Fundamentals of a Solar-thermal \( \text{Mn}_2\text{O}_3/\text{MnO} \) Thermochemical Cycle to Split Water

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23 May 2005  

Project ID No. PDP44

This presentation does not contain any proprietary or confidential information
Overview

Timeline
- 6-1-2005
- 5-31-2009
- 0%

Budget
- Total Project Funding
  - $1,095,000 DOE
  - $270,000 Cost share
- Funds received in FY04
  - $0

Barriers
- J. Rate of Hydrogen Production
- M. Materials Durability
- N. Materials and systems Engineering
- P. Diurnal Operation Limitation
- Q. Cost
- R. System Efficiency
- T. Renewable Integration
- V. High and Ultrahigh Temperature Thermochemical Technology
- W. High Temperature Materials
- Y. Solar Capital Cost

Partners
Swiss Federal Research Institute (ETH-Zurich)
Objectives

• Develop an understanding of the Mn$_2$O$_3$/MnO solar-thermal thermochemical cycle through theoretical and experimental investigation

• Based on the above, develop a process flow diagram and carry out an economic analysis of the best process option
Approach

• Develop an initial process flow diagram based on available published information regarding the cycle; simulate integrated process; identify key areas for research and development
• Develop and carry out an experimental plan to evaluate the feasibility of all steps in the cycle
• Carry out CFD modeling and simulation to develop an understanding of solar-thermal reactor transport mechanisms
• Analyze cost and efficiency metrics for integrated cycle performance; provide final process flow diagram based on best scenario
Technical Accomplishments/Progress/Results

- Literature surveyed
- Preliminary flow sheet developed based on literature information (conventional processing)
- Very preliminary economics carried out
- Preliminary key areas identified for research (based on preliminary simulations and economics)
- Experimental work plan being developed
Literature Surveyed


**Literature Cycle**

Concentrated Solar Energy

\[ \text{Mn}_2\text{O}_3 \rightarrow 2\text{MnO} + \frac{1}{2}\text{O}_2 \]

**Metal Oxide Decomposition**

NaOH

\[ \text{MnO + NaOH} \rightarrow \frac{1}{2}\text{H}_2 + \text{NaMnO}_2 \]

**H}_2 Liberating Step**

\[ \text{NaMnO}_2 + \frac{1}{2}\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{Mn}_2\text{O}_3 + \text{NaOH} \]

**Water Splitting**

\[ \text{H}_2 \text{ (product)} \]

\[ \text{O}_2 \text{ (vent)} \]

\[ \text{MnO (solid)} \]

\[ \text{H}_2 \text{O (vapor)} \]

\[ \text{NaMnO}_2 \]
Preliminary Flowsheet Development

• Based on literature only, a preliminary PFD was developed for the Mn$_2$O$_3$/MnO solar-thermal thermochemical cycle

• Only the most obvious and conservative unit operations were considered for this initial pass
Process Design Premises

- $\text{Mn}_2\text{O}_3$ dissociated (80%) in air at 1835 K
- NOx considered formed and dealt with via 640 K SCR
- Molten salt heat recovery system considered
- $\text{H}_2$ production step carried out at reduced P; $\text{H}_2$ removed to shift equilibrium to right (100%)
- 90% conversion assumed on water splitting step
- Multi-effect evaporator considered to recover NaOH
- $\text{H}_2$ supplied to pipeline at 300 psig
Process Economics Premises

- Economics by study estimate (factor) method using major purchased equipment costs (Lang’s Factor)
- Base Case = 24 MW\textsubscript{th} plant size; Integrated to 150,000 kg H\textsubscript{2}/day
- 15 yr plant lifetime; 2453 hours per year (28 % on-sun)
- 12.5 % target IRR
- 25 % contingency
- Working capital = 18 % of FCI
- Equity funded
- 1.9% inflation; 7 yr MACR depreciation
- 228 operators in 150,000 kg H\textsubscript{2}/day plant
**Hydrogen Production**

Net Flow: \[ H_2O \rightarrow H_2 + \frac{1}{2} O_2 \]

**Water Splitting**

\[ 2NaMnO_2 + H_2O \rightarrow Mn_2O_3 + 2NaOH \]

**Solar Thermal Decomposition**

\[ Mn_2O_3 \rightarrow 2MnO + \frac{1}{2} O_2 \]

**Hydrogen Production**

\[ 2MnO + 2NaOH \rightarrow H_2 + 2NaMnO_2 \]
Safety, Environmental, and Health Considerations

Environmental Considerations

• Nitrogen oxides (NO\(_x\)) potentially formed at high temperature in solar thermal reactor

• NO\(_x\) can be reduced via selective catalytic reduction (SCR).

\[
\begin{align*}
4NO + 4NH_3 + O_2 & \rightarrow 4N_2 + 6H_2O \\
6NO_2 + 8NH_3 & \rightarrow 7N_2 + 12H_2O
\end{align*}
\]

