Robust and Energy Efficient Dual Stage Membrane Based Process for Enhanced CO_2 Recovery

DE-FE0013064

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Project Overview

Media and Process Technology Inc. (M&P)
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M&P Dual Stage Membrane Process

Project Overview

Funding: ***Overall project budget: $2.5MM including $500,000 (20%) cost share***

Overall Project Performance Dates: ***October 1, 2013 - September 30, 2016***

Project Participants:

- ***Media and Process Technology…Membrane manufacturer/supplier and technology developer***
- ***University of Southern California…Membrane reactor expertise***
- ***Technip Stone and Webster Process Technology Inc…Engineering and system design, analysis and economics***

Overall Project Objectives:

1. ***Conduct bench scale testing of innovative process scheme for power generation with CO_2 capture and sequestration (CCS).***
2. ***Carbon molecular sieve membrane as a "one-box" membrane reactor for CO conversion and H_2 recovery***
3. ***Pd-alloy membrane for residual H_2 recovery from "captured" high pressure CO_2***

Technology Background

Media and Process Technology Inc. (M&P)
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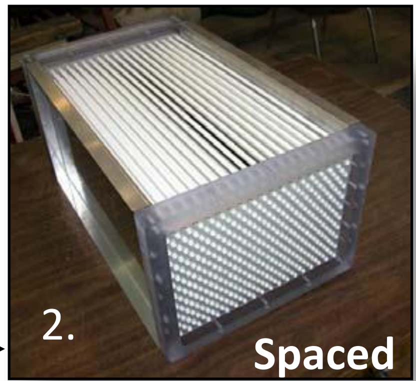
M&P Commercial Ceramic Membranes

Multiple Tube Membrane Bundles – versatile, low cost

Example: conventional micro- and ultrafiltration



Ex: porous heat exchangers & catalytic membrane reactors

Single tubes

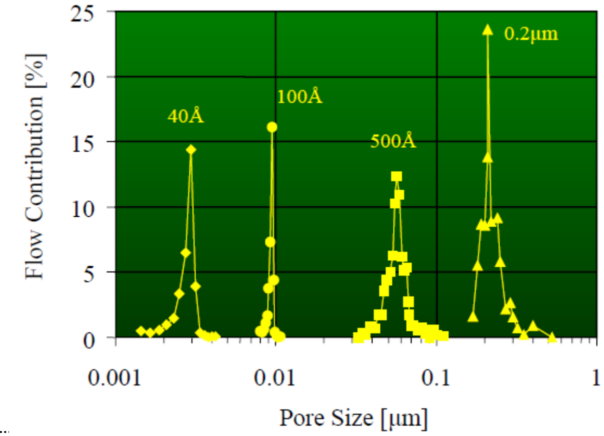
Ex: high pressure intermediate temperature gas separations

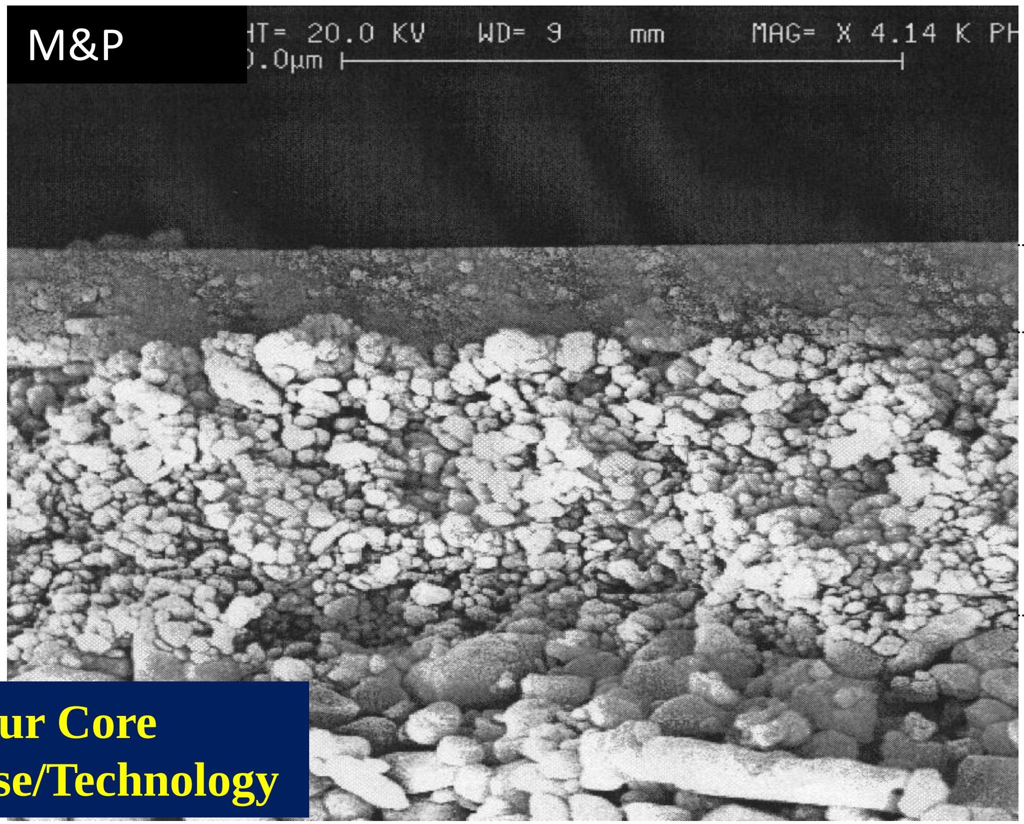
Our Core Expertise/Technology

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

M&P Commercial Ceramic Membranes

Thin Film Deposition for Pore Size Control





40Å to 100Å Pore Size Layer

500Å Pore Size Sublayer

0.2µm Pore Size Sublayer

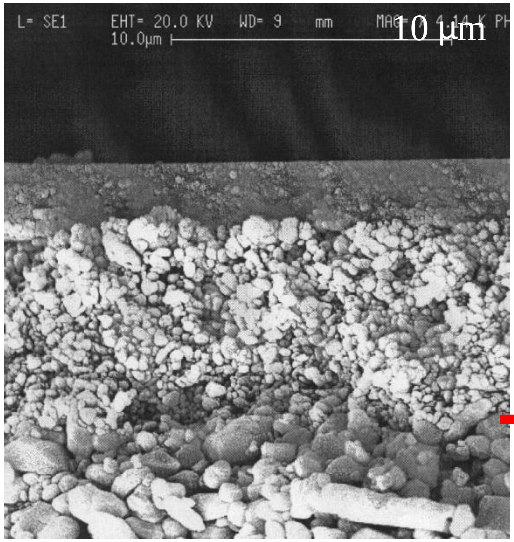
Our Core Expertise/Technology

#2: Our core expertise allows us to deposit a near perfect thin film on less-than desirable, but low cost porous tubular substrate.

