

II.1.2 Fundamentals of a Solar-thermal Hydrogen Production Process Using a Metal-Oxide Based Thermochemical Water Splitting Cycle

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Objectives

- A fundamental understanding of the Mn_2O_3/MnO and ferrite-based ($MxFeyO_4$) solar-thermal thermochemical cycles to split water through theoretical and experimental investigations.
- A process flow sheet and an economic analysis for the best process options.

Technical Barriers

This project addresses the following technical barriers from the High-Temperature Thermochemical, Solar-Driven Production of Hydrogen section (3.1.4.2.7) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

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

Technical Targets

- Cost of Hydrogen (delivered, untaxed, 2005\$, by 2015) at \$3/kg

Accomplishments

- Preliminary process flowsheet developed and simulated.
- Very preliminary economics carried out.
- Preliminary key areas identified for research (based on preliminary simulations and analysis).
- Preliminary experimental workplan underway for primary thermochemical cycle reactions.

Introduction

The most benign and renewable method for obtaining hydrogen is by using sunlight to split water. Splitting water directly with solar-thermal energy is not practical since the temperature required in order to obtain high conversion is above 4,000 K. Another huge challenge is the requirement to separate gaseous hydrogen from oxygen at these temperatures. Multi-step thermochemical cycles which split water through a series of two or more chemical reactions provide an opportunity for carrying out the high temperature step in the process at more modest temperatures of less than 2,000 K. In addition, with thermochemical cycles, oxygen and hydrogen are removed in separate steps, thus avoiding the recombination issues. The Mn_2O_3/MnO and ferrite cycles allow lower operating temperatures compared to other thermochemical metal oxide cycles and are of particular interest.

Approach

The approach taken to assess the technical and economic feasibility is:

1. Develop an initial process flow diagram based on available public information regarding the cycle; simulate integrated process; and identify key areas for research and development.
2. Develop and carry out an experimental plan to evaluate the feasibility of all steps in the cycle.
3. Carry out computational fluid dynamics (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.

Results

The literature was surveyed and a preliminary process flow sheet was developed using conventional process equipment (Figure 1). A very preliminary economic study was carried out in order to identify key areas for research and an experimental work plan is underway for the major reactions.

The three primary steps in the cycle include:

- $Mn_2O_3 \rightarrow 2 MnO + \frac{1}{2} O_2$ (metal oxide decomposition; Step 1)
- $MnO + NaOH \rightarrow \frac{1}{2} H_2 + NaMnO_2$ (hydrogen liberation; Step 2)
- $NaMnO_2 + \frac{1}{2} H_2O \rightarrow Mn_2O_3 + NaOH$ (water splitting; Step 3)

Regarding the preliminary process flow sheet (Figure 1), solar energy is supplied to the solar-thermal reduction reactor from three 8 MW_{th} heliostat fields. The overall efficiency of the heliostat fields and secondary concentrators is approximately 65% and the solar concentration is approximately 3,000 suns. The optimal tower height for these heliostat fields is 125 m. The reactor efficiency is determined by accounting for reradiation losses and, for a concentration of 3,000 suns and a temperature of 1,868 K, is approximately 58.6%. Thus a total of 9,142 kW_{th} is available to heat the reactants. The solids feed to the reactor has a flow rate of 24,560 kg/hr and consists of approximately 85 mole percent Mn₂O₃ and 15 mole percent NaMnO₂. It is assumed that the solar-thermal reduction reaction is

