Pre-combustion CO_2 Capture with Membranes: Lessons Learned from Field Trials

Tim Merkel, VP Technology, MTR

RITE Membrane Symposium, Tokyo, Japan

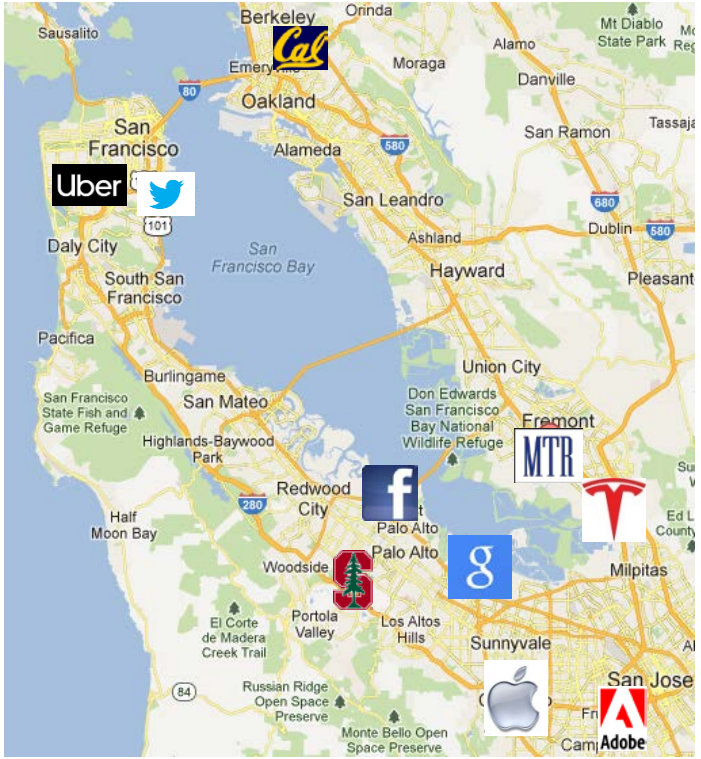
January 18, 2019

Outline

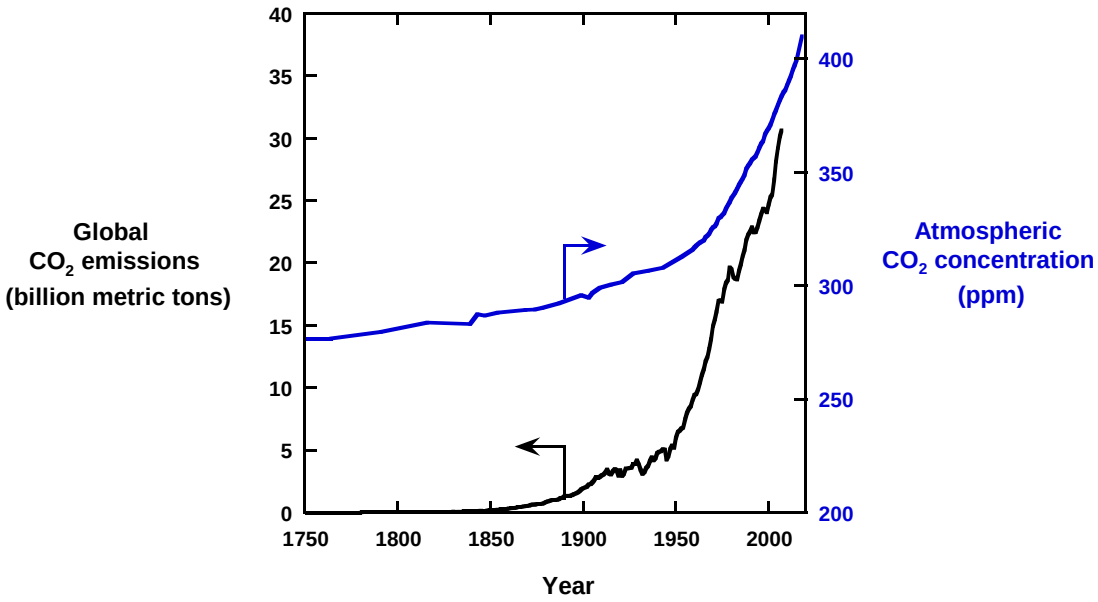
- Introduction/background
- MTR's CO_2 capture program
- Update on pre-combustion capture with membranes
- Conclusions and lessons learned

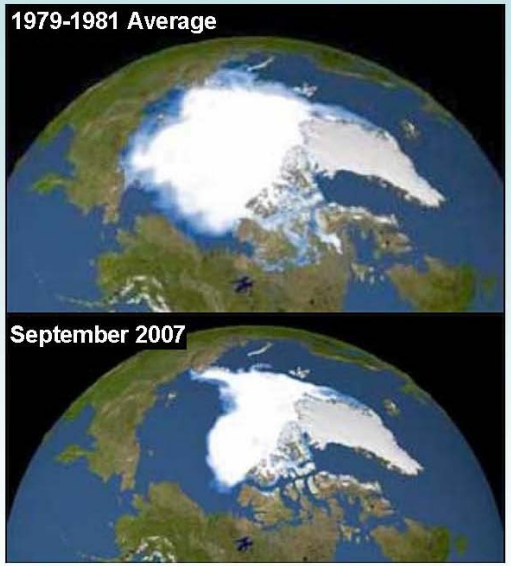
MTR Introduction

- Started in 1982, privately-held, based in Newark, California
- Commercial products in petrochemical, natural gas and refinery industries; >300 systems installed worldwide
- Expertise in membrane materials, formation, processes, field installation and operations
- Worked with U.S. DOE for last decade on application of membranes to CO_2 capture



CO_2 Emissions are Changing the Climate





The Arctic ice cap reached its smallest extent ever in 2007 (top), about 50% of its size in the 1950s.

