Performance Estimates for Sulfur-based Thermochemical Hydrogen Cycles using OLI

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OLI Simulation Conference
Hyatt Hotel, Morristown, NJ
October 23-24, 2007
Outline

- Background
- The Sulfur Cycles
- Thermal Efficiency Considerations
- HyS Flowsheet Analysis Using OLI-MSE
  - Properties Modeling Challenges
  - Application Example
  - Results of Analysis
Our Energy Future

- World energy needs are growing rapidly
- There is a finite supply of oil and gas
- Alternative energy supplies need to be developed soon
- Environmental concerns are increasing
- America needs energy security & diversity
  - Petroleum imports will exceed 75% by 2025

WE NEED A SUSTAINABLE ENERGY SYSTEM
The “Hydrogen Economy” Could Be One Solution

- Broad-based use of hydrogen as a fuel
  - Energy carrier analogous to electricity
  - Produced from variety of primary energy sources
  - Can serve all sectors of the economy: transportation, power, industry and buildings
  - Replaces oil and natural gas as an end-use fuel
  - Makes renewable and nuclear energy “portable”

- Advantages:
  - Inexhaustible
  - Clean
  - Universally available to all countries
Hydrogen Can Be Made From Domestic Resources

- Biomass
  - Water
    - Hydro
    - Wind
    - Solar
    - Geothermal
- Nuclear
- Oil
- Coal
- Natural Gas

- Transportation
- Distributed Generation

High Efficiency & Reliability
Zero/Nearest Zero Emissions

With CO₂ Sequestration
Hydrogen Economy Will Need a Lot of Hydrogen

- **National Academy of Engineering Report (2004) estimates:**
  - Use of \(\text{H}_2\) for all light-duty vehicles in 2050 will require 110 MM tons per year
  - 12-fold increase over current use
  - Energy content = 13.5 Quad
  - Power content = 450 GW\(_{\text{th}}\)

- **Will require multiple primary sources**
  - Fossil fuels with \(\text{CO}_2\) sequestration
  - Renewable energy with electrolysis
  - **Nuclear water-splitting**
Centralized Nuclear Hydrogen Production Plant

Thermochemical Process

\[ \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \]

Intermediate Heat Exchanger

Primary Coolant Circulator

Intermediate Loop Circulator

Modular Helium Reactor

High Capacity Pipeline

Time of Day/Month

H\(_2\) Storage

Industrial H\(_2\) Users

Hydrogen Fueled Future

Distributed Power

Transport Fuel

SRNL
DOE Nuclear Hydrogen Initiative

- Parallel development of technology to make hydrogen from nuclear energy via
  - Electrolysis (electricity input)
  - High Temperature Electrolysis (heat and electricity input)
  - Thermochemical cycles (heat input)
  - Hybrid thermochemical cycles (heat and electricity input)

- What is a thermochemical cycle?
  - Chemical process
  - Series of chemical reactions that combine to split water
  - All intermediate species regenerated
  - True thermochemical cycles use only heat to drive process
  - Hybrid cycles use both heat and electricity
Status of Thermochemical Cycles

- Major design challenges due to large material flows, corrosive chemicals, impurities, reactant separation, high temperature heat exchange, and costs
- Currently in lab-scale development stage
- Two leading cycles:
  - Sulfur-Iodine (SI) process
  - Westinghouse or Hybrid Sulfur (HyS) process
Sulfur-iodine (SI) Thermochemical Cycle for Production of H₂

Inputs:
- Water
- Heat (>800°C)

Outputs:
- Hydrogen
- Oxygen
- Waste heat

At least 115 different thermochemical cycles have been proposed.
Hybrid Sulfur (HyS) Cycle

Inputs:
- Water
- Heat (>800°C)
- Electricity

Outputs:
- Hydrogen
- Oxygen
- Waste heat

The only 2-step, all-fluids thermochemical cycle – based on sulfur oxidation and reduction
Efficiency Benchmark for Thermochemical Cycles

- Alkaline electrolysis (AE) provides an efficiency benchmark
  - Mature technology
  - 65-70% LHV efficiency
- Coupled with PWR/LWR
  - Thermal efficiency of Rankine cycle power generation is ~33%
  - Net thermal efficiency is 21-23%
- Coupled with HTGR
  - Thermal efficiency of Brayton cycle power generation is ~46%
  - Net thermal efficiency is 30-32%

More complex TC cycles become attractive compared to PWR/LWR- (or HTGR-) coupled AE when LHV efficiency is ≥ 26-29% (or 36-40%)
HyS Electrolyzer Requires Much Less Power than Alkaline Electrolyzer

- **Water electrolysis reactions:**
  \[
  \begin{align*}
  \text{H}_2\text{O}(l) & \rightarrow \frac{1}{2} \text{O}_2(g) + 2 \text{H}^+ + 2 \text{e}^- \quad \text{anode reaction} \\
  2 \text{H}^+ + 2 \text{e}^- & \rightarrow \text{H}_2(g) \quad \text{cathode reaction} \\
  \hline
  \text{H}_2\text{O}(l) & \rightarrow \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \quad \text{net reaction}
  \end{align*}
  \]

