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

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2010 NETL CO_2 Capture Technology Meeting

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Project Overview

Award number #: DE-FE0001124

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

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

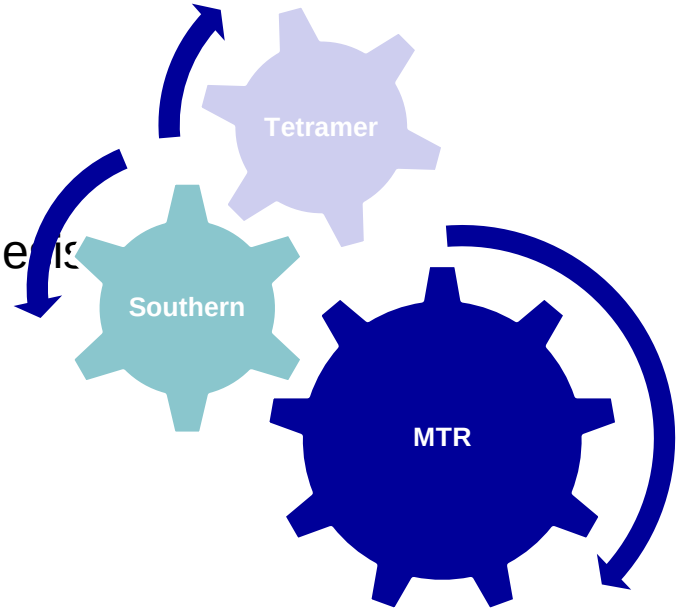
DOE program manager: Richard Dunst

Project team:

MTR --- membrane and process development

Tetramer Technologies --- specialty polymer synthesis

Southern Company NCCC --- field test



<u>Project scope:</u> 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.

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Project Objectives

- 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^oC)
- Membrane performance evaluation
  - Evaluate membrane performance and lab-scale membrane modules using simulated syngas
  - Evaluate membrane stamps in the field using coal-fired syngas
- 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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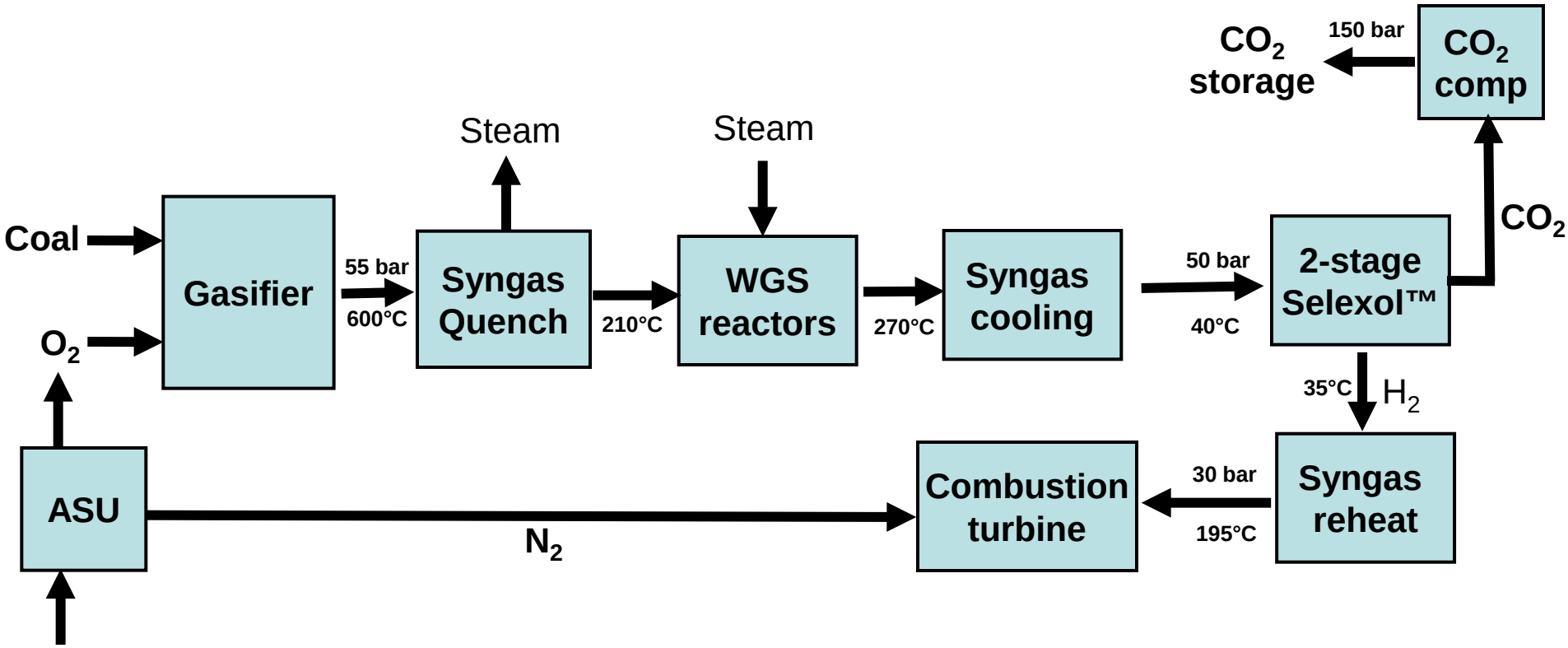
Membrane Options for Syngas Cleanup



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

1. Ciferino, J. and Marano, J, "Novel Integration of Gas Separation Membranes for CO_2 Capture from IGCC Power Plants," presented at AIChE New Orleans, April 2008.

