Solar-Driven Photocatalytically-Assisted Water Splitting

Florida Solar Energy Center – Cocoa, FL

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DOE Prime Contract Number: DE-FG36-07GO17002
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This presentation does not contain any proprietary, confidential, or otherwise restricted information
Overview

Timeline

- Start date: Sept. 2007
- End date: Oct. 2011
- Percent complete: 15%

Budget

- Total project funding
  - DOE share: $4M
  - Contractor share: $1M
- $300k received in FY07
- Funding for FY08: $1M

Barriers

- Barriers addressed
  U. High-Temperature Thermochemical Technology
  V. High-Temperature Robust Materials
  W. Concentrated Solar Energy Capital Cost
  X. Coupling Concentrated Solar Energy & Thermochemical Cycles
- H₂ Production Target: $3.00/kg

Partners

Project lead:
Solar System Development
- FSEC at UCF
  Reactor/Receiver & Process Development
Objectives

• Evaluate photo/thermo-chemical water splitting cycles that employ the visible portion of the solar spectrum for production of hydrogen

• Select a cycle that has the best potential for cost-effective production of hydrogen from water – DOE target of $3.00/kg H₂

• Demonstrate technical feasibility of the selected cycle using solar input in a bench-scale reactor

• Demonstrate pre-commercial feasibility via a fully-integrated pilot-scale solar hydrogen production system

• Perform economic analysis of the selected cycle.
Project Participants

• Science Applications International Corp.
  – Contract Management
  – Solar Concentration System Development & System Integration

• Florida Solar Energy Center at UCF
  – Photo/Thermo-Chemical Cycle Evaluation/Selection
  – Reactor/Receiver & System Design

• IPHE partnership
Project Phases

• PHASE 1: Sub-cycle testing & evaluation

• PHASE 2: Bench-scale testing of the complete cycle & pilot plant design

• PHASE 3: Pilot-scale demonstration
## Milestones, Schedule & Deliverables

<table>
<thead>
<tr>
<th>Month-Year</th>
<th>Type</th>
<th>Description</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sep ‘08</td>
<td>Report</td>
<td>Select preferred water-splitting cycle, based on cost &amp; performance evaluations</td>
<td>Complete</td>
</tr>
<tr>
<td>Sep ‘08</td>
<td>Report</td>
<td>Preliminary design of solar concentrator for pilot-scale test system</td>
<td>ongoing</td>
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<tr>
<td>Mar ‘09</td>
<td>Report</td>
<td>Summary of experimental results &amp; economic analysis, with H₂ cost estimate &amp; recommendations for bench scale system</td>
<td>ongoing</td>
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<tr>
<td>Mar ‘09</td>
<td>GO/ NO-GO To Phase 2</td>
<td>Optimal high temperature water-splitting cycle selected for bench-scale testing &amp; non-federal cost share in place for Phase 2</td>
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<tr>
<td>Mar ‘10</td>
<td>Report</td>
<td>Summary of bench-scale reactor &amp; solar system test results</td>
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</tbody>
</table>
| Mar ‘10    | GO/ NO-GO To Phase 3 | Bench-scale results prove to be technologically feasible to support scale-up to pilot-scale demonstration & reveal no major technical hurdles  
Economic analysis shows that the projected cost of hydrogen from this technology will meet 2010 target of < $3/kg |            |
| Sep ‘10    | Report             | Design of pilot-scale solar concentrator & pilot-scale receiver/reactor                                                                                                                                                     |            |
| Apr ‘11    | Report             | Completion of concentrator installation; demonstration of dish operation with receiver                                                                                                                                 |            |
| Sep ‘11    | Report             | Final report with results of all testing and development, final cost estimates, & recommendations for further development                                                                                           |            |
Phase 1 Approach

• Sub-cycle Testing & Evaluation
  – Photo/Thermo-Chemical Cycle Analysis
  – Lab Testing of Selected Cycle
  – Report - Preferred Cycle Selection
  – Reactor/Process Configuration

• Solar Concentrator Design
  – Concentrator Specifications
  – Preliminary Concentrator Design
  – Subsystem Tests
  – Report - Prelim. Solar Concentrator Design