Source: http://ecology.com/, NASA images

Recent records set include, highest global mean surface temperature, highest number of “extreme” warm events, highest global mean sea surface temperature, highest sea level, lowest sea ice

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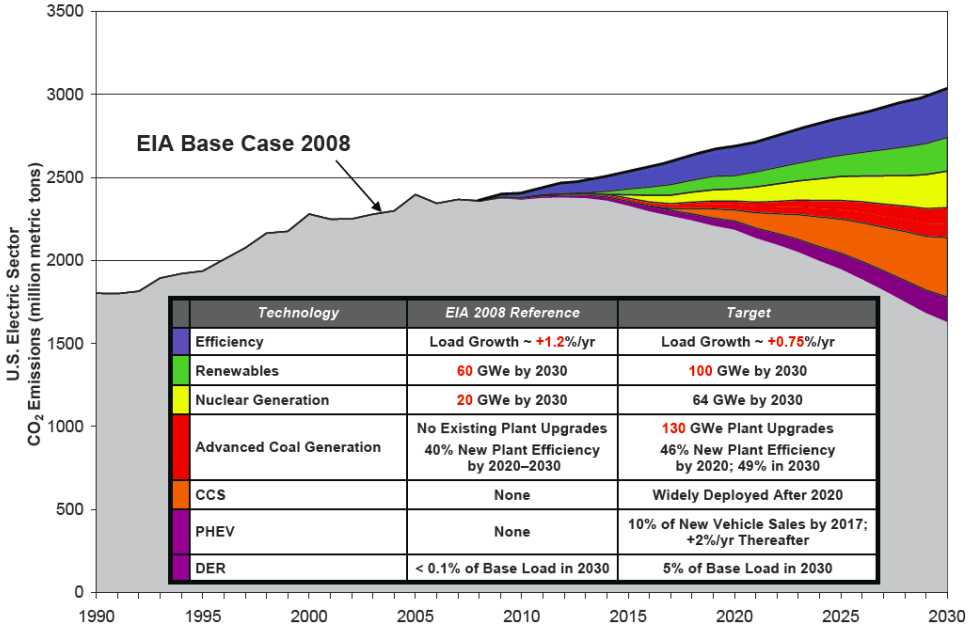
Impacts of Climate Change are Global

- Summer 2018 heatwave produced the highest temperature recorded in Japan (41.1 °C)
- During this period, >130 deaths were attributed to heat-related causes, and >71,000 hospitalizations for heat stroke
- Future impacts of climate change on Japan include more intense heat waves and typhoons, sea level rise/flooding, changes to crop and fish production, etc.

CO_2 Capture from Large Point Sources is Part of the Answer

- Studies show climate change mitigation is more expensive without CO_2 capture from power facilities
- Capture from industrial sources (cement, steel) is required; no renewable alternative
- Biofuel with CCS is lowest cost means of achieving negative emissions



Technology	EIA 2008 Reference	Target
Efficiency	Load Growth ~ +1.2%/yr	Load Growth ~ +0.75%/yr
Renewables	60 GWe by 2030	100 GWe by 2030
Nuclear Generation	20 GWe by 2030	64 GWe by 2030
Advanced Coal Generation	No Existing Plant Upgrades 40% New Plant Efficiency by 2020–2030	130 GWe Plant Upgrades 46% New Plant Efficiency by 2020; 49% in 2030
CCS	None	Widely Deployed After 2020
PHEV	None	10% of New Vehicle Sales by 2017; +2%/yr Thereafter
DER	< 0.1% of Base Load in 2030	5% of Base Load in 2030

"Today, deploying CCS technology is costly. Tomorrow, not deploying CCS technology will exert an even greater cost." – DOE Fossil Forward report

