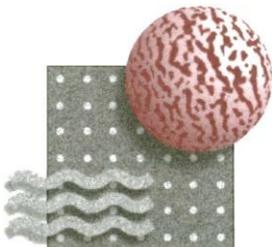
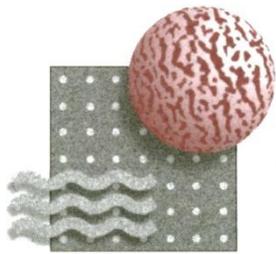


# **Robust & Energy Efficient Dual-Stage Membrane-Based Process for Enhanced Carbon Dioxide Recovery**

DE-FE0013064

- **Dr. Paul KT Liu, Media and Process Technology Inc.  
1155 William Pitt Way, Pittsburgh, PA 15238**
- **Professor Theo T. Tsotsis, University of Southern California**
- **Dr. Eric C. Wagner, Technip Stone & Webster Process Technology, Inc.**





# MPT Commercial Ceramic Membranes

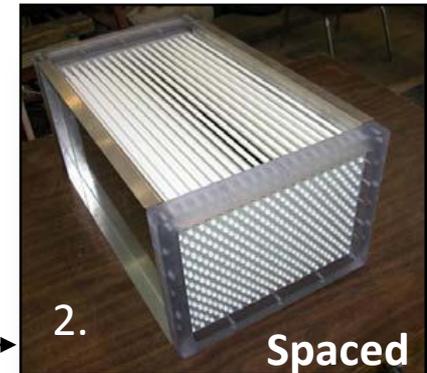
*Various Multiple Tube Elements – versatile, low cost*



Single tubes



*Ex: conventional MF & UF*



*Ex: porous heat exchangers & catalytic membrane reactors*

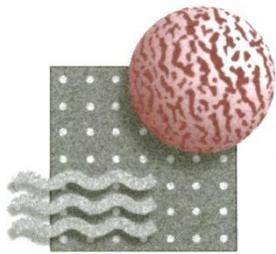


*Ex: high pressure intermediate temperature gas separations*

**Our Core Technologies**



1. Packaging membrane tubes into commercially viable modules for field use.

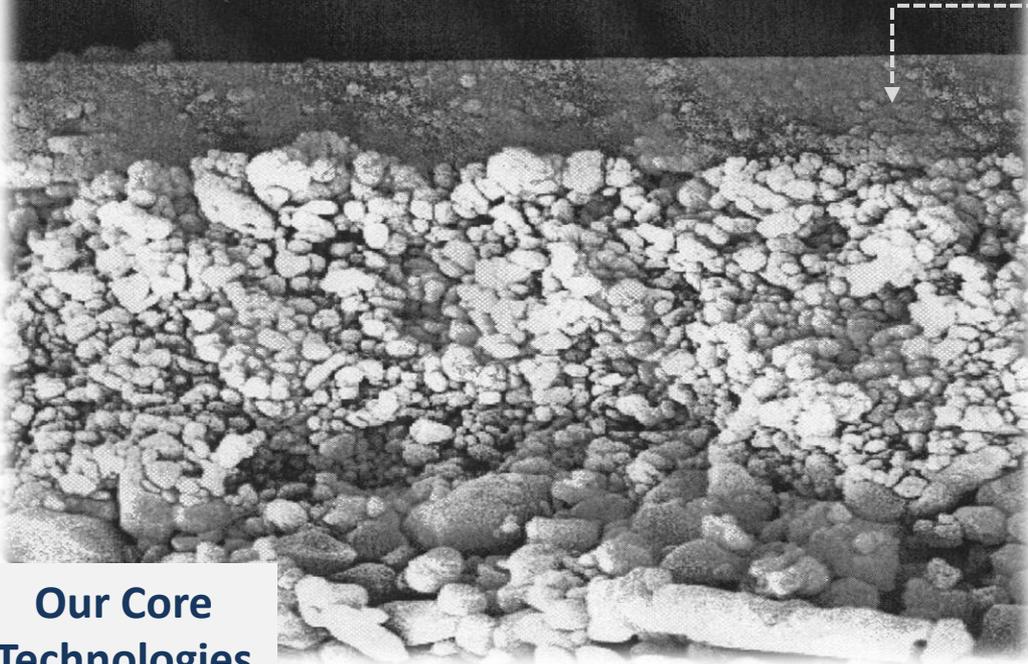


# MPT Commercial Ceramic Membranes

*Our Low Cost vs Conventional Expensive Tubular Substrate*

L= SF1 EHT= 20.0 KV WD= 9 mm MAG= X 4.14 K P  
10.0µm

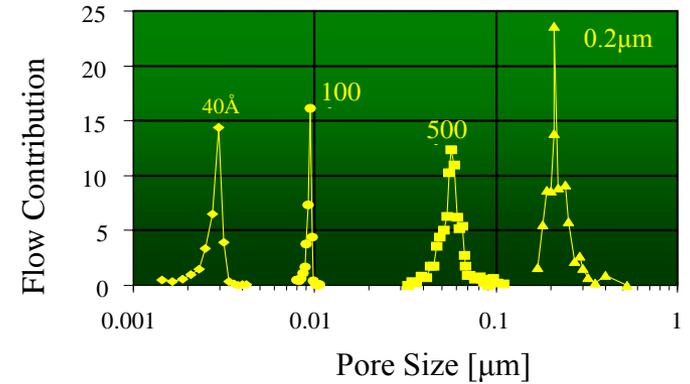
**MPT**



**Our Core Technologies**



2. depositing a near perfect thin film on less-than desirable, but low cost porous substrate.

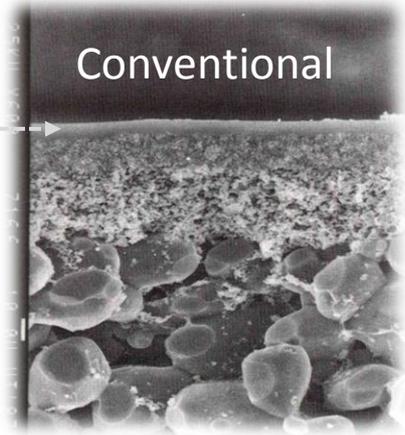


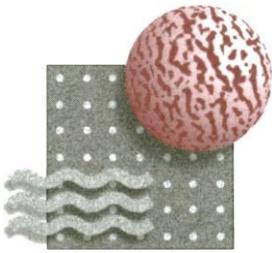
40Å to 100Å  
Layer

500Å  
Sublayer

0.2µm  
Sublayer

Conventional





# Media and Process Technology Inc.

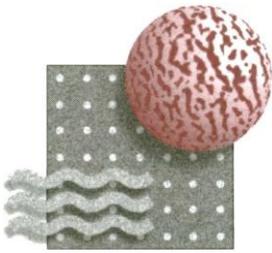
## *Our Facilities*



**Production/ Field Testing Facility  
Leechburgh, PA**

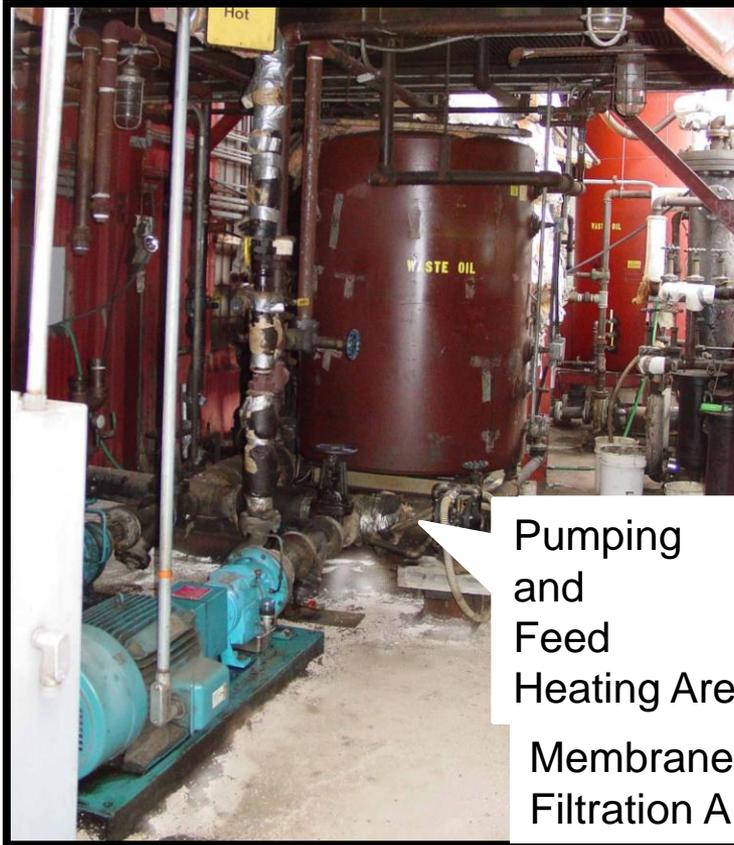


**R&D Facility  
Pittsburgh, PA**



# Media and Process Technology Inc.

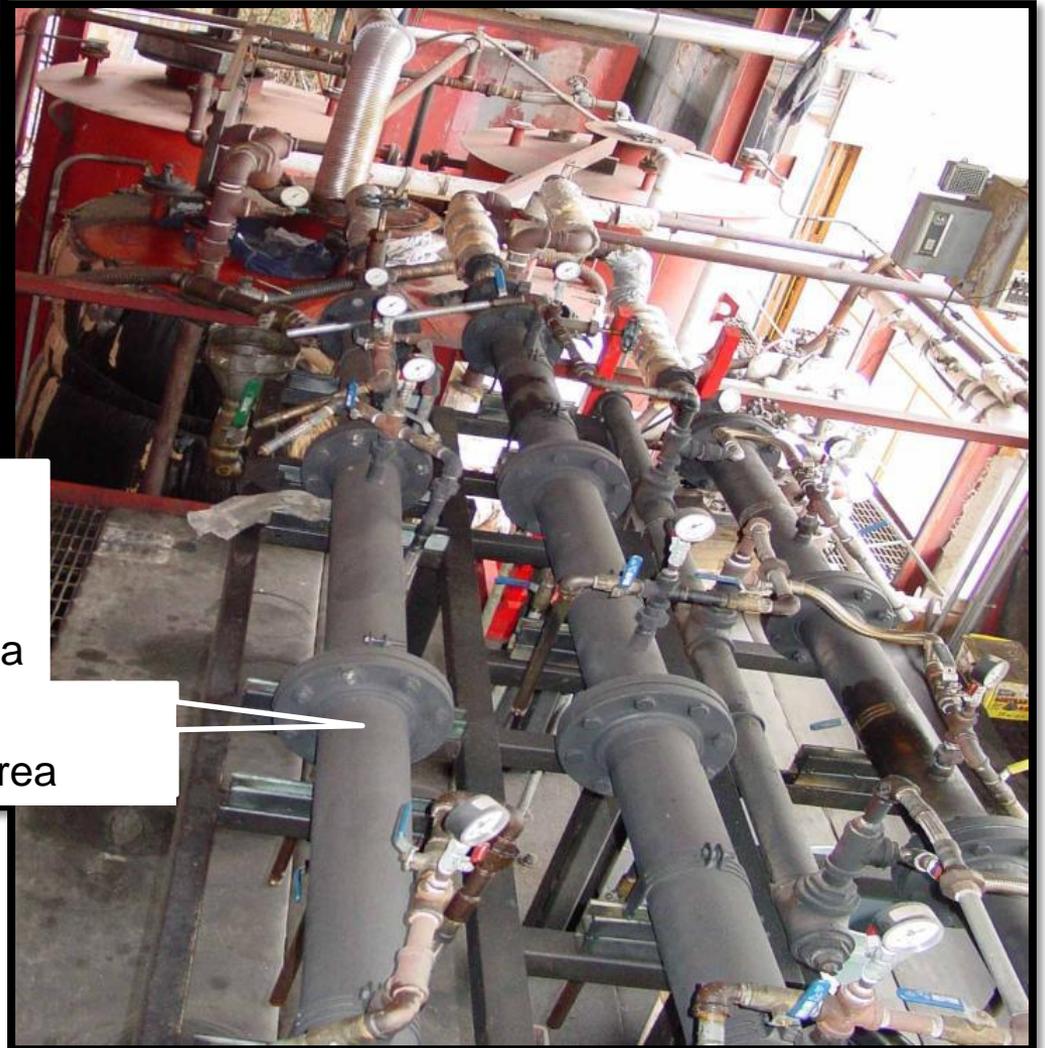
*Waste Motor Oil Filtration for Recycle and Reuse using MPT Ceramic Membrane*



Pumping  
and  
Feed  
Heating Area

Membrane  
Filtration Area

Our ceramic membrane performs effectively at 25-200°C and >100 psi for liquid filtration.

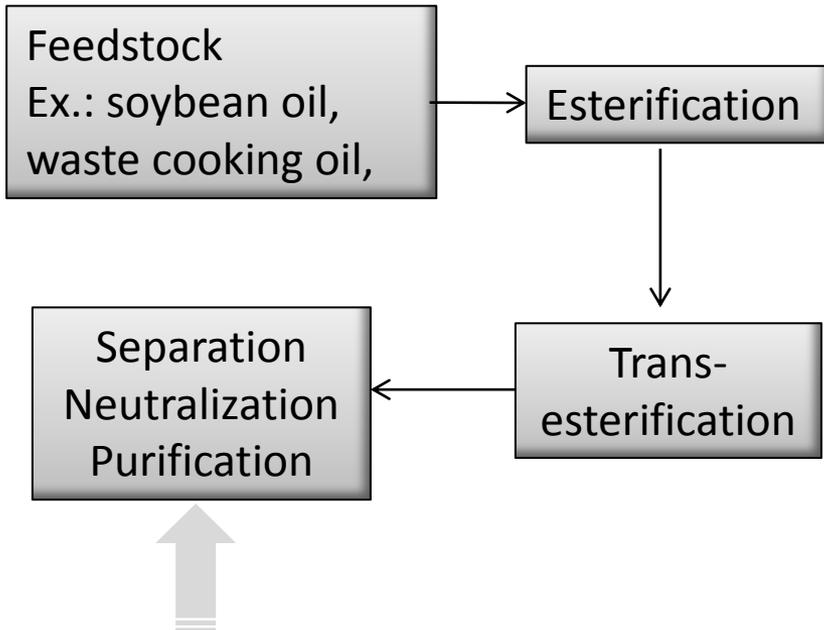


# Our Ceramic Membrane-based Process as End-of-The-Pipe Treatment

an effective, economical and simple tool for biodiesel producers  
to adapt to lower quality feedstock

## Major Unit Operations

### Biodiesel Production from Generic Feedstock

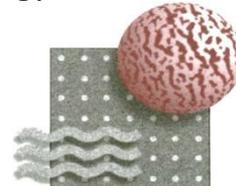


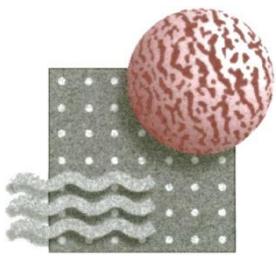
as end-of-the-pipe treatment to meet the CSFT (cold soak filtration test) without using selective adsorbents.



- Projected biodiesel production in US is 1 bgy in 2013.