• Economic Evaluation
Technical Accomplishments/Progress/Results

• Completed cycle analyses
• Selected cycle for further development
• Validated hydrogen production photo-process
• Validated oxygen production sub-cycle chemistry
• Evaluated reactor/receiver options
• Evaluated solar collector configurations
**S-NH$_3$ Solar Water Splitting Cycle**

**H$_2$ Production Step**
- Photocatalytic
- Operates at $\lambda<520$ nm
- Requires $\sim$20% of solar spectrum

**O$_2$ Production Process**
- Thermocatalytic
- Operates at $\lambda>520$ nm
- Requires $\sim$80% of solar spectrum
Aspen Flowsheet of S-NH₃ Cycle

\[(\text{NH}_4)_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{H}_2\]

Photocatalytic Reaction

\[\text{SO}_2 + 2\text{NH}_3 + \text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_3\]

Chemical Absorption

\[\eta_1 \ (\text{LHV}) = 51\% \text{ with heat recovery}\]

\[(\text{NH}_4)_2\text{SO}_4 + \text{ZnO} \rightarrow \text{ZnSO}_4 + 2\text{NH}_3 + \text{H}_2\text{O} @ 250^\circ\text{C}\]

\[\text{ZnSO}_4 \rightarrow \text{ZnO} + \text{SO}_2 + \frac{1}{2}\text{O}_2 @ 900^\circ\text{C}\]

Heat Recovery & Steam Generation

High & Low Temp. Reactors
Comparison of S-NH$_3$ Cycle Efficiency to Other HT Cycles

# DOE Hydrogen Program, FY'05 Progress Report, High Temp. Thermochemical/Solar Hydrogen Generation
Photocatalyst Screening for Hydrogen Production

\[
(NH_4)_2SO_3(aq) + H_2O(l) \rightarrow (NH_4)_2 SO_4(aq) + H_2(g)
\]
Setup for Photocatalytic H₂ Production Experiments
Stability of the Photosystem in Hydrogen Generation Step

Photolyte: 1M [(NH₄)₂SO₃]
Photocatalyst: Pt/Pd doped CdS - 1wt%/0.4wt% of CdS
Photocatalyst loading: 0.5 g CdS in 300 mL of photolyte
Temperature= 25°C
Photon Efficiency as a Function of Single Metal Dopant Loading

Photolyte: 1M (NH$_4$)$_2$SO$_3$

Photocatalyst loading: 0.5g CdS in 300 mL of photolyte
Effect of Photocatalyst Doping

Photocatalyst loading: 0.5 g CdS in 300 mL photolyte: 1M (NH₄)₂SO₃
Effect of Photolyte Temperature

- Photolyte: 1M [(NH₄)₂SO₃]
- Photocatalyst loading: 0.5g CdS in 300 mL photolyte
- Dopant loading: Pt-M (Pt=1wt% of CdS)
- Co-dopant loading: M= Pd or Ru (0.4 wt% of CdS)
Sub-Cycle for Oxygen Production

\[
\text{(NH}_4\text{)}_2\text{SO}_4(s) + \text{ZnO}(s) \rightarrow 2\text{NH}_3(g) + \text{ZnSO}_4(s) + \text{H}_2\text{O}_g
\]

\[
\text{ZnSO}_4(s) \rightarrow \text{SO}_2(g) + \text{ZnO}(s) + \frac{1}{2}\text{O}_2(g)
\]
Experimental Methodology

Investigated thermocatalytic decomposition of:

- Pure $\text{(NH}_4\text{)}_2\text{SO}_4$
- $\text{ZnO}):(\text{NH}_4\text{)}_2\text{SO}_4 = 1.5:1$ (molar ratio)
- $\text{ZnSO}_4$

In the temperature range of 100°C-900°C.

