II.F.3 Solar Hydrogen Production with a Metal Oxide-Based Thermochemical Cycle

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Subcontractors:
- Jenike and Johanson, San Luis Obispo, CA
- University of Colorado, Boulder, CO

Project Start Date: June 2004
Project End Date: Project continuation and direction determined annually by DOE

Fiscal Year (FY) 2011 Objectives

- Characterize reactive materials suitable for thermochemical hydrogen production under realistic operating conditions (e.g. temperature, atmosphere, heating rate).
- Develop a particle-based thermochemical reactor suitable for deployment on a central receiver platform and embodying several key design features.
- Evaluate the likely system level performance of the reactor concept and identify energy losses and opportunities for performance improvement.

Technical Barriers

This project addresses the following technical barriers from the production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(U) High-Temperature Thermochemical Technology

(V) High-Temperature Robust Materials

(X) Coupling Concentrated Solar Energy and Thermochemical Cycles

Progress toward the technical targets is shown in Table 1. Hydrogen cost from the particle reactor system has not yet been evaluated because the system level design is not complete and this is needed as the basis for an economic analysis. Heliostat cost reduction is not actively funded by this project, but is an element of the DOE Solar Program. The thermochemical efficiency for the particle reactor has been estimated to be 37% using commercially available cerium oxide reactant powder. This material is not the ideal from a thermodynamic perspective and will likely be improved upon as the project progresses. The reactor itself can be configured for any particulate reactant.

TABLE 1. Progress towards Meeting Technical Targets for Solar Drive High Temperature Thermochemical Hydrogen Production

Characteristic	Units	2012 Target	2017 Target	SNL 2011 Status
Hydrogen Cost	$/gasoline gallon equivalent H_2	6	3	N/A
Heliostat Cost	$/m^2	140	80	N/A
Process Efficiency	%	30	>35	30% estimated[1]

[1] This number is the product of receiver efficiency (solar in to heat available, ~82%) and thermochemical efficiency (heat available to lower heating value H_2 ~37%).
N/A - not available

Additional project targets outside of those listed in Table 1 are given as follows:

- Thermochemical Cycle (reactive materials): Oxidation and reduction reactions must reach 90% completion within two minutes.
- Reactor: Demonstrated conversion efficiency for the prototype reactor (5 kW_{th}) must be in excess of 20% at a pressure greater than 10 Pa.
- System: Estimated system level efficiency including collection and conversion losses must be in excess of 19% annual average for a dish system and 14% for a tower system.

Accomplishments

- Reactor
  - A detailed reactor performance model was developed and indicates that heat to hydrogen conversion efficiency in excess of 37% is possible using a cerium oxide-based thermochemical cycle.
  - Evaluated the compatibility of cerium oxide reactant with reactor construction materials including Al_2O_3, SiC, and Haynes 214 at nearoperational temperatures. SiC and Haynes 214 showed minimal or no interaction to 1,400°C, Al_2O_3 showed no interaction to 1,450°C.
  - Designed a particle conveyor system (subcontract with Jenike and Johanson) suitable for moving a powder reactant vertically in a packed bed arrangement. This configuration is required to achieve the best-case efficiency in the particle reactor. Prototype construction of the conveyor is currently in progress.

- Materials
  - A laser-based heating method was incorporated into our stagnation flow reactor that enables rapid thermal processing of sample materials. Heating rates in excess of 100°C/s are achievable at 500 W/cm^2 (5,000 suns).
  - The thermal reduction of various CeO_2 reactive structures, comprised of powders, felts, and fully dense forms, was characterized at operating pressures and heating rates relevant to solar thermochemical applications. It was determined that for CeO_2 reactive structures with characteristic dimensions less than 1 mm, oxygen evolution kinetics would likely not limit use of this material in the proposed reactor configurations.
  - Experiments to characterize the thermal reduction and water splitting kinetics for the following material structures and chemistries have been conducted: CeO_2 felt, CeO_2 and Mn-doped CeO_2 powder, atomic layer deposition (ALD) thin film Fe_2O_3/CeO_2, ALD thin film Fe_2O_3/m-ZrO_2, ALD thin film Fe_2O_3/Al_2O_3 (hercynite). We are in the process of analyzing the complete data set.
- System
  - A general system level model was developed to estimate the annual average hydrogen production efficiency of the particle reactor system. Results show that an annual average solar-to-hydrogen conversion efficiency of 24% is possible in a dish based system with a cerium oxide reactant.
  - A separate system model that includes a more detailed description of the reactor (temperature dependent properties, rigorous treatment of chemical reactions) was developed in ASPEN.