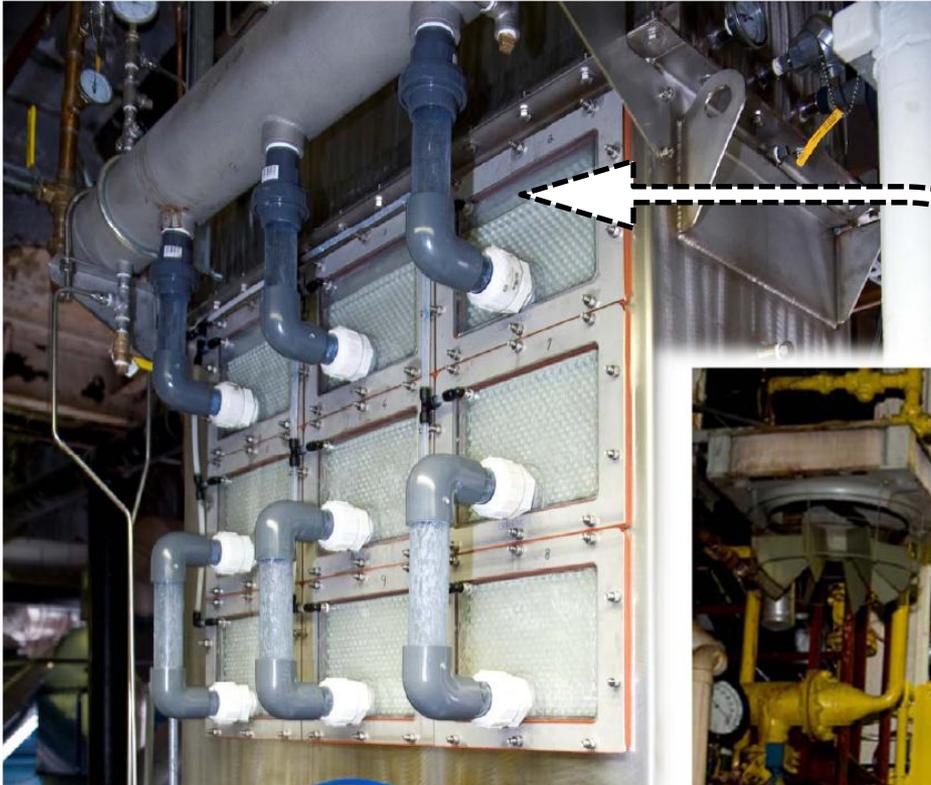
**Media and Process Tech Inc.**



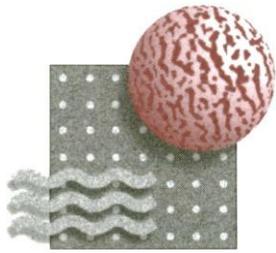


# MPT Commercial Ceramic Membranes

*Vapor phase applications: energy and water recovery from combustion flue*



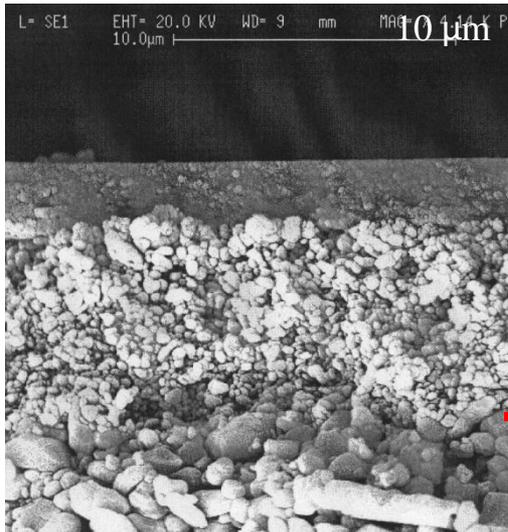
As a porous heat exchanger, our ceramic membrane has demonstrated the enhancement of boiler efficiency from ~80 to >90%



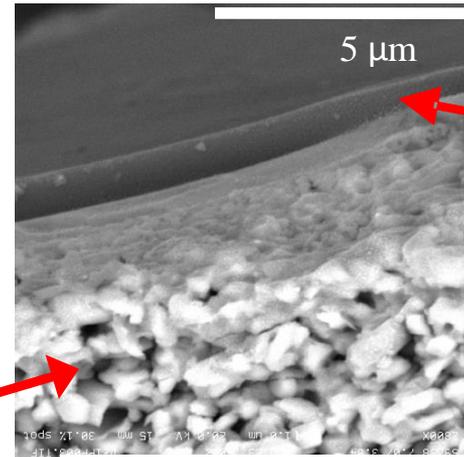
# MPT Advanced Inorganic Membranes

*Specific thin film deposition for advanced separations*

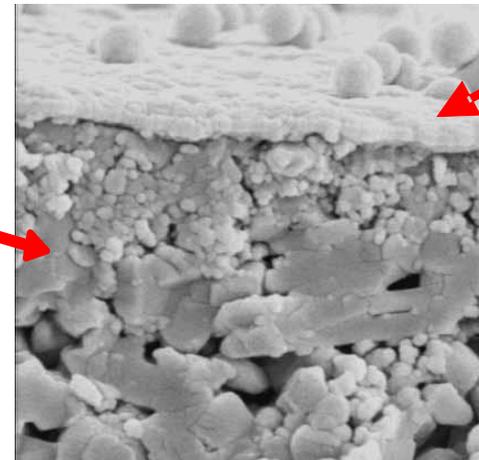
## Inorganic Substrate



Ceramic  
Substrate



Carbon  
molecular  
sieve  
(porous,  
sulfur  
resistance)

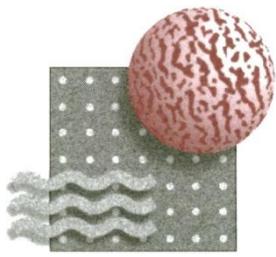


Palladium  
(dense,  
excellent  
selectivity)

Others,  
including  
zeolites,  
flourinated  
hydrocarbons,  
etc.

## Unique feature of Supported Membranes

Low cost,  
e.g., no Pd supply challenge



# MPT Advanced Inorganic Membranes

## *CMS and Pd Membrane Elements*



**CMS thin film  
deposition on  
various elements**

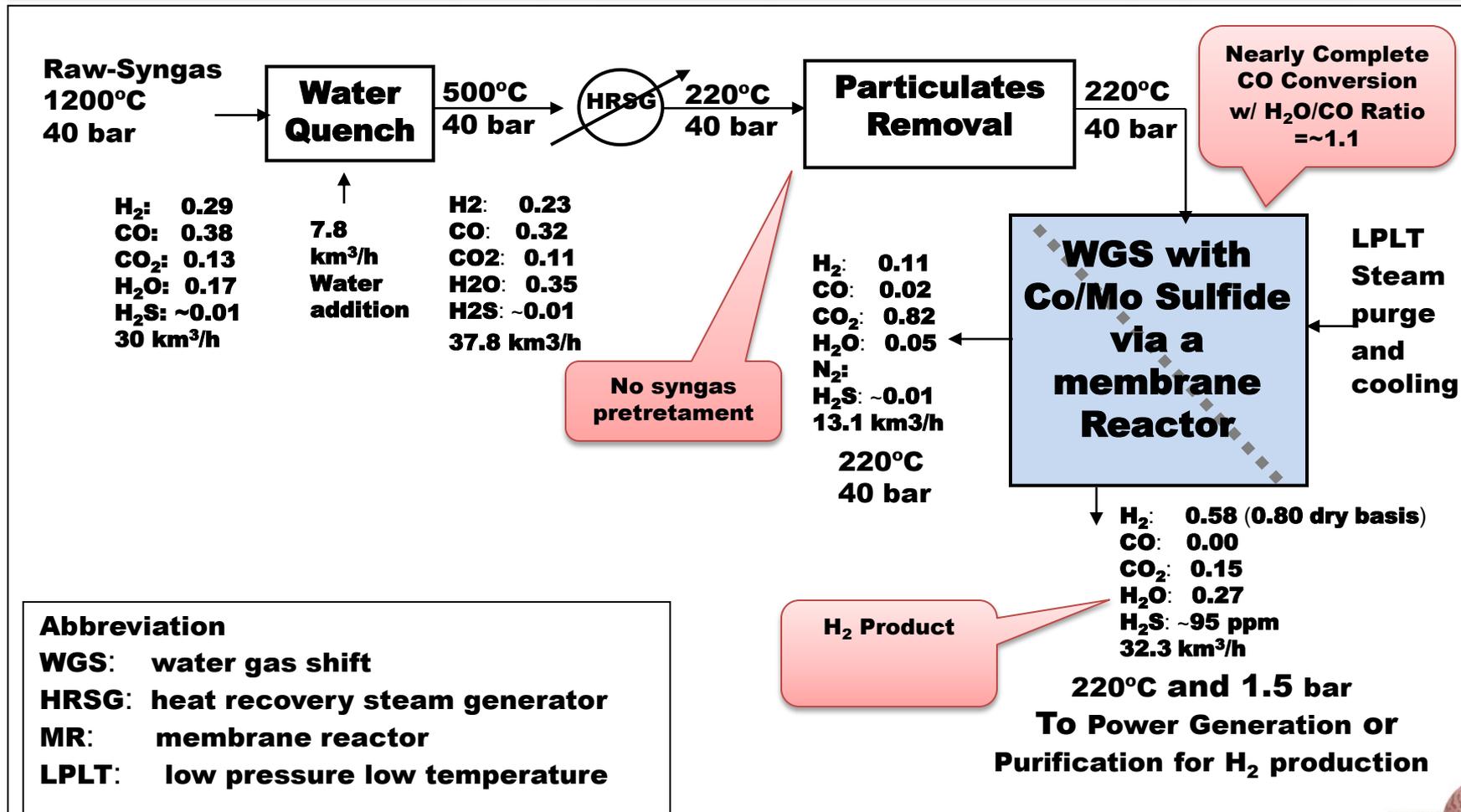


**Pd thin film  
deposition on  
various elements**

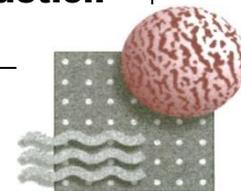


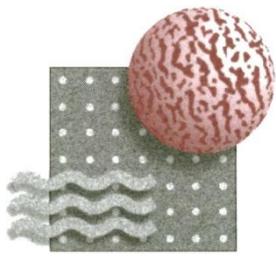
# Block Flow Diagram for the One Box Process for H<sub>2</sub> production and/or power generation

Basis: 300 MW IGCC plant (simplified, unoptimized, for illustration purposes only)



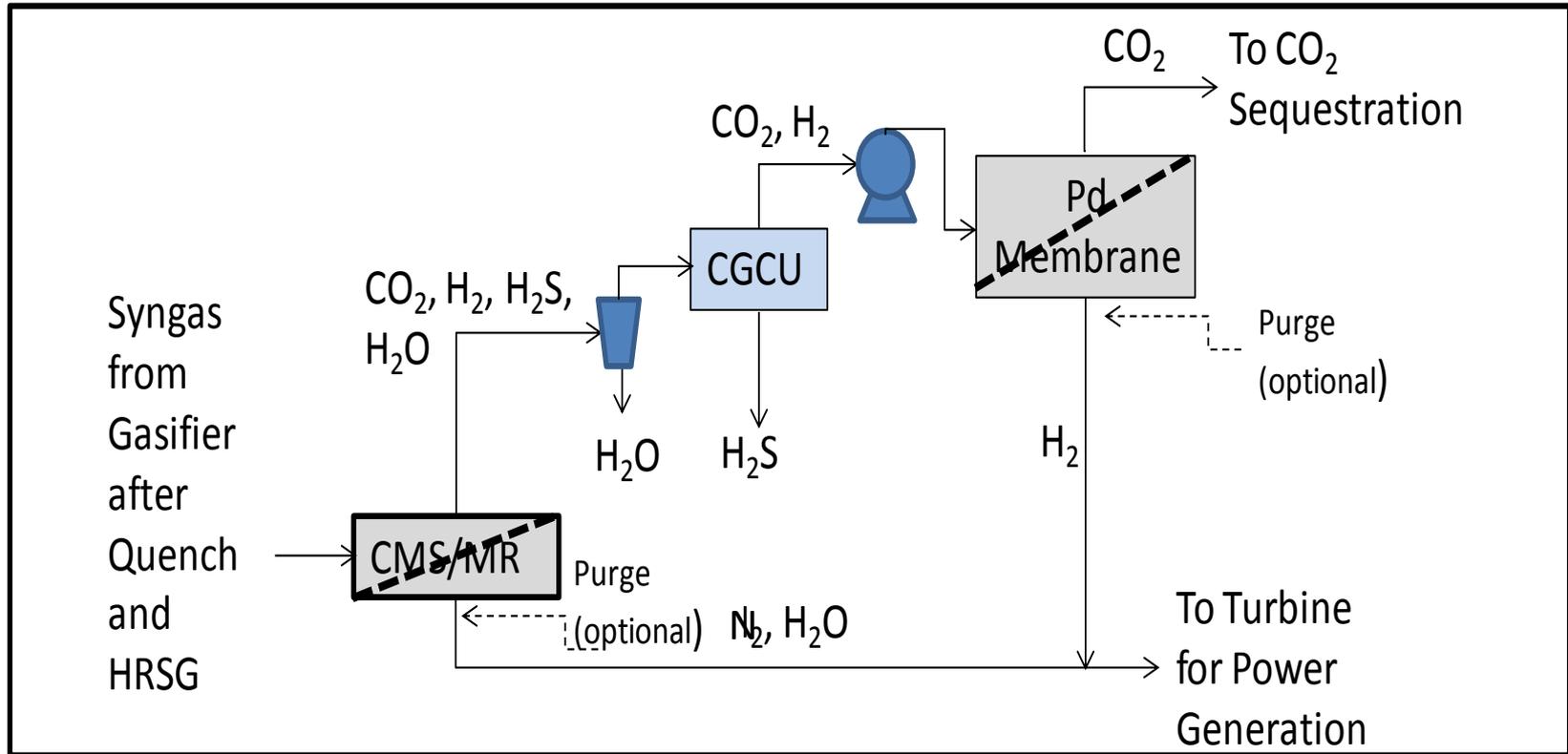
H<sub>2</sub> selective carbon molecular sieve (CMS) membranes as one-box process that accomplishes the warm gas clean-up of coal-derived syngas, the WGS and H<sub>2</sub> recovery in one single unit.



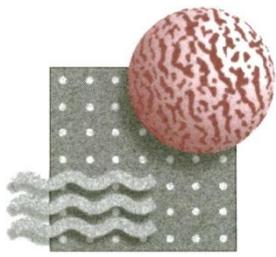


# MPT Advanced Inorganic Membranes

## Dual Stages for IGCC with CCS

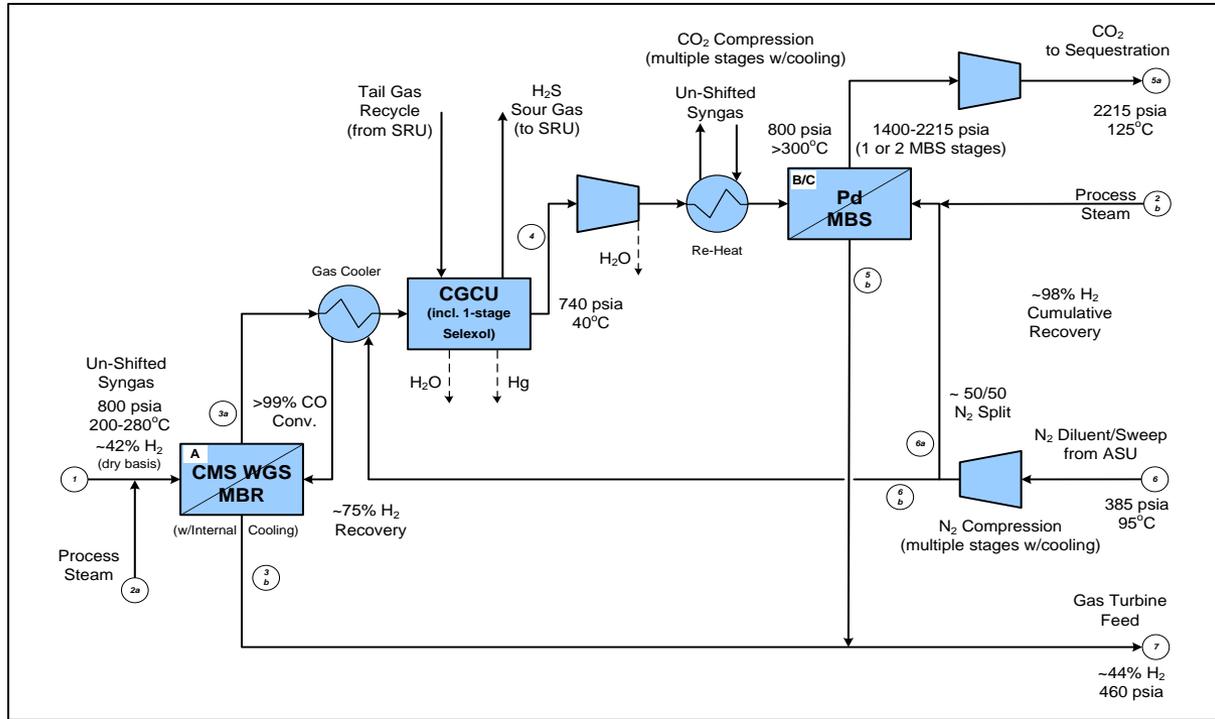


- ❑ Our unique two-stage process avoids the capital and compression costs associated with the conventional two stage operation.
- ❑ The strengths of CMS and Pd membranes are fully utilized while their weaknesses are compensated for by the synergy that is being created by this novel two-stage process.



