for process intensification
- Warm/cool syngas cleanup membranes offer fewer operating challenges

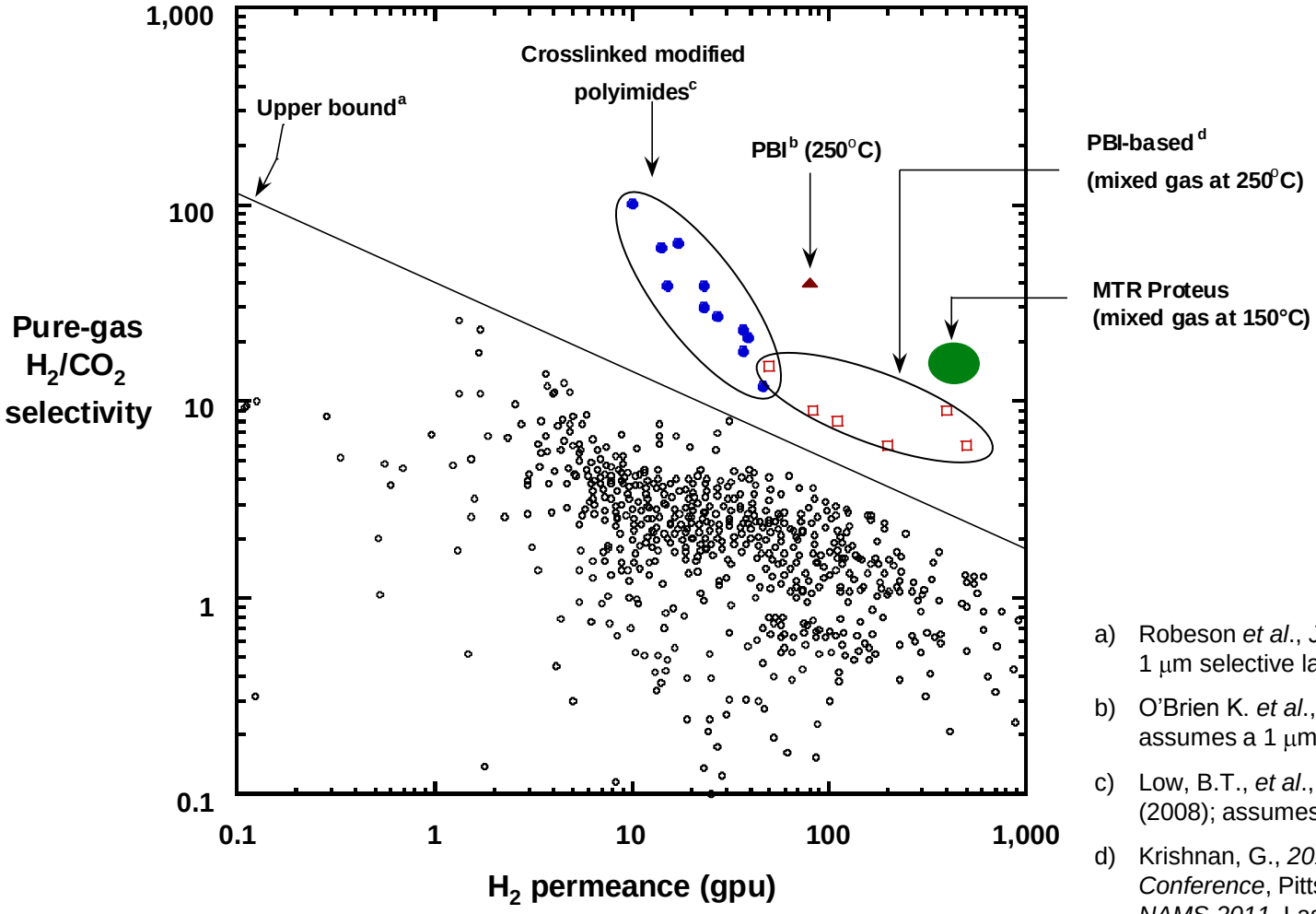
H_2-Selective Membranes Offer Advantages



H_2-selective membrane advantages:

- Can operate warm/hot to reduce the need for heat exchange
- Can use nitrogen sweep to maintain permeate fuel gas at turbine pressure
- Water goes with fuel gas; reduces CO_2 dehydration costs

New High-Temperature Polymer Membranes Show Promise



a) Robeson *et al*., *JMS 320,* 390-400 (2008); assumes a 1 μm selective layer.

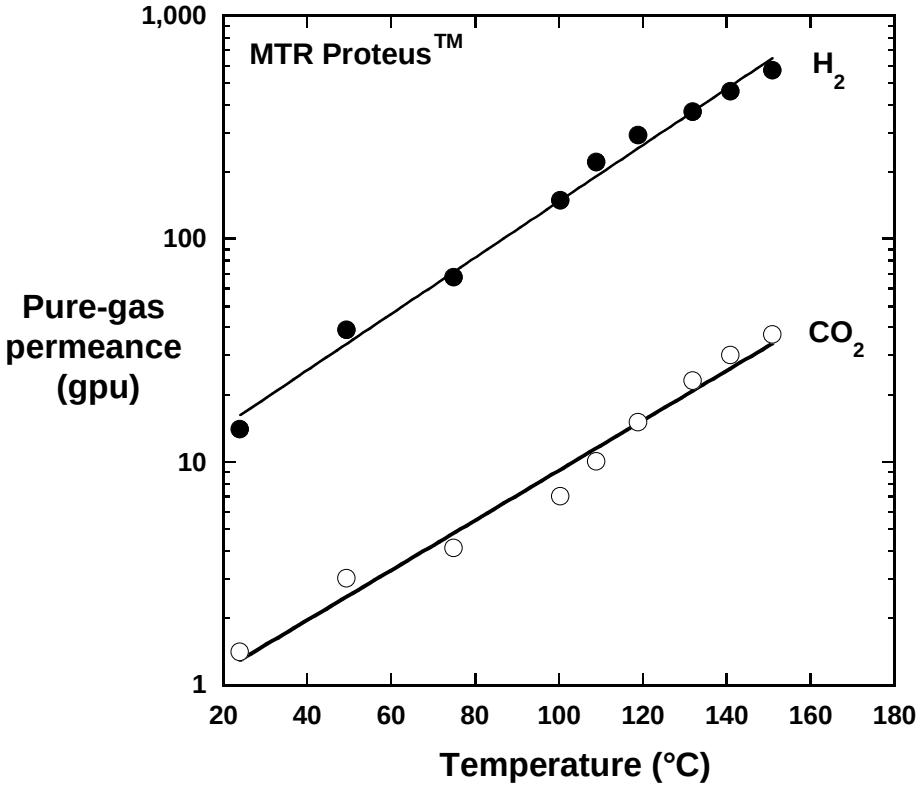
b) O'Brien K. *et al*., *DOE NETL project fact sheet 2009*; assumes a 1 μm selective layer.

c) Low, B.T., *et al*., *Macromolecules 41(4)*, 1297-1309 (2008); assumes a 1 μm selective layer.

