



# Membrane Reactor for Hydrogen Production

**AICHE 2008 Annual Meeting, Philadelphia, PA**



Photo courtesy of  
Pall Corporation

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This presentation does not contain any proprietary or confidential information

- **Pall Corporation**
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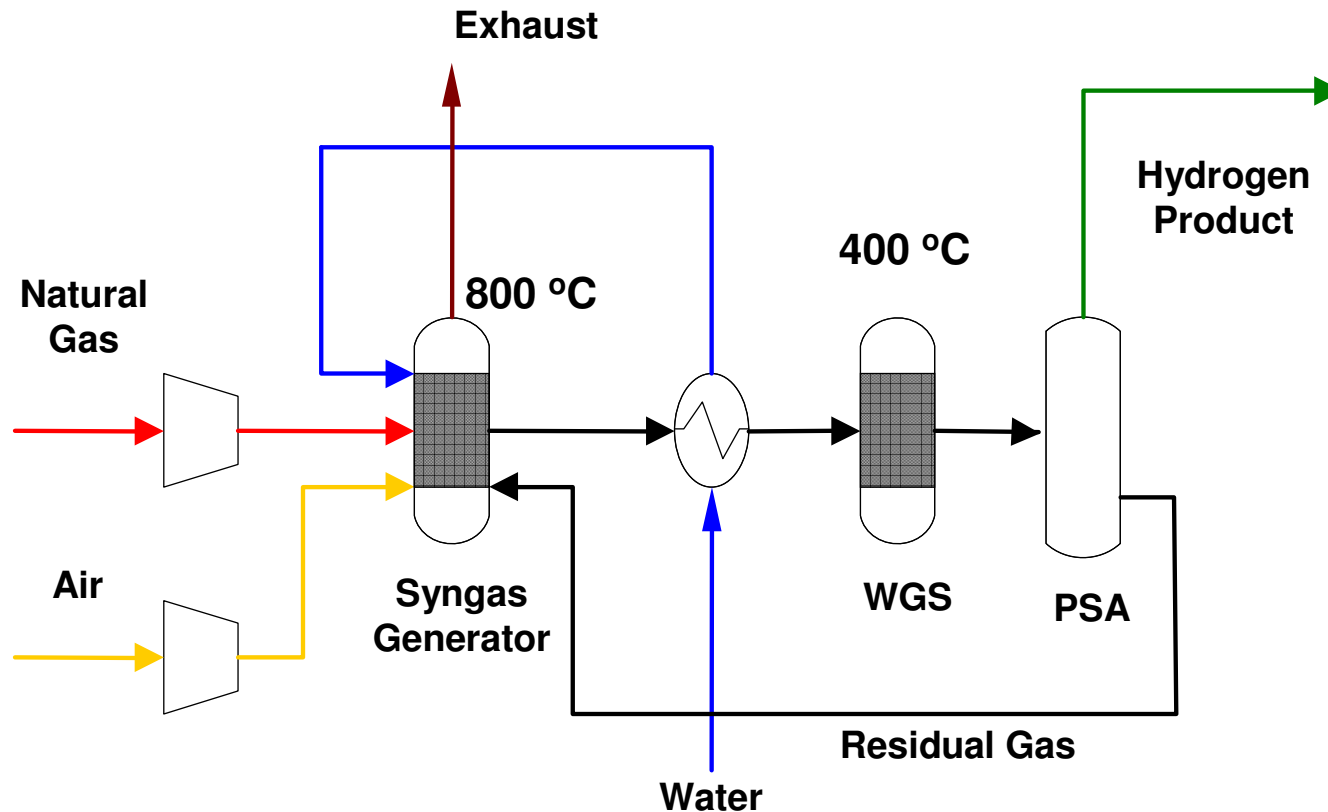
- Drivers for Hydrogen Production and CO<sub>2</sub> capture
- Process intensification / Membrane reactor concept
- Status of Pd-alloy composite membrane at Pall
  - Inorganic substrate development
  - Composite Pd-alloy membrane development
- Membrane reactor model simulations
  - WGS Membrane reactor experimental studies
- Pall's capabilities and future activities

## Two major drivers for hydrogen production

- Hydrogen as energy carrier – Transportation, Power/heat generation, and Chemical production
- Pre-combustion CO<sub>2</sub> capture and hydrogen production has potential to reduce GHG emissions

## Hydrogen Production

- Can be produced from multiple pathways – natural gas, coal, biomass and renewables
- Near term hydrogen production from Natural Gas
- Longer term hydrogen production from Coal and renewable energy sources (biomass, solar, wind)



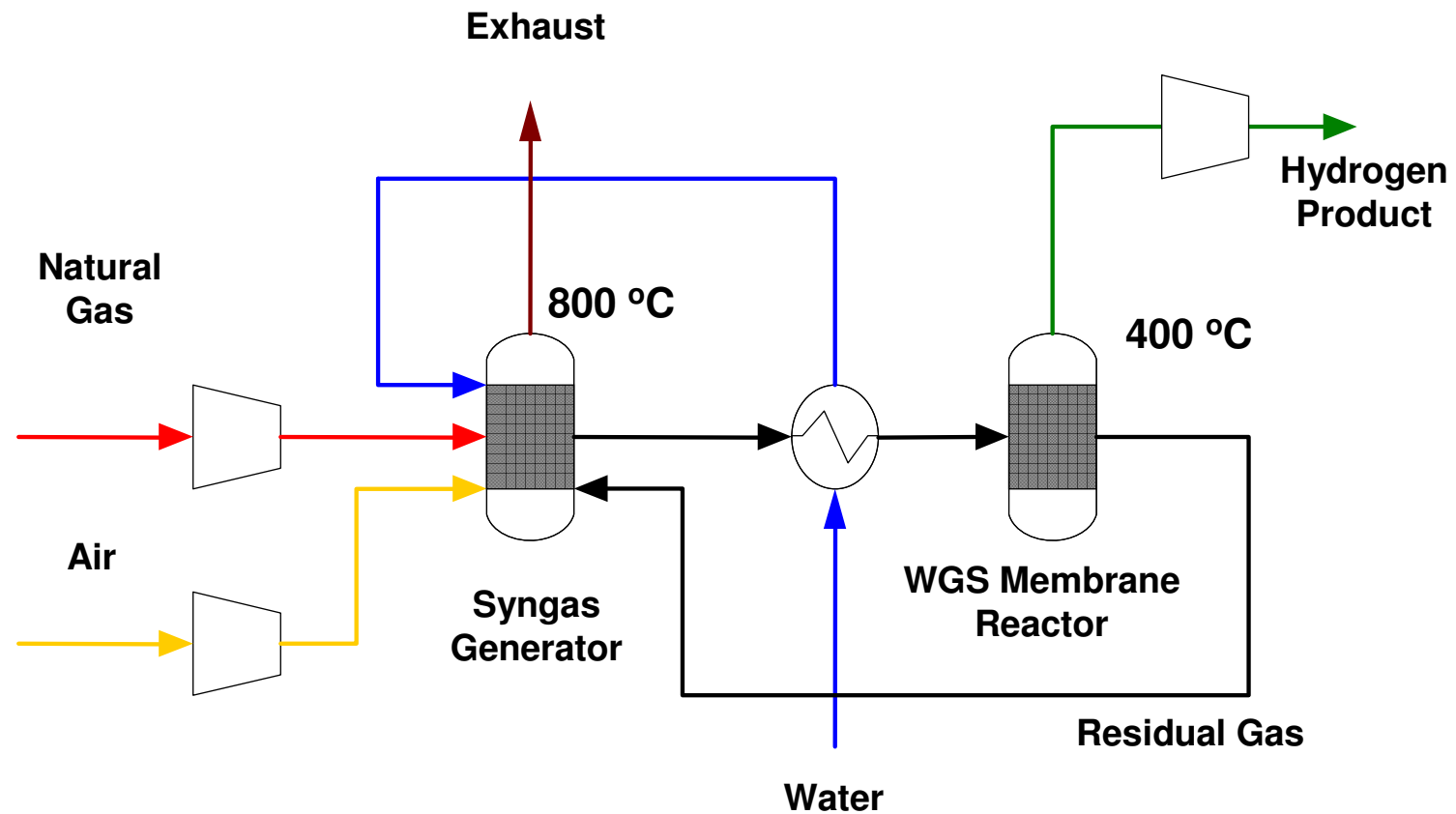
## Current State:

