Robust and Energy Efficient Dual Stage Membrane Based Process for Enhanced CO$_2$ Recovery

DE-FE0013064

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• Dr. Eric C. Wagner, Technip Stone & Webster Process Technology, Inc.
Project Overview
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
M&P Commercial Ceramic Membranes

Multiple Tube Membrane Bundles – versatile, low cost

1. Close-packed
   Example: conventional micro- and ultrafiltration

2. Spaced
   Ex: porous heat exchangers & catalytic membrane reactors

3. Candle Filter
   Ex: high pressure intermediate temperature gas separations

Our Core Expertise/Technology

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

Carbon molecular sieve (porous, sulfur resistance)

Palladium (dense, excellent selectivity)

Ceramic Substrate
5 μm

Important Features of MPT Inorganic Membranes
- Low cost commercial ceramic support
- High packing density, tube bundle
- Module/housing for high temperature and pressure use

Others, including zeolites, flourinated hydrocarbons, etc.
- **M&P Dual Stage Membrane Process**
  - *Proposed Process: Dual Membrane Stages for IGCC with CCS*

- **Diagram Description:**
  - Syngas from Gasifier after Quench and HRSG.
  - CO$_2$, H$_2$, H$_2$S, H$_2$O to CGCU.
  - CO$_2$, H$_2$ to Pd Membrane.
  - N$_2$, H$_2$O to Turbine for Power Generation.
  - CO$_2$ to CO$_2$ Sequestration.
  - H$_2$ to (optional) Purge.

- **Points:**
  - **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.**
**Preliminary Economic Analysis for IGCC + CCS via Dual Stage**

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

<table>
<thead>
<tr>
<th>Case Descriptions</th>
<th>Production</th>
<th>HHV Efficiency</th>
<th>Required Selling Price</th>
<th>CO₂ Capture</th>
<th>CO₂ Avoided</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Electricity, MWh/Ton</td>
<td>Hydrogen, M SCF/Ton</td>
<td>Efficiency, %</td>
<td>Electricity, mills/kWh</td>
<td>Hydrogen, $/MM Btu</td>
</tr>
<tr>
<td>1a: IGCC w/o CCS - 1-Stage Selexol™ (base case)</td>
<td>2.66</td>
<td>-</td>
<td>39.0</td>
<td>76.3</td>
<td>-</td>
</tr>
<tr>
<td>2a: IGCC w/CCS - 2-Stage Selexol™</td>
<td>2.23</td>
<td>-</td>
<td>32.6</td>
<td>105.5</td>
<td>-</td>
</tr>
<tr>
<td>3a: IGCC w/CCS - CMS &amp; Pd Membranes &amp; 1-Stage Selexol™</td>
<td>2.37</td>
<td>-</td>
<td>34.6</td>
<td>95.1</td>
<td>-</td>
</tr>
</tbody>
</table>

**Note:** Avoided Cost = (COE/MWh w/capture - COE/MWh w/o capture)\( t \) (tonne CO₂ emitted/MWh w/o capture - tonne CO₂ emitted /MWh w/capture); for H₂ production, COE is replaced with the RSP of H₂ 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.**
Field Test at US DOE’s NCCC: CMS Performance Stability

M&P Carbon Molecular Sieve (CMS) Membrane

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
H₂ ~ 10 to 30%
CO ~ 10%
CO₂ ~10%
N₂,H₂O ~Balance

Trace Contaminants
NH₃ ~ 1,000ppm
Sulfur Species ~ 1,000ppm
HCL, HCN, Naphthalenes/Tars, etc.

Performance stability of a multiple tube CMS membrane bundle during H₂ recovery from NCCC slip stream testing. He and N₂ Permeances measured periodically during >400 hr test.
Experimental Results, Simulation, and Predictions

Experimental Results with Model Predictions

**CO Conversion and H₂ Recovery**

- CO Conversion
- H₂ Recovery

Predicted Performance at High Pressure

**Enhanced CO conversion and H₂ Recovery at high pressures**

Operating Conditions: 300°C at 5 atm
M&P Pd-Alloy Membranes

Pd-Alloy Membranes for Residual $H_2$ Recovery

- 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 for Various Parts and Alloys