unaffected by the presence of the NaMnO₂ although this assumption has not been verified in the literature. An air stream with a flow rate of 623.6 kg/hr consisting of 79 mole percent N₂ and 21 mole percent O₂ is compressed from atmospheric pressure to 207 kPa and is mixed with the solids feed. The combined feed is then preheated to 1,273 K and fed to the solar thermal reactor. The solar thermal reduction reaction reaches 80% conversion in the reactor. Furthermore, approximately 1% of the N₂ is converted to NO and 1% is converted to NO₂. As will be discussed later, these conversions of N₂ are likely overestimates of the actual amount of NO_x that is formed in the reactor. The products enter the cooling zone of the reactor at 1,835 K and 186.3 kPa. There are four heat exchangers in the cooling zone of the reactor. The first heat exchanger is used to preheat the entering reactants. The second heat exchanger transfers heat to a molten salt system at a rate of 5,324 kJ/s thereby lowering the product temperature to 984 K. The third heat exchanger in the cooling zone of the reactor preheats the ammonia for use in the selective catalytic reduction (SCR) system from 325 K to 620 K. The temperature of the product stream is lowered to 799 K in this step. In the final heat exchanger the products transfer heat at a rate of 1,479 kJ/s to the molten salt system. The temperature of the products is thus lowered to 533 K and their pressure decreases to 103.6 kPa prior to exiting the cooling zone of the reactor. This product has a flowrate of approximately 25,190 kg/hr and consists of 63% MnO, 17% oxygen, 8% Mn₂O₃, 7% NaMnO₂, 5% N₂ and trace amounts of NO and NO₂ (NO_x).

This product stream enters the baghouse filter at 533 K and 103.6 kPa. The solids are filtered out in the baghouse resulting in a solids stream with a flow rate of 22,790 kg/hr and a composition of 81% MnO, 10% Mn₂O₃ and 9% NaMnO₂. The gas stream from the baghouse filter has a flow rate of 2,396 kg/hr and consists of 77% O₂, 22% N₂, and trace amounts of NO_x. The solid stream is sent via a solids conveying system to a storage tank. The gas stream is mixed with ammonia at a temperature of 620 K and 122 kPa and fed to the SCR system where the nitrogen oxides are reduced over a catalytic bed of TiO₂ and V₂O₅ with small amounts of WO₃. The product from the SCR system has a mass flow rate of 2,420 kg/hr and consists of 76% O₂, 22% N₂, 1.4% H₂O, 0.1% ammonia and small amounts of NO_x. The levels of NO_x in this stream are on the order of 800ppm. This concentration of NO_x is not suitable for release to the environment. However, as will be discussed later, it is likely that the concentration of NO_x in the system was overestimated by a factor of ten or more and therefore the high value of 800 ppm is probably not physically realistic.

The MnO is mixed with a 50% sodium hydroxide solution and fed to the first of two rotary kilns that are heated by natural gas. The first rotary kiln operates at

