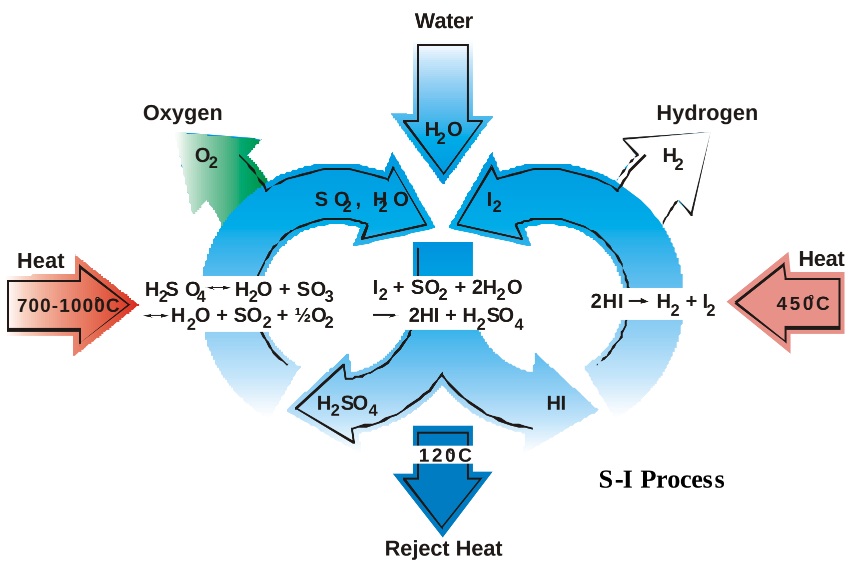
Thermochemical Production of Hydrogen

Thermochemical production of hydrogen involves the separation of water into hydrogen and oxygen through chemical reactions at high temperatures. Ideally, water can be separated directly (thermolysis), however this process requires temperatures in excess of 2500°C.

$$H_2O \Rightarrow H_2 + 1/2\ O2 \qquad > 2500°C$$

Because these temperatures are impractical, thermochemical water-splitting cycles achieve the same result (i.e., separation of water into hydrogen and oxygen) at lower temperatures. A thermochemical water-splitting cycle is a series of chemical reactions, some at rather high temperatures. Chemical are chosen to create a closed loop where water can be fed to the process, oxygen and hydrogen gas are collected, and all other reactants are regenerated and recycled.

Recent studies conducted through the Nuclear Energy Research Initiative (NERI) have identified more than 100 thermochemical water-splitting cycles. A few of the most promising cycles have been selected for further research and development, based on the simplicity of the cycle, the efficiency of the process, and the ability to separate a pure hydrogen product.



Of the identified thermochemical processes, the sulfur family of processes, including sulfur-iodine (S-I) and hybrid-sulfur, appear to have the highest efficiencies and hence the most promising. As shown in the figure, the S-I cycle uses iodine (I_2) and sulfur dioxide (SO_2) as chemical catalysts to split water. First, water reacts with I_2 and SO_2 to form hydrogen iodide (HI) and sulfuric acid (H_2SO_4).

$$I_2 + SO_2 + 2H_2O \Rightarrow 2HI + H_2SO_4 \qquad \sim 120°C$$

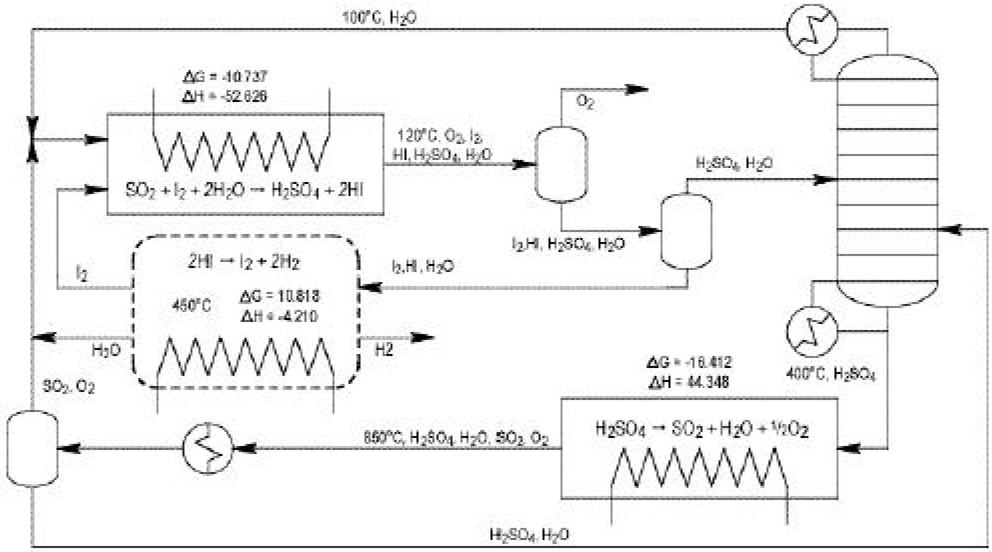
Then the HI and H_2SO_4 are separated from each other. The I_2 and SO_2 are then recovered from the HI and H_2SO_4 and recycled, and hydrogen and oxygen gases are collected.

$$H_2SO_4 \Rightarrow H_2O + SO_2 + ½\ O_2 \qquad > 850°C$$

$$2HI \Rightarrow H_2 + I_2 \qquad \sim 450°C$$

The reaction that requires the greatest heat input is the thermal decomposition of H_2SO_4, typically at temperatures in the range of 850°C. High temperatures are necessary to produce large quantities of hydrogen in a cost-effective manner, because the efficiency of the process (hydrogen produced per unit of heat input) decreases rapidly with temperature.

There are several process variations. Preliminary designs of the process completed under DOE NERI (see figure below) rely heavily on the use of distillation to separate system



Sulfur-Iodine Process Flow Diagram

components. Distillation adds considerably to capital costs as well as energy consumption. The identification and development of membranes that can be used in the process may improve process efficiency in two ways, through more cost-effective separations and by increasing reaction rates.

Another leading candidate is the hybrid-sulfur process. This process uses the same high-temperature step as the S-I process but replaces the lower-temperature chemical reactions with an electrolytic cell.

$$SO_2 + 2H_2O \Rightarrow H_2SO_4 + H_2 \qquad \text{Electolysis: 80ºC}$$

The power requirements for this electrochemical step are much less than direct electrolysis of water. The process adds the complication of an electrolysis step but reduces the complexity of the chemical plant.

Other thermochemical cycles that use other chemical systems may also be feasible for large-scale cost-effective hydrogen production. For example, the calcium-bromine cycle (Ca-Br) is being investigated as part of another DOE NERI project. The advantage of the Ca-Br process is a lower temperature requirement (~750°C). However, unlike the S-I and sulfur-hybrid processes, which contain only gases and liquids, the Ca-Br contains solids. In current designs the Ca-Br process is a batch process