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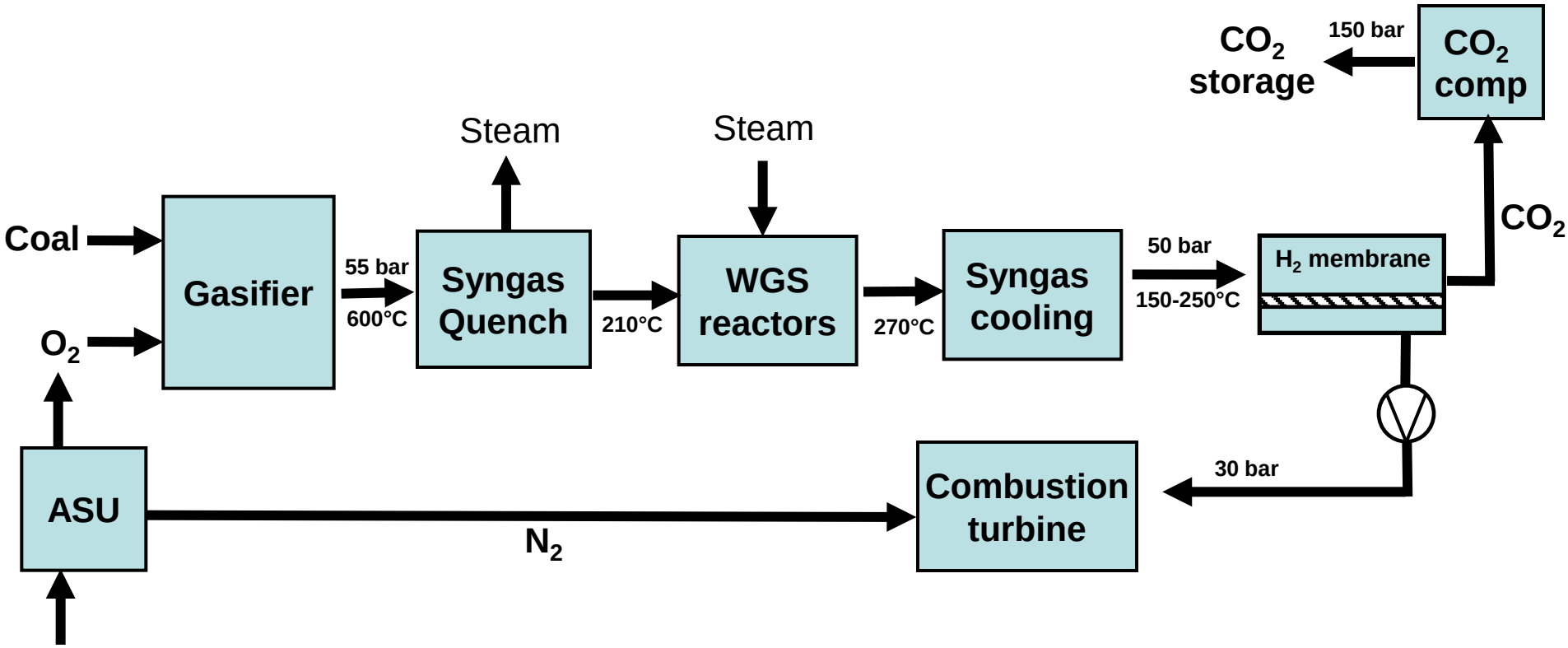

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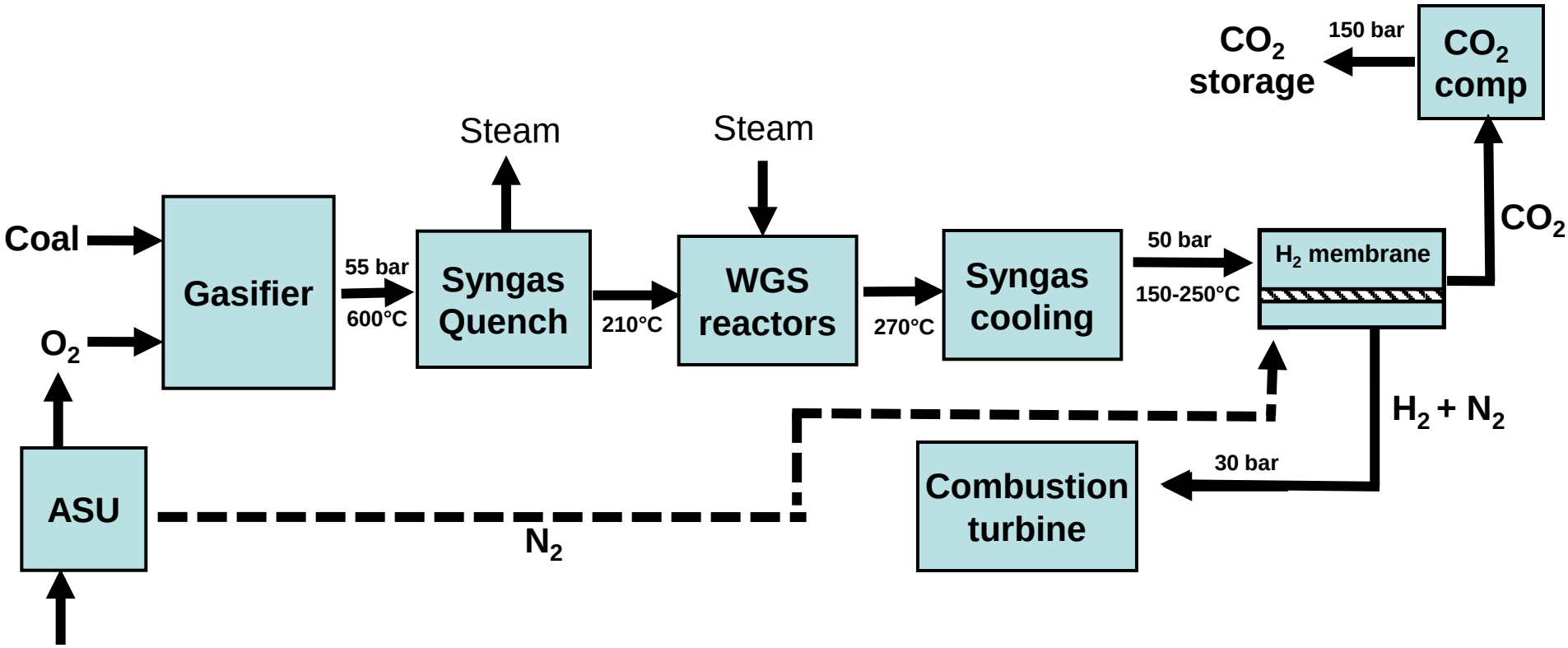

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Pros and Cons of Membranes for Syngas Cleanup

Advantages:

- Simple design; small footprint
- Energy efficient compared to sorption processes
- No water used; no leakage or disposal of chemical solvents

Challenges:

- Membrane reactor for hot/warm gas cleanup --- difficult operating conditions, stability in presence of contaminants
- Inorganic membranes --- lack of reproducible, low-cost module fabrication technology
- Polymer membranes --- thermal stability of membrane materials for hot/warm gas cleanup

