# Analysis of Solar Thermochemical Water-Splitting Cycles for Hydrogen Production

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## Objectives

- Analyze thermochemical water-splitting cycles (TCWSCs) suitable for solar interface from the viewpoint of thermodynamics, chemical process engineering, costs and their potential environmental impact.
- Develop a more precise method for determining the thermal efficiency of TCWSCs.
- Build chemical process engineering flowsheets for prospective solar-driven TCWSCs.

## 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 R,D&D Plan:

- V.  High- and Ultra-High-Temperature Thermochemical Technology
- W.  High-Temperature Materials
- Y.  Solar Capital Cost

## Approach

- Review all published papers, reports, patents, etc. in the past $25^+$ years that relate to thermochemical water-splitting cycles, in general, and solar driven cycles, in particular.
- Use FactSage$^{TM}$ program to perform chemical equilibrium calculations.
- Employ HYSYS/ASPEN Plus chemical process simulation (CPS) program for developing process flowsheet, process analyses and optimization.
- Compare the performance characteristics and costs of the University of Tokyo-3 (UT-3) and sulfur-iodine (S-I) TCWSCs.
- Identify processes that especially benefit from the solar interface.
- Use chemical process flowsheet analysis to identify new processes/cycles or modifications of the existing cycles that improve performance and facilitate better interface with solar heat source.

## Accomplishments

- Examined cycle efficiency calculation methods and developed a technique based on chemical process simulation flowsheet (see list of publications).
- Used HYSYS CPS to analyze the sulfuric acid decomposition process of a solar driven sulfur-iodine TCWSC.

- Developed two new flowsheets for decomposing sulfuric acid in the solar based S-I cycle (see list of publications).
- Completed flowsheet simulation of sulfuric acid purification and decomposition using HYSYS steady-state processor.
- Evaluated kinetic models for sulfur trioxide decomposition using HYSYS simulation tool.
- Performed thermodynamics analyses of the decomposition of sulfuric acid and sulfur trioxide at various temperatures and pressures (see list of publications).
- Developed a new Sulfur-Ammonia (S-A) TCWSC based on sulfuric acid decomposition.

## Future Directions

- Develop and optimize a completed flowsheet for the S-I cycle and precisely determine its thermal efficiency and costs.
- Analyze purification process of aqueous hydroiodic acid (HI) solution.
- Carry out Aspen Plus process flowsheet analysis of separation of HI and $H_2SO_4$ and investigate the possibility of a newer and simpler process scheme.
- Perform thermodynamic calculations involving HI decomposition and the $SO_2 + I_2$ reaction.
- Determine phase equilibrium involving HI and $H_2SO_4$.

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## Introduction

In the course of the past several decades, many thermochemical cycles have been devised for production of hydrogen from water. It has been shown that thermochemical water splitting cycles (TCWSCs) have potential to deliver overall system efficiencies in excess of 40%. Among the most studied TCWSCs are sulfur-halogen cycles. Figure 1 depicts a simple schematic diagram of the sulfur-halogen TCWSCs. Presently there are two potential high temperature heat sources available for use with thermochemical processes. They are solar thermal concentrator and central receiver systems, and nuclear reactors (i.*e.* high temperature gas-cooled reactors, HTGR). The U.S. DOE, under the Nuclear Energy Research Initiative (NERI) Program, has funded several efforts aimed at hydrogen production using nuclear power.

One major program is underway at General Atomics (GA) Corp., in collaboration with the University of Kentucky (UK) and Sandia National Laboratories (SNL), to assess the technoeconomics of $H_2$ production using HTGR. GA/UK/SNL reports provided a starting point for this evaluation of thermochemical water-splitting cycles suitable for solar interface and capable of providing efficient and cost-effective means of $H_2$ production from water. After analyzing more than 100 different thermochemical water splitting cycles, the GA/UK/ SNL study narrowed the prospective cycles to two; namely, the University of Tokyo's UT-3 and GA's Sulfur-Iodine cycle. At FSEC, we have selected and analyzed, in detail, three thermochemical processes. They are 1) sulfur family cycles, especially GA's S-I cycle; 2) the UT-3 cycle; and 3) the SynMet process developed at the Paul Scherrer Institute (PSI), Switzerland.