# MPT Advanced Inorganic Membranes

## Preliminary Economic Analysis for IGCC + CCS via Dual Stage



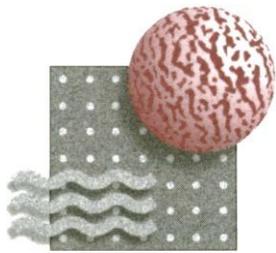
**Table 1 Process Schemes Selected for Performance and Economic Analysis for Power Generation**

| Case Descriptions                                      | Production  |           | HHV Efficiency | Required Selling Price |           |             |          | CO <sub>2</sub> Capture | CO <sub>2</sub> Avoided |
|--|-------------|-----------|----------------|------------------------|-----------|-------------|----------|-------------------------|-------------------------|
|  | Electricity | Hydrogen  |                | Electricity            | Hydrogen  | Electricity | Hydrogen |                         |                         |
|  | MWh/Ton     | M SCF/Ton | %              | mills/kWh              | \$/MM Btu | % Increase  |          | %                       | \$/tonne                |
| 1a: IGCC w/o CCS - 1-Stage Selexol™ (base case)        | 2.66        | -         | 39.0           | 76.3                   | -         | -           | -        | 0                       | -                       |
| 2a: IGCC w/CCS - 2-Stage Selexol™                      | 2.23        | -         | 32.6           | 105.5                  | -         | 38          | -        | 90                      | 42.46                   |
| 3a: IGCC w/CCS - CMS & Pd Membranes & 1-Stage Selexol™ | 2.37        | -         | 34.6           | 95.1                   | -         | 25          | -        | 98                      | 24.64                   |

Note:  $Avoided\ Cost = (COE/MWh_{w/capture} - COE/MWh_{w/o\ capture}) / (tonne\ CO_2\ emitted/MWh_{w/o\ capture} - tonne\ CO_2\ emitted/MWh_{w/capture})$ ;

for H<sub>2</sub> production, COE is replaced with the RSP of H<sub>2</sub> and the basis of MWh is replaced by M SCF.

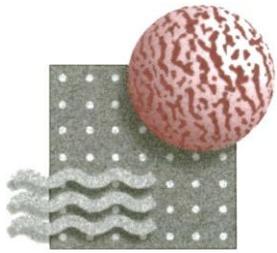
Ref.: *Cost and Performance Baseline for Fossil Energy Plants, Volume 1: Bituminous Coal and Natural Gas to Electricity*, DOE/NETL-2010/1397, Revision 2, November 2010.



# Kick-off Meeting for DE-FE0013064

## *Robust & Energy Efficient Dual-Stage Membrane-Based Process for Enhanced Carbon Dioxide Recovery*

- 1. Introduction/Background of The Contractor and The Project (MPT)**
- 2. 1<sup>st</sup> Stage: CMS Membrane for Bulk Contaminants Removal and Bulk Hydrogen Recovery (MPT)**
  - Current Technology Status; Potential Technical Challenges; Proposed Technical Activities*
- 3. 1<sup>st</sup> Stage: CMS Membrane as WGS Membrane Reactor (USC)**
  - Current Technology Status; Potential Technical Challenges; Proposed Technical Activities*
- 4. 2<sup>nd</sup> Stage: Pd Membrane for Enhanced Hydrogen Recovery through CO<sub>2</sub> Compression Train for CCS (MPT)**
  - Current Technology Status; Potential Technical Challenges; Proposed Technical Activities*
- 5. Engineering, Economics and Environmental Analysis (Technip)**



# M&P H<sub>2</sub> Selective CMS Membranes

## *Mixture Separations with Our CMS Membrane at 250°C*

| Gas mixture composition  |  |                          |
|--|--|--------------------------|
| Gas  | Permeance m <sup>3</sup> /(m <sup>2</sup> h bar) | Separation Factor (S.F.) |
| (1) H <sub>2</sub> :CO:CO <sub>2</sub> :CH <sub>4</sub> :H <sub>2</sub> S = 39.5%:15.2%:32.4%:12.2%:0.7%                             |  |                          |
| H <sub>2</sub>   | 1.37   | 1.0                      |
| CO   | 0.02   | 68.5                     |
| CO <sub>2</sub>  | 0.05   | 27.4                     |
| CH <sub>4</sub>  | 0.01   | 137.0                    |
| H <sub>2</sub> S   | 0.01   | 137.0                    |
| (2) H <sub>2</sub> :CO:CO <sub>2</sub> :CH <sub>4</sub> :H <sub>2</sub> S = 45.36%:4.52%:38.91%:11%:0.21%                            |  |                          |
| H <sub>2</sub>   | 1.40   | 1.0                      |
| CO   | 0.02   | 70.0                     |
| CO <sub>2</sub>  | 0.04   | 35.0                     |
| CH <sub>4</sub>  | 0.01   | 140.0                    |
| H <sub>2</sub> S   | 0.01   | 140.0                    |
| (3) H <sub>2</sub> :CO:CO <sub>2</sub> :CH <sub>4</sub> :H <sub>2</sub> O:H <sub>2</sub> S = 42.45%:4.233%:36.4%:10.29%:6.43%:0.197% |  |                          |
| H <sub>2</sub>   | 1.56   | 1.0                      |
| CO   | 0.02   | 78.0                     |
| CO <sub>2</sub>  | 0.05   | 31.2                     |
| CH <sub>4</sub>  | 0.01   | 156.0                    |
| H <sub>2</sub> O   | 1.1  | 1.4                      |
| H <sub>2</sub> S   | 0.01   | 156.0                    |

Though selectivity is not as high as some competitive polymeric and metallic membranes (Pd-based), our CMS membrane is inert and robust, and is suitable for intermediate temperature applications

# M&P H<sub>2</sub> SELECTIVE CMS MEMBRANES

## QA/QC Performance Testing of CMS Full Scale Bundles

*CMS Bundles: 86 tube, 3.25" Collar, Full Ceramic*

*QA/QC Testing Conditions*

*Temperature: 220 to 250°C*

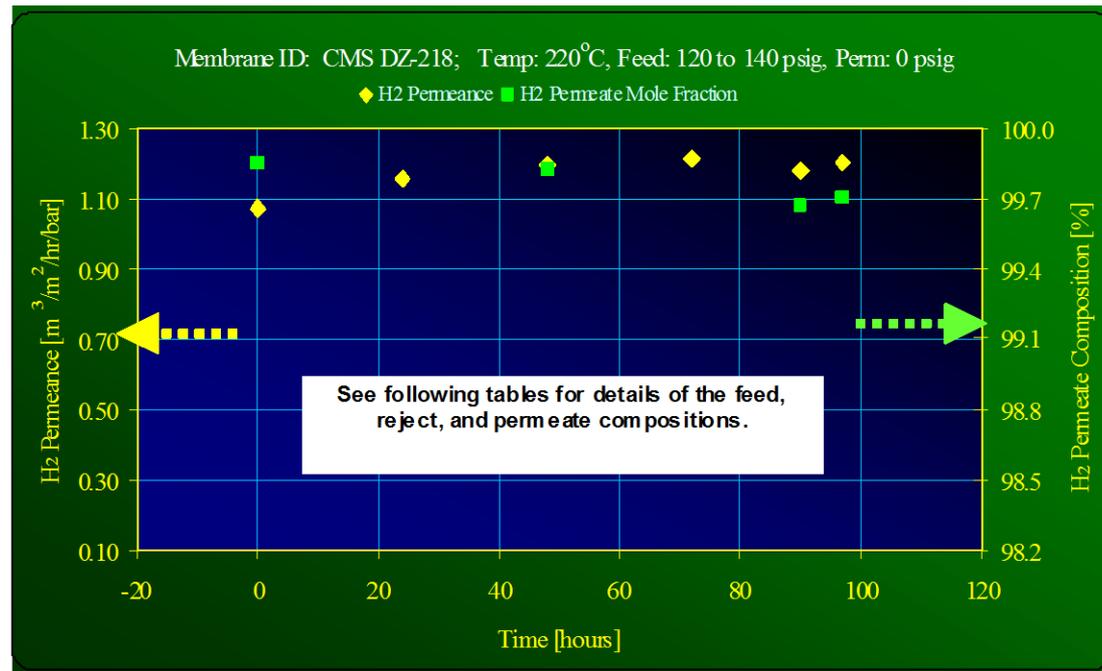
*Pressure: 20 to 50psig*



| Membrane ID | He Permeance [m <sup>3</sup> /m <sup>2</sup> /hr/bar]           | N <sub>2</sub> Permeance [m <sup>3</sup> /m <sup>2</sup> /hr/bar] | He/N <sub>2</sub> Selectivity [-] | Comments                |
|-------------|---|---|-----------------------------------|-------------------------|
| 3-1 to 3-5  | Off-spec bundles. Initial facility setup and deposition trials. |   |                                   |                         |
| 3-6         | 2.0   | 0.020   | 100                               |                         |
| 3-7         | 2.8   | 0.015   | 187                               |                         |
| 3-8         | 1.8   | 0.020   | 91                                |                         |
| 3-9         | 2.6   | 0.025   | 102                               |                         |
| 3-10        | 1.0   | 0.005   | 200                               | Overdeposited           |
| 3-11        | 1.6   | 0.011   | 142                               |                         |
| 3-12        | 1.5   | 0.020   | 77                                | Repair of damaged tubes |
| 3-13        | 2.3   | 0.018   | 126                               |                         |
| 3-14        | 2.8   | 0.025   | 117                               |                         |

# CMS Membrane Field Testing

Membrane performance is stable in a 100 hour challenge test conducted at a refinery pilot facility using VGO hydrocracker off-gas in the presence of significant H<sub>2</sub>S, NH<sub>3</sub>, and higher hydrocarbon contamination.



## Gas Stream Compositions, Stage Cut and H<sub>2</sub> Recovery During the VGO Hydrocracker Pilot Test

At time = 3 hours

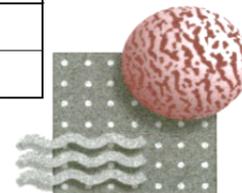
| Gas                           | Composition [%] |        |            | H <sub>2</sub> /Slow Selectivity |
|-------------------------------|-----------------|--------|------------|----------------------------------|
|                               | Feed            | Reject | Permeate   |                                  |
| H <sub>2</sub> S              | 5.2             | 32.0   | 0.03       | 163                              |
| H <sub>2</sub>                | 89.9            | 38.9   | 99.88      | 1                                |
| C <sub>1</sub>                | 2.1             | 12.2   | 0.08       | 123                              |
| C <sub>2</sub>                | 0.88            | 5.4    | 0.01       | ~600                             |
| C <sub>3</sub> +              | 1.88            | 11.6   | ND         | >1,000                           |
| <b>Stage Cut</b>              |                 |        | <b>85%</b> |                                  |
| <b>H<sub>2</sub> Recovery</b> |                 |        | <b>92%</b> |                                  |

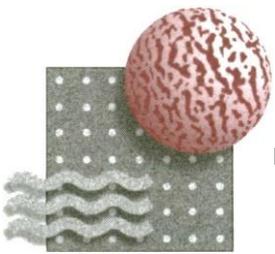
At time = 100 hours

| Gas                           | Composition [%] |        |            | H <sub>2</sub> /Slow Selectivity |
|-------------------------------|-----------------|--------|------------|----------------------------------|
|                               | Feed            | Reject | Permeate   |                                  |
| H <sub>2</sub> S              | 4.8             | 24.5   | 0.16       | 74                               |
| H <sub>2</sub>                | 90.8            | 50.6   | 99.70      | 1                                |
| C <sub>1</sub>                | 1.9             | 9.9    | 0.06       | 123                              |
| C <sub>2</sub>                | 0.81            | 4.2    | 0.01       | ~600                             |
| C <sub>3</sub> +              | 1.66            | 10.7   | ND         | >1,000                           |
| <b>Stage Cut</b>              |                 |        | <b>80%</b> |                                  |
| <b>H<sub>2</sub> Recovery</b> |                 |        | <b>85%</b> |                                  |

Milestone #4

Media and Process Tech Inc.

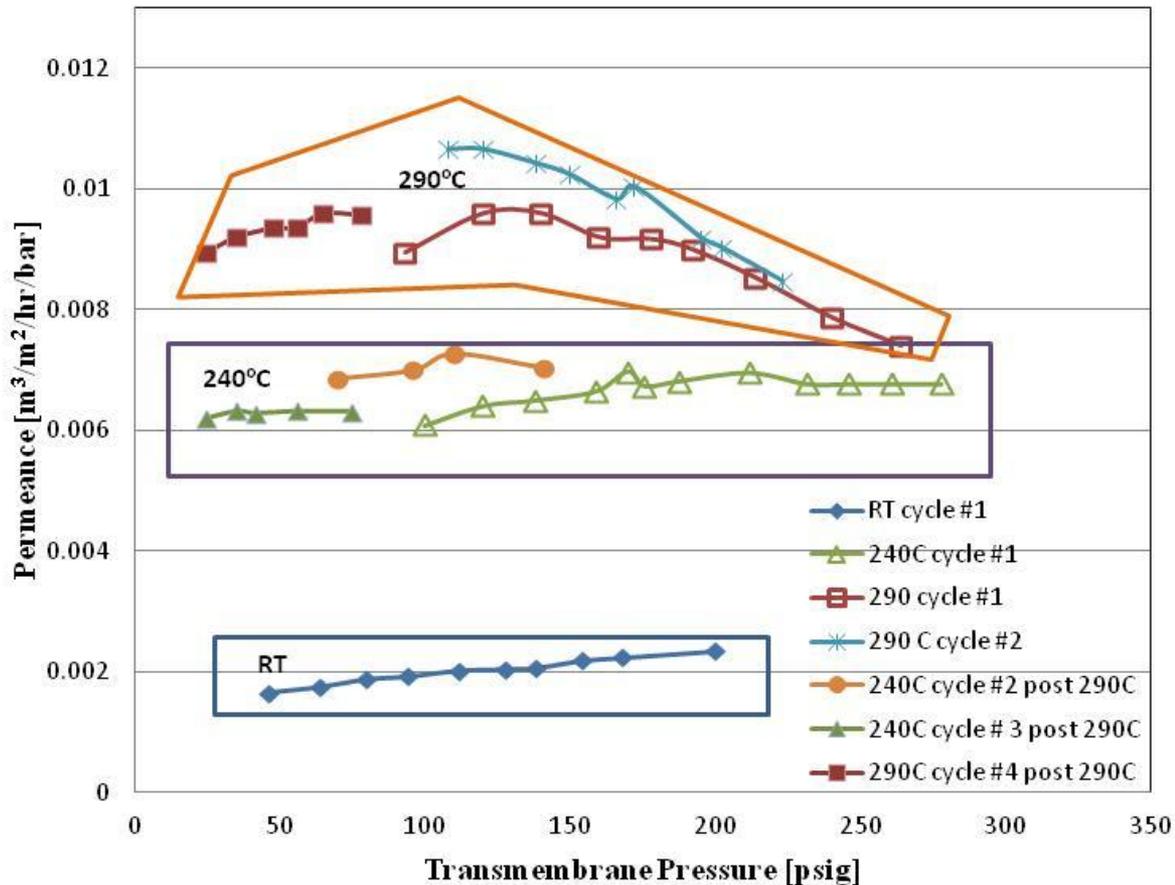




# MPT H<sub>2</sub> Selective CMS Membranes

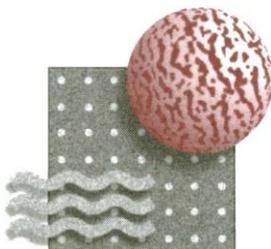
## 86-tube CMS Bundle in Pilot Scale Module

*CMS Tube Bundle N<sub>2</sub> Permeance versus Temperature and Pressure*



*CMS Bundle in High Pressure Housing*





# MPT H<sub>2</sub> Selective CMS Membranes

---

*Testing Results: Slip Stream from NCCC (PSDF) Coal/Biomass Gasifier*

## **PSDF Field Test Objectives**

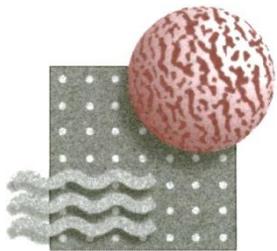
Demonstrate hydrogen production/recovery from coal gasifier off-gas.