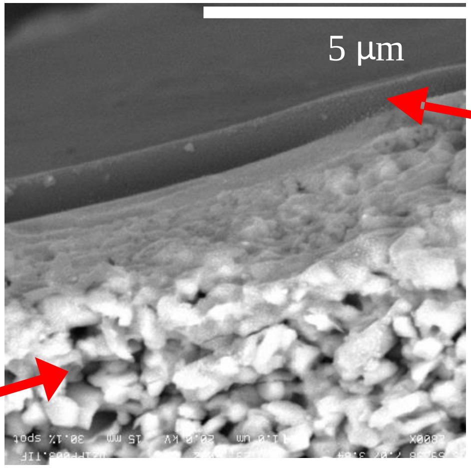
M&P Advanced Inorganic Membranes

Specific thin film deposition for advanced separations

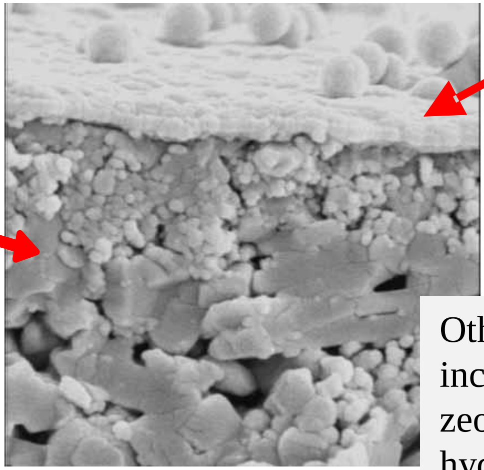
Inorganic Substrate



Ceramic Substrate



Carbon molecular sieve (porous, sulfur resistance)



Palladium (dense, excellent selectivity)

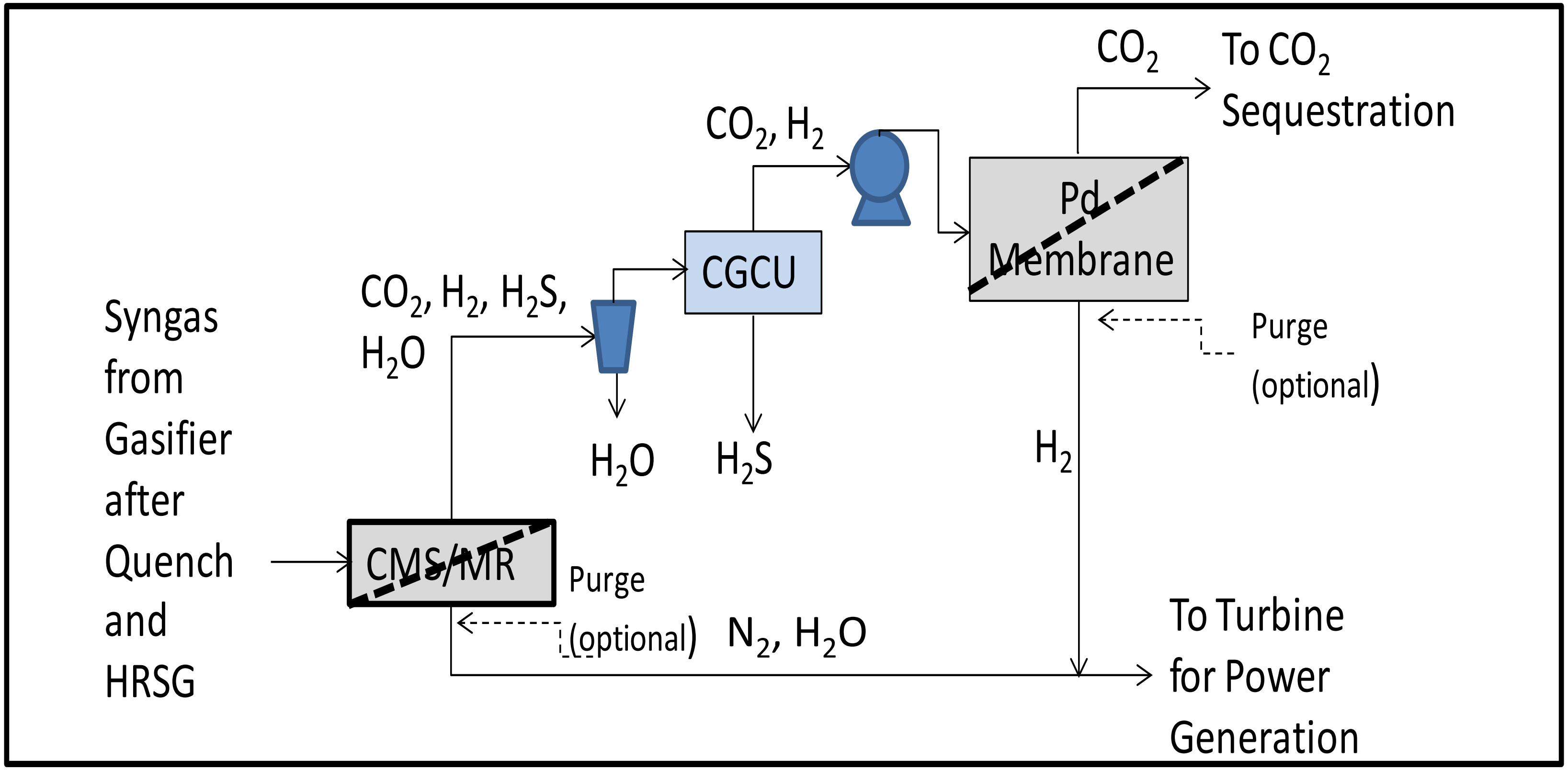
Others, including zeolites, flourinated hydrocarbons, etc.

Important Features of MPT Inorganic Membranes

- Low cost commercial ceramic support
- High packing density, tube bundle
- Module/housing for high temperature and pressure use

M&P Dual Stage Membrane Process

Proposed Process: Dual Membrane 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.**

M&P Dual Stage Membrane Process

Preliminary Economic Analysis for IGCC + CCS via Dual Stage

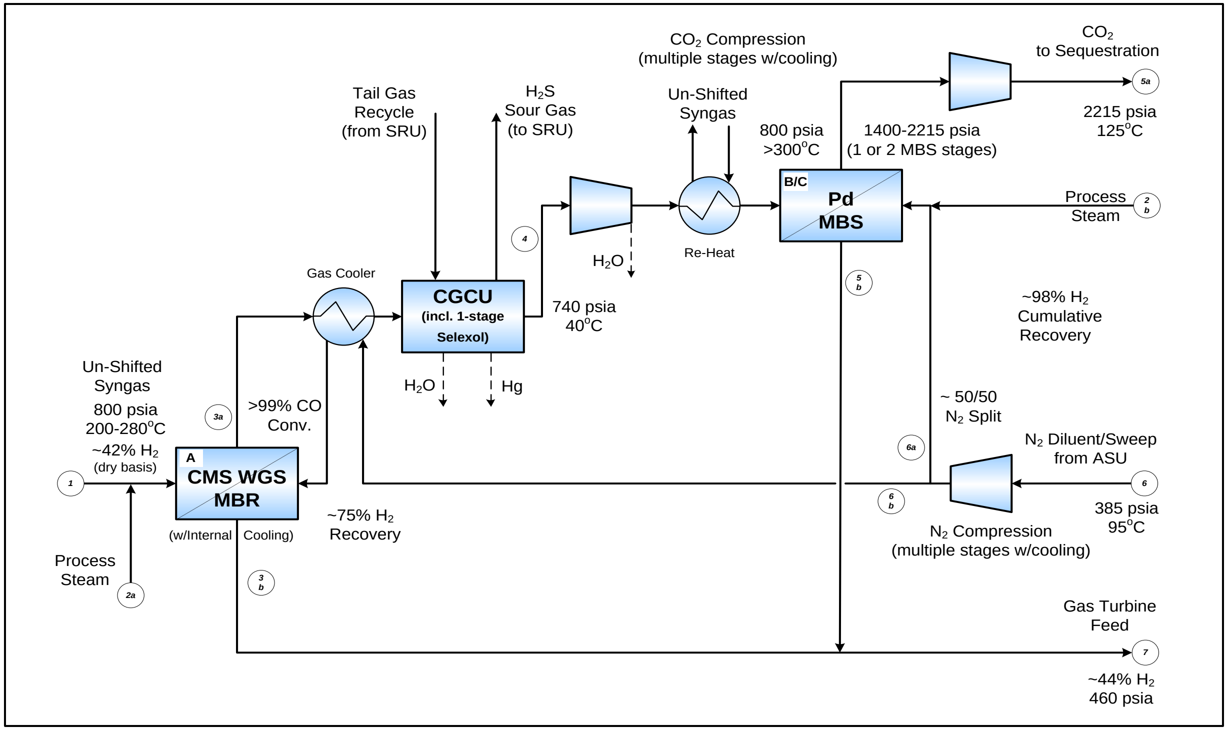


Table 1 Process Schemes Selected for Performance and Economic Analysis for Power Generation

