Development of Hydrogen Selective Membranes/Modules as Reactors/Separators for Distributed Hydrogen Production

DE-FG36-05GO15092

PD _26_ Liu

Paul KT Liu
Media and Process Technology Inc.
1155 William Pitt Way
Pittsburgh, PA 15238

May 18 – 22, 2009

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

- **Project Start Date**
  7/1/05
- **Project End Date**
  6/30/08 (no cost extension applied)
- **Percent Complete**
  95%

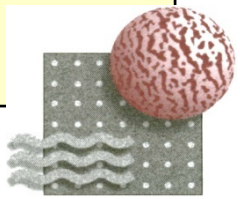
#1 Testing/Analysis: few (or no) commercial scale membrane- and membrane reactor-based processes in operation

#2 Permeate Flux/Selectivity: no net cost advantages by the membrane-based process according to case studies in DOE H2A analysis

#3 Stability: lack of long term membrane performance stability demonstrated

- **Total project funding**
  - DOE Share: $1,530,713.
  - Contractor Share: $382,678.
- **Previous Funding received:**
  $100K(FY05), $225K(FY06), $566K(FY07)
- **Funding received in FY08**
  $639K
- No catalyst development activities due to funding limitation in the beginning of the project

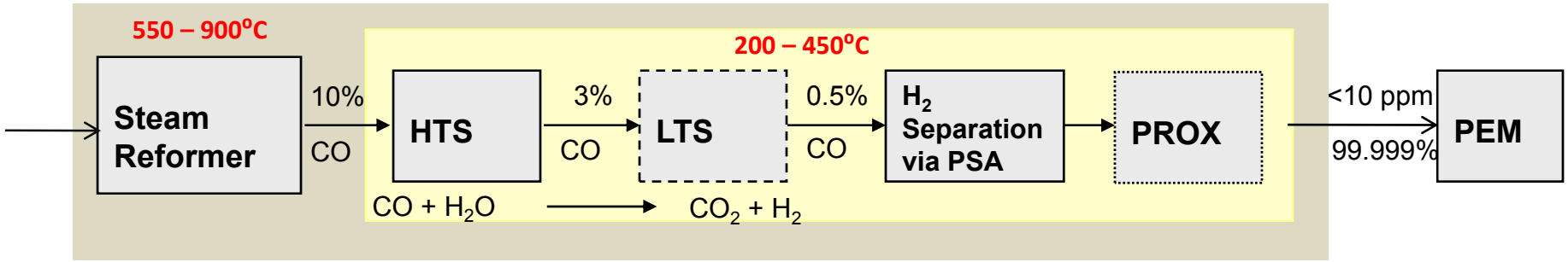
- **Professor Theo T. Tsotsis**
  University of Southern California,
  Catalytic membrane reactor expert
- **Dr. Babak Fayyaz-Najafi** Chevron ETC,
  End User Participant
- **Dr. Hugh Stitt,** Johnson Matthey,
  Catalyst Manufacturer
- **Dr. Pat Hearn**, Ballard Corp,
  Fuel Processing End User



Overall Project Objectives

1. **Develop, fabricate and demonstrate field implementable hydrogen selective membranes/modules**
2. **Achieve process intensification of conventional hydrogen production**
3. **Reduce cost for distributed hydrogen production**

Example of Conventional Process - Steam Methane Reforming (SMR)



Overall Technical Approach

Process Intensification (Objective #2)

Membranes/Module Development (Objective #1)

1. Reduce HTS/LTS reactors & inter-stage coolers into a single stage **LTS/MR** operation

2. Process synthesis to overcome the dilemma of **high H_2 purity vs high H_2 recovery ratio** for a membrane-based process

3. Process improvement/optimization to meet **economic** targets

Pilot & Field Tests (Objective #3)

HTS: High Temperature Shift
LTS: Low Temperature Shift
PROX: Preferential Oxidation
PEM: Proton Exchange Membrane Fuel Cell
MR: Membrane Reactor

Specific Objectives and Technical Approach for FY08-09

Based upon the experimental results obtained from previous years in the performance of our membranes and membrane reactors, we have focused on activities below :

- **Performing economic analysis (Barrier #2)**
  - determined capital and operating costs for hydrogen production based upon the membrane/module and the process developed
  - identified areas of improvement/modification for cost reduction
  - pursued the 2nd iteration of membrane/module development to satisfy areas identified

- **Conducting tests using the PDU testing facility at USC and pilot testing unit at M&P (Barrier #1)**
  - verified the performance based upon process simulation, and
  - provided experimentally substantiated inputs for H2A analysis

- **Fabricate field implemental membranes/modules for field testing by end users (Barrier #1&3)**
  - fabricating 150 scfh H_2 separator for field test in 2nd Q

TECHNICAL ACCOMPLISHMENTS – FY08-09

- **Limited Economic Advantages by the Membrane-based Process**

  Our membrane reactor process (HiCON, combining WGS/H_2 Separation via CMS membranes) delivers minor cost benefit, in comparison with conventional (WGS + PSA) process according to H2A analysis. Case studies in DOE H2A analysis show similar results. Hydrogen produced at a low pressure is the main cause.

- **Innovative Solution to Deliver H_2 at Higher Pressure**

  Innovative concept, permeate purging with high pressure steam generated from waste heat and then separation of steam via condensation, to deliver higher pressure hydrogen product, e.g., 100 psig, from the membrane process has been developed. This innovation reduces the electricity-driven compression requirement with the reutilization of waste heat.

- **Membrane Development/Modifications (2nd Iteration) to Implement Innovation**

  Pd thin film supported on our commercial ceramic substrate/module has been developed to implement the above innovation. This Pd membrane is low cost, steam stable, and able to sustain the high pressure , i.e., ≥300 psig, uniquely qualified for the proposed innovation. Its long term operation stability, e.g., >30 thermal cycles (room to 350°C) and >2 months on-stream (H_2+H_2O), has been demonstrated.

TECHNICAL ACCOMPLISHMENTS – FY08-09 (cont'd)

- **Economic Analysis of the Improved Process**
  The H2A analysis on the improved process demonstrates cost savings potential for a typical membrane-based process. Our preliminary, un-optimized analysis (via PRO/II) exhibits ~5% cost reduction by our membrane-based production process. Optimization is presently underway.

- **Pilot-scale Membrane Bundle/Module Development and Testing**
  Pilot scale membrane bundle/housing has been prepared and tested under multiple thermal/pressure cycles, ready for field test. Hydrogen recovery using a pilot scale module (i.e., 0.1 m^2, 21 scfh/hr at 50 psig) has been successfully fabricated and its performance is consistent with the results obtained from the single tube bench top unit, e.g., ≥99.5% purity at 93% recovery.