- **Standard cell potential, \( E^\circ = -1.229 \text{ V} \) at 25°C**

- **SO2-depolarized electrolysis (SDE) reactions:**
  \[
  \begin{align*}
  2 \text{H}_2\text{O}(l) + \text{SO}_2(\text{aq}) & \rightarrow \text{H}_2\text{SO}_4(\text{aq}) + 2 \text{H}^+ + 2 \text{e}^- \quad \text{anode reaction} \\
  2 \text{H}^+ + 2 \text{e}^- & \rightarrow \text{H}_2(g) \quad \text{cathode reaction} \\
  \hline
  2 \text{H}_2\text{O}(l) + \text{SO}_2(\text{aq}) & \rightarrow \text{H}_2\text{SO}_4(\text{aq}) + \text{H}_2(g) \quad \text{net reaction}
  \end{align*}
  \]

- **Standard cell potential, \( E^\circ = -0.158 \text{ V} \) at 25°C
  \[
  = -0.173 \text{ V in 30% H}_2\text{SO}_4 \\
  = -0.262 \text{ V in 50% H}_2\text{SO}_4
  \]
Actual SDE Potentials Look Promising

- Lu and Ammon (Westinghouse) data for 50% H$_2$SO$_4$ anolyte sat’d with SO$_2$ at 1 atm, 50°C
- Sivasubramanian et al. (University of South Carolina) data for dry, gaseous SO$_2$ feed at 1 atm, 80°C
- Steimke and Steeper (SRNL) data for 32% H$_2$SO$_4$ anolyte sat’d with SO$_2$ at 4 atm, 70°C
- Current development goal is 0.6V at 0.5 A/cm$^2$, 20 bar, and 90°C
Energy Allowance for H₂SO₄ Decomposition

- SDE cell voltage thermal equivalent at 46% conversion efficiency \((Q_{th} \text{ to } W_e)\)
  - \(0.6 \text{ V} \approx 252 \text{ kJ/mol H}_2\)
  - \(0.7 \text{ V} \approx 294 \text{ kJ/mol H}_2\)

- Energy consumption for different net thermal efficiencies
  - 36% LHV \(\approx 672 \text{ kJ/mol H}_2\)
  - 40% LHV \(\approx 605 \text{ kJ/mol H}_2\)

- H₂SO₄ decomposition heat requirement
  - at 0.6 V, \(672 - 252 = 420 \text{ kJ/mol H}_2\) allowance for 36% LHV efficiency
  - \(605 - 252 = 353 \text{ kJ/mol H}_2\) allowance for 40% LHV efficiency
  - H₂SO₄ decomposition heat input needs to be \(\leq 420 \text{ kJ/mol}\) to achieve net thermal efficiencies of 36% or higher (LHV basis)
  - Can consume up to \(\sim 420 \text{ kJ/mol}\) and still be attractive
OLI-MSE Model an Obvious Choice for Modeling Sulfuric Acid Properties

- Sulfur cycles involve sulfuric acid over wide T-p-x range
  - 0-900°C
  - 0.01-90 bar
  - 0-98 wt% H₂SO₄

- OLI-MSE model fits sulfuric acid VLE data accurately over entire range

- OLI-MSE can be used in conjunction with Aspen Plus™ for Sulfur-based cycle flowsheet simulations

SO$_2$-H$_2$O LLE Inevitable for HyS at High Pressures

- SO$_2$-H$_2$O binary exhibits complex phase behavior
  - Hydrates
  - Immiscibility
- LLE possible at conditions typical for H$_2$SO$_4$ decomposition product
  - 15-120°C temperatures
  - 2-35 bar pressures
- HyS temperatures too high for hydrate formation
- OLI-MSE model predicts SO$_2$-H$_2$O LLE with reasonable accuracy
Solubility of SO₂ in Sulfuric Acid at 20°C, 1 atm Partial Pressure

- SO₂-H₂O-H₂SO₄ ternary also has complex phase behavior
- Solubility of SO₂ in sulfuric acid varies with concentration
  - Broad minimum at 30-50 mol%
  - Increases rapidly with concentration above 50 mol%
- OLI-MSE model reproduces this behavior reasonably well
  - Predicts extra peak at low temperatures for SO₂ solubility in sulfuric acid
  - Speciation may need revision
SO₂ Immiscibility Possible Over Entire H₂SO₄ Concentration Range

- LLE occurs at sufficiently high pressures and SO₂ levels
- Ternary diagrams published by Francis (1965) *
  - SO₂ solubility is 26% in pure H₂O, H₂O solubility is 1.5% in pure SO₂
  - SO₂ minimum solubility is 17% in 94-96% H₂SO₄
  - Dashed line in diagram 16 indicates isopycnic (both liquid phases have equal density)
  - SO₂ completely miscible with 30% oleum
  - HyS process operates in 0-95% H₂SO₄ range

HyS Cycle Simplified Flowsheet

- Power Generation
- HTGR Nuclear Heat Source
- Electrolyzers and Auxiliaries
- Sulfuric Acid Decomposition
- Sulfur Dioxide / Oxygen Separation