Case Descriptions	Production		HHV	Required Selling Price				CO_2	CO_2
	Electricity	Hydrogen	Efficiency	Electricity	Hydrogen	Electricity	Hydrogen	Capture	Avoided
	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_2 production, COE is replaced with the RSP of H_2 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.

M&P Carbon Molecular Sieve (CMS) Membrane

Field Test at US DOE's NCCC: CMS Performance Stability

NCCC Slip Stream

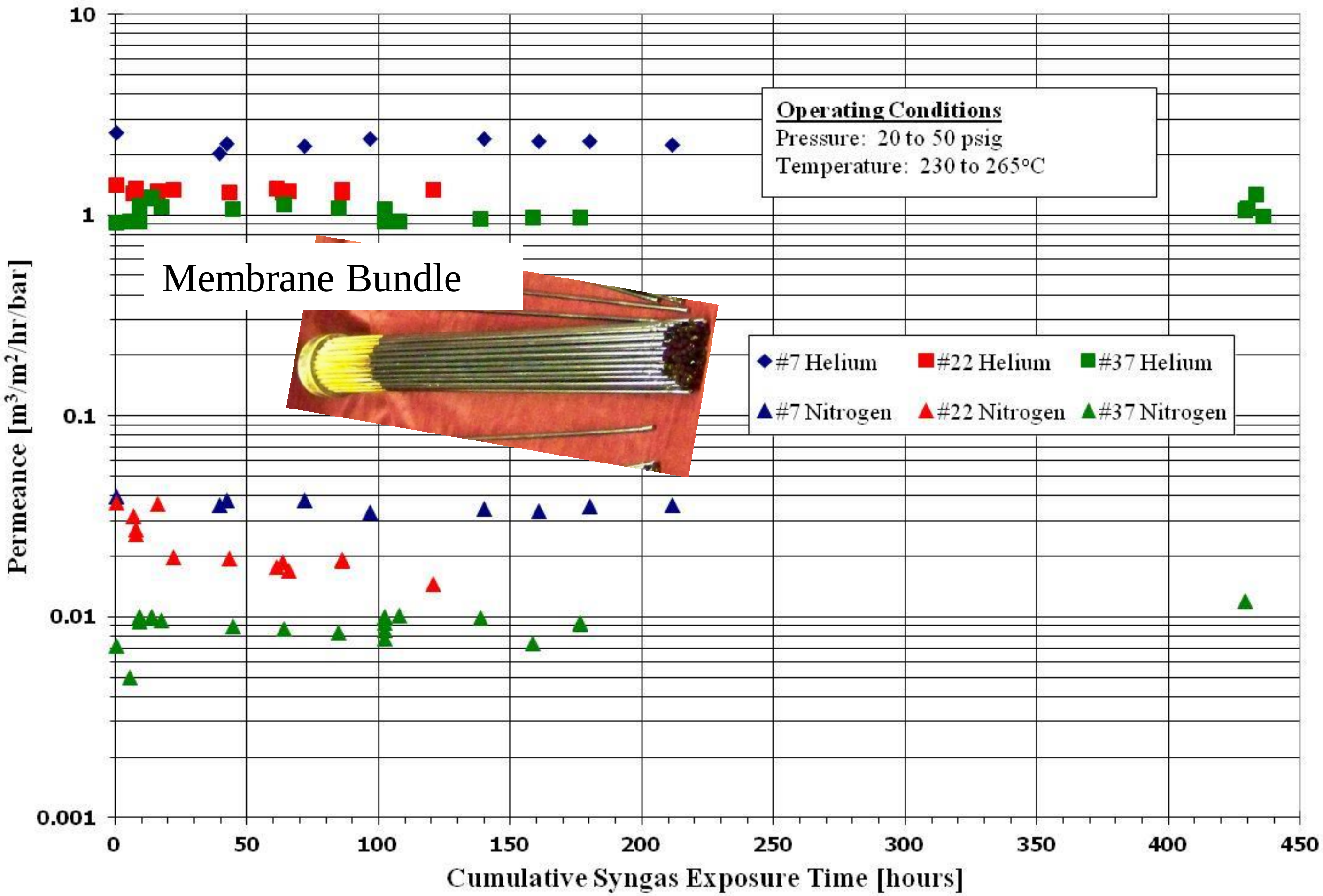
Membrane
86-tube CMS

Operating Conditions
T~ 250 to 300°C
P~ 200 to 300 psig

Pretreatment
Particulate trap, no other gas cleanup.

Composition
H_2 ~ 10 to 30%
CO ~ 10%
CO_2 ~10%
N_2,H_2O ~Balance

Trace Contaminants
NH_3 ~ 1,000ppm
Sulfur Species ~ 1,000ppm
HCL, HCN, Naphthalenes/Tars, etc.



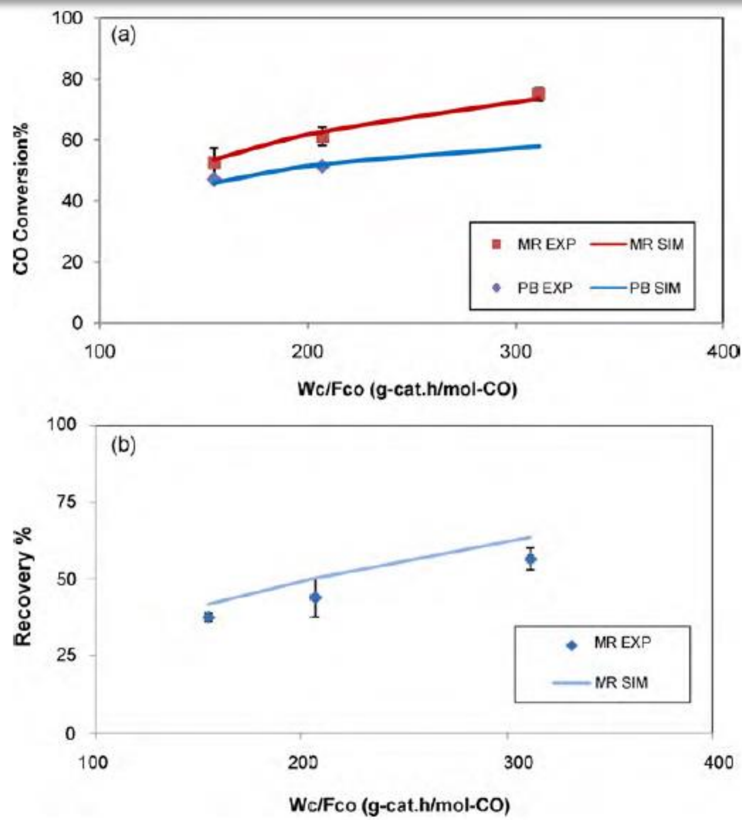
Performance stability of a multiple tube CMS membrane bundle during H_2 recovery from NCCC slip stream testing. He and N_2 Permeances measured periodically during >400 hr test.