> 90 % of H<sub>2</sub> is produced from NG by this process

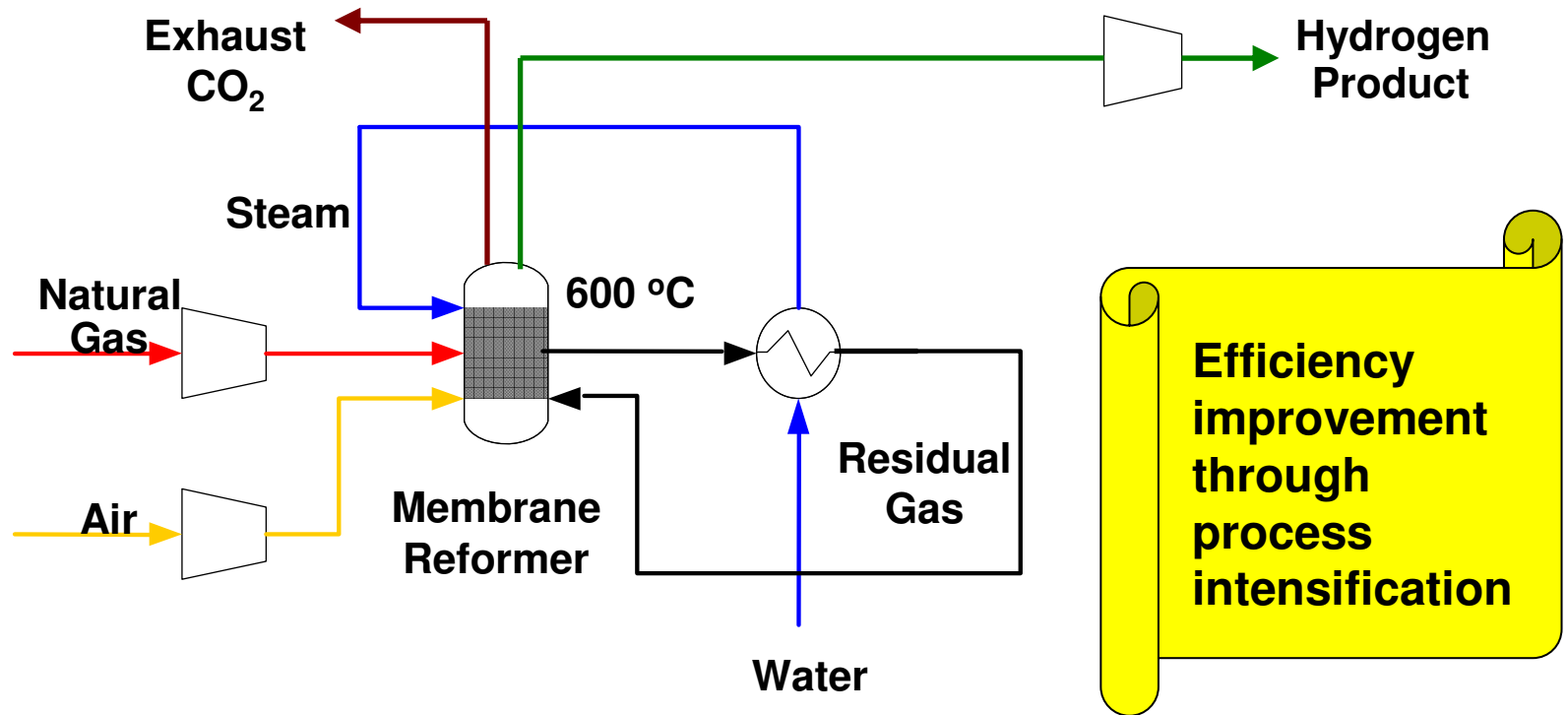
Very efficient on large scale

## Future State:

Combining hydrogen generation and separation (**process intensification**) can potentially reduce capital and operating cost of hydrogen production at various scales

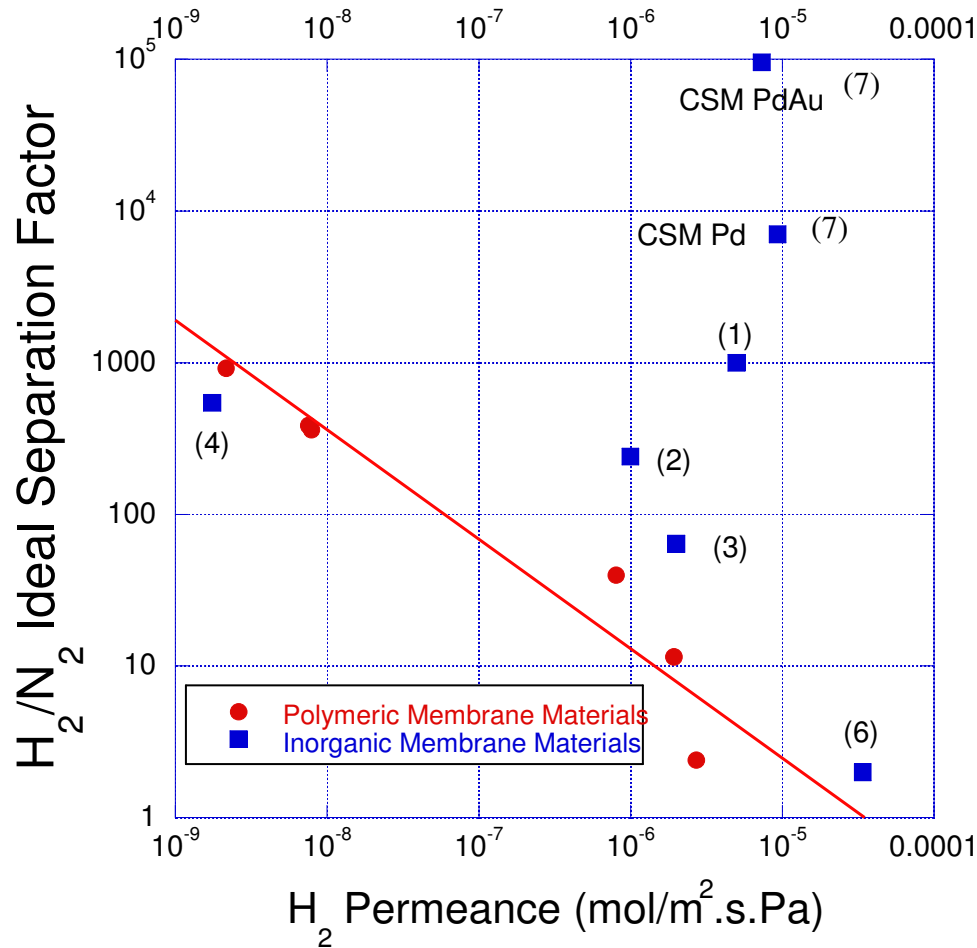


- Increased conversion due to equilibrium shift
- Compact system, smaller footprint
- Simpler operation and lower operating/energy costs
- Need compressor for high pressure hydrogen product



**Efficiency improvement through process intensification**

- ✓ Compact unit, smaller footprint → Lower capital cost  
Milder conditions
- ✓ Increased hydrogen yield → Greater energy efficiency,  
Less steam → Lower cost of H<sub>2</sub> production
- ✓ Need high temperature inorganic membrane for H<sub>2</sub> separation



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5. Polymer line from : Robeson, L. M., *J. Membr. Sci.*, **62**, 165(1991).
6. Wu, J. C. S. et al., *J. Membr. Sci.*, **77**, 85(1993).
7. Hatlevik, Ø., Gade, S. K., Keeling, M. K., Thoen, P. M. and J. D. Way, "Palladium and Palladium Alloy Membranes for Hydrogen Separation and Production: History, Fabrication Strategies, and Current Performance," submitted to *Separation and Purification Technology*, Sept. 2008.