- **Preparation of Hydrogen Separator for Field Testing**
  A pilot scale hydrogen selective membrane/module (150 scfh H_2, 1.5 m^2) has been currently under preparation, which will be delivered to our end user (Ballard) in June '09 for field testing using reformate generated from ATR.

TECHNICAL ACCOMPLISHMENTS – FY08-09 (cont'd)

- **Applications for other reforming process with our carbon molecular sieve (CMS) membranes**

  Our carbon-based hydrogen selective membrane has been upgraded. Its permeate flux is comparable or better than the Pd/Cu foil at the comparable temperature range. Its stability in the presence of contaminants, e.g., H_2S, has been field tested , ideally suitable for use with other reformates, where the Pd based membrane may be lack of material stability.

Economic Analysis via H2A analysis: Technical Challenges for Membrane-based Processes

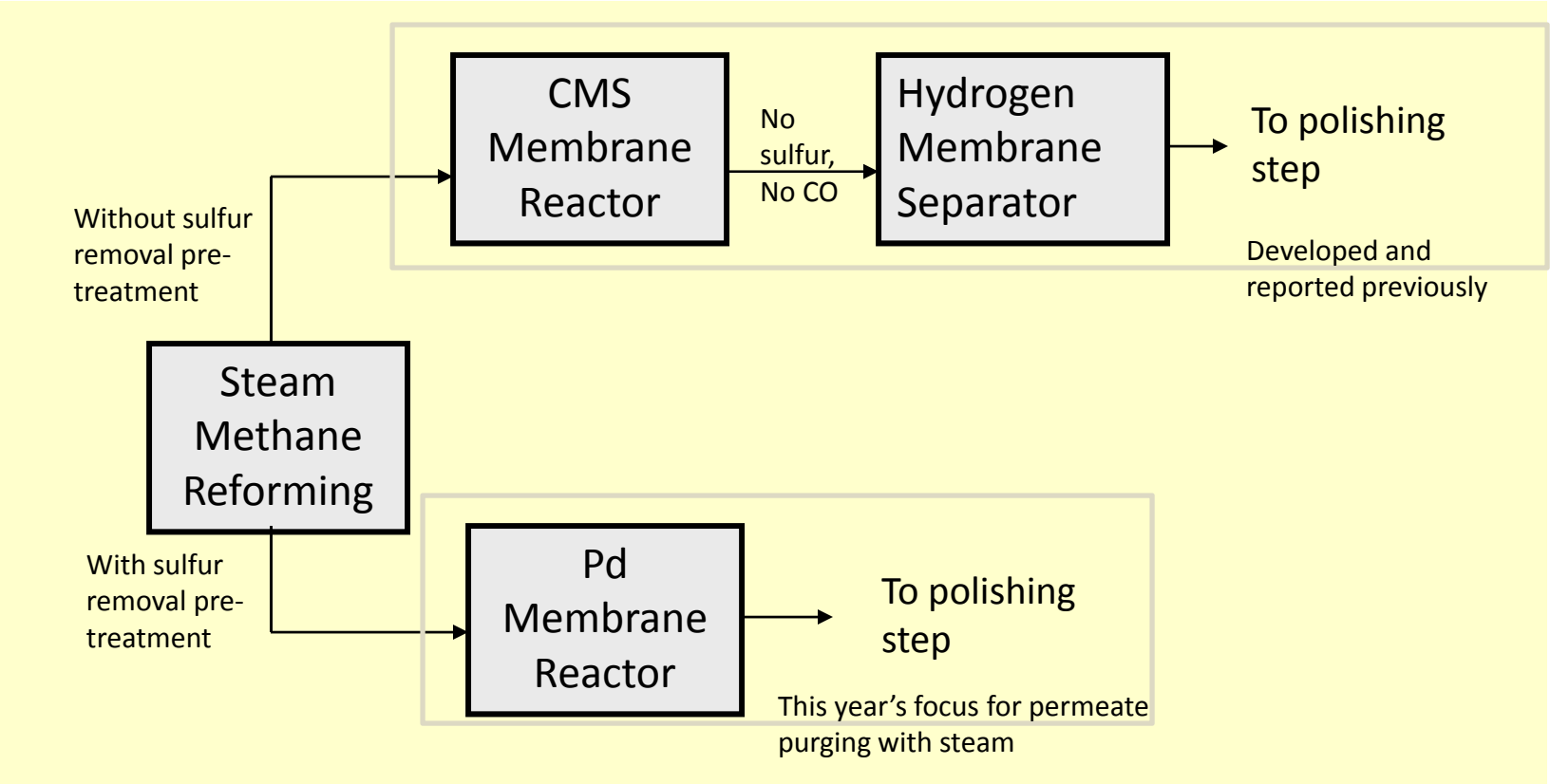
H2 Production Cost Contributio based upon DOE H2A Case Studies		
Cost Component	SMR + PSA ($/kg H_2)	Ultimate MR* ($/kg H_2)
Capital Costs	0.45	0.32
Decommissioning Costs	0.00	0.00
Fixed O&M	0.16	0.13
Feedstock Costs	0.91	0.96
Other Raw Material Costs	0.00	0.00
Byproduct Credits	0.00	0.00
Other Variable Costs (including utilities)	0.10	0.19
Total	**1.61**	**1.59**

Assumptions used for H2A

Cases	Methane Conversion [%}	H_2 Recovery [%]
SMR + PSA	82	75
Ultimate MR	97	90

- The ultimate membrane reactor offers the capital cost advantages; however, no net cost advantage is demonstrated due to the penalty in H_2 compression cost.
- For Hydrogen production with CO_2 sequestration requirement, or for on-site fuel cell power generation, this penalty is eliminated.
- For distributed H_2 production requiring 6,250 psi recompression, cost reduction for MR is necessary to become competitive.
- During this year, compression with minimum parasitic energy consumption has been explored.

M&P Membrane Reactor Scheme



Unique Advantages of our Membranes/Membrane Reactors

1. Low temperature operation (WGS-LTS), thus, no exotic engineering/materials are required to develop for a membrane reactor and separator.
2. Our commercial low cost ceramic membranes/modules as platform ; thus, capital cost can be justified due to low permeate flux at a low temperature.