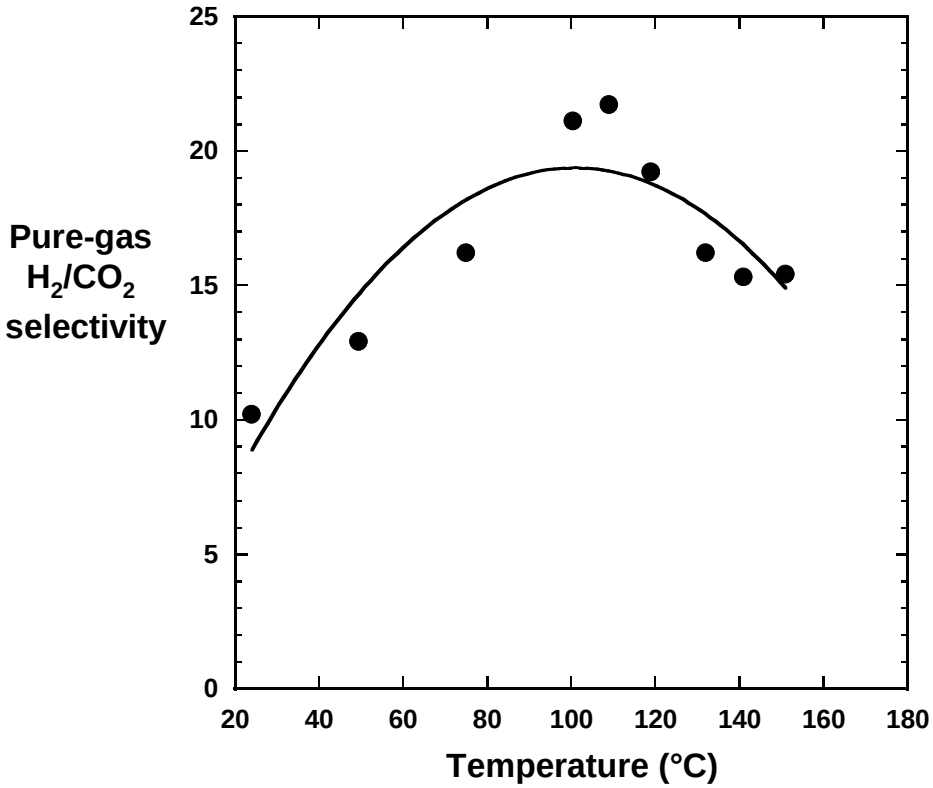
d) Krishnan, G., *2010 NETL CO_2 Capture Technology Conference*, Pittsburgh, PA and Klaehn, J., et al., *NAMS 2011*, Las Vegas, NV.

High temperature improves performance

Permeance



Selectivity



- Membranes have very low permeance and modest H_2/CO_2 selectivity at room temperature
- Increasing temperature improves permeance and selectivity; selectivity maximum?

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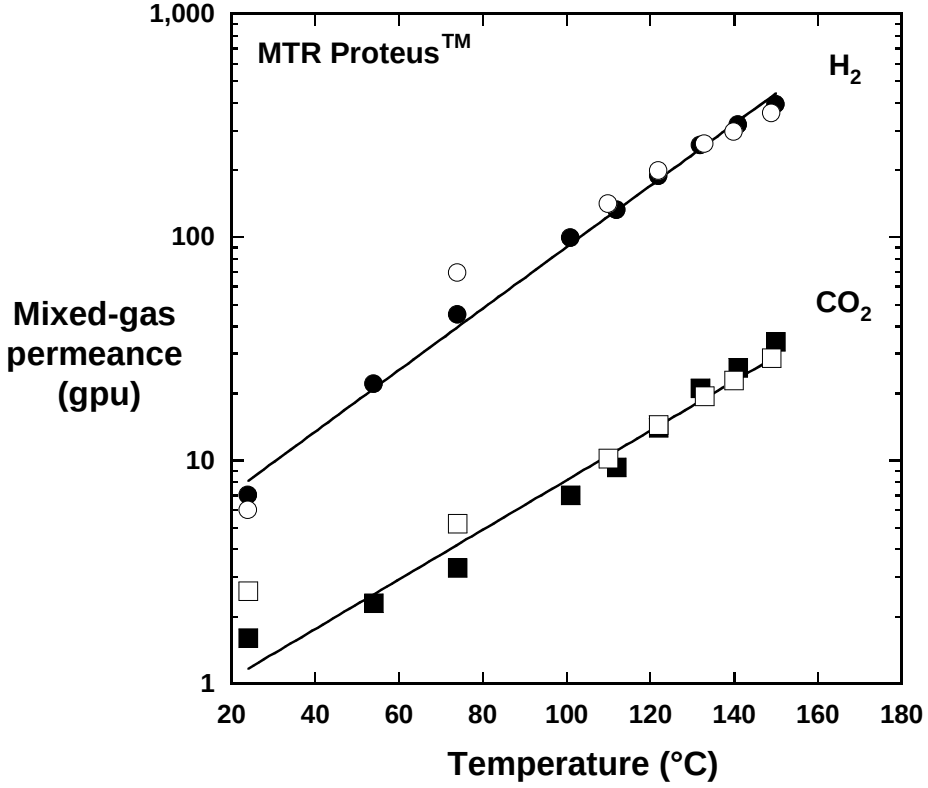
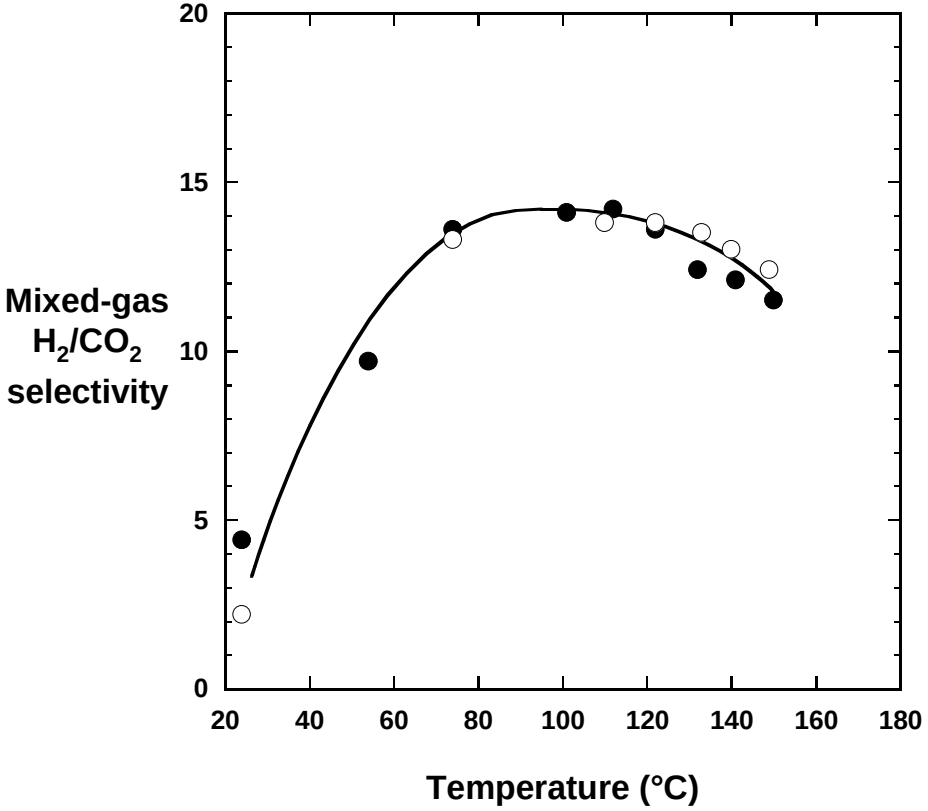
Temperature cycling gives reproducible results