Graph courtesy of Prof. Doug Way and CSM group

## **Self supporting membrane structures**

- Need membrane of sufficient thickness for structural integrity and strength e.g. tubes or flat sheets > 25  $\mu\text{m}$
- Expensive, Niche applications – small H<sub>2</sub> purifiers

## **Composite membrane structures**

- Thin films on substrates
- Substrate provides structural integrity and strength
- Deposition of thin Pd-alloy films by various techniques ~ 1 – 5  $\mu\text{m}$
- Better seals for High T – High P applications
- Lower cost – thin Pd layer, less membrane area

## Components of a Composite Membrane

### 1) Porous stainless steel

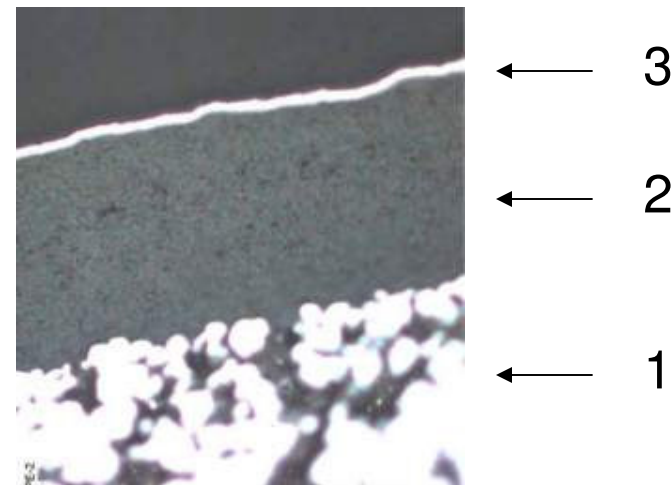
- Provides mechanical support that can withstand the operating conditions of the process
- Critical features: permeability, weld configuration, mechanical, thermal and chemical compatibility

### 2) Diffusion barrier

- Enables formation of functional layer
- Critical features: surface properties, material, gas permeability, number of defects

### 3) Pd alloy membrane

- Functional layer provides for gas separation
- Critical features: thickness, alloy composition, durability and number of defects



Excellent adhesion to zirconia layer, uniform thickness, and surface contour following of Pd-alloy metal film

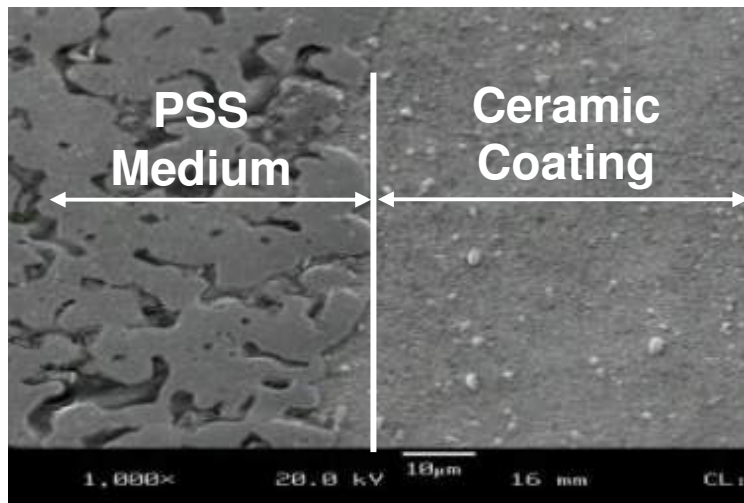


## Ceramic / PSS composite substrate for Pd alloy membranes

### It's all about the substrate



Porous stainless steel tube with  $ZrO_2$  ceramic coating: Extensive development work done to optimize the composite structure and surface properties to enable formation of a high quality Pd alloy or other functional layer.



- **All welded design**  
No polymer seals, Higher temp. capabilities
- **Thermal expansion**  
Uniform thermal expansion with the housing and module components
- **Cost**  
All metal design with welded fittings, allows for direct welding to a tube sheet. This eliminates the need for intricate sealing mechanism and reduces overall module cost

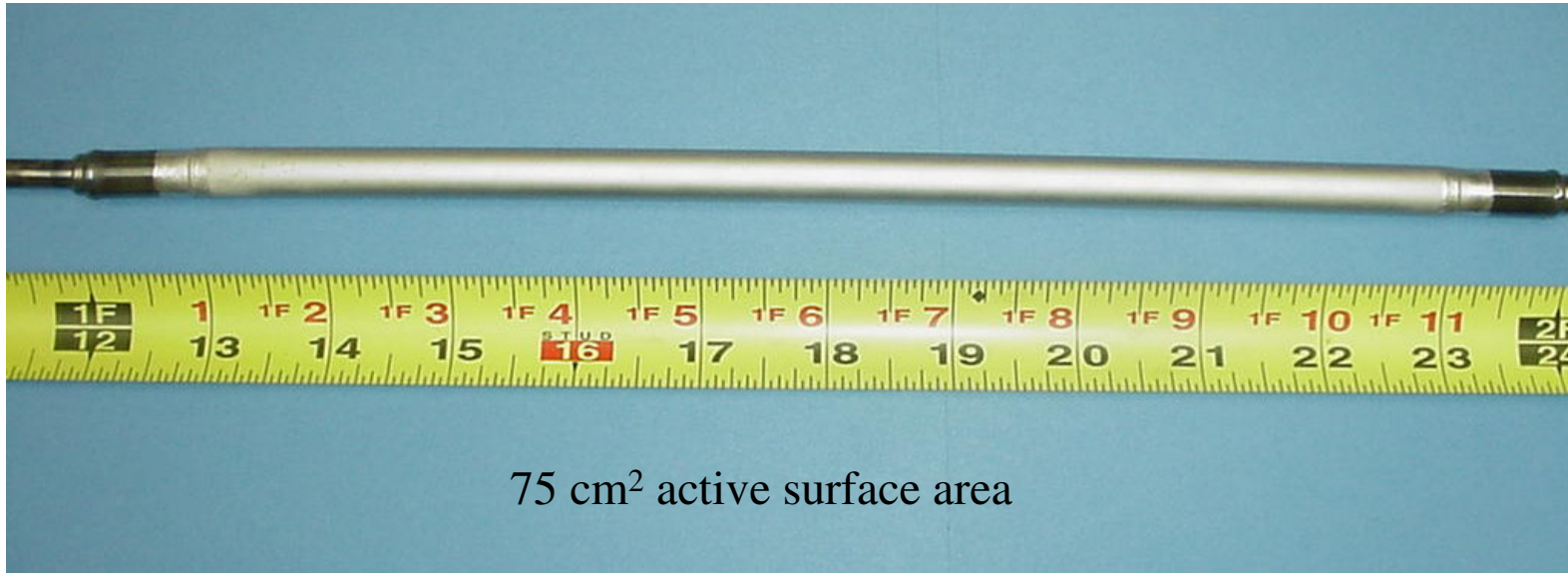


**Durability : Pall Gas/Gas separation supports have been exposed to multiple thermal cycles with no detrimental effects to the composite structure**

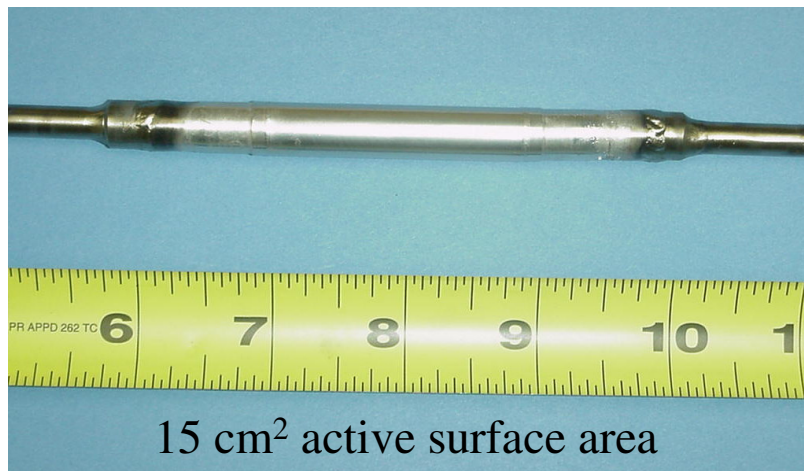
- Ceramic layer stable and maintains adhesion to metallic substrate through thermal cycles
- Composite tube with 310SC can be used up to 550 °C in pure H<sub>2</sub> and up to 400°C in air or inert gases