USC CMS Membrane for WGS-MR

Experimental Results, Simulation, and Predictions

Experimental Results with Model Predictions

CO Conversion and H_2 Recovery

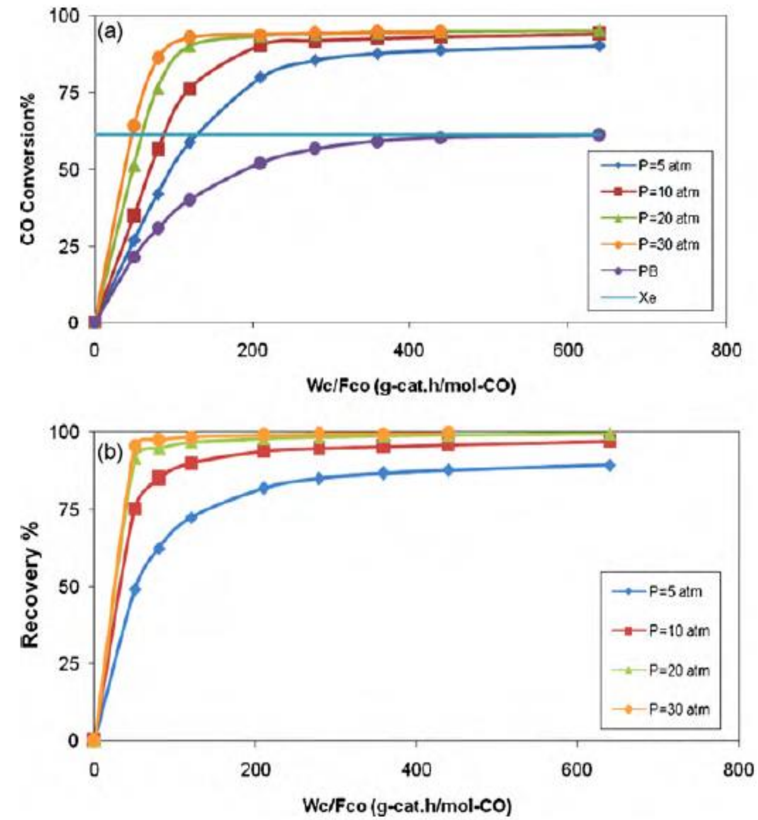


Operating Conditions: 300°C at 5 atm

Predicted Performance at High Pressure

Enhanced CO conversion and

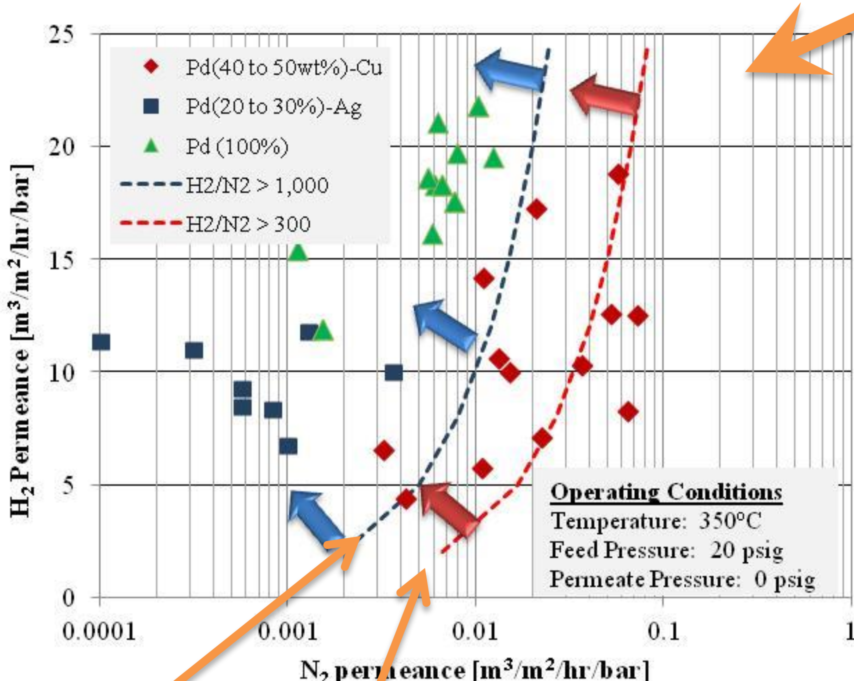
H_2 Recovery at high pressures



M&P Pd-Alloy Membranes

Pd-Alloy Membranes for Residual H_2 Recovery

H_2 and N_2 Permeance for Various Parts and Alloys

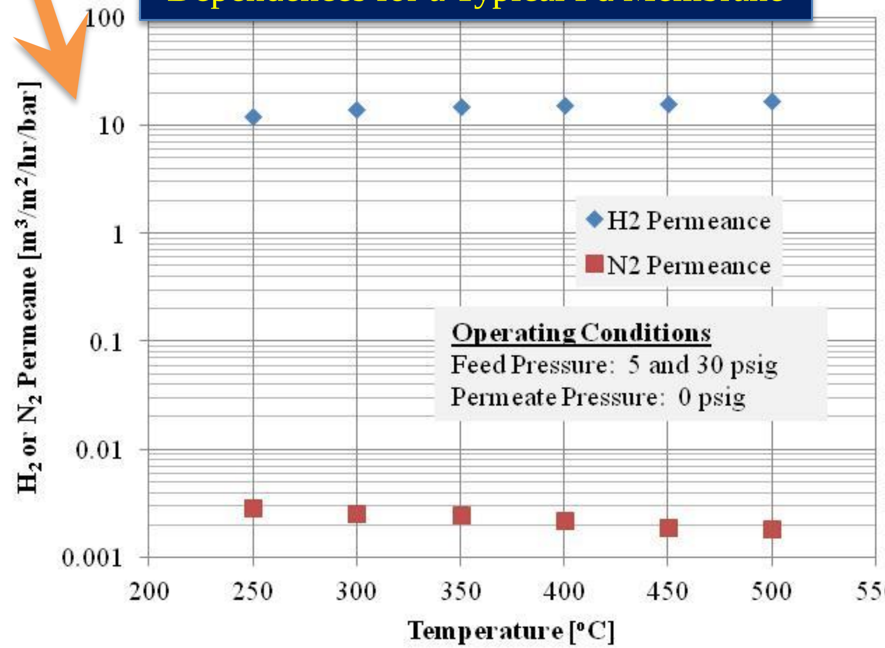


H_2/N_2 = 1,000

H_2/N_2 = 300

- **Ultra-high selectivity NOT necessary.**
  H_2/CO_2 > 300 is adequate to achieve high H_2 recovery with high CO_2 rejection (for CCS)
- **High Permeance at Low Temperature**
  Matches CCS CO_2 compression temperature; not necessary to heat