Introduction

Solar-powered thermochemical water splitting produces hydrogen using only water, heat from the sun, and chemicals that are completely re-cycled so that only hydrogen and oxygen are produced and only water and solar thermal energy are consumed in the cycle. All known thermochemical cycles face obstacles that could include extremely high temperature, highly corrosive chemicals, difficult separations of chemicals during sequential cycle steps, multiple reaction steps necessary to close the cycle, or side reactions with stable products that poison the process upon recycling, Many of these barriers can be overcome, but generally at the expense of energy efficiency, consumption of feedstocks other than water, and possibly much higher temperature to drive reactions to completion. All of these measures add cost to the product, inhibit acceptable production rates, or prevent the realization of plant designs with acceptable lifetimes. Overcoming these barriers is made even more difficult by turning to solar radiation for the driving energy source, primarily because of its transient nature and relatively low power density. The low power density characteristic of solar power requires large collector areas and efficient concentrators to drive energy-intensive processes like water splitting.

The ultimate success of solar thermochemical hydrogen production is contingent on developing suitable reactive materials and on incorporating these materials into an efficient solar thermochemical reactor. Currently, SNL and the University of Colorado are working together to identify and characterize prospective thermochemical cycles and associated reactive materials. Recent efforts have focused on ferrites, cerium oxide, and hercynite as potential candidate material "families". Additional research and development efforts are directed at reactor and system level challenges related to collecting and applying solar thermal energy to the water splitting function within each of these cycles. Solar thermochemical reactors for ultra-high temperature processes (T >1,300°C) are being developed and tested by SNL.

Approach

Metal oxide-based materials, such as those containing cerium oxide or iron oxide (ferrites), have demonstrated the capability of splitting water in a two-step cycle consisting of a high temperature, oxygen-liberating thermal reduction reaction (up to 1,500°C) and a lower temperature, hydrogen-producing water oxidation reaction (<1,000°C). In order to achieve large hydrogen production volumes in a practical device these two reactions should be run in a continuous manner. In addition, in order to achieve high efficiency it is desirable to maximize the extent of reaction and essential to recover sensible heat between the high and low temperature reactions (recuperation). Also, any practical solar-driven reactor will operate continuously for thousands of hours without requiring service. Any reactive materials used in such a reactor must demonstrate an acceptable level of chemical and mechanical durability.

We are developing a particle-based reactor concept suitable for continuous hydrogen production on-sun in either a central receiver or parabolic dish configuration. Our technical efforts are organized into three tasks:

- **Reactor Development:** This task focuses on the reactor design, performance estimation and eventual validation at the prototype level (5-10 kW_{th}). Specific areas of effort include the design of high temperature solar reactor components along with material compatibility studies to evaluate interactions between the thermochemical reactant and products and materials used in reactor construction.
- **Materials Characterization:** Although materials are available today that can achieve performance levels near the DOE targets, there is considerable room for improvement. In this task we use a unique experimental capability to evaluate the performance of prospective

materials under controlled conditions similar to what might be found during on-sun operation. This system, based on a laser heated reaction chamber, allows for the evaluation of reaction thermodynamics and kinetics of prospective thermochemical cycles.

- **System Level Analysis:** The ultimate goal of this project is to produce hydrogen efficiently from solar energy. In this task we estimate the performance of thermochemical technologies at the system level, identifying energy losses and calculating annual average hydrogen production efficiency based on the collection platform and facility location.

Results

The results from FY 2011 show that the combination of our particle reactor concept and cerium oxide-based reactive materials has the potential to achieve performance near the 2012 and 2017 DOE targets. Meeting these targets with actual hardware during on-sun operation will require additional effort in FY 2012 and beyond.