M&P Commercial Ceramic MEMBRANES - Low Cost

for harsh environment applications

Developmental Work Required

1. Deposition of an additional thin film for hydrogen separation
2. Fabrication of bundle/housing suitable for working environment

Examples of Commercial Installations

- Oil filtration applications at 150°C and 80 psi
- Water vapor recovery from flue gas at ~75°C

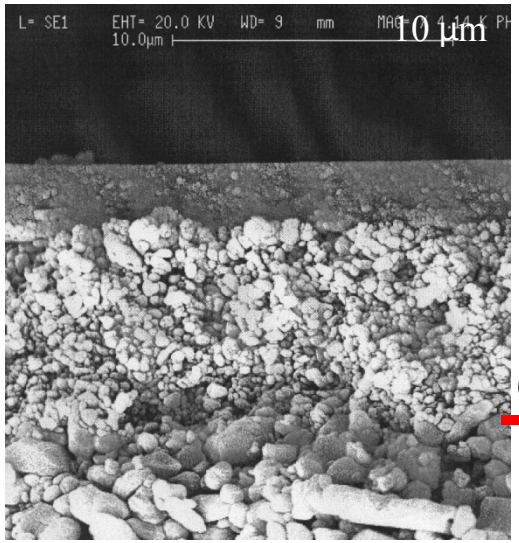
Proposed Applications

- Hydrogen recovery from reformate
- Water gas shift (WGS) membrane reactor at 200 to 350°C

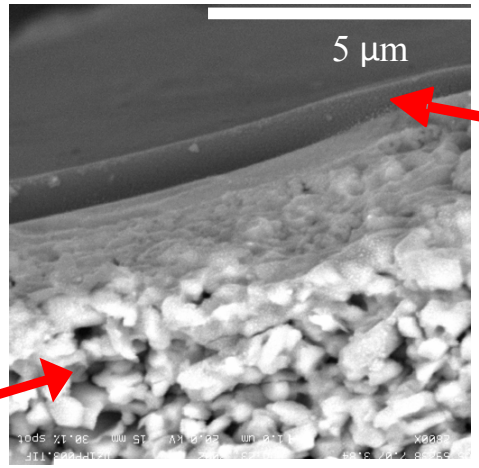
M&P Emerging Inorganic Membranes

M&P's Core Technology: Thin film deposition on porous substrates

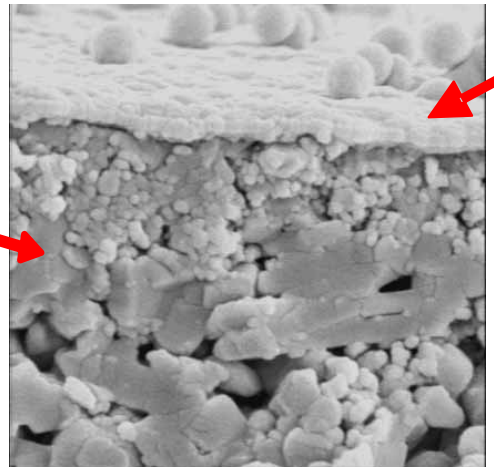
Inorganic Substrate



Ceramic Substrate



Carbon molecular sieve (porous, sulfur resistance)



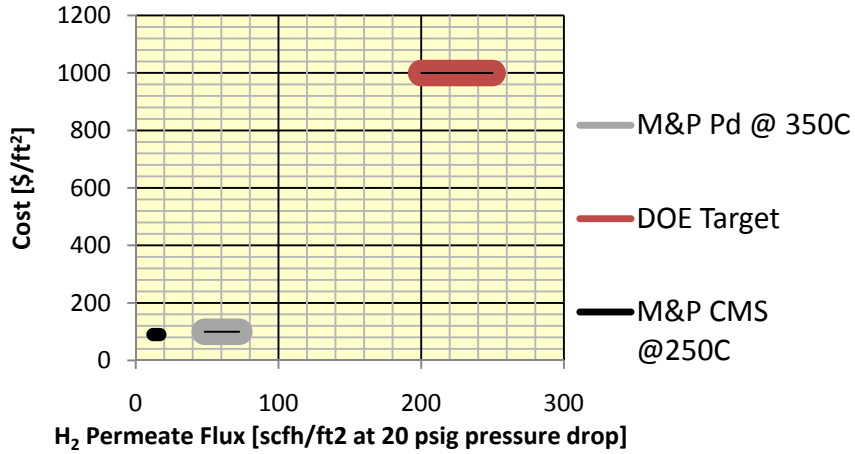
Palladium (dense, excellent selectivity)

Unique features of <u>Supported Membranes</u>

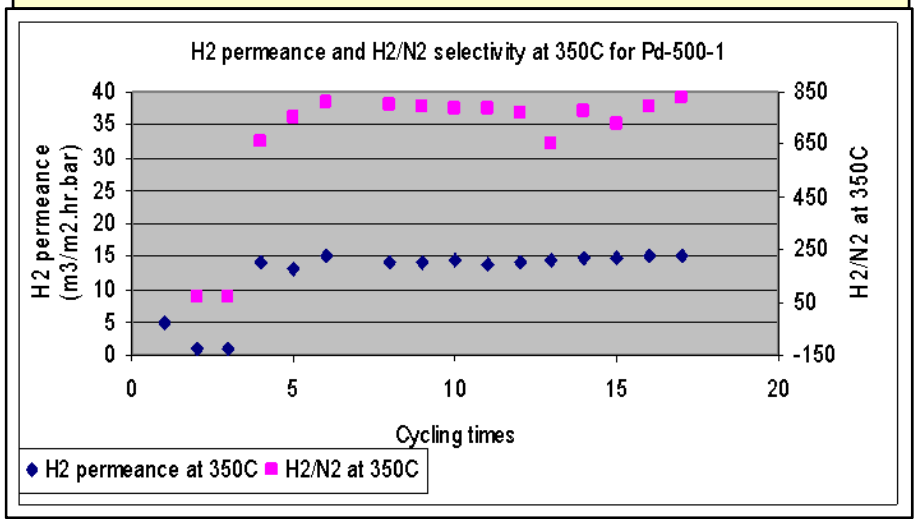
- Low cost, no Pd supply challenge
- Module/housing for high temperature/pressure use

Evaluation of M&P Hydrogen Selective Pd Membranes: Results

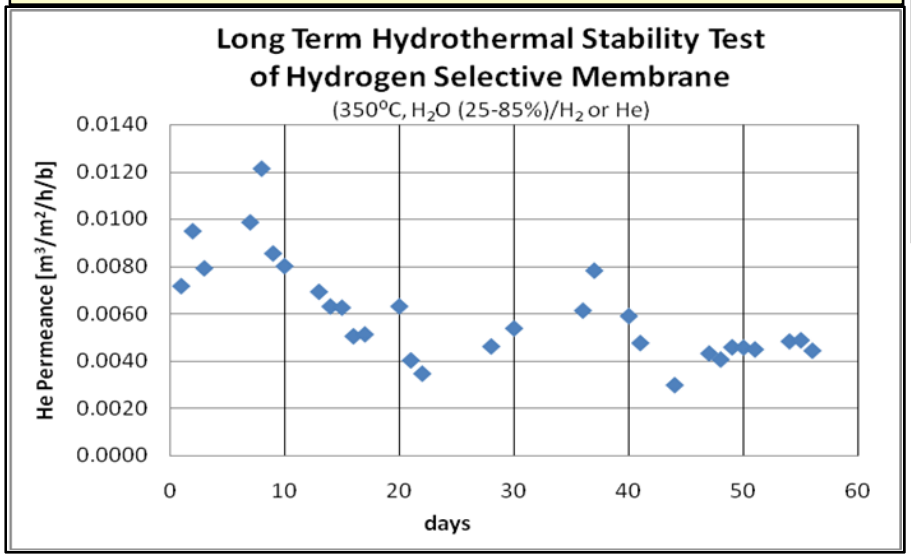
1. Performance Characterization (typical)



2. Thermal Cycling Stability



3. Thermal/Hydrothermal Stability



1. Our Pd membranes have been comprehensively evaluated under multiple temperature cycles and extended thermal/hydrothermal test.
2. Our cost/performance ratio meets/exceeds the DOE target. More importantly, the membrane is prepared on existing commercial ceramic membrane products.

