Composite Pd and Alloy Porous Stainless Steel Membranes for Hydrogen Production and Process Intensification

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Worcester Polytechnic Institute  
Department of Chemical Engineering  
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Project ID: PD007

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

Timeline

- Start: 5/7/2007
- Finish: 5/6/2010
- 100% Complete

Budget

- Total Project Cost: $1,602,922
  - DOE Share: $1,256,226
  - Recipient Share: $346,696
- Funding Received:
  - FY08: $442,785
  - FY09: $420,638
  - FY10: $392,803

Barriers

- Barriers Addressed:
  - Long-term selectivity stability & re-producibility
  - H$_2$ flux targets
  - Mixed gas & long-term WGS reaction studies
  - Steady-state & unsteady-state CMR modeling simulations
  - Process intensification analysis & process control strategies
  - Absorbent selection & PSA system build-up and testing

Technical Targets**

<table>
<thead>
<tr>
<th>Year</th>
<th>H$_2$ Flux [scfh/ft$^2$] $^\S$</th>
<th>Temp. [°C]</th>
<th>ΔP max. [psi]</th>
<th>H$_2$ Purity</th>
<th>Sulfur Tolerance</th>
</tr>
</thead>
<tbody>
<tr>
<td>2010</td>
<td>200</td>
<td>300-600</td>
<td>400</td>
<td>99.5%</td>
<td>20 ppm</td>
</tr>
<tr>
<td>2015</td>
<td>300</td>
<td>250-500</td>
<td>800-1000</td>
<td>99.9%</td>
<td>&gt;100 ppm</td>
</tr>
</tbody>
</table>

$^\S$ @ 100 psi ΔP H$_2$ partial pressure

CO Tolerance: Yes; WGS Activity: Yes

Subcontractor

- Adsorption Research Inc. (ARI)

** DOE-NETL Test Protocol v7 – 05/10/2008
Project Objectives & Relevance

- Synthesis of composite Pd and Pd/alloy porous Inconel membranes for WGS shift reactors with long-term thermal, chemical and mechanical stability with special emphasis on the stability of hydrogen flux and selectivity.
- Demonstration of the effectiveness and long-term stability of the WGS membrane shift reactor for the production of fuel-cell quality hydrogen.
- Research and development of advanced gas clean-up technologies for sulfur removal to reduce the sulfur compounds to <2 ppm.
- Development of a systematic framework towards process intensification to achieve higher efficiencies and enhanced performance at a lower cost.
- Rigorous analysis and characterization of the behavior of the resulting overall process system, as well as the design of reliable control and supervision/monitoring systems.
- Assessment of the economic viability of the proposed intensification strategy through a comprehensive calculation of the cost of energy output and its determinants (capital cost, operation cost, fuel cost, etc.), followed by comparative studies against other existing pertinent energy technologies.
Approach: Coal Gasification & CMR

H₂ Production via the Conventional Technology:

Coal Gases → HTS → LTS → PrOx → PSA → H₂

Coal Gases → Sulfur Removal → Advª Sulfur Clean-up → WGS → H₂

Novel Catalytic Membrane Reactor (CMR):
## Project Schedule & Milestones

<table>
<thead>
<tr>
<th>Tasks</th>
<th>Year 1</th>
<th>Year 2</th>
<th>Year 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q1 Q2 Q3 Q4</td>
<td>Q1 Q2 Q3</td>
<td>Q1 Q2 Q3</td>
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<tr>
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<td>Q1 Q2 Q3</td>
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</tr>
<tr>
<td>Gas Clean-up &amp; Fast PSA using Structured Adsorbent</td>
<td>M1 G1</td>
<td>M2</td>
<td>M3</td>
</tr>
<tr>
<td>Membrane Synthesis</td>
<td>M4</td>
<td>M5</td>
<td>G2</td>
</tr>
<tr>
<td>Membrane Characterization &amp; Reactor Performance</td>
<td>M6</td>
<td>M7</td>
<td></td>
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<tr>
<td>Membrane Reactor Modeling</td>
<td>M8</td>
<td>M9</td>
<td>M10</td>
</tr>
<tr>
<td>Process Intensification</td>
<td></td>
<td></td>
<td>M11</td>
</tr>
<tr>
<td>Process Control System; Design &amp; Implementation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Process Monitoring System; Design &amp; Implementation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Program Management &amp; Reporting</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Tasks Overview
- **Membrane Reactor Modeling**: M1, G1, M2, M3, M4, M8, M9, M10, M11
- **Process Intensification**: M5, G2, M7, M11
- **Process Control System; Design & Implementation**: M6
- **Process Monitoring System; Design & Implementation**: M10
- **Program Management & Reporting**: M11
**Membrane Properties & Permeation Test Set-up**

- **Membrane:**
  
  Pd supported on porous Inconel (media grade 0.1 µm)

- **Method of Preparation:**
  Electroless Plating

- **Geometry:**
  
  Tubular (Plated on the outside of a tube)

- **Membrane Area:**
  
  ≈ 25 cm²

Similar setup equipped w/ pre-heater, mixer, cold trap & GC was utilized for the mixed gas & WGS reaction tests
Excellent long-term H₂/He selectivity stability was achieved over a total testing period of ~3550 hours (>147 days).
Reproducible Long-Term Selectivity Stability: Membranes #030 7.9 µm Pd, #031 7.0 µm Pd & #033 8.7 µm Pd

Excellent leak mitigation and re-producible long-term H₂/He selectivity stability via high temperature pre-Annealing (at 550°C/He/12h) and surface Polishing (pAP) treatments

- **#030 7.9 µm Pd**
  - H₂/He ≅ ∞ at 450°C
  - H₂ purity: ≥ 99.999%
  - 1400 hours (>58 days)

- **#031 7.0 µm Pd**
  - H₂/He ≅ 4500 at 450°C
  - H₂ purity: ≥ 99.99%
  - 2200 hours (>90 days)

- **#033 8.7 µm Pd**
  - H₂/He ≅ 9725 at 450°C
  - H₂ purity: ≥ 99.99%
  - 800 hours (>32 days)

Also delivered a ½” OD, 12” long Pd/Inconel membrane for DoD-Ballards

Technical Accomplishments
Technical Accomplishments

- Mixed gas permeation testing for an additional ~3000 hours at ~400°C & at a ΔP range of 1-14 atm (P_{Low}=1 atm) w/ stable H₂ Flux, H₂/He Selectivity & no significant increase in He leak after successive testing at 400°C
- Below 10 scfh, high recovery (>90%) and no significant/additional inhibiting effect of ~19% steam or CO on H₂ flux
- Permeate: H₂ only, no other gases were detected
- Retentate: High-pressure CO₂ !!!
Progress Towards DOE H₂ Flux Targets

Membrane _032_3.5 µm Pd High-P Flux Data
(As of 12/05/2008)

At 442°C & at a ∆P of 100 psi (P$_{\text{High}}$ = 115 psia & P$_{\text{Low}}$ = 15 psia), the H$_2$ flux of the 3-5 µm thick Pd/Inconel membrane #032 was as high as ~359 scfh/ft$^2$ at the end of ~285 hours of testing with H$_2$/He selectivity of ~450 (H$_2$ purity ≥99.8%), which exceeded the DOE’s 2010 and 2015 H$_2$ flux targets.
Mixed Gas Testing of AA-6

**Temperature dependent permeance inhibition due to CO observed at 350 and 400°C, insignificant above 400°C**

**Gas boundary layer resistance observed by comparison of Mixture A (high diffusivity H₂/He) and Mixture B (low diffusivity H₂/CO₂)**

**H₂ recovery of up to 92% achieved at low GHSV**

**Pₜₐₜₜ = 212 psia**
**Pₜₜ₂ = 116 psia**

(Membrane: AA-6)
**Area = 0.025 ft²**
**Selectivity > 2200**
High CO conversion, in significant excess of EQ, was achieved for all experiments.