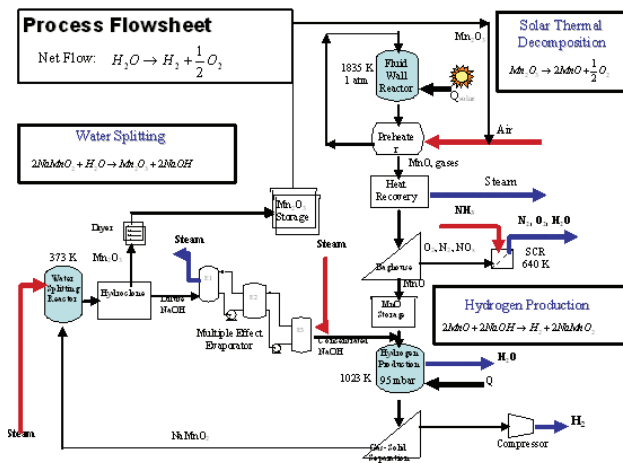


FIGURE 1. Mn₂O₃/MnO Preliminary Process Flow Sheet

low temperature (140°C) and its purpose is to boil off the excess water that was introduced with the 50% NaOH solution. The rotary kiln evaporates off 3,745 kg H₂O per hour. The solid product from the first rotary kiln has a temperature of 413 K (140°C) and is at approximately atmospheric pressure. The composition of this solids stream is approximately 44% MnO, 44% NaOH, 5% Mn₂O₃, 5% NaMnO₂, and 3% water. This product enters a second rotary kiln. This rotary kiln operates under reduced pressure (95 mbar). The reaction of MnO with NaOH has been demonstrated experimentally as an effective method of the production of pure hydrogen. The only products of this reaction are α-NaMnO₂ and hydrogen. The energy to heat this rotary kiln is provided by burning natural gas and 100% conversion is assumed. This is a key area of potential improvement to the process as hydrogen cannot be produced cleanly if natural gas is burned. The vapor product from the second rotary kiln has a temperature of 663 K and a pressure of 9.5 kPa (95 mbar). The composition of this vapor is approximately 89% H₂ and 11% water vapor. The vapor is cooled to 45°C and then sent to a series of compressors, heat exchangers and liquid/vapor separators. The heat exchangers are used as intercoolers between the compressors so that the temperature in the compressors is kept at or below 204°F. The liquid vapor separators are necessary because as the vapor is compressed, some of the water content is condensed out. This condensed liquid must be removed from the vapor before the vapor can be sent to the next compressor. The final product from this compression sequence has a pressure of 300 psi, a temperature of 354 K and a composition of about 99.5% hydrogen. This product, with a flowrate of 235 kg/hr, is sent to a hydrogen pipeline.

The solid product from the second rotary kiln has a mass flow rate of 31,430 kg/hr and a composition of around 90% NaMnO₂ and 10% Mn₂O₃. This product is mixed with a large excess of water (approximately a molar ratio of 55 moles of water to 1 mole of solids). The mixture is fed to the third and final reactor where 90% conversion of NaMnO₂ is assumed. There is some experimental evidence of the formation of birnessite (Na_{0.58}Mn₂O₄) from this reaction, but it is ignored for the purposes of this simulation. This third reaction occurs at approximately atmospheric pressure and a temperature of 373 K. The product from this step consists of approximately 97% water, 2% NaOH and 1% Mn₂O₃. The solid Mn₂O₃ is separated from the liquids in a hydroclone. The solid product has a composition of 79% Mn₂O₃, 14% NaMnO₂ and 7% water. The product is dried and then recycled back to the solar-thermal reduction reactor. The recycle stream has a flowrate of 24,560 kg/hr and a temperature of 378 K. The recycle stream contains 85% Mn₂O₃ and 15% NaMnO₂.

The liquid product from the hydroclone has a flow rate of 228,100 kg/hr and a composition of 98%

water and 2% NaOH (3.8% by weight). This product is concentrated using a multiple effect evaporator with five effects to a 50% solution of NaOH. The concentrated NaOH solution has a flow rate of 12,850 kg/hr and a temperature of approximately 300 K. This solution is recycled back to the first rotary kiln in order to complete the process loop.

The key advantages of this cycle include: (1) a relatively low operating temperature of less than 1,650°C, (2) seemingly easier separations at high temperature due to the fact that MnO is a solid at the highest temperature in the cycle, and (3) that, thermodynamically, the metal oxide decomposition step can be carried out in air.

The key disadvantages of the process include: (1) the corrosive nature of NaOH, (2) the difficult separation of Mn₂O₃ from NaOH, (3) inefficiencies due to the fact that the cycle involves three steps instead of two, and (4) that multiple oxide species (i.e. MnO, Mn₂O₃, NaMnO₂) are involved in the process, complicating separations and recovery.

A thermodynamic free energy minimization study of the Step 1 reaction (dissociation) indicated that the high temperature reaction could actually be carried out at reduced temperature less than 1,300°C, if the pressure was reduced. In order to evaluate this possibility, a set of thermogravimetric experiments was carried out at 500 mtorr pressure. The results are shown in Figure 2. Mn₂O₃ is converted to Mn₃O₄ at 750°C and is then converted to MnO at 1,310°C. Color changes (Mn₂O₃ was black, Mn₃O₄ was rust colored, MnO was green), measured oxygen content of the products, and x-ray diffraction (XRD) analysis (Figure 3) indicated that reaction went to completion. Studies are continuing to investigate the reaction at temperatures approaching 1,200 °C. A lower temperature operation would significantly reduce the capital cost of the process by