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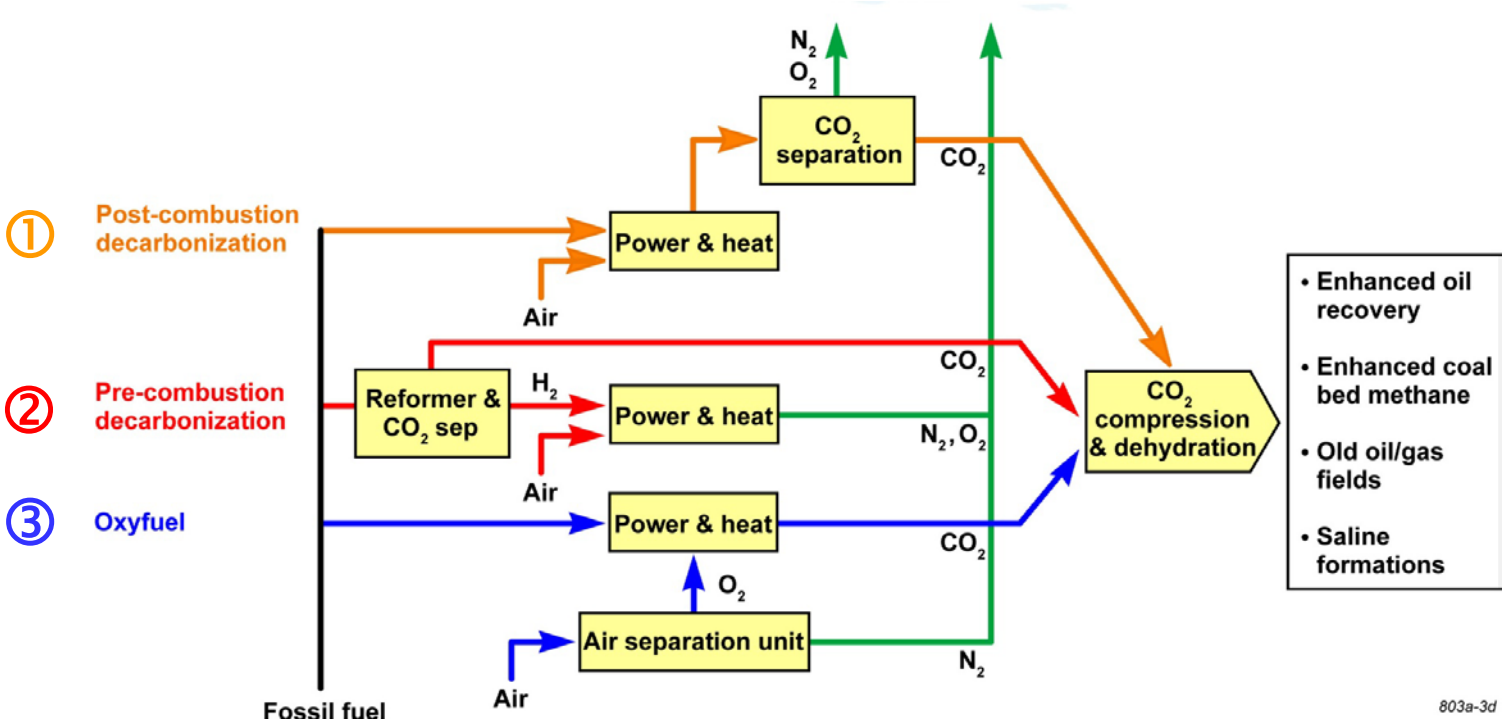
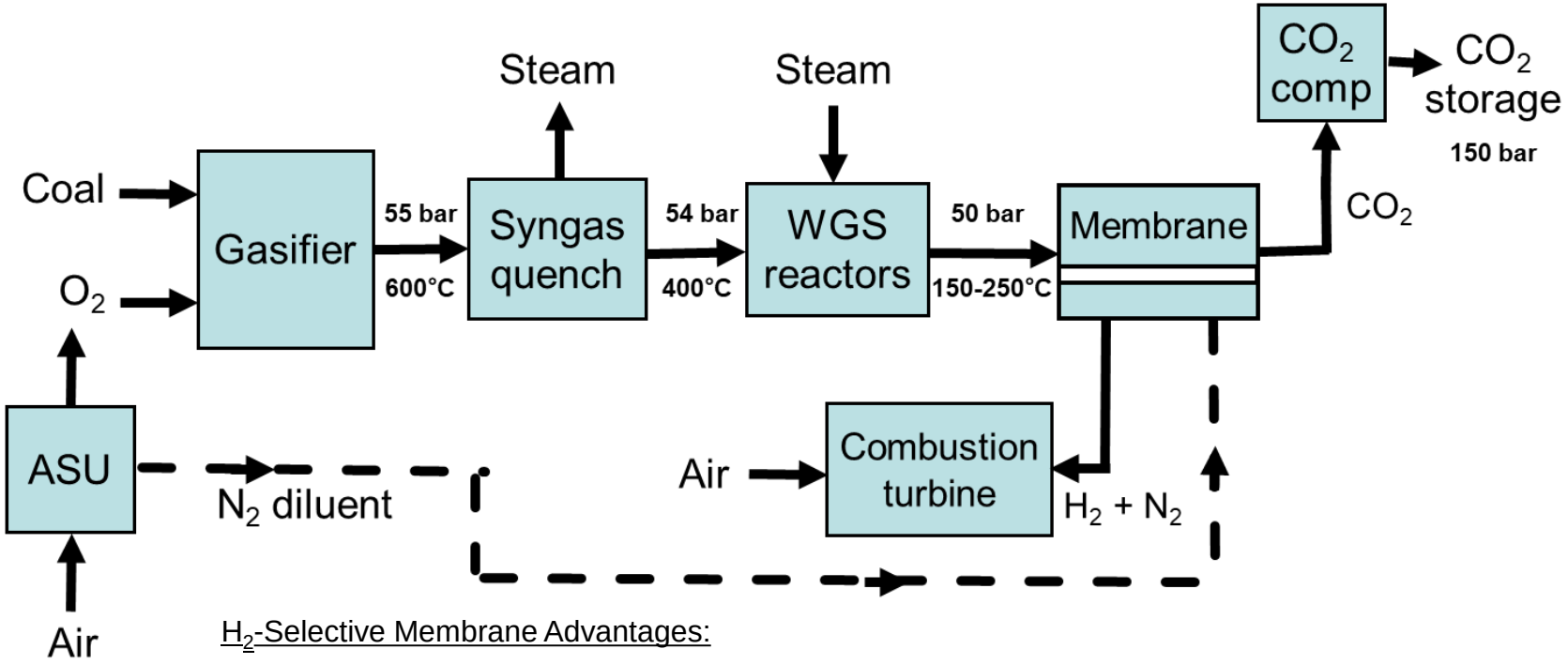
CO_2 Capture Options for Fossil Fuel Power



All options have opportunities for membranes; today, I will focus on pre-combustion capture

Pre-Combustion CO_2 Capture Membranes



<u>H_2-Selective Membrane Advantages:</u>

- Can operate warm/hot to reduce the need for heat exchange
- CO_2 is maintained at pressure; less compression compared to standard AGR
- Water goes with fuel gas; reduces CO_2 dehydration costs