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$H_2/N_2 = 1,000$

$H_2/N_2 = 300$

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H$_2$ and N$_2$ Permeance Temperature Dependences for a Typical Pd Membrane

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Operating Conditions:
- Temperature: 350°C
- Feed Pressure: 20 psig
- Permeate Pressure: 0 psig

H$_2$ or N$_2$ Permeance ($m^3/m^2/hr/bar$)

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Operating Conditions:
- Feed Pressure: 5 and 30 psig
- Permeate Pressure: 0 psig

---

Temperature [°C]
M&P Pd-Alloy Membranes

*Multiple Tube Bundles High Performance Tube Sheet and Seals*

**High Pressure Tube Sheet**
- Pd Bundle and Ceramic Tube Sheet

**High Performance Package**
- N₂ Flux (Leak Rate) v. Pressure and Temperature

**2nd Generation Module Design**
- Latest Module Design with Graphite Packing

Graph showing H₂ Permeance Region (-15 to 25)

- Bundle ID: MCC12-31
- Description: 12-tube Pd-Ag Bundle Candle Filter Configuration

Graph showing permeance vs. pressure for different temperatures and configurations:
- RT + o-ring
- RT Graphite
- 150°C Graphite
- 250°C Graphite
- 350°C Graphite
Technical Approach/Project Scope
Project Technical Approach

Overview of Project Technical Approach - Workplan

**Budget Period 1**

Task 1. Project Management and Planning

**Budget Period 2**

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 H₂ Recovery for field test: Focus here is design and fabrication of the pilot scale Pd module.

**Budget Period 3**

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
<table>
<thead>
<tr>
<th>Task</th>
<th>Yr I</th>
<th>Yr II</th>
<th>Yr III</th>
<th>Cost per Task</th>
<th>Cost per BP</th>
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<tr>
<td><strong>Task 2.0 Establish performance database for CMS-WGS/MR (USC)</strong></td>
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<tr>
<td>Subtask 2.1 Modification of the present lab-scale WGS?MR system</td>
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<tr>
<td>Subtask 2.2 Generation of performance database</td>
<td></td>
<td></td>
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<tr>
<td>Subtask 2.3 Verification of existing mathematical model</td>
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<tr>
<td>Task 3.0 Preparation of CMS membrane reactor for bench scale test (MPT)</td>
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<tr>
<td>Subtask 3.1 Optimization of CMS membrane separation performance</td>
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<td>Subtask 3.2 Conceptual design on CMS membrane/module/housing to function as a WGS/MR</td>
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<tr>
<td>Subtask 3.3 Fabrication and evaluation of CMS-WGS/MR</td>
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<tr>
<td>Subtask 3.4 Technical input for membrane reactor design/fabrication (Technip)</td>
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<table>
<thead>
<tr>
<th>ID</th>
<th>Title</th>
<th>Planned Date</th>
<th>Verification Methods</th>
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<tbody>
<tr>
<td>A</td>
<td><strong>Generation of the performance database</strong></td>
<td>12th</td>
<td>Report with the database including parameters listed in p. 39 of FOA</td>
</tr>
<tr>
<td>B</td>
<td><strong>Verification of the mathematical model</strong></td>
<td>18th</td>
<td>Report summarizing the deviation for all tests performed</td>
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<tr>
<td>D</td>
<td><strong>Conceptual design for the CMS/MR</strong></td>
<td>12th</td>
<td>CAD drawing of the MR, and parameters listed in p. 39 of FOA</td>
</tr>
</tbody>
</table>
## Task

<table>
<thead>
<tr>
<th>Task</th>
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<td><strong>BP 3</strong></td>
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<tr>
<td>Task 4.0 Prepare a Pd alloy membrane separator for the 2nd stage hydrogen recovery (MPT)</td>
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<tr>
<td>Task 5.0 Evaluate gas permeation and catalytic reaction under extremely high pressure (USC)</td>
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<tr>
<td>Subtask 5.1 Experimental Verification</td>
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<tr>
<td>Subtask 5.2 Membrane and membrane reactor simulation support</td>
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<td>0.67</td>
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<tr>
<td>Task 6.0 Field test with the CMS-WGS/MR and Pd membrane gas separator (MPT)</td>
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<td>Subtask 6.1 Operation of the bench-scale membrane reactor</td>
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<tr>
<td>Subtask 6.2 Long term operation stability</td>
<td>E</td>
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<td></td>
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</tbody>
</table>

