HydroGEN Seedling: High-Temperature Reactor Catalyst Material Development for Low-Cost and Efficient Solar-Driven Sulfur-Based Processes

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Subcontractor:
University of South Carolina, Columbia, SC

HydroGEN node laboratories:
- Idaho National Laboratory, Idaho Falls, ID
- Savannah River National Laboratory, Aiken, SC
- National Renewable Energy Laboratory, Golden, CO

Project Start Date: October 1, 2017
Project End Date: September 30, 2020

Overall Objectives

- Develop a new catalyst for the sulfuric acid decomposition, achieving nominal reaction yields about 30% higher than the current state of the art.
- Demonstrate reduced catalyst performance degradation for >400 h, achieving a 50% improvement compared to the current state of the art.
- Develop a novel solar-driven hybrid sulfur (HyS) process flowsheet, demonstrating solar-to-hydrogen overall efficiency ≥20%.
- Develop a novel direct solar receiver-reactor concept, allowing for a direct solar-driven sulfuric acid decomposition, with experimental demonstration of an electrically heated laboratory-scale system.
- Identify a solar thermochemical plant configuration demonstrating reduced overall hydrogen production costs, showing a viable path to \$2/kg H_2.

Fiscal Year (FY) 2018 Objectives

- Develop a novel baseline catalytic formulation for the sulfuric acid decomposition occurring at T ≈800°C and achieve nominal reaction yields approximately 20% higher than the current state of the art (i.e., 0.28 mol $SO_2/g_{Cat}/h$).
- Demonstrate reduced catalyst performance degradation for about 70–100 h, achieving a degradation ≤0.015%/h.
- Develop a novel solar-driven HyS process flowsheet, demonstrating solar to hydrogen efficiency >18%.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan,[1] with particular reference to the thermochemical hydrogen production technologies:

- High-temperature catalyst activity and degradation
- Plant construction materials, being able to stand harsh environment with sulfur-based compounds at temperatures on the order of 800°C
- Efficient and low-cost integration of the thermochemical plant with the solar plant
- Efficient and cost-effective solar HyS plant configuration.

Technical Targets

This project is conducting both fundamental development of novel catalytic formulations for

[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

sulfuric acid high-temperature decomposition reactions and engineering and system design and analysis of the solar-driven HyS cycle. Insights gained from this work will be applied to develop novel solar-driven hydrogen production systems that meet the following targets:

- H_2SO_4 decomposition catalyst nominal yield: 0.3 mol $SO_2/g_{Cat}/h$
- H_2SO_4 decomposition catalyst degradation: 0.0125%/h
- Solar-to-hydrogen efficiency: 20% (DOE target).
- Hydrogen production cost: $2/kg H_2 (DOE target).

FY 2018 Accomplishments

- Identified and tested a novel catalytic formulation (referred to as CAT2), showing increased activity (1.8 mol $SO_2/g_{Cat}/h$) and reduced degradation, with essentially no degradation for the 72-hour test.
- Identified and simulated a novel direct receiver reactor configuration, demonstrating the feasibility of a direct solar-driven H_2SO_4 decomposition reactor with enhanced performance compared to the previous bayonet-based baseline reactor.
- Developed a novel solar HyS integrated flowsheet based on optimized solar tower plant configuration and on vapor-fed SO_2 depolarized electrolyzer (SDE) section, showing preliminary thermochemical efficiencies ≈37.8% and solar-to-hydrogen efficiencies exceeding the target (≈20.5%).

INTRODUCTION

The HyS process, driven by solar power, has great potential to reach high-efficiency and low-cost hydrogen production without greenhouse gas emissions. The high-temperature section of the HyS cycle, which operates the catalytic decomposition of sulfuric acid into sulfur dioxide, oxygen, and water, is a fundamental part of the cycle affecting the overall plant efficiency and cost [1, 2]. Therefore, a high-performance catalyst (i.e., low cost, high catalytic activity, and low degradation catalyst) is of critical importance to achieve high efficiency and low hydrogen cost. Research and development has highlighted that a Pt-based monometallic catalyst had unacceptable catalytic activity and performance degradation for a high-efficiency and low-cost hydrogen production process [3]. A high-efficiency solar receiver-reactor system, which incorporates the new catalyst, also needs to be developed to achieve the required plant efficiency and cost. Greenway Energy (GWE) and the University of South Carolina (USC), partnering with HydroGEN node laboratories Idaho National Laboratory (INL), Savannah River National Laboratory (SRNL), and National Renewable Energy Laboratory (NREL), propose the development of a new catalyst formulation, included in a novel solar receiver-reactor concept, to be tested experimentally in the last part of the project.