## **Characterization Data of Composite Support**

- ✓ First bubble in IPA is > 30 psi
- ✓ Air permeability @ 1000 cc/min ~ 7 psi
- ✓ Zirconia coating pore structure is 70 nm
- ✓ Base metallic tube pore structure is 2 microns in average



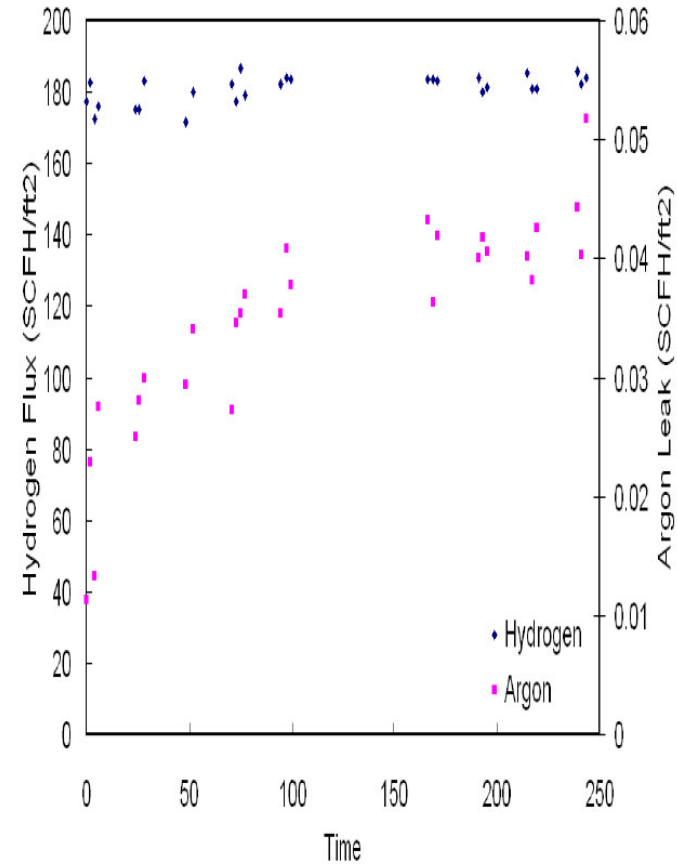
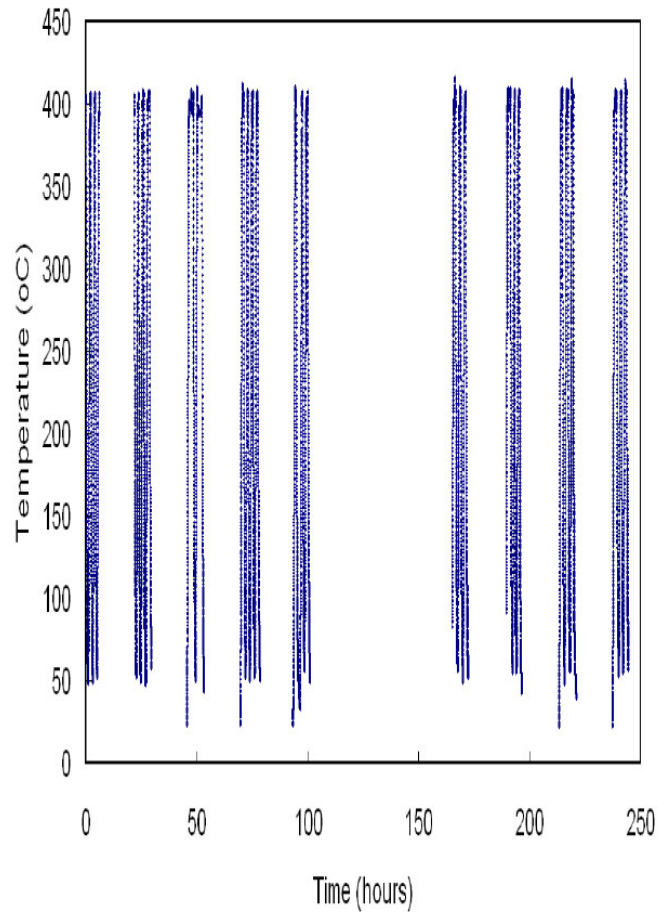
75 cm<sup>2</sup> active surface area