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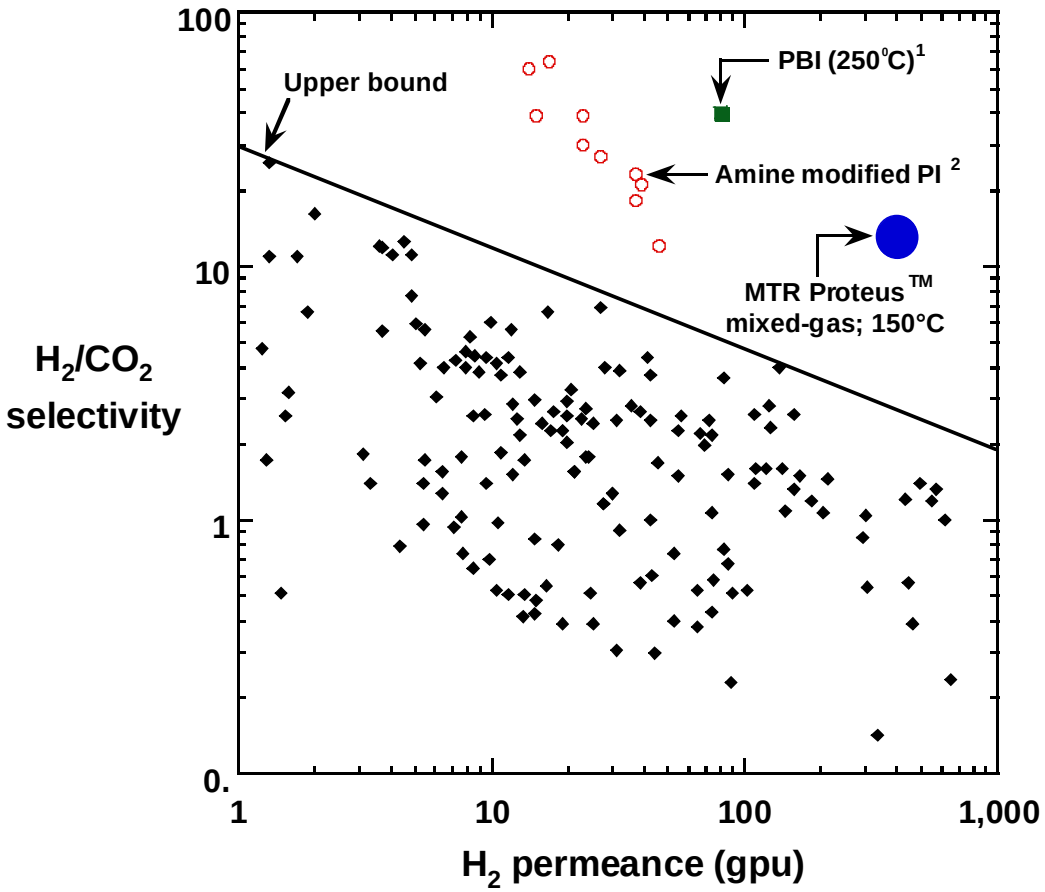
New high-temperature membranes show promising performance



Permeance conversions:

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

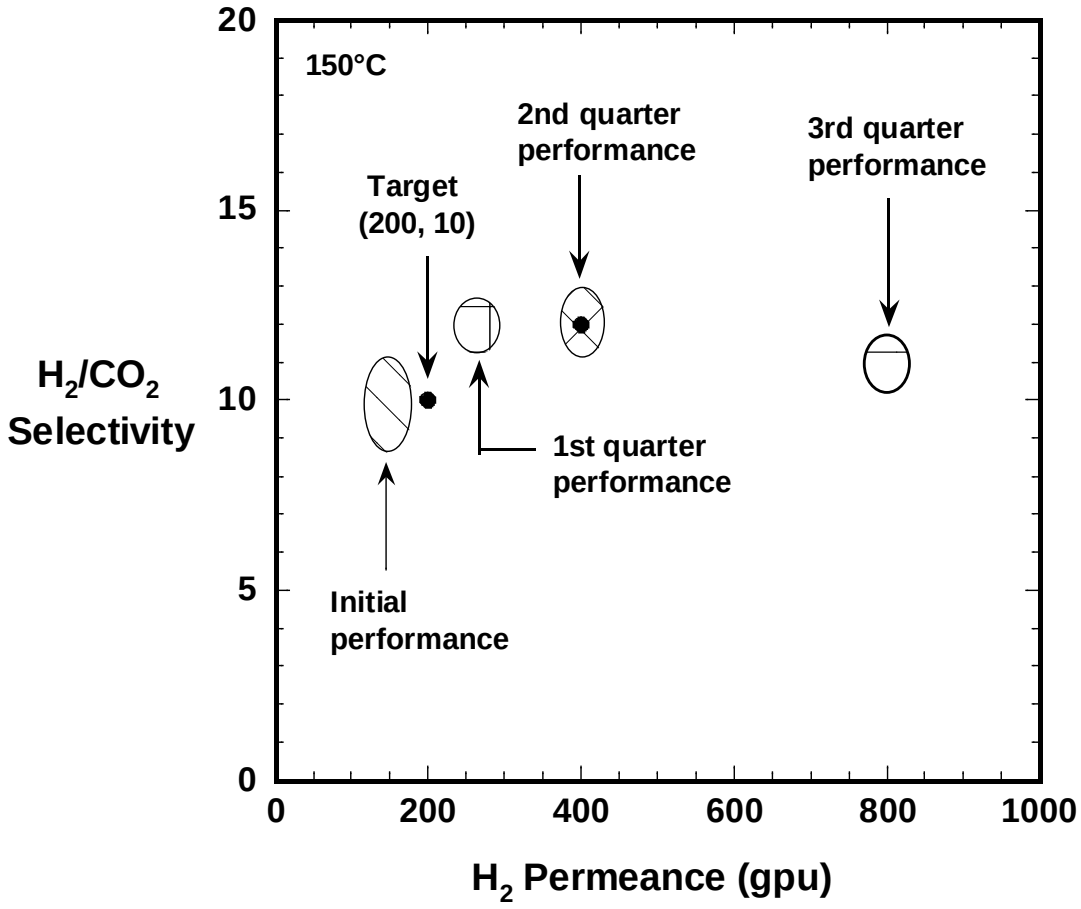
1 ft^3(STP)/(h ft^2 psi) = 1,600 gpu

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

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

1. O'Brien K. et al., **"**Fabrication and Scale-Up of PBI - Based Membrane System for Pre-Combustion Capture of Carbon Dioxide," DOE NETL project fact sheet 2009.
2. Low, B.T., et al., "Simultaneous Occurrence of Chemical Grafting, Cross-linking, and Etching on the Surface of Polyimide Membranes and Their Impact on H_2/CO_2 Separation," *Macromolecules 41*(4),1297-1309 (2008).