APPROACH

The work is carried out based on a three-level approach: (1) the first level analyzes the fundamental mechanisms of the H_2SO_4 catalytic decomposition, aiming to synthesize and produce a novel catalyst; (2) the second level analyzes the engineering and system aspects of the solar reactor for the sulfuric acid decomposition, proposing an innovative direct solar receiver-reactor; and (3) the third level focuses on high-level solar thermochemical process analysis, proposing new HyS flowsheets and novel solar plant integration layout. A novel catalyst preparation technique, developed by USC, uses a combination of strong electrostatic adsorption, which permits formation of very small metal particles with a narrow distribution of sizes, and electroless deposition (ED) to produce controlled bimetallic catalysts. This will result in limiting the catalyst deactivation by using very small particles of a high-surface free energy core metal with a catalytically active outer metal shell deposited by ED. A new laboratory-scale decomposition reactor will also be designed and tested (during Phase 3 of the project) to assess the nominal performance and the long-term degradation. The solar-driven HyS cycle will also be modeled, integrating the down-selected reactor concept with the other HyS interfaced equipment. A large-scale solar-driven process configuration will be identified, modeled, and optimized to achieve solar efficiencies ≥20% and hydrogen costs ≤$2/kg H_2.

GWE and USC are partnering with three HydroGEN node laboratories: INL to perform the catalyst testing, SRNL to develop the HyS flowsheet, and NREL to design and assess the performance of the interfaced solar plant and the solar balance-of-plant equipment.

RESULTS

Catalyst Material Development and Testing

Several materials were examined and tested, including both monometallic and bimetallic formulations. Table 1 shows a list of the selected materials, including the novel formulations developed at USC (currently being patented) referred to as CAT0 (monometallic formulation), CAT1 (bimetallic initial formulation), and CAT2 (bimetallic enhanced formulation). Each material was tested with sulfuric acid at approximately 90 wt% in water, T = 800°C, and P = 1 bar.

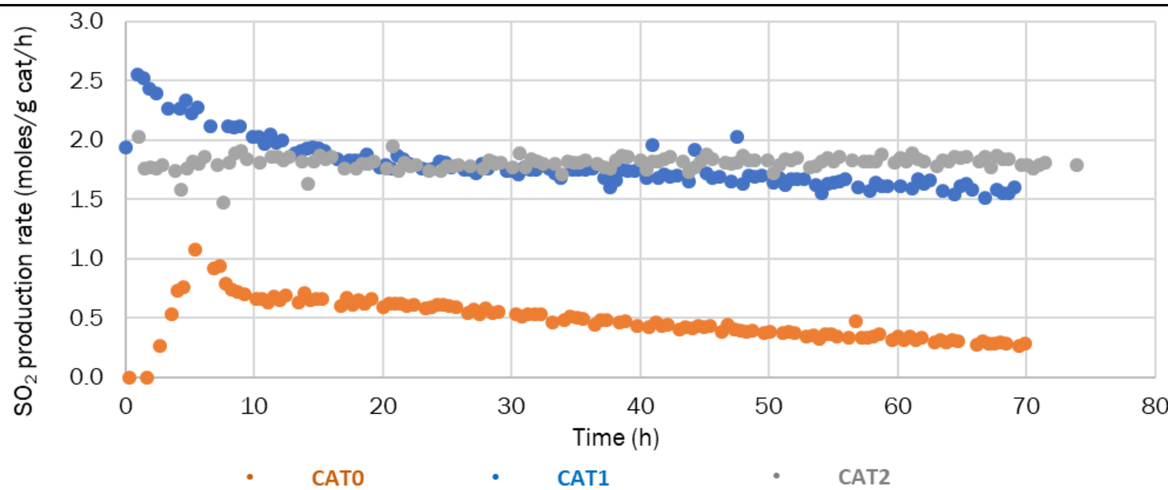
Monometallic formulations, based on 1% Pt/TiO_2, were able to achieve the nominal activity target but could not maintain the same level of performance over time, failing to achieve the performance duration target. Therefore, work moved forward with the bimetallic catalysts, identified by comparing the surface free energy of the two elements and synthesized using the ED approach.

Table 1. List of Catalyst Formulations Tested at INL

Catalyst	Classification	Source
1% Pt/TiO_2	Monometallic	USC
1% Pt/TiO_2	Monometallic	Johnson-Matthey
5% Ir/TiO_2	Monometallic	USC
5% Ru/TiO_2	Monometallic	USC
1% Pt/5% Ir/TiO_2	Bimetallic	USC
1% Pt/10% Ir/TiO_2	Bimetallic	USC
CAT0	Monometallic	USC (novel formulation)
CAT1	Bimetallic	USC (novel formulation)
CAT2	Bimetallic	USC (novel formulation)

The main results achieved during the first year of the project for novel bimetallic formulations are shown in Figure 1, highlighting the performance of the down-selected catalytic materials.

