Techverse, Inc.
Advancing Energy Technologies

Integrated Membrane Reactor for Pre-Combustion CO_2 Capture

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Project Overview – DOE SBIR Phase I

- Funding - $150,000
- Project Duration - June 9, 2014 – March 8, 2015
- Project Partners - Pall Corporation

  Membrane Fabrication

  Southern Research Institute

  Membrane testing

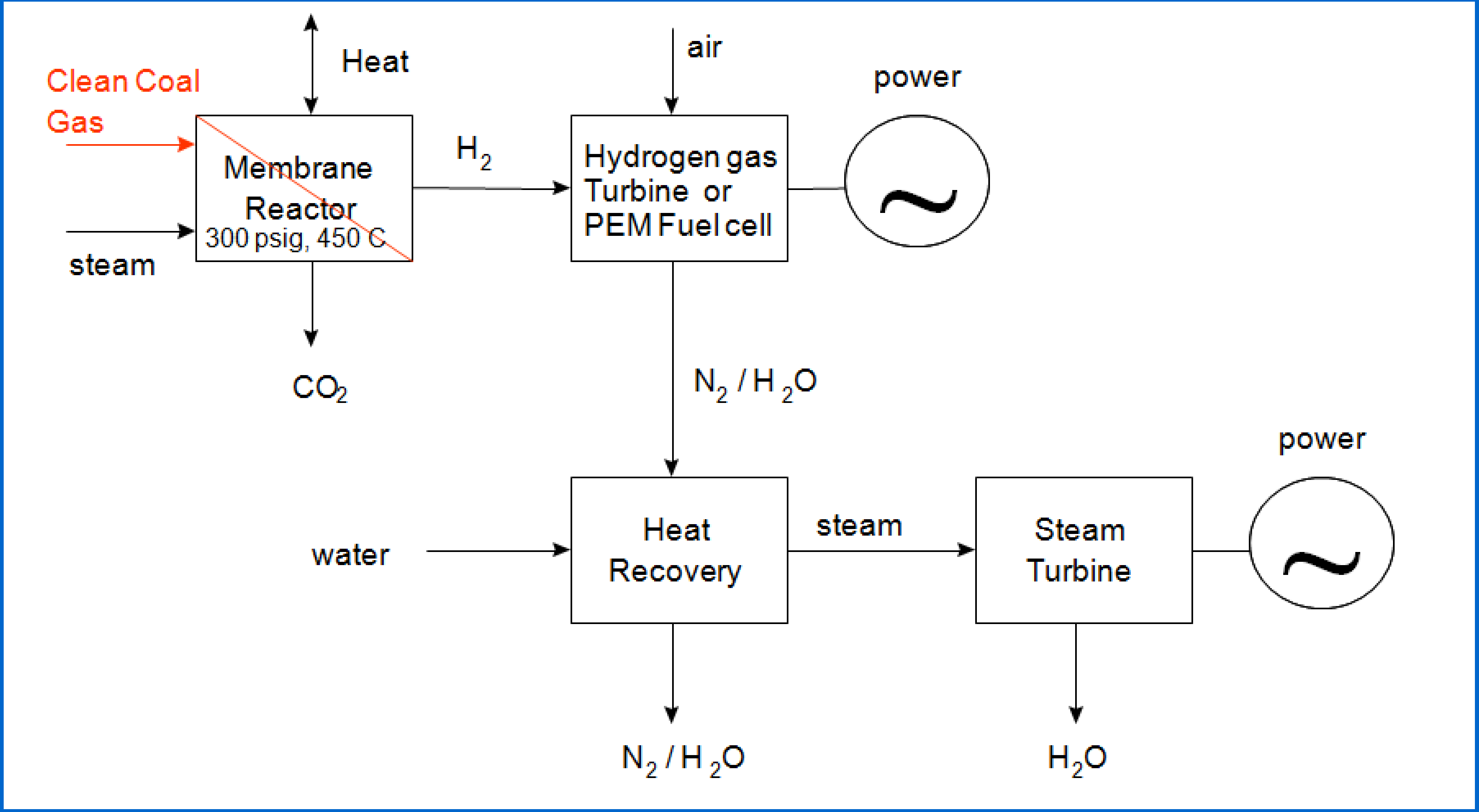
  CB&I - E-Gas Technology

  Gasifier Industry perspective, no-cost

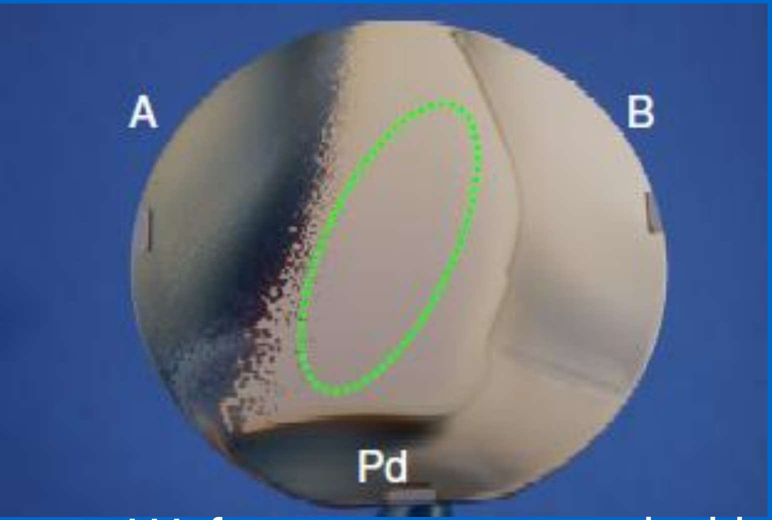
Proposed Carbon Capture Approach

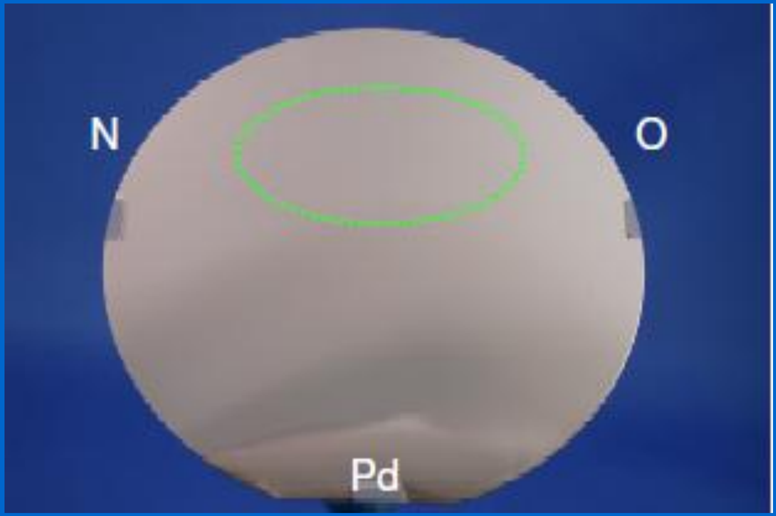
- Pre-combustion CO_2 capture from syngas in advanced gasification based power generation
- Process intensification - Membrane reactor process
- Syngas fuel value is converted to hydrogen by high temperature WGS reaction ($CO + H_2O \Leftrightarrow CO_2 + H_2$) with simultaneous H_2/CO_2 products separation
- Pd-alloy Membrane selective for H_2 separation
- Membrane tolerant to carbon and sulfur in syngas
- CO_2 captured at a high pressure