H_2 and N_2 Permeance Temperature Dependences for a Typical Pd Membrane



M&P Pd-Alloy Membranes

Multiple Tube Bundles High Performance Tube Sheet and Seals

High Pressure Tube Sheet

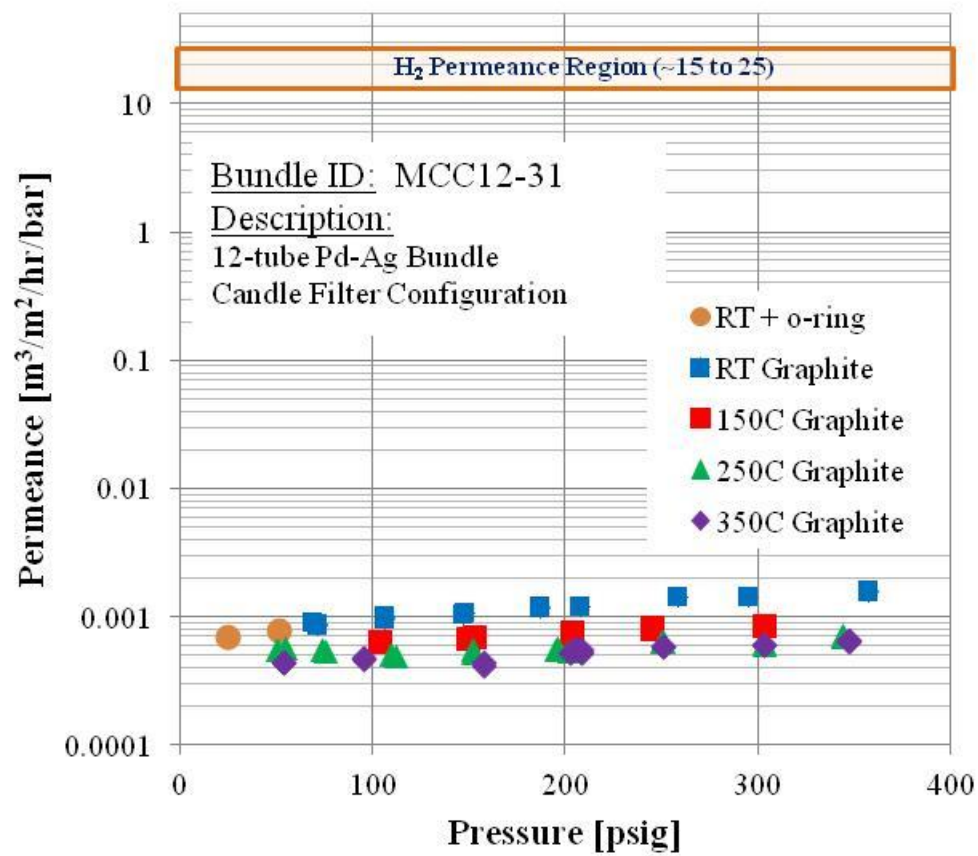
Pd Bundle and Ceramic Tube Sheet

2nd Generation Module Design

Latest Module Design with Graphite Packing

High Performance Package

N_2 Flux (Leak Rate) v. Pressure and Temperature



Technical Approach/Project Scope

Media and Process Technology Inc. (M&P)
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Project Technical Approach

Overview of Project Technical Approach - Workplan

Budget Period 1	Budget Period 2	Budget Period 3

Task 1. Project Management and Planning

Task 2. Establish Performance Database: Focus here is to complete the membrane performance database under more severe operating conditions in the presence of simulated WGS contaminants at long times. Also reactivate the bench top WGS-MR system for Task 3 activities.

Task 3. CMS WGS-MR experimental verification and modeling under extreme conditions: Focus here is bench scale testing of the CMS WGS-MR at gasifier conditions and includes model development/verification.

Task 4. Preparation of CMS WGS-MR for field test: Focus here is design and fabrication of the pilot scale (86-tube bundle) WGS-MR.

Task 5. Preparation of Pd Module for 2nd Stage H_2 Recovery for field test: Focus here is design and fabrication of the pilot scale Pd module.

Task 6. NCCC Field Testing: Focus here is testing at the NCCC of the two stage process for demonstration and operational stability.

Task 7. Process Design and Engineering: Focus here is

Task 8. Conduct Economic and Environmental Analysis: Focus here is

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

C	Operation under extremely pressure	Modify existing in-house mathematical model to be able to simulate the permeation and reaction kinetics within 15% uncertainty in comparison with the experimental results obtained from the pressure ranging from 10 to 40 bar.	end of 24th month	Report with the experimental results including parameters listed in p. 39 of FOA
E	Field test	Complete the field test documenting MR performance and long term operation for >720 hrs	end of 27th month	Test report including updated parameters listed in p. 39 of FOA

Task	Yr I				Yr II				Yr III				Cost per Task ($)	Cost per BP ($million)
	1	2	3	4	1	2	3	4	1	2	3	4		
	BP 1						BP 2			BP 3				
Task 5.0 Evaluate gas permeation and catalytic reaction under extremely high pressure (USC)													50,000	0.68
Subtask 5.2 Membane 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	

Total Budget: $2.5 millions

F	Design, and engineering Analysis	Complete process design and engineering study for power generation with >90% CO_2 capture and >95% purity following Attachment 3 requested by this FOA	end of 36th month	Report with design and engineering analysis according to the format in Attachment 3 requested by this FOA
G	Economic & environmental Analysis	Complete the economic and environmental analysis for power generation with the format following Attachment 3&4 requested by FOA	end of 36 months	Report with economic/environmental analysis according to Attachment 3&4 requested by this FOA format

M&P Dual Stage Membrane Process

Project Risk and Risk Mitigation Strategies

Description of Risk	Probability	Impact	Risk Management Mitigation and Response Strategies
Technical Risks:			
Insufficient Long term performance stability of the membrane - Pd alloy membrane	moderate	low	Built-in pressure sensor, flow meter and on-line gas analysis are equipped for the field test unit. Thus, in case the risk takes place, operator will be notified and then a replacement membrane will be installed to continue the operation while the damaged membrane will be sent back to our lab for post-mortem analysis.
Insufficient Long term performance stability of the membrane - CMS membrane	low	low	Built-in pressure sensor, flow meter and on-line gas analysis are equipped for the field test unit. Thus, in case the risk takes place, operator will be notified and then a replacement membrane will be installed to continue the operation while the damaged membrane will be sent back to our lab for post-mortem analysis.
Chemical stability of Pd alloy membranes	low	low	Built-in pressure sensor, flow meter and on-line gas analysis are equipped for the field test unit. Thus, in case the risk takes place, operator will be notified and then a replacement membrane will be installed to continue the operation while the damaged membrane will be sent back to our lab for post-mortem analysis.
Contaminants leak through the CMS membrane as a rougher	moderate	low	Installation of a guard beds after the CMS membrane as currently practiced by the catalyst industry.
Ceramic-to-metal joint failure	moderate	low	built-in pressure sensor, flow mete and on-line gas analysis are equipped for the field test unit. Thus, in case the risk takes place, operator will be notified and the a replacement membrane will be installed to continue the operation while the damaged membrane will be sent back to our lab for post-mortem analysis. Our long term risk mitigation will be the use of the standard candle filter mode without purge. The hydrogen recovered will thus be recompressed for the turbine use.
Resource Risks:			
Worldwide Pd supply vs demand for the proposed application	low	low	With our proposed process scheme, we will maximize the recovery of hydrogen by the rougher. Thus, the demand for Pd membrane would be reduced significantly. Our mitigation solution is to increase the guard beds service life to maximize the recovery of hydrogen in the rougher.
Overspending of the allocated budget for a given task	low	low	Overspending will be alarmed in our monthly accounting report. MPT and its subcontractor have been in collaboration for >20 yrs; MPT has the small company mentality while USC work will be performed by the graduate students. Both institutions have the attitude of getting "things" done even extra effort is necessary. Technip has been involved in the engineering and design of the hydrogen plant for decades. The cost estimate to get the work done is very reliable.
Management Risks:			
Lack of effective and timely coordination to get the task completed intime according to the project needs	low	low	Weekly meeting will be held with the USC team to discuss the progress and plan for the subsequent week. Thus, corrective action can be taken when necessary. With Technip experience in hydrogen production plan construction management and design, we will prepare a comprehensive step-by-step task to manage the progress.

