ENHANCED HYDROGEN PRODUCTION INTEGRATED WITH CO$_2$ SEPARATION IN A SINGLE-STAGE REACTOR

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This presentation does not contain any proprietary or confidential information
## Overview

### Timeline
- **Project start date:** Oct 2003
- **Project end date:** Sept 2005
- **Percent complete:** 50%

### Barriers
**Technical Target:**
- Cost reduction of H₂ production from fossil fuels. For natural gas sources
  - $3.00/ggeH₂ (by 2005)
  - $1.50/ggeH₂ (by 2010)

**Technical Barriers:**
- Cost effective CO₂ avoidance
- Reduction in impurities (CO, H₂S)
- Selectivity towards H₂ capture
- Desired Operating Temp range
- Cost of H₂ production

### Budget
- **Total project funding:** $501,300
  - **DOE share:** $399,713
  - **Contractor share:** $101,587
- **Funding for FY04:** $160,000
- **Funding for FY05:** $200,000

### Partners
Ohio State University
Project Objectives

To assist DOE in the development of hydrogen production technologies by maximizing H₂ production from fossil fuels

- To develop a high temperature reaction based process from syn gas (CO + H₂) which:
  - Maximizes H₂ production at high temperature & pressure (current year)
  - Maximizes H₂ purity by enhancing water-gas-shift reaction
  - Creates a sequestration ready CO₂ stream

- To identify process conditions for maximizing CaO reactivity
  - Thermodynamic analyses for optimizing carbonation, hydration and sulfidation
  - Testing of mesoporous calcium sorbents
  - Optimizing carbonation and calcination reactions (current year)
  - Multicyclic testing (current year)
Overall Technical Approach

- In-situ CO$_2$ removal from the Water gas mixture
- Drive the equilibrium limited WGS reaction forward

✓ Maximize H$_2$ production
✓ High T/P/Purity H$_2$ possible
✓ Reduce Steam consumption
✓ Remove CO and CO$_2$ to ppm levels
✓ Integrated CO$_2$ separation making this H$_2$ Production process CO$_2$ sequestration ready as well
✓ In membrane reactors, H$_2$ production limited by WGS catalysis and not H$_2$ diffusion

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]
Approach: Experimental

• Integral bed for simultaneous WGS and Carbonation
  – Breakthrough studies for extent/purity of hydrogen production
  – Sorbent reactivity
  – Catalyst activity (blank testing)
  – Catalyst deactivation avoidance

• MSB-TGA testing
  – Extent of carbonation (High pressures)
  – Multicyclic carbonation-calcination reaction testing
  – Competing carbonation/sulfidation reactions

• Sub-atmospheric calcination
  – Vacuum calcination
  – Steam calcination
Carbonation Calcination Reaction System (CCR)

Regenerable metal oxides
- Carbonation
  \[ \text{MO} + \text{CO}_2 \rightarrow \text{MCO}_3 \]
- Calcination
  \[ \text{MCO}_3 \rightarrow \text{MO} + \text{CO}_2 \]

Equilibrium \( P_{\text{CO}_2} \) for carbonation (atm)

- 0.0001
- 0.001
- 0.01
- 0.1
- 1

Carbonation Calcination

\[ \text{CaO} + \text{CO}_2 \leftrightarrow \text{CaCO}_3 \]

Computed from HSC Chemistry v 5.0

\(^a\)15.3% MEA, \(^b\)AC, 1393 m\(^2\)/g, \(^c\)AC: Norit R1, \(^d\)Silica Gel, \(^e\)AC 1018 m\(^2\)/g

\(^a\)Song et al., 1996; \(^b\)Heuchel et al., 1999; \(^c\)Dreisbach et al., 1999; \(^d\)Zhang et al., 1998; \(^e\)Sarkar and Bose, 1997
Reaction Schemes

Reaction phase:

**WGSR:**  \( CO + H_2O \rightarrow CO_2 + H_2 \)

**Carbonation:**  \( CaO + CO_2 \rightarrow CaCO_3 \)

Regeneration phase:

**Calcination:**  \( CaCO_3 \rightarrow CaO + CO_2 \)

Parasitic Reactions:

**Hydration:**  \( CaO + H_2O \rightarrow Ca(OH)_2 \)

**Sulfidation:**  \( CaO + H_2S \rightarrow CaS + H_2O \)

- High Steam/CO
- \( H_2/CO \) ratio can be improved
- But can never maximize \( H_2 \) production
- Further CO cleanup required for PEM fuel Cells (ppm levels)
Thermodynamic Analyses