Membrane performance has improved significantly



- Mixed-gas performance at 50 psig, 150°C with a 50%/50% H_2/CO_2 mixture

Field Tests at the National Carbon Capture Center (NCCC)

- 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
- Two types of membranes were tested
  - CO_2-selective Polaris™ modules (tested at 40°C, 165 -190 psia)
  - H_2-selective Proteus™ membranes (tested at 120°C or 135°C, 165 – 190 psia)
- Total of three field tests to date; each test lasted 3 to 6 weeks
  - November 2009, April 2010 and August 2010
- Two types of syngas streams were provided
  - Unshifted syngas: 10%H_2, 69%N_2, 1%CH_4, 7%CO, and 13%CO_2
  - Shifted syngas: 13%H_2, 69%N_2, 1%CH_4, 2%CO, 15%CO_2 and 780ppm H_2S.

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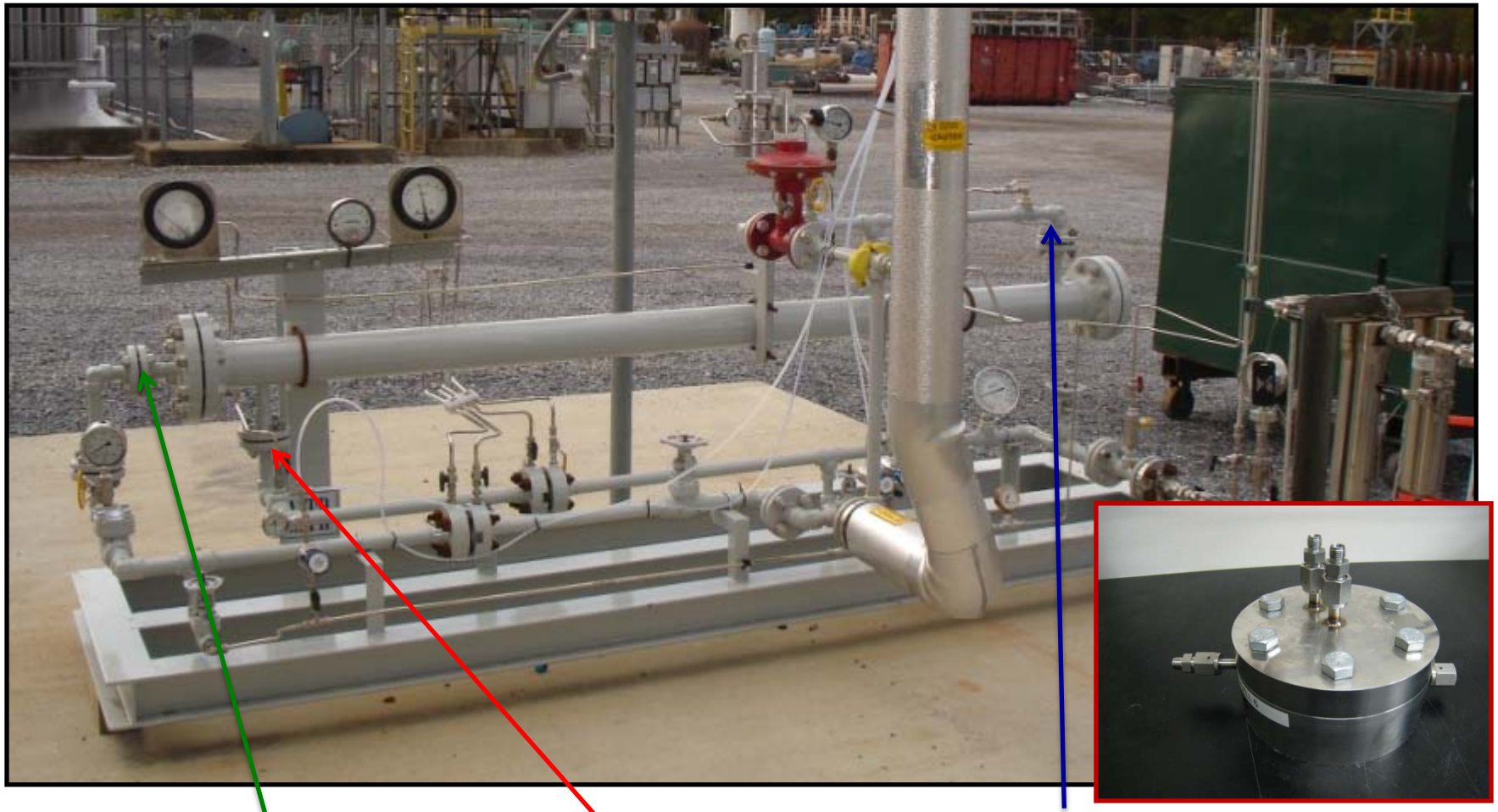
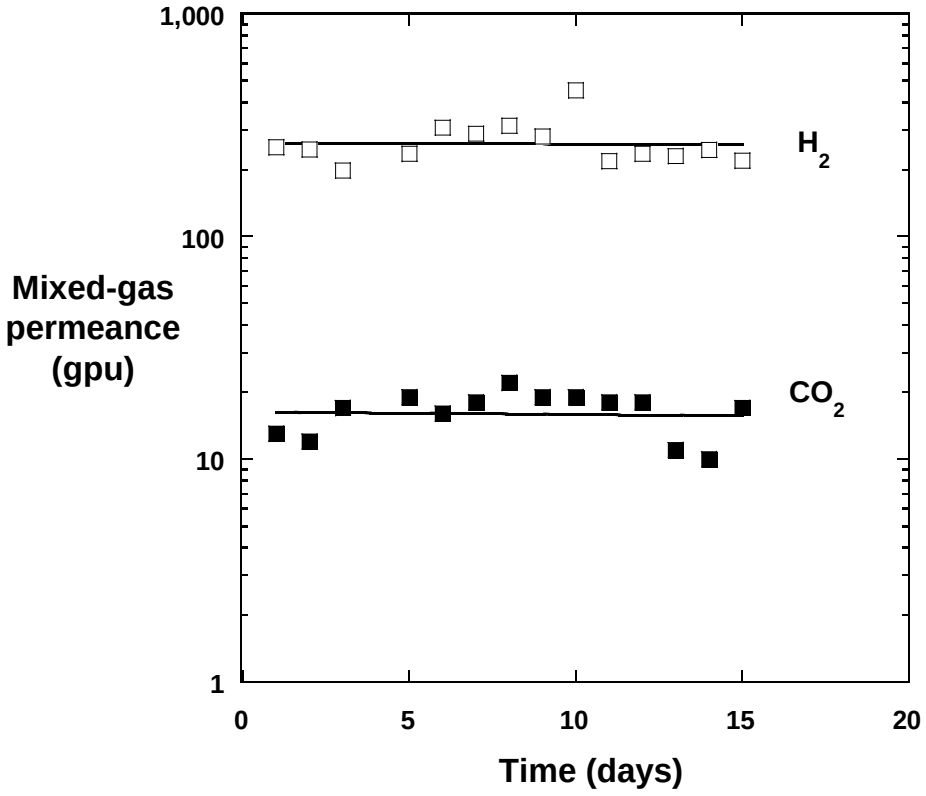
MTR Test Unit at NCCC