Progress and Current Status of Project

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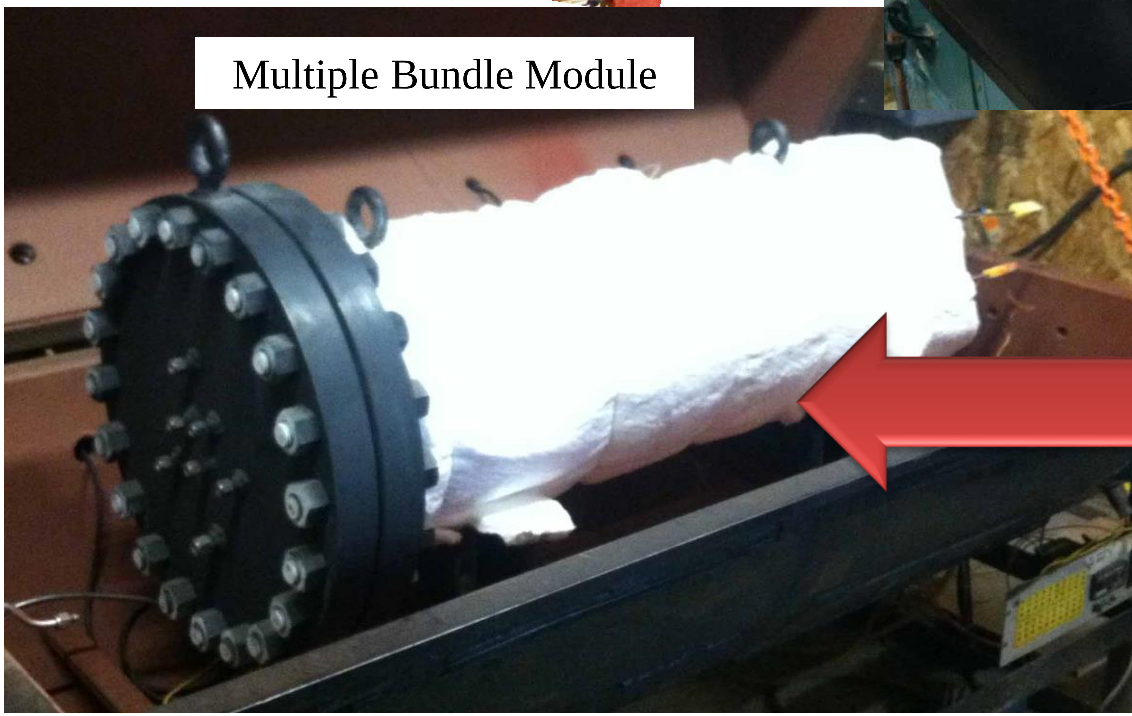
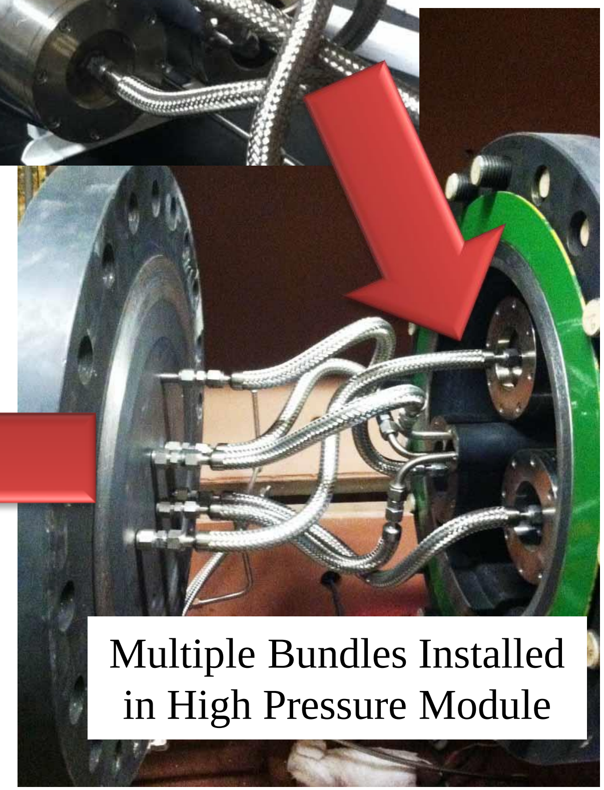
M&P H_2 CMS Selective Membranes

