Water-Gas Shift
Membrane Reactor Studies

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H₂ Membrane Reactor Concept

*WGS Reaction: CO + H₂O ⇌ CO₂ + H₂
*High-T for favorable kinetics
*Membrane removes H₂ to “shift” unfavorable equilibrium to produce more H₂

Pure Hydrogen

Synthesis Gas...
(H₂, CO₂, CO, plus H₂O,)

High Pressure CO₂
Project Rationale

• Designing WGS membrane reactors requires the consideration of reaction kinetics and mass transport phenomena
  – Forward and Reverse Water-Gas Shift Kinetics
  – Catalytic Effect of Reactor Materials, Membrane Materials
  – Need for Heterogeneous Catalysis?
  – Hydrogen Flux and Selectivity Through Membrane
  – Durability of Membrane in Extreme Environments

• Lab-scale approach
  – Address scientific issues using mainly thick (i.e. 10’s of microns), easy-to-manufacture membranes of precise composition
  – Incorporate the optimal alloy composition into membrane reactors of various geometries that have high flux with a highly permeable support
Objectives

• Evaluate water-gas shift (WGS) reaction kinetics and membrane flux using industrial gas mixtures and conditions

• Test the feasibility of enhancing the WGS at high temperature without added catalyst particles by using a membrane reactor

• Determine the catalytic effect of metal shell materials (e.g. Inconel) and membrane surfaces (e.g. Pd) on the WGS reaction
Budget

• Funding determined yearly thru submission of Annual Operating Plan proposals to EERE

• FY04 Funding = $200k

• EERE funding is 50% contribution to overall project; the other 50% is from FE
Project Timeline

10/01 - 10/03 11/03-08/04 09/04-09/06

Phase I  Phase II  Phase III

1  2  3  4  5  6  7  8

- **Phase I – Hi-T, Hi-P WGS Reaction Kinetics**
  1. Complete reverse WGS reaction kinetics study
  2. Complete forward WGS reaction kinetics study
  3. Determine catalytic effects of membrane/reactor materials

- **Phase II – Membrane Reactor Development**
  4. Fabricate different Pd membrane reactor prototypes
  5. Determine feasibility of Pd membrane reactor prototypes

- **Phase III – WGS Membrane Reactor Testing**
  6. Complete baseline testing of Pd-Cu membrane reactor
  7. Complete validation testing of optimized WGS MR system
  8. Operate WGS MR in presence of contaminants (e.g. H₂S)
Technical Barriers and Targets

• **Barrier A**: Fuel Processor Capital Costs—specifically single-step shift w/integrated membrane technology
  - Related 2005 Targets: Purification at a Cost of $0.11/kg H₂ and H₂ Efficiency of 82%

• **Barrier AB**: H₂ Separation & Purification—specifically membrane separation with the shift reaction in one unit operation
  - Related 2005 Targets: Flux Rate of 100 scfh/ft², Cost of $100-150/ft², Durability of 50,000 hours, Operating Temperature of 300-600°C, and Parasitic Power of 3.0 kWh/1000 scfh
NETL Hydrogen Separation Facilities

- 3 H₂ Membrane Test Units
- Constructed FY99 to FY02
- Temperatures to 900°C
- Pressures to 400 psi
- Disk & tubular membranes
- 1/4” to 1/2” membranes
- Feed gas flexibility
- Membrane separation & reactor configurations
- “Clean” and “sulfur-laden” gas feedstocks
- Online analysis of products by GC
Project Safety

• Safety vulnerability is addressed thru NETL’s Safety Analysis & Review System (SARS). This process identifies, analyzes, minimizes all ES&H hazards. It ensures that all projects have a SARS Permit before operations begin.

• Management of changes is also addressed for any project or facility modifications thru the NETL SARS process.

• All H$_2$-related reactors are contained in purge vessels thru which an inert gas (N$_2$) is continually streaming.

• Gas alarm systems are in place in areas where gases such as H$_2$, H$_2$S, CO, CO$_2$, etc. are in use.
FY04 Approach

• Conduct baseline testing of the fWGS reaction at high pressure with no catalyst in the 300-900°C range in the prototype Pd & PdCu membrane reactors.

• Re-design the PdCu membrane reactor to maximize membrane area and minimize thickness in order to enhance conversions of CO and H₂O to H₂ and CO₂.

