

HIGH EFFICIENCY SOLAR PRODUCTION OF HYDROGEN FROM WATER

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1. Introduction

Science Applications International Corp. (SAIC) and the Florida Solar Energy Center (FSEC) of the University of Central Florida have teamed to develop an advanced solar thermochemical water-splitting cycle for hydrogen production that utilizes the “quantum boost” effect of sunlight [1]. The approach chosen by the SAIC-FSEC team is to concentrate on multi-step thermochemical water-splitting cycles that incorporate at least one step utilizing solar (visible and near-UV) photons directly. The program objectives are to generate hydrogen at above 40% efficiency and at less than \$3/kg. The thermochemical cycle chosen for further development is a hybrid sulfur-family cycle that incorporates reactions involving ammonia. The cycle utilizes the quantum portion of the sunlight to photocatalytically produce hydrogen. By employing quantum boost, the high-energy photons within the solar spectrum are utilized directly rather than thermalized, reducing the energy requirements for the high-temperature portions of the cycle. Because the photocatalytic reaction only uses the ultraviolet/visible portion of the solar spectrum, it has been proposed to split the solar beam into high-energy photons and thermal radiation using hot or cold mirrors and other approaches. SAIC has been investigating solar field configurations appropriate to supply solar energy to this cycle, including heliostat/central receiver, parabolic dishes, and other geometries.

2. Background

Ninety-five percent of hydrogen is presently produced from fossil fuels. In order for the U.S. to move towards a non-carbon hydrogen fuel infrastructure, reliable, cost effective, and renewables-based hydrogen production processes must be developed. There are several processes for using solar energy to produce hydrogen. These processes and their attributes are shown in Table 1.

Table 1. Comparison of Solar Hydrogen Production Processes

Process	Attributes
Natural photosynthesis	< 1% solar energy conversion efficiency
Direct decomposition	Temp. > 2,500°C & high temp. materials, gas recombination issue, degradation of photonic energy to heat
Photoelectrochemical	<15% solar to H ₂ efficiency, bias voltage is needed, photo-electrode corrosion issues, no efficient & stable photocatalyst has been found

PV-electrolysis	High potential, $\Delta E > 1.23$ V requirement, high cost of PV cells
Photocatalysis	Need for high band gap photocatalysts $E_g > 3.0$ eV, $< 5\%$ UV in terrestrial insolation, recombination of H_2 & O_2
Thermochemical	High efficiency ($> 50\%$), H_2 & O_2 are produced in separate processes

Thermochemical water splitting cycles (TCWSCs) are of particular interest because they can produce overall system efficiencies of 40-50% (compared to 28-32% for advanced electrolysis and direct thermal-to-hydrogen systems). Presently, there are two prospective high temperature heat sources suitable for thermochemical process interface. They are solar thermal concentrators and nuclear power (*i.e.* high temperature gas-cooled reactors). A universal drawback to almost all high-temperature thermochemical cycles investigated to date is that they utilize only the thermal component of the heat source. The solar spectrum is unique in that it contains significant amounts of high-quality photonic energy; by degrading or neglecting the quantum component of the solar spectrum these cycles are limited in their overall energy conversion efficiency. This neglect of the high-energy photonic component also requires the reactions to run at very high temperatures, significantly limiting the choice of materials and solar concentrating systems and the practicality of the approaches in general.

In recent years, considerable research in solar thermochemical cycles has focused on two-step oxidation/reduction cycles involving metal oxides (e.g., ZnO) used in combination with high-temperature solar concentrators. The temperatures required are often well above 1000°C, and efficiencies are low. The SAIC/FSEC approach is significantly more efficient than the other proposed hydrogen production processes and thus may lead to a cost effective method of producing hydrogen from the ultimate renewable resources – *i.e.* water and sunlight.