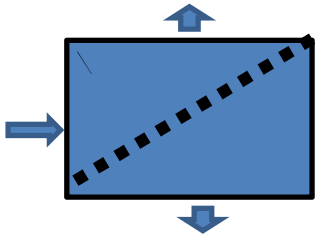
Separation Performance of Pd Membranes: Results

in Pilot-Scale Modules (0.1 m^2)

Synthetic Reformate from ATR

Reject [liter/min]	9.7
H_2 [vol%]	23.9
N_2	47.5
CH_4	8.8
CO_2	19.8

350°C, 53.5 psi, 11.9 liter/min	
H_2 [vol%]	37.7
N_2	38.9
CH_4	7.2
CO_2	16.2



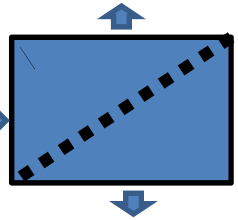
Permeate [liter/min]	2.2
H_2 [vol%]	97.9
N_2	1.7
CH_4	0.26
CO_2	0.16

H_2 Recovery [%]	48.5
H_2 Permeance [$m^3/m^2/hr/bar$]	4.5
H_2/N_2 selectivity (estimated)	421

Synthetic Reformate from SMR

Reject [liter/min]	4.8
H_2 [vol%]	16.1
CO_2	83.9

350°C, 89 psig, 14.2 liter/min	
H_2 [vol%]	72
CO_2	28

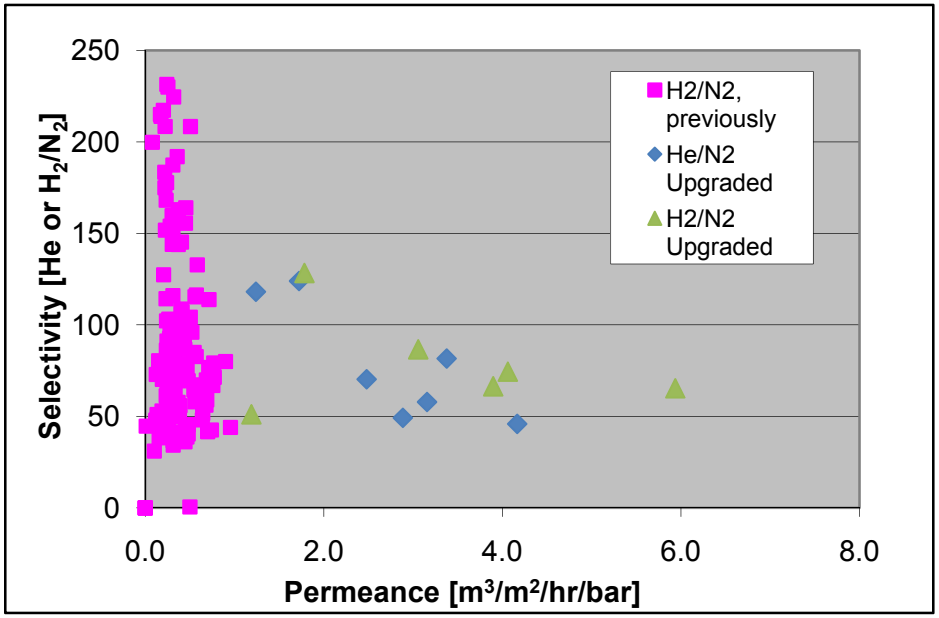


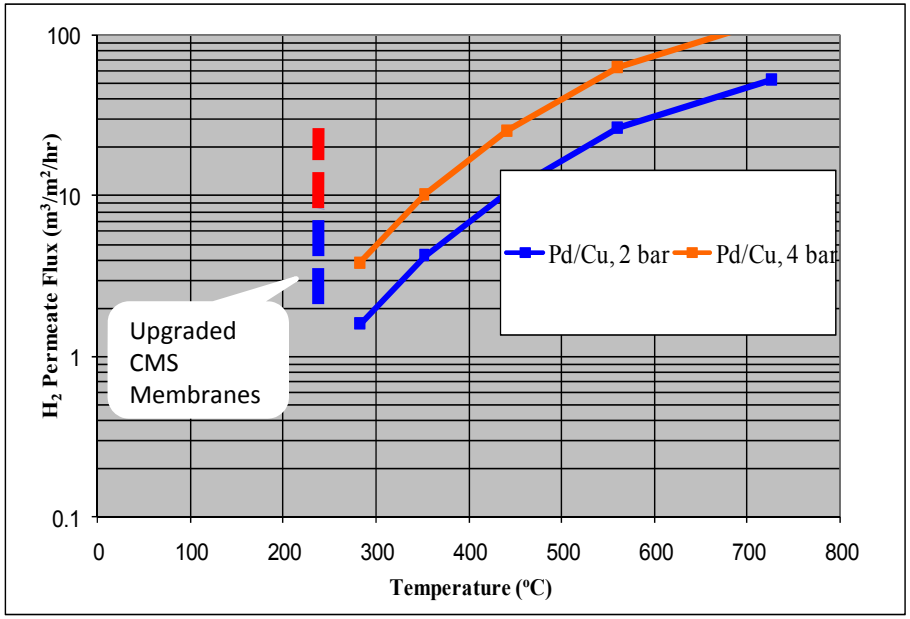
Permeate [liter/min]	9.4
H_2 [vol%]	99.5
CO_2	0.6

H_2 Recovery [%]	92.6
H_2 Permeance [$m^3/m^2/hr/bar$]	3.5
H_2/CO_2 selectivity (estimated)	540

- The H_2 purity and the H_2 recovery ratio meet the specifications required by our end user for fuel processing via ATR and the requirement for distributed hydrogen production via SMR after post treatment (presented in previous presentations).
- The selectivity and permeance obtained from the mixtures above are similar to those obtained from single components.

Performance Improvement of CMS Membranes in FY08-09





- Excellent chemical stability/sulfur resistance of CMS membranes. This membrane has been field tested successfully under coal gasification off-gas without pre-treatment.
- CMS membrane can now be deposited on the outside of the tube, which results in about 2 time increase in surface area, and then throughput.