• Determine H₂ permeance of PdCu in the presence of major gasifier components, such as CO, H₂O, CO₂.
FY04 Accomplishments

• Completed forward WGS kinetics study
  – Gas phase kinetics
  – Correlation developed for high T, high P fWGS reaction

• Determined catalytic effect of membrane and reactor shell materials
  – Inconel – example of reactor shell material
  – Pd and Pd/Cu – examples of membrane materials

• Evaluated effect of CO and H2O on H2 permeability

• Fabricated 3 types of Pd MR for trials
  – Pd flat disk in Inconel: assessment of effect of side reactions
  – Thin Pd tubes: effect of temperature, pressure, reactant ratio

• Incorporated WGS kinetics results into MR model
Forward WGS Kinetics

- Inconel walls catalyze the reaction
- Gas-phase reaction appears to be slow

\((x_{\text{CO}})_0 = 0.72, (x_{\text{H}_2\text{O}})_0 = 0.28, (x_{\text{CO}_2})_0 = (x_{\text{H}_2})_0, \tau \sim 0.5 - 1 \text{ s}\)
CO not a Poison for Pd Membranes at Hi-T

- Physical, transient drop due to C deposition–permeability restored
- H₂O doesn’t exert any effect on H₂ permeation (not shown)

T = 900°C, Pretentate= 220 psig, Ppermeate= 5 psig, H₂/CO/He (~33% ea)
Inconel Enhances Kinetics & Pd Removes H₂

**Good synergy between Inconel & Pd**

**Side reactions on Inconel are significant**

\[ \text{Conversions:} \]

<table>
<thead>
<tr>
<th>Reactor</th>
<th>CO₂/H₂</th>
<th>CO</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Blank Reactor</strong></td>
<td>4.10</td>
<td>14.2%</td>
<td>79.7%</td>
</tr>
</tbody>
</table>

\[ \text{Conversions if only WGS in quartz reactor} \]

- CO: 77.16%
- H₂O: 55.78%

\[ \text{CO}_2 / \text{H}_2 = 5.84 \]

\[ \text{CO}_2 / \text{H}_2 = 4.10 \]

\[ \text{H}_2 \text{ removed by membrane}^* \approx 24.2\% \]

* \[ \left( \frac{F_{H_2, \text{permeate}}}{F_{H_2, \text{permeate}} + F_{H_2, \text{retentate}}} \right) \times 100 \]

\[ T = 900^\circ \text{C}, P = 16 \text{ bar}, \tau = 2.5 \text{ s}, y_{\text{CO},0} = 0.85, y_{\text{H}_2\text{O},0} = 0.15 \]
Pd or PdCu membrane surfaces enhance the WGS

- Exposure of the Pd to O₂ to remove C roughens the membrane
- This increases surface area and enhances conversion activity,
- Need to operate at conditions where C deposits do not form

SEM images of fresh (top) & oxidized (bottom) Pd packing shows increase in roughness; PdCu displays a similar behavior

\[ T = 900^\circ C, \ P = 1 \ \text{bar}, \ \tau = 0.7 \ \text{s}, \ \gamma_{\text{CO},0} = 0.70, \ \gamma_{\text{H}_2\text{O},0} = 0.30 \]
1) Helix design used to optimize surface-to-volume ratio
2) Graph shows CO conversions above equilibrium
3) In summary, WGS w/ membrane reactor yields more H2 than conventional WGSR at hi-temperature
Interactions, Collaborations, Papers

- Synetix (Johnson-Matthey) in the UK: Dr. Jim Abbott – informal exchange of WGS information
- Princeton Environmental Institute: Dr. Tom Kreutz – membrane reactor systems analyses
- Collaborations with ultra-thin Pd/Cu membrane developers: Dr. Doug Way (Pd/Cu/porous ceramic), Dr. Robert Buxbaum (Pd/Cu/dense metals), and Dr. Ed Ma (Pd/Cu/porous SS)

- F. Bustamante et al., “Hi-T, Hi-P WGS Reaction in a Membrane Reactor,” AIChE Mtg., San Francisco, 11/03
- R. Enick et al., “Towards the Development of Robust Water-Gas Shift Reactors,” ACS Mtg., New York, 8/03
- F. Bustamante et al., “Hi-T Kinetics of the Homogeneous rWGS Reaction,” AIChE Journal, 05/04
Responses to Reviewers’ Comments Last Year

• **Summary Comment** — “emphasize feasibility of hi-temp WGS under realistic operating conditions”

• **Response** — project focus has shifted from kinetics studies to actual WGS membrane reactor testing using syngas components, reactor materials, high T&P, novel reactor designs

• No weaknesses specified in reviewers comments
Future Plans

• FY04
  – Conduct baseline testing of Pd membrane reactor (MR) to determine feasibility of prototype design
  – Fabricate Pd-Cu MR based on results of Pd testing and begin baseline testing

• FY05
  – Complete baseline testing of Pd-Cu MR
  – Determine effect of syngas components and impurities (S, Cl, NH3, etc.) on WGS MR
  – Complete initial validation tests under gasification conditions