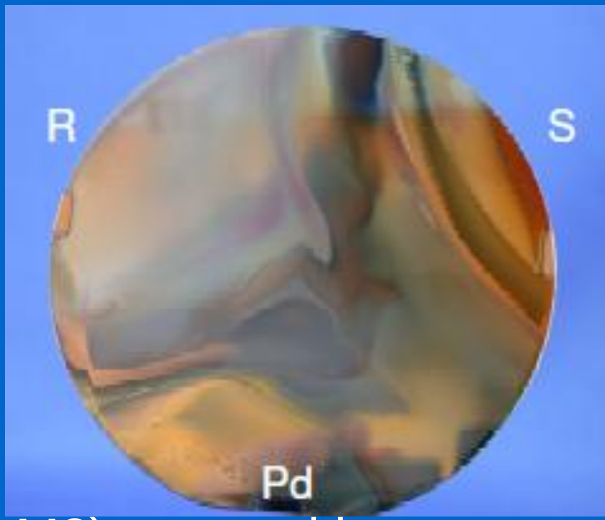
Membrane Reactor Based Power Generation



Identification of Ternary Pd-alloy Compositions







- Wafers were prepared with full range of ternary alloy (Pd-M1-M2) compositions
- Wafers were exposed to simulated coal syngas compositions (24 hr, 170 ppm H_2S)
- Analysis of wafers revealed composition map unaffected by the exposure
- Membranes of promising ternary compositions were then tested for permeation
  - Syngas - 1.3% CO, 3% H_2O, 36% H_2, 11% CO_2, 20 ppm H_2S, balance nitrogen
  - Both S/C tolerance as well as high H_2 flux and selectivity are necessary
- Within a family of ternary alloy, performance can depend on specific composition

Advantages of the Proposed Approach

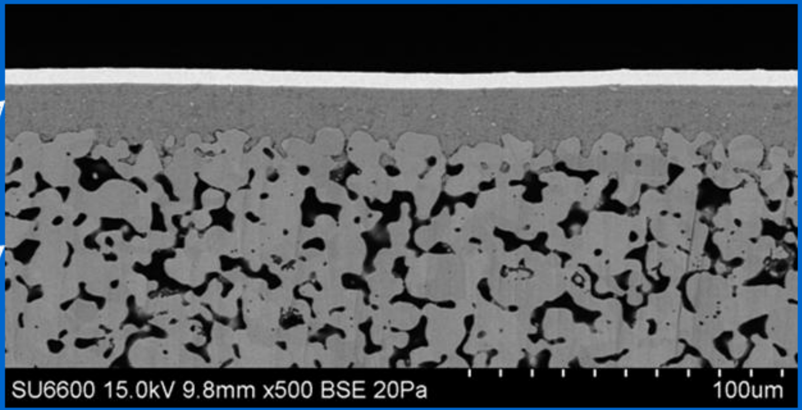
- Near complete CO conversion, maximum CO_2 recovery, and a smaller compact unit
- High temperature H_2/CO_2 separation improves thermal efficiency of power generation
- Process Intensification of reaction and separation –
  - Fewer units and lower capital costs,
- Lower operating costs by eliminating the costs of a separate CO_2 removal process,
- Lower steam to carbon ratio than conventional WGS
- Produces high purity H_2 for PEM fuel cells, and
- CO_2 in a compressed form for sequestration.

Phase I Project Objectives –

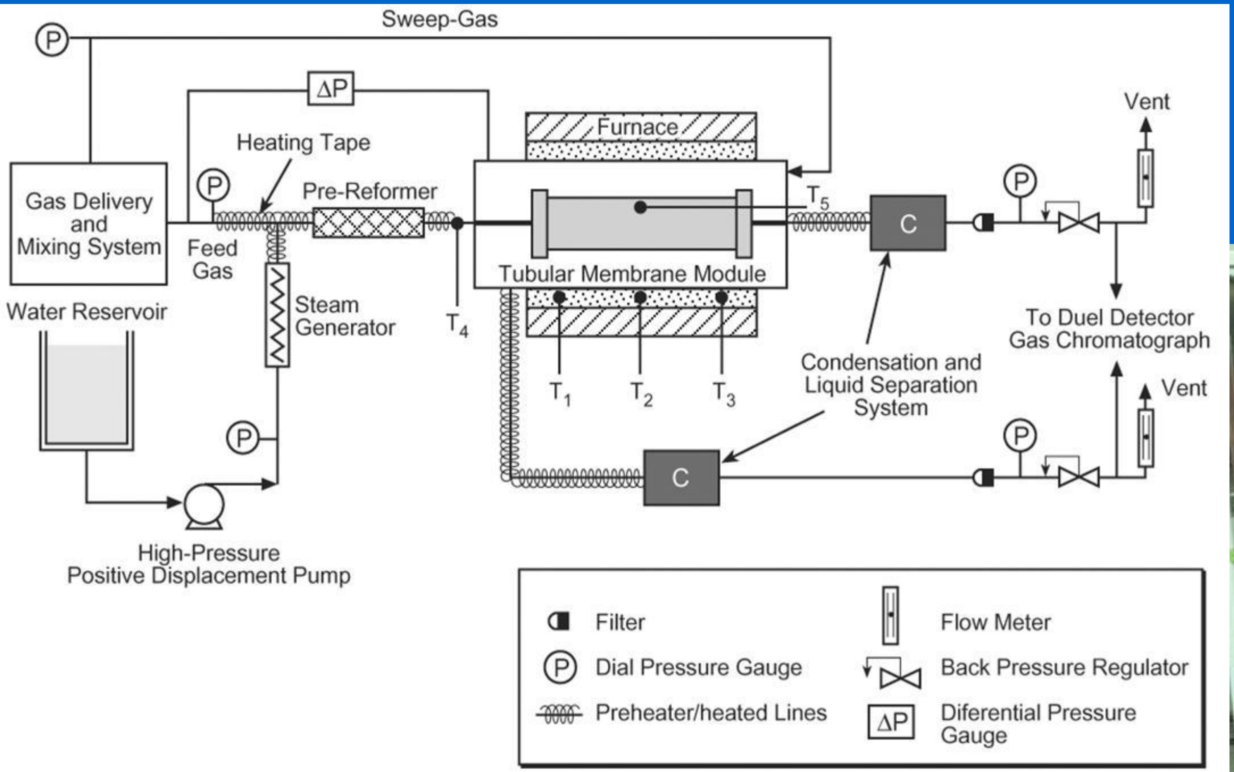
- Confirm stability and long term durability of promising candidate membranes in coal gas
- Demonstrate process intensification maximizing CO conversion, hydrogen recovery and CO_2 capture
- Develop a prototype membrane reactor design for further scale-up and demonstration in Phase II
- Conduct Technical and Economic Analysis of the Membrane Reactor Process to determine approaches to meet performance/cost targets of >90% CO_2 Capture and <$40/ton of CO_2 Captured