$\text{CaO} + \text{CO}_2 \rightleftharpoons \text{CaCO}_3$

$\text{CaO} + \text{H}_2\text{O} \rightleftharpoons \text{Ca(OH)}_2$

Equilibrium Temperature for H$_2$O (°C)

Equilibrium Partial Pressure for H$_2$O (atm)

Equilibrium Temperature for CO$_2$ (°C)

Equilibrium Partial Pressure for CO$_2$ (atm)
### Fuel Gas Compositions

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Moving Bed, dry</th>
<th>Moving Bed slagging</th>
<th>Fluidized Bed</th>
<th>Entrained Flow, slurry</th>
<th>Entrained Flow, dry</th>
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</thead>
<tbody>
<tr>
<td>Fuel</td>
<td>air</td>
<td>Oxygen</td>
<td>Oxygen</td>
<td>Oxygen</td>
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<tr>
<td>Fuel</td>
<td>Sub Bituminous</td>
<td>Bituminous</td>
<td>Lignite</td>
<td>Bituminous</td>
<td>Bituminous</td>
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<td>Pressure (psi)</td>
<td>295</td>
<td>465</td>
<td>145</td>
<td>615</td>
<td>365</td>
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<tr>
<td>CO</td>
<td>17.4</td>
<td>46</td>
<td>48.2</td>
<td>41</td>
<td>60.3</td>
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<tr>
<td>H2</td>
<td>23.3</td>
<td>26.4</td>
<td>30.6</td>
<td>29.8</td>
<td>30</td>
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<tr>
<td>CO2</td>
<td>14.8</td>
<td>2.9</td>
<td>8.2</td>
<td>10.2</td>
<td>1.6</td>
</tr>
<tr>
<td>H2O</td>
<td>...</td>
<td>16.3</td>
<td>9.1</td>
<td>17.1</td>
<td>2</td>
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<td>N2</td>
<td>38.5</td>
<td>2.8</td>
<td>0.7</td>
<td>0.8</td>
<td>4.7</td>
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<td>CH4+ HCs</td>
<td>5.8</td>
<td>4.2</td>
<td>2.8</td>
<td>0.3</td>
<td>...</td>
</tr>
<tr>
<td>H2S + COS</td>
<td>0.2</td>
<td>1.1</td>
<td>0.4</td>
<td>1.1</td>
<td>1.3</td>
</tr>
</tbody>
</table>

- Typical gasifier $P_{CO_2}$: 0.4 - 4.3 atm
- Equilibrium Temperature: 830 - 1000 °C
- Operate below $T_{eq}$ for carbonation to occur
- Typical gasifier $P_{H_2O}$: 12 - 20 atm
- Equilibrium Temperatures: 550 - 575°C
- Operate above $T_{eq}$ to prevent hydration of CaO
Solids loading: 2.56 wt%  
$\text{CO}_2$ flow rate: 5 scfh

$\text{CO}_3^{2-}$ and $\text{HCO}_3^{-}$ ions  
$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3$

*Agnihotri et al., (1999)
Optimization of Sorbent Morphology

Optimization of Surface area and Zeta potential\(^1\)

Comparison of PSD of PCC with other natural lime based sorbents\(^2\)

\(^1\text{Gupta and Fan, (2002); } \ ^2\text{Gupta et al (2004)}\)
**Effect of Initial Sorbent Morphology (carbonation of CaO sorbents)**

![Table of BET surface area and PV values](image)

- **Name** | **BET SA (m²/g)** | **PV (cc/g)**
  - LC
  - LC-CaO | 17.79 | 0.078
  - Dolomite | 1.822 | 0.004
  - FCD-CaO | 29.85 | 0.08
  - PCC | 36.8 | 0.11
  - PCC-CaO | 12.79 | 0.027

- **Two-regime heterogeneous Gas-Solid reaction**
  - Rapid kinetic regime
  - Slow product layer diffusion regime

Carbonation in TGA at 700 °C under 100 % CO₂
Comparison of High Temperature Sorbents

Number of cycles

Wt % CO₂ capture (g-CO₂ / g-sorbent)