A 1% Pt–10% Ir/TiO_2 support has been identified as a possible enhanced material for the Pt bimetallic catalyst on TiO_2 support. This formulation can exceed the nominal conversion target (0.28 mol $SO_2/g_{Cat}/h$) but cannot meet the degradation performance target (0.015%/h). A novel bimetallic catalyst formulation has been identified, developed, and tested, referred to as CAT2. This material was able to exceed both the nominal activity target (measured nominal activity of about 1.8 mol $SO_2/g_{Cat}/h$) and the degradation performance target for 72-hour tests (essentially absence of degradation observed for 72-hour tests) as shown in Figure 1. The use of co-ED, depositing Pt and Ir contemporarily, is also being examined with different Pt and Ir concentrations and different deposition conditions. Results will be available as part of the next phases of the project. A mixed Rh-Pt catalyst was also examined, with results showing poor performance in comparison with pure Pt-based formulations.



Test conditions included temperature: 800°C, pressure: 1 bar, and H_2SO_4 concentration: 91.28 wt%

Figure 1. Novel catalyst formulation tests

Novel Direct Solar Reactor/Receiver Concept

A novel sulfuric acid decomposition reactor concept has been developed by GWE and NREL. The concept is based on a suitable modification of an NREL solar receiver, adopted for concentrated solar power plants to produce electricity, as shown in Figure 2.

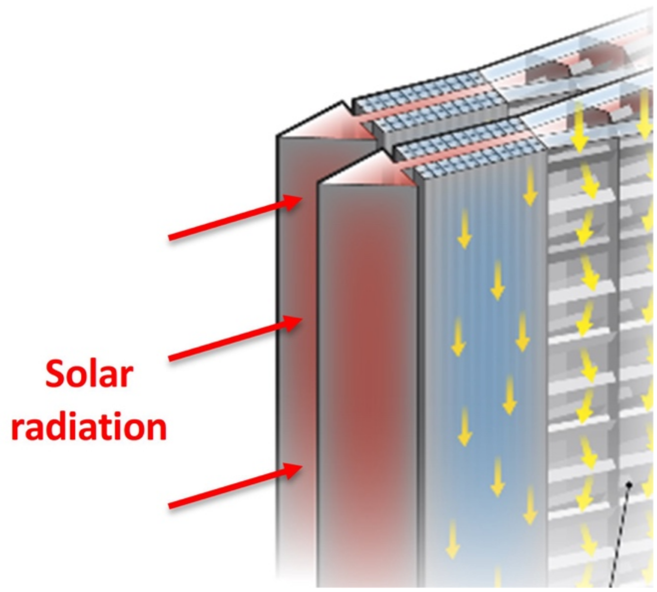


Figure 2. Novel integrated solar receiver-reactor for sulfuric acid decomposition

The concentrated sulfuric acid mixture flows in the external parallelepipedal region, in direct contact with the external wall heated by the concentrated solar radiation. The decomposed mixture flows in a counter-current arrangement in the internal parallelepipedal region, allowing internal heat recovery and exchange with the inlet sulfuric acid mixture. The proposed reactor concept allows (1) effective external solar heat transfer and internal heat recovery to be accomplished in a single highly intensified unit, (2) removal of solar intermediate heat exchangers, with the solar power transferred directly from the receiver to the HyS working fluid, and (3) high exergetic efficiency and potential cost reduction. A detailed transport phenomena computational fluid dynamics (CFD) reactive model has been developed in finite volume environment (STAR-CCM+), including mass, energy, and momentum balance equations integrated with suitable kinetics expressions [4]. Different operating conditions, including temperatures, pressures, and H_2SO_4 concentrations, were examined. Temperature and SO_2 concentration profiles obtained in the catalytic decomposition region (decomposition of SO_3 into SO_2 and O_2) of a single unit reactor are shown in Figure 3. Results demonstrate the feasibility of the proposed concept, highlighting (1) excellent internal heat recovery between the reacting mixture and the reacted mixture, (2) absence of temperature decrease during the endothermic decomposition of the SO_3 into SO_2, and (3) linear decomposition of SO_3 into SO_2 throughout the catalytic decomposition region.