Ternary Pd-Alloy Synthesis

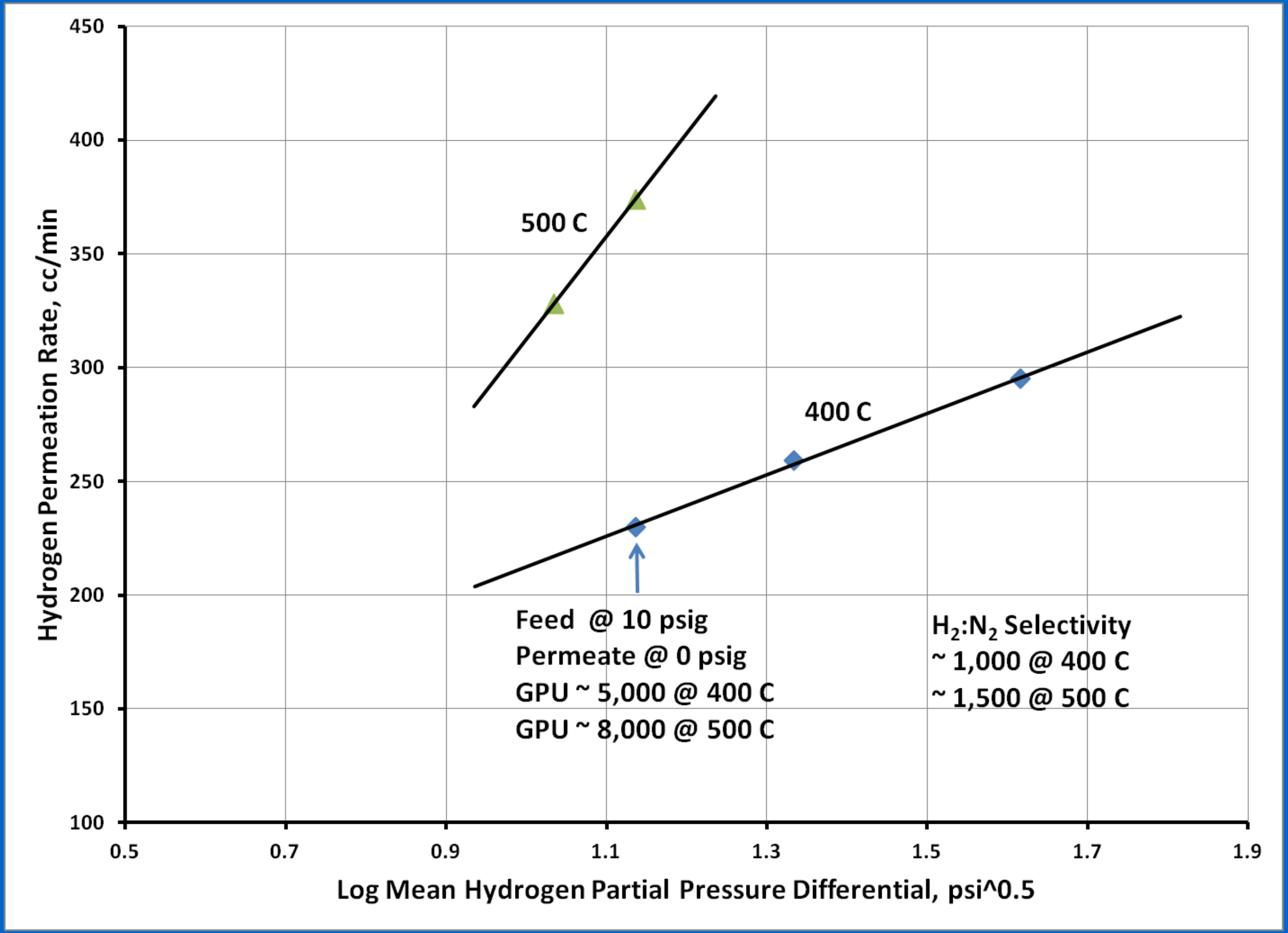
- Two Pd-alloy compositions: Pd-A-B and Pd-C-D
- Membrane area ~ 15 cm^2, Thickness ~ 5 microns
- Non-porous extension tubes welded at both ends