- Assuming 1 micron thickness of Pd/Cu membrane,
- Permeate flux data source: Morreale, B.D., etc, JMS, 241(2004) 219
- Feed Pressure as indicated, Permeate Pressure: 1 atm

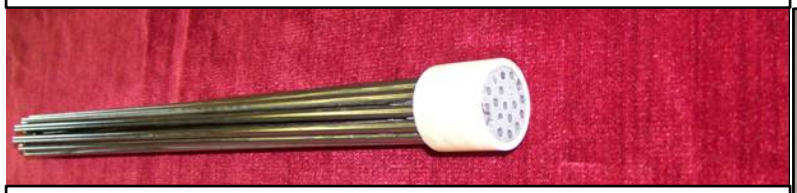
For lower temperature applications, i.e., ≤300°C, the permeance of our upgraded CMS membrane is competitive or better than that of the Pd alloy foil. While Pd membranes offer extremely high selectivity, our CMS membranes offer sulfur resistance.

Accomplishments:
MEMBRANE BUNDLE AND HOUSING PREPARATION/TESTING

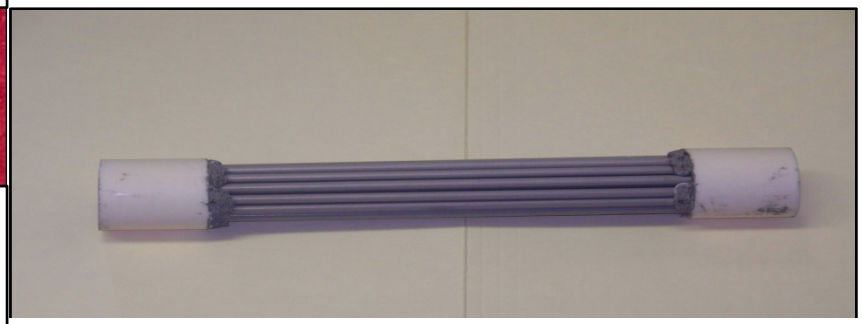
These membranes and modules were adapted from our existing commercial ceramic membrane products and modules.

Our full-scale ceramic membrane module (3 - 4" dia, prototype) for gas applications

Pilot Scale Membrane Bundle and Housing for High Pressure Intermediate Temperature Applications



- 1.5" Dia Bundles (top & right) and Housing (bottom),
- 20 x 5mm Membranes in candle filter configuration for CMS membrane (above)
- 20 x 5mm Membranes in two-end mounted configuration for Pd membrane (right)
- Thermal cycling tested at 20 to 220°C
- Pressure cycling tested at 0 to 1000 psig



Unique Features
- low cost
- existing engineering/materials know-how

Our Accomplishments
- successfully thermal/pressure cyclic tested

Media and Process Tech In.

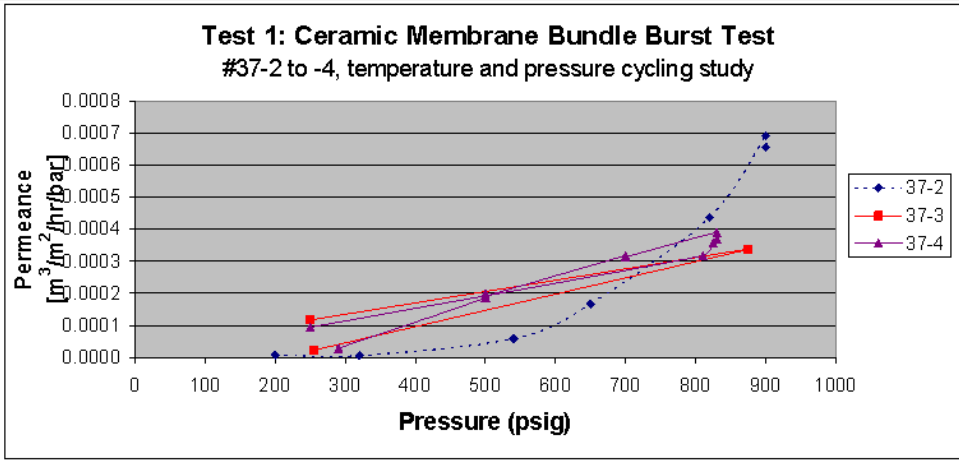
Evaluation of Pilot-Scale M&P Hydrogen Selective Membranes: Results

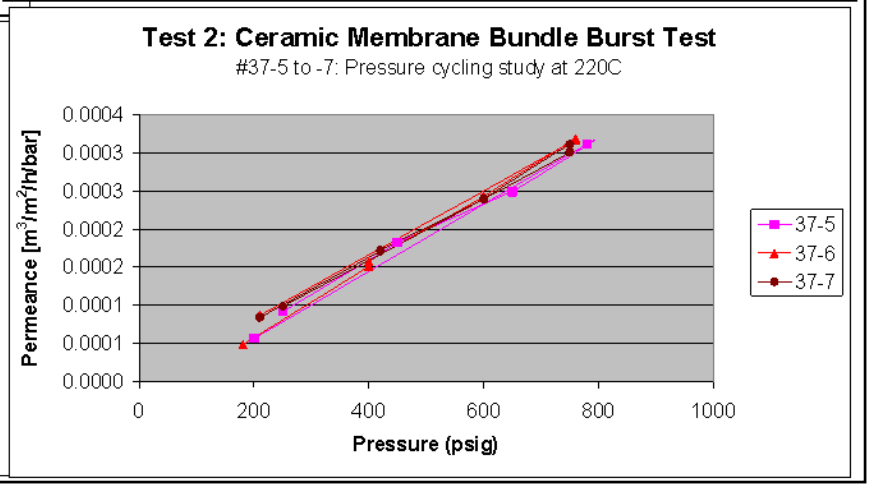
Burst Pressure Testing of M&P Ceramic Membrane Modules

at 220°C and up to 800 psi

Test ID	Beginning temp	Heating to	Beginnging pressure	Peak pressure	Ending Pressure	Idle Condition		Test Descirption
						Temp	Pressure	
37-1	20	20	14.7	800	14.7	20	14.7	Initiial quick test at room temperature
37-2	20	20	14.7	800	14.7	20	14.7	Pressure cycling at room temperature
37-3	20	220	14.7	800	14.7	20	14.7	Heating up to 220C, then pressure cycling, then cooling
37-4	20	220	14.7	800	14.7	220	14.7	Heating up to 220C, then pressure cycling,

Test ID	Beginning temp	Heating to	Beginnging pressure	Peak pressure	Ending Pressure	Idle Condition		Test Descirption
						Temp	Pressure	
37-5	220	220	250	800	14.7	200	200	Pressure cycling at 220C
37-6	220	220	180	800	14.7	220	210	Pressure cycling at 220C
37-7	220	220	210	800	14.7	220	250	Pressure cycling at 220C





