II.G.2 Sulfur-Iodine Thermochemical Cycle

Paul Pickard (Primary Contact), Benjamin Russ[1]
Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185
Phone: (505) 845-3046; Fax: (505) 284-4276
E-mail: pspicka@sandia.gov
[1] General Atomics

DOE Technology Development Manager:
Stephen Kung
Phone: (301) 903-8074; Fax: (301) 903-0180
E-mail: Stephen.Kung@nuclear.energy.gov

DOE Project Officer: Melissa Bates
Phone: (208) 526-4652
E-mail: batesmc@id.doe.gov

Contract Number: DE-FC07-09ID14929

Project Start Date: April, 2006
Project End Date: April, 2009

Objectives

- Evaluate the potential of the sulfur-iodine (S-I) thermochemical cycle for large-scale hydrogen production using nuclear energy.
- Perform an integrated lab scale (ILS) experiment to demonstrate closed-loop operation of the S-I cycle.
- Provide the technical basis for the DOE Nuclear Energy assessment of the S-I cycle for thermochemical hydrogen production using advanced nuclear reactors.

Technical Barriers

This project addresses the following technical barriers for the Nuclear Hydrogen Initiative:

- Process chemistry and thermodynamic data information for evaluation of S-I cycle efficiency and operational characteristics.
- High-temperature, corrosion resistant materials for extended service under thermochemical process conditions.
- Thermochemical hydrogen production economics.

Technical Targets

This project is directed at the demonstration of the S-I thermochemical cycle to address large-scale hydrogen production using nuclear energy. This work includes the investigation of the primary reaction processes, the evaluation of materials of construction, and evaluation of the cost implications of candidate design choices.

Accomplishments

Several hydrogen production experiments have been conducted this past year using the extractive distillation process developed by General Atomics. Following the initial run in April 2008, improved diagnostics and a smaller hydrogen iodide (HI) reaction vessel was incorporated to facilitate operation and control of the HI decomposition section. Multiple stand alone operations, to examine pressure dependence of H_2 production and materials behavior were conducted successfully. Parametric studies to confirm the pressure dependence of hydrogen production were conducted including a hydrogen production experiment using Commissariat à l'Énergie Atomique (CEA) Bunsen section feed material that produced approximately 75 liters/hr. All primary reactions involved in the extractive distillation process for HI decomposition (iodine extraction, HI distillation, HI decomposition, HI recycle), have now been demonstrated.

The counter-current Bunsen reactor section developed by CEA was operated several times to produce the necessary HIx (heavy) phase and H_2SO_4 (light) phase acid compositions near expected values. Significant diagnostic and hardware modifications were implemented to facilitate operations. The December 2008 run produced a HIx (heavy) phase composition that was fully consistent with flowsheet specifications. The SO_2/O_2 separation section operated reliably in multiple operations and in conjunction with the H_2SO_4 acid decomposer.

H_2SO_4 decomposition experiments were completed up to 900°C, to explore temperature, pressure, and flow rate dependencies. Multiple operations were conducted with no corrosion issues identified.

✧ ✧ ✧ ✧ ✧

Introduction

The U.S. Department of Energy and the CEA are investigating the S-I thermochemical cycle as one of the promising methods for production of hydrogen from advanced nuclear reactors. The focus of this collaborative effort is the construction and operation of an ILS experiment that will provide the technical basis for the evaluation of this cycle. The ILS experiment will investigate the operational characteristics, performance potential and provide input for the cost implications of this cycle to support future technology selection decisions for nuclear hydrogen production. The first thermochemical cycle to be investigated in an ILS experiment is the S-I thermochemical cycle. The ILS for S-I is being conducted as an International Nuclear Energy initiative (INERI) project and is a collaborative effort involving Sandia National Laboratories (SNL), General Atomics (GA), and the CEA. The CEA is designing and testing Section 1, the primary (Bunsen) reaction section. GA is developing and testing Section 3, the HI decomposition section. SNL is developing and testing Section 2, the high temperature H_2SO_4 decomposition section.

Approach

- Flowsheet analysis of the SI-cycle process to evaluate alternative configurations.
- Experiments to investigate the chemistry of the three major reactions for the S-I cycle.
- Develop improved materials and heat exchanger designs for service in high temperature corrosive environments.
- Design and construct an ILS apparatus to provide a test bed for S-I cycle evaluation.
- Perform ILS experiments to evaluate closed-loop operation.
- Develop system designs, sizing, and materials for a nominal megaWatt pilot-scale experiment.