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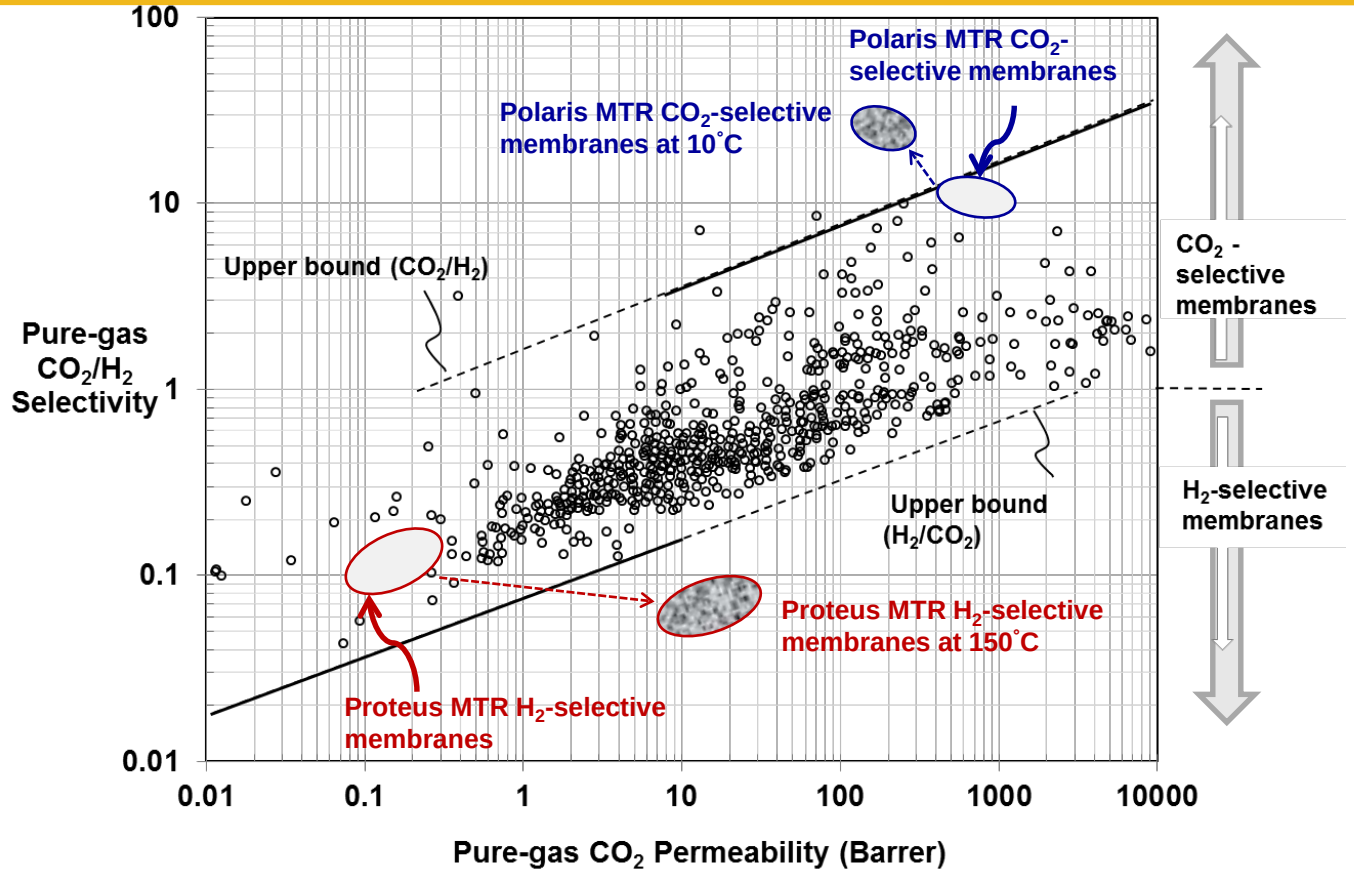
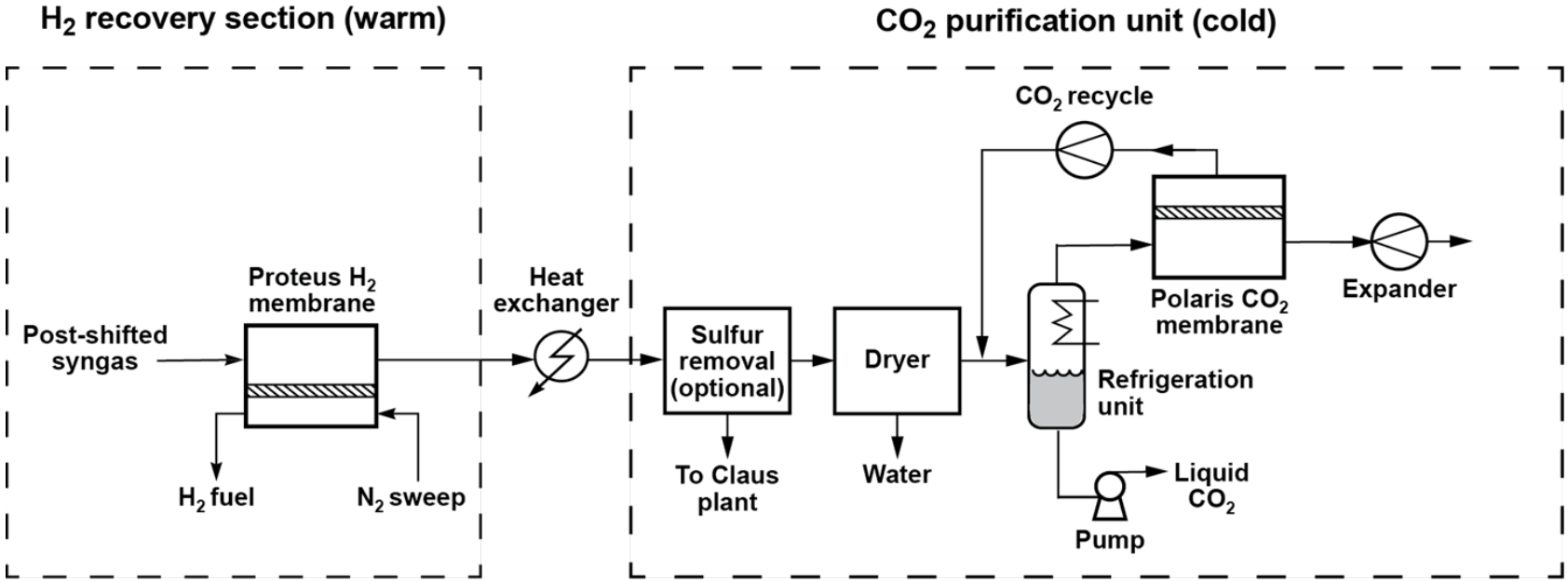
MTR Pre-Combustion Membranes