Reactor Development – The particle reactor being developed in this project uses cerium oxide powder in a two-step redox cycle to continuously produce hydrogen from solar energy and water. A schematic of the reactor concept is shown in Figure 1. Key attributes of the reactor are recuperation of sensible heat between the reaction steps, continuous flow, direct absorption of solar energy by the reactant, and the spatial separation of pressure, temperature, and reaction products within the device.

Our preliminary work in FY 2011 focused on estimating the likely level of reactor performance achievable in a mature technology. For this study we assumed that the reactant would be CeO_2, which has been shown to be suitable for two-step thermochemical hydrogen production, but is not considered to be ideal due to the relatively small amount of oxygen exchanged per mole of reactant. Even so, with recuperation the performance of the reactor in terms of the conversion of thermal energy to chemical energy in the form of a hydrogen product can exceed 40% at a thermal reduction pressure in excess of 100 Pa (Figure 2). With improved materials this level of performance can be even higher.

Efforts to design a reactor prototype at the 5-10 kW_{th} level have focused on identifying a suitable means of conveying a packed powder vertically within the reactor. To this end a contract was placed with Jenike and Johanson, specialists in the field of powder conveyance. They identified a conveyor based on the "Old's Elevator" approach in which particles are moved by friction up a stationary central screw by contact with a rotating cylindrical housing. A conceptual design of the conveyor system, included rotary airlocks and cyclone separators, is shown in Figure 3. This system will be modified during the final solar prototype design stage.

Our reactor design efforts also included a study of the compatibility of various construction materials with cerium oxide powder. We have shown that several materials including Haynes 214 and Al_2O_3, are compatible with cerium oxide up to 1,400°C. Our hope is that it will eventually be possible to use a metal like Haynes 214 for the main components of the screw conveyor as this would minimize difficulties with fabrication. This may not be possible at a temperature much in excess of 1,200°C due to material strength issues. We are therefore continuing to investigate options for fabricating the conveyor components from suitable ceramic materials.

Materials Characterization – A number of experiments were conducted that focused on the characterization of pure cerium oxide reactive materials. In this work, a

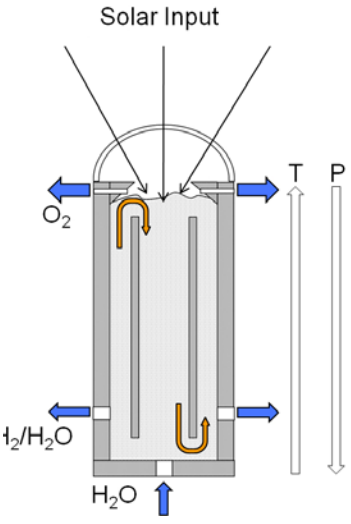


FIGURE 1. A schematic of the particle reactor concept. Particles must be conveyed vertically as a packed bed within the reactor. Concentrated solar energy enters from the top.

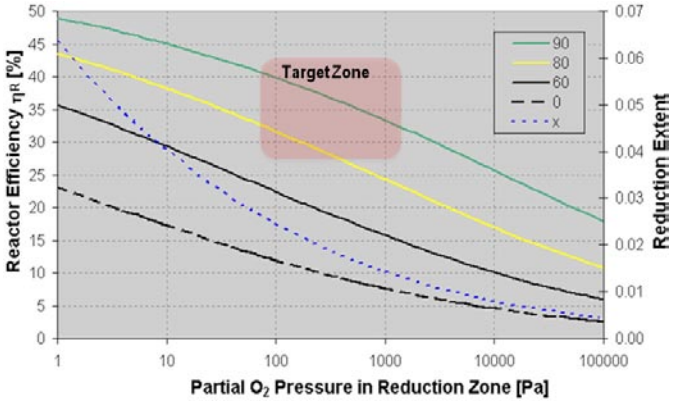


FIGURE 2. Predicted performance of the particle reactor using pure CeO_2 reactant. Reactor efficiency is analogous to the DOE "process efficiency" number.

