Fundamentals of a Solar-thermal
Mn$_2$O$_3$/MnO Thermochemical Cycle
to Split Water

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Project ID No. PDP15
Overview

Timeline
• 6-1-2005
• 5-31-2009
• 25% completed

Budget
• Total Project Funding
  $330,000 DOE ($180,00 via UNLV)
  $82,500 Cost share
• Funds received in FY05
  $110,000 ($60,000 via UNLV)

Barriers
 AU. High-Temperature Thermochemical Technology
 AV. High-Temperature Robust Materials
 AW. Concentrated Solar Energy Capital Cost
 AX. Coupling Concentrated Solar Energy and Thermochemical cycles

Partners
Swiss Federal Research Institute (Aldo Steinfeld)
Objectives

• Research and develop a cost effective 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 underway for major reactions
**Literature Cycle**

- **Concentrated Solar Energy**
  - $Mn_2O_3 \rightarrow 2MnO + \frac{1}{2}O_2$
  - Metal Oxide Decomposition

- **Water Splitting**
  - $NaMnO_2 + \frac{1}{2}H_2O \rightarrow \frac{1}{2}Mn_2O_3 + NaOH$
  - **H₂ Liberating Step**

- **H₂ (product)**
  - $MnO + NaOH \rightarrow \frac{1}{2}H_2 + NaMnO_2$
  - $NaMnO_2$

- **O₂ (vent)**
  - $H_2$ and $O_2$ are produced from the splitting of water and the decomposition of metal oxides.
Mn$_2$O$_3$/MnO Solar Cycle

- **Advantages**
  - Relatively low temperature (~1650 °C, or lower)
  - All solid/liquid species → no recombination
  - Can be performed in air

- **Disadvantages**
  - Corrosive nature of NaOH
  - Energy-efficient separation of NaOH/Mn$_2$O$_3$ difficult
  - Three step cycle has decreased efficiency
  - Multiple oxide species involved
Goals

• Perform high temperature reaction with small particles in an aerosol flow reactor
• Verify hydrogen formation when NaOH is added to MnO at elevated temperatures
• Optimize hydrolysis and separation of reaction products for recycle into 1\textsuperscript{st} and 2\textsuperscript{nd} steps
• Identify kinetics/mechanism
Key Challenges

• Solve separation problem in 3^{rd} step for favorable economics: Currently 1 molar solution for 90% leaching necessary!

• Investigate effect of sodium carry-over to high-temperature reaction (10% residual)
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

• Mn$_2$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
• H$_2$ production step carried out at reduced P; H$_2$ removed to shift equilibrium to right (100%)
• 90% conversion assumed on water splitting step
• Multi-effect evaporator considered to recover NaOH
• H$_2$ supplied to pipeline at 300 psig
Simplified Process Flowsheet:

**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**

\( 2MnO + 2NaOH \rightarrow H_2 + 2NaMnO_2 \)
Process Simulation
Key Areas for Research

• Kinetics of $\text{Mn}_2\text{O}_3 \rightarrow 2 \text{MnO} + \frac{1}{2} \text{O}_2$ at reduced pressure to determine how low of a temperature the high step reaction can be carried out at (increases process efficiency)

• Demonstrate $2^{\text{nd}}$ and $3^{\text{rd}}$ steps in the cycle and verify pinch points

• Develop an alloy ($\text{Mn}_x\text{Metal}_y\text{O}_z$) providing for a Na salt with improved solubility in water (i.e. to reduce the amount of water that needs to be distilled off to recover NaOH)
Experimental Work

- Rapid dissociation kinetics ($\text{Mn}_2\text{O}_3 \rightarrow 2\text{MnO} + \frac{1}{2}\text{O}_2$) investigation underway (SHGR funding in Yr 1)
- $\text{MnO} + \text{NaOH} \rightarrow \frac{1}{2}\text{H}_2 + \text{NaMnO}_2$; preliminary H$_2$ liberating step experiments carried out
- $\text{NaMnO}_2 + \frac{1}{2}\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{Mn}_2\text{O}_3 + \text{NaOH}$; preliminary water splitting step experiments carried out
Mn$_2$O$_3$ TGA Decomposition