MTR Dual Membrane Process



- Process uses both hydrogen and CO_2-selective membranes operating at preferred conditions
- Compared to 2-stage Selexol (Case 2 of DOE Bituminous Baseline Study), MTR process shows 27 MW_e net power improvement and 7.4% lower COE

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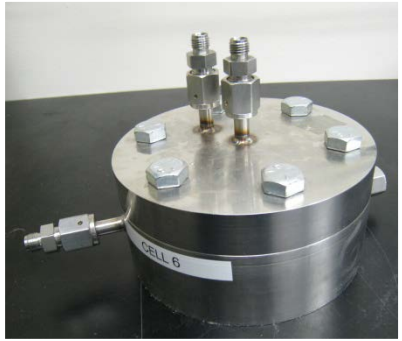
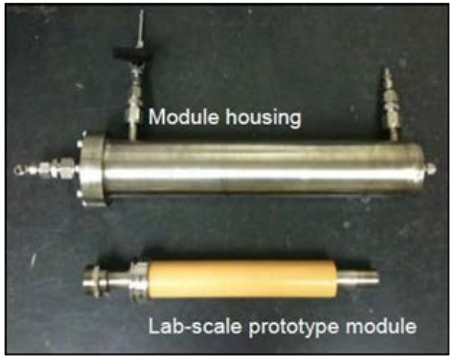
Stages of Membrane Development

1) Membrane stamps
Area: 0.0030 m^2; Flow: 1 lb/h



2) Lab-scale module
Area: 0.13 m^2; Flow: 10 lb/h

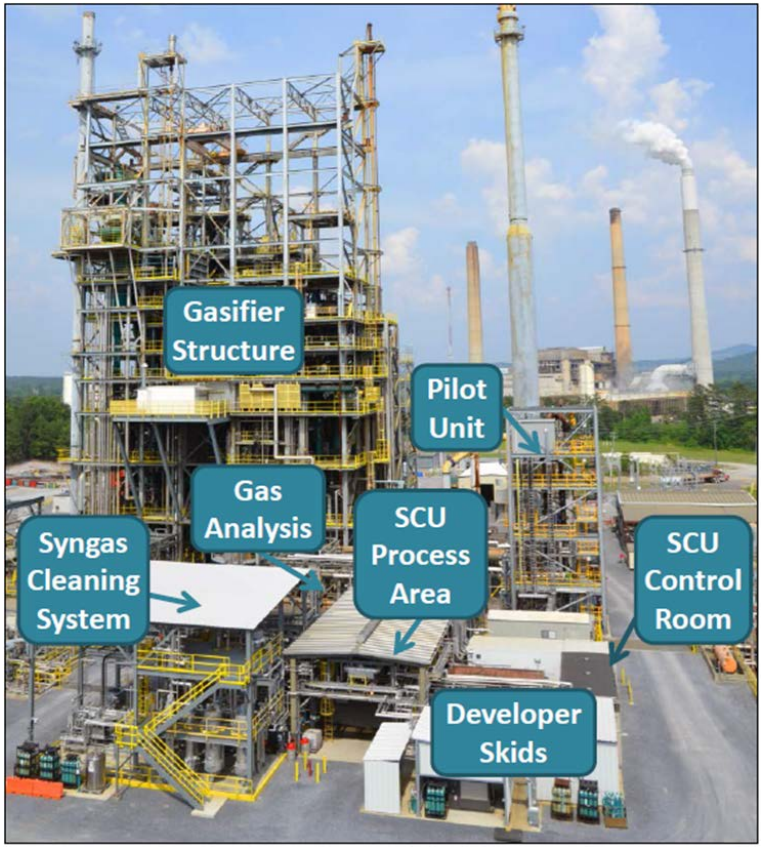


3) Semi-commercial module
Area: 1 - 4 m^2; Flow: 50 lb/h

4) Commercial-sized module
Area: 20 – 50 m^2; Flow: 500 lb/h

- A membrane stamp with good performance is the first step in the development process
- R&D effort and costs roughly scale with the feed flow rate
- To go from step 1 to 4 generally takes 3 to 5 years

Field Tests at the US National Carbon Capture Center (NCCC)



- 6 MW_e Transport Gasifier producing 20,000 lb/hr of coal-derived syngas
- In operation from 1996 - 2017
- Supported slipstream testing from 5 to 500 lb/h
- Tailored air-blown syngas
  - Shifted or unshifted (WGS)
  - Sour or sweet syngas (H_2S)
  - H_2 enrichment available
- MTR conducted membrane testing from 2009 to 2017