Evidence of coke formation was only observed in experiments with low H₂O/CO = 1.1.

Flux @ 450°C = 35.7 scfh/ft² (ΔP of 14.7 psi)
**WGS CMR**$_{11.6 \, \mu m \, Pd}$ : Syngas Feed

- **Feed Conditions**
  - 22.7% CO, 22.0% H$_2$, 9.9% CO$_2$, 45.4% H$_2$O
  - H$_2$O:CO = 2:1
  - T (°C): 400, 450
  - $P_{\text{Total}} = 206$ psia
  - (Membrane: AA-8)
  - Selectivity > 1500

- **Technical Accomplishments**
  - CO conversion approached ‘dynamic equilibrium’ as time factor increased above ~12 lb$_{cat} \ast h/\text{lb-mol}$
  - At low time factor, H$_2$ recovery and CO conversion were limited by the H$_2$ permeance of the membrane

- **Flux @ 450°C = 44.0 scfh/ft$^2$ (ΔP of 14.7 psi)**
### Technical Accomplishments

- **Stable CO conversion and H₂ recovery** were observed for up to 80 hours.
- **Stable H₂ permeance** after WGS test.
- **Significant selectivity decline** after test.

### Feed Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>CO</td>
<td>22.7%</td>
</tr>
<tr>
<td>H₂</td>
<td>22.0%</td>
</tr>
<tr>
<td>CO₂</td>
<td>9.9%</td>
</tr>
<tr>
<td>H₂O</td>
<td>45.4%</td>
</tr>
<tr>
<td>H₂O/CO</td>
<td>2.0</td>
</tr>
<tr>
<td>GHSV (h⁻¹)</td>
<td>4500</td>
</tr>
<tr>
<td>T (°C)</td>
<td>450</td>
</tr>
</tbody>
</table>

### Membrane: AA-8R

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selectivity (F_{H₂}/F_{He})</td>
<td>4000</td>
</tr>
<tr>
<td>After WGS Experiment</td>
<td>400 (-90%)</td>
</tr>
<tr>
<td>Permeance (scfh/ft² psi⁰.⁵)</td>
<td>27.9</td>
</tr>
<tr>
<td>After WGS Experiment</td>
<td>26.6 (-4.6%)</td>
</tr>
</tbody>
</table>

### Flux @ 450°C = 44.3 scfh/ft² (ΔP of 14.7 psi)
The permeability had a more prevalent effect on the adiabatic reactor H₂ recovery.

The adiabatic reactor could achieve high X₇O and R₇H₂ only at low inlet flow rates due to admitting the feed at low temperature to protect the membrane. (X₇O = 85% and R₇H₂ = 90% at GHSV = 1600h⁻¹).

Isothermal MR performance surpasses the adiabatic MR for the current reaction conditions.

Feed: Slurry-feed coal-derived syngas*

Adiabatic:
#1 T_{feed} = 300°C
#2 T_{feed} = 260°C
P_{Rxn} = 220 psia
P_{Tube} 14.7 psia
T_{Iso-Rxn} = 450°C
α_{H₂/He} = ∞
GHSV = 8081h⁻¹
Process Intensification - Effect of Bulk Catalyst Density

**Isothermal MR**

(T = 450°C / \( P_{Rxn} = 220 \text{psia} / \text{GHSV} = 1600 \text{h}^{-1} \))

- \( X_{CO} - \rho_{Bulk,Max} \)
- \( X_{CO} - 8\% \rho_{Bulk,Max} \)
- \( P_{H2} - \rho_{Bulk,Max} \)
- \( P_{H2} - 8\% \rho_{Bulk,Max} \)

**Adiabatic MR**

(T_{feed} = 260°C / \( P_{Rxn} = 220 \text{psia} / \text{GHSV} = 1600 \text{h}^{-1} \))

- \( T - \rho_{Bulk,Max} \)
- \( T_{Reaction} - 8\% \rho_{Bulk,Max} \)
- \( P_{H2} - \rho_{Bulk,Max} \)
- \( P_{H2} - 8\% \rho_{Bulk,Max} \)

- Packing the reactor with less catalyst would not affect the production specifications and would reduce the cost.