## Approach

Our approach was to develop detailed flowsheets of the candidate TCWSCs and processes. We have considered the following systems:

**i. Bunsen reaction involving iodine and thermal decomposition of HI.** As depicted in Figure 1, in addition to the sulfuric acid decomposition step, the following reactions are employed:

$SO_2 + I_2 + 2H_2O = 2HI(aq) + H_2SO_4 (aq)$
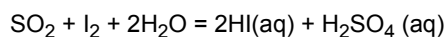
followed by thermal decomposition of hydroiodic acid:

$2HI = H_2 + I_2$
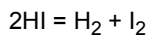
This is the General Atomics process with the revised cycle having improved energetics and an overall efficiency of about 50%. A variation of this TCWSC is the so-called Bowman-Westinghouse cycle that employs a reaction involving bromine (instead of iodine) and electrolysis of hydrobromic acid (in lieu of thermal decomposition of HI). The electrolytic decomposition of HBr requires a cell voltage of about 0.80 V (for acid concentration of 75 wt%).
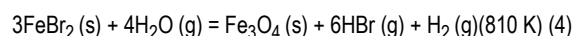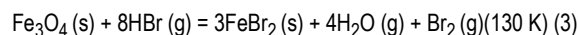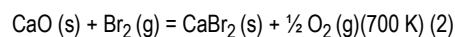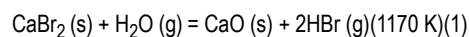
One problem with the Westinghouse cycle involves the pH effects during electrolysis of sulfur dioxide in aqueous solution. At low solution pH, sulfur forms instead of hydrogen. To avoid sulfur formation, one has to maintain a high solution pH that requires a reduction in acid concentration in the solution. Low acid flow rates translate into low hydrogen evolution rates. In summary, we note that the hydrogen production rate depends on the solution pH, while pH is dependent on sulfur dioxide concentration. To avoid sulfur formation, the electrolytic process has to maintain low acid concentration levels to keep pH levels high. This in turn leads to a decrease in $H_2$ production rate. Low sulfuric acid concentration will also require a more intensive and costly acid separation and concentration step, reducing the efficiency of $H_2SO_4$ decomposition to sulfur dioxide and oxygen (see Figure 1). The acid decomposition step consumes a major portion of the input energy to the cycle.

**ii.UT-3 thermochemical cycle.** This thermochemical hydrogen production cycle has been developed by Kameyama and Yoshida (at the
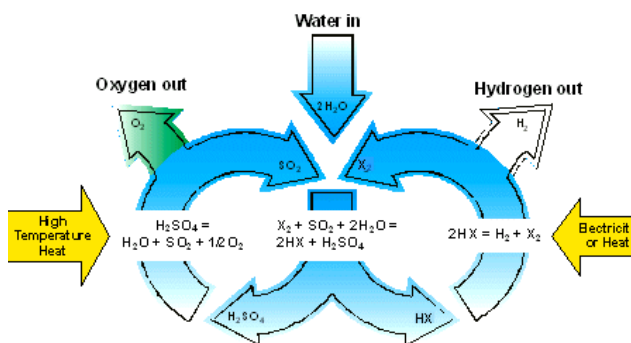


**Figure 1.** Schematic Diagram of Sulfur-Halogen Cycle (X= iodine or bromine)

University of Tokyo). The UT-3 process is one of the most studied thermochemical hydrogen production cycles in the world. It should be noted that the UT-3 process is being developed for coupling to nuclear power reactors. The reported cycle efficiency is in the range of 40 to 50%. The cycle involves the following four gas-solid reactions:

$CaBr_2$ (s) + $H_2O$ (g) = CaO (s) + 2HBr (g)(1170 K)(1)

CaO (s) + $Br_2$ (g) = $CaBr_2$ (s) + ½ $O_2$ (g)(700 K) (2)

$Fe_3O_4$ (s) + 8HBr (g) = $3FeBr_2$ (s) + $4H_2O$ (g) + $Br_2$ (g)(130 K) (3)

$3FeBr_2$ (s) + $4H_2O$ (g) = $Fe_3O_4$ (s) + 6HBr (g) + $H_2$ (g)(810 K) (4)

Reaction (1) has been the slowest step, kinetically, amongst the four reactions; thus, it is rate-limiting for the whole cycle. Since it is necessary that all of the reactions proceed at the same rate for continuous operation of the cycle, the slow rate of hydrolysis of calcium bromide adversely affects the whole process efficiency. Another undesirable feature of the UT-3 cycle is that it is a gas-solid type process consisting of a pair of hydrolysis (endothermic) and Br reduction (exothermic) reactions that occur in four series reactors. In order to conduct these processes as in fixed bed reactors, the gases must alternatively flow in opposite directions. In other words, a given reactor must run an endothermic reaction in one direction for about two hours and then an exothermic one in the opposite direction for the next two hours, and so forth.