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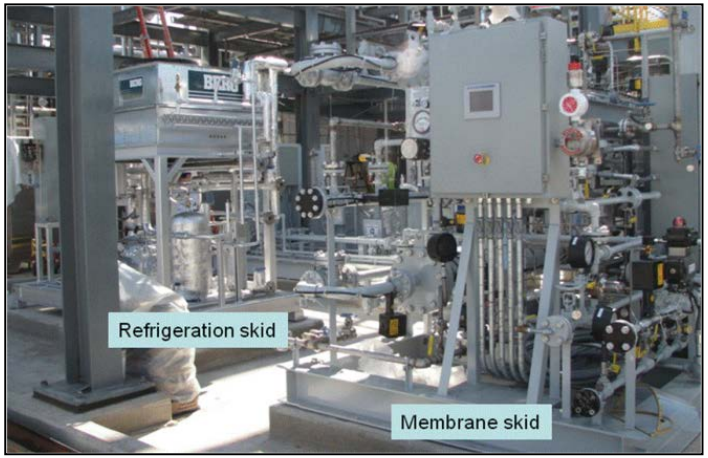
Field Tests at the US National Carbon Capture Center (NCCC)

Bench-scale module test skid

Pilot-scale liquid CO_2 skid



- Polaris CO_2-selective membrane
  - Stamp testing started in 2009; by 2013 commercial-sized modules evaluated; in total >5000 hours of testing with syngas
- Proteus H_2-selective membrane
  - Initial stamp tests in 2010; semi-commercial modules by 2014; >8000 hours testing

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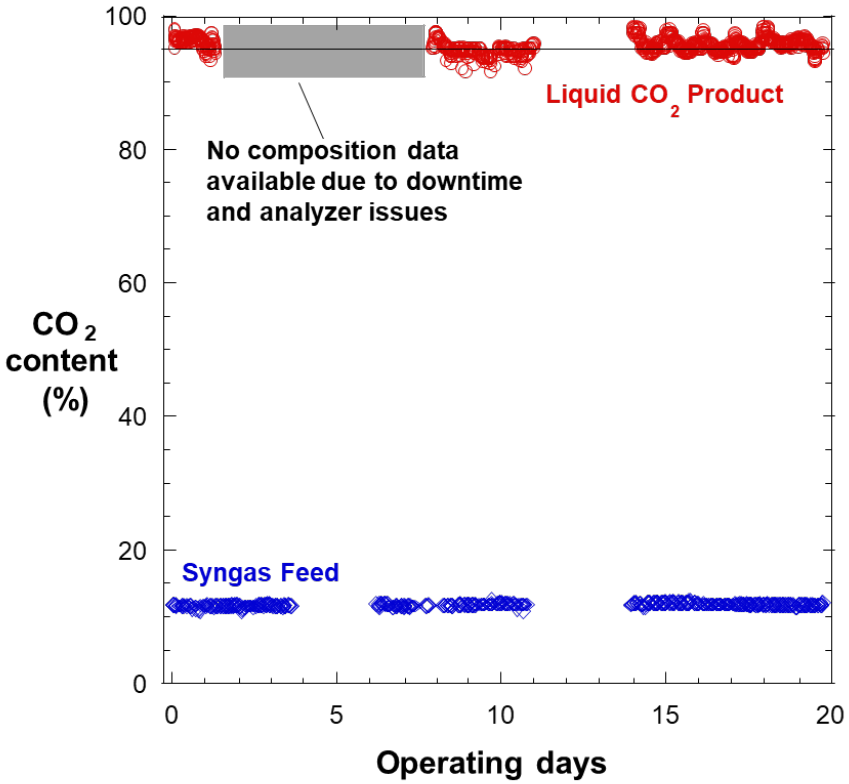
Commercial Polaris Modules Used to Produce Liquid CO_2



- 8-inch diameter, commercial-sized Polaris modules tested with coal-derived syngas
- Liquid CO_2 (>97%) produced from ~12% syngas feed
- Captured >900 lb/day of liquid CO_2 (400 kg/day)

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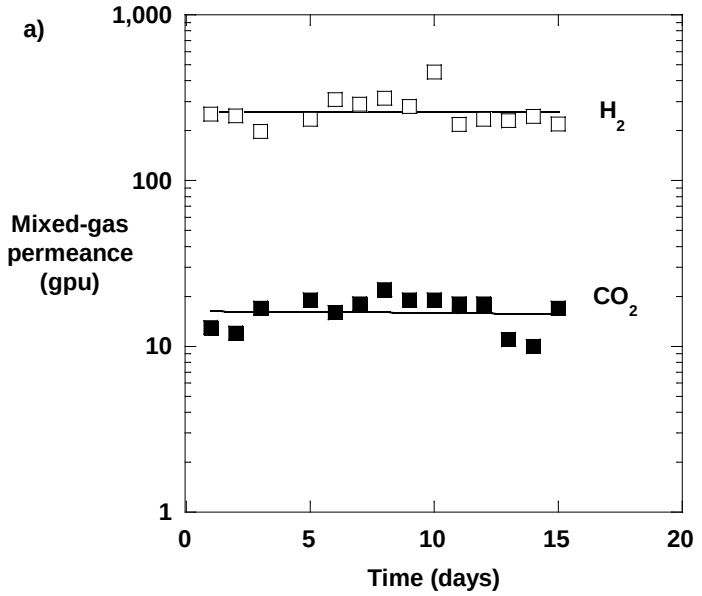
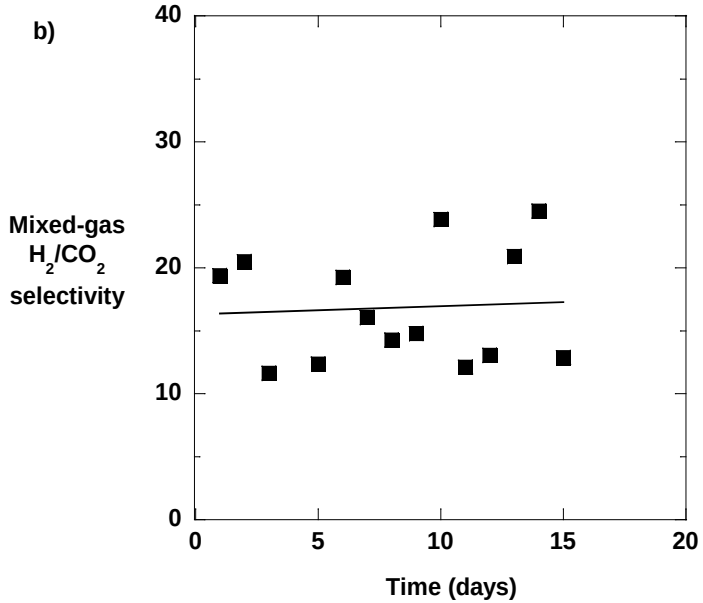
Proteus Gen 1 Test Data from NCCC