Permeance

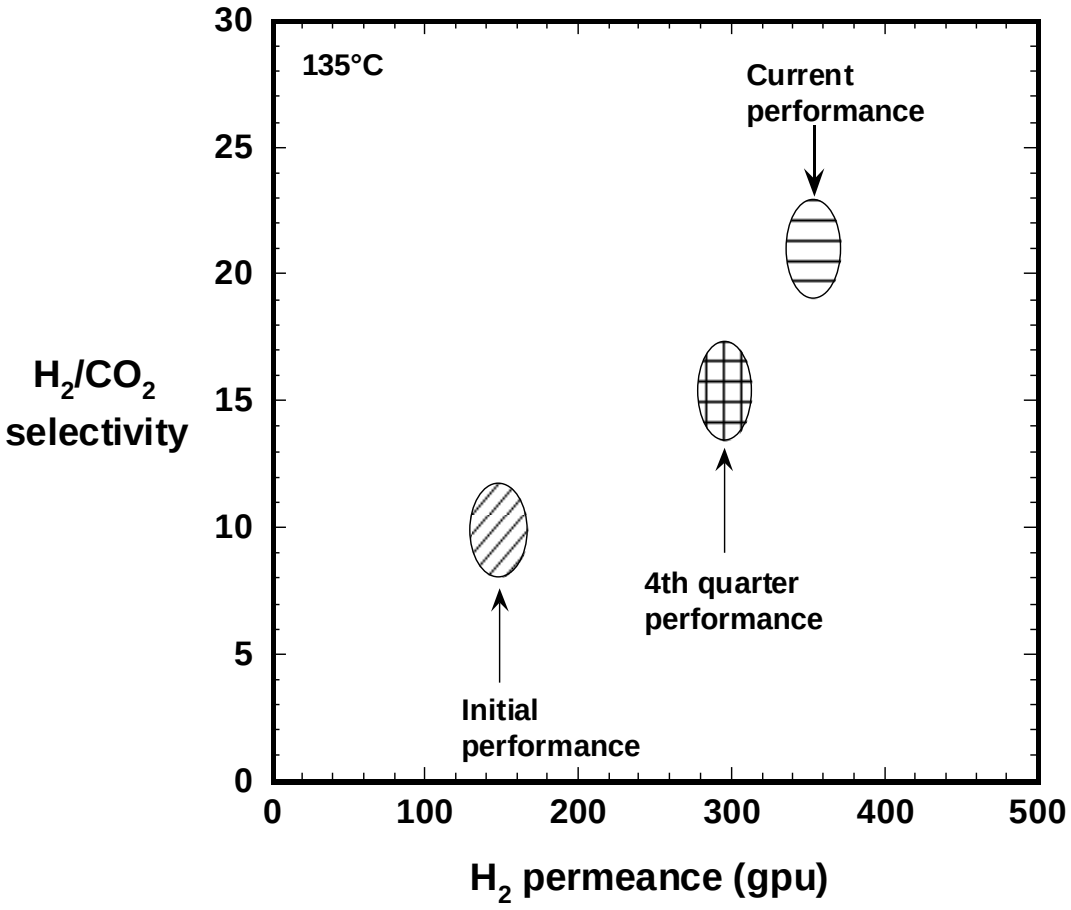


Selectivity



- Closed symbols = cycle 1; open symbols = cycle 2; both cycles show selectivity maximum
- Mixed-gas selectivities are slightly lower than pure-gas values

Significant Progress During this Project



- Membrane performance at 50 psig, 135°C with a 50%/50% CO_2/H_2 mixture

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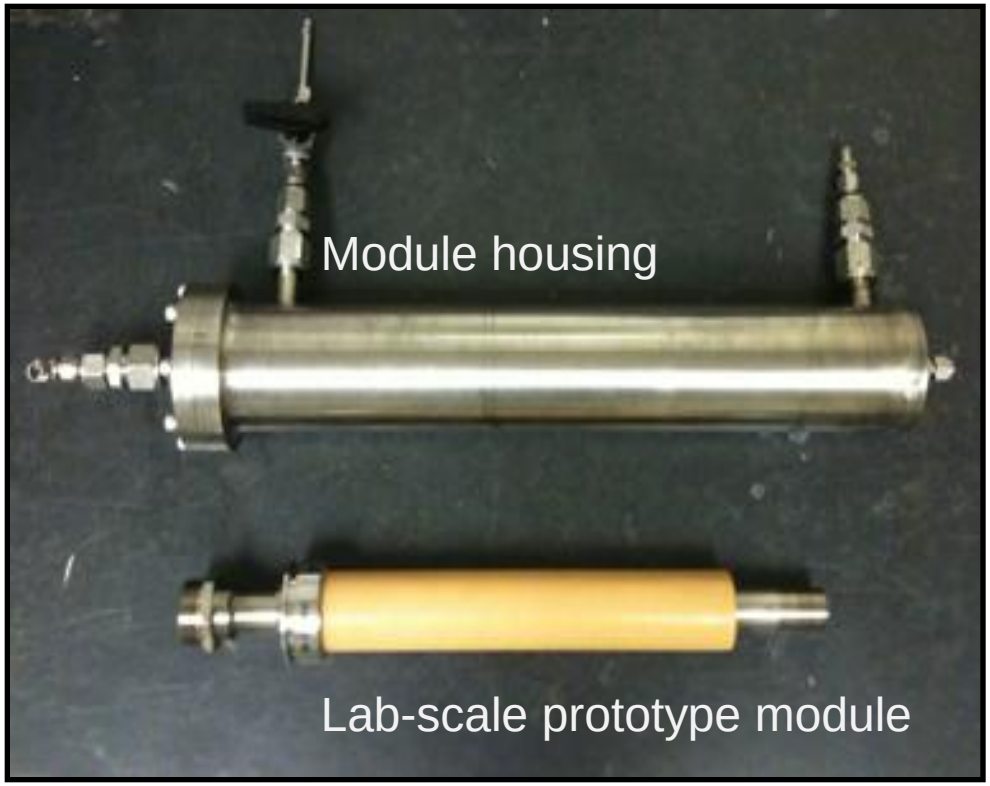
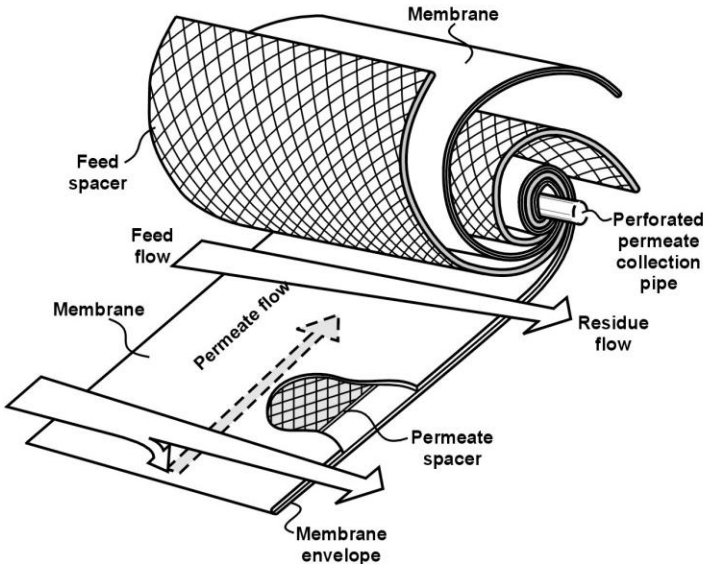
Development of Lab-scale Module