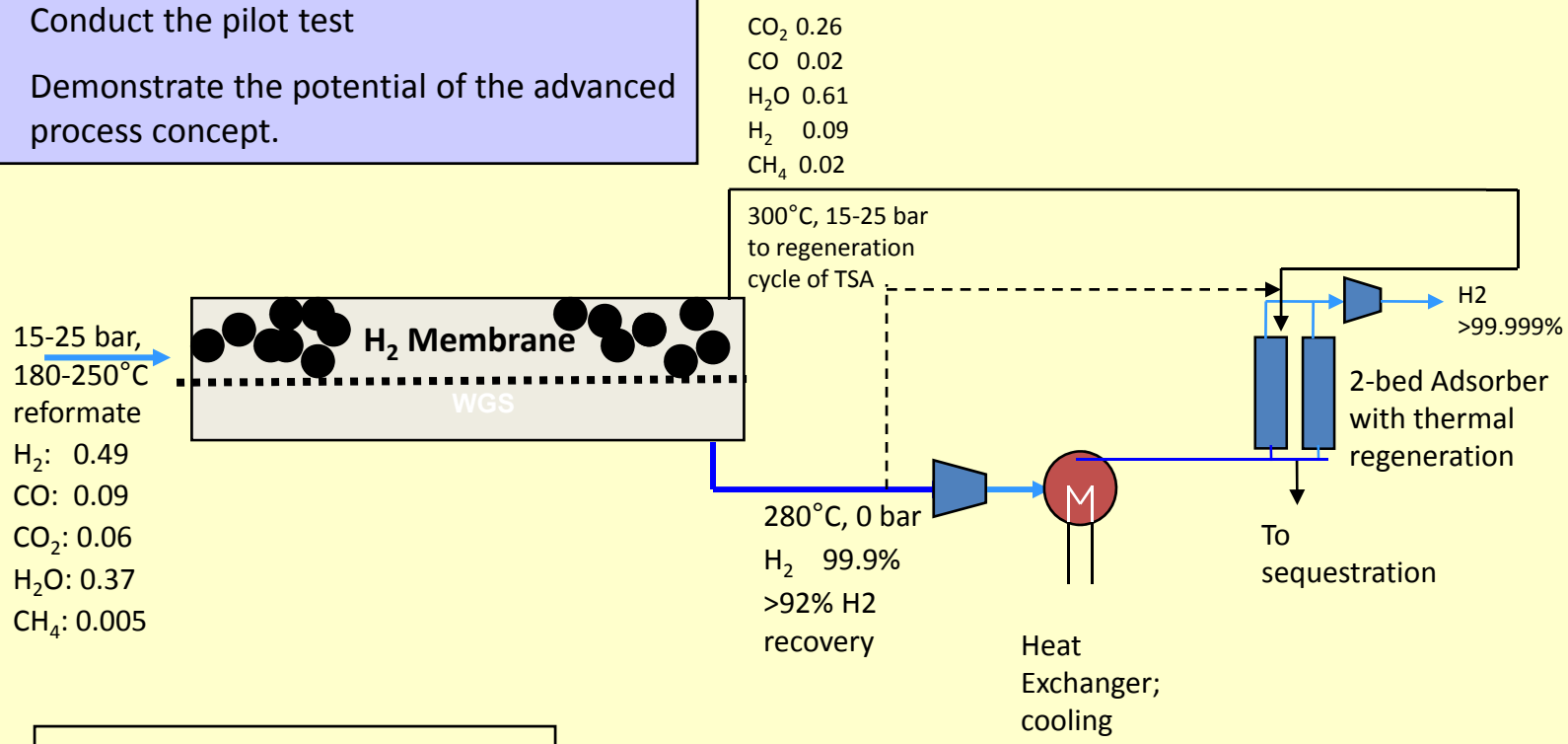
- The pilot-scale bundle/housing has been subject to multiple temperature/pressure cycles under conditions harsher than the proposed application environment.

Hydrogen Production Process based upon M&P Hydrogen Selective Membranes

Our HICON Process: CO Conversion, H_2 Recovery and Polishing Step

Process Development Activity Focus in FY08-09

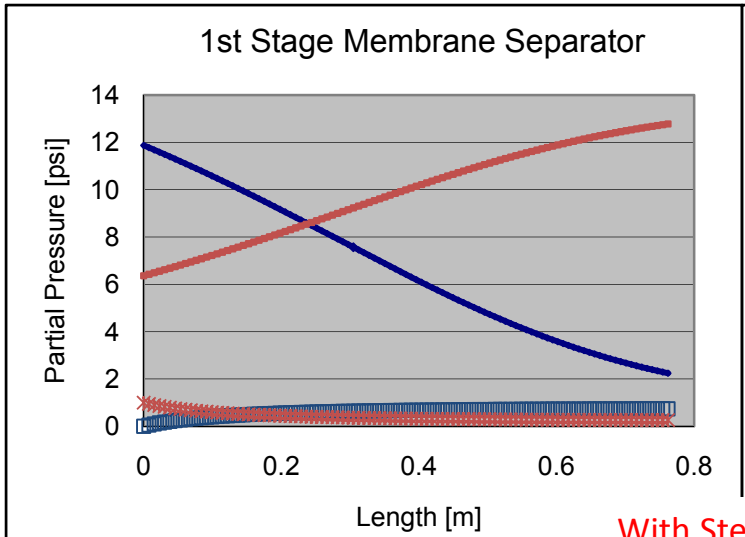
1. Conduct the pilot test
2. Demonstrate the potential of the advanced process concept.