## **Gasifier Off-gas Composition to the CMS Membrane:**

H<sub>2</sub> Content ca. 10 to 30%, balance primarily CO<sub>2</sub>, N<sub>2</sub>, CO.

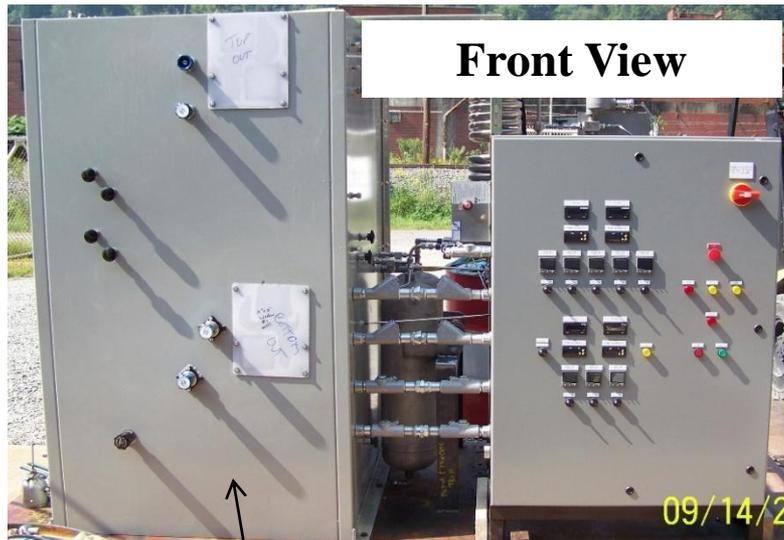
The trace contaminants typically encountered at PSDF includes:

- NH<sub>3</sub> ~1000ppm
- Sulfur Species ~1000ppm
- HCl < 5ppm
- HCN ~20ppm
- Naphthalenes (and other condensable higher hydrocarbons) also high concentration contaminant



# MPT H<sub>2</sub> Selective CMS Membranes

*NCCC (PSDF) Field Test Unit*



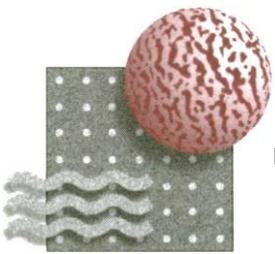
**Front View**

Cabinet for Membrane Bundles



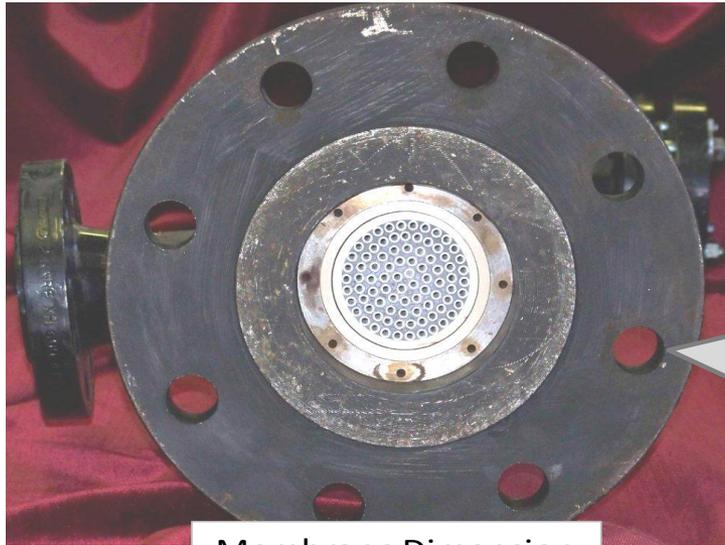
**Installed NCCC**

The Unit meets Class 1, Div.2 requirement. The field test is scheduled to begin on Oct 15, 2011 for two months at US DOE's NCCC testing facility, to be fed with actual coal gasifier off-gas directly to our membrane without pre-treatment.



# MPT H<sub>2</sub> Selective CMS Membranes

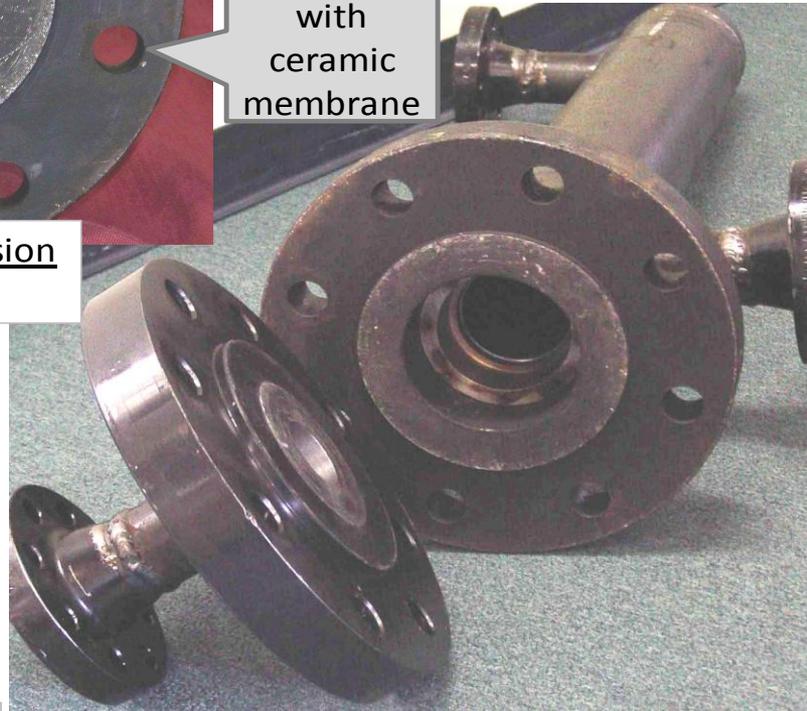
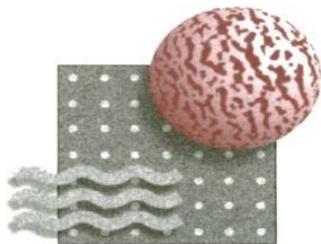
## *CMS Membrane Bundle in Field Test Module*



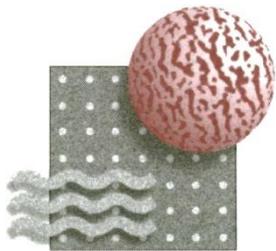
**M&P Full-Scale Hydrogen  
Selective Membrane and  
Housing Rated for 1000 psi use**

End view  
packed  
with  
ceramic  
membrane

Membrane Dimension  
3" dia x 30"L

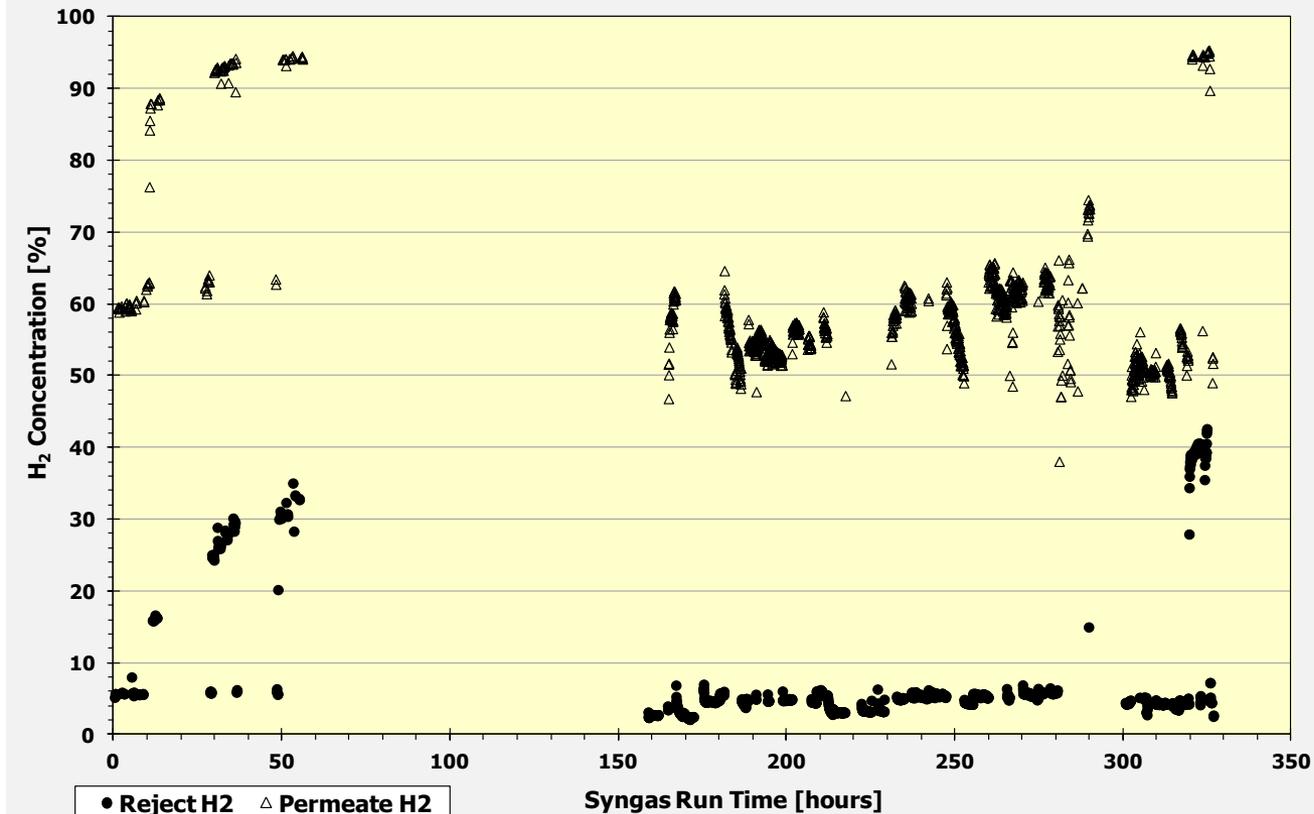


**Media and Process Tech Inc.**



# MPT H<sub>2</sub> Selective CMS Membranes

## *Performance of a CMS Bundle at NCCC (PSDF)*



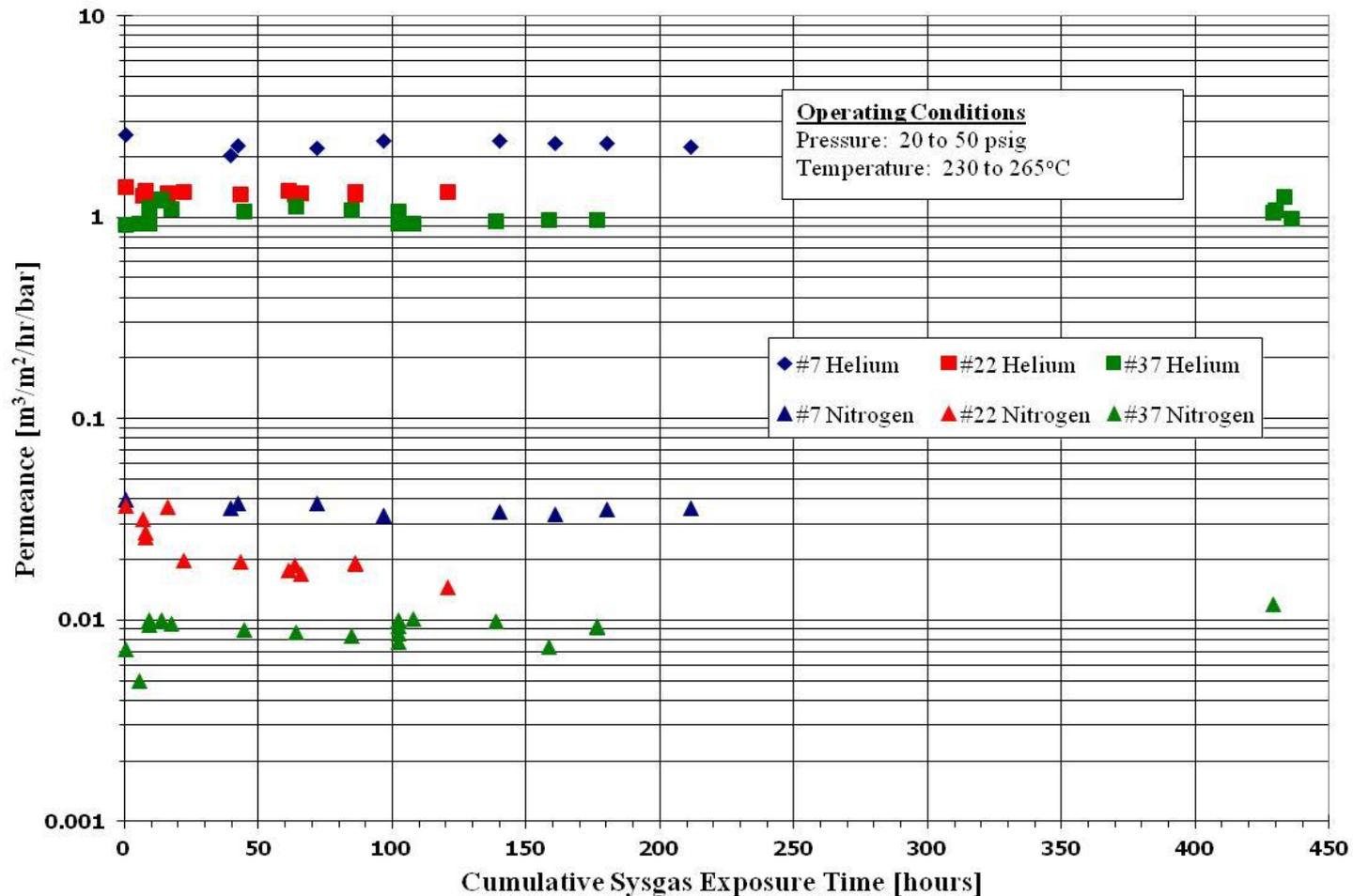
Hydrogen was enriched from 20-30% to >90-9%, consistent with the prediction based upon single components obtained in the lab.