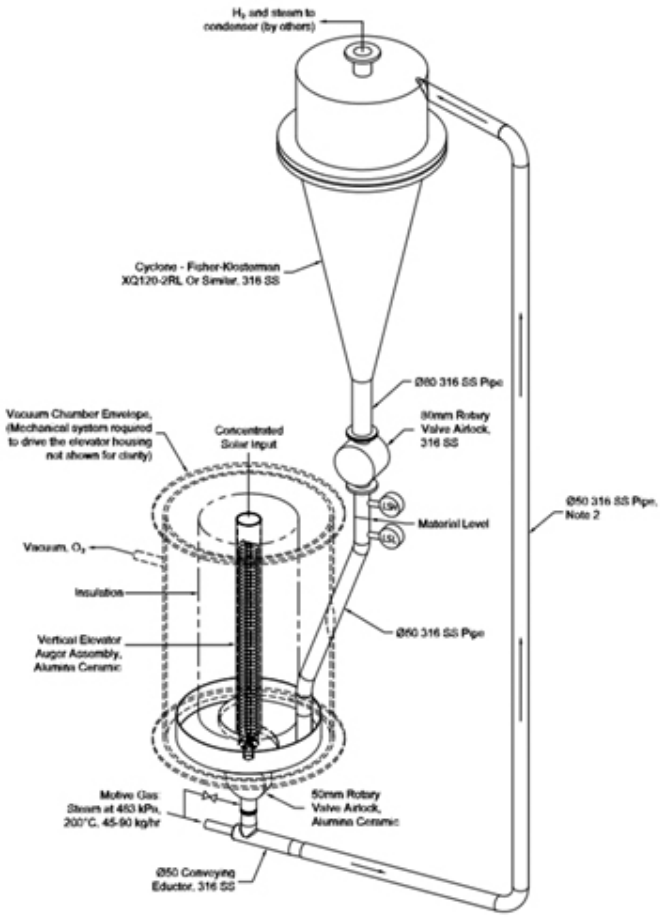
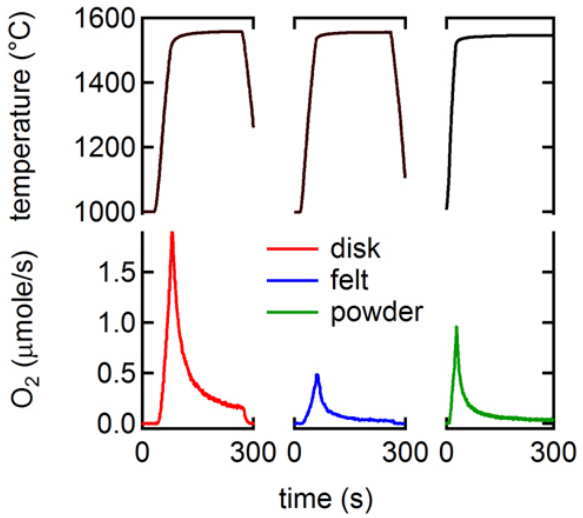


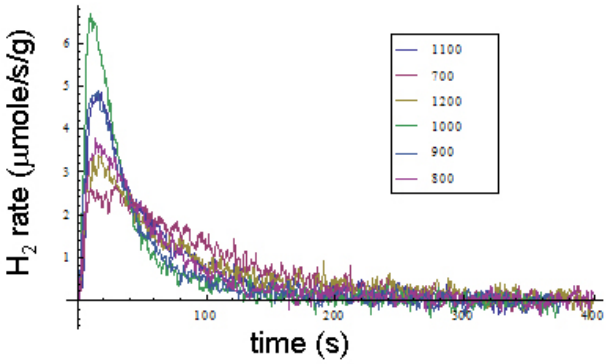
FIGURE 3. Conveyor system preliminary design.