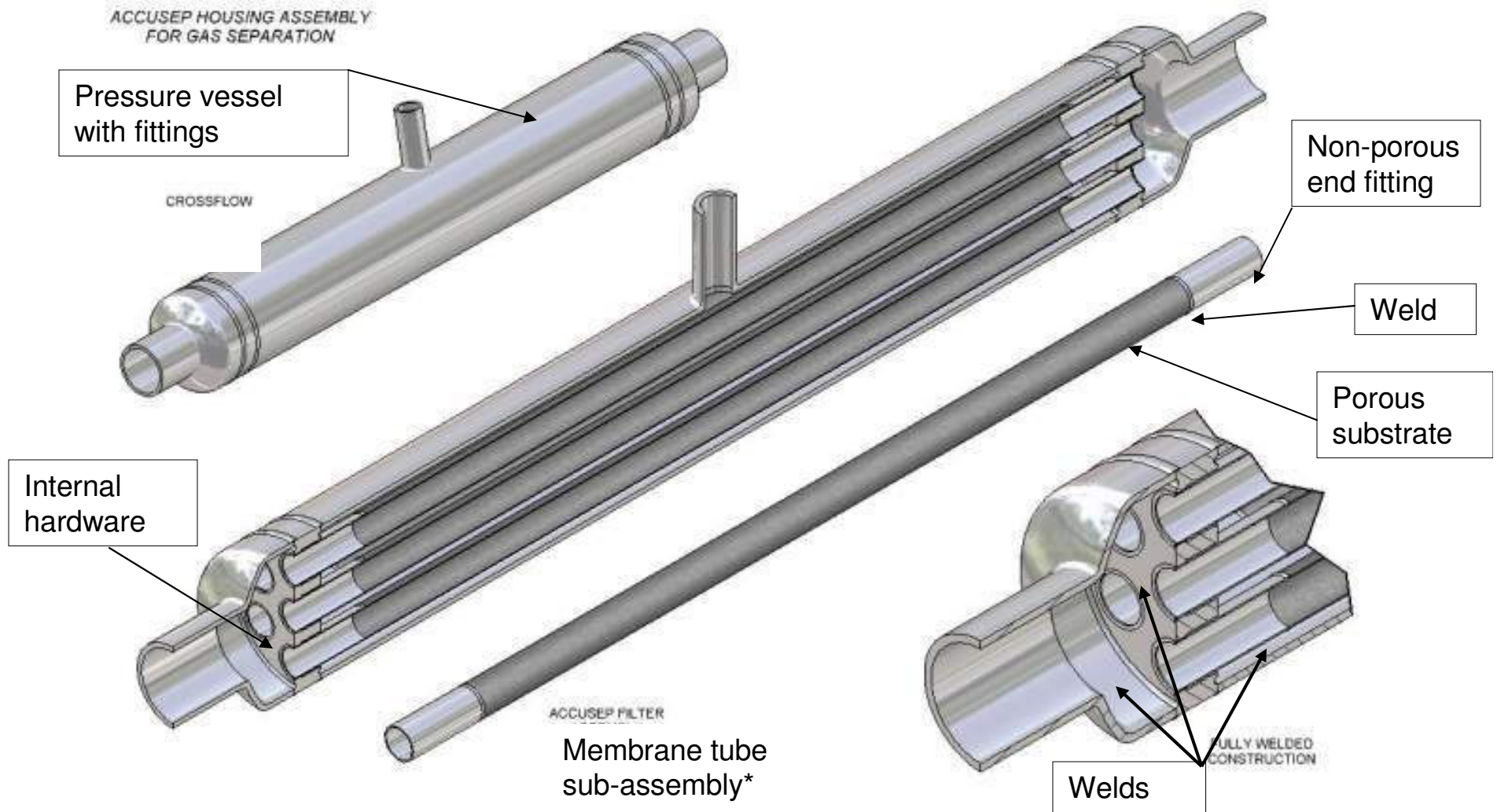
15 cm<sup>2</sup> active surface area

## Typical Performance Data

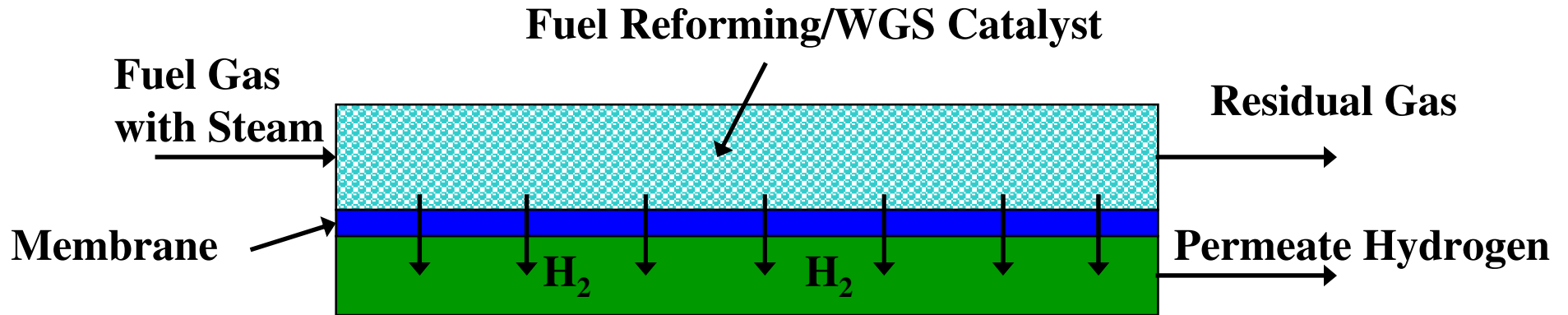
- **H<sub>2</sub> flux 150-180 SCFH/ft<sup>2</sup>**
  - **H<sub>2</sub>/Ar SF 10,000 – 20,000**
- Under test conditions**
- **Pure gas permeation**
  - **400°C**
  - **Feed 20 PSIG**
  - **Permeate atmospheric**



Thermal Cycle: Air → Air → Argon → Hydrogen → Air  
 Temperature (C): 25 → 400 → 400 → 400 → 25  
 Pressure (psig): 0 → 20 → 20 → 20 → 0