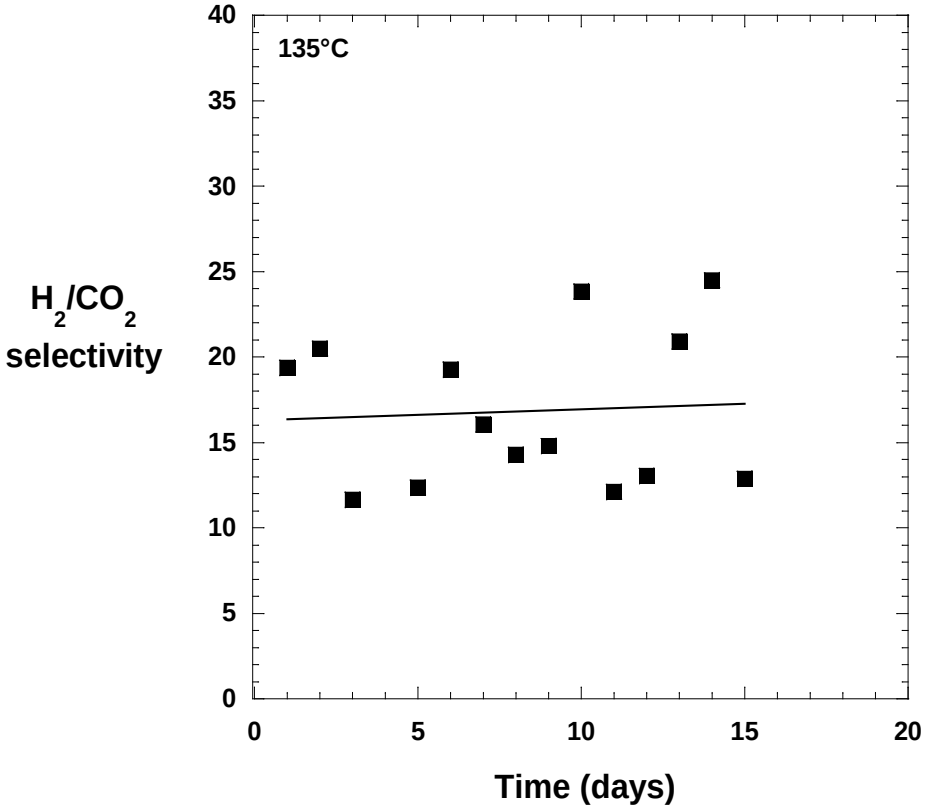


NCCC Results 1:
Stable Performance with Desulfurized Syngas

Permeance



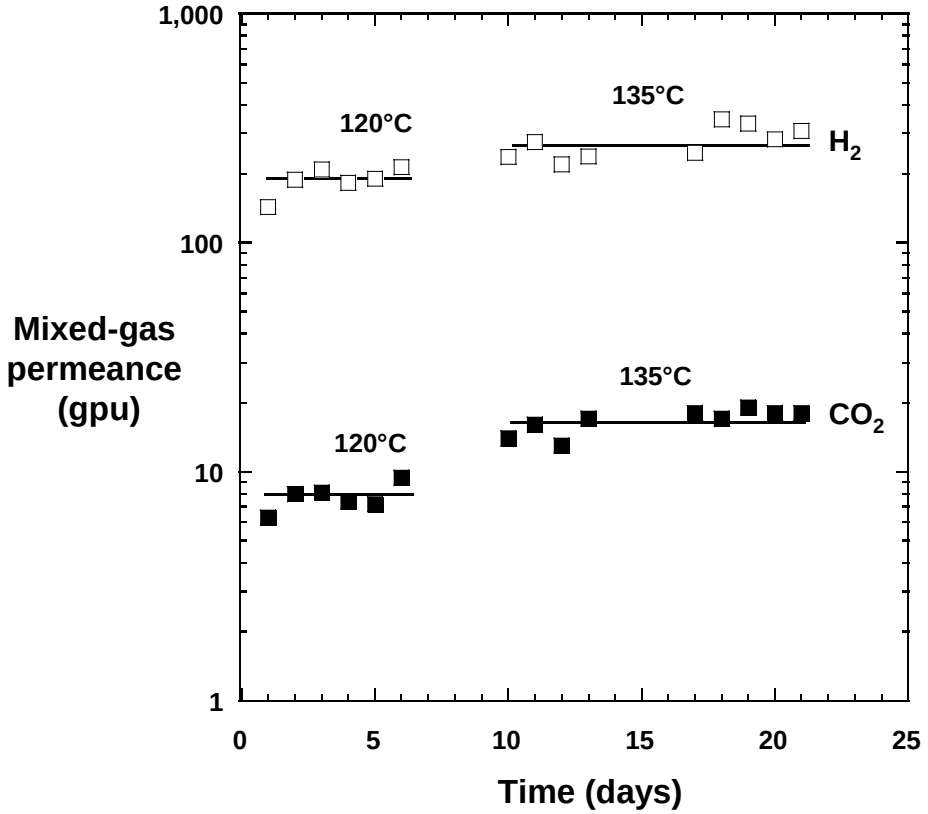
Selectivity



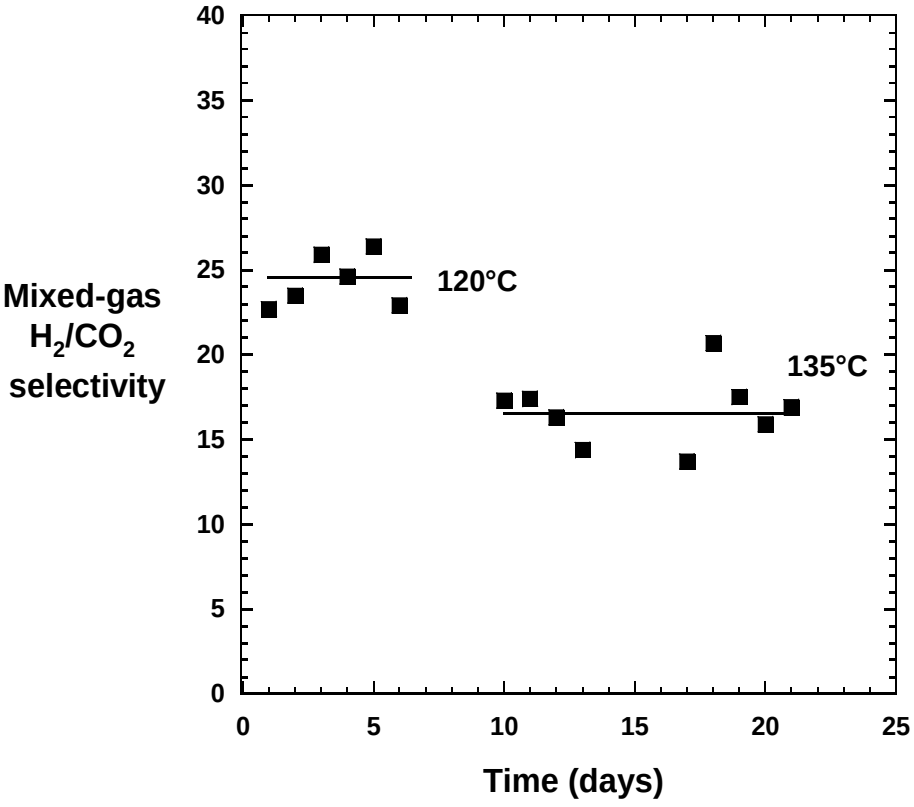
- Tests were conducted on membrane stamps (area = 30.2 cm^2) with a coal-derived syngas mixture at 150 psig and 135°C. Average H_2 permeance = 260 gpu and H_2/CO_2 selectivity = 16.

NCCC Results 2:
Stable Performance with High Sulfur Syngas