- Lab-scale prototype module: 12'' length with a membrane area of 0.14 m^2
- Module components were stable after cycling from 20 to 160°C

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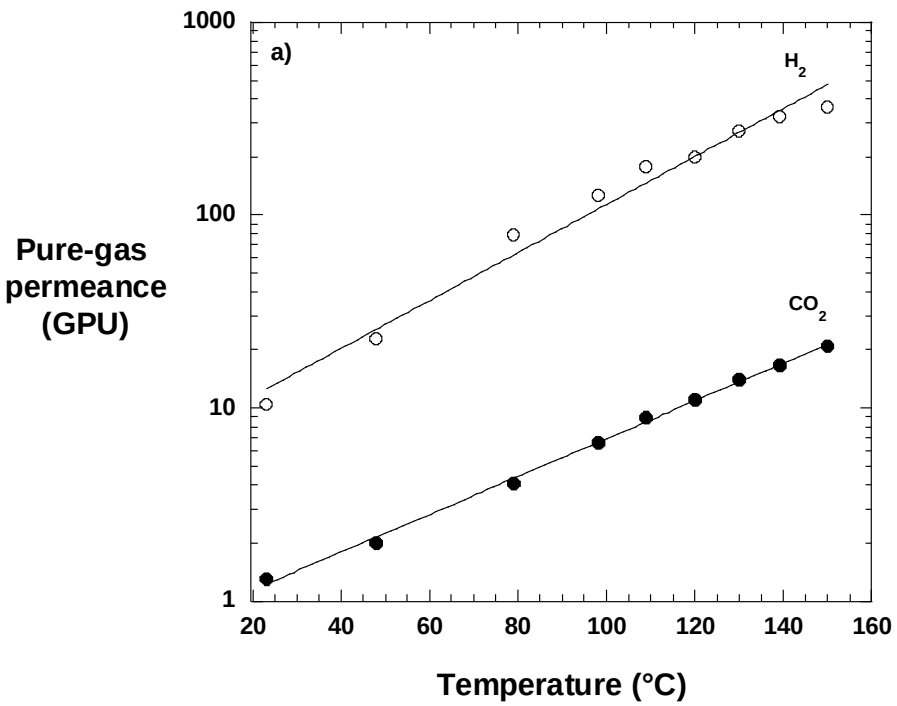
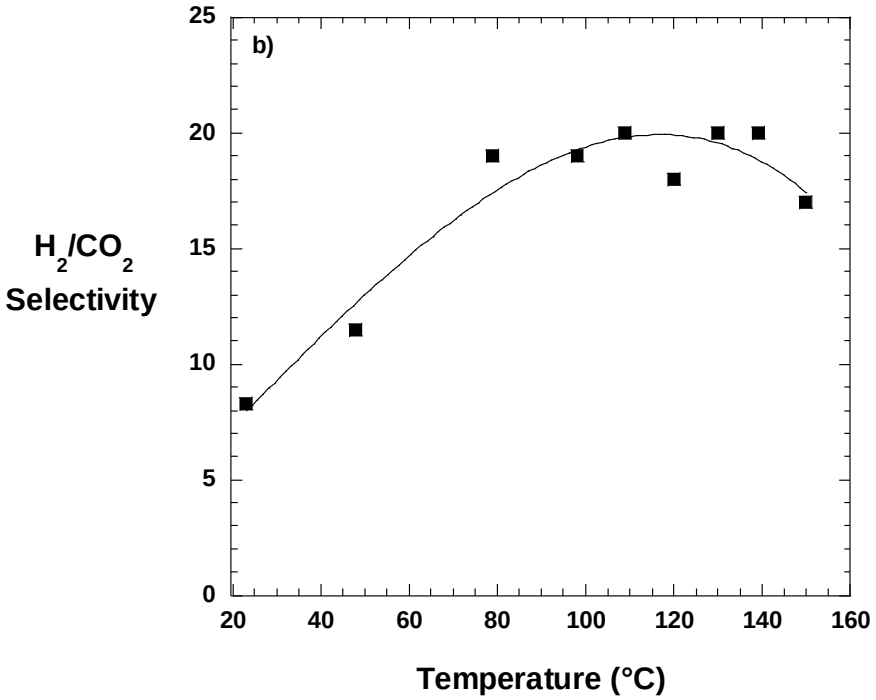
Performance of Lab-scale Modules

Permeances



Selectivity



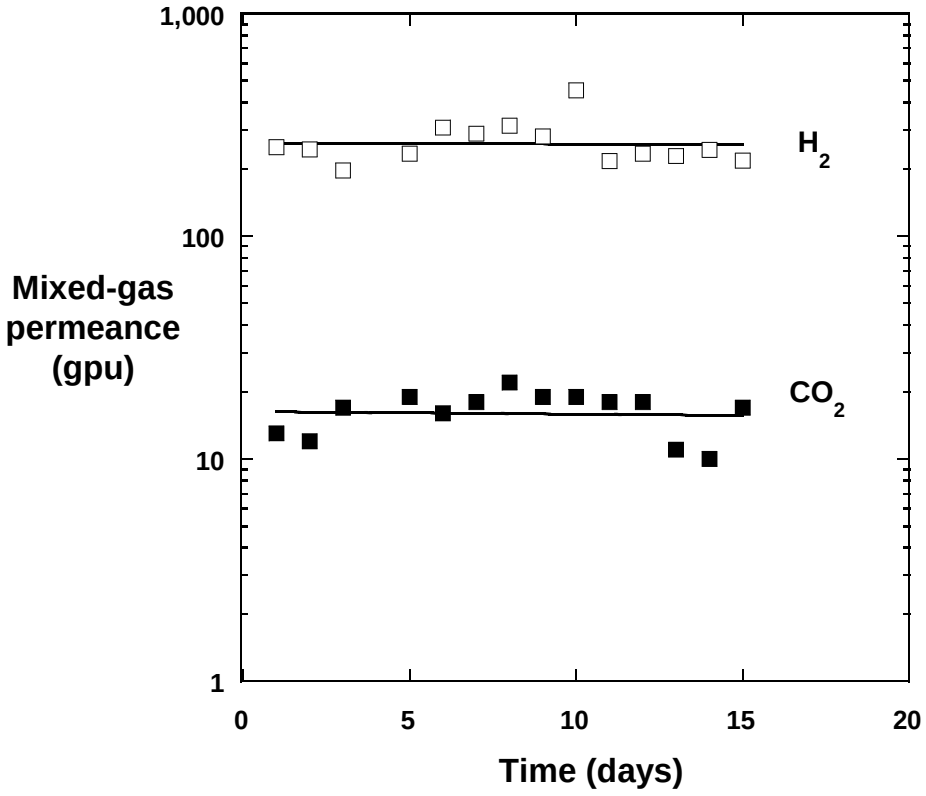
- Performance of lab-scale module is consistent with performance of membrane stamps.