Hydrogen concentration (dry-basis) in the permeate and reject sides during the testing of the “full-scale” CMSM module fed with air blown coal-fed gasifier off-gas at ~250 °C and ~14.8 bar. The feed rate was maintained in the range of 150 to 250 l/min. The typical feed composition during this run is 6.49% H<sub>2</sub>, 74.03% N<sub>2</sub>, 9% CO, 9% CO<sub>2</sub>, 0.9% CH<sub>4</sub>, and 312 ppm H<sub>2</sub>S. During the beginning (2-50 hr) and the ending periods (near 350 hr), the feed was artificially spiked with bottled hydrogen to simulate the feed hydrogen concentration of the oxygen-blown gasifier to the “one-box” process.

# MPT H<sub>2</sub> Selective CMS Membranes

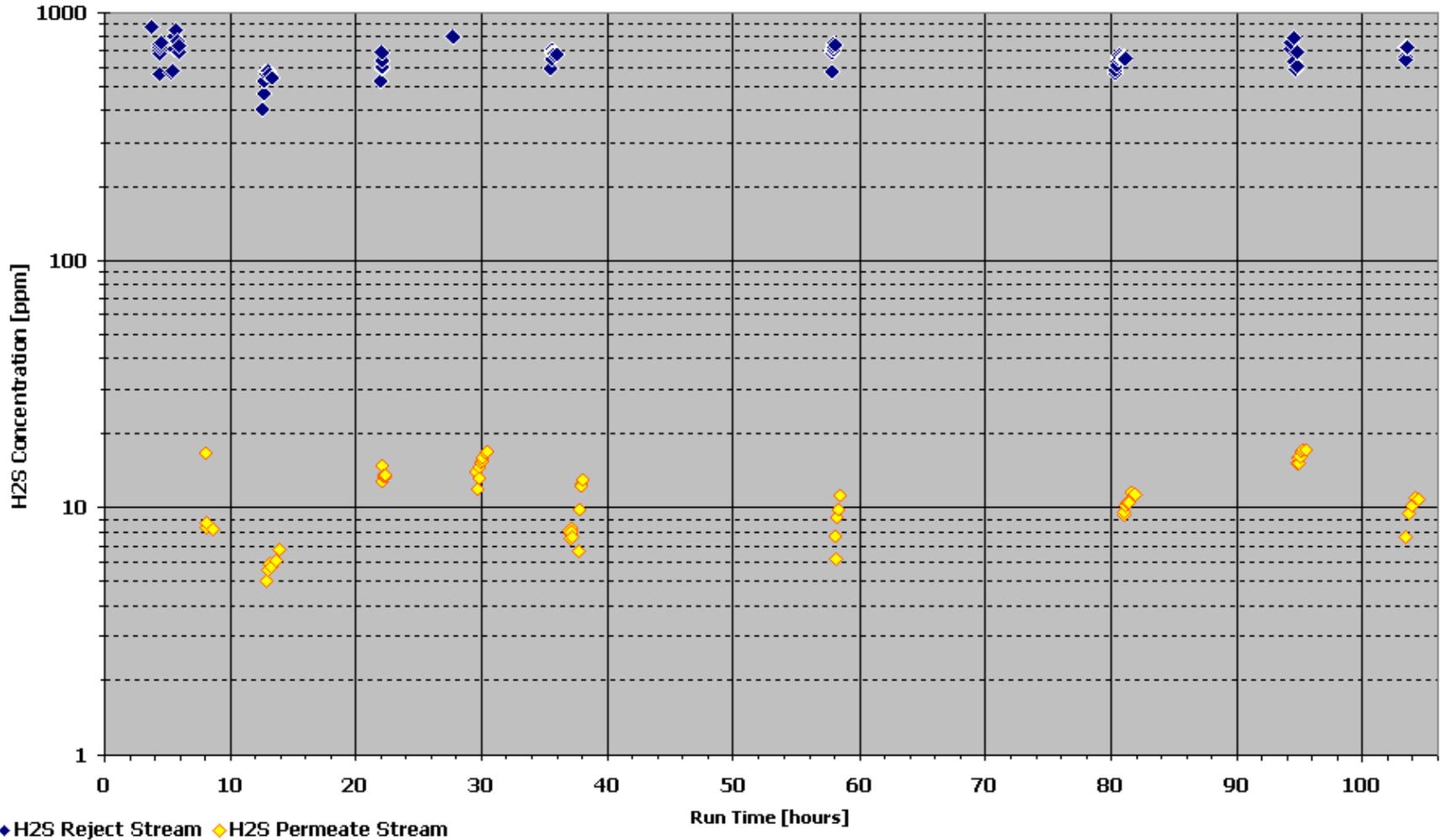
## Performance Stability of the B3-7 Bundle

### He and N<sub>2</sub> Permeance Stability Following Gasifier Off-gas Exposure



# MPT H<sub>2</sub> Selective CMS Membranes

## *H<sub>2</sub>S Removal with the B3-7 Bundle*



# 1<sup>st</sup> Stage, CMS Membranes as a WGS Membrane Reactor (WGS-MR): Current Technology Status

- CMS membranes tested for pressures up to 60 psig and temperatures up to 300 °C in the WGS/MR in the presence of simulated coal-derived syngas containing NH<sub>3</sub>, H<sub>2</sub>S and model organic vapor and tar compounds
- Kinetics of sulfided Co-Mo WGS catalyst tested for the same region of pressure/temperature conditions
- Both membranes and catalysts performed well and stably for continuous experiments lasting more than 6 weeks
- WGS/MR model developed and used successfully to model the experimental data

# Comparison of Experimental Results vs. Model Predictions for WGS/MR using CMS Membranes (Co/Mo Sulfided Catalyst)

## CO Conversion and Hydrogen Recovery

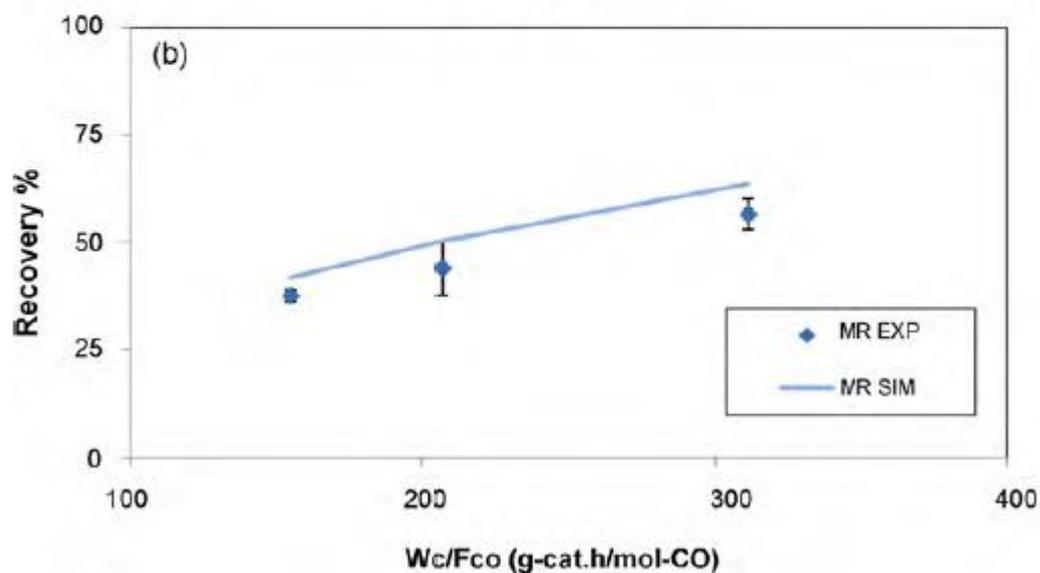
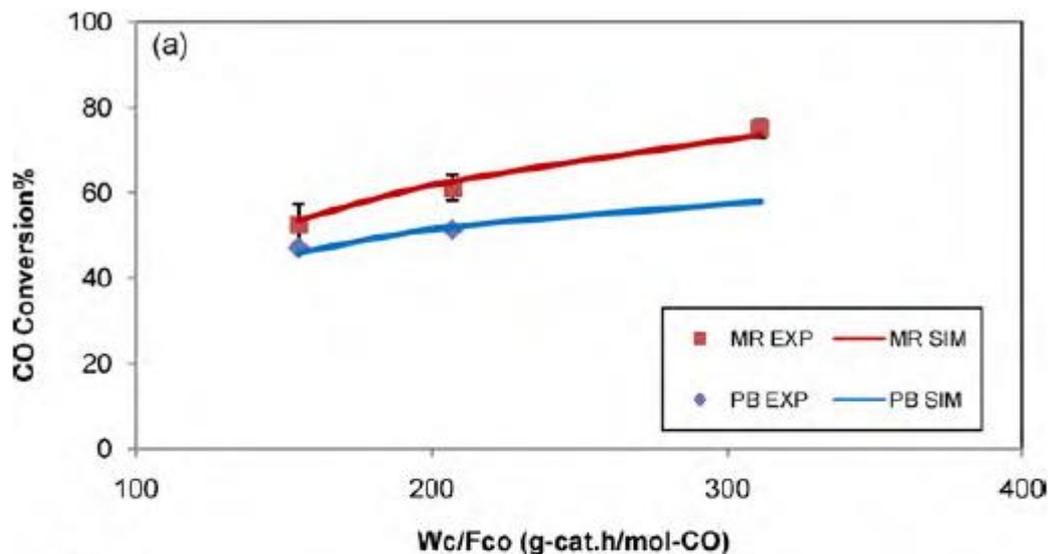


Fig. 10. Comparison of the experimental (a) conversion and (b) recovery with the model predictions at  $T = 300^\circ\text{C}$ ,  $P = 5$  atm and sweep ratio = 0.3 using CMS#2.

Temperature ( $^\circ\text{C}$ ): 300

Pressure (atm): 5

Weight of catalyst (g): 12

$W/F_{\text{CO}}$  (g-cat.h/mol-CO): 150 -311

Feed Composition

$\text{H}_2:\text{CO}:\text{CO}_2:\text{CH}_4:\text{H}_2\text{O}:\text{H}_2\text{S}$   
2.6:1:2.14:0.8:1.2:0.05

*J. Membr. Sci.*, 363, 160 (2010);  
*Ind. Eng. Chem.*, 10.1021/ie402603c  
(2014)

## Comparison of Experimental Results vs. Model Predictions for WGS/MR using CMS Membranes (Co/Mo Sulfided Catalyst)

### Reject and Permeate Stream Compositions

*J. Membr. Sci.*, 363, 160  
(2010); *Ind. Eng. Chem.*,  
10.1021/ie402603c (2014)

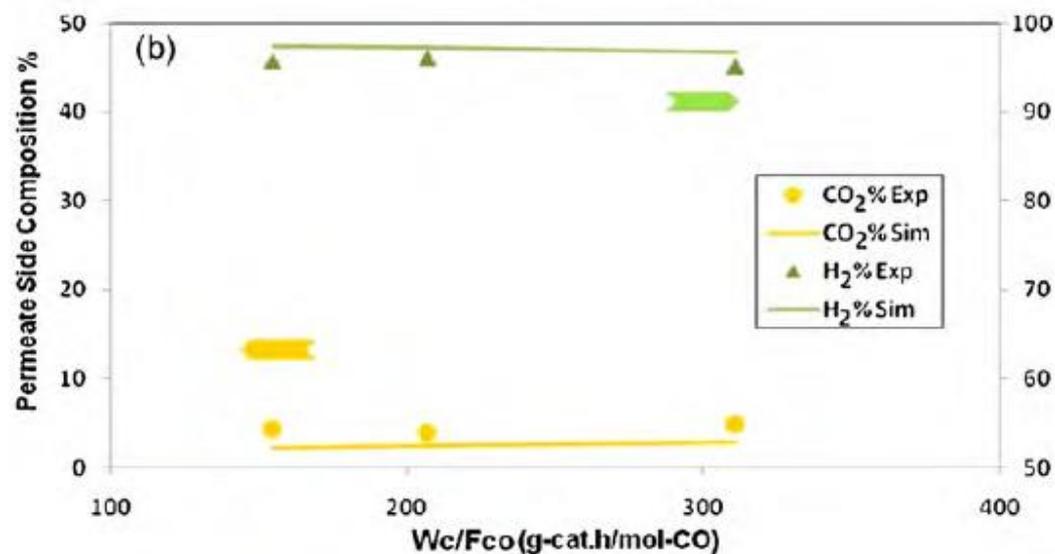
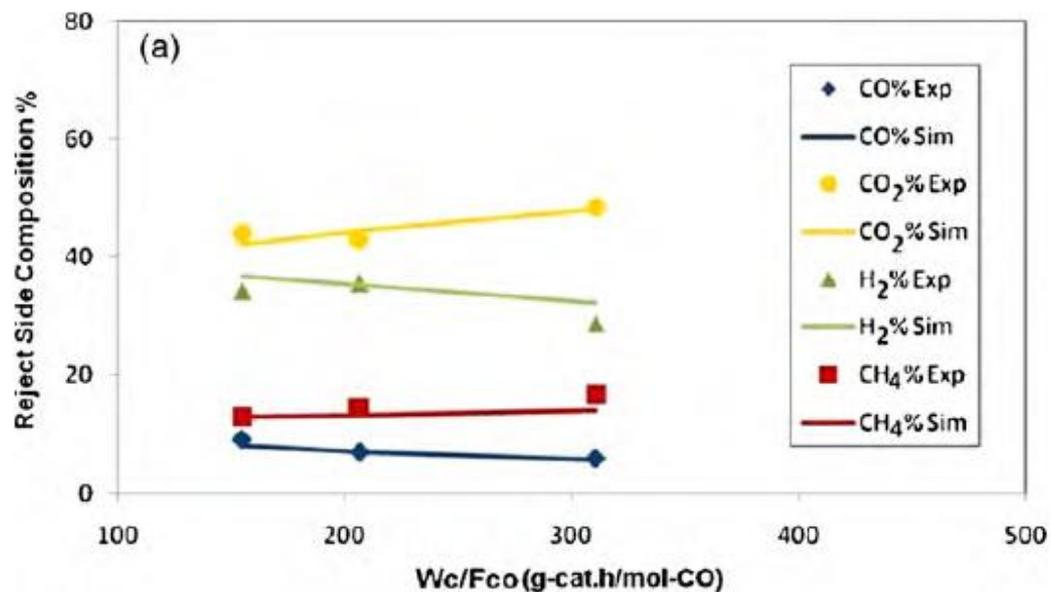
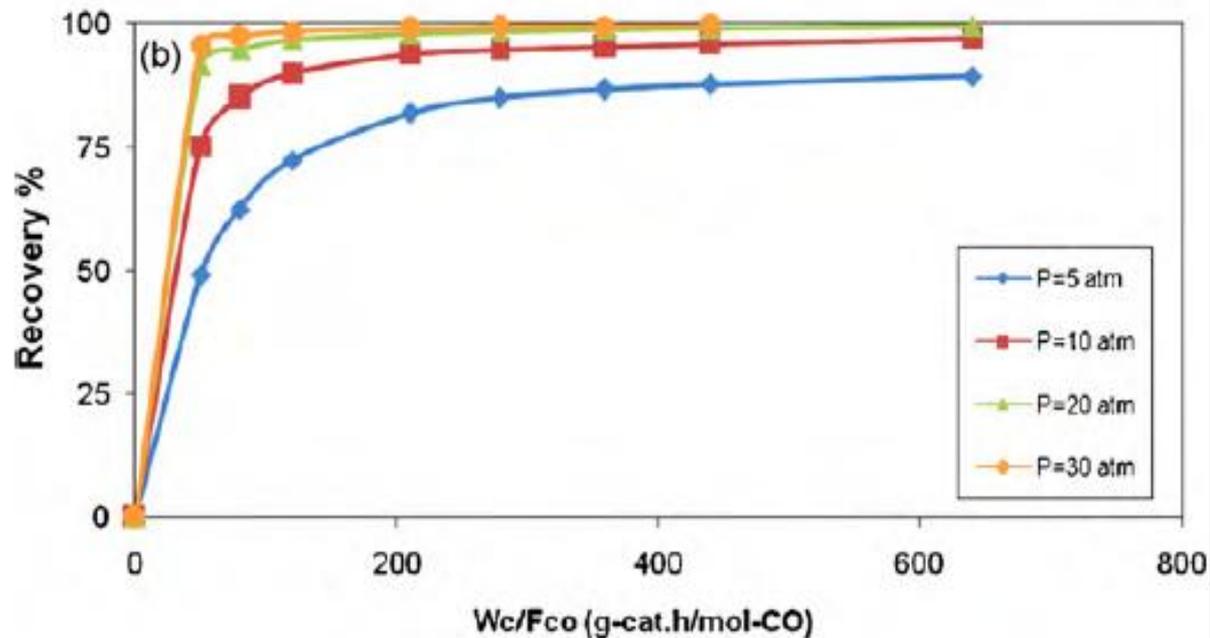
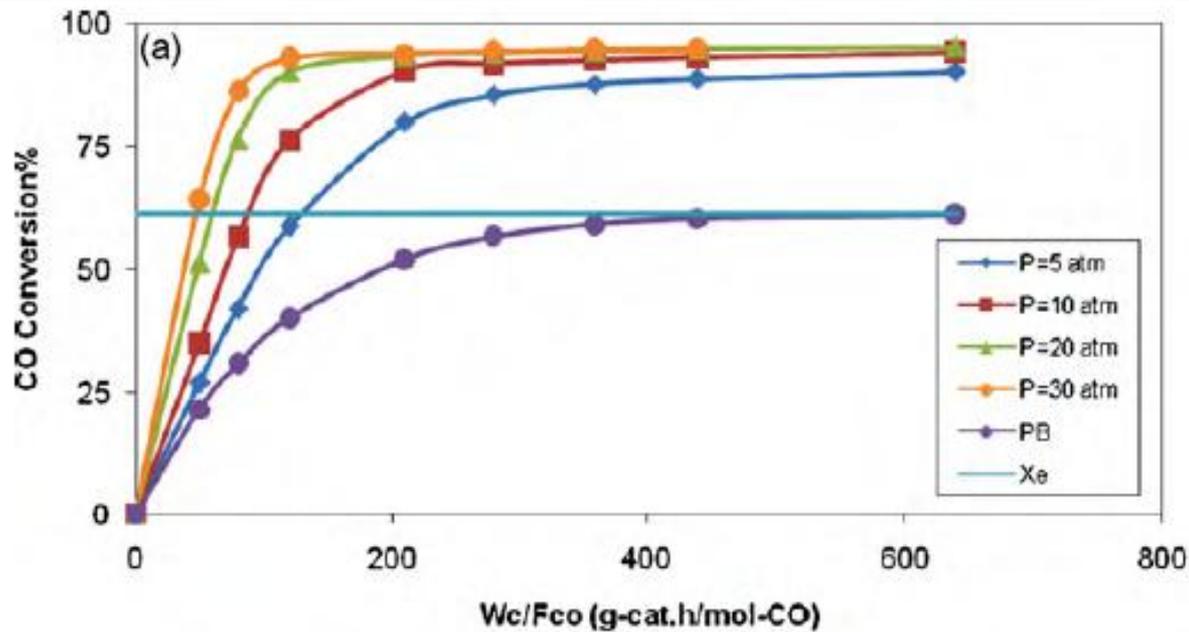