Permeance

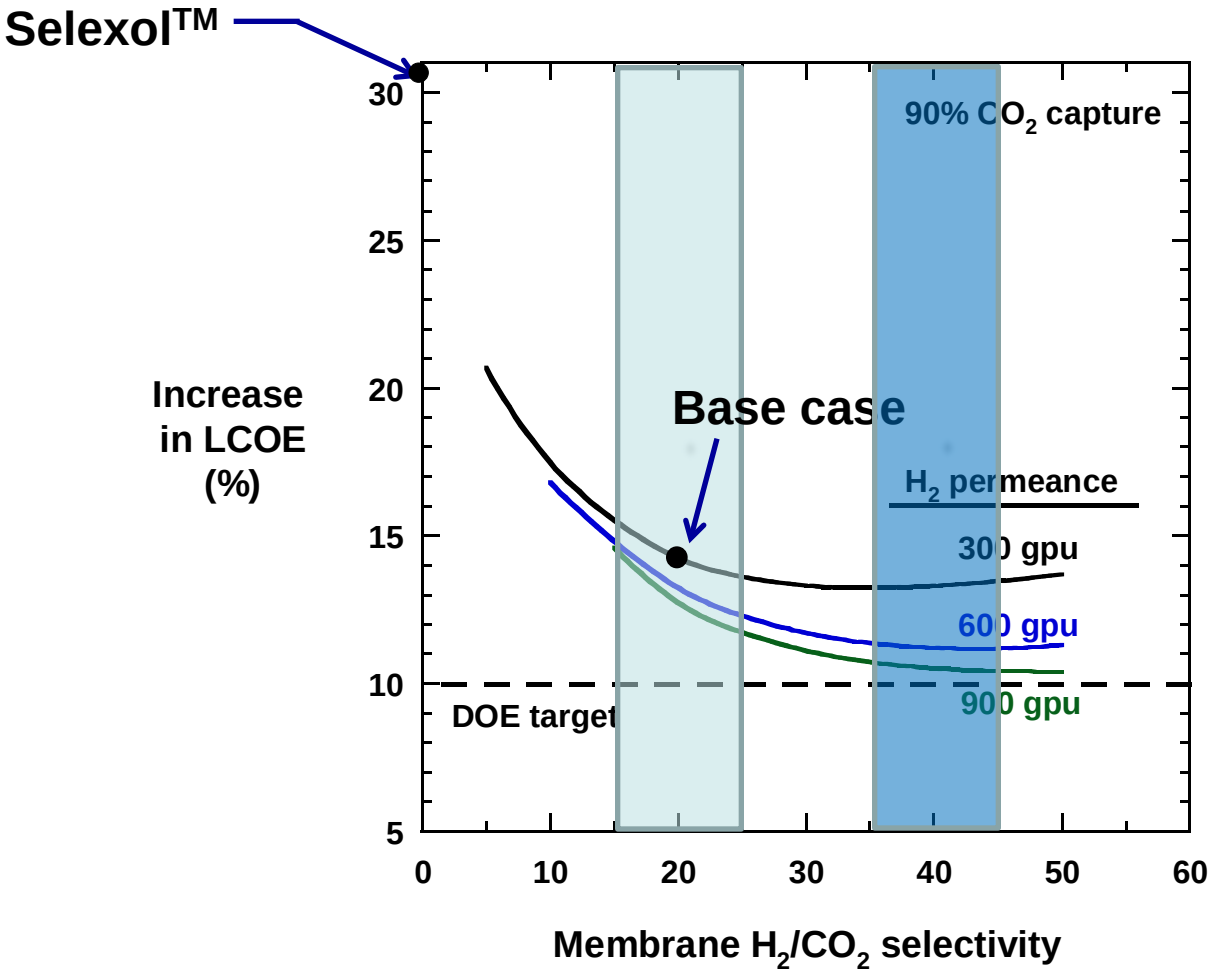


Selectivity



- Tests were conducted on membrane stamps (area = 30.2 cm^2) with a coal-derived shifted syngas mixture at 175 psig and 120°C or135°C.
- H_2 content was enriched from ~10% to ~60 – 80%.
- H_2/gas selectivities (CH_4, N_2, CO and H_2S) are higher than H_2/CO_2.

Current membranes show potential to approach the DOE LCOE target



- 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.