Field Tests at NCCC

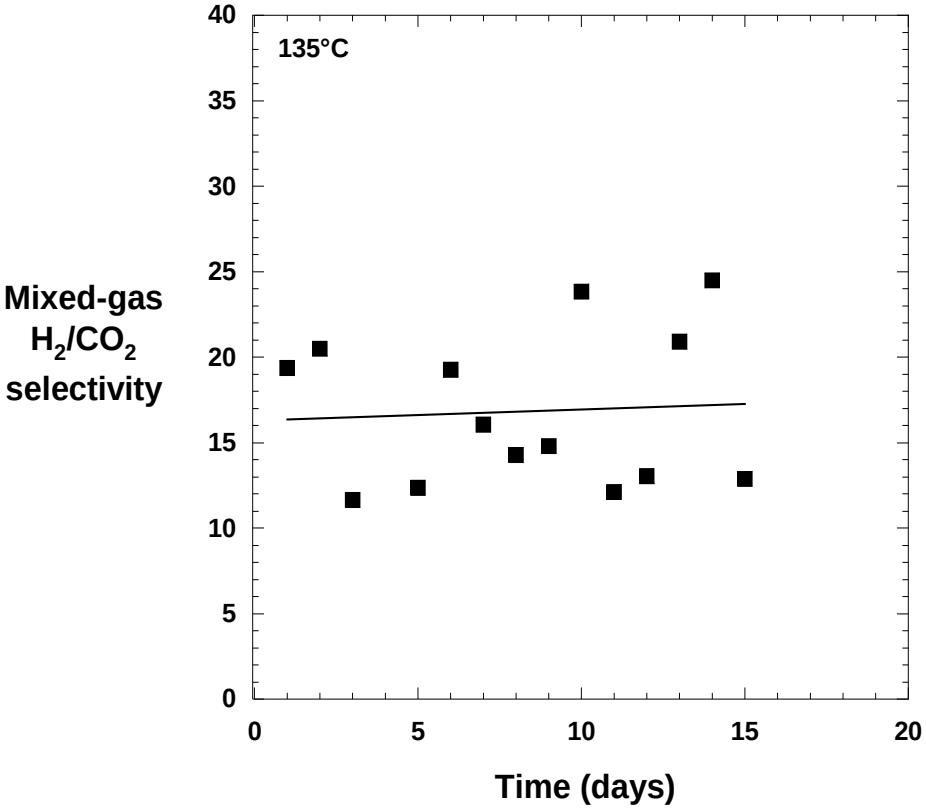
- MTR pilot testing at the National Carbon Capture Center (NCCC) run by Southern
- Feed is coal-derived syngas at 180 psia shifted or unshifted and with or w/o sulfur compounds

NCCC Results 1:
Stable Performance with Desulfurized Syngas

Permeance



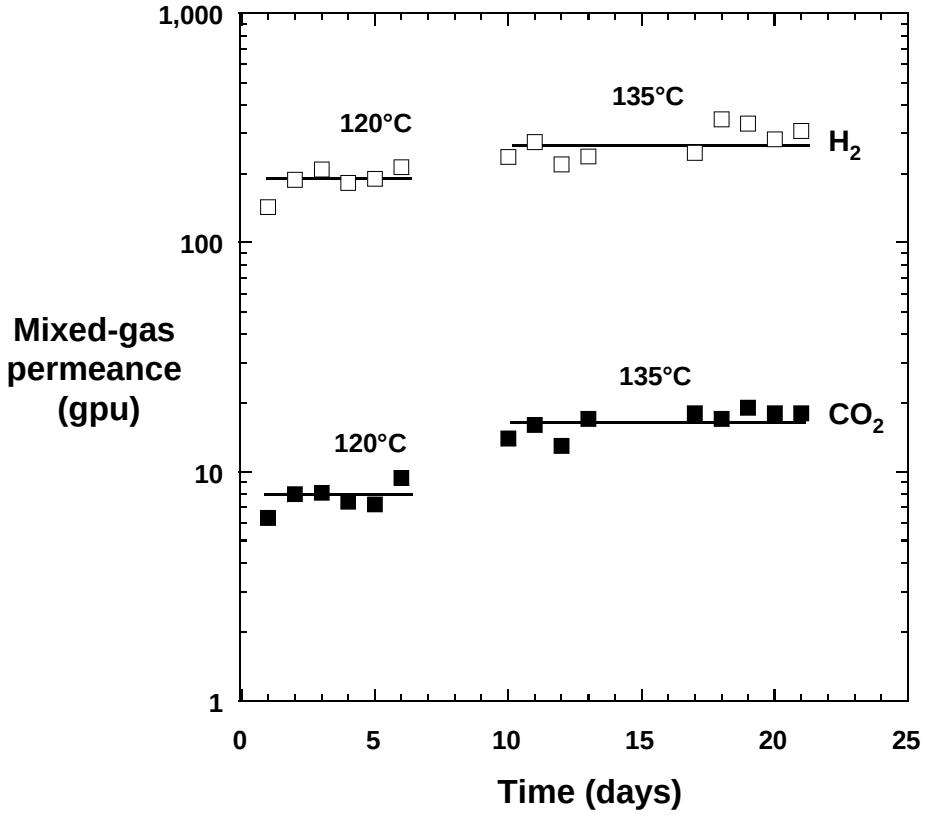
Selectivity



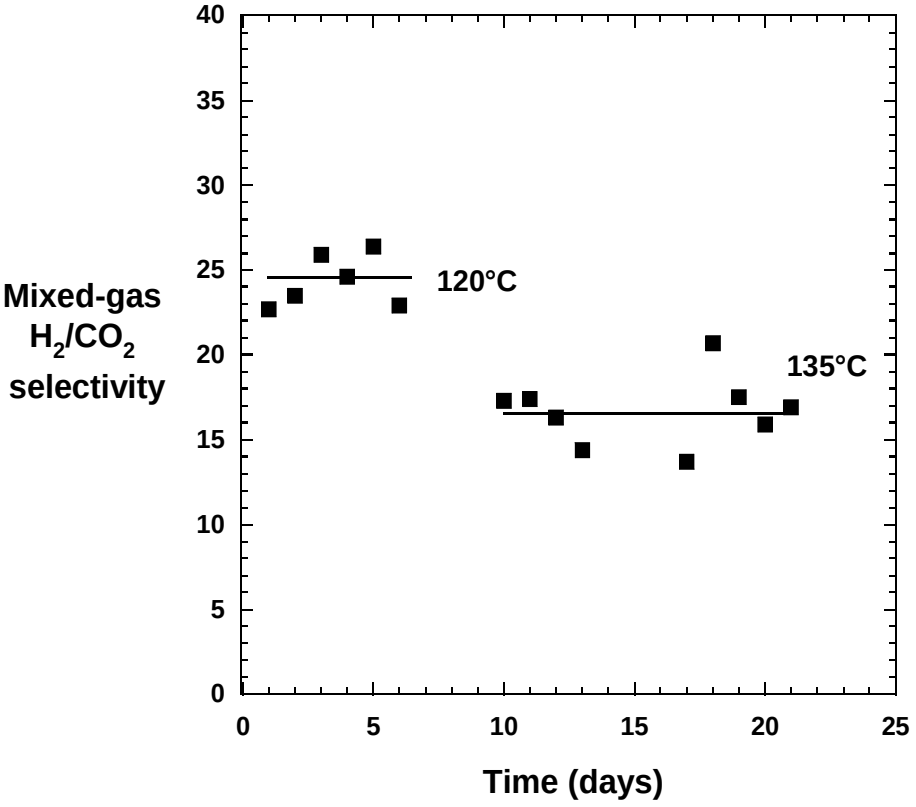
- Tests were conducted on membrane stamps (area = 30.2 cm^2) with a coal-derived syngas mixture at 150 psig and 135°C. Average H_2 permeance = 260 gpu and H_2/CO_2 selectivity = 16.