### 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

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Media and Process Tech Inc.
## Task Breakdown

<table>
<thead>
<tr>
<th>Task</th>
<th>Task Description</th>
<th>Year I</th>
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<tr>
<td>Subtask 5.2 Membrane and membrane reactor simulation support</td>
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</tr>
<tr>
<td>Task 7.0 Conduct process design and engineering study (Technip &amp; MPT &amp; USC)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F Design, and engineering Analysis</td>
<td>Complete process design and engineering study for power generation with &gt;90% CO₂ capture and &gt;95% purity following Attachment 3 requested by this FOA</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>G Economic &amp; environmental Analysis</td>
<td>Complete the economic and environmental analysis for power generation with the format following Attachment 3&amp;4 requested by FOA</td>
<td></td>
<td></td>
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<td></td>
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</table>

**Total Budget: $2.5 millions**
### Project Risk and Risk Mitigation Strategies

<table>
<thead>
<tr>
<th>Description of Risk</th>
<th>Probability</th>
<th>Impact</th>
<th>Risk Management Mitigation and Response Strategies</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Technical Risks:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Insufficient Long term performance stability of the membrane - Pd alloy membrane</td>
<td>moderate</td>
<td>low</td>
<td>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.</td>
</tr>
<tr>
<td>Insufficient Long term performance stability of the membrane - CMS membrane</td>
<td>low</td>
<td>low</td>
<td>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.</td>
</tr>
<tr>
<td>Chemical stability of Pd alloy membranes</td>
<td>low</td>
<td>low</td>
<td>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.</td>
</tr>
<tr>
<td>Contaminants leak through the CMS membrane as a rougher</td>
<td>moderate</td>
<td>low</td>
<td>Installation of a guard beds after the CMS membrane as currently practiced by the catalyst industry.</td>
</tr>
<tr>
<td>Ceramic-to-metal joint failure</td>
<td>moderate</td>
<td>low</td>
<td>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. 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.</td>
</tr>
<tr>
<td><strong>Resource Risks:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Worldwide Pd supply vs demand for the proposed application</td>
<td>low</td>
<td>low</td>
<td>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.</td>
</tr>
<tr>
<td>Overspending of the allocated budget for a given task</td>
<td>low</td>
<td>low</td>
<td>Overspending will be alarmed in our monthly accounting report. MPT and its subcontractor have been in collaboration for &gt;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 &quot;things&quot; 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.</td>
</tr>
<tr>
<td><strong>Management Risks:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack of effective and timely coordination to get the task completed intime according to the project needs</td>
<td>low</td>
<td>low</td>
<td>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.</td>
</tr>
</tbody>
</table>
Progress and Current Status of Project

Media and Process Technology Inc. (M&P)
1155 William Pitt Way
Pittsburgh, PA 15238 - 1678
M&P H₂ CMS Selective Membranes

Pilot Module Photographs: 3-CMS Membrane Bundles

Membrane Bundle

Membrane Bundle Enclosure

Multiple Bundle Module

Multiple Bundles Installed in High Pressure Module
M&P H₂ 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

Operating Conditions
T~ 250 °C
P~ 20 to 100 psig
He(60%), balance N₂

Mixed Gas/Pure Gas He Permeance [-]

Gas Feed Rate [liters/min]
M&P H₂ Selective Membranes

Key Technical Hurdles Focused on Long Term Stability

**CMS Bundle Long Term Stability**

- **Part ID:** 86 Tube Bundle CMS J-1  
  **Temperature:** 250°C  
  **Pressure:** 20 psig

- **Part ID:** 86 Tube Bundle CMS J-2  
  **Temperature:** 250°C  
  **Pressure:** 20 psig

**Pd-Alloy Bundle Long Term Stability**

- **Part ID:** PdAg-T63  
  **Temperature:** 350°C  
  **Pressure:** 20 psig

**Pd-Alloy H₂ Thermal Cycling**

- **Part ID:** PdCu-9  
  **Temperature:** cycle RT to 350°C  
  **Pressure:** 20 psig
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
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
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.

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.
End