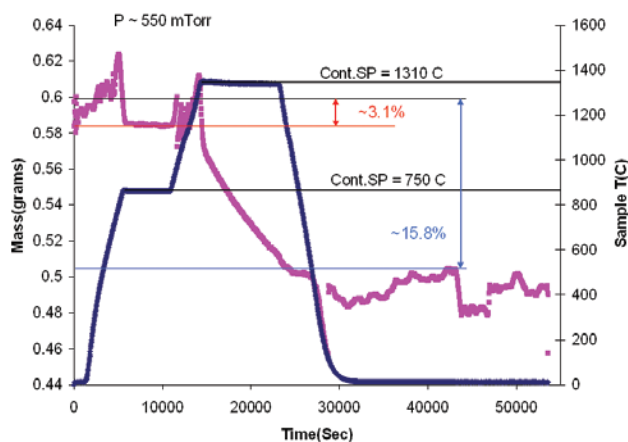


FIGURE 2. Thermogravimetric Analysis Results for Mn₂O₃ Decomposition (P ~ 500 mtorr)

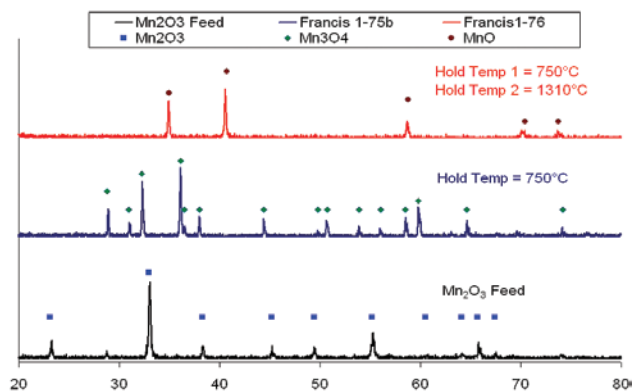


FIGURE 3. XRD Results for Thermogravimetric Analysis Products

reducing the number of heliostats required to provide sunlight and would also reduce the complexity of materials issues associated with the high temperature step.

The hydrogen generation step (Step 2) was also experimentally validated. A horizontal tube furnace was set up with a mass spectrometer to analyze product gases. MnO and NaOH were loaded into a quartz boat and argon was flowed through the tube over the boat of reactants. At 700°C, hydrogen began to be liberated (Figure 4), in line with the thermodynamic considerations. A conversion of 84% of the MnO was determined based on integration of the hydrogen generation peak per the mass spectrometer. An XRD of the reaction products indicated the presence of NaMnO₂ and residual MnO. These results were consistent with the mass spectrometer results, confirming significant hydrogen generation at 700°C.

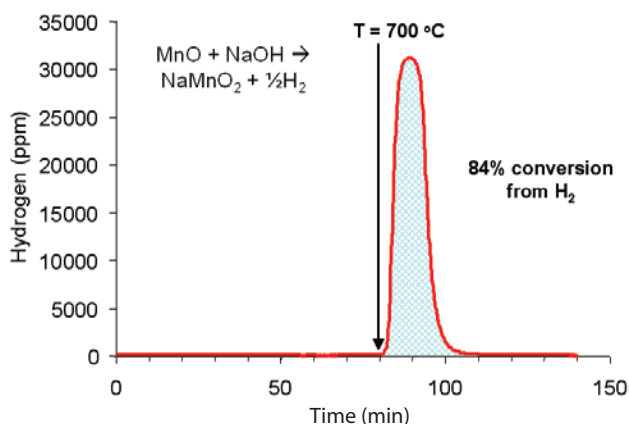


FIGURE 4. Mass Spectrometer Hydrogen Signal for Hydrogen Generation Step

Conclusions and Future Directions

- The Mn₂O₃ dissociation step can be completed at temperatures below 1,300°C if the reaction is carried out at a 500 mtorr reduced pressure.
- The hydrogen generation step is fast and can be driven to completion at temperatures slightly above 700°C.
- Work will continue in the evaluation of all three process steps, but with an emphasis on Steps 2 and 3 where research will be directed toward improving the separation of Mn₂O₃ from NaOH.

FY 2006 Publications/Presentations

1. Presented at the 2006 DOE Program Review (Washington, DC).