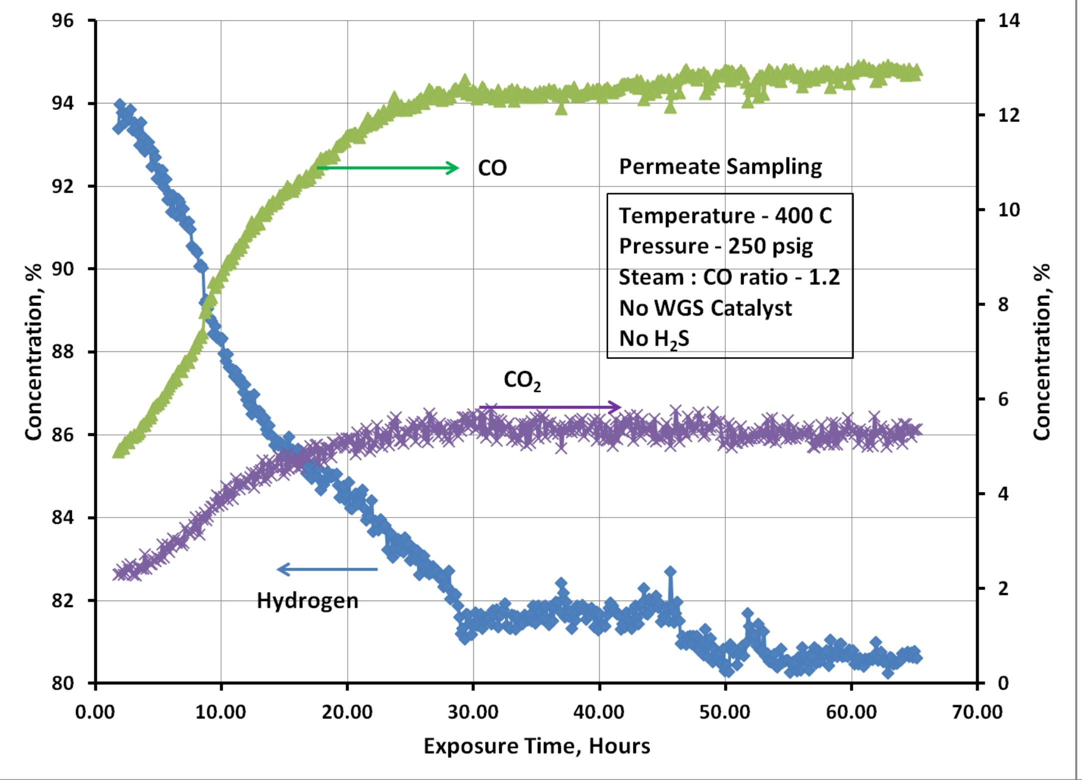
Membrane Test System Schematic and Skid

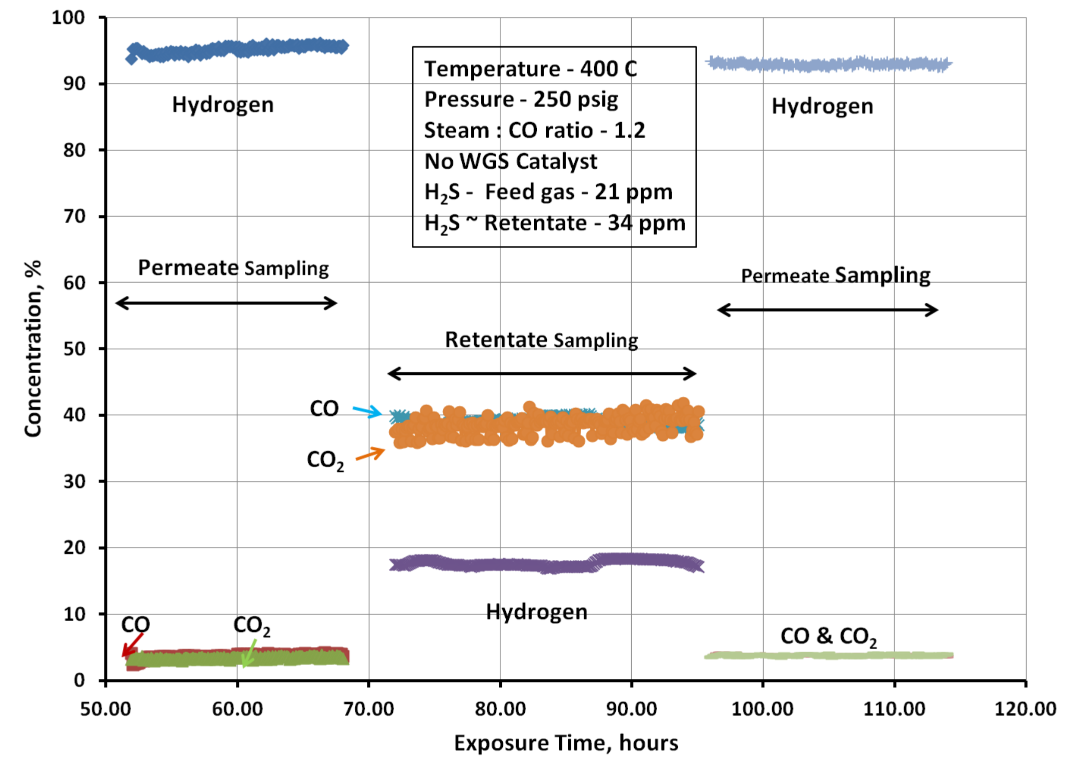


Hydrogen Flux Rate with Temperature Pd-A-B membrane



