Sorption-Enhanced Reforming

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Hydrogen Statistics

• Annual Production Rate  ca. 75 Mt
• Growth Rate  ca. 10%/yr
• Oil Equivalent  4.5 Mb/day
• Raw Material  48% natural gas
  30% oil
  18% coal
  4% electrolysis

• Current Uses  ca. 50% NH$_3$ production
  ca. 50% petroleum refining
  Others: methanol, metallurgical

• Future Uses  Power Generation: IGCC, SOFC
  Transportation: PEM Fuel Cells

The Hydrogen Economy ???
• Other Raw Materials

  *Natural Gas*
  Coal
  Biomass

• Candidate Sorbents

  *Calcium Based*
  K-treated Hydrotalcite
  $\text{Li}_2\text{ZrO}_3$
  $\text{Li}_4\text{SiO}_4$
  $\text{Na}_2\text{ZrO}_3$
Standard Reforming

Reforming

\[ \text{CH}_4(g) + 2\text{H}_2\text{O}(g) \rightarrow 3\text{H}_2(g) + \text{CO}(g) \quad \Delta H_r^o = 226 \text{ kJ/mol} \]

Water-Gas Shift

\[ \text{CO}(g) + \text{H}_2\text{O}(g) \rightarrow \text{H}_2(g) + \text{CO}_2(g) \quad \Delta H_r^o = -38 \text{ kJ/mol} \]

Combined

\[ \text{CH}_4(g) + 3\text{H}_2\text{O}(g) \rightarrow 4\text{H}_2(g) + \text{CO}_2(g) \quad \Delta H_r^o = 188 \text{ kJ/mol} \]
Standard Reforming

Reformer

Shift Reactors

Purification Options

Flue Gas

CH₄/H₂O Feed

Supplemental Energy

Fuel/Air

PSA Units

Pressure Swing Adsorption

99.5+% H₂

Wet Scrubbing

95+% H₂ Trace CO, CO₂

PSA Off-Gas

H-T Shift

L-T Shift

Scrubber/Stripper

Methanator or PROX
Sorption Enhanced Reforming

Reforming
\[ \text{CH}_4(g) + \text{H}_2\text{O}(g) \rightarrow 3\text{H}_2(g) + \text{CO}(g) \quad \Delta H_r^0 = 226 \text{ kJ/mol} \]

Water-Shift
\[ \text{CO}(g) + \text{H}_2\text{O}(g) \rightarrow \text{H}_2(g) + \text{CO}_2(g) \quad \Delta H_r^0 = -38 \text{ kJ/mol} \]

Carbonation
\[ \text{CaO}(s) + \text{CO}_2(g) \rightarrow \text{CaCO}_3(s) \quad \Delta H_r^0 = -188 \text{ kJ/mol} \]

Overall
\[ \text{CH}_4(g) + 3\text{H}_2\text{O}(g) + \text{CaO}(s) \rightarrow 4\text{H}_2(g) + \text{CaCO}_3(s) \quad \Delta H_r^0 = -13 \text{ kJ/mol} \]
Sorption Enhanced Reforming Process

Hydrogen Product

Sorbent Purge

Sorbent Makeup

Spent Sorbent

Regenerated Sorbent

Reformer

Reactor

Hydrator

Regenerated Gas

Regeneration Gas + CO₂

Natural Gas/Steam

Purge

Makeup

Energy

Regeneration Gas

Regeneration Energy
Advantages

Simplification (or in some cases elimination) of the H₂ purification section.

Elimination of the shift reactor(s) and shift catalysts.

Replacement of high temperature, high alloy steels in the reforming reactor with less expensive materials of construction.

Reduction or possible elimination of carbon deposition in the reforming reactor.

Reduced energy requirement.

Production of pure, sequestration ready, CO₂.
Thermodynamics

Hydrogen Yield

- Temperature
- Pressure
- Steam to Carbon Ratio (S/C)

Sorbent Regeneration
Effect of Temperature

\[ P = 15 \text{ bar, } (S/C) = 4 \]
Effect of Pressure

\[(S/C) = 4\]
Effect of Feed Composition (S/C) 
P = 5 bar

![Graph showing the effect of feed composition on hydrogen mole fraction at 5 bar pressure. The graph plots temperature in °C on the x-axis and hydrogen mole fraction on the y-axis. Three curves are shown for different S/C ratios: (S/C) = 2, (S/C) = 3, and (S/C) = 6. The mole fraction decreases as temperature increases for all S/C ratios.]
Hydrogen Impurities

P = 15 bar, (S/C) = 4

Component Mol Fraction (Dry Basis)

Temperature, °C
Sorbent Regeneration

CaO(s) + CO₂(g) ⇌ CaCO₃(s)

EQUILIBRIUM CO₂ Pressure, bar

Temperature, °C

Carbonation

Calcination
Experimental Results

• Fixed-Bed Reactors
• Fluid-Bed Reactors
• TGA (carbonation/calcination only)

