IV.I.2 Fundamentals of a Solar-thermal Mn_2O_3/MnO Thermochemical Cycle to Split Water

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Objectives

- Develop an understanding of the Mn_2O_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

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section 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 Target

Solar-thermal Production Costs

This project is conducting fundamental studies of the solar-thermal dissociation of water using a 3-step Mn_2O_3/MnO thermochemical cycle. Insights gained from these studies will be applied toward the development of hydrogen production that meet the DOE 2015 hydrogen production cost target of $3/gge at the plant gate using concentrated solar power.

Approach

The University of Colorado (CU) is teaming with the ETH-Zurich (Swiss Federal Research Institute) to develop a fundamental understanding of the solar-thermal dissociation of water using a 3-step Mn_2O_3/MnO thermochemical cycle and carry out experimentation using a high-temperature, solar thermal heat source to drive a manganese-oxide based thermochemical water-splitting cycle. The Mn_2O_3/MnO 3-step cycle (Figure 1) has a number of advantages relative to other cycles including (1) lower temperatures (< 1700°C) for thermal dissociation of the oxide, (2) standard industrial separation of dissociated solid MnO from gaseous O_2, (3) no noxious gases to deal with, (4) the ability to conduct the high temperature dissociation in air, avoiding inert gas usage, recovery, and recycle, and (5) a simple intermediate solid (MnO) which can be easily stored or processed independently to produce H_2 during off-sun times.

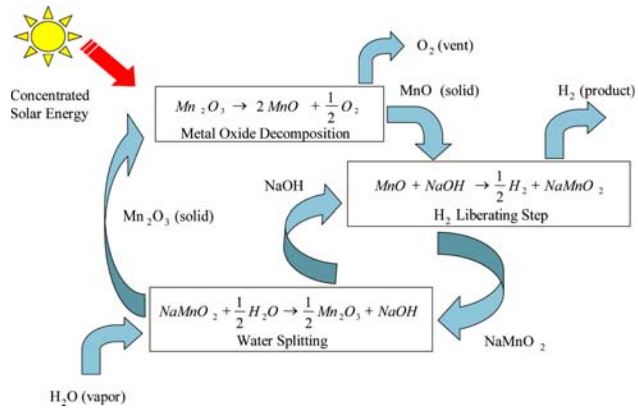

Figure 1. 3-Step Mn_2O_3/MnO Solar-thermal Thermochemical Cycle to Split Water

All three steps in the cycle will be investigated and the processing steps will be integrated by the end of the project with Mn_2O_3 being formed and reused in the recycle step. The initial feasibility of carrying out the high temperature (1550 to 1950°C) thermal reduction of Mn_2O_3 to MnO will be carried out at CU using an existing 10-cm inside diameter x 46 cm long hot zone, electrically-heated aerosol flow reactor. The reactor will be modified to incorporate compatible materials to prevent reaction of reactants and products with reactor materials. The reactor is completely instrumented (gas chromatograph/mass spectrometer, non-dispersive infrared, O_2 analyzer) and off-line characterization is available for analysis of the solid phase product (X-ray defraction, LECO fixed C/O, PSD, surface area, etc.). An improved solar-thermal transport reactor will be designed and constructed at CU for interfacing to the High-Flux Solar Simulator (HFSS) at ETH-Zurich where a temperature of at least 2000°C will be possible. Additional lab testing will be done to evaluate the supporting reactions in the cycle.

During the first year, research is focusing on proof-of-concept feasibility analysis. If the cycle appears feasible, a positive decision will be made for construction of the solar-thermal reactor and extensive testing as well as a more thorough understanding of the kinetics and thermodynamics of each cycle reaction will be developed. An analytical model of the reactor and process will be developed as well. In addition, a flow sheet will be developed for a full-scale process plant (see Figure 2 for preliminary flowsheet), material and energy balances will be carried out, equipment will be priced, and an economic profitability analysis will be done. The design/economics will be an ongoing aspect of the work and will be updated annually. Team meetings will be held at CU and at ETH-Zurich each year.

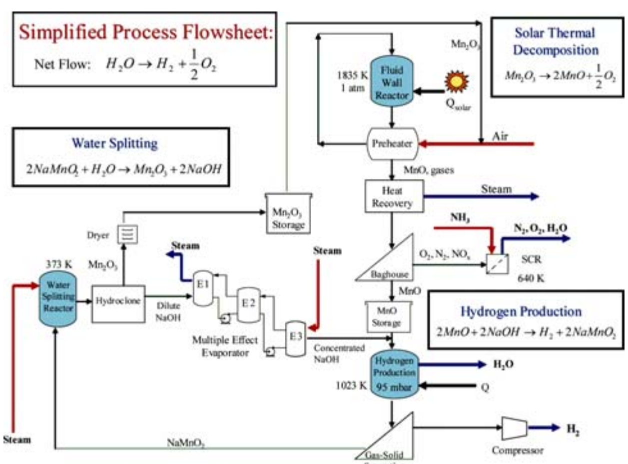

Figure 2. Preliminary Process Flow Sheet Using Conventional Process Equipment

The technology impact of the research may be significant. The reaction kinetics and efficiencies for the rapid high temperature reduction of Mn_2O_3 to MnO, the H_2 formation, and the Mn_2O_3 recovery will be identified. An improved efficiency solar-thermal aerosol reactor capable of achieving at least 2000^oC will be designed and demonstrated. The chemistry and solar-thermal heat source will be integrated at the ETH-Zurich HFSS facility using a CU/ETH-Zurich designed/constructed reactor. The feasibility of using a tubular transport reaction tube will be evaluated and the process design/economic evaluation of the process will be carried out. Hence, appropriate materials of construction will be evaluated for this high temperature use.

Accomplishments

- Key areas for research were identified:
  - Integration of a single set of secondary reaction steps with multiple solar fields/reactors for carrying out the high temperature step needs to be done in order to take advantage of the economics of scale
  - NaOH recovery step needs to be evaluated using alternative technologies such as a MnFe or MnCo alloy to improve process efficiency
  - Rapid $Mn_2O_3 \rightarrow 2MnO + 1/2O_2$ needs to be done in air at low temperature with in-situ NOx mitigation
  - Heliostat costs need to be reduced