Fig. 6. Compositions of (a) reject and (b) permeate side at  $P=3$  atm and sweep ratio = 0.3.

**Simulations  
for WGS/MR  
using  
a CMS Membrane  
Under a  
Coal Gasification  
Environment  
(Co/Mo sulfided Catalyst)**

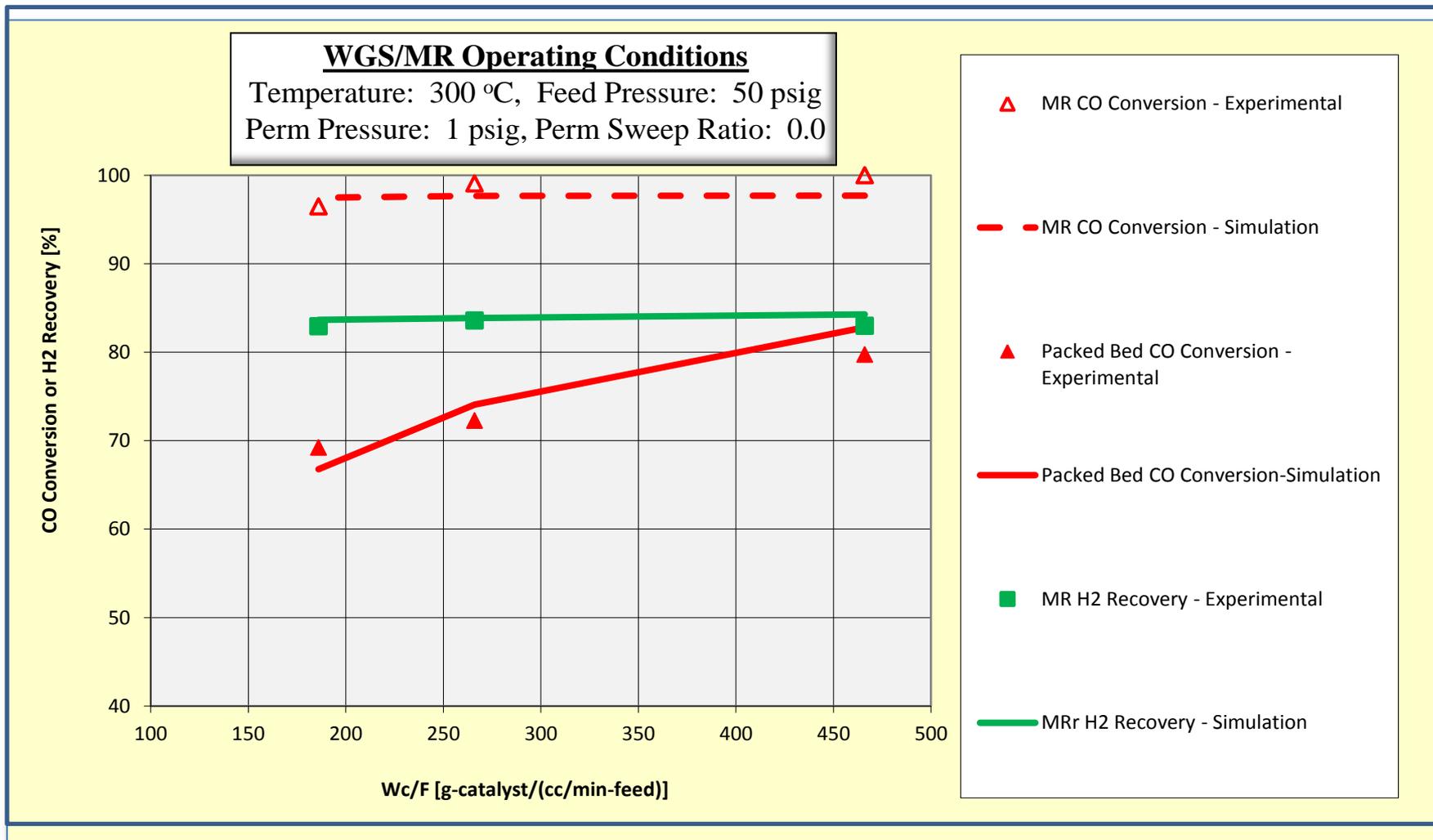


**Effect of Pressure on the  
CO Conversion and  
Hydrogen Recovery**

*J. Membr. Sci.*, 363, 160 (2010); *Ind. Eng. Chem.*, 10.1021/ie402603c (2014)

# WGS-LTS Membrane Reactor using a Palladium Membrane

Experimental results using methane steam reformat *at 50 psig and with no sweep*



- Our experimental results demonstrate >99% conversion and >99.9% purity at >83% hydrogen recovery is possible by our WGS-MR using Pd membranes.

# 1<sup>st</sup> Stage, CMS Membranes as a WGS Membrane Reactor (WGS-MR): Proposed Technical Activities

## 1. Task 2. Establish Performance Database for CMS-WGS/MR

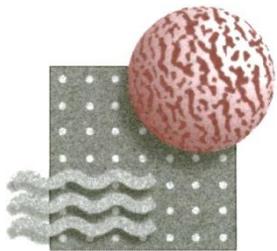
- Subtask 2.1: Modification of the Present Laboratory-Scale WGS/MR System*
- Subtask 2.2: Generation of the Performance Database*
- Subtask 2.3: Verification of the Existing Mathematical Model and Simulations of the Performance of the Bench-Scale System*

## 2. Task 5. Evaluate Gas Permeation and Catalytic Reaction CMS Membrane as WGS Membrane Reactor

- Subtask 5.1: Experimental Verification*
- Subtask 5.2: Membrane and MR Simulation Support*

## 3. Task 7. Provide Technical Support for Process Design and Engineering Study

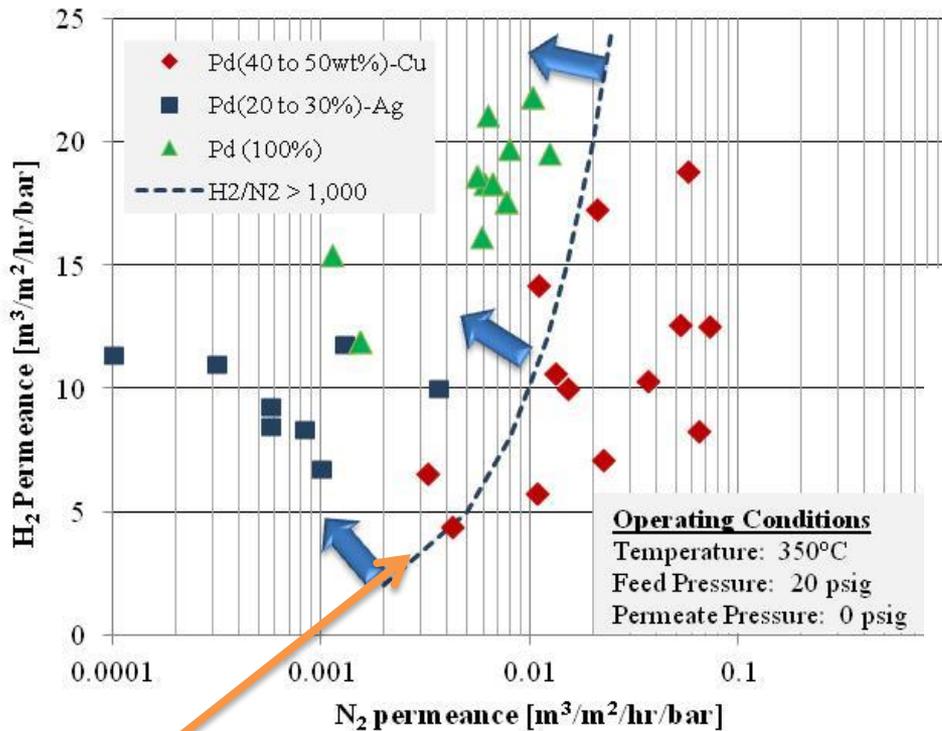
## 4. Task 8. Provide Technical Support for Environmental and Economic Analyses



# MPT H<sub>2</sub> Selective Pd Alloy Membranes

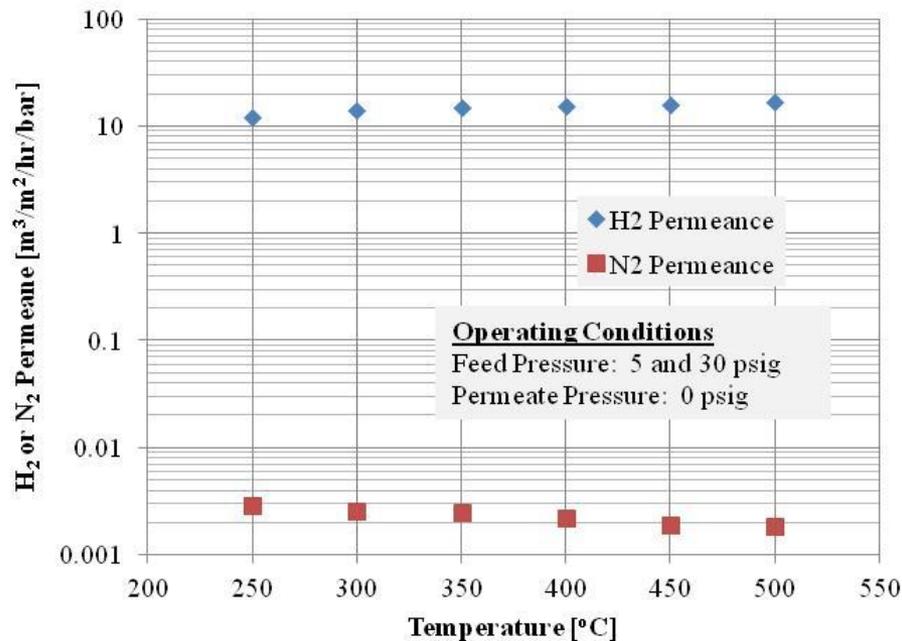
## General Performance: H<sub>2</sub> and N<sub>2</sub> Permeance

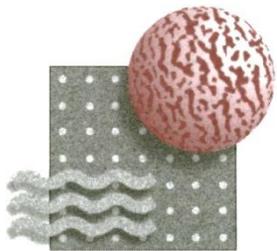
### H<sub>2</sub> and N<sub>2</sub> Permeance for Various Parts and Alloys