laser-based heating method was used in conjunction with a stagnation flow reactor equipped with a mass spectrometer to investigate both the thermal reduction and oxidation reactions for cerium oxide powders, dense pellets, and felts. The rate of oxygen evolution during thermal reduction was measured for: (1) a powder having a ~5 µm particle diameter, (2) a 1,000 µm thick fully dense pellet, and (3) a felt with ~10 µm fiber diameter. Tests were conducted at a peak temperature slightly above 1,500°C and a heating rate in excess of 100°C/s. The results are illustrated in Figure 4 and show that the reaction rate and ultimate extent of thermal reduction was independent of the length scale over the range evaluated. The rate of the hydrogen-producing water splitting reaction using cerium oxide felt was measured over a range of temperatures in an attempt to characterize the optimal operating point for this type of reactive structure. These tests showed that the peak hydrogen production reaction rate varies with temperature, reaching a maximum near 1,000°C, but the overall amount of hydrogen production per unit mass of reactant was independent of reaction temperature (Figure 5). In the case of reaction at 1,000°C, the amount of time required for 90% completion is less than 90 seconds, which is consistent with



form	mass (mg)	mole O (×10^{-6})	δ
disk	960	220	0.0394
felt	207	48	0.0398
powder	454	91	0.0350

FIGURE 4. Thermal reduction behavior observed for various forms of CeO_2.



temperature (°C)	total H_2 (µmole/g)	peak H_2 (µmole/s/g)
1200	274	3.27
1100	273	4.76
1000	249	6.51
900	229	4.75
800	235	3.60
700	285	2.64

FIGURE 5. Rate of H_2 production for thermally reduced CeO_2 felt.

the operational requirements of a solar thermochemical reactor. Thirty cycles were run over which the production characteristics remained constant, which indicates that there was no degradation of the reactive material or its physical structure. A number of other chemistries for solar thermochemical water splitting were also evaluated this FY, including modified cerium oxide and ALD-ferrite-coated reactive structures. Analysis of the data is ongoing and will be completed before the end of FY 2011.

System Level Analysis – The focus of the system level analysis was to identify all energy losses within the solar collection and reactor sub-systems and then estimate the annual average conversion efficiency of sunlight to hydrogen. The analysis was based on hourly meteorological data for a design location in Daggett, CA. System performance was calculated for each hour of an entire year and the energy inputs and hydrogen outputs summed over the year to determine the efficiency. Figure 6 is a summarized output showing principal energy losses within the system. It is important to note that 42% of the solar energy available to the parabolic dish collector is lost during collection and not available to power the thermochemical reaction. Although this may be improved slightly, the parabolic dish is a very efficient optical platform and large gains in collection efficiency are not likely. This fact is a compelling argument in support of dedicating significant effort to reactor design in order to maximize its efficiency.

The current system model, which was constructed in Excel, was provided to researchers at Pacific Northwest National Laboratory for inclusion in their ASPEN-based studies. We have also begun developing our own reactor models in ASPEN with the intent of eventually simulating the entire system (annual performance) with this code.

Conclusions and Future Directions

The progress made in FY 2011 will provide a strong foundation for continued work in FY 2012 that will hopefully culminate in the on-sun demonstration of a particle reactor prototype. Specific conclusions and future directions for each of the three main project elements are given as follows:

Reactor Development – In FY 2011 we have shown that the particle reactor concept can meet the DOE performance targets and are well on our way to completing the design of a 5-10 kW_{th} prototype system. In FY 2012 and beyond we will focus our efforts on completing the design and performing on-sun testing of the reactor. Past experience has shown that when dealing with thermochemical fuel production hardware it is essential to test systems under realistic condition to identify technical challenges that are not apparent when performing more idealized preliminary analysis and simulation activities.

Materials Characterization – In FY 2011 we experimentally characterized several promising reactive materials under operating conditions similar to what would be expected in a solar thermochemical reactor. In FY 2012 and beyond we will define a standard performance evaluation process and metrics that can be used to more easily compare various candidate materials. We will also continue to characterize promising new redox chemistries for non-volatile metal oxide cycles using the laser-based heating method incorporated into the stagnation flow reactor, subject to the material characterization protocols developed in FY 2012.