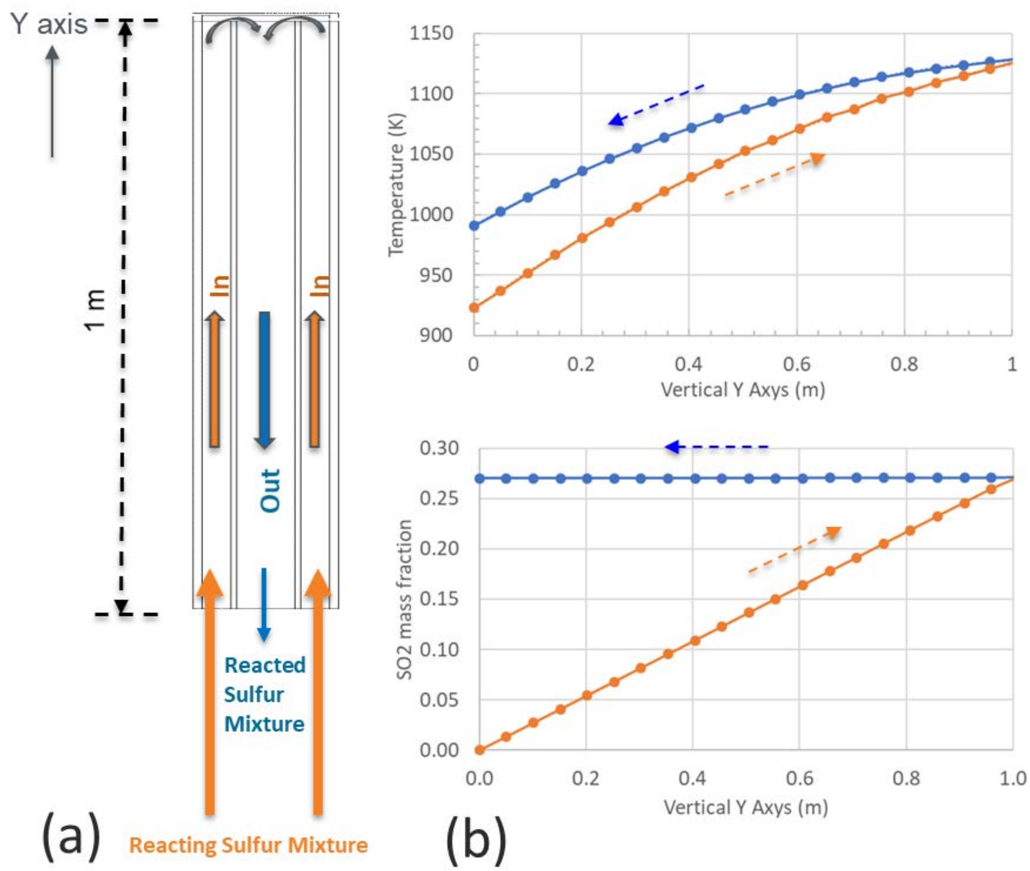


Figure 3. CFD simulation results of the novel reactor: (a) back view of the reactor, (b) temperature and SO_2 concentration profiles

Solar HyS Plant Flowsheet and Integration

A novel solar-driven HyS thermochemical flowsheet has been developed, introducing (1) a vapor-fed SDE section approach for the low-temperature section, and (2) chemical sulfur-based storage (H_2SO_4 and SO_2), replacing expensive and less-efficient thermal energy storage. By this approach the low-temperature electrochemical section will be designed to work continuously, while the high-temperature section will be designed to work on-sun based on the availability of the solar radiation. The novel HyS flowsheet has been initially developed and simulated using ASPEN Plus, resulting in the following preliminary results: (1) high-temperature section thermal duty: 345.3 kJ_{th}/mol H_2, (2) high-temperature section electric duty, mainly required for the SO_2 separation and recirculation: 10.5 kJ_e/mol H_2, and (3) low-temperature section electric duty: 112.4 kJ_e/mol H_2 with 110.2 kJ_e/mol H_2 required for the SDE. This results in a thermochemical efficiency (assuming an electric efficiency of 41.6%) of 37.8% (based on the low heating value of the hydrogen). The solar plant, to be coupled with the thermochemical plant, has been designed using SolarPILOT software examining different power conditions. An optimum solar power condition of 200 MW was assessed based on the cost of the heliostat field and of the solar tower (Figure 4). The 200-MW plant heliostat efficiency was calculated using Solar PILOT, resulting in 63.9%, and the novel receiver efficiency was projected to be on the order of 85%. Therefore, the overall solar-to-hydrogen efficiency has been preliminarily estimated to be equal to 20.5%. More refined calculations will be carried out during the first quarter of FY 2019 as part of one of the milestones of the project.