H<sub>2</sub>/N<sub>2</sub> = 1,000

### H<sub>2</sub> and N<sub>2</sub> Permeance Temperature Dependences for a Typical Pd Membrane

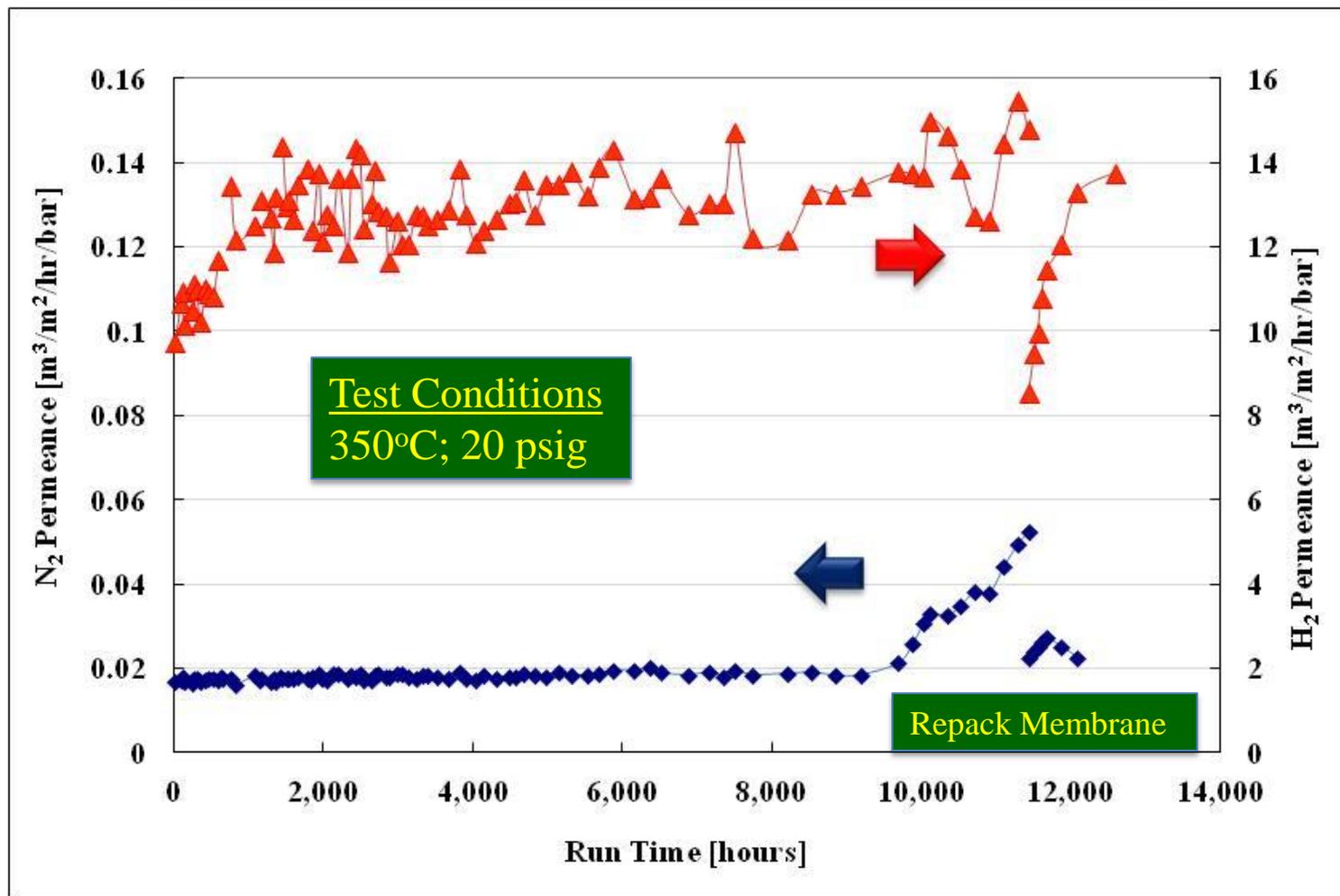


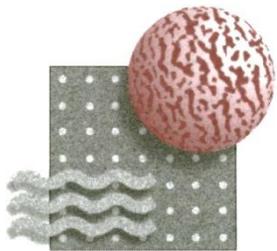


# MPT H<sub>2</sub> Selective Pd Alloy Membranes

*Long Term Thermal Stability in the Presence of H<sub>2</sub>*

## Thermal Stability in the Presence of H<sub>2</sub>

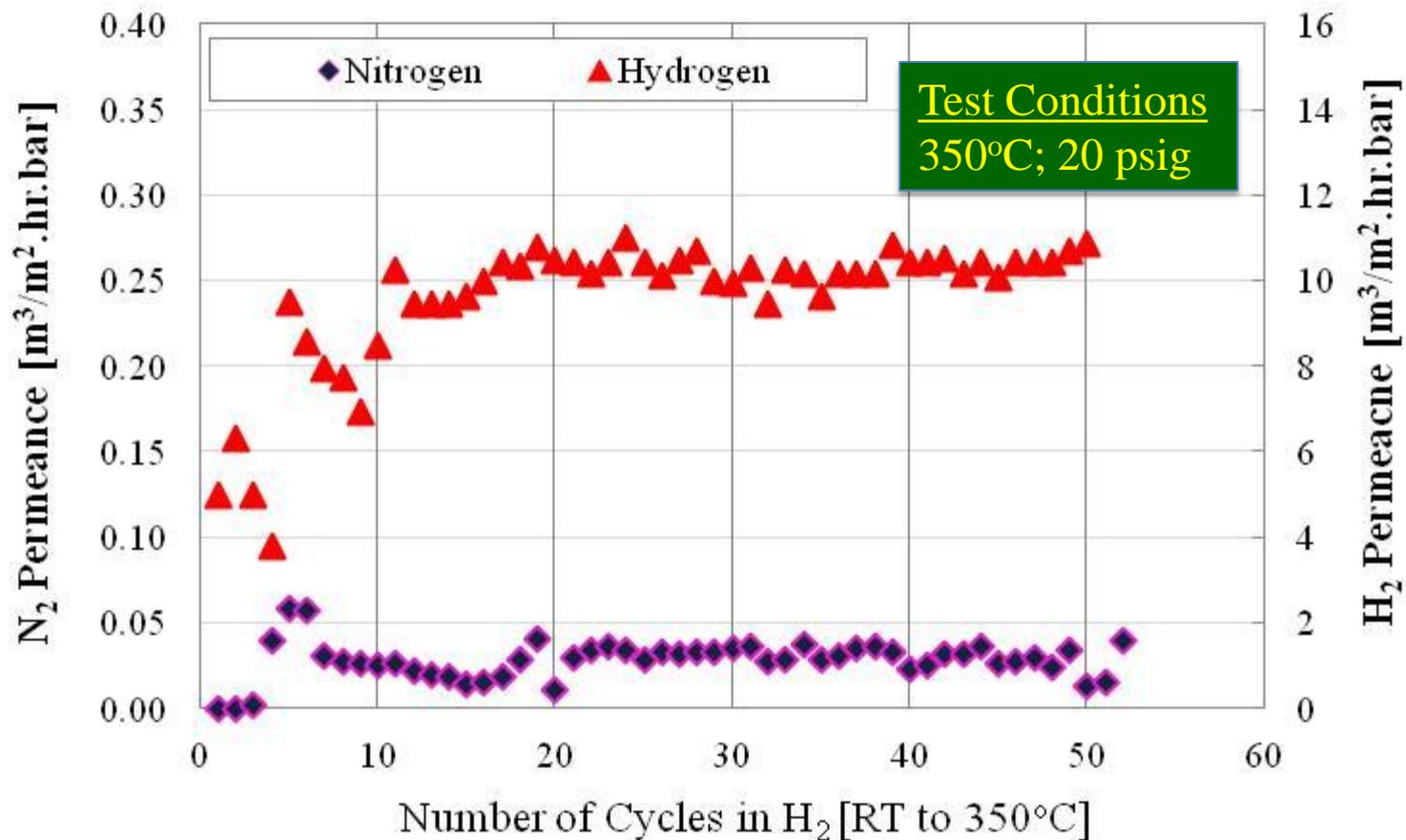


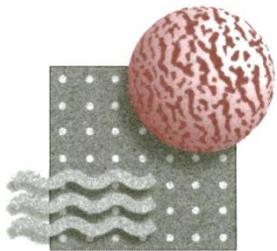


# MPT H<sub>2</sub> Selective Pd Alloy Membranes

*Simulated Startup and Shutdown Operation. Pd-Cu Alloy Membrane*

## Thermal Cycling in the Presence of N<sub>2</sub> and H<sub>2</sub>

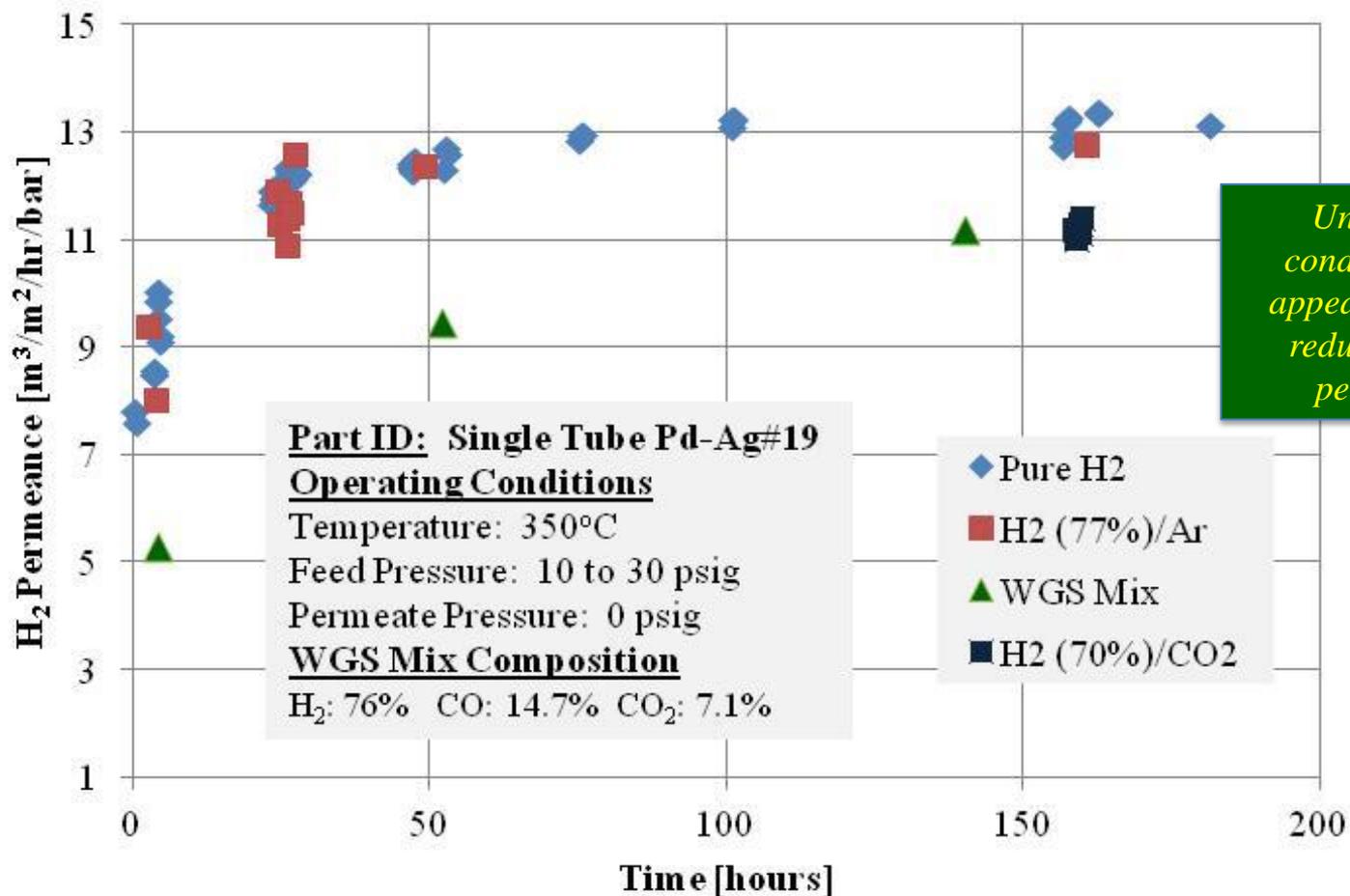


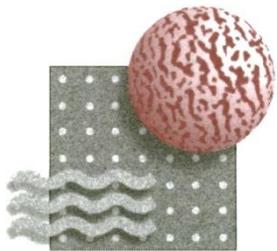


# MPT H<sub>2</sub> Selective Pd Alloy Membranes

## Mixed Gas Testing

### H<sub>2</sub> Permeance in Various Mixed Gas Systems





# MPT H<sub>2</sub> Selective Pd Alloy Membranes

*Multiple Tube Bundles for Fuel Cell Applications*

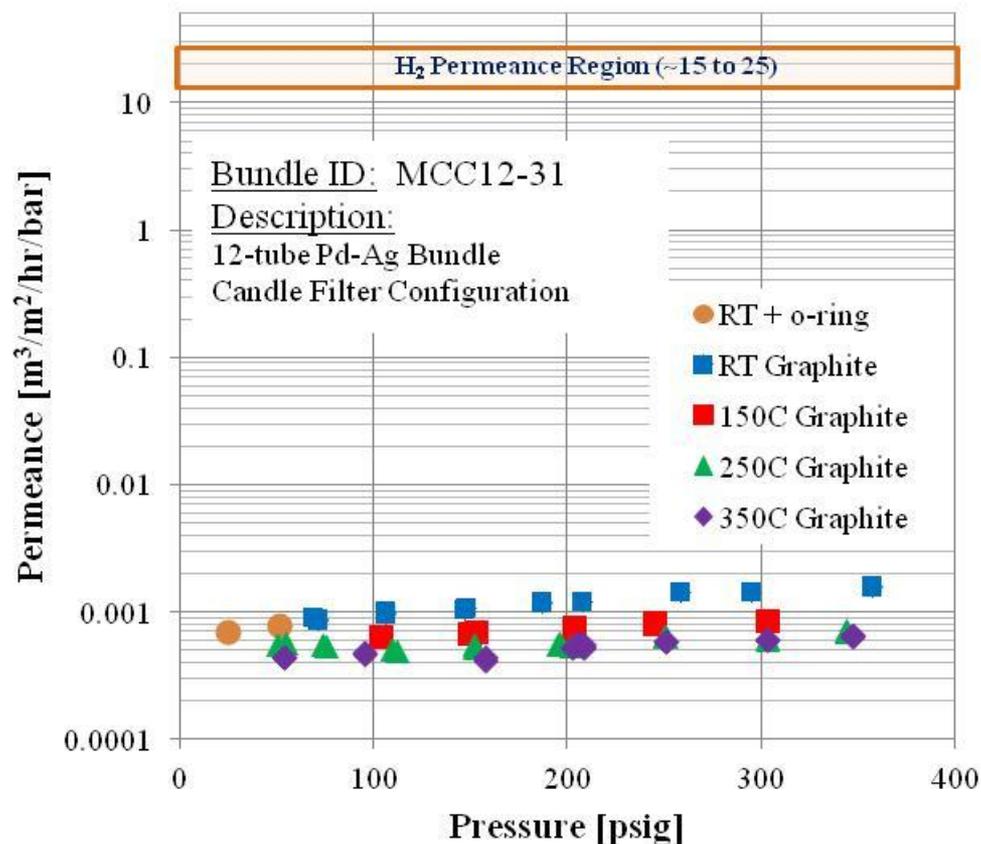
## High Pressure Tube Sheet

Pd Bundle and Ceramic Tube Sheet



## High Performance Package

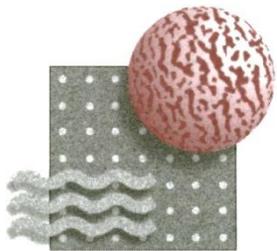
N<sub>2</sub> Flux (Leak Rate) v. Pressure and Temperature



## 2<sup>nd</sup> Generation Module Design

Latest Module Design with Graphite Packing





# MPT H<sub>2</sub> Selective Pd Alloy Membranes

*Performance Benchmarking: Competing substrates*

## Porous Stainless Steel (PSS) Supported Composite Pd Membranes

### PSS: Single Tube Membrane Performance

**Table 1 – Characteristics of composite Pd and Pd–Au membranes tested at NCCC.**

| Membrane #        | Thickness Pd–Au $\mu\text{m}$ | He leak at 25 °C $\text{Ncm}^3 \text{min}^{-1} \text{bar}^{-1}$ | H <sub>2</sub> permeance at 450 °C $\text{Nm}^3 \text{m}^{-2} \text{h}^{-1} \text{bar}^{-0.5}$ | H <sub>2</sub> /He selectivity 450 °C, $\Delta P = 1 \text{ bar}$ |       |
|-------------------|-------------------------------|---|--|---|-------|
| M-01 <sup>a</sup> | After 1st plating             | 6.9–0   | 0.5  | 31.7  | >1563 |
|                   | After 2nd plating             | 8.2–0.15  | <0.1 <sup>b</sup>  | 27.8 <sup>c</sup>   | N.A.  |
| M-03              | After 1st plating             | 5.9–0   | 9  | 27.7  | >218  |
|                   | After 2nd plating             | 7.0–0.2   | <0.1 <sup>b</sup>  | 26.1 <sup>c</sup>   | N.A.  |
| M-04              | After 1st plating             | 12–0  | 2.2  | 22.3  | >248  |
|                   | After 2nd plating             | 13.2–0  | <0.1 <sup>b</sup>  | 20.7 <sup>c</sup>   | N.A.  |

a M-01 weld nuggets were plated with an extra 10  $\mu\text{m}$  thick Au layer.