3. Project Overview

This project consists of a three-phase program of research and development leading to demonstration of a cost-effective high-temperature solar water-splitting cycle for hydrogen production using state-of-the-art high-flux solar concentrators. The project has as its primary goal the development of a cycle that not only uses solar flux for heating but also includes a “solar boost” from photon absorption in the chemical process. This approach has the potential to be more energy efficient and therefore more cost-effective than cycles that only use thermal energy for production of hydrogen from water. Secondary goals are to build and operate a pilot-scale solar hydrogen production system to demonstrate practical implementation of the selected cycle, and to verify the cost-effectiveness of this approach for commercial production of H_2 from water.

The project is divided into three phases.

- Phase 1: Cycle Testing and Preliminary Evaluation

- Phase 2: Bench-Scale Testing and Design
- Phase3: Pilot-Scale Demonstration

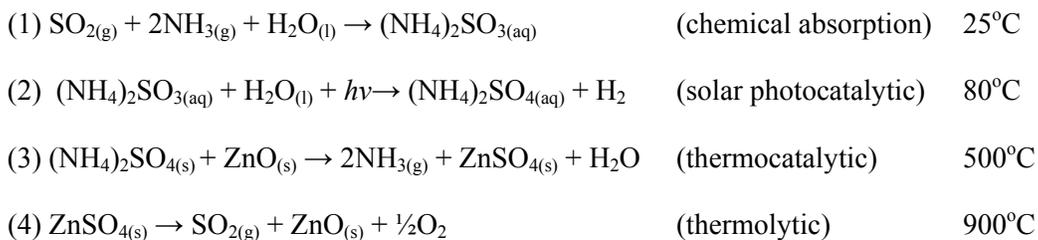
In the first phase, started in September 2007, laboratory testing and evaluation are being conducted. Thermodynamic and chemical equilibrium analysis of potential solar thermochemical cycles that include a photo-assisted step has been performed. The results are being combined with preliminary economic analyses to select a preferred cycle for further development. In the second phase, a bench-scale solar concentrator and reactor system will be used for on-sun validation of the selected process with continuous flow of materials, and a pilot-scale system will be designed. Finally, the third phase will include the fabrication of a fully-integrated pilot-scale solar hydrogen production system including an optimized solar concentrator system and solar reactor (with recycle loops included). The pilot-scale system will be operated to demonstrate the complete solar water-splitting process with a net reaction of water + sunlight → hydrogen and oxygen. Economic analyses will be completed to verify feasibility of the system to deliver hydrogen at less than \$3/kg.

The specific objectives of the project are shown below.

- Determine thermochemical and economic characteristics of potential solar-boosted water-splitting cycles
- Select a cycle that has the best potential for cost-effective production of hydrogen from water
- Demonstrate technical feasibility of the selected cycle(s) using solar input in bench-scale reactors
- Demonstrate pre-commercial feasibility through economic analysis of the selected cycle and demonstration of a fully-integrated pilot-scale solar hydrogen production system.

4. Hybrid Sulfur-Ammonia Thermochemical Cycle

Researchers at the FSEC have developed a hybrid sulfur-ammonia photo-thermochemical water-splitting cycle with an optional ZnSO₄-ZnO sub-cycle for the oxygen production step [2,3]. The cycle consists of the following four reactions:



Experimental and process simulation results obtained to date [4, 5] indicate that the FSEC cycle has the capability to reach a 1st Law efficiency of about 57%.

Reaction (1) in the S-NH₃ cycle is a chemical absorption step involving reaction between SO₂ and NH₃ to form aqueous (NH₄)₂SO₃. Reaction (2) is a step in which SO₃²⁻ ions are oxidized to SO₄²⁻ in water, generating hydrogen. Reaction (2) is a light-driven step and can occur either photocatalytically (subject to visible light) or photolytically under UV irradiation. Experimental data obtained to date show that it is possible to perform Reaction (2) with energy conversion efficiencies above 32% using doped cadmium sulfide (CdS) as the photocatalyst.

Reactions (3) and (4) are thermally-driven, high-temperature reactions that result in oxygen production and regeneration of SO₂, ZnO, and NH₃. Other cycles use a high-temperature sulfuric acid concentration and decomposition step that imposes severe materials stability requirements. The ZnO/ZnSO₄ sub-cycle, on the contrary, involves only solids and gases so species separations are simpler and none of the materials are difficult to handle.