• Single Cycle
• Multicycle
Fixed-Bed Reactor Results: Calcined Dolomite Sorbent

- Component Concentration (% dry basis)
- Time (minutes)
- Sorbent Conversion

- Start-up prebreakthrough
- Breakthrough
- Postbreakthrough

- $T = 650^\circ$C
- $P = 15$ bars
- $(S/C) = 4$
- 12% CH$_4$
- N$_2$ diluent

- CH$_4$, CO
- Sorbent Conversion
Fixed-Bed Reactor Results:
Reagent CaCO$_3$ Sorbent

100 % Conversion of CH$_4$ to H$_2$

Mol Percent H$_2$ (Dry Basis)

Temperature, °C

100 % Conversion of CH$_4$ to H$_2$

P = 15 atm
(S/C) = 4
6% CH$_4$
N$_2$ diluent
Fluid-Bed Reactor Results:
Dolomite, 600ºC, 1 bar, (S/C) = 3

Johnsen et al., CES, 2006, 61,1195
Fixed-Bed Reactor: 
Multicycle Results

Calcination: INSITU

$P = 1 \text{ atm}$

$T = 800 \degree \text{C}$

$500 \text{ sccm}$

$100\% \text{ N}_2$

Time, min

$\% \text{H}_2$ (Dry Basis)
Fluid-Bed Reactor:
Four Cycle Results

Johnsen et al., CES, 2006, 61,1195
Stability of Naturally Occurring Sorbents: Carbonation/Calcination Only

Bandi et al., 2002, 5th Intl. Symp. On Gas Cleaning
300-Cycle Results

Carbonation
100% CO₂
850°C

Calcination
100%N₂
850°C

Sun, P. et al., AIChE J., 2008, 54, 1668
Alterations in Pore Structure

After initial calcination. After 30 carbonation/calcination cycles.

Grasa et al., ChemEngJ, 2008, 137, 561
Improved Durability

- Synthetic Sorbent
- Synthetic Mixed Sorbent/Catalyst
- Sorbent Reactivation
Synthetic Sorbent: CaO (75%)/Ca$_{12}$Al$_{14}$O$_{33}$ (25%), Carbonation/Calcination Only

CaO-CA-2
1000°C calcination during preparation
Carbonation:
650°C, 1 atm,
16% CO$_2$/N$_2$,
30 min
Calcination
850°C, 1 atm
100% N$_2$
5 min

Li et al., IECRes, 2006, 45, 1911
Multicycle Results: CaO (75%)/\(\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}\) (25%), Parallel Fixed-Bed Reactors

Carbonation:  
630 °C  
1 bar  
(S/C) = 5

Calcination:  
850 °C  
1 bar  
100% Argon

Li et al., IECRes, 2006, 45, 1911
Durability: CaO/ \( \text{Ca}_{12}\text{Al}_{14}\text{O}_{33} \) vs. Dolomite

IFE, Norway
Nanocrystalline CaO/Calcium Aluminate

Spray-dried particle before calcination → Porous channel → Spray-dried particle after calcination

Fang, KIER presentation, July 2009
Reactivation by Hydration: Carbonation/Calcination Only

Three Limestones: Havelock, Purbeck, Cadomin

Fluid Bed
Carbonation: 750°C, 1 atm
14% CO₂ in N₂
Calcination: 750°C, 1 atm
100% N₂
Hydration: Overnight at 20°C,
1 atm, in Air with
\( P_{\text{CO₂}} \approx 0.023 \text{ bar} \)

Fennell, et al., JInstEnergy, 2007, 80, 116
Process Simulations and Economics

CH₄ to H₂

– Ochoa-Fernandez et al.,
  GreenChem, 2007, 9, 654

CH₄ to H₂ to Electricity

– Reijers et al., WorldHydrogen
  Energy Conf., Lyon, France, 2006

Coal to Electricity

– MacKenzie et al., Energy&Fuels,
  2007, 21, 920

– Li et al., AIChEJ, 2008, 54, 1912

-- Abanades et al., EnvSciTech,
  2007, 41, 5523
# Production of 99.9% H₂

<table>
<thead>
<tr>
<th>Standard Reforming</th>
<th>Sorption Enhanced Reforming</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Process Units</strong></td>
<td></td>
</tr>
<tr>
<td>Reformer</td>
<td></td>
</tr>
<tr>
<td>HT Shift</td>
<td></td>
</tr>
<tr>
<td>LT Shift</td>
<td></td>
</tr>
<tr>
<td>PSA</td>
<td></td>
</tr>
<tr>
<td><strong>Carbon Capture</strong></td>
<td>79%</td>
</tr>
<tr>
<td><strong>Efficiency (without capture)</strong></td>
<td>86%</td>
</tr>
<tr>
<td>(vs 88% literature)</td>
<td></td>
</tr>
<tr>
<td><strong>Efficiency (with capture)</strong></td>
<td>71%</td>
</tr>
<tr>
<td>(MEA scrubbing)</td>
<td></td>
</tr>
<tr>
<td><strong>Efficiency (with capture)</strong></td>
<td>79%</td>
</tr>
<tr>
<td>(CO₂ compressor)</td>
<td></td>
</tr>
</tbody>
</table>

Ochoa-Fernandez et al., GreenChem, 2007, 9,654
**CH₄ to H₂ to Electricity**

Design Basis: Natural gas combined cycle based on 380 MWe Siemens V94.3A gas turbine coupled with steam cycle

Standard steam-methane reforming:

\[ \eta = 57.1\% \text{ without CO}_2 \text{ capture} \]
\[ \eta = 48\% \text{ with 85}\% \text{ CO}_2 \text{ capture using MEA} \]

Sorption Enhanced H₂ Production using CaO sorbent:

- Hydrogen Production: 600°C, 17 bar, H₂O/CH₄ = 3
- Sorbent Regeneration: 1000°C, 17 bar, H₂O/CO₂ = 1.8

\[ \eta = 52.6\% \text{ with 85}\% \text{ CO}_2 \text{ capture} \]

Reijers et al., WorldHydrogen Energy Conf., Lyon, France, 2006
Coal to Electricity

• Order-of-Magnitude Economic Study
• 360 MWe Pressurized Fluid Bed Combustor
• 85% CO₂ Capture

• Capture Cost  $23.70/metric ton CO₂ (Canadian)

• MEA Capture Cost  $39 – $96/metric ton CO₂ (range from 11 literature sources)

MacKenzie et al., Energy & Fuels, 2007, 21,920
# Coal to Electricity

<table>
<thead>
<tr>
<th>Process</th>
<th>COE, ¢/kWh</th>
<th>η, % HHV</th>
</tr>
</thead>
<tbody>
<tr>
<td>*Amine, subcritical</td>
<td>8.16</td>
<td>25.1</td>
</tr>
<tr>
<td>*Amine, supercritical</td>
<td>7.69</td>
<td>29.3</td>
</tr>
<tr>
<td>*Amine, ultra supercritical</td>
<td>7.34</td>
<td>34.1</td>
</tr>
<tr>
<td>*Oxyfuel</td>
<td>6.98</td>
<td>30.6</td>
</tr>
<tr>
<td>IGCC</td>
<td>6.51</td>
<td>31.2</td>
</tr>
<tr>
<td>Limestone (X = 0.1)</td>
<td>6.54</td>
<td>31.0</td>
</tr>
<tr>
<td>Dolomite (X = 0.14)</td>
<td>6.31</td>
<td>31.2</td>
</tr>
<tr>
<td>75CaO/25Ca_{12}Al_{14}O_{33} (X = 0.27)</td>
<td>6.35</td>
<td>32.8</td>
</tr>
</tbody>
</table>

Li et al., AIChEJ, 2008, 54, 1912
# Coal to Electricity

<table>
<thead>
<tr>
<th></th>
<th>Units</th>
<th>Existing Plant</th>
<th>Oxifuel Plant</th>
<th>Calcium Looping</th>
</tr>
</thead>
<tbody>
<tr>
<td>Efficiency</td>
<td>kWh/kWh</td>
<td>43</td>
<td>32</td>
<td>35.6</td>
</tr>
<tr>
<td>CO2 Capture</td>
<td>%</td>
<td>---</td>
<td>95</td>
<td>86</td>
</tr>
<tr>
<td>CO2 Emission Factor</td>
<td>kgCO2/kWhe</td>
<td>795</td>
<td>53</td>
<td>134</td>
</tr>
<tr>
<td>Cost of Electricity</td>
<td>US$/kWhe</td>
<td>0.039</td>
<td>0.057</td>
<td>0.049</td>
</tr>
<tr>
<td>Avoided Cost</td>
<td>US$/tCO2</td>
<td>---</td>
<td>23.8</td>
<td>15.5</td>
</tr>
</tbody>
</table>

Abanades et al., EnvSciTech, 2007, 41, 5523
Pratt & Whitney Rocketdyne is Developing Improved Hydrogen Generator

Rocketdyne Hydrogen Generator

Advantages Over SMR Technology

- 90% Size Reduction (vs. SMR Fired Box)
- 30-40% Lower Equipment Cost
  - No High Temperature Fired Box
  - No Shift Required
  - No Desulphurization Required
  - Smaller PSA – Less Purification
- 5-20% Higher Hydrogen Yields
  - Steam Neutral
  - Concentrated CO₂ Stream for enhanced oil and gas recovery

60 MMscfd Capacity

Pratt & Whitney
A United Technologies Company

Non-Proprietary Data

Pratt & Whitney Rocketdyne
Hydrogen Generator 03-07-07/301jh-4
Zecomix: ENEA – Italy
Synergy with Cement Manufacture

Rodriguez et al., EnvSciTech, 2008, 42, 6980
Related R&D Activities

- Australia
- Austria
- Canada
- China
- Germany
- Greece
- Israel
- Italy
- Japan

- Mexico
- Netherlands
- New Zealand
- Norway
- Spain
- South Korea
- Sweden
- United Kingdom
- United States
- Others?
Conclusions

Carbonation: All looks good
Regeneration: No problem
**Sorbent Durability**
Process Sim.: Favorable numbers
Process Devel.: Moving ahead
Next: Reports of new developments at the

1st Meeting of the

High Temperature Solid Looping Cycles Network