Milestones

- Confirmed that composite membranes made from novel polymers give hydrogen permeances of at least 200 gpu and H_2/CO_2 selectivities of greater than 10 in bench-scale tests as well as in field tests.
- Completed scale up of composite membranes on a commercial coater.
- Identified the membrane performance requirement in order to meet the DOE program targets. Determined the overall technical and economic competitiveness of the proposed process as compared to alternative technologies.
- Develop bench-scale membrane modules and demonstrate module performance and lifetime consistency with small-scale membrane stamp studies.

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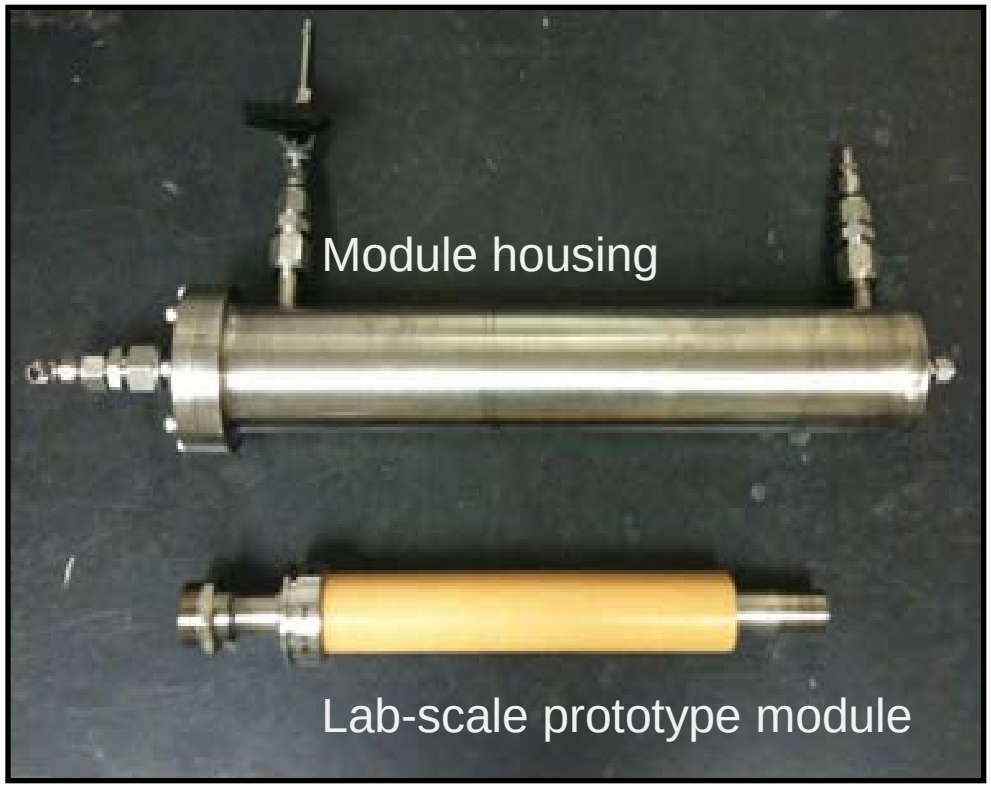
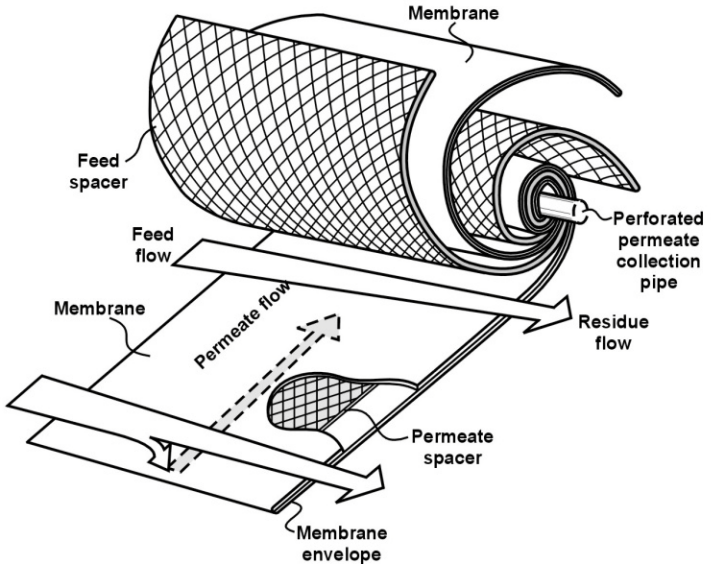
Lab-scale module development is on-going