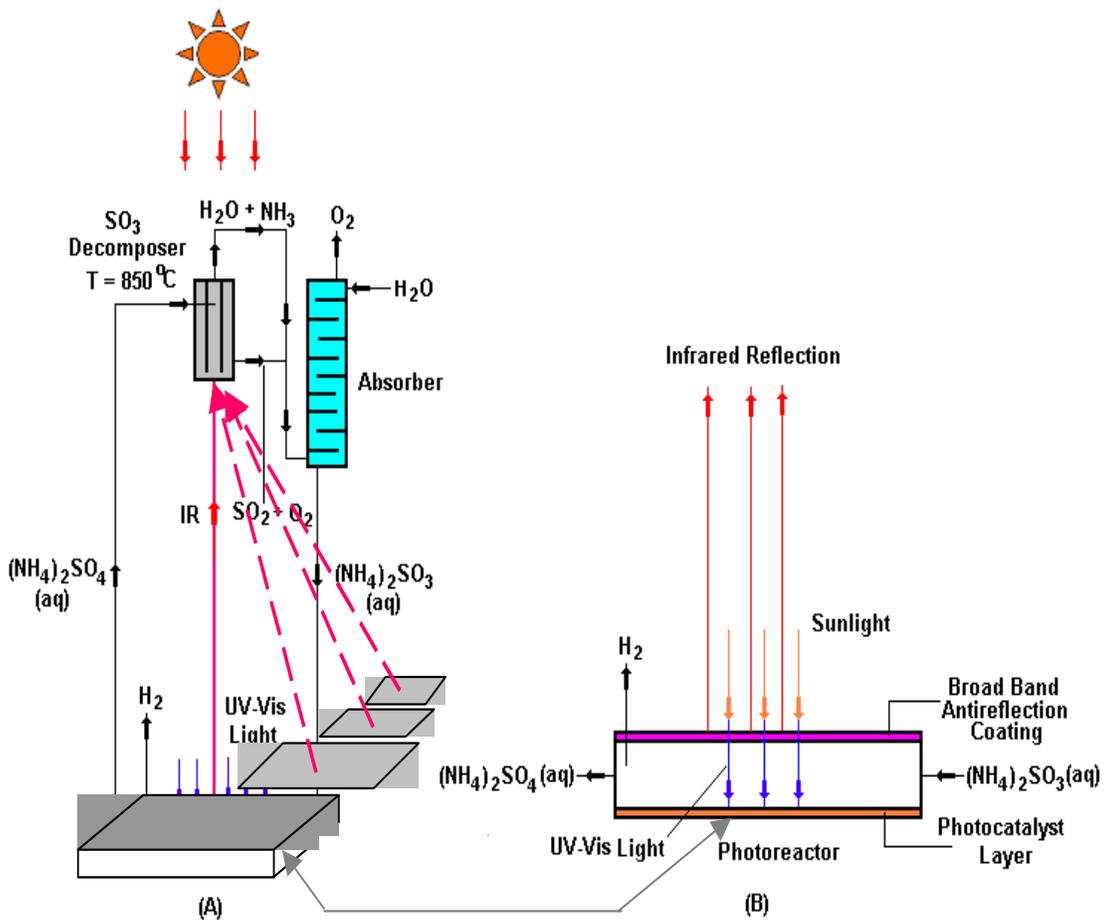


Fig. 2: Schematic diagram of FSEC's S-NH₃ photo-thermochemical water splitting cycle [from 6]

Fig. 2 shows a simple schematic diagram of one possible configuration of the S-NH₃ cycle, depicting the manner in which the thermal (*i.e.* near infrared (NIR) and infrared (IR)), and the UV/visible portions of solar radiation may be separated

using a spectral splitting mirror. The thermal part of the sunlight is concentrated into a high temperature thermocatalytic reactor/receiver that operates the oxygen production step, while the photonic (UV and visible light) portion passes through a coating layer and drives the photocatalytic hydrogen generation reaction.