Membrane Durability in Syngas with and without H_2S

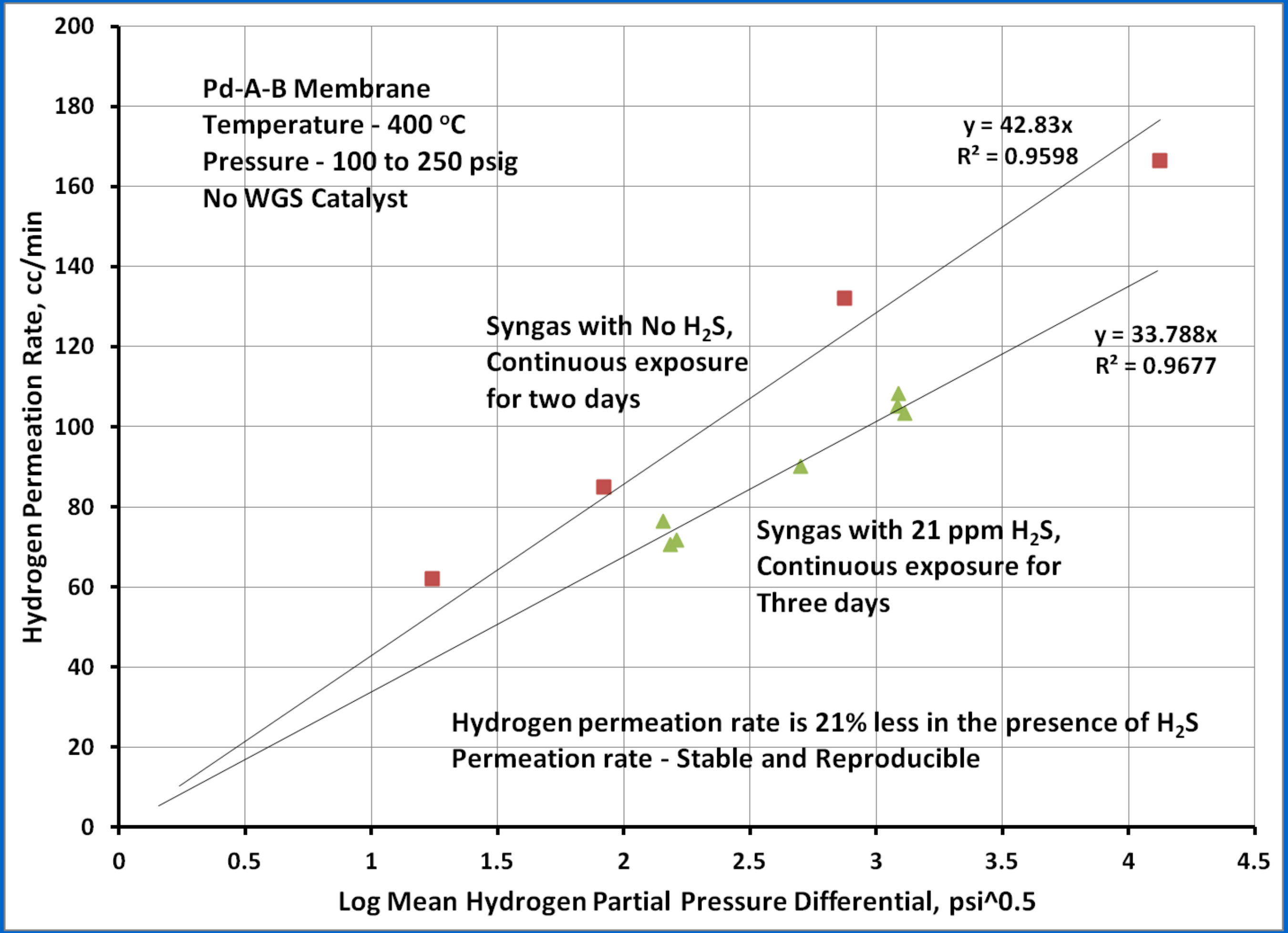




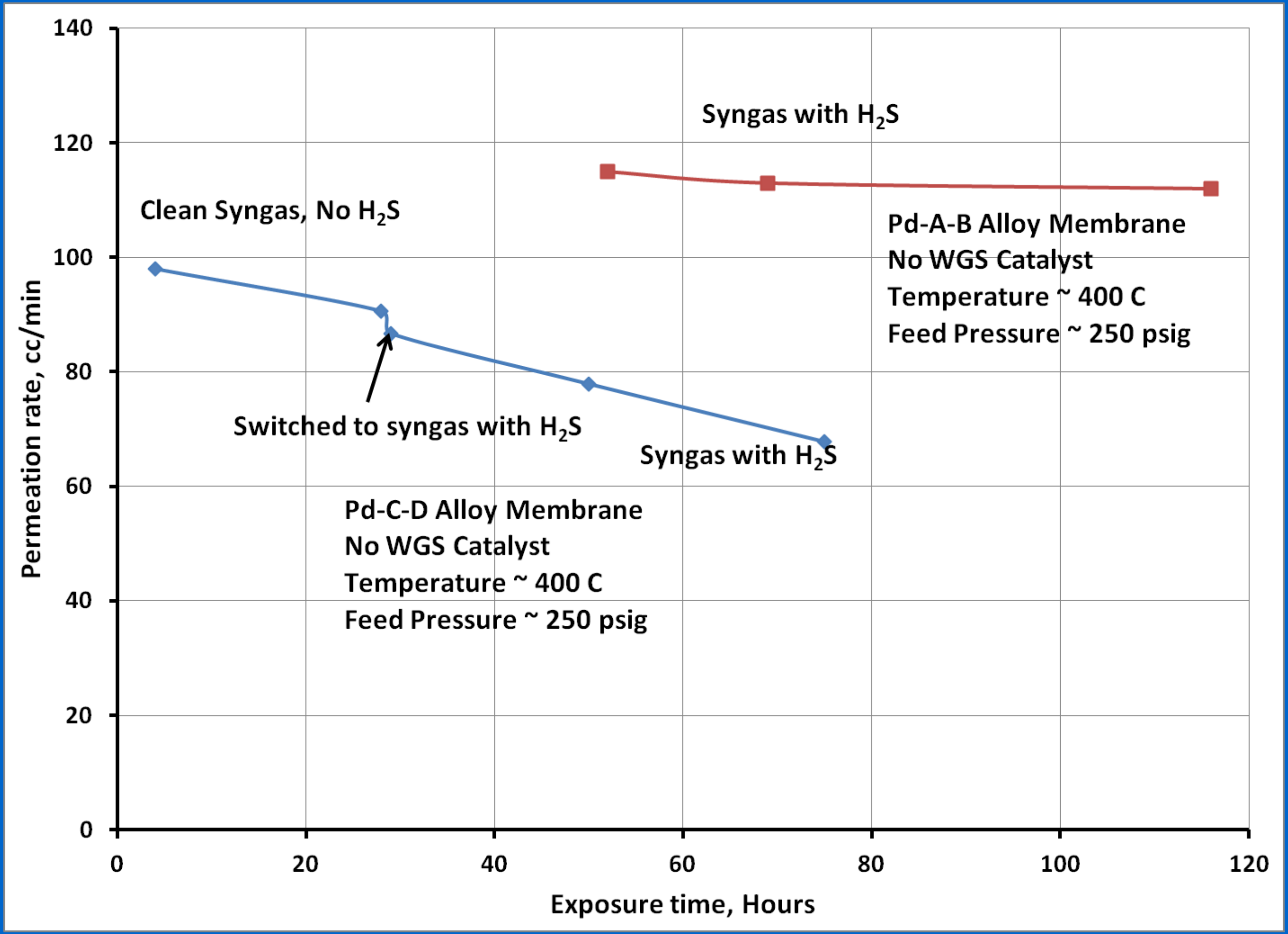
Pd-Au Binary Alloy Membrane **Pd-A-B Ternary Alloy Membrane**