Membrane Stamp Permeance

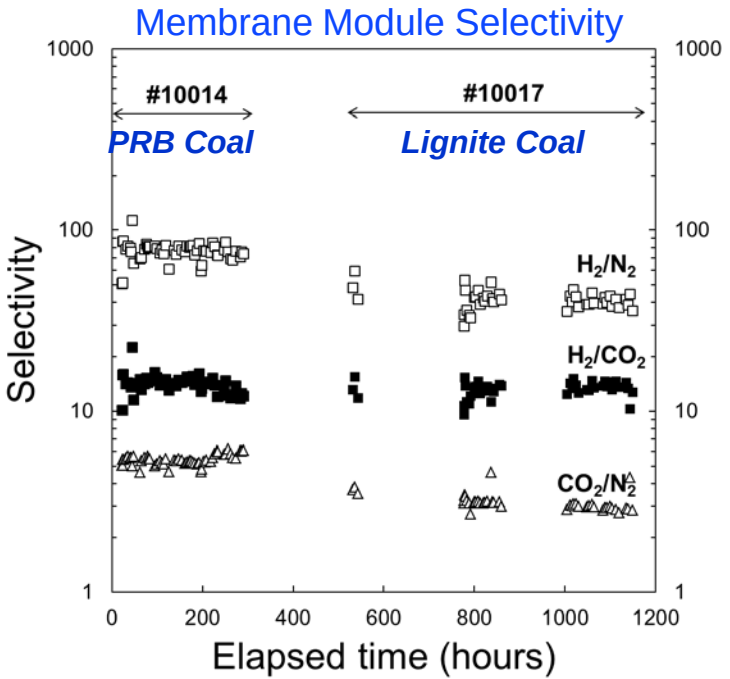


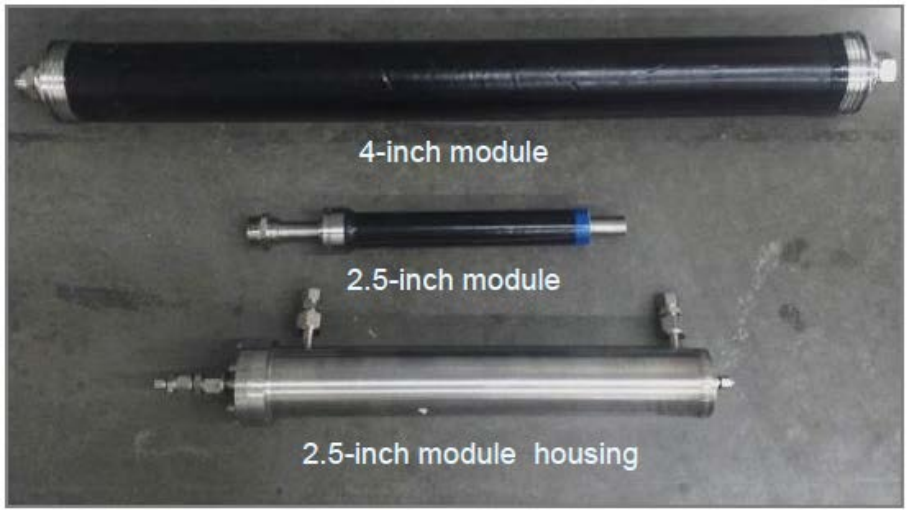
Membrane Stamp Selectivity



- Feed is shifted syngas: ~13% H_2, 13% CO_2, 70% N_2, 2.5% CO, 1.5% CH_4, 800 ppmv H_2S, 165-180 psig, 120 - 140°C
- Average H_2 permeance: 230 gpu; average H_2/CO_2 selectivity: 15

Proteus Gen 1 Modules Tested at NCCC





- Initial modules were defective; module components (glues, spacers) changed to handle high temperature, wet conditions
- Optimized modules tested a NCCC show H_2/CO_2 selectivity = 15, consistent with stamps

Proteus Gen 1 at Commercial Pilot Plants

Primus Green Energy

Alberta Innovates / Enerkem

- Commercial-sized modules are being tested with real syngas in commercial pilot plants
- Applications are H_2 recovery in bio-waste to ethanol process and syngas ratio adjustment in gas to liquids process