5. Solar Collector Field Design

SAIC has started evaluation of solar collector designs suitable for the FSEC's hybrid sulfur-ammonia water splitting process. Based upon the preliminary laboratory results, requirements for the solar collectors of a potential hydrogen production system are as follows:

- Provide photons of wavelength <520 nm at approximately one-sun concentration for the hydrogen-producing photoreactor
- Provide heat to the photoreactor to maintain it at approximately 80°C
- Provide thermal energy at approximately 400°C and 825°C for thermal decomposition reactions to produce oxygen

The relative amounts of energy required for the hydrogen (photocatalytic) and the oxygen (high-temperature) production stages depend on the efficiencies of those production steps. Based solely on the heats of formation, the split is approximately 20% for the hydrogen production step and 80% for oxygen production. An efficiency of over 32% for the hydrogen production step has already been demonstrated at FSEC, and improved catalysts are expected to yield further increases [6, 7]. The photocatalytic portion of the reaction takes place at about 80°C . The heat necessary for maintaining the reactor at that temperature comes from photons that are not utilized by the photocatalytic reaction and become thermalized.

The efficiency of the oxygen production step is expected to be closer to 60-80%, based on evaluations of similar reactions. At a temperature of 825°C , the solar receiver efficiency will be reduced so the overall oxygen production efficiency from sunlight to chemicals will be less. The high temperatures needed for the oxygen production stage require a concentrating solar collector system with approximately 1000-1500 suns of concentration. Therefore, flat plate, evacuated tube, and parabolic trough collectors were eliminated from consideration. In this range of concentrations and temperature, only dish concentrators and heliostat/central receiver configurations are suitable.

Because FSEC's cycle uses only UV/visible photons in the hydrogen generation cycle, SAIC assessed the potential for "splitting" the solar spectrum so that the high-energy UV-visible light can be used to drive the photocatalytic portion of the process and the remaining portion of the spectrum can be utilized to operate the thermocatalytic oxygen evolution sub-cycle. To spectrally separate light, dichroic mirrors are typically used, made of thin layers of materials with varying refractive index. "Hot" mirrors reflect low-energy radiation and allow high-energy photons to pass through, and "cold" mirrors reflect high-energy photons and pass through low-energy radiation [8]. Five solar collector field configurations were

considered in the preliminary evaluation – three dish-type systems and two central receiver/heliostat configurations:

1. Dish concentrator with hot mirrors focusing to a receiver at the focal point, with a photocatalytic reactor directly behind the mirrors (Fig. 3).

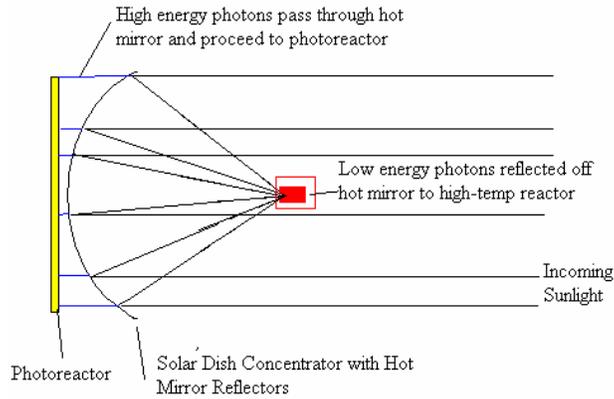


Fig. 3: Collector Concept #1 – Dish with Hot Mirrors

2. Dish concentrator with full-spectrum mirrors focusing to a thermal receiver at the focus. A conical cold mirror near the focus intercepts the high-energy photons and redirects them to a cylindrical photoreactor concentric to the axis of the dish (Fig. 4).