System Level Analysis – In FY 2011 we developed an annual system performance model that shows all major

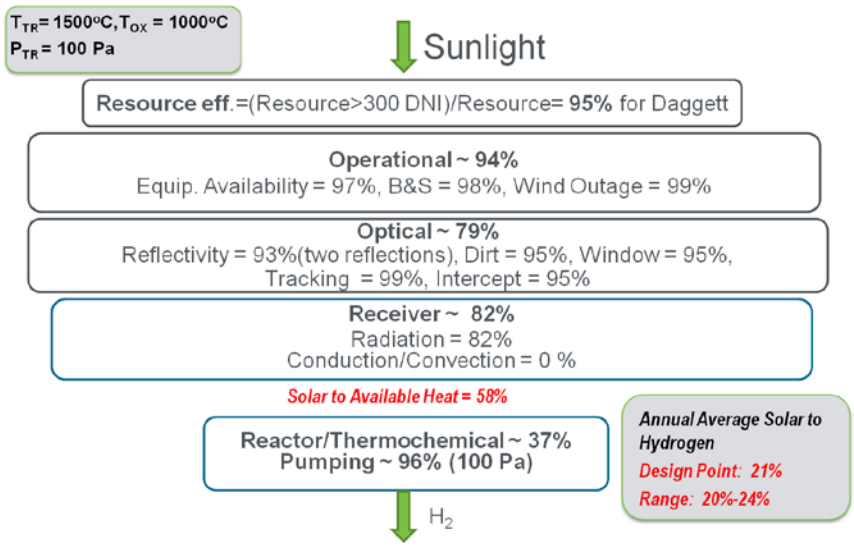


FIGURE 6. System level energy flow and annual average efficiency calculation.

energy losses in the system and enables the calculation of an annual average hydrogen production efficiency, a much more valuable number than a design point efficiency. In FY 2012 and beyond we will extend this model to a central receiver-based system configuration that will show the potential, and challenges, associated with scaling the particle reactor concept to larger sizes.

Definition of Terms

- Thermochemical Efficiency: This is the efficiency of the conversion of heat within the reactor to chemical fuel based on the lower heating value (LHV) of hydrogen. It does not include solar losses or energy losses from the receiver that are accounted for separately.
- Receiver Efficiency: The fraction of solar energy entering the reactor that is converted into useable heat available to the reactor. This term essentially accounts for radiation and convection losses from the receiver.
- Process Efficiency: The fraction of solar energy entering the reactor that is converted into chemical energy in the form of hydrogen on an LHV basis. This number is the product of receiver efficiency and thermochemical efficiency.
- Annual Average Efficiency: The total energy contained in hydrogen (LHV basis) produced over an entire year divided by the solar energy striking the collection system (mirrors) over the same period of time.
- Resource Efficiency: This quantity is the total solar energy that could be collected divided by the amount available over a year. Accounts for periods when the system is not operated by design.
- Operational Efficiency: The fraction of the total energy actually collected divided by the amount that could be collected over a year. This accounts for "wasted" energy when the collectors are not operating during the daytime due to weather outages or system maintenance.
- Optical Efficiency: The fraction of energy reaching the aperture of the reactor divided by the amount actually collected by the concentrator. Accounts for all reflection and transmission losses.

FY 2011 Publications/Presentations

1. Two abstracts submitted and accepted for presentation at SolarPaces 2011. Full papers are to be completed by July 31st, 2011.

2. A project summary was presented at the Annual Merit Review in Washington, D.C.

3. An invited talk entitled "*High temperature splitting of water and carbon dioxide using complex oxides as a route to solar fuels*" will be presented at the 242nd ACS National Meeting, Division of Fuel Chemistry, in August of 2011.

4. An abstract has been accepted for presentation at the 5th International Conference on Energy Sustainability hosted by the ASME in August of 2011.

5. "*Hydrogen Production via Chemical Looping Redox Cycles Using Atomic Layer Deposition-Synthesized Iron Oxide and Cobalt Ferrites*", Jonathan R. Scheffe, Mark D. Allendorf, Eric N. Coker, Benjamin W. Jacobs, Anthony H. McDaniel, Alan W. Weimer in Chemistry of Materials 2011 23 (8), 2030-2038.