- ↓\( \rho_{Bulk} \)  ➸  Controlled \( T_{Rxn \ rise} \)  ➸  \( V_{\text{effective}} \) increased from 40% to 80% of the \( V_{\text{total}} \)

\[
\rho_{Bulk,\text{max}} = \frac{W_{\text{Cat,Max}}}{V_{\text{Reactor}}}
\]

<table>
<thead>
<tr>
<th>GHSV =3200h^{-1}</th>
<th>Isothermal</th>
<th>Adiabatic</th>
</tr>
</thead>
<tbody>
<tr>
<td>( %\rho_{Bulk,Max} )</td>
<td>8</td>
<td>100</td>
</tr>
<tr>
<td>PBR</td>
<td>MR</td>
<td>PBR</td>
</tr>
<tr>
<td>( X_{CO}[%] )</td>
<td>79.5</td>
<td>97</td>
</tr>
<tr>
<td>( F_{H2} [\text{scfh}] )</td>
<td>0.89</td>
<td>1.1</td>
</tr>
</tbody>
</table>
Dusty Gas Model (DGM) for the multi-component gas diffusion

- $\text{H}_2 + \text{CO} + \text{H}_2\text{O} + \text{CO}_2$

Separation Factor:

$$S_F = \frac{\left[ \frac{x_{\text{H}_2}}{x_{\text{CO}} + x_{\text{H}_2\text{O}} + x_{\text{CO}_2}} \right]_{\text{Permeate Side}}}{\left[ \frac{x_{\text{H}_2}}{x_{\text{CO}} + x_{\text{H}_2\text{O}} + x_{\text{CO}_2}} \right]_{\text{Reaction Side}}}$$

Technical Accomplishments:

- $\alpha_{\text{H}_2/\text{He}}$ does not affect $X_{\text{CO}}$ within the range of $50 - 50 \times 10^3$.
- Experimental $\alpha_{\text{H}_2/\text{He}} \geq 1000$ (Data obtained under this project)
- No detectable CO in the permeate side of the Pd-based membrane with $\alpha_{\text{H}_2/\text{He}} = 1000$
The main objective of the proportional integral controller was to reduce the CO fractions at the reactor exit by manipulating the inlet steam flow rate to enhance the MR performance by increasing the CO conversion. (Assume $\alpha_{H_2/He} = \infty$)

**Regulator Problem [Disturbance rejection]**

$P_T = 220 \rightarrow 147$ psia

**Servo Mechanism Problem [Set-point tracking]**

Set point $= 1.9 \rightarrow 0.9 \% \ CO^{\text{Dry}} @ \text{Rxn side exit}$

$PBR f_{CO} = 7\%$ (Dry basis)

**Tuning Targets**

- Smooth transition
- Energy efficient
- (Less steam)
- Fast & stable response
- No oscillation

Controller tuning for $K_c$ - RP
Optimum $K_c = 0.006$ and $\tau_I = 1.25$ s

$X_{CO} = 97.1\% \ & \ H_2O:CO = 3.3$

Controller tuning for $K_c$ - SP
Optimum $K_c = 0.009$ and $\tau_I = 1$ s

$X_{CO} = 97.3\% \ & \ H_2O:CO = 6.8$
Collaborations

Adsorption Research Inc. (ARI); sub
(Through telephone conversations and quarterly report to the prime)

