High Temperature Solar Splitting of Methane to Hydrogen and Carbon

Allan Lewandowski (NREL)
Alan Weimer (University of Colorado, Boulder)

Team Members:
CU: Jaimee Dahl, Karen Buechler, Chris Perkins
NREL: Carl Bingham, Judy Netter

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Thermal Decomposition of Methane

- Demonstrated by Thagard in late 70’s
  - electrically heated, porous wall reactor
- Simple in concept
  - essentially single step to end products
- Extremely high reaction rates at 1600-2000°C
- Various end-product configurations possible
- Co-products both have economic value

\[ \Delta H_{1800^\circ C} = -76 \text{ kJ/mole} \]

\[ \Delta H_{1800^\circ C} = -394 \text{ kJ/mol C} \]

\[ \text{CH}_4 + \rightarrow \text{C} + 2\text{H}_2 \]

-890 kJ/mol CH\(_4\)  \(\rightarrow\)  -572 kJ/2mol H\(_2\)
Project Goals

• Near term
  – Current status:
    • 70-95% CH₄ conversion to H₂ @ 1850°C
    • $0 -12/kg depending on process configuration and co-product value
  – Targets:
    • 70% conversion on a continuous basis
    • $3/kg for fleet fueling station with carbon black at tire market price

• Long-term
  – < $2/kg for water-splitting cycles
Historical Perspective

• Initiation of Project: FY2000
  – University of Colorado awarded competitive DOE GO subcontract

• Significant Results:
  – FY00: demonstrated proof-of-concept at HFSF
  – FY01: achieved 80% conversion in new reactor
  – FY02: demonstrated fluid-wall (aerosol) reactor
  – FY03: achieved 94% conversion
    • Limited funding to complete Ph.D. thesis experimental work

• Overall:
  • very high reaction rates demonstrated
  • no technical showstoppers
  • near-term commercialization opportunities
Why Use Solar Energy?

- Environmentally benign energy source
  - little or no CO₂ emissions (depending on process)
- High concentrations possible (>1000 W/cm²)
  - high temperatures easily achieved (>3000 °C)
  - reduced reactor size; low thermal mass
- Rapid heating rates (>>1000 °C/s)
  - quick start/stop operation
- Abundant resource (both US and worldwide)
  - Sufficient to power the world (if we choose to)
- Advantages tradeoff against collection area
  - this is true for all technologies using sunlight
  - heliostat costs are significant fraction of capital
    - importance depends on overall process efficiency
World Class Direct Resource in US

- **World Class area in US:**
  \[
  5.8 \times 10^5 \text{ km}^2 
  \]
  \[
  \rightarrow 6 \text{ kWh/m}^2/\text{day} 
  \]

- **Annual US Energy Usage:**
  \[
  2.9 \times 10^{13} \text{ kWh} \quad \text{(Year 2000 EIA data)} 
  \]
  \[
  \rightarrow \eta=10\%, \text{ area required:} 
  \]
  \[
  1.3 \times 10^5 \text{ km}^2 \quad \text{(50\% of Arizona)} 
  \]

- **Annual World Energy Usage:**
  \[
  1.2 \times 10^{14} \text{ kWh} 
  \]
  \[
  \rightarrow \eta=10\%, \text{ area required:} 
  \]
  \[
  5.5 \times 10^5 \text{ km}^2 
  \]
  \[
  \quad (95\% \text{ of Arizona + Nevada}) 
  \]
Vision for Solar Thermal Processing

• Apply advantages to a clean hydrogen economy producing hydrogen from water

• Near-term (0-5 years): Methane as transition fuel
  – Identify/develop promising processes
    • e.g. NG dissociation, dry reforming
  – Develop aerosol flow reactor and process understanding
    • technical and economic
  – Introduce solar technology on small scale in appropriate markets/locations (SW United States)
    • HCNG fleet fueling stations

• Longer-term (3-15 years): Move to water as the fuel
  – Initially through thermochemical cycles
    • e.g. 2-step metal oxide reduction, others as identified
  – Eventually to direct, high-temperature splitting/separation
    • significant materials separation issues need to be overcome
  – If renewable electric power is ever cheap enough: electrolyzers
Potential Application Areas

- **Bulk Hydrogen**
  - large-scale systems, pipeline feeds
- **Distributed Fleets**
  - fueling stations
  - HCNG a near-term possibility
- **Industrial User/Supplier**
  - Semiconductor industry
- **Syngas**
  - add reformer to system
- **Utility plants**
  - power and hydrogen
- **Carbon black plant**
- **Stranded gas/capped wells**
Technical Challenges

• Compatibility with on/off nature of sunlight
  – short start-up & shut-down times
  – semi-continuous operation
• High efficiency reactor design for high temperature
• Materials of construction
• Thermophoretic deposition of carbon black

Non-technical Challenges

• Co-product marketing (outlet for carbon black)
• Poor fit to a single business
Aerosol Flow Reactor Concept

T~1800 °C

Sun

N.G.(CHₙ) → C + (x/2)H₂

Particle Feed

Feed N.G. (CHₙ)

H₂ Sweep

Porous Graphite Tube

Solid Graphite Absorber

Quartz Envelope

H₂, C, CHₓ
System Concept
Hydrogen Production

T~1800 °C

Feed N.G. (CHₙ)

4 kg

Particle Feed

Recycle CHₓ

Recycle H₂

Hydrogen to Storage or pipeline

1 kg

Indirect Solar H₂

0.44 kg

Hydrogen to Storage or pipeline

N.G. (CHₓ) → C + (x/2)H₂

sun

H₂, C, CHₓ

3 kg C

sales

Baghouse Filter

Reformer

21.9 kW e⁻

Electrolyzer

Air in

Air out

H₂O in

H₂O

Carbon Conversion Fuel Cell

7.5 kg CO/H₂

Carbon Conversion

Reactor

3 kg C

sales

H₂, C, CHₓ

1 kg

Electrolyzer

H₂O

in

O₂

N.G. (CHₓ)
Reactor System

Process Gas and Particles

Purge Gas Out

Cooling Water

Secondary Concentrator

Purge Gas In

Process Gas and Particles
Conversion as a Function of Reactor Wall Temperature for Various Initial Methane Flow Rates
Energy use and GHG Emissions
(H₂ Supplied as High-pressure Gas)

Steam-reforming Plant + Liquid H₂ + Transport

\[ \text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2 \]

+310 MJ/kg of H₂
+20.42 kg CO₂-eq/kg H₂

(Spath and Amos, 2002)

Solar-thermal NG Dissociation Distributed Plant

\[ \text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \]

(carbon is sold)
+38 MJ/kg of H₂
+3.46 kg CO₂-eq/kg H₂

(carbon is converted to H₂)
+218 MJ/kg of H₂
+14.2 kg CO₂-eq/kg H₂

Fossil fuel avoided = 272 MJ/kg H₂
CO₂ avoided = 17 kg CO₂/kg H₂

Fossil fuel avoided = 82 MJ/kg H₂
CO₂ avoided = 6.22 kg CO₂/kg H₂
# Economic Studies
*(Speth and Amos 2002)*

## Fueling Stations
*(H₂ @ 3000psig; $0.66/kg C)*

<table>
<thead>
<tr>
<th>Collector Area (m²)</th>
<th>Capital Cost ($M)</th>
<th>H₂ Selling Price ($/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>&quot;Out the Gate&quot; Compressed/Stored</td>
</tr>
<tr>
<td>2,188 (1.8 acres)</td>
<td>4.42</td>
<td>12.30 (250 kg/day)</td>
</tr>
<tr>
<td>2.15</td>
<td>3.35 (462 kg/day)</td>
<td>-----</td>
</tr>
<tr>
<td>8,750 (7 acres)</td>
<td>8.93</td>
<td>8.04 (750 kg/day)</td>
</tr>
<tr>
<td>4.34</td>
<td>2.61 (1141 kg/day)</td>
<td>-----</td>
</tr>
</tbody>
</table>

*Basis: $3.92/1000 scf NG; 15% IRR, 20 yr life, Equity funded*
## Economic Studies

*(CU analysis)*

### Semi-conductor Plant

(300 psig, $4.35/kg current contract price)

<table>
<thead>
<tr>
<th>Collector Area (m²)</th>
<th>Capital Cost ($M)</th>
<th>H₂ Selling Price ($/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>985 (0.8 acre)</td>
<td>$1.46</td>
<td>3.92 (240 kg/day total; 75 kg/day stored)</td>
</tr>
</tbody>
</table>

### Small Utility

(co-gen 1.6 MW electricity & H₂ out the gate)

<table>
<thead>
<tr>
<th>Collector Area (m²)</th>
<th>Capital Cost ($M)</th>
<th>H₂ Selling Price ($/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7,800 (6.2 acres)</td>
<td>$4.96</td>
<td>3.22 (1743 kg/day; electricity @ 5 ¢/kWh)</td>
</tr>
</tbody>
</table>

*Basis: $3.92/1000 scf NG; 15% IRR, 20 yr life, Equity funded*
Collaborations

• In the US
  – 10 industrial partners (in-kind cost share)

• Outside of the US
  – IEA SolarPACES, Task II, Solar Chemistry (AL is US Coordinator)
  – Paul Scherrer Institute, Switzerland
  – Swiss Federal Institute of Technology (ETH), Zurich
2002 Review Panel Comments

- Team took exception to the use of a carbon fuel cell to extend hydrogen production into dark hours
  - Response: the carbon fuel cell is a long-term technology that was considered as an option for use of the carbon byproduct and is not essential to the overall concept technically or economically.

- “...inclusion...in the hydrogen program portfolio is important in that it keeps the technology area broad, maximizes options for commercial use, and complements other dissociation technologies.”
HCNG Fleet Opportunity in Desert SW United States

• First Fueling Station: Phoenix Area
  – Pinnacle West is already in business
    • HCNG, NG, H₂; H₂ by electrolysis w/off-line e⁻
  – Arizona Public Service, Municipal Vehicles, Taxis, Bus Lines, ...

• Combined Fleet Facility with Industrial H₂ users
  – Intel & Motorola are heavy users
  – Tucson, Albuquerque, Las Vegas, Denver, Colorado Springs, Salt Lake City, ...

• Potential scale-up scenario
  – H₂ Enriched NG (HCNG) (20 – 35% H₂) for Fleets
  – Increased H₂ Content HCNG (50% or more)
  – Fuel Cell Vehicles (100% H₂) or IC engines running on H₂
    • Carbon Conversion Fuel Cell Marketed
One-step HCNG Process Today (21+ % conversion)

\[
\text{sun} \quad \text{CH}_x \rightarrow \text{C} + 35\% \text{H}_2 / 65\% \text{CH}_x
\]

1 kg 0.16 kg 0.84 kg
## Economic Impact of Fleet Station Development

<table>
<thead>
<tr>
<th>Number of 327 fill-up HCNG Fleet Stations</th>
<th>Total Annual Revenue ($M)*</th>
<th>% North American Carbon Black Market</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>141</td>
<td>1%</td>
</tr>
<tr>
<td>200</td>
<td>706</td>
<td>5%</td>
</tr>
<tr>
<td>400</td>
<td>1,413</td>
<td>10%</td>
</tr>
<tr>
<td>1600</td>
<td>5,648</td>
<td>40%</td>
</tr>
</tbody>
</table>

*based on capital cost of $3.2M per station and operating costs of $2.3M/year

### Carbon Black Market

- **World Market:** ~ 8 billion kg/year
- **Tire & industrial rubber:** 92% of World Market
  - 7.3 billion kg/yr
- **North American Market:** 25% of World Market
  - 1.8 billion kg/year
Solar Examples

Enhanced oil recovery, early 80’s

Large solar furnace, France

Small central receiver, Israel

30 MW th Solar Plant, CA
Preliminary HCNG Field Design for Fleet Fueling Station Application

- Phoenix Area
- ~ 6,546 kg/day HCNG
- ~ 327 fill-ups/day (@ 20 kg/fill-up)
- ~ 1250 kg C/day
- ~ 0.57 hectares (1.4 acres)

- ~ 1.1 MW$_{th}$
- ~ 5 cm ID x 48 cm reactor
- ~ 122 heliostats (~1770 m$^2$)
- Overall optical $\eta$~70%
  - peak flux >3000 suns
Next Step Applications/Options

- Industrial \( H_2 \) to Semi-conductor Plants in SW, etc.
- Co-generating Utilities
  - \( H_2 \) and electricity
- Coal Bed Methane Conversion
  - largest reserves in the world are in the Four Corners Region of the desert SW United States)
- Biogas Conversion
  - waste landfill biogas, etc.
- Dry Reforming of \( CO_2 \) Contaminated Gas Wells
- Water-splitting cycles
Water-splitting Cycles

• **2 Step metal oxide reduction**
  - high temperature endothermic reduction
  - lower temperature exothermic reaction with water
  - Ongoing European solar projects

• **Thermochemical cycles**
  - originally studied with nuclear reactors in mind
  - recent General Atomics study identified 2 candidates
    • adiabatic UT-3
    • Sulfur – iodine
  - GA proposing to identify others with higher temperature operation using solar thermal power

• **Direct water splitting**
  - requires $T>2500^\circ C$, high temperature separation
  - $\Delta H_{2500^\circ C} = 238 \text{ kJ/mole}$
2ZnO $\rightarrow$ 2Zn + O$_2$
$\Delta H_{1700^\circ C}$ = 557 kJ/mol

Zn + H$_2$O $\rightarrow$ ZnO + H$_2$
$\Delta H_{450^\circ C}$ = -107 kJ/mol

Overall Chemistry
2H$_2$O $\rightarrow$ 2H$_2$ + O$_2$

Idealized Concept
ZnO reduction

T $\sim$ 1700 $^\circ$C
CH$_4$+ZnO recycle

CH$_4$+ZnO $\rightarrow$ Zn+2H$_2$+CO

$\Delta H_{900^\circ C} = 440$ kJ/mol

Zn+H$_2$O $\rightarrow$ ZnO+H$_2$

$\Delta H_{450^\circ C} = -107$ kJ/mol

Intermediate Concept
ZnO reduction

Overall Chemistry
CH$_4$+2H$_2$O $\rightarrow$ 4H$_2$+CO$_2$

Reformer

H$_2$O

H$_2$

H$_2$O

CO

3H$_2$

3H$_2$, CO

PSA

CO$_2$ (44 kg)

(16 kg)

(8 kg)

T~1800 $^\circ$C

sun
Dry Reforming Experiments

- Application to high CO$_2$ containing gas wells and landfill gas processing

$$\text{CO}_2 + 2\text{CH}_4 \rightarrow \text{C} + 2\text{CO} + 4\text{H}_2$$

Feed Gas: 0.90% CH$_4$; 0.45% CO$_2$

<table>
<thead>
<tr>
<th>Flux (kW/m$^2$)</th>
<th>% CO$_2$</th>
<th>% CH$_4$</th>
<th>% CO</th>
<th>% H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>0.45</td>
<td>0.84</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1500</td>
<td>0.23</td>
<td>0.20</td>
<td>0.35</td>
<td>1.55</td>
</tr>
<tr>
<td>2000</td>
<td>0.11</td>
<td>0.07</td>
<td>0.62</td>
<td>1.60</td>
</tr>
</tbody>
</table>
Chemically-assisted Solar-thermal Water Splitting

\[
\begin{align*}
\text{CH}_4 + \text{ZnO} & \rightarrow \text{Zn} + 2\text{H}_2 + \text{CO} \\
\Delta H_{900^\circ C} &= 440 \text{ kJ/mol} \\
\text{Zn} + \text{H}_2\text{O} & \rightarrow \text{ZnO} + \text{H}_2 \\
\Delta H_{450^\circ C} &= -107 \text{ kJ/mol} \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2 \\
\text{CH}_4 + 2\text{H}_2\text{O} & \rightarrow 4\text{H}_2 + \text{CO}_2
\end{align*}
\]
Summary

• Splitting methane using concentrated sunlight is technically feasible
• Various system configurations and applications have economic potential
• Technical concept can be extrapolated to other chemical reactions and to water splitting
• A near-term application, business opportunity and path forward have been identified
• Continued funding is warranted
Project Team

Al, Karen

Sarah

Judy, Al, Jaimee, Carl, Fabian