NCCC Results 2:
Stable Performance with High Sulfur Syngas

Permeance



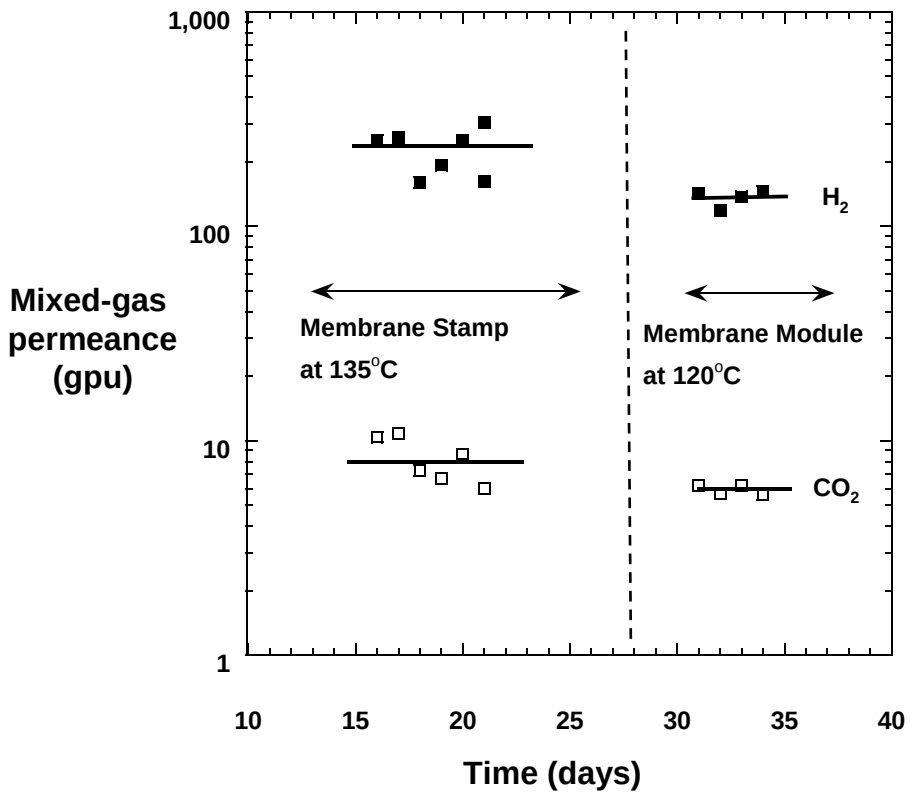
Selectivity



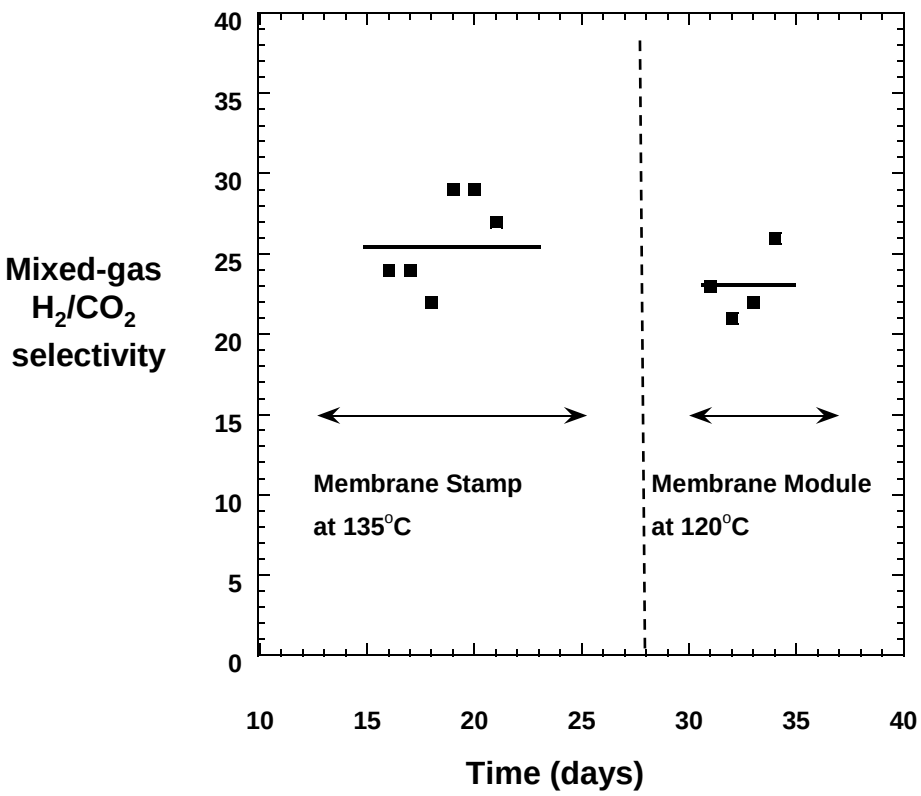
- Tests were conducted on membrane stamps with a coal-derived shifted syngas mixture containing 780 ppm H_2S at 175 psig and 120°C or 135°C.
- H_2/gas selectivities (CH_4, N_2, CO and H_2S) are higher than H_2/CO_2; water permeates with H_2

NCCC Results 3: Module Field Tests

Permeance



Selectivity



- Tests were conducted on a membrane stamp and a membrane module with a coal-derived shifted syngas mixture at 175 psig and 135°C and 120°C respectively.
- H_2 content was enriched from ~12% to ~ 80% for a membrane stamp and ~ 60% for a membrane module.

Key Field Test Findings

- Bench and field tests show that the performance of MTR Proteus™ membranes exceeds the project targets.
- NCCC field results demonstrate the membrane performance is stable at high temperature (up to 150°C) treating coal-derived syngas containing up to 780 ppm H_2S.
- Average field performance gives a mixed-gas H_2/CO_2 selectivity of 15-25, and a hydrogen permeance of 150-300 gpu at 120-150°C.
- 10 lb/h small module tests is on-going; full-scale modules require 500 lb/h syngas.