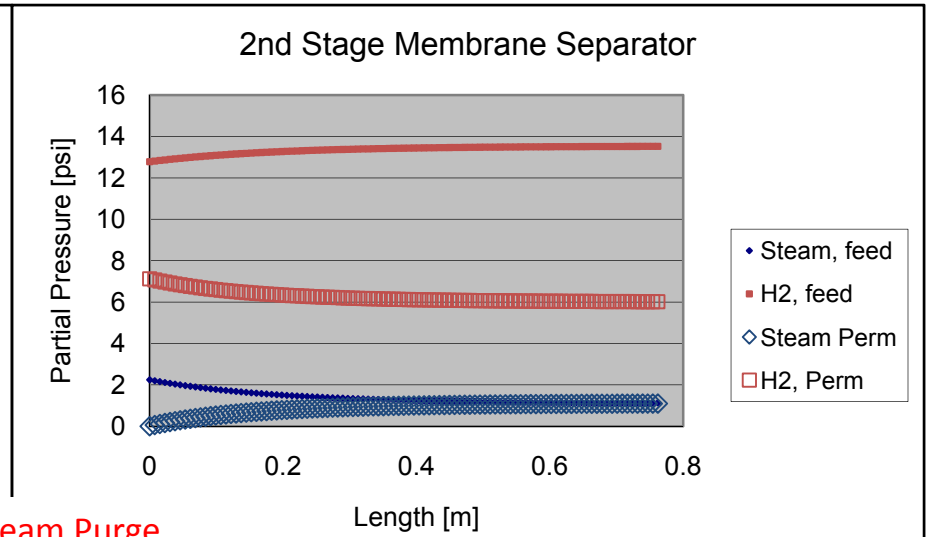


M&P HiCON Process

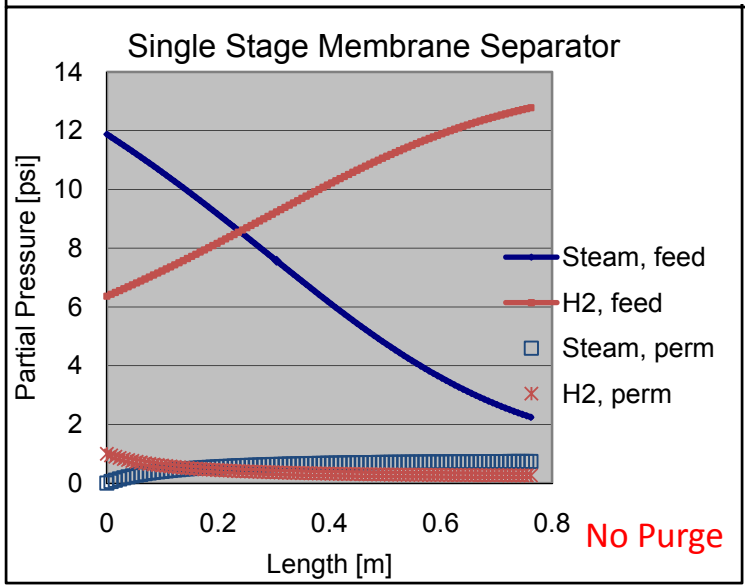
Experimental results for key process components were presented in previous presentations.

Delivery of High Purity Hydrogen Permeate at Higher Pressure with Minimum/No Parasitic Energy Consumption: Accomplishments





With Steam Purge



No Purge

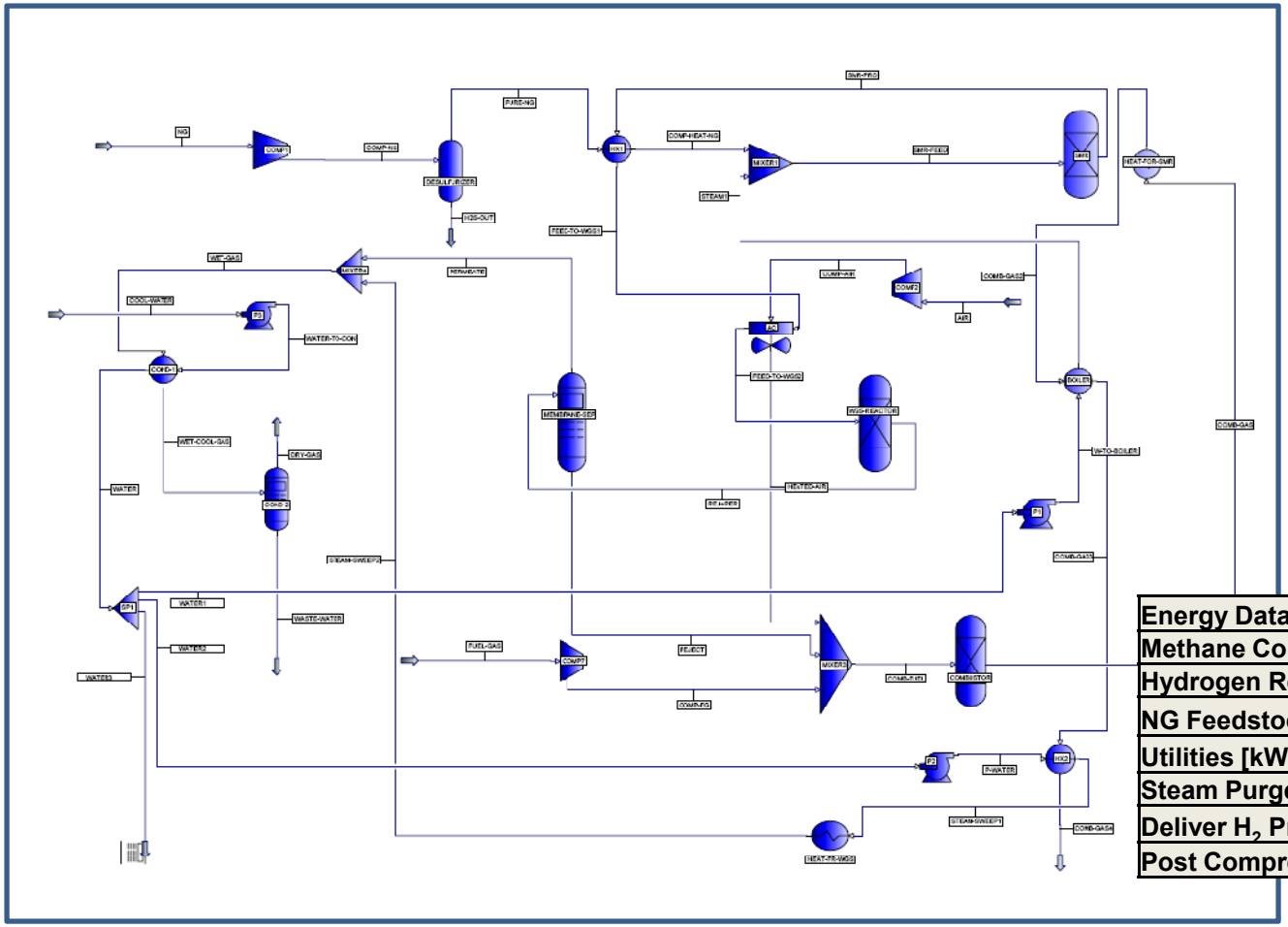
Parameters	1st stage	2nd Stage	Cumulative	Single [control]
Feed Pressure [psig]	300	300	300	300
Permeate Pressure [psig]	90	90	90	0
Steam Purge Ratio [% feed]	18	18	36	0
H_2 Recovery [%]	74	16	90	90
H_2 Purity [%]	99.88	99.7	99.849	99.935
Membrane Surface Area [m^2]	1	0.5	1.5	0.63

To deliver the hydrogen product at a higher pressure with our proposed steam purge as shown here, membrane surface area requirement increases to achieve a similar recovery ratio. Thus a low cost membrane is a must.

Media and Process Tech Inc.