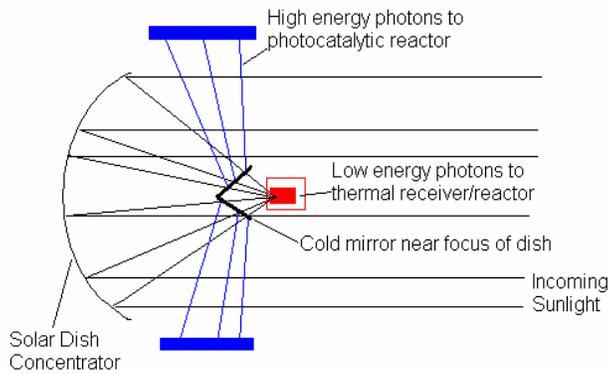


Fig. 4: Collector Concept #2 – Dish with Cold Mirror

3. Conical concentrator with hot mirror reflectors. Photoreactor either immediately behind the hot mirrors (at ~ 0.7 suns) or flat on a plate perpendicular to the sun (at ~ 1 sun). Thermal reactor in a tubular configuration along the axis of the cone (Fig 5).

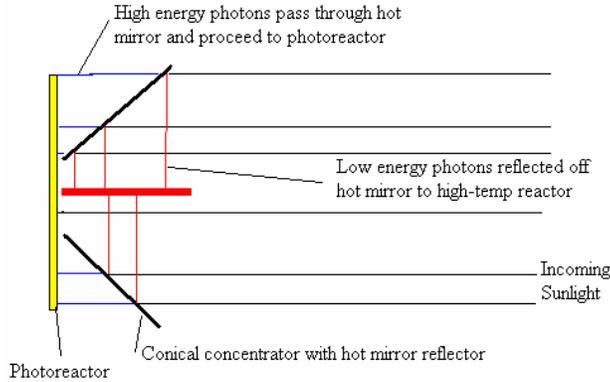


Fig 5: Collector Concept #3 – Conical Concentrator with Hot Mirror

4. Heliostat field with hot mirror heliostats. Photoreactors behind the mirrors on the heliostats or on the ground around and under the heliostats. Thermal receiver at the central receiver tower (Fig. 6).

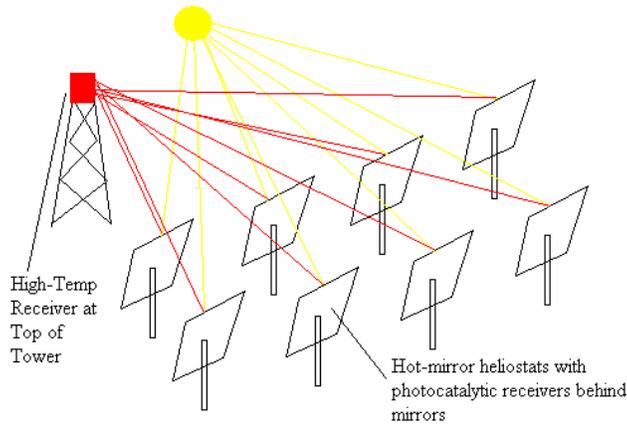


Fig 6: Collector Concept #4 – Hot Mirror Heliostat Field

5. Solar dish or heliostat/central receiver with full spectrum mirrors focusing to thermal receiver. Separate photoreactor in the form of a flat-plate (e.g., UV-visible light transparent plastic film [11]) collector or a solar pond near the dish/heliostat field (Fig. 7)

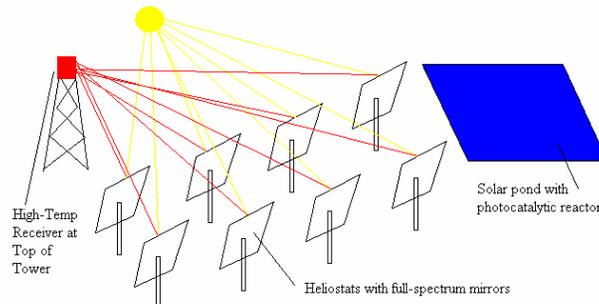


Fig. 7: Collector Concept #5 – Separate Thermal and Photonic Collectors

The preliminary evaluation of the solar collector configurations resulted in the following conclusions:

- Hot mirror configurations are unlikely to be cost-effective due to the cost of dichroic mirrors (up to several hundred dollars per square meter, much more than the total cost of conventional heliostat or dish systems [9, 10]).
- Due to the scale and complexity of equipment needed for handling materials in the process, dish systems were unlikely to be suitable. In particular, solids-handling equipment would be difficult to scale down to the size of a single dish of 100-200 m² and difficult to design so it could track with a dish over a range of elevation angles from 0° to near 90°.
- Cold mirror heliostat systems are difficult to design because the high-energy photons must be spread out again to near one-sun to be used in the photoreactor
- Configuration #5 reduces the size of the high-temperature solar field by 30-40% because it eliminates losses from the hot- or cold-mirrors and permits the whole solar spectrum to be used in the high-temperature reactor. This has a direct effect on the system capital cost.

The final result was selection of a heliostat/central receiver system with a separate one-sun hydrogen reactor, as the baseline configuration for continued study. SAIC is continuing to evaluate advanced concepts such as holographic beam splitters in order to avoid eliminating potential long-term winners, but the separate low-temperature/high-temperature system appears optimum for the near term.

The photoreactor in Concept #5 could take the form of a series of thin plastic tubes through which the reactants flow. In a prior project SAIC produced such low-cost reactors for UV-catalysis to detoxify organic materials in water [11]. PVDF plastic film was used to form the reactor, which provided high UV transmittance and good chemical resistance. If more thermal energy were needed than that provided by the thermalized high-energy photons, a potential approach would be to float the photocatalytic reactor on a solar pond that would provide additional heat to maintain it at operating temperature.

Having determined that a heliostat field is most appropriate, the requirement for 1000-1500 suns of concentration in turn either drives the heliostat field to a large size (e.g., 100MW or larger) or the heliostats to a smaller size. The conventional wisdom has been that larger heliostats are more cost-effective on a \$/m² basis due to economies of scale in drives. Therefore, heliostats have tended toward 100 m² to 150 m² in area [11]. The assumption that bigger is better is being addressed by SAIC in more detail in the preliminary design stage. Smaller heliostats, if they can be produced cost-effectively, have advantages of producing smaller images on the receiver and giving more control over the flux profile on the receiver. They can also result in a smaller minimum system size for the processing plant (perhaps 1MW instead of 100MW).

Finally, the requirement to attain temperatures of 825°C in the receiver leads to consideration of a cavity receiver with a secondary optical concentrator to minimize its aperture size. This, in turn, leads to consideration of a North-field configuration of the heliostats in order to maximize their effectiveness in getting their energy into such an aperture. SAIC is also considering the potential in such concepts as “beam-down” central receiver designs.

A direct approach to improving the cost-effectiveness of the hydrogen production system involves the realization that the solar concentrator (heliostat) field is typically the largest single cost component of the entire system. If we reduce the cost of heliostats, the cost of hydrogen will be directly reduced. Therefore, SAIC has undertaken an effort aimed at evaluating low-cost heliostat designs. One that appears to have significant promise is to replace the steel heliostat structure with one formed from glass-reinforced concrete (GRC). GRC has a cost that is orders of magnitude less than steel, is available everywhere in the world, can be formed and shaped into complex shapes easily using low-cost equipment, and concrete has demonstrated literally millennia of successful resistance to weathering (e.g., the dome of the Pantheon in Rome, built in 125 A.D.). Fig. 8 shows a prototype model heliostat based on a GRC structure that is under evaluation.



Fig. 8. GRC Heliostat Model

6. Status and Prospects

SAIC and FSEC have already made significant progress toward developing a cost-effective hydrogen production technology based on a solar thermochemical process with a “quantum boost” feature. FSEC is developing improved catalysts that will increase the hydrogen production efficiency beyond the 32% already achieved, and evaluating the kinetics and chemistry of the dark reactions. SAIC’s

evaluation of solar collector field configurations has resulted in designs that may significantly reduce the capital cost of the hydrogen production plant. The evaluation of GRC heliostat structures promises to reduce capital costs even more. Work is continuing at both organizations to optimize and improve the components and sub-systems of this cycle with the aim of demonstrating a pilot-scale hydrogen production plant within only a few years.

7. References

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