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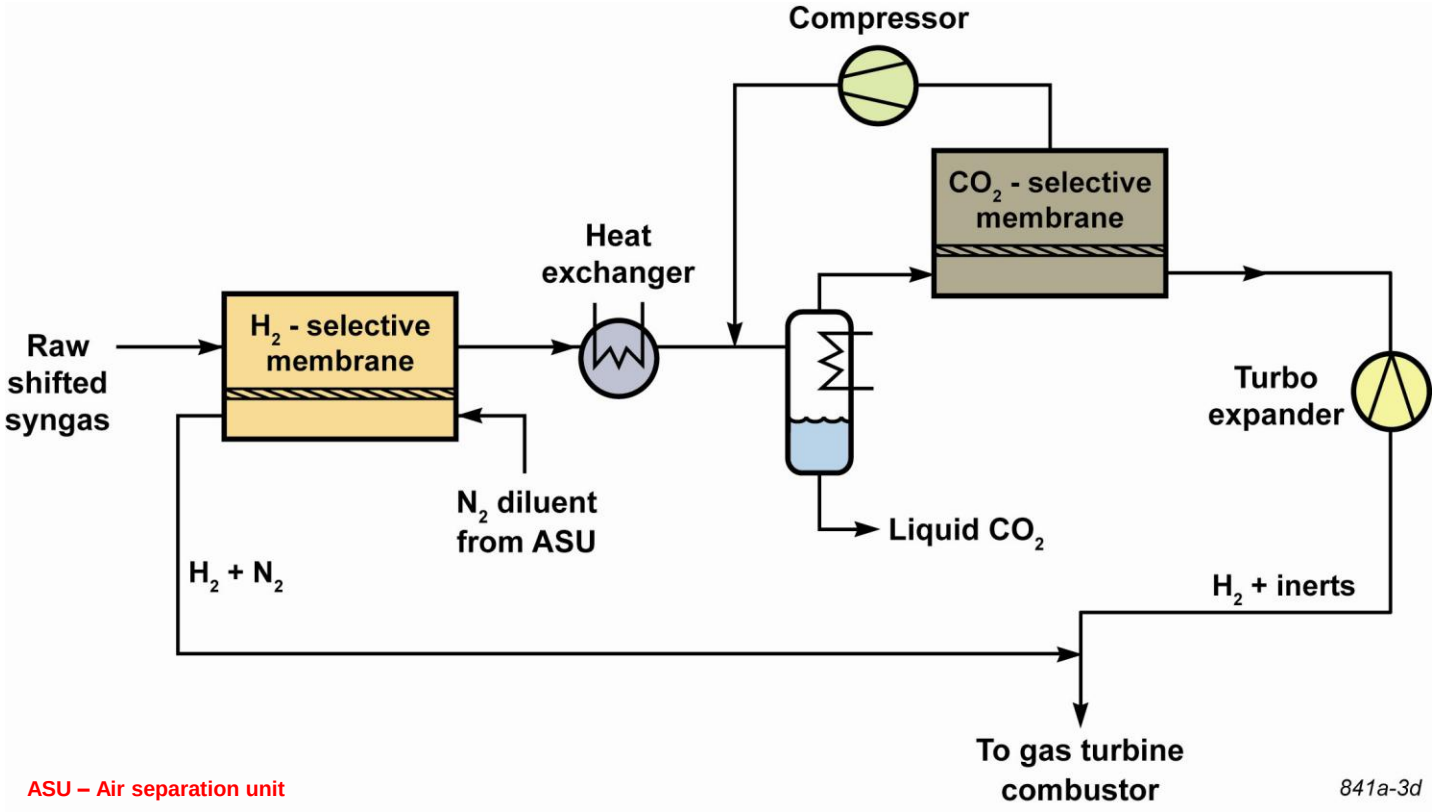
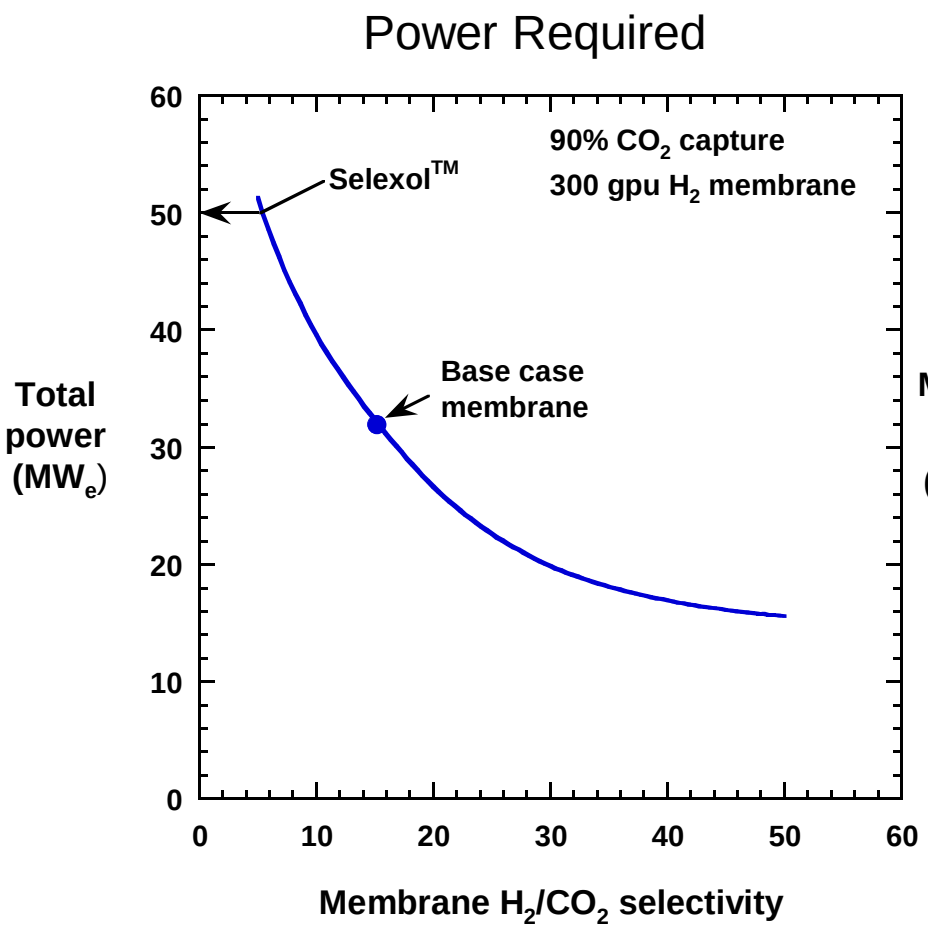
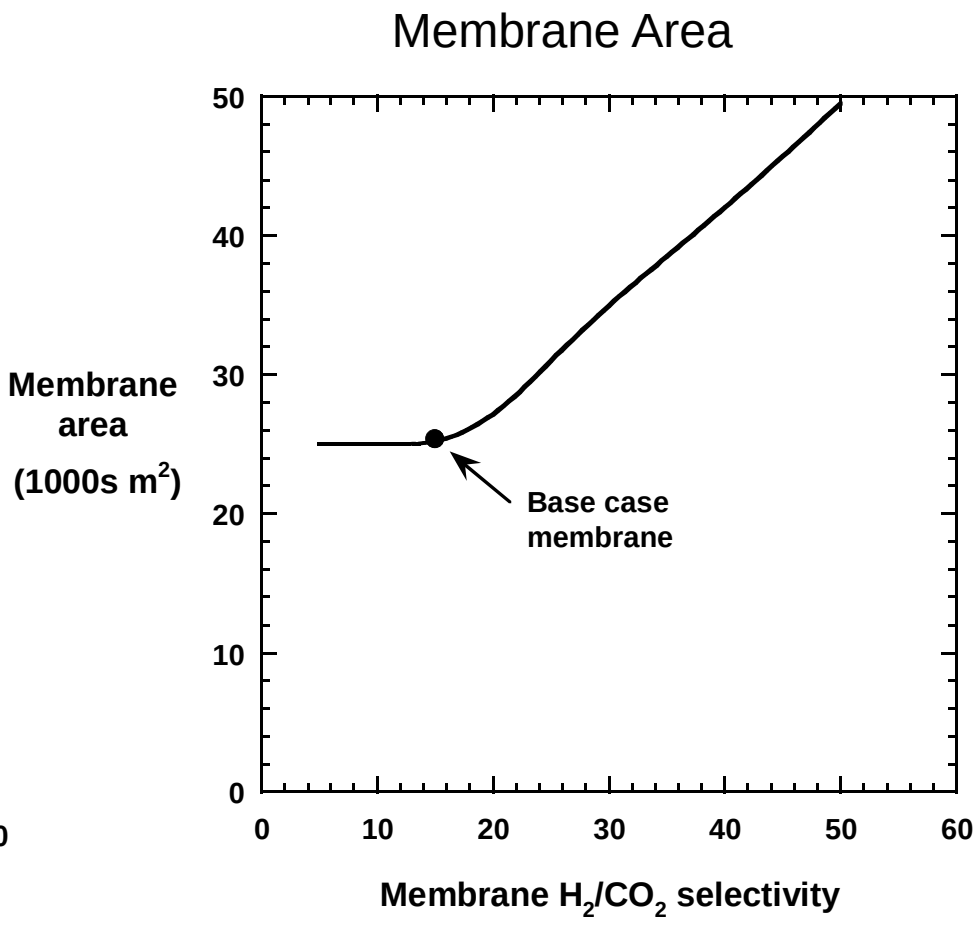
A Possible Process Design