Our Overall Process Scheme

Membrane-based Hydrogen Production Process with Higher Pressure Permeate



Basis

Ours: PRO/II Calculation

SMR+PSA: DOE H2A analysis

Energy Data	*SMR + PSA*	*Ours*
Methane Conversion [%]	82	82
Hydrogen Recovery [%]	75	90
NG Feedstock [NM³/ kg H_2]	4.49	4.3
Utilities [kWh/kg/H_2]	1.11	1.54
Steam Purge Ratio [-]	NA	0.3
Deliver H_2 Pressure [psig]	300	90
Post Compression [psig]	5,280	5,280

H2A Analysis: Accomplishments

Conventional Process:	SMR + WGS + PSA
Ultimate Membrane Reactor:	SMR/MR
Our Proposed Process:	SMR + WGS/MR at 250°C with higher H_2 delivered Pressure, e.g., 90 psig

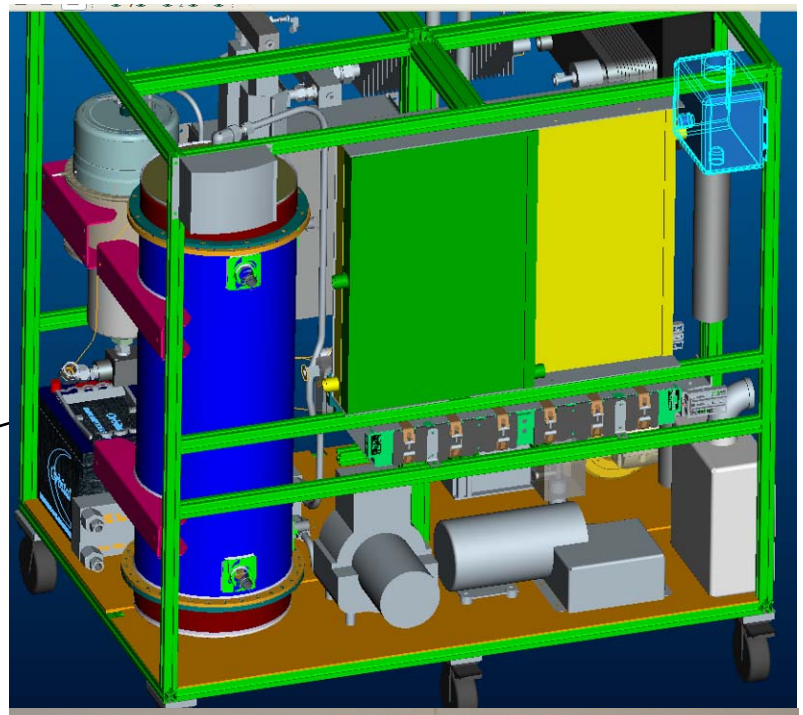
Specific Item Cost Calculation based upon DOE H2A Case Studies

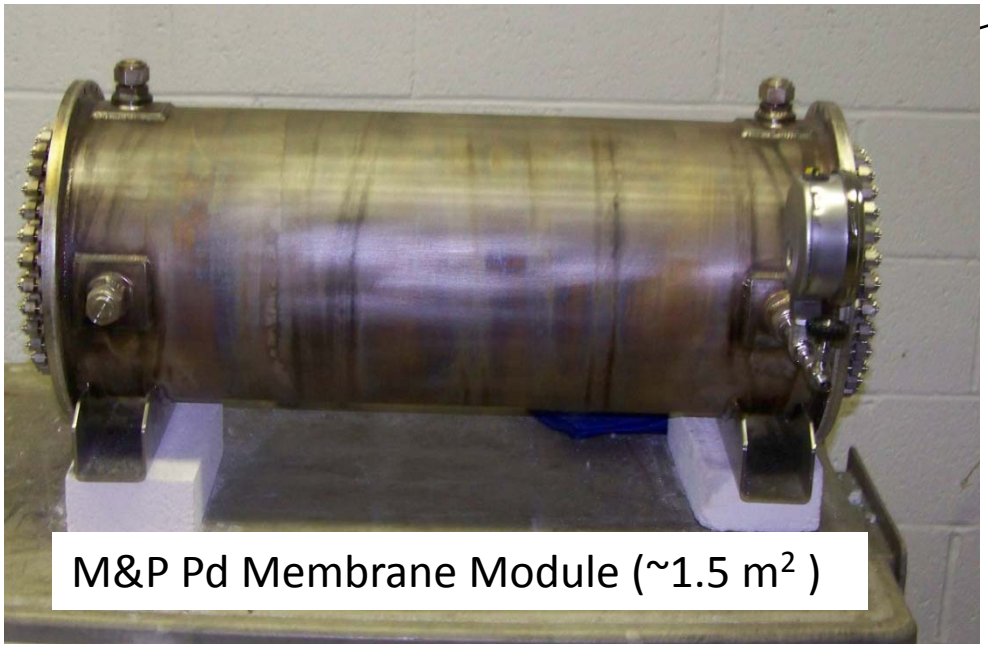
Cost Component	Hydrogen Production Cost Contribution ($/kg), SMR + PSA	Hydrogen Production Cost Contribution ($/kg), Ultimate MR*	Hydrogen Production Cost Contribution ($/kg), Ours
Capital Costs	0.45	0.32	0.40
Decommissioning Costs	0.00	0.00	0.00
Fixed O&M	0.16	0.13	0.14
Feedstock Costs	0.91	0.96	0.87
Other Raw Material Costs	0.00	0.00	0.00
Byproduct Credits	0.00	0.00	0.00
Other Variable Costs (including utilities)	0.10	0.19	0.13

Our innovation shows potential to achieve further cost reduction for the membrane-based process. No optimization has been performed on process simulation, which will be complete by the end of this project to finalize the ultimate cost savings potential.

Field Test Activities in FY08-09

M&P H_2 Selective Membranes for fuel processing to produce 152 scfh Hydrogen
Picture: Design of 5 kWh fuel-cell power generation unit (courtesy of Ballard Corp)





M&P Pd Membrane Module (~1.5 m^2)

M&P Palladium Membrane Bundle

Current Status: scheduled to demonstrate in June 2009

Summary and Conclusions – FY08-09

- Demonstrated potential to alleviate economic barriers by membrane-based process with our innovation
- Developed and comprehensively tested low cost Pd membranes supported on our ceramic substrate
- Demonstrated successfully separation performance of our Pd membrane in pilot scale units.
- Preparing H_2 selective membranes/modules for field testing

Work Plan for Rest of Project Period

Membrane Module/Housing Development

1. Complete membrane/module fabrication for field test by the end user for hydrogen recovery from fuel processing reformate.
2. Complete pilot test module fabrication for field test for membrane reactor applications.

Process Simulation & Optimization

1. Complete the optimization study on the delivery of membrane permeates at higher pressures and determine its cost savings potential via H2A analysis.

Field Test Activities

1. Complete the field test for hydrogen separation with our existing end user to demonstrate its commercial viability in the field.
2. Select an end user to complete the field test for membrane reactor study.