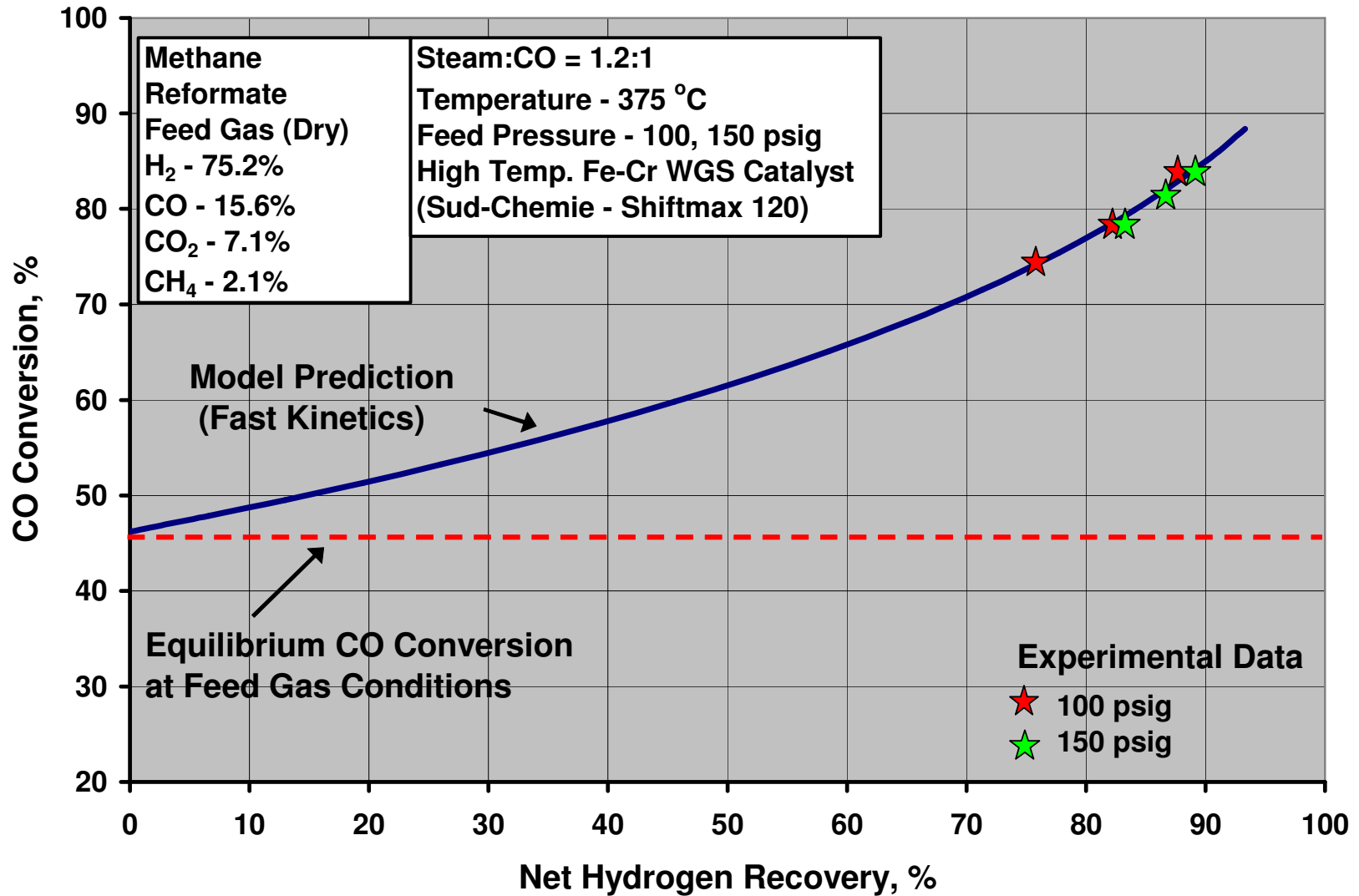


\* Pd alloy membrane not shown, typically on the OD of the tube



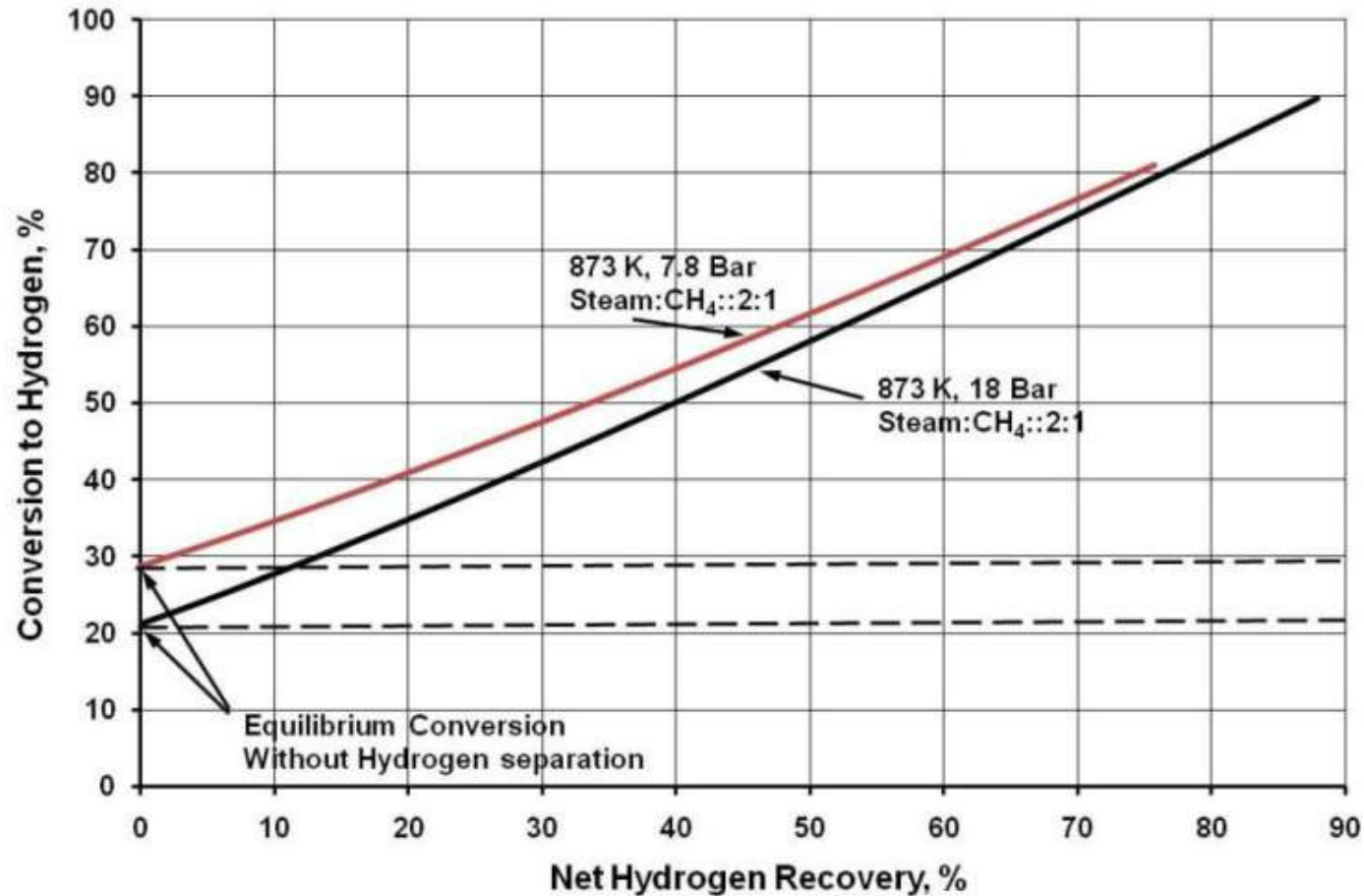
## Model Assumptions

- Temperature and total pressure constant on both sides
- Reaction kinetics faster than hydrogen permeation
- Feed side is in dynamic equilibrium
- Hydrogen flux determined by local driving force