The UT-3 cycle has been investigated extensively for almost 25 years since it was first proposed in 1978. It has also been fully detailed in flowsheets, and many issues related to the reaction chemistry and kinetics of individual processes, as well as the process separation issues, have been studied in detail. The overall efficiency of the improved adiabatic UT-3 process has been reported as 40% to 50%. However, difficulties remain with UT-3 cycle requiring further improvements. Examples include 1) heat-transfer and temperature control - reactions 1 and 4 are hydrolytic reactions, which require energy input, while reactions 2 and 3 are exothermic, requiring heat removal from the reactors; 2) steady-state operation - circulation time period for the UT-3 cycle has been reported to be two hours; 3) separation issues - to cool down exothermic

reactors and sweep the reaction products out of reaction zones, excess steam is needed; 4) packed reactor design; 5) process lifetime issues; etc.

**iii.  Zn/ZnO process.**  This is the so-called "SynMet" process developed at PSI.  The process combines ZnO-reduction and $CH_4$-reforming within a solar reactor.  It consists of a gas-particle vortex flow confined to a solar cavity receiver that is exposed to concentrated solar irradiation.  A 5-kW reactor has been built at PSI and subjected to tests in a high-flux solar furnace.  Natural gas is used as a reducing agent to process ZnO according to the following overall reaction:

$$ZnO + CH_4 = Zn + 2H_2 + CO(5)$$
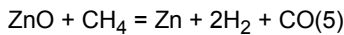
The process reforms methane in the absence of catalysts and is being optimized to produce syngas especially suited for methanol synthesis, and co-production of Zn and syngas avoids $CO_2$ emissions in the traditional carbothermal reduction of ZnO.  Even though the PSI process is the only system developed for direct solar interface, it is not, however, a typical TCWSC, per se.

## Results

In order to mitigate problems discussed above, a new sulfur-ammonia cycle has been conceived that is a better fit to solar power source and does not suffer from acid solubility issues.  A schematic diagram of the cycle is depicted in Figure 2.  A flowsheet of the cycle is given in Figure 3.  Ammonium sulfite is fed to a photocatalytic reactor, where sulfite ions are oxidized into sulfate ions while water is reduced to $H_2$.  Ammonium sulfate is then decomposed into

ammonia gas and, at the same time, water also boils off.  Through the decomposer, liquid sulfuric acid is introduced into the acid vaporizer to generate gaseous sulfur trioxide and water.  The product sulfuric trioxide is then reduced to produce sulfur dioxide gas and oxygen in a reduction reactor.  Small amounts of sulfuric acid remaining can be separated from the gaseous mixture containing sulfur dioxide, oxygen and water with an acid separator.  Sulfuric acid so separated is then recycled, and sulfur dioxide and oxygen are mixed with ammonia and chemically adsorbed to produce ammonium sulfite, which is then fed into the photocatalytic reactor to begin a new cycle.

In the adsorption unit, oxygen is separated from the stream.  The chemical reactions involved in the proposed sulfur-ammonia cycle are:
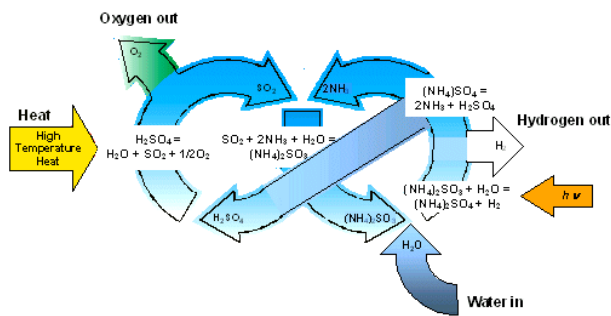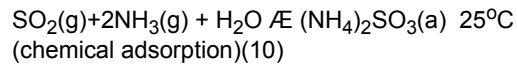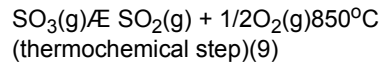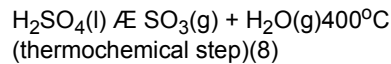
$(NH_4)_2SO_3(a) + H_2O \text{Æ} (NH_4)_2SO_4(a) + H_2(g)$ 80°C (photocatalytic step)(6)