- N_2 sweep on H_2-selective membrane greatly reduces energy requirements
- CO_2-selective membrane increases the operating temperature of the CO_2 purification/liquefaction step → reduces material costs and process complexity

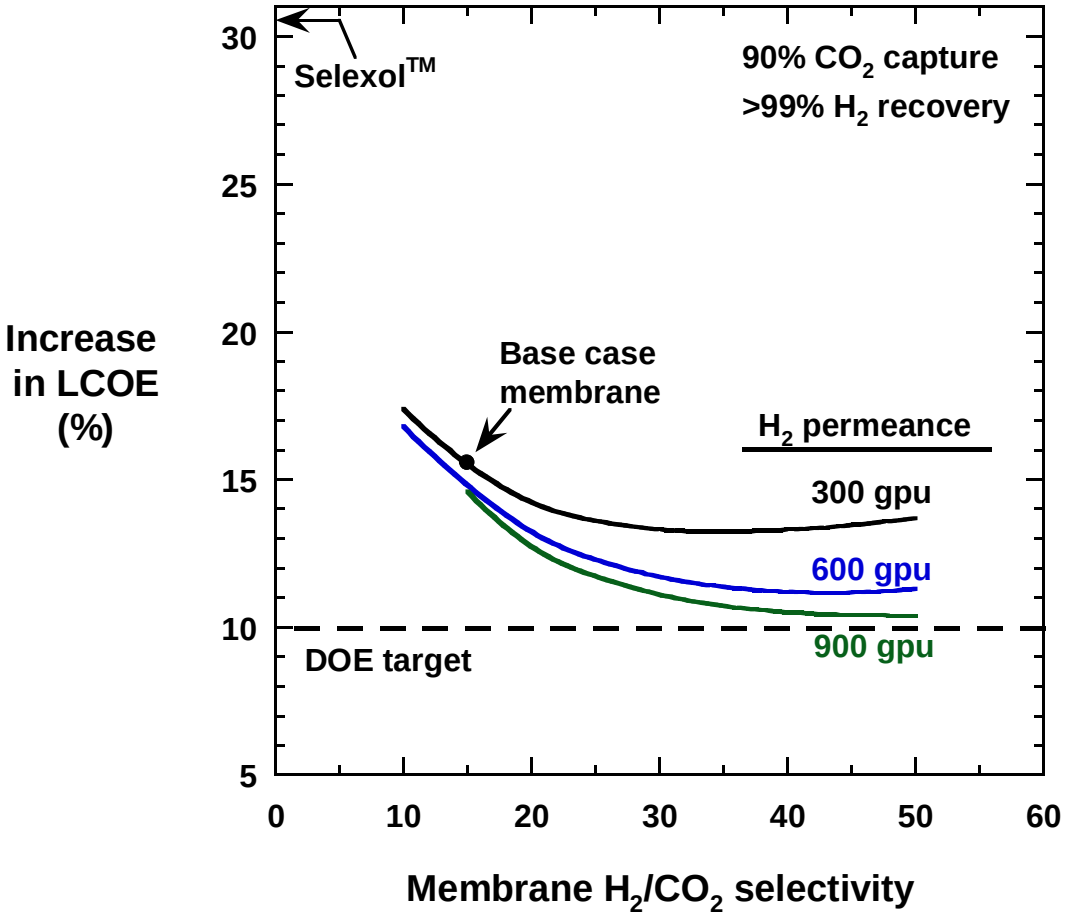
Higher H_2/CO_2 selectivity is beneficial





Calculations are for shifted syngas from a GE gasifier (case 2 in the DOE Bituminous Coal Baseline Report, DOE/NETL-2007/1281). Power includes compression to liquid CO_2.

Membranes can approach the DOE target



- Need H_2/CO_2 > 10 for 90% CO_2 capture
- Calculations are for shifted syngas from a GE gasifier (Case 2 in the DOE Bituminous Coal Baseline Report)
- Selexol™ installation and contingency factors were used for the membrane cases
- Calculations assume H_2S can be co-sequestered with CO_2. If not, add 5 points to LCOE

Next Steps

- Continue membrane improvements
- Develop commercial-scale modules
- Conduct relevant field tests
- Identify other H_2/CO_2 applications where these membranes can be used
- Test membrane modules

  at NCCC in 2011/12

  → 10 lb/h syngas run

  → 50 lb/h syngas run

Summary

- H_2-selective membranes have greater potential for cost and energy savings compared to CO_2-selective membranes
- Current membranes show H_2/CO_2 selectivities >20 with H_2 permeances > 200 gpu
- The best current design uses a hot H_2-selective sweep membrane combined with a cold CO_2-selective membrane to reduce CO_2 purification/liquefaction costs
- Current membranes give an increase in LCOE of ~15%, approaching DOE targets
- Higher H_2/CO_2 selectivity helps performance, especially up to 20; above this value, higher H_2 permeance is more beneficial

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Acknowledgements

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