PCCᵃ
LCᵃ
Li₄SiO₄ᵇ
PbOᶜ
CaOᶜ
CaO (microns)ᵈ
CaO (sub-microns)ᶠ

dolomiteᵉ

**Experimental Setup**

**Combined WGSR and Carbonation**

**Fixed Bed of catalyst and CaO mixture**
- Süd-Chemie: HTS catalyst
- Fe$_2$O$_3$ supported on chromium oxide

**Sorbents**
- PCC (tailored)
- Linwood hydrate (natural)

- 1500 sccm
- 3 % CO
- Steam/CO = 3
- 600 °C
WGS Catalyst Testing w/o Sorbent

\[ K_{WGS} = \frac{[CO_2][H_2]}{[CO][H_2O]} \]

Thermodynamic equilibrium

CO Conversion

Partial Pressure Ratios

CO Conversion (%)

Reaction Temperature

0.5 g HTS catalyst, 3% CO  H\textsubscript{2}O/CO ratio = 3, Total flow = 1.5 slpm
Performance of Linwood Hydrate

T = 600 °C, 3% CO, 9% H₂O, Total flow = 1.5 slpm

100% conversion: < 10 secs
90% conversion: 900 secs
Performance of PCC

- 100% conversion: 240 secs (4 min)
- 90% conversion: 1000 secs (16.5 min)
- Final breakthrough: 2500 secs (42 min)

\[ T = 600 \, ^\circ\text{C}, \, 3\% \, \text{CO}, \, 9\% \, \text{H2O}, \, \text{Total flow} = 1.5 \, \text{slpm} \]
Comparison of PCC and LH

T = 600 °C, 3% CO, 9% H2O, Total flow = 1.5 slpm
Sub-atmospheric Calcination

Schematic diagram of the calciner reactor setup

- Vacuum Pump 1
- Diluent Gas
- Vacuum Pump 2
- Vent
- Data Acquisition System (DAS)
- Ceramic Tube Reactor
- Rotary Seal
- Rotary Supports
- Sorbent Calcination zone
- Reactor Baffles
- Furnace
- Motor Drive
- Rotary Supports
- NDIR CO₂ Analyzer (0-2500 ppm)
- NDIR CO₂ Analyzer (0-20 %)
- Pressure Gauge 1
- Pressure Gauge 2
- Vacuum Pump 2
Sub-atmospheric Calcination

- Effect of vacuum on calcination rate
- Higher vacuum favors the rate
- PCC calcines faster than LC
- Lower calcination temperature favors sorbent morphology

- Effect of diluent gas flow rate
- 0-1000ml/min of He
- Calcination of 10g LC
- 28”Hg vacuum
- T=880 °C
Future Work (FY 2005)

MSB Testing

– Multicyclical Testing that includes:
  • Carbonation
    – Simulated WG mixtures
    – Effect of Pressure
  • Calcination
    – N$_2$/H$_2$O/CO$_2$/Vacuum combination

– Effect of H$_2$S:
  • Competing sulfidation and carbonation
  • Effect of steam to prevent sulfidation
  • Optimization of $X_{CO_2}/X_{H2S}$
Future Work (FY 2005)

• **Breakthrough Testing**
  
  – **Hydrogen Generation**
    
    • Purity of hydrogen
      – Thermal Conductivity
      – Density
      – Specific Heat
    
    • CO exit concentration
    • CO\textsubscript{2} exit concentration

• **Multicyclic Catalyst Performance**
  
  – Catalyst maintained under inert gas
    
    • No exposure to CO\textsubscript{2}, H\textsubscript{2}O
Future Work (FY 2005)

- **H₂ Enriched Gas Outlet**
- **SynGas Inlet**

**CLOSED**

- Vacuum
- Nitrogen
- Vacuum
- Nitrogen
- Vacuum

**Calcium Oxide**

**WGS Catalyst**
Publications and Presentations

Presentations:


Gupta, H; Iyer, M.V.; Sakadjian, B.B.; and Fan, L.-S., “The Role of CaO in Maximizing Hydrogen Production from Fossil Fuels” Fuel Cell Seminar, San Antonio, TX, 2004


Publications:

Hydrogen Safety

Most significant hydrogen hazard associated with this project is

- The experiments involved in this project use a gas mixture consisting of CO, H₂, H₂O, H₂S, CO₂ and N₂.
- High temperatures (100-700°C) and pressure (1-20 bars)
- The most significant hydrogen hazard associated with this project is the combustion/explosion of hydrogen inside and/or outside the reactor. In addition, carbon monoxide could pose a similar safety hazard.
Hydrogen Safety

Our approach to deal with this hazard is

- Minimize gas flow rates and reactor footprint
- Double sash well-ventilated walk-in hood (81 fpm)
- 13 ppmv Hydrogen in the vicinity of reactor
- Manual controls are outside the hood