Pilot Module Photographs: 3-CMS Membrane Bundles

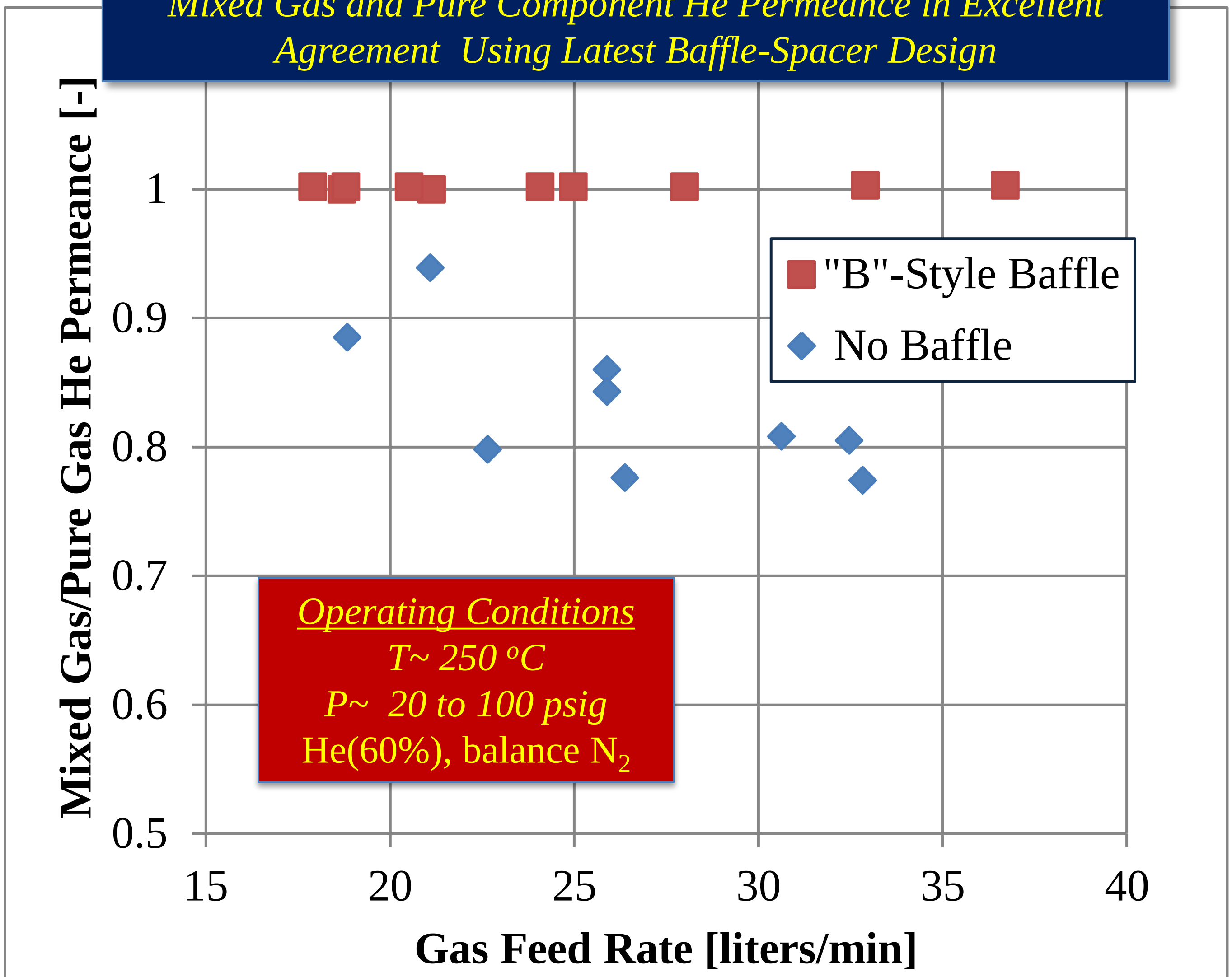


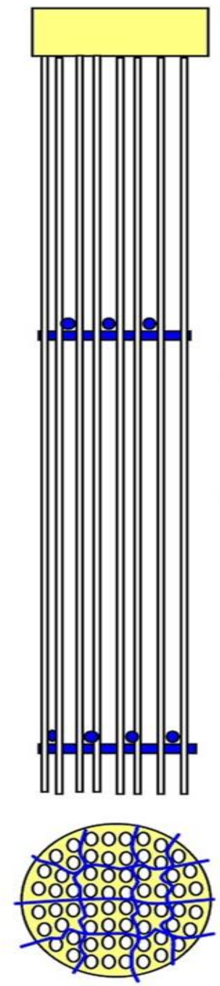


M&P H_2 CMS Selective Membranes

Feed Flow Distribution in CMS Membrane Bundles

Mixed Gas and Pure Component He Permeance in Excellent Agreement Using Latest Baffle-Spacer Design

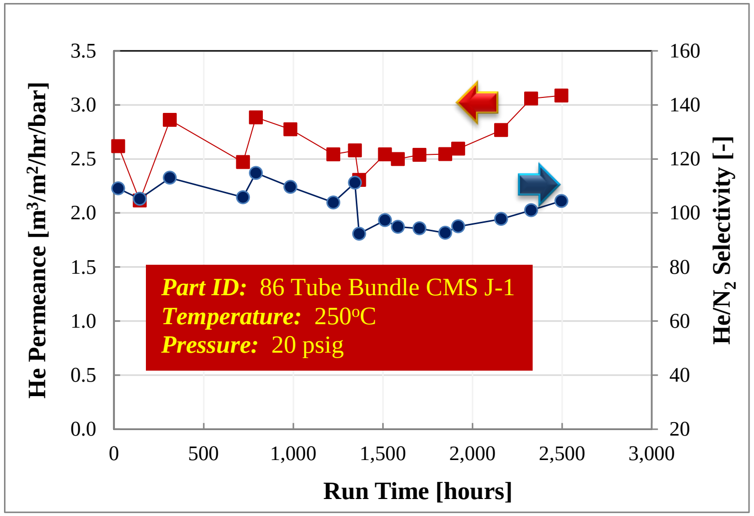


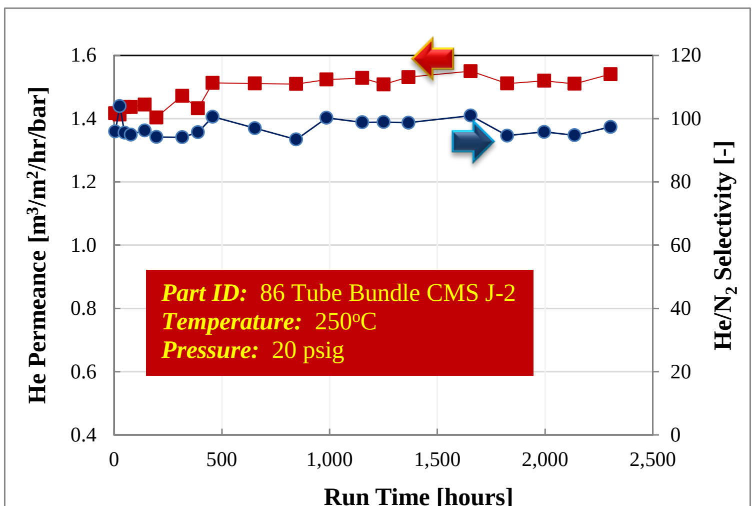


M&P H_2 Selective Membranes

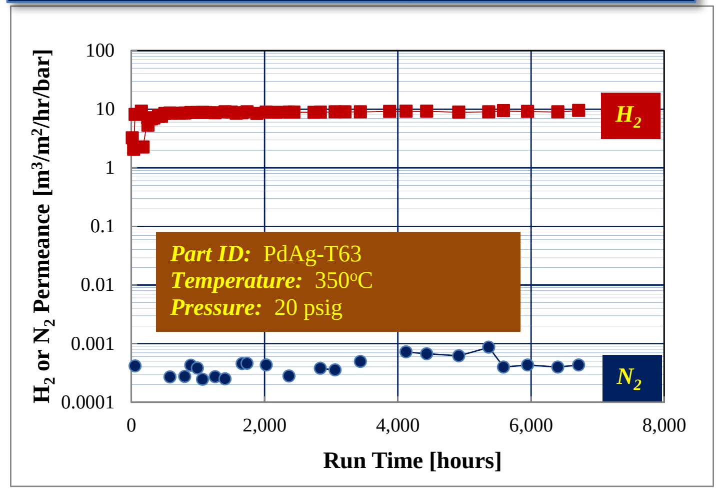
Key Technical Hurdles Focused on Long Term Stability