ZrO$_2$ crucible in argon @ 10 deg C/min

\[ 3\text{Mn}_2\text{O}_3 \rightarrow 2\text{Mn}_3\text{O}_4 + \frac{1}{2}\text{O}_2 \]

Expected: -3.4%  Actual: -3.7%

\[ 2\text{Mn}_3\text{O}_4 \rightarrow 6\text{MnO} + \text{O}_2 \]

Expected: -10.1%  Actual: -12.9%
TGA Decomposition Challenges

- Product sinters to crucible
  - No product analysis possible
- Solution → run under vacuum
  - Performed some preliminary runs
    - Have had initial problems keeping balance stable
  - Can obtain 500 mtorr atmosphere during run
Effect of Reduced Pressure
• 10 °C/min to 1310°C
• Sample mass = 600 mg
• Some sintering of product to crucible
• Dark greenish color (as MnO)
• Oxygen = 21.6% (MnO = 22.6%)

• 10 °C/min to 1200°C
• Sample mass = 870 mg
• No sintering of product to crucible
• Partial reaction – product contains both Mn₂O₃ (brownish-red color) and MnO (dark greenish color)
Experimental Results
Support Thermodynamics

**Reaction 1**

\[ \text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4 \]

\[ T = 650^\circ\text{C} \quad P = 550 \text{ mtorr} \]

**Reaction 2**

\[ \text{Mn}_2\text{O}_3 \rightarrow \text{MnO} \]

\[ T = 1220^\circ\text{C} \quad P = 0.1 \text{ atm} \]
Reduced Pressure Studies
Summary

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Argon Flow</th>
<th>Vacuum (500 mtorr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3\text{Mn}_2\text{O}_3 \rightarrow 2\text{Mn}_3\text{O}_4 + \frac{1}{2}\text{O}_2$</td>
<td>1330 °C</td>
<td>750 - 850 °C</td>
</tr>
<tr>
<td>$2\text{Mn}_3\text{O}_4 \rightarrow 6\text{MnO} + \text{O}_2$</td>
<td>1580 - 1620 °C</td>
<td>1200 - 1310 °C</td>
</tr>
</tbody>
</table>

- Performing decomposition under reduced pressure conditions **does** reduce reaction temperatures
- Product oxygen mass content analyses indicate **full conversion** to MnO
Horizontal Tube Furnace

- For study of 2\textsuperscript{nd} and 3\textsuperscript{rd} steps
- Pull sample into hot zone at desired temperature
- Online mass spectrometer
MnO + NaOH $\rightarrow$ NaMnO$_2$ + $\frac{1}{2}$H$_2$

$T = 700$ °C

84% conversion from H$_2$

H$_2$ is produced

Mass Spectrometer Hydrogen Signal
XRD Product Analysis

MnO + NaOH → NaMnO₂ + ½H₂
MnO + NaOH $\rightarrow$ NaMnO$_2$ + $\frac{1}{2}$H$_2$
NaMnO$_2$ + H$_2$O $\rightarrow$ $\frac{1}{2}$Mn$_2$O$_3$ + NaOH

**Challenges**
- Optimize hydrogen production step
  - Grinding MnO/NaOH mixture appears to increase conversion
- Separation of Mn$_2$O$_3$/NaOH solid species

**Further options**
- Temperature based phase separation
- Mixed manganese oxides
  - Prepare Mn$_x$Fe$_{1-x}$O and Mn$_x$Zn$_{1-x}$O with sol-gel process
  - Verify hydrogen production with these mixed oxides
  - Investigate the separation efficiency with NaOH
    - Compare to Mn$_2$O$_3$/NaOH separation efficiency
Conclusions/Summary

• The Mn$_2$O$_3$/MnO cycle provides an opportunity for low cost renewable H$_2$
  - air in high temperature (HT) step
  - HT < 1250 °C (possible metal alloy receiver)
  - little MnO/O$_2$ recombination concern
• Significant development needs made relative to process integration at large scale, NaOH recovery and NOx mitigation
Major Collaboration

- ETH-Zurich is working with CU on the design of a solar-thermal transport tube reactor to interface to their High Flux Solar Simulator
  - reactor design
  - heat transfer modeling
  - experimentation
Acknowledgement

• DOE Hydrogen Program