$(NH_4)_2SO_4(a) \text{Æ} 2NH_3(g) + H_2SO_4(l)$ 350°C (thermochemical step)(7)

$H_2SO_4(l) \text{Æ} SO_3(g) + H_2O(g)$ 400°C (thermochemical step)(8)

$SO_3(g) \text{Æ} SO_2(g) + 1/2O_2(g)$ 850°C (thermochemical step)(9)

$SO_2(g) + 2NH_3(g) + H_2O \text{Æ} (NH_4)_2SO_3(a)$  25°C (chemical adsorption)(10)
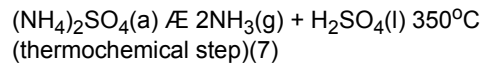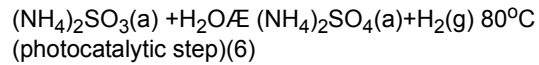


**Figure 2.**  Schematic Diagram of Sulfur-Ammonia Cycle
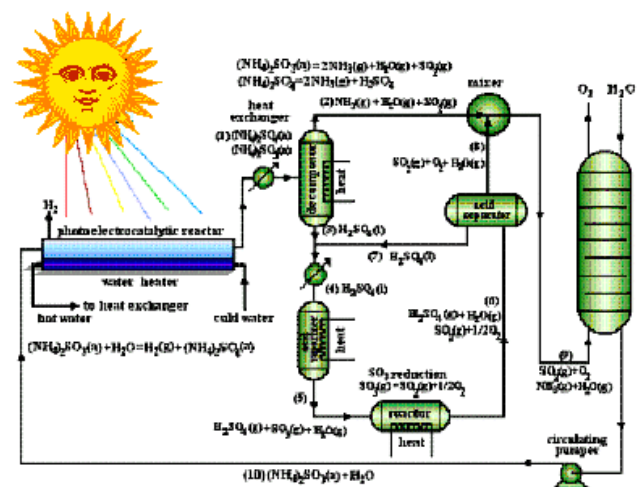


**Figure 3.**  Process Flowsheet for the Proposed Sulfur-Ammonia Cycle

Among these reactions, Reactions (6), (7) and (10) are unique to this new cycle. Reactions (8) and (9) are common to all sulfur family cycles.

If reaction (6) is carried out at a temperature of 80 ~ 90°C, the concentration of ammonium sulfate is about 50 wt% (assuming complete conversion of sulfite to sulfate ions). This concentration is six times higher than in the Bowman-Westinghouse cycle. Since pH in ammonium sulfate or ammonium sulfite solutions is higher than that of pure sulfuric acid or sulfurous acid at the same concentration of anions, sulfite ion oxidation can be conducted in a higher concentration solution without elemental sulfur repercussion. Furthermore, higher sulfuric acid concentration will ease acid separation and concentration as well as improve process energetics. Moreover, increased acid concentration will increase the sulfite ion oxidation rate. Interestingly, the solubilities of sulfite and sulfate ions are comparable at 30°C. However, at temperatures higher than 30°C, ammonium sulfite has higher solubility in water than ammonium sulfate. If reaction (6) is operated at 80°C, the concentration of sulfite ions becomes higher than sulfate ions, thus increasing the oxidation rate.

The energy required to separate the products of reaction (7), i.e. ammonia and sulfuric acid, can be provided by reaction (10), so there is no net energy input. This is not, however, the case with the S-I cycle that requires energy input for HI decomposition. The S-A cycle is well suited to solar input as a heat source and ultraviolet (UV) light. The UV part of solar spectrum is of great value for the photolytic and/or photocatalytic redox reactions. In the photocatalytic reactor, sulfite ions are oxidized to sulfate ions while hydrogen is generated. The photoreactor consists of two segments. The first layer adsorbs UV light, promoting a redox reaction. Because neither sulfite nor sulfate can adsorb visible light, a second under-layer can be used to adsorb concentrated long wavelength light, heating and decomposing sulfur trioxide to sulfur dioxide.