Results

During the past year, the focus has been on characterizing the individual process sections and on coupling the operation of the three sections in a closed loop. All three sections have been operated successfully multiple times and partially integrated operations have been conducted.

Bunsen Reaction

The final Bunsen reaction experiments focused on demonstrating repeatable successful, controlled operation of the Bunsen reactor and its associated components. Prior to the final experimental run, a team of engineers and technicians from CEA were on site to make several modifications to the Skid 1 hardware to enhance the reliability of the system. The primary modifications dealt with the HIx (lower phase) product flow control. These modifications allowed for a successful Bunsen reactor during March of 2009. The operations demonstrated the successful control of both the upper and lower phase product flows, reactor pressure and temperature control as well as the reactant flow control (water, sulfur-dioxide and iodine). Samples of the process fluids from the experiment have been analyzed. The upper phase material was dilute, at 12 wt% H_2SO_4, while the lower phase was close to target at 40 wt% HI. The concluding experiments for phase 3 testing of the S-I ILS process have been completed.

Sulfuric Acid Decomposition

The SNL acid decomposition process has been operated several times in stand-alone mode and while integrated with the CEA process section. Stand-alone tests verified process operation after completion of process modifications. The integrated tests with the CEA section involved production of sulfur dioxide and subsequent transfer to the CEA skid. Parametric operations evaluated the effect of decomposition temperature on acid decomposition efficiency. All tests were performed at a pressure of 2 bar absolute with 41 mole percent acid feed. The results from varying the decomposition temperature from 650 to 850°C are given in Table 1.

TABLE 1. Results for Temperature Effect on Decomposition Efficiency

Acid decomposition temperature (°C)	O_2/SO_2 ratio	Gas (SO_2 + O_2) flow rate (L/hr)
850	0.48	2.4 ± 0.1
800	0.5	2.2 ± 0.1
750	0.47	1.8 ± 0.1
700	0.56	1.1 ± 0.2
650	No SO_2 detected	0

The results match analytical estimates of sulfur dioxide production as a function of temperature. No gas was produced at 650°C. The data indicate for maximum

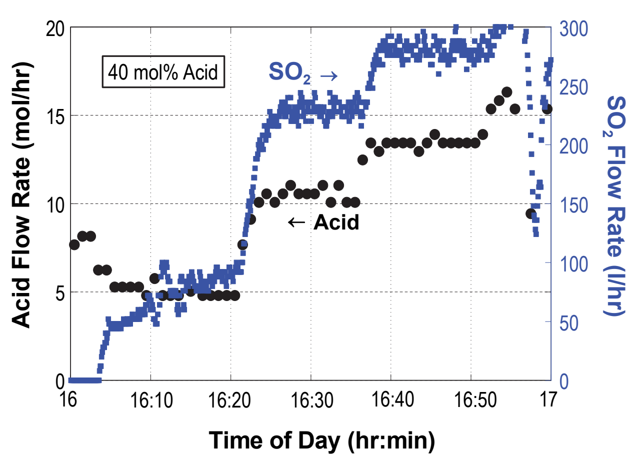

FIGURE 1. SO_2 Production versus Acid Flow Rate (40 m/o, 850°C)