- 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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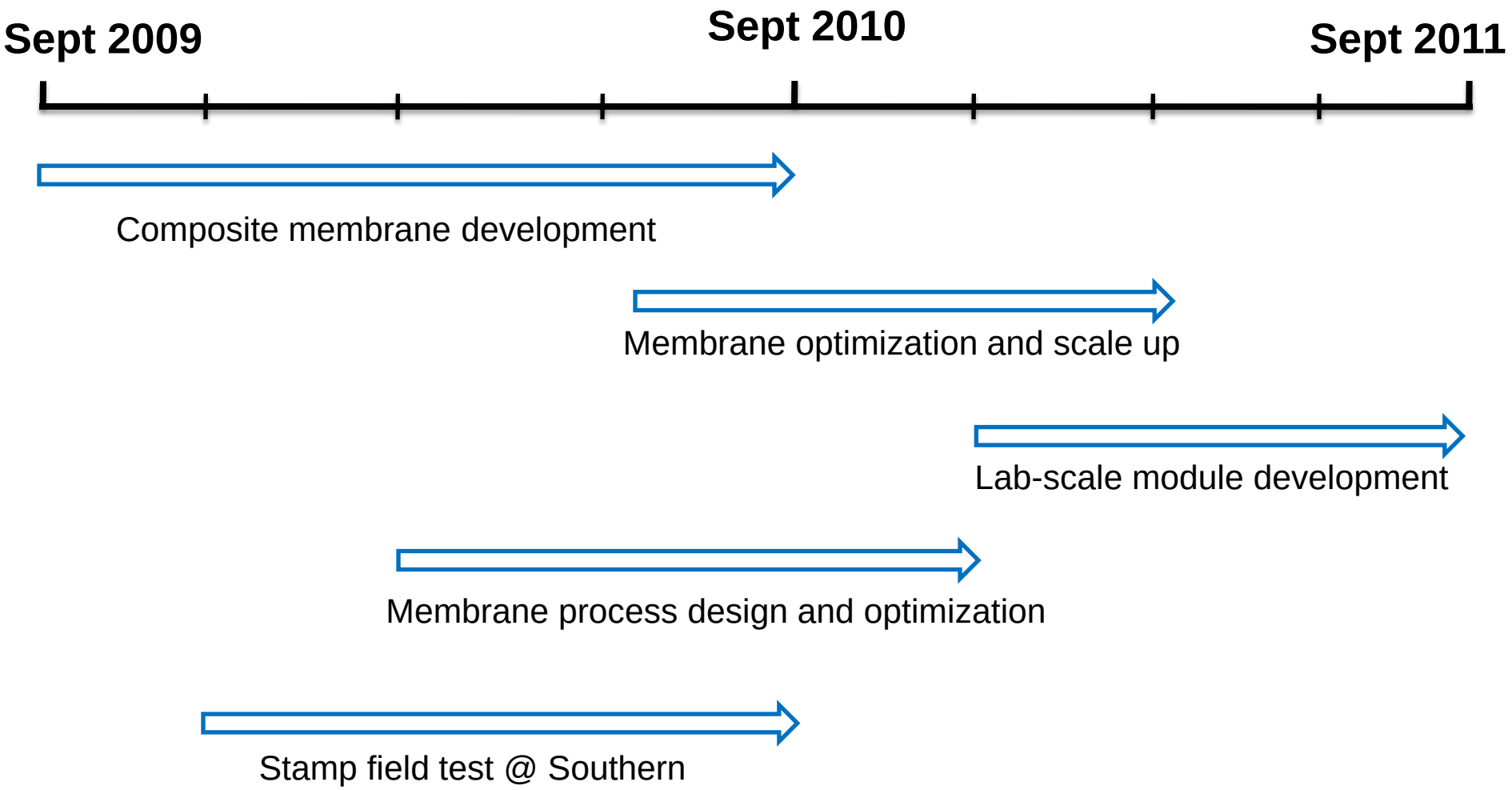
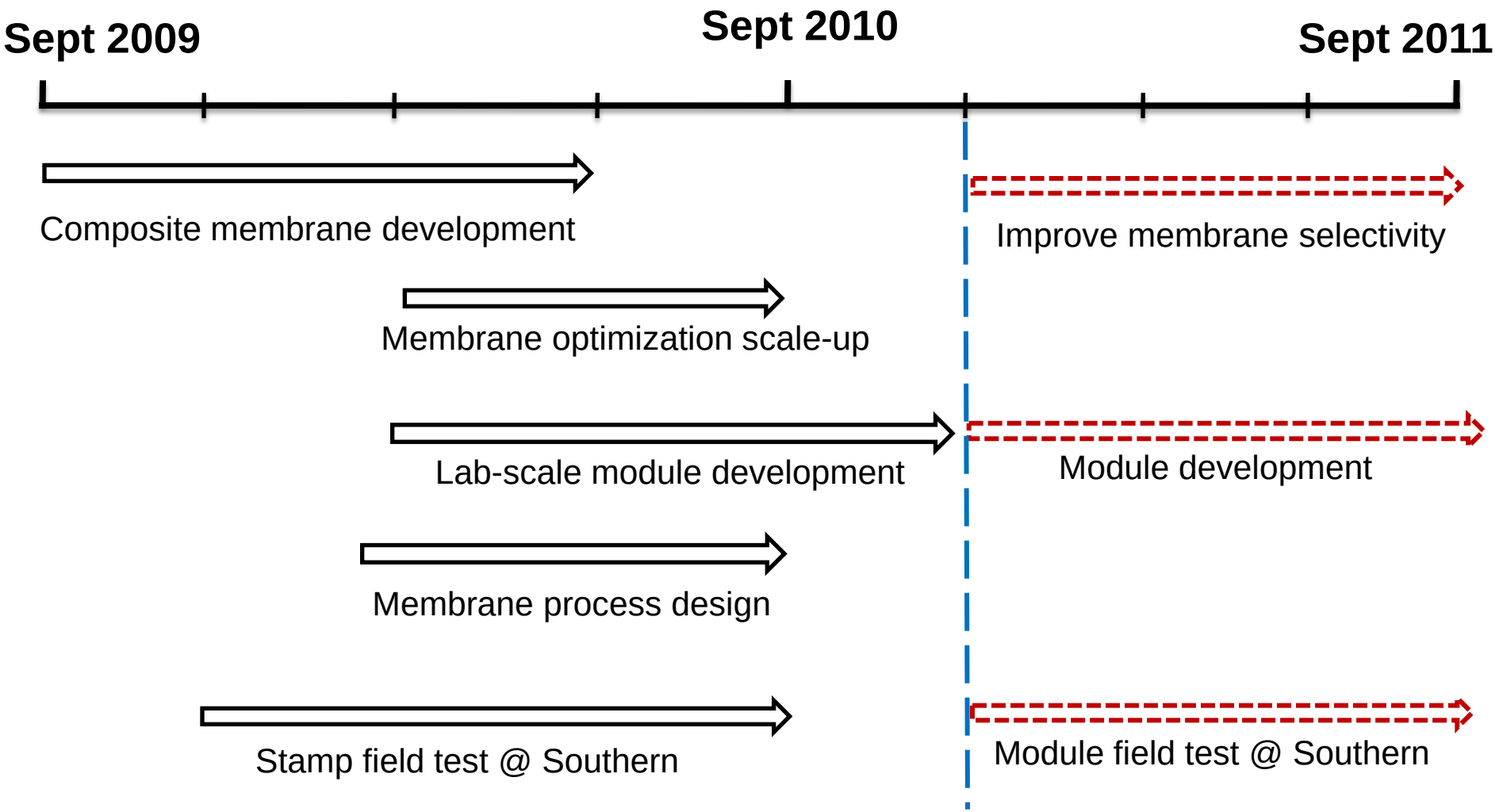
Project timeline: original



Project Timeline: update



Next Steps toward Commercialization

- Improve membrane performance
- Develop commerical-scale modules
- Evaluate long-term high temperature stability

- Test membrane modules

  at NCCC in 2011

  → 50 lb/h syngas run

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Summary

- 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 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.
- Current membrane performance yields an increase in LCOE of ~15%. Higher H_2/CO_2 selectivity and higher H_2 permeance are both needed to achieve DOE LCOE targets.

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Acknowledgements

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  National Energy Technology Laboratory
  - Richard Dunst

- **Southern Company**
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- **Tetramer Technologies**
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  - Viktor Klep, Adam Haldeman