- ARI completed adsorption selection & property measurement for Zeolite 5A, Zeolite 13X, NaY and Hisiv3000
- The equilibrium isotherms measurements & the transient uptake tests to evaluate both short-time and long-time diffusion behavior of the adsorbents 5A, 13X, NaY and Hisiv3000 were conducted at 200 and 230°C for CO₂, COS, H₂S and the water vapor.
- Completed the pressure swing adsorption (PSA) system and demonstrated the cyclic operation at 200°C & 200 psia with 5A to ensure the accuracy of the simulations.
- For a three-component mixture, showed a recovery of 99+% of helium when a recycle of the blow-down gas was used.
Proposed Future Work (FY10 & FY11)

- Scaling-up to 1” & 2” OD Membranes
- Continue WGS reaction and mixed gas testing studies
- Complete 2010 technical target screening and qualification tests* phase 1 and phase 2
- Synthesis of thin separation layers to achieve higher H₂ flux using support with minimum mass transfer resistance
- Continue Pd/Au alloying studies to improve H₂ flux
- Conduct long-term sulfur poisoning & recovery experiments
- Further refinement & improvement of the CMR model
- Continue process intensification & performance assessment analyses coupled with process control strategies
- Initiate economical analysis for the proposed process intensification framework
- Complete testing of a Pressure Swing Adsorption (PSA) system (sub: ARI)

* Table 4 in DOE-NETL Test Protocol v7 – 05/10/2008
Project Summary

- Achieved excellent long-term H₂/He selectivity stability of essentially infinite over a total testing period of ~3550 hours (>147 days) at 300-450°C & at a ΔP of 15-100 psi (P_{Low}=15 psia).
  - Conducted an additional ~3000 hours of mixed gas permeation testing (61.7% H₂, 37.1% CO₂ & 1.2% CO w/ and w/o 19% Steam) at 400°C & ΔP of 1-14 atm (P_{Low}=1 atm) that resulted in stable H₂ flux and minimal inhibition effects of steam, CO₂ and CO at T > 400°C & low total flow rates (≤ 5000 sccm).
- At 450°C, the long-term H₂/He selectivity stability was successfully re-produced with several membranes with H₂ purity ≥99.99% over a testing period of 30-90 days.
- Flux of ~359 scfh/ft², which exceeded the DOE’s 2010 and 2015 H₂ flux targets [T=442°C & ΔP of 100 psi (with P_{Low}=15 psia)].
- Reduced the number of synthesis steps for the large scale preparation for potential commercialization of WPI’s composite Pd-based membrane production technologies.

- Completed mixed gas & WGS testing of composite Pd/Inconel membranes:
  - Effects of temperature dependent CO inhibition and gas boundary layer mass transfer resistance were isolated in mixed gas experiments.
  - 98% CO conversion and 81% H₂ recovery were achieved in a 18.1 µm thick Pd-based CMR operated at 450°C, ΔP=200 psi (P_{Low}=15 psia) and GHSV_{stp} = 2900 h⁻¹, with a CO and steam feed, exceeding the equilibrium conversion of 93%.
  - 95% CO conversion and 83% H₂ recovery were achieved for over 80 hours of WGS testing in a 13.1 µm thick Pd-based CMR operated at 450°C, ΔP=200 psi (P_{Low}=15 psia) and GHSV_{stp} = 4500 h⁻¹, with syngas feed, exceeding the equilibrium conversion of 76%.
Successfully completed steady-state MSR & WGS reaction modeling studies & process intensification analysis:

- Studied the effect of permeability in Adiabatic & Isothermal membrane reactor, Adiabatic feed temperature, catalyst loading and changes in CO conversion, and the effect of selectivity on H₂ purity and CO conversion by utilizing the Dusty Gas Model.