H₂ Product
H₂SO₄, H₂O
H₂O, SO₂
O₂ By-product
H₂O Feed
H₂ Product
H₂O, SO₂, O₂
H₂O, SO₂, O₂
H₂O Feed
SRNL SDE Configuration

- Nafion® or other proton exchange membrane
- Gas diffusion carbon electrodes
- Membrane electrode assembly (MEA) construction
- Porous carbon flow fields
- Recirculating acid anolyte
- No catholyte needed

Anode

\[ \text{H}_2\text{SO}_4(aq) \]

Cathode

\[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(g) \]

\[ \text{SO}_2(aq) + \text{H}_2\text{O}(l) \rightarrow \text{SO}_3(aq) + \text{H}_2\text{O}(l) \]

\[ \text{SO}_2(aq), \text{H}_2\text{O}(l) \]

PEM Separator

\[ \text{SO}_3(aq) + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{SO}_4(aq) \]
Bayonet Decomposition Reactor Design

- Bayonet reactor consists of one closed ended tube co-axially aligned with an open ended tube to form two concentric flow paths
- Heat applied externally
- Liquid fed to annulus, vaporized, passed through catalyst bed
- Product returns through center, heats feed through recuperation
- Advantages include internal heat recuperation, only one connection at cool end, corrosion resistance, and low fabrication cost
- Silicon carbide bayonets are an off-the-shelf item (thermocouple tubes)
- Developed at Sandia Nat’l Lab’s

Bayonet Reactor Feed Heating and Product Cooling Curves

High-temperature heating target

Recuperation

Heat rejection target

86 bar, 870°C, 80 mol% H₂SO₄ feed, 10°C min ΔT, 1-kmol H₂/s production

328.7 MW

69.8 MW
High-temperature Heat Requirement for H₂SO₄ Bayonet Decomposition Reactor

870°C peak process temperature, 900°C secondary helium temperature
HyS Flowsheet Example Specifications

- PEM electrolyzer with 47% H₂SO₄ feed containing 15.1% SO₂ at 80°C and 21 bar makes 50% H₂SO₄ product at 92°C and 20 bar with 20% conversion at 600 mV
- 3 successive vacuum flash steps remove unreacted SO₂
- 3 partial vaporization steps concentrate acid to 80 wt% at increasing pressure to allow recuperation
- Bayonet decomposition reactor at 870°C and 86 bar with 80% H₂SO₄ feed makes H₂O, SO₂, and O₂ at 47% conversion
- Unconverted acid at 69% is recycled to concentration train
- Vapor product is cooled and let down to 21 bar
  - SO₂-H₂O condensate collected and mixed with recycled anolyte
  - O₂ vapor scrubbed with water removed in concentration train
Composite Curves for HyS Flowsheet Example (Excluding Bayonet Reactor) – 1-kmol H₂/s Basis

- High-temperature heating target: 79.2 MW
- Heat rejection target: 282.4 MW
- Pinch Point: 282.4 MW
- Recuperation:
Results of Efficiency Analysis

- High-temperature heating target for flowsheet example
  - 328.7 MJ/kmol H₂ needed for H₂SO₄ decomposition
  - Additional 79.2 MJ/kmol H₂ needed for H₂SO₄ concentration
  - Total minimum heat requirement is 407.9 MJ/kmol H₂

- Power requirement for electrolysis and pumps/compressors
  - 115.8 MJ/kmol H₂ needed for SDE
  - Additional 16.8 MJ/kmol H₂ needed for shaft work
  - Total electric power requirement is 132.5 MJ/kmol H₂

- Efficiency estimates:
  - PWR/LWR-generated power at 33% efficiency gives 29.9% LHV efficiency
  - HTGR-generated power at 46% efficiency gives 34.7% LHV efficiency

- Optimization (ongoing) should boost efficiency to desired range
Summary

- Splitting water to make hydrogen using nuclear energy is one possible component of a sustainable energy future.
- Sulfur-based thermochemical cycles are being developed under the Nuclear Hydrogen Initiative as a means to split water using a high-temperature heat source like a nuclear reactor.
- Inherently more complex thermochemical cycles must outperform simpler water electrolysis to be attractive.
- Sulfur-based cycles present stream properties modeling challenges that can be successfully handled using the OLI-MSE model.
- Aspen-OLI is being used to simulate Hybrid Sulfur process flowsheets to evaluate and optimize the net thermal efficiency.
- Preliminary results based on electrolyzer and decomposition reactor performance extrapolated from development experiments suggest that sufficiently attractive net thermal efficiency should be attainable.
Acknowledgements

- This work sponsored by U.S. Department of Energy under Contract No. DE-AC09-96SR18500
- Funding provided by the DOE Office of Nuclear Energy, Science & Technology under the Nuclear Hydrogen Initiative
  - Mr. Carl Sink
- Consultation
  - Dr. William A. Summers (SRNL)
  - Dr. Edward J. Lahoda (Westinghouse Electric Co.)
  - Dr. Paul M. Mathias (Fluor Corp.)
  - Prof. John P. O’Connell (University of Virginia)
  - Prof. John W. Weidner (University of South Carolina)