Feed Syngas Composition – H_2 – 33%, CO – 45%, CO_2 – 17%, Ar – 5%, H_2S- 21 PPM

H_2 permeation rate in Syngas with and without H_2S



H_2 Permeation rate with Alloy composition

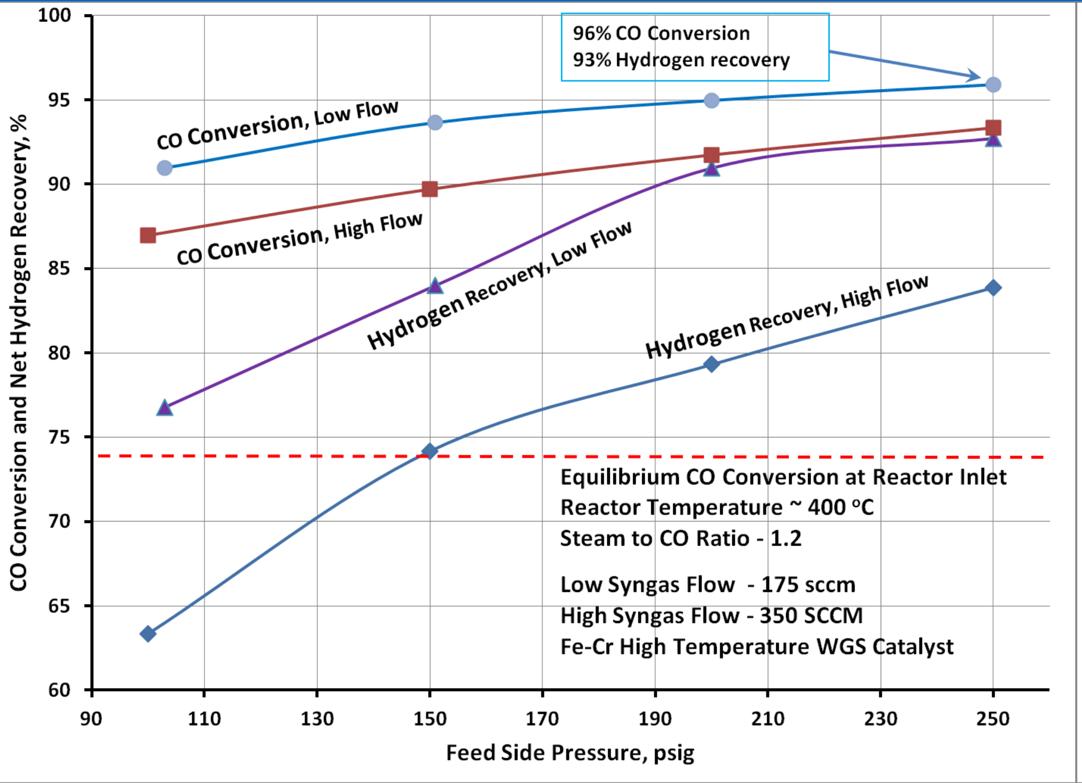


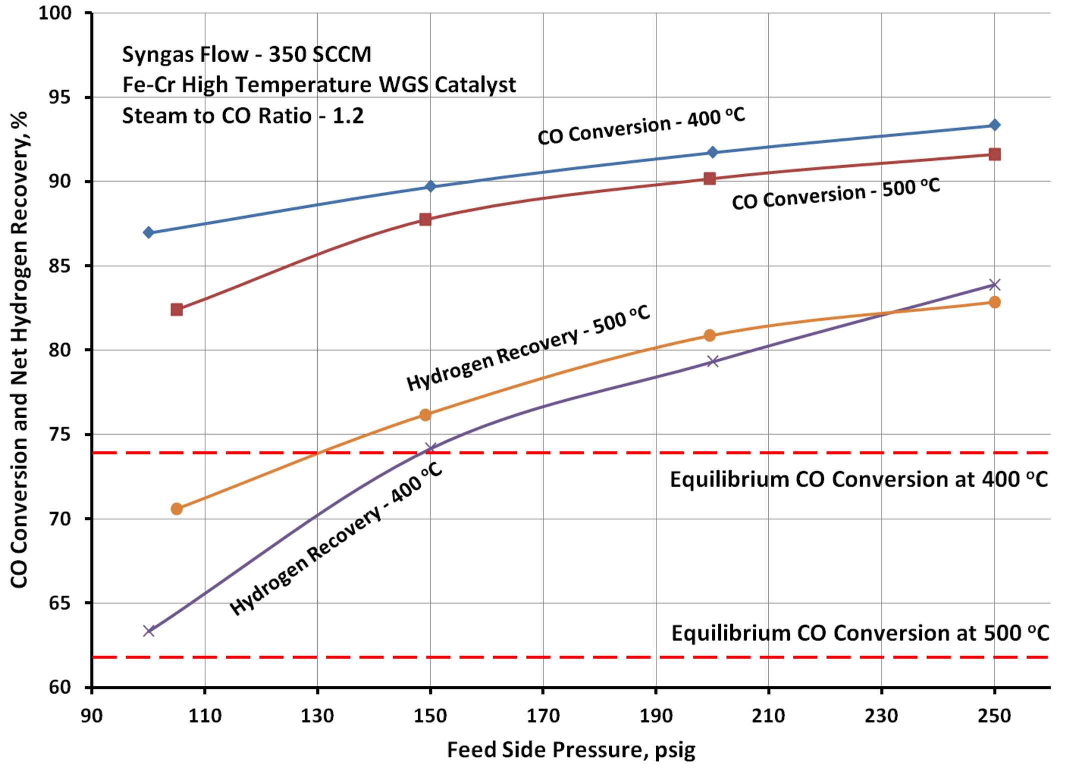
Pd-A-B ternary alloy Exhibited stable Permeation Rate even in the presence of H_2S.

Whereas, Pd-C-D alloy permeation rate declined with time in syngas. regardless of H_2S.

Pd-A-B ternary alloy membrane was therefore selected for WGS Membrane Reactor Experiments

WGS Membrane Reactor Experimental Results
Effect of Feed Flow Rate and Temperature