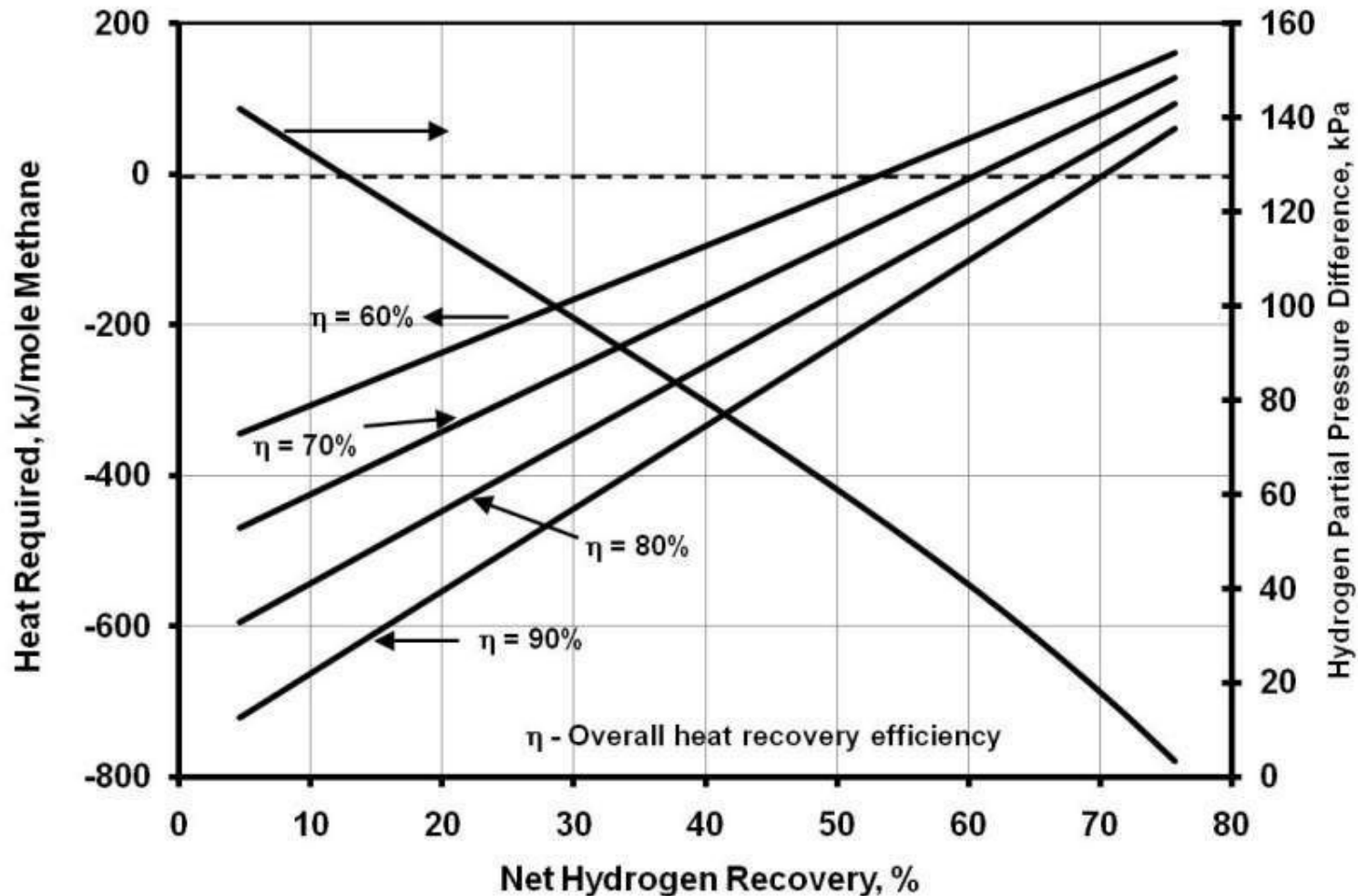


**Demonstrated > 80% Net Recovery of Hydrogen with >80% CO conversion**

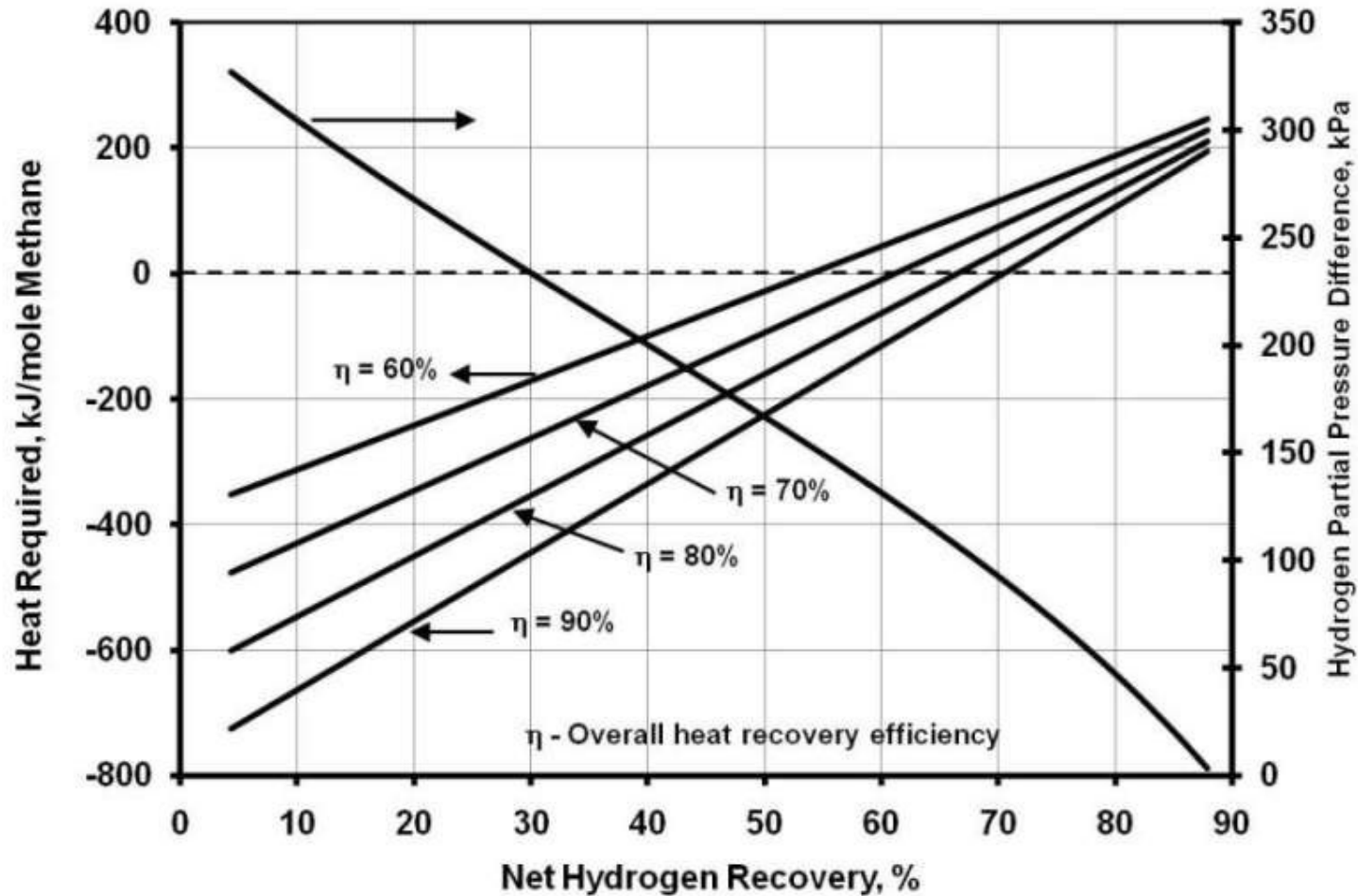
# Predicted Methane Conversion increase @ T – 600 C, Steam:C::2:1, P-100, 250 psig



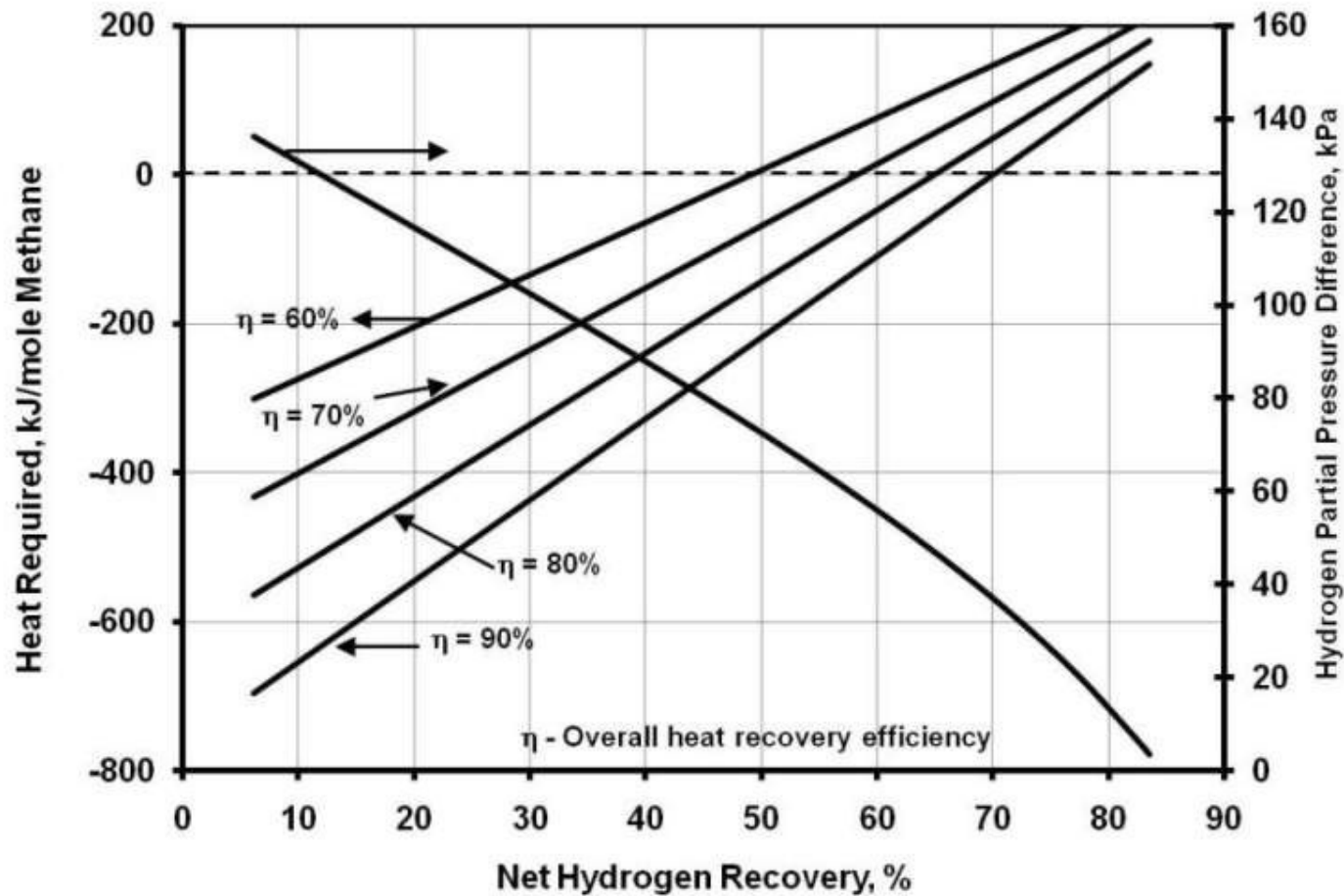
Effect of Pressure – Greater H<sub>2</sub> recovery and yield in spite of unfavorable equilibrium



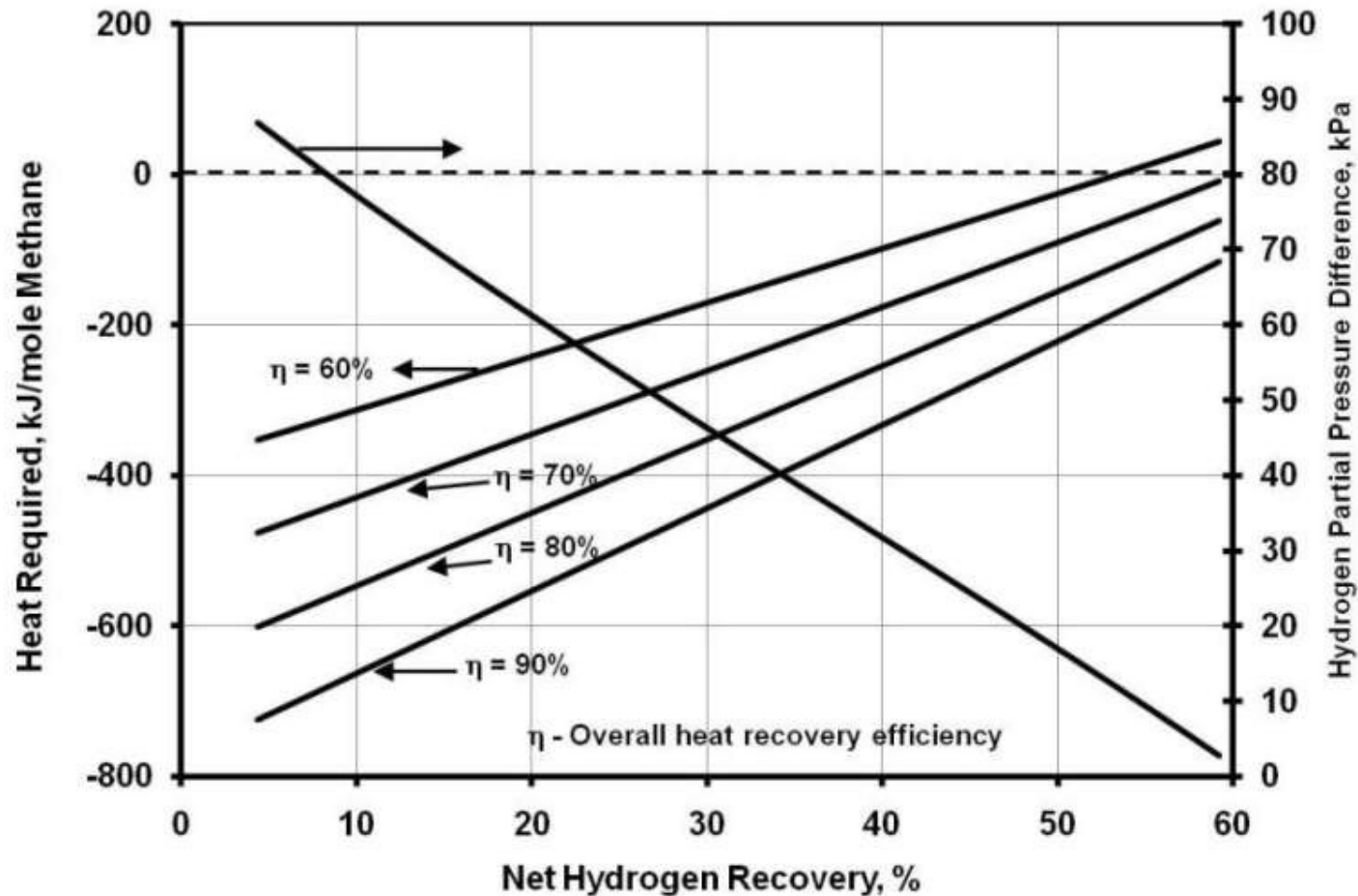
Recovery of sensible and combustion heat of Residual Gas  
 Net heat requirement analysis



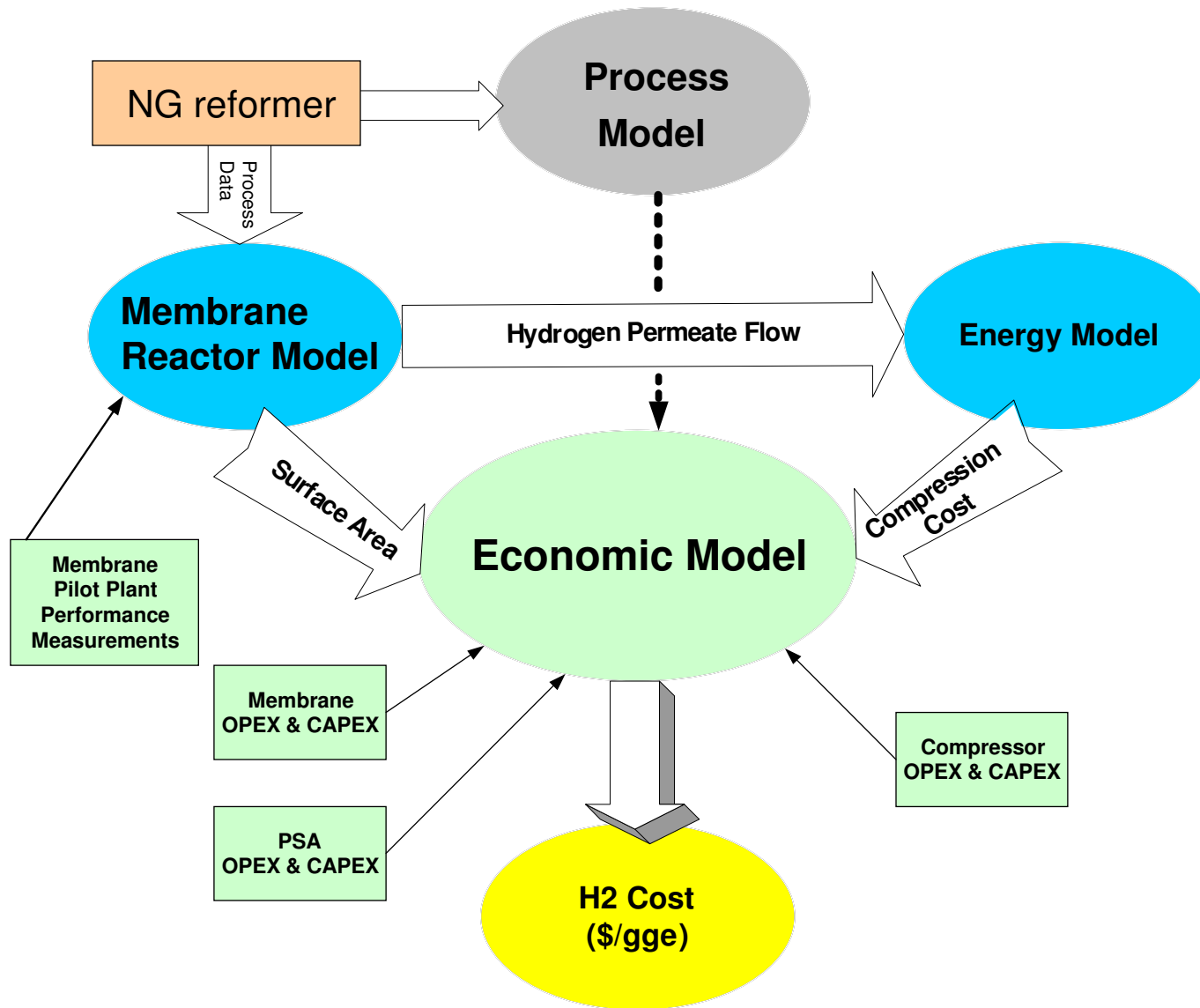
Effect of Pressure – Greater H<sub>2</sub> partial pressure  
Less Membrane Area requirement



Higher Steam:C ratio – Greater H<sub>2</sub> partial pressure  
 Less Membrane Area requirement  
 Relatively small energy penalty



Lower Temperature – Lower H<sub>2</sub> partial pressure – less conversion  
**(strong effect)**      Low hydrogen recovery





## **Basis: 100 Kg/day (1650 SCFH)**

- Membrane module area ~ 10 ft<sup>2</sup>
- Membrane Module cost with DOE Target ~ \$7,500
  - Cost of metal ~ \$ 235 (October 2008 prices)
- Capital cost reduction by replacing PSA/WGS ~ \$ 40,000
- DOE H<sub>2</sub>A Forecourt Model – Capital cost portion ~ \$3.06/kg H<sub>2</sub>
- Potential reduction in capital cost contribution ~ \$0.36/kg H<sub>2</sub>
- Penalty for 50% additional compressor cost ~ \$ 0.08/kg H<sub>2</sub>
- Additional benefits not yet quantified
  - Increased hydrogen yield
  - Reduced operational cost
  - Reduced energy costs

## **Capital Cost**

- High flux membrane to reduce required membrane area and pressure vessel size
- High efficiency modules to maximize use of membrane area
- Commercial scale manufacturing process for Pd alloy membranes
- Process integration to reduce balance of plant cost
- Process intensification (ex: membrane reactors) to minimize catalyst and hardware cost

## **Operating Cost**

- High separation factor membranes that maximize H<sub>2</sub> recovery
- Process integration to minimize the energy penalty for CO<sub>2</sub> capture

## **Maintenance Cost**

- Durable palladium alloys that can tolerate severe process conditions, abrupt startups & shutdowns, and contaminants in feed streams

Research



Development



Commercialization



**Thank You !**