Successfully completed unsteady-state WGS reaction modeling studies and implemented process control strategies:

- Characterized the reactor’s dynamic behavior via detailed simulation studies based on the lumped reactor model approximation & showed that the transient state ended in 10 seconds with $X_{\text{CO,iso}} = 97\%$ when the coal-derived syngas feed was used.
- Model-based analysis of the automatically controlled MR was able to recover the disturbed system due to pressure drop from 220 to 147 psia in 20 seconds and kept $X_{\text{CO,iso}}$ at 97%. The CO fraction of 2% was reduced to 1% with the application of the servo mechanism controller.
- The retentate stream consisted of mostly CO₂ and H₂ would be ready to be sequestered at high pressure after the energy value of the remaining H₂ is used.

Completed property & isotherm measurements for the selected adsorbents (Sub, ARI).
Completed the PSA system construction and initiated PSA testing at 200°C and a feed pressure of 200 psia (with $P_{\text{low}} = 1$ atm) (Sub, ARI).
# Project Summary Table: Permeation Results

<table>
<thead>
<tr>
<th>DOE Targets§</th>
<th>Current WPI Membranes (1/2&quot; OD, 2.5&quot; Length, ~24 cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2010</td>
<td>2015</td>
</tr>
<tr>
<td>Flux [scfh/ft²]</td>
<td>200</td>
</tr>
<tr>
<td>ΔP (psi) H₂ partial pressure (P&lt;sub&gt;Low&lt;/sub&gt;=15 psia)</td>
<td>100*</td>
</tr>
<tr>
<td>Temperature [°C]</td>
<td>300-600</td>
</tr>
<tr>
<td>H₂/He Selectivity</td>
<td>n/a</td>
</tr>
<tr>
<td>Total Test Duration [hours]</td>
<td>n/a</td>
</tr>
<tr>
<td>Thickness [µm]</td>
<td>n/a</td>
</tr>
<tr>
<td>WGS Activity</td>
<td>Yes</td>
</tr>
<tr>
<td>CO Tolerance</td>
<td>Yes</td>
</tr>
<tr>
<td>S Tolerance [ppm]</td>
<td>20</td>
</tr>
<tr>
<td>H₂ Purity</td>
<td>99.5%</td>
</tr>
<tr>
<td>ΔP Operating Capability (Max. Sys. Pressure, psi)</td>
<td>400</td>
</tr>
</tbody>
</table>

§ DOE-NETL Test Protocol v7 - 05/10/2008, * Standard conditions are 150 psia hydrogen feed pressure and 50 psia hydrogen sweep pressure

** Maximum pressure tested, however, the ΔP can be higher since previous WPI membranes were tested up to 600 psi under MSR reaction conditions.
# Project Summary Table: Mixed Gas & WGS Reaction Results

<table>
<thead>
<tr>
<th></th>
<th>DOE Targets§</th>
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<td>2015</td>
</tr>
<tr>
<td>Flux [scfh/ft²]</td>
<td>200</td>
<td>300</td>
</tr>
<tr>
<td>ΔP (psi) H₂ partial pressure (P&lt;sub&gt;Low&lt;/sub&gt;=15 psia)</td>
<td>100**</td>
<td>100**</td>
</tr>
<tr>
<td>Temperature [°C]</td>
<td>300-600</td>
<td>250-500</td>
</tr>
<tr>
<td>H₂/He Selectivity</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Total Test Duration [hours]</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Thickness [µm]</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>WGS Activity</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>CO Tolerance</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>S Tolerance [ppm]</td>
<td>20</td>
<td>&gt;100</td>
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<tr>
<td>H₂ Purity</td>
<td>99.5%</td>
<td>99.99%</td>
</tr>
<tr>
<td>ΔP Operating Capability (Max. System Pressure, psi)</td>
<td>400</td>
<td>800-1000</td>
</tr>
</tbody>
</table>

§ DOE-NETL Test Protocol v7 - 05/10/2008

* R - repaired by mechanical treatment and Pd plating

** Standard conditions are 150 psia hydrogen feed pressure and 50 psia hydrogen sweep pressure