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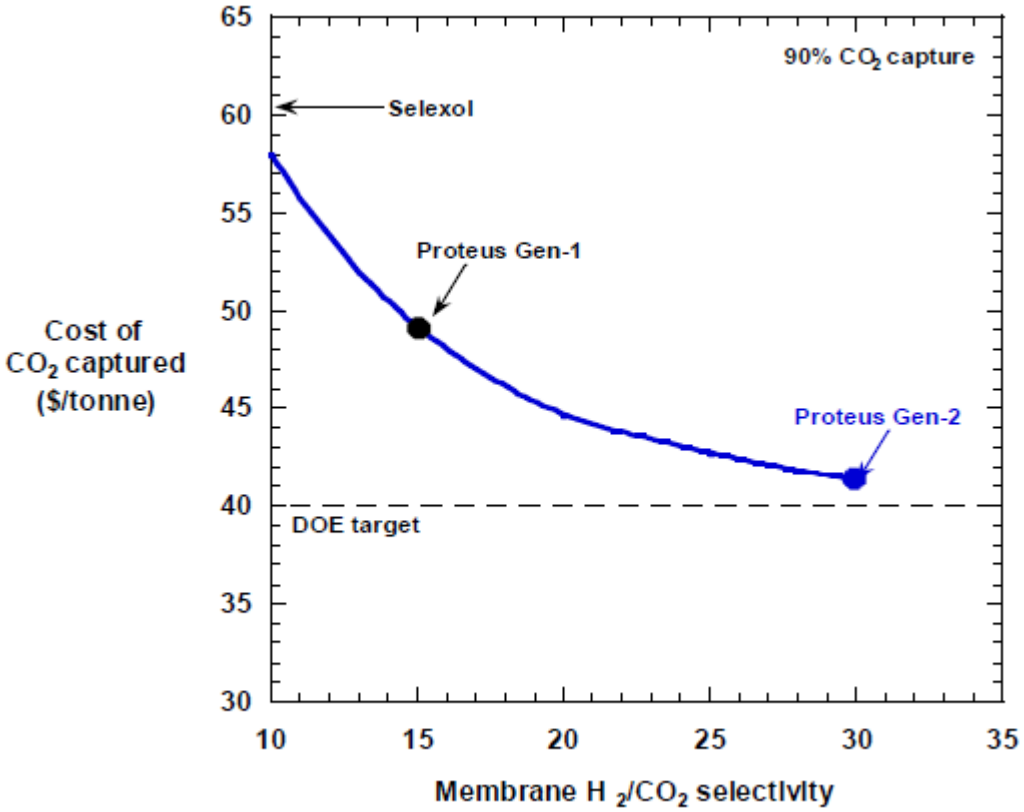
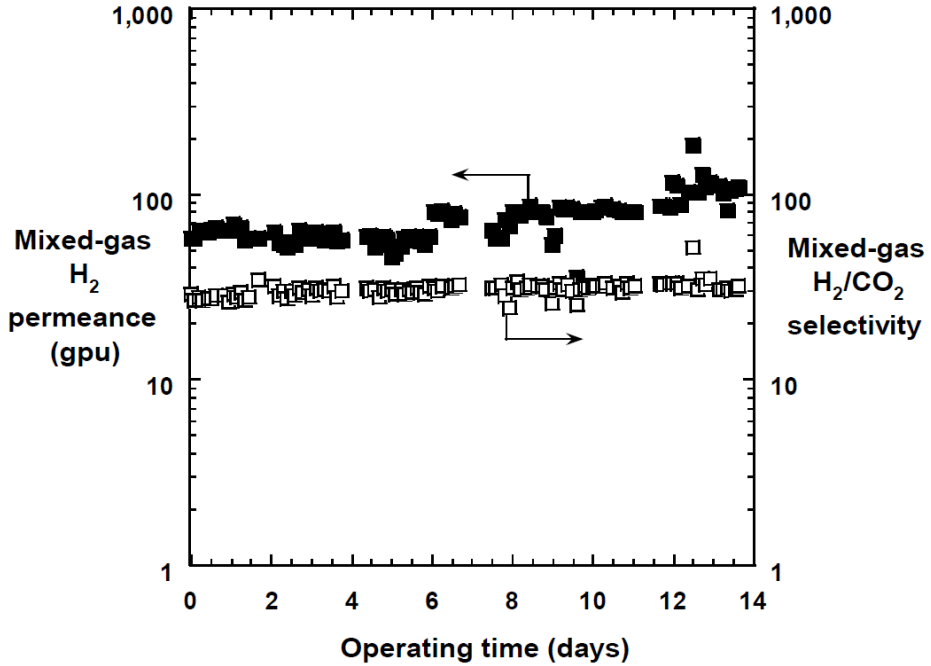
Higher H_2/CO_2 Selectivity Lowers Costs



- Methodology from DOE Bituminous Baselines Study with updated costs used
- Improvements in H_2/CO_2 selectivity are important to reduce costs
- Recently, we have started a new DOE project to produce higher selectivity membranes

Proteus Gen 2 Shows Higher H_2/CO_2 Selectivity

Membrane Stamp Data from NCCC



- All membrane components were changed to allow higher temperature operation (200 °C)
- Selective layer was “tightened” to give higher selectivities
- H_2/CH_4, H_2/N_2, H_2/CO selectivities were all > 100
- H_2/H_2S selectivity > 50
- Average H_2/CO_2 selectivity = 32

Future Work – Gen 2 Module Tests at EERC

- Current work on new DOE project is focused on developing module components (glues, spacers, etc) capable of operating at 200 ºC
- Module tests will be conducted at the Energy and Environmental Research Center (EERC) in North Dakota
- Syngas will come from an oxygen-blown gasifier using PRB coal
- Follow-on project will combine Proteus Gen 2 modules with Polaris for integrated CO_2 capture using the dual membrane process

Summary

- Membranes have some advantages for pre-combustion CO_2 capture and H_2 purification
- Portions of MTR dual membrane process have been tested at various scales at NCCC over several years
- Gen-2 Proteus membranes show promising results up to 200°C
- NCCC testing has allowed for optimization and scale up of Proteus and Polaris membranes in a real world syngas environment
- Proteus module development continues with industrial pilot system field tests

Acknowledgments

- Funding from DOE NETL under contract DE-FE0006138 and AI under contract AI-2089
- NCCC for assistance with ongoing gasifier slipstream testing
- Alberta Innovates, Enerkem, City of Edmonton, and Primus Green Energy for demonstration-scale testing