Catalyst: TiO\(_2\) / V\(_2\)O\(_5\) / WO\(_3\)

Safety and Health Considerations

• Corrosive chemicals (NaOH, NH\(_3\))

• Flammability hazards (H\(_2\), O\(_2\))

• Central nervous system effects from prolonged exposure (MnO, Mn\(_2\)O\(_3\))
## Material Balance Summary*

<table>
<thead>
<tr>
<th></th>
<th><strong>Base Case: Single 24 MW&lt;sub&gt;th&lt;/sub&gt; solar thermal reactor</strong></th>
<th><strong>95 solar thermal reactors (each 24 MW&lt;sub&gt;th&lt;/sub&gt;) Single Back-end</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Products</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>235 kg/hr (1,579 kg/day), $20.27/kg</td>
<td>22,325 kg/hr (150,024 kg/day), $9.04/kg</td>
</tr>
<tr>
<td>Low Pressure Steam</td>
<td>2,491 kg/hr</td>
<td>236,645 kg/hr</td>
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<tr>
<td><strong>Raw Materials and Utilities</strong></td>
<td></td>
<td></td>
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<tr>
<td>Ammonia</td>
<td>25 kg/hr</td>
<td>2,329 kg/hr</td>
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<tr>
<td>Low pressure steam</td>
<td>46,295 kg/hr</td>
<td>4,398,025 kg/hr</td>
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<tr>
<td>Cooling water</td>
<td>64,390 kg/hr</td>
<td>6,117,050 kg/hr</td>
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<tr>
<td>Natural Gas</td>
<td>21,275 scf/hr</td>
<td>2,021,082 scf/hr</td>
</tr>
<tr>
<td>Electricity</td>
<td>846 kWh/hr</td>
<td>80,370 kWh/hr</td>
</tr>
</tbody>
</table>

* Preliminary Process Design (12.5% IRR; 15 year lifetime)
Possible Cost Reducing Areas

• Equipment
  – Mult. Effect Evaporator – 16% total BMC
  – Heliostats – 12% total BMC
  – NOx Reactor – 11% total BMC
  – Salt System – 2.3% total BMC

• Variable costs
  – Ammonia – 19% TVC
  – Steam – 48% TVC
  – Natural Gas – 17% TVC
Cost Reductions Applied Individually

Cost Reduction from Base, $/kg

Price of H₂, $/kg

Type of Action

Scale Up | MEE | NOx Reactor | Heliostats | Lower RK Temp | Salt System
Sensitivity Analysis: TPI and Fixed Operating Costs (TFC)

15 year plant
All cost reductions except with multiple effect evaporator

Cost of Hydrogen ($/kg)

% Change in Total Fixed Costs, and Total Permanent Investment
Impact of Cost Reductions

• All cost reductions except multiple effect evaporator:
  – $829 million TPI
  – $6.58/kg for 12.5% IRR (15 yr lifetime)
  – 8.8% ROI, 11.4 years PBP

• All cost reductions (40 yr plant life)
  – $764 million TPI, $3.01/kg for 10 % IRR
  – Break Even: $1.50/kg H₂ selling price
Key Areas for Research

- Integration of single secondary reaction step with multiple solar fields/reactors ($11+/kg)
- NaOH recovery step using alternative technologies such as membrane separation, …($4+/kg)
- Rapid $\text{Mn}_2\text{O}_3 \rightarrow 2 \text{MnO} + \frac{1}{2} \text{O}_2$ in air and in-situ mitigation of NOx ($2/kg$)
- Reduced heliostat costs ($1/kg$)
- Kinetics of $\text{Mn}_2\text{O}_3 \rightarrow 2 \text{MnO} + \frac{1}{2} \text{O}_2$ (lowest temperature) ($1/kg$)
- Consider alternative secondary reaction steps
Experimental Work Plan Development

- Rapid dissociation kinetics ($\text{Mn}_2\text{O}_3 \Rightarrow 2\text{MnO} + \frac{1}{2}\text{O}_2$) investigation underway (STCH funding in Yr 1)
- $\text{MnO} + \text{NaOH} \Rightarrow \frac{1}{2}\text{H}_2 + \text{NaMnO}_2$; $\text{H}_2$ liberating step experiments being planned
- $\text{NaMnO}_2 + \frac{1}{2}\text{H}_2\text{O} \Rightarrow \frac{1}{2}\text{Mn}_2\text{O}_3 + \text{NaOH}$; water splitting step experiments being planned
Hydrogen Safety

• At this stage of the project, H₂ quantities involved in the experiments are so minimal as to pose no H₂ safety risks
• The most significant current hazard is associated with ultra-high temperature (> 1500°C) operations
• Hazards mitigated with personnel training, well documented SOPs, and internal safety reviews
Conclusions/Summary

• The Mn$_2$O$_3$/MnO cycle provides an opportunity for low cost renewable H$_2$
• Significant development needs made relative to process integration at large scale, NaOH recovery and NOx mitigation
Acknowledgement

• DOE Hydrogen Program