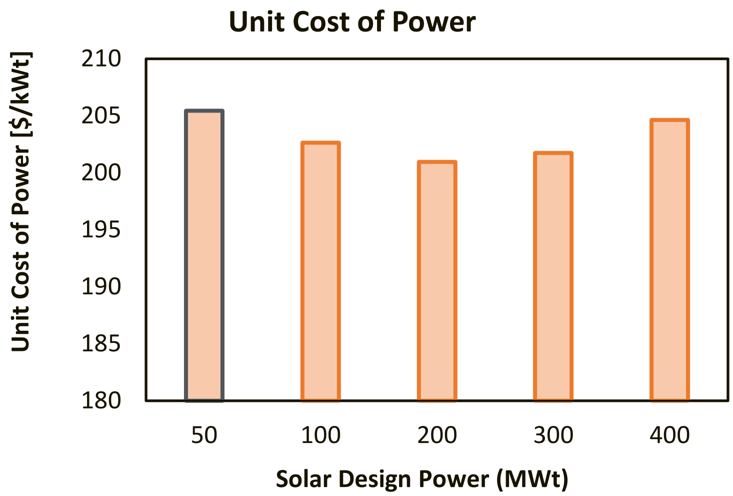


Figure 4. Techno-economic analysis results of the solar plant for different solar powers

CONCLUSIONS AND UPCOMING ACTIVITIES

The project has identified a novel catalytic formulation, currently being patented, for the decomposition of sulfuric acid at temperatures on the order of 800°C. Compared to the current state of the art, the new catalyst showed higher nominal activity and essentially absence of degradation during 72-hour tests. A novel efficient and potentially low-cost solar-driven receiver-reactor concept has also been developed and simulated to carry out the H_2SO_4 decomposition. CFD simulation results demonstrated excellent technical performance of the proposed concept in terms of temperature and concentration results. A preliminary solar thermochemical process analysis showed the potential of the integrated solar plant to achieve solar-to-hydrogen efficiencies on the order of 20%, thus meeting the DOE target.

Future work will be carried out on (1) optimization of the novel catalytic formulation, with duration tests up to 400–500 hours, (2) fabrication of the novel reactor at laboratory scale, with electrically heated experimental tests, and (3) detailed assessment of the techno-economic performance of the integrated solar thermochemical plant, including equipment design, cost assessment, and additional sensitivity analyses and process optimization.

The collaboration with the HydroGEN node laboratories involved in the project (i.e., INL, SRNL, and NREL) was instrumental to achieve the project targets and objectives. In particular, INL is world-renowned laboratory to perform sulfuric acid decomposition tests at high temperatures and at various operating conditions. USC has been working in strict conjunction with INL to develop and test the new catalysts. SRNL knowledge on HyS process flowsheeting and development was fundamental to set up a novel flowsheet and assess the thermochemical process efficiency under different operating conditions. GWE and SRNL have been working together to perform the HyS equipment design and cost evaluation. The presence of NREL in the project was also of primary importance to identify the solar plant techno-economic performance and to integrate the solar plant with the thermochemical process. GWE and NREL identified the novel reactor concept with involvement of USC in the CFD simulation of the proposed concept.

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. Record of Invention by NREL and GWE: Ma, Z., et al., NREL Record of Invention ROI-18-62, 2018.
2. Invention disclosure by USC and INL: Monnier, J., et al., USC ID no. 1372, 2018.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. C. Corgnale et al., "Solar Driven Thermo-Electrochemical Hybrid Sulfur Process for Hydrogen Production," ECS AiMES Meeting 2018, Cancun (Mexico), October 2018. https://ecs.confex.com/ecs/aimes2018/meetingapp.cgi/Paper/112622.
2. C. Corgnale et al., "Numerical Modeling of a Novel Solar Driven Sulfuric Acid Decomposition Reactor," ECS AiMES Meeting 2018, Cancun (Mexico), October 2018. https://ecs.confex.com/ecs/aimes2018/meetingapp.cgi/Paper/112623.

REFERENCES

1. C. Corgnale et al., *Int. J. Hydrogen Energy* 36 (2011): 11604–11619.
2. C. Corgnale et al., *Solar Hybrid Sulfur Cycle Water-Splitting Process*, SRNL-STI-2015- 00546, Revision 0 (2015).
3. L.M. Petkovic et al., *Applied Catalysis A: General* 338 (2008): 27
4. C. Corgnale et al., *Int. J. Hydrogen Energy* 42 (2017): 20463–20472.