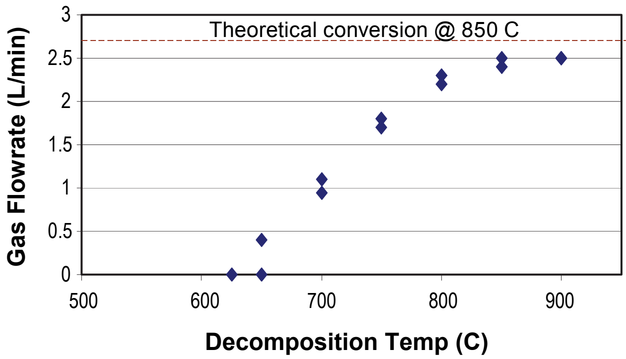

FIGURE 2. Production of SO_2/O_2 as a Function of Decomposition Temperature

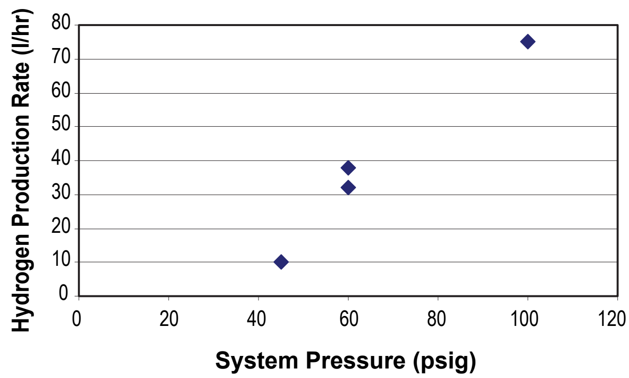

FIGURE 3. H_2 Production Rate as a Function of Pressure

conversion under the conditions of the test the acid decomposer must be operated at 800°C or higher. These data are shown in Figures 1 and 2.

HI Decomposition

The primary variable investigated during this period is the operating pressure which determines the HI recycle rate and therefore the effective hydrogen production rate. Several runs have been conducted at pressures ranging from 45-200 psig. The primary affects of the pressure are 1) the hydrogen production rate and 2) the HI distillation boiler temperature. The system pressure affects H_2 production rate by affecting the HI recycle. As the decomposition step is only 20% efficient, the un-reacted HI needs to be recycled in order to achieve the target production rates. This recycle is achieved by cooling the HI/H_2 stream to ~5°C after the iodine has been removed. The vapor pressure of HI at this temperature is 66.15 psia. As the system pressures exceed this value, the percentage of HI liquefied increases as the vapor fraction of HI decreases by Henry's Law:

$$Y_{HI} = P_{HI}/P_{tot}$$

As the total pressure increases, a larger fraction of HI is condensed to liquid, and recycled back to the reactor. The hydrogen production as function of pressure is shown in Figure 3.

ILS Status

These experiments conclude the phase 3 testing of the ILS. While the final tests focused on the successful operation of the Bunsen reactor, previous experiments had confirmed the integrated operation capabilities of the entire loop.

Conclusions and Future Directions

The DOE–CEA project on the ILS was completed in April 2009. The ILS equipment is being cleaned and put in safe shutdown condition, and the system will be decommissioned in Fiscal Year 2010. The results from the project included several partially integrated runs conducted to produce H_2 at up to 75 l/hr. Bunsen operations produced correct lower phase compositions, but Iodine flow challenges limited reliability. The HI section operations show extractive distillation works well, but it is complex and considered to be too costly for large-scale applications. Initial experiments on reactive distillation show promise as a more efficient and lower cost alternative distillation path. The SNL SiC bayonet acid decomposer has operated routinely with no materials issues. Among the observations from these experiments is the difficulty in finding affordable and reliable components at small scales. A larger scale experiment would allow wider component and materials options. Materials issues encountered in the HI section study identified critical areas for future development.

FY 2009 Publications

1. Moore, R.C., E. Parma, Russ, B., Sweet, W., Helie, M., Pons, N., and P. Pickard. (2008) "An Integrated Laboratory-Scale Experiment on the Sulfur-Iodine Thermochemical Cycle for Hydrogen Production", 4th International Meeting on High Temperature Reactor Technology, Washington, D.C., September 2008.

FY 2009 Presentations

1. April 2008, NHA Meeting (Sacramento) "Status of the INERI Sulfur-Iodine Integrated Loop Experiment".

2. October 13–18, 2008, Pacific Basin Nuclear Conference (Aomori, Japan), "S-I Integrated Lab Scale Demonstration Update".

3. October 13–18, 2008, Pacific Basin Nuclear Conference (Aomori, Japan), "Status of the INERI Sulfur-Iodine Integrated Loop Experiment".

4. 18 June, 2008,World Hydrogen Energy Conference, (Brisbane, Queensland). "Demonstrating Production of Hydrogen using the Sulfur-Iodine Hydrogen Cycle"

5. November 2008, AIChE, (Philadelphia, PA) "Status of the INERI Sulfur-Iodine Integrated Loop Experiment".

6. January 2009, MIT-CEA Nuclear H_2 workshop, (Paris, France) "Assessment of Thermo-Chemical Water Splitting Processes for Industrial Hydrogen Production".