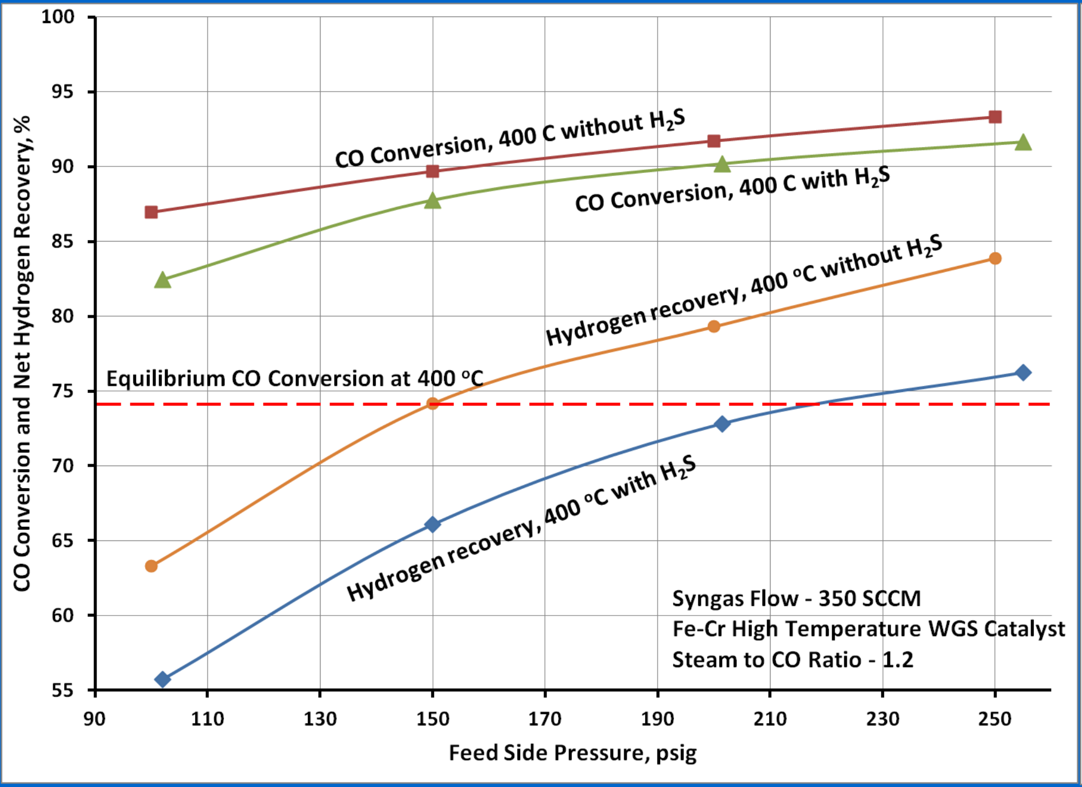


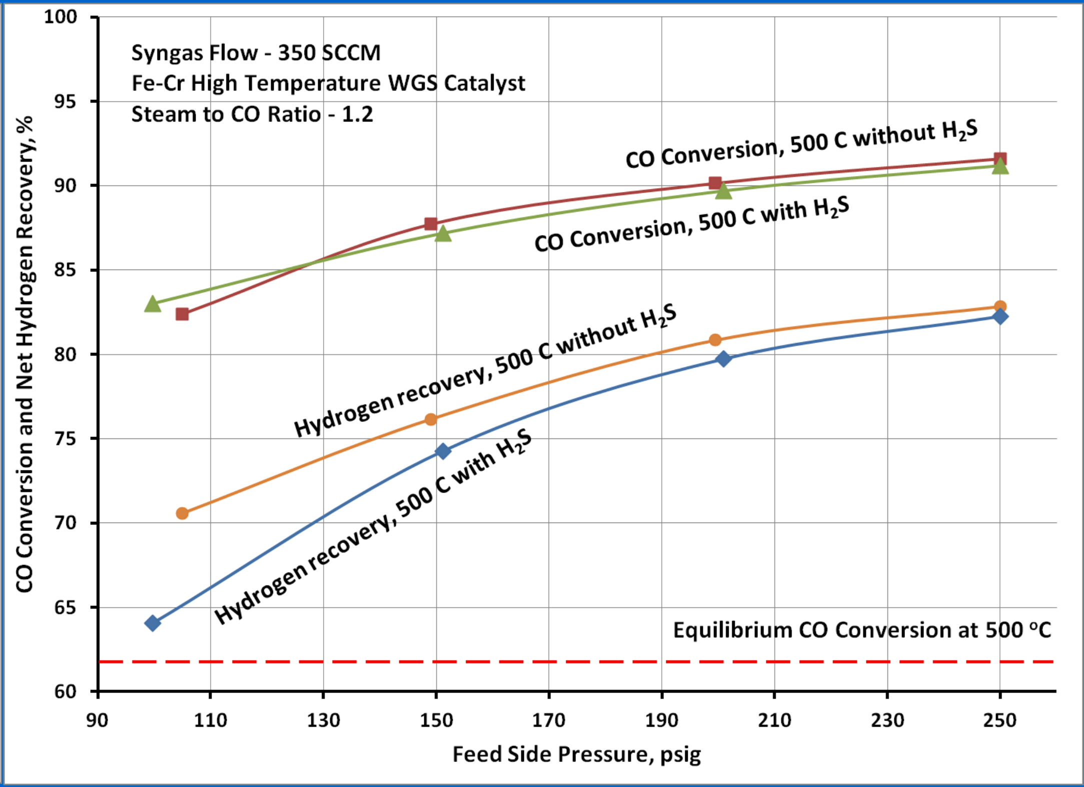


- Demonstrated 96% CO conversion and 93% Net Hydrogen recovery
- High CO conversion (>90%) in spite of unfavorable equilibrium at 500 °C
- Steam to CO ratio – 1.2

WGS Membrane Reactor Results (Cont.)

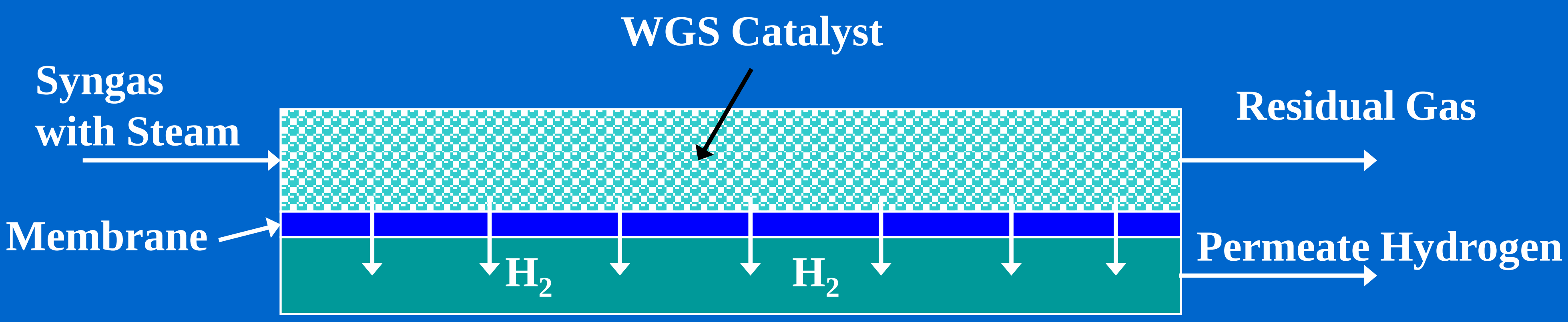
Effect of H_2S at 400 ºC and 500 ºC Temperature





- Effect of H_2S on membrane performance is small at 400 ºC and minimal at 500 ºC
- Results indicate that Membrane Reactor will be Effective in 400 – 500 ºC range