CMS Bundle Long Term Stability

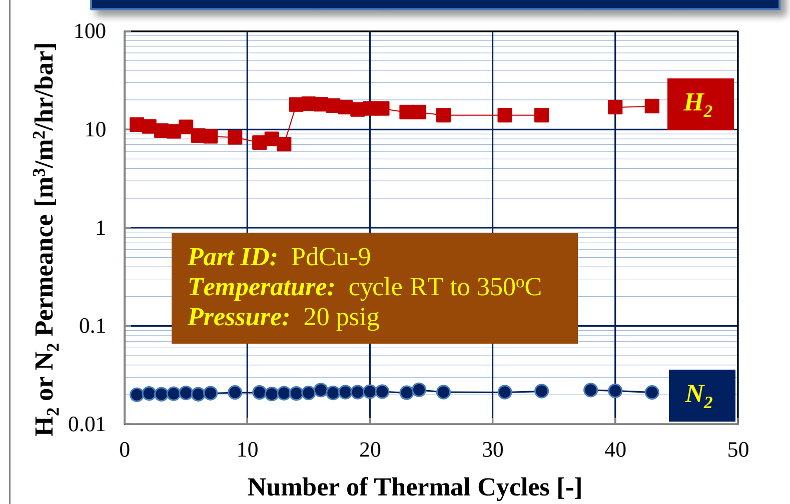




Pd-Alloy Bundle Long Term Stability



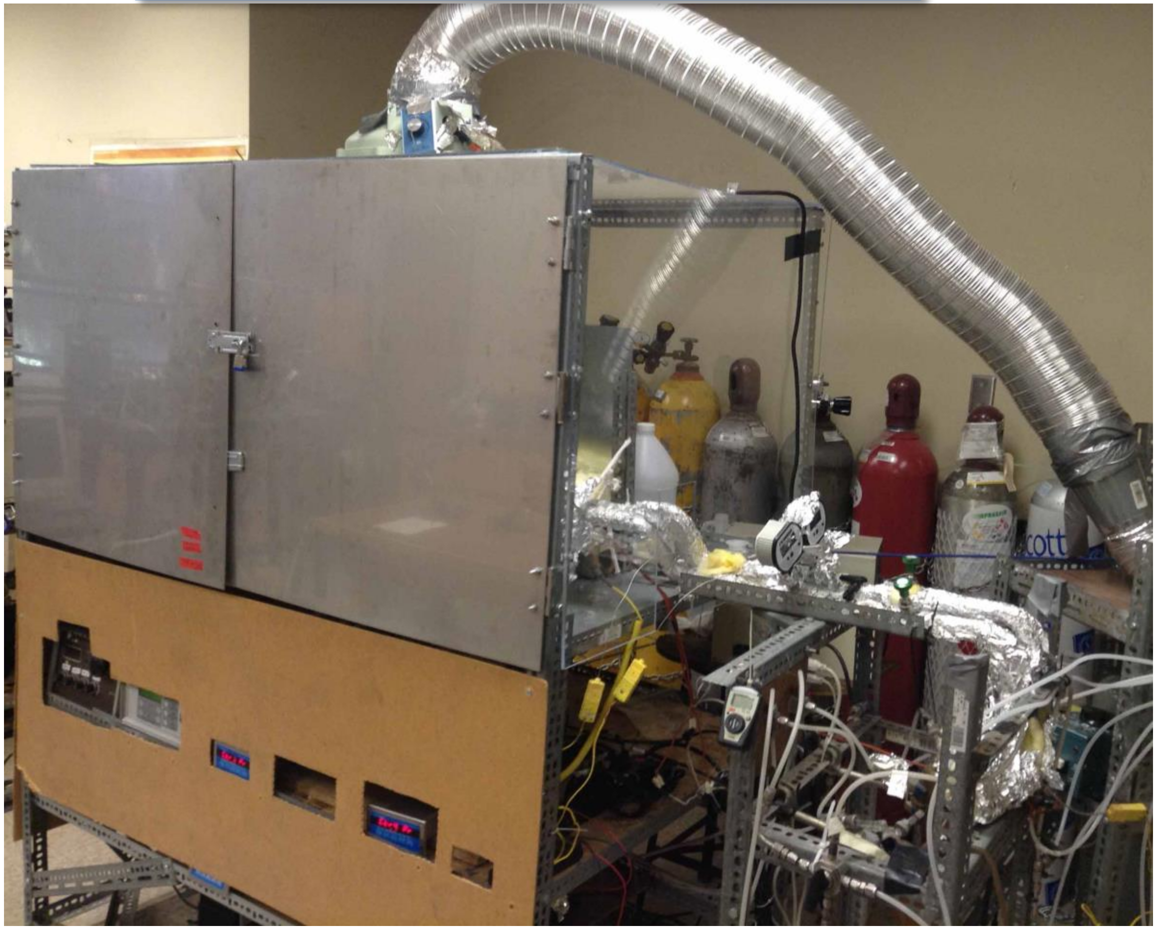
Pd-Alloy H_2 Thermal Cycling



USC WGS-Membrane Reactor

Experimental Setup for WGS-MR at High Pressure

High Pressure System Completed
WGS-MR System



High Pressure Module Completed
CMS Membrane in Reactor Module

Future Plans

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M&P Dual Stage Membrane Process

Next Step

Near Term (next 3 to 6 months):

- ***WGS-MR Kinetics, Stability, and Modeling at High Pressure***
- ***Complete the performance database (CMS and Pd…primarily LT stability)***
- ***WGS-MR module design for field testing at the NCCC (CMS Bundle)***
- ***Optimize the CMS membrane performance for H_2 permeance and CO_2/H_2S rejection.***
- ***High pressure mixed gas H_2/CO_2 performance testing with Pd-alloy membranes***

Intermediate Term (3 to 16 months):

- ***WGS-MR Field Testing at the NCCC***
- ***Extreme pressure testing of the various membrane and module components***

Longer Term (>16 months):

- ***Engineering design and analysis of the overall process scheme***
- ***Economic and pollution prevention/CO_2 capture analysis***

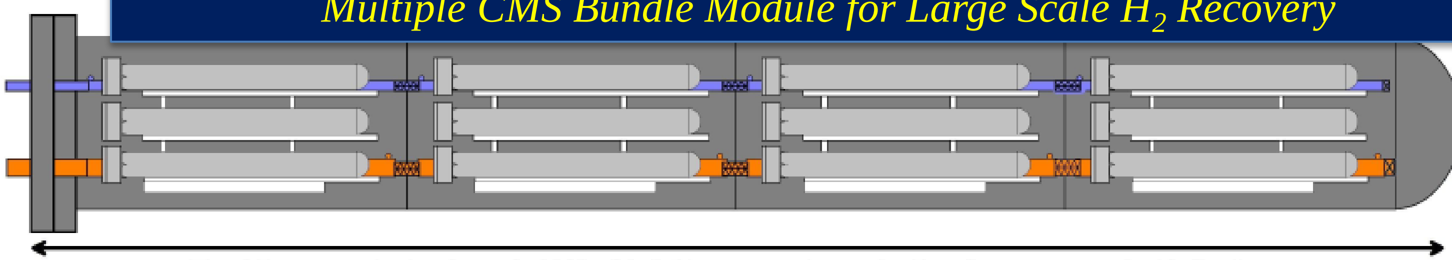
M&P Dual Stage Membrane Process

Commercial Opportunities

CMS Membrane in Refinery Waste Gas H_2 Recovery

- ***Recover H_2 from various refinery waste gases***
- ***We offer high performance and long term stability in highly contaminated gases***
- ***Primary driver is H_2 value…most significant opportunities outside the US.***

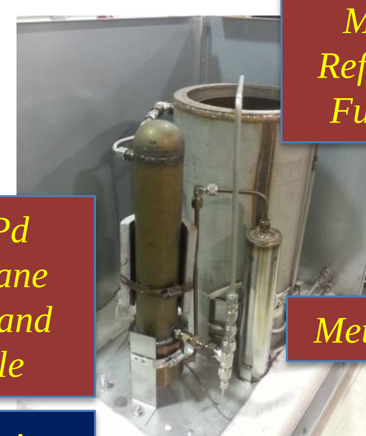
Multiple CMS Bundle Module for Large Scale H_2 Recovery



Total Pressure Jacket Length 200" of 24" Pipe, 4 sections of 7 Bundles connected with flexlines.

Pd-alloy Membranes for H_2 Purification:

- ***High purity H_2 for fuel cell power generators***
- ***High purity H_2 for specialty gas applications***
- ***Primary driver is cost.***



H_2 Purifier for Fuel Cell Application

End

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