## Conclusions

TCWSCs employing solar energy as a heat source can be attractive due to their relatively higher efficiency. The UT-3 cycle is a pure thermochemical process that has been under investigation for close to 25 years. Bowman-Westinghouse sulfur is a hybrid cycle in which an electrolytic process and a thermal decomposition of sulfuric acid are combined to co-produce hydrogen and oxygen. The main drawback of the Bowman-Westinghouse cycle is that the electrolysis step requires low concentration of sulfuric acid, leading to higher energy consumption in the acid concentration and separation process. A new sulfur-ammonia thermochemical cycle was proposed for decomposing water into hydrogen and oxygen. The cycle consists of three steps: 1) photocatalytic oxidation of ammonium sulfite to generate ammonium sulfate while water is reduced to hydrogen utilizing both thermal and UV portion of the solar spectrum; 2) ammonium sulfate decomposition into ammonia and sulfuric acid, with the latter undergoing the same reduction process as that in the Bowman-Westinghouse sulfur cycle; and 3) chemical co-adsorption of ammonia and sulfur dioxide to produce ammonium sulfite, which is then recycled to produce $H_2$ and ammonium sulfate.

The new cycle has the potential for achieving high overall efficiency by using readily available and inexpensive chemicals. Solar energy is used as a heat source, and UV portion is utilized for a photocatalytic redox reaction. Prior experimental results obtained at FSEC indicate that photolytic and/or photocatalytic oxidation of sulfite ions occurs at acceptable rates with no occurrence of side reactions.

## FY 2003 Publications/Presentations

1. Muradov, N.Z. and A. T-Raissi, "Hydrogen Production via Catalytic Reformation of Unconventional Methane Containing Feedstocks," Paper submitted for presentation and publication at the HYPOTHESIS Symposium held in Porto Conte, Italy, September 7-10, 2003.

2. T-Raissi, A. "Photocatalytic Oxidation of Terpenic VOCs," Invited paper submitted for presentation at the 2nd AOP (II EPOA) International Conference held at Campinas, Brazil, August 25-27, 2003.

3. T-Raissi, A. "Hydrogen Storage in Ammonia and Aminoborane Complexes," Presentation at the 2003 Hydrogen Program Annual Review, Berkeley, CA , May 21, 2003.

4. T-Raissi, A. "System Analysis of $H_2$ Production and Utilization at KSC," Presentation at the NASA Hydrogen Review Meeting at Tampa, FL, January 15, 2003.

5. T-Raissi, A. "Analysis of Alternate Hydrogen Production Processes," Presentation at the NASA Hydrogen Review Meeting at Tampa, FL, January 15, 2003.

6. T-Raissi, A. "Hydrogen Storage in Amine Borane Complexes," Presentation at the NASA Hydrogen Review Meeting at Tampa, FL, January 15, 2003.

7. T-Raissi, A. and C. Huang, "Technical Analysis of Hydrogen Production," A semi-annual contract report to U.S. DOE under DEFC3600GO10603, February 2003.

8. T-Raissi, A., et al. "Task IV-2, System Analysis of Hydrogen Production and Utilization at KSC," Interim contract report on NASA NAG3-2751, January 2003.

9. Huang, C. and A. T-Raissi, "Task IV-6, Analysis of Alternative Hydrogen Production Processes," Interim contract report on NASA NAG3-2751, January 2003.

10. T-Raissi, A., et al. "Task III-3, Hydrogen Storage in Amine Borane Complexes, Part II - Molecular Modeling of Hydrogenation of Borazine to Cyclotriborazane," Interim contract report on NASA NAG3-2751, January 2003.

11. T-Raissi, A. "Cryogenics Tasks, NASA KSC Update and System Analysis, and Analysis of Alternate Hydrogen Production Processes," Presentation at the NASA-GRC Program Review Meeting, Cleveland, OH, September 3-4, 2002.

12. T-Raissi, A. "Chemical Storage - Overview," Keynote speech at the DOE Hydrogen Storage Workshop, Argonne National Laboratory, Argonne, IL, August 14, 2002.

13. T-Raissi, A. "System Analysis of $H_2$ Production Concepts - Overall System Analysis," Presentation at the NASA-Hydrogen Research at Florida Universities Program Review Meeting held at FSEC, July 16-17, 2002.

## Special Recognitions & Awards/Patents Issued

1. T-Raissi, A., et al. "Apparatus for decoupled thermo-photocatalytic pollution control," U.S. Patent No. 6,551,561, April 22, 2003.

2. T-Raissi, A., et al. "Apparatus and method for low flux photocatalytic pollution control," U.S. Patent No. 6,531,035, March 11, 2003.

3. Recipient of 2002-03 I&C Award for Excellence in Research, UCF.

4. Director of the FSEC's Hydrogen R&D Division as of August 31, 2002.