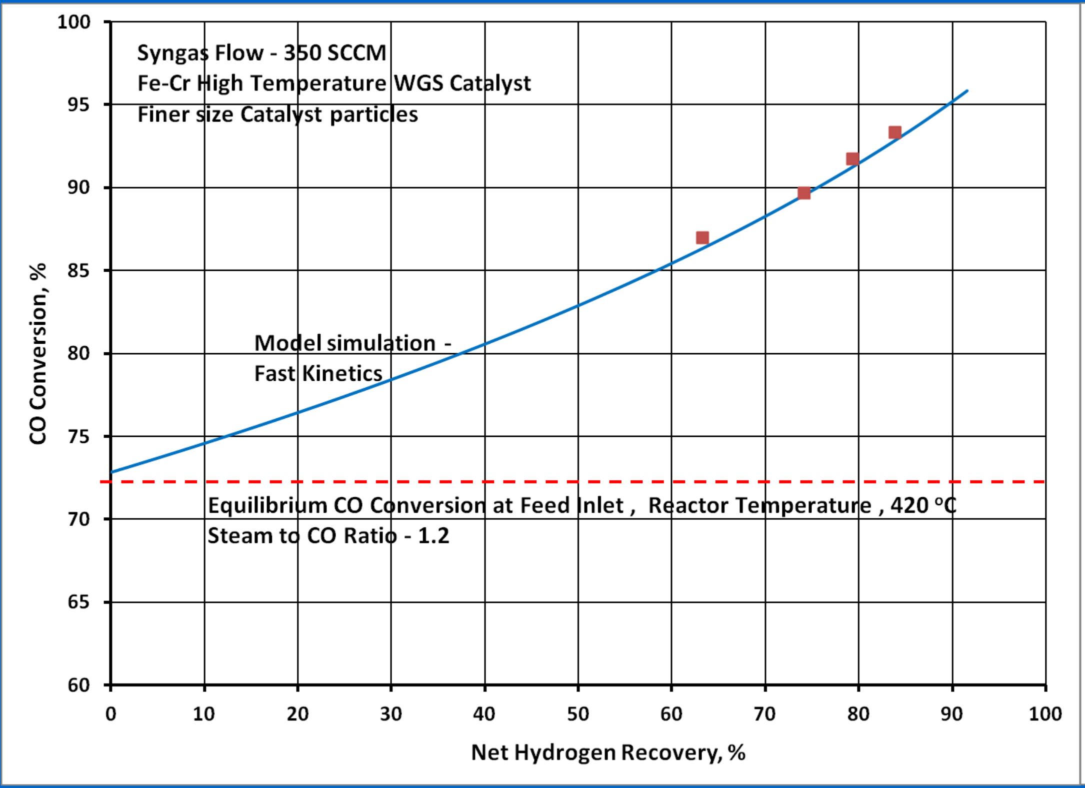
Techverse Membrane Reactor Model

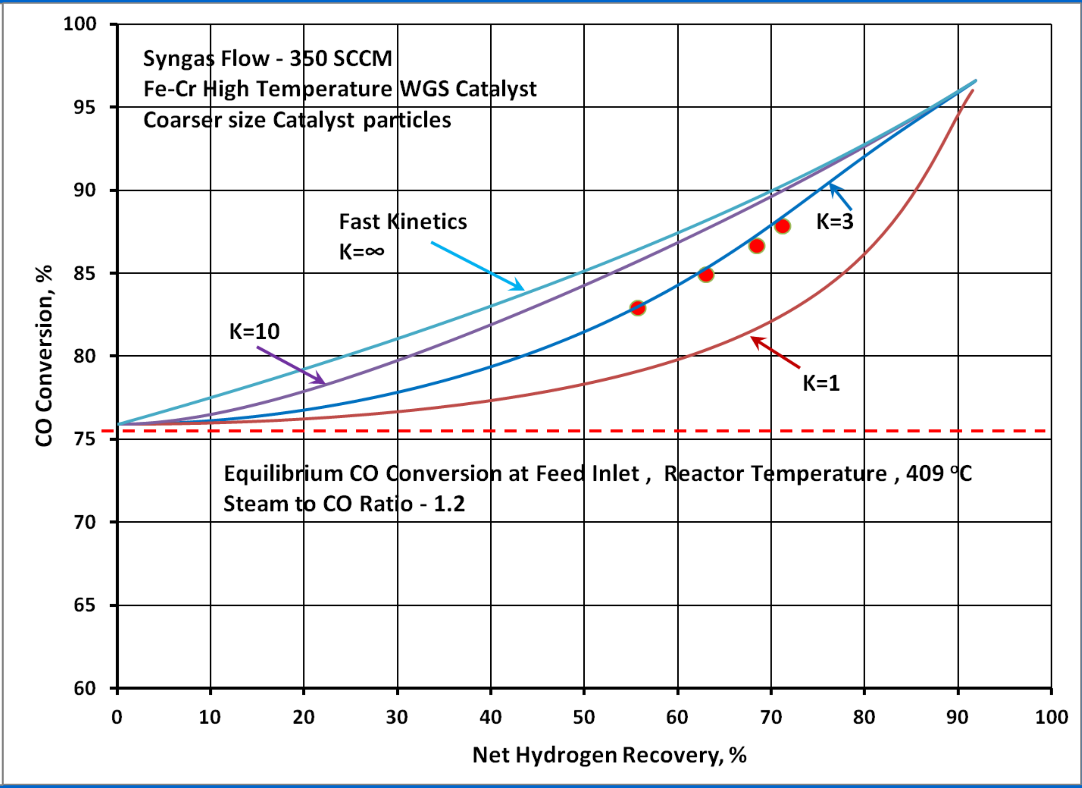


Model Assumptions:

- One-dimensional linear geometry
- Constant feed and permeate side pressures along the reactor
- Includes heat of reaction, effect on kinetics and permeation
- Extent of reaction limited by equilibrium considerations
- Hydrogen flux determined by local driving force

Model Simulation Results - Examples

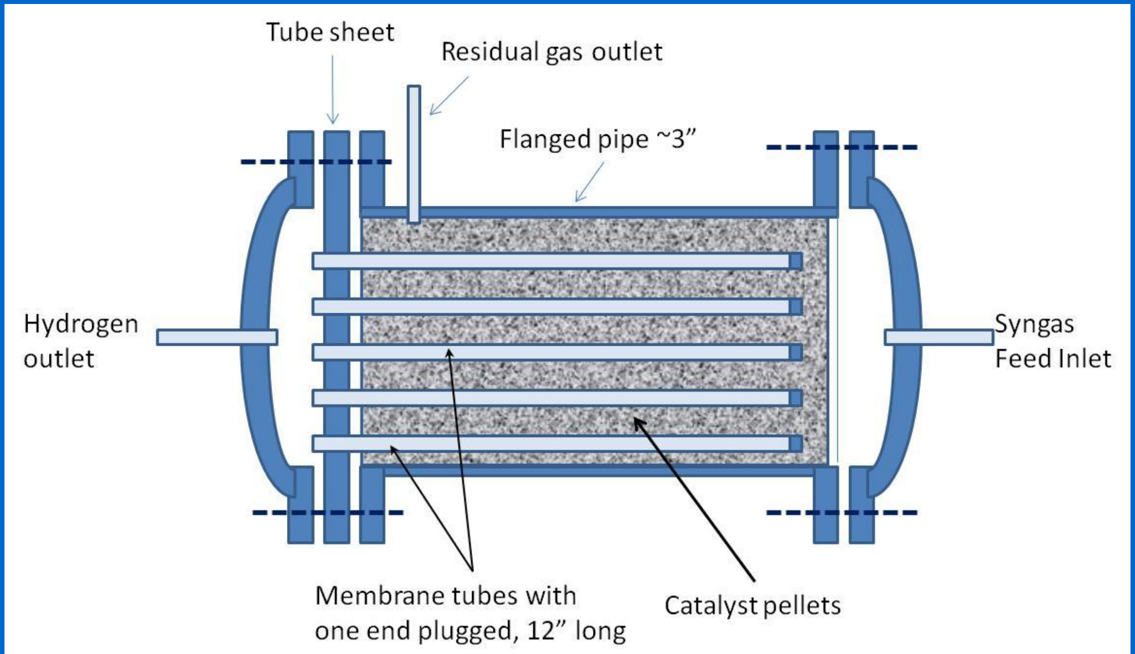




- Model simulations accurately predicted effect of reaction kinetics
- Membrane reactor model includes heat transfer or adiabatic operation

Prototype Membrane Reactor Module Design

- Process capacity ~ 1 scfm syngas (oxygen blown gasifier)
- Steam to CO ratio – 1.2, Temperature - 400 ^oC, Pressure - 300 psig
- 12-tube module with 12” length membrane tubes



Techno-Economic Analysis

- Estimated membrane module costs:
  - 5 µm membrane < $500/ft²$, 2.5 µm < $250/ft²$
- To be competitive with SOTA (Selexol process) (DOE/NETL-401/113009)
  - ($/GPU-cm^2)x1000 < 0.4 and a H_2/CO_2 selectivity >40
  - For 5,000 GPU with 5 µm membrane, cost target <$1,860/ft^2
- For capital cost similar to conventional WGS reactors/Selexol/PSA
  - Membrane cost target - $ 2,850/ft^2 (DOE/NETL-2010/1434)
- Cost target for <$40/ton CO_2 in Natural Gas Combined Cycle plant
  - $560/ft^2 (Jansen et al. Energy Procedia, 2009, vol. 1, p 253-260, GHGT-9 Conference)
- Pd-A-B alloy membrane has excellent potential to meet cost target

Future Development / Testing / Commercialization

- Optimize membrane synthesis – composition, thickness
- Membrane scale-up to 12” length
- Testing for additional syngas contaminants
  - Tar, ammonia, higher H_2S, COS
- Fabrication of multi-tube module
  - Testing of multi-tube module in simulated syngas
- Testing of multi-tube module on a gasifier slip stream