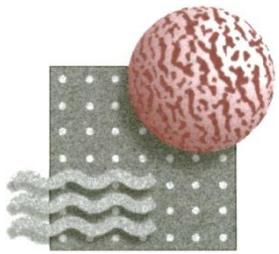
b 0.1  $\text{Ncm}^3 \text{min}^{-1} \text{bar}^{-1}$  detectable minimum leak.

c Estimation taking into account Pd thickness and support mass transfer resistance.

Ma et. al., International Journal of H<sub>2</sub> Energy, 37 (2012) 14577-14568.

### MPT Ceramic: Multiple Tube Bundle Performance

|                              |        |    |    |                   |        |
|------------------------------|--------|----|----|-------------------|--------|
| MCC12-31<br>(12 tube bundle) | 2x ELP | ~5 | NA | 35 to 45 at 350°C | >3,000 |
|------------------------------|--------|----|----|-------------------|--------|



# MPT H<sub>2</sub> Selective Pd Alloy Membranes

Overall Comparison: Pd-PSS vs Pd-Ceramic of Ours

## Disadvantages/Limitations of Pd-PSS Composite Membranes

Costly substrate: Sintered fine powdered metal in H<sub>2</sub> atmosphere.

“Poor” quality substrate: Multiple references describe problems and attempted solutions.

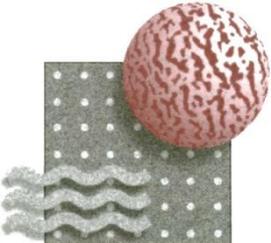
Intermediate Layer problems: Delamination and high surface roughness.

Thick Pd Layer: ...to overcome the substrate and intermediate layer problems.

End seals and joints. Leaking and failure at the Pd layer/substrate end seals.  
Unproven technology.

Lower flux: Thick Pd layer yields lower flux.

High operating temperature: ...to overcome the lower flux problems.



# MPT H<sub>2</sub> Selective CMS Membranes

## CMS Membrane Challenge Areas:

- **Optimize Pore Size Tuning**

Pore size tuning to maximize H<sub>2</sub> permeance with the rejection of H<sub>2</sub>S; thus, hydrogen extraction can be maximized in Stage I for turbine applications

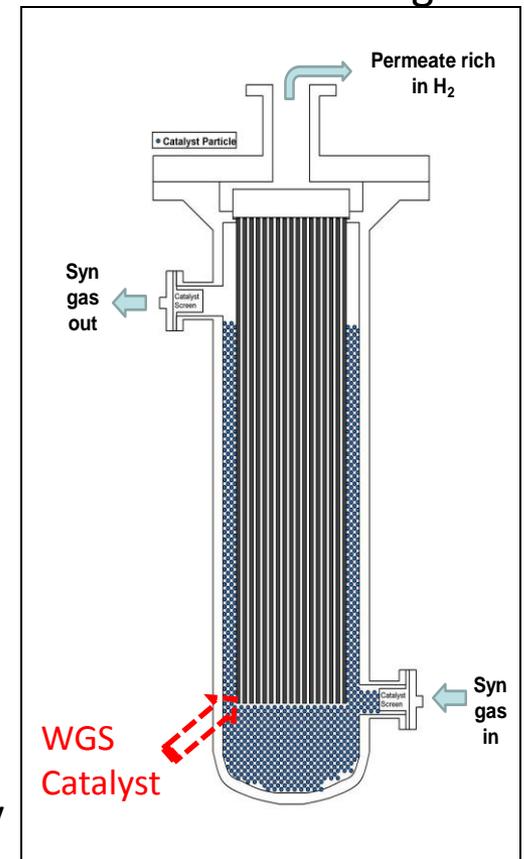
- **Reactor Design and Catalyst Packing**

Our current designs focus on a solid positive seal, consistent flow path, and optimized free flow distribution. While it does have space for catalyst to be loaded into the vessel, it is not optimized for use as a reactor bed.

Improvements in reactor design and catalyst packing should include:

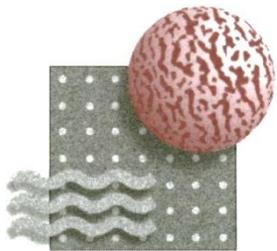
- catalyst bed flow distribution optimizations
- ability to monitor internal bed conditions
- efficient catalyst loading/unloading capability
- and others

## Current MR usage



## **1<sup>st</sup> Stage, CMS Membranes as a WGS Membrane Reactor (WGS-MR): Potential Technical Challenges**

- Catalysts and membranes may not perform adequately in the high-pressure region
- Reaction kinetics derived at low pressures may not fit high-pressure experimental data
- Mathematical model may need to be revised to describe MR experiments at high pressures



# MPT H<sub>2</sub> Selective Pd Alloy Membranes

*Pd Membrane Challenge Area A: Very Large Surface Area Requirements*

**Pd Challenge #A: H<sub>2</sub> Recovery in CCS = Enormous Scale Membrane Application**

**Objective: Minimize the Membrane Area and Cost**

## Approach

### **Minimize the Pd Layer Thickness**

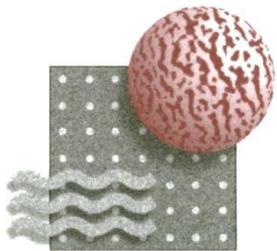
- 1. Higher flux**
- 2. Less metal**

#### *Delivers*

- a. Smaller scale**
- b. Overall cost reduction is 2-fold**

### **Requires Maximized (Optimized) Substrate Flux**

- 1. High flux Pd requires very high flux substrates**
- 2. Defects more problematic**
- 3. Strength may suffer (thinner substrate)**



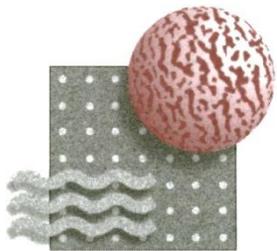
# MPT H<sub>2</sub> Selective Pd Alloy Membranes

*Composite Membrane Engineering: Next Generation Substrates*

**Larger pore size higher flux substrates under development**

**Table A-1. H<sub>2</sub> permeances obtained with Pd thin films supported on MPT commercial and experimental ceramic substrates**

| Parameters<br>Substrates        | Overall H <sub>2</sub><br>Permeance<br>[m <sup>3</sup> /m <sup>2</sup> /hr/bar <sup>0.5</sup> ] | Apparent Substrate<br>Resistance<br>Contribution [%] | Ideal Selectivity<br>H <sub>2</sub> /N <sub>2</sub> [-] | Substrate Pore<br>Size [μm] |
|---------------------------------|---|--|---|-----------------------------|
| MPT Commercial<br>Ceramic Tube  | 36.8  | 66   | >5,000  | 0.5                         |
| MPT High Permeance<br>Substrate | 55.8  | 48.4   | 350 to 500  | 2                           |
| MPT Developmental<br>Substrate  | 104   | 3.8  | 100 to 150  | 10                          |



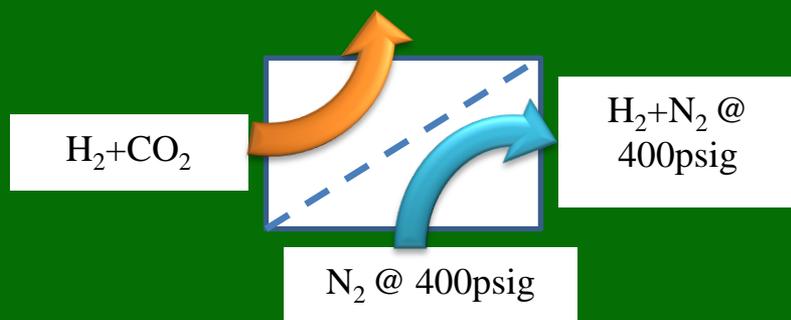
# MPT H<sub>2</sub> Selective Pd Alloy Membranes

*Pd Membrane Challenge Area B: Permeate Sweep with Inert Gas and/or Steam*

## Challenge B: Prefer High Pressure H<sub>2</sub> as Turbine Fuel Supply

**Pd Membrane Permits Selective Transfer of H<sub>2</sub> to High Pressure Sweep Gas**

### Approach

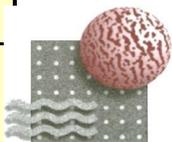


### Concepts: Example Bundle Open Both Ends



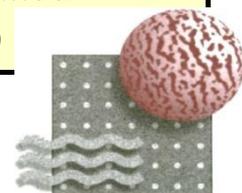
| Task   | Yr I |   |   |   | Yr II |   |   |   | Yr III |   |   |   | Cost     | Cost        |
|--|------|---|---|---|-------|---|---|---|--------|---|---|---|----------|-------------|
|  | 1    | 2 | 3 | 4 | 1     | 2 | 3 | 4 | 1      | 2 | 3 | 4 | per Task | per BP      |
|  | BP 1 |   |   |   | BP 2  |   |   |   | BP 3   |   |   |   | (\$)     | (\$million) |
| Task 2.0 Establish performance database for CMS-WGS/MR (USC)                         |      |   |   |   |       |   |   |   |        |   |   |   | 200,000  | 1.15        |
| Subtask 2.1 Modification of the present lab-scale WGS?MR system                      |      |   |   |   |       |   |   |   |        |   |   |   |          |             |
| Subtask 2.2 Generation of performance database                                       |      |   |   | A |       |   |   |   |        |   |   |   |          |             |
| Subtask 2.3 Verification of existing mathematical model                              |      |   |   |   |       |   | B |   |        |   |   |   |          |             |
| Task 3.0 Preparation of CMS membrane reactor for bench scale test (MPT)              |      |   |   |   |       |   |   |   |        |   |   |   | 577,595  |             |
| Subtask 3.1 Optimization of CMS membrane separation performance                      |      |   |   |   |       |   |   |   |        |   |   |   |          |             |
| Subtask 3.2 Conceptual design on CMS membrane/module/housing to function as a WGS/MR |      |   |   | D |       |   |   |   |        |   |   |   |          |             |
| Subtask 3.3 Fabrication and evaluation of CMS-WGS/MR                                 |      |   |   |   |       |   |   |   |        |   |   |   |          |             |
| Subtask 3.4 Technical input for membrane reactor design/fabrication (Technip)        |      |   |   |   |       |   |   |   |        |   |   |   |          |             |

| ID | Title                                  | Planned Date | Verification Methods   |
|----|--|--------------|--|
| A  | Generation of the performance database | 12th         | Report with the database including parameters listed in p. 39 of FOA |
| B  | Verification of the mathematical model | 18th         | Report summarizing the deviation for all tests performed             |
| D  | Conceptual design for the CMS/MR       | 12th         | CAD drawing of the MR, and parameters listed in p. 39 of FOA         |



| Task  | Yr I |   |   |   | Yr II |   |   |   | Yr III |   |   |   | Cost     | Cost        |
|---|------|---|---|---|-------|---|---|---|--------|---|---|---|----------|-------------|
|   | 1    | 2 | 3 | 4 | 1     | 2 | 3 | 4 | 1      | 2 | 3 | 4 | per Task | per BP      |
|   | BP 1 |   |   |   | BP 2  |   |   |   | BP 3   |   |   |   | (\$)     | (\$million) |
| Task 4.0 Prepare a Pd alloy membrane separator for the 2nd stage hydrogen recovery (MPT)    |      |   |   |   |       |   |   |   |        |   |   |   | 140,721  | 0.67        |
| Task 5.0 Evaluate gas permeation and catalytic reaction under extremely high pressure (USC) |      |   |   |   |       |   |   |   |        |   |   |   | 50,000   |             |
| Subtask 5.1 Experimental Verification   |      |   |   |   |       |   |   |   |        |   |   |   |          |             |
| Subtask 5.2 Membrane and membrane reactor simulation support                                |      |   |   |   |       |   |   |   |        |   |   |   |          |             |
| Task 6.0 field test with the CMS-WGS/MR and Pd membrane gas separator (MPT)                 |      |   |   |   |       |   |   |   |        |   |   |   | 293,936  |             |
| Subtask 6.1 Operation of the bench-scale membrane reactor                                   |      |   |   |   |       |   |   |   |        |   |   |   |          |             |
| Subtask 6.2 Long term operation stability   |      |   |   |   |       |   |   |   |        |   |   |   |          |             |

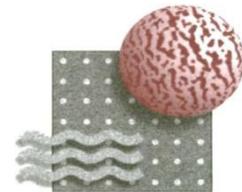
| ID | Title                            | Planned Date | Verification Methods                                     |
|----|----------------------------------|--------------|--|
| C  | Operation under extreme pressure | 24th         | including parameters listed in p. 39 of FOA              |
| E  | Field test                       | 24th         | Test report including updated parameters listed in p. 39 |



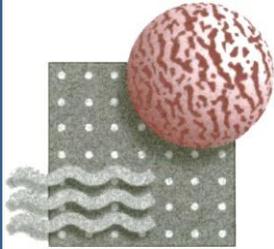
| Task  | Yr I |   |   |   | Yr II |   |   |   | Yr III |   |   |   | Cost     | Cost        |
|---|------|---|---|---|-------|---|---|---|--------|---|---|---|----------|-------------|
|   | 1    | 2 | 3 | 4 | 1     | 2 | 3 | 4 | 1      | 2 | 3 | 4 | per Task | per BP      |
|   | BP 1 |   |   |   | BP 2  |   |   |   | BP 3   |   |   |   | (\$)     | (\$million) |
| Task 5.0 Evaluate gas permeation and catalytic reaction under extremely high pressure (USC) |      |   |   |   |       |   |   |   |        |   |   |   | 50,000   | 0.68        |
| Subtask 5.2 Membrane and membrane reactor simulation support                                |      |   |   |   |       |   |   |   |        |   |   |   |          |             |
| Task 7.0 Conduct process design and engineering study (Technip & MPT & USC)                 |      |   |   |   |       |   |   |   |        |   |   | F | 273,881  |             |
| Task 8.0 Conduct Economic and Environmental Analyses (Technip & MPT & USC)                  |      |   |   |   |       |   |   |   |        |   |   | G | 273,881  |             |

| ID       | Title                                      | Planned Date | Verification Methods   |
|----------|--|--------------|--|
| <b>F</b> | <b>Design and Engineering Analysis</b>     | 36th         | analysis according to the format in Attachment 3 requested by this FOA |
| <b>G</b> | <b>Economic and Environmental Analysis</b> | 36th         | analysis according to Attachment 3&4 requested by this FOA format      |

Total Budget: \$2.5 millions



# >20 year Experience in High Temperature High Pressure Membrane-based Gas Separations

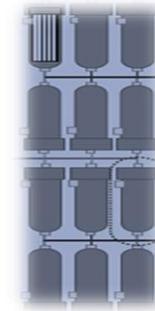
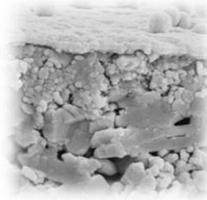
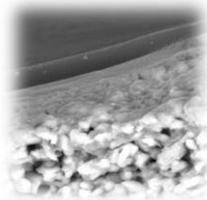


- ❑ A Commercial Ceramic Membrane Manufacturer
- ❑ A Ceramic Membrane Module & Housing Designer

- ❑ Transport Phenomena for Fluid through Porous Media
- ❑ A Reaction Engineer specializing in Membrane Reactor



## One-Box Process



## Field Implementable High Temperature Membrane-based Gas Separation Process

Bench (small pilot) Scale Field Test with Real Coal-derived Syngas



Engineering, Economic, & Environmental Analysis

**Technip**

(formerly KTI)

the world leader in the design and construction of the conventional hydrogen production facilities

Next Step: Field Test/Demonstration