Employing following analytical techniques:

- TG-DTA
- TPD-MS
- GC-MS/UV-Vis
# Thermocatalytic Decomposition of (NH$_4$)$_2$SO$_4$/ZnO – Summary of Reaction Product Analysis

<table>
<thead>
<tr>
<th>Method</th>
<th>T/ °C</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>700</th>
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<td>NH$_3$</td>
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<td>SO$_3$</td>
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<td>H$_2$O</td>
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<td>GC-MS/UV-Vis</td>
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<td>SO$_3$</td>
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<td>NH$_3$</td>
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ZnO/(NH₄)₂SO₄ Thermocatalytic Decomposition – Reaction Mechanisms

Step 1 (T< ~400°C):

\[(\text{NH}_4)\text{SO}_4(s) \rightarrow \text{NH}_3(g) + \text{NH}_4\text{HSO}_4(s)\]

\[\text{NH}_4\text{HSO}_4(s) + \text{ZnO}_4(s) \rightarrow \text{NH}_3(g) + \text{H}_2\text{O}(g) + \text{ZnSO}_4(s)\]

Step 2 (T<~800°C):

\[\text{ZnSO}_4(s) \rightarrow \text{ZnO}_4(s) + \text{SO}_3(g)\]

Step 3 (T>~800°C):

\[\text{ZnSO}_4(s) \rightarrow \text{ZnO}_4(s) + \text{SO}_2(g) + {1\over 2}\text{O}_2(g)\]
Solar Hydrogen Production
Heliostat Cost Reduction

Heliostats are the largest single cost component in the solar hydrogen production system

Identified potential for cost savings using a GRC (Glass-Reinforced Concrete) heliostat structure:

• Very low cost material ($0.15/kg)
• Easy to process (automated spray on mold)
• Excellent weathering and stiffness
• Excellent design flexibility (molded-in reinforcing ribs and mounts; pre-tensioning is possible)

Preliminary design:

• Small (10-15 m²) heliostat, factory-produced, PV self-powered, with wireless communication to minimize field wiring costs
• Factory-made, surface-installed concrete track foundation to simplify installation
Solar Hydrogen Production
Preliminary System Comparison

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<tbody>
<tr>
<td>Baseline Hybrid Sulfur (HyS) System (Kolb): Heliostat/Central Receiver</td>
<td>1.30</td>
<td>6.50</td>
<td>381.2</td>
<td>3.00</td>
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<tr>
<td>Dish concentrator</td>
<td>0.85</td>
<td>3.42</td>
<td>409.2</td>
<td>3.13</td>
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<tr>
<td>FSEC S-NH₃ Cycle w/ Solar Boost:</td>
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<tr>
<td>Dish concentrators w/cold mirror</td>
<td>0.83</td>
<td>3.33</td>
<td>644.3</td>
<td>3.33</td>
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<tr>
<td>Heliostat w/hot mirror</td>
<td>1.06</td>
<td>5.31</td>
<td>810.6</td>
<td>4.12</td>
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<tr>
<td>Heliostat-separate photoreactor</td>
<td>0.84</td>
<td>5.90</td>
<td>435.1</td>
<td>2.33</td>
</tr>
<tr>
<td>Advanced GRC Heliostat-separate rxr</td>
<td>0.84</td>
<td>5.90</td>
<td>417.4</td>
<td>2.25</td>
</tr>
</tbody>
</table>

• Results:
  • FSEC process hydrogen cost <$3/kg
  • Hot/cold mirror systems more expensive
  • FSEC process with separate photoreactor shows cost advantage over baseline (HyS)
  • Advanced heliostat improves costs further
  • GRC prototype heliostat cost estimated at 17% less than conventional glass/metal heliostat ($105/sq.m vs. $126/sq.m)
Future Work

- Close & complete analyses of S-NH₃ cycle
- Complete H₂ production photocatalyst screening
- Reduce noble metal loading on the photocatalyst
- Develop immobilized photocatalyst formulations
- Conclude oxygen production process optimization
- Analyze & design the high temperature reactor/receiver system
- Complete solar collector system analysis & design
- Perform technoeconomic & H2A analysis of the S-NH₃ cycle
Summary

• S-NH₃ photo/thermochemical water splitting cycle has been validated for solar hydrogen production
• S-NH₃ cycle utilizes the thermal portion of solar spectrum for the production of O₂ while the high energy photonic part of sunlight is used for hydrogen generation
• The 1st law efficiency of the S-NH₃ cycle was calculated using Aspen flowsheeting & shown to be 51%
• A large number of doped & polymer stabilized CdS based photocatalysts have been synthesized and evaluated for H₂ production from aqueous ammonium sulfite solutions
• Heliostat field appears to be the preferred solar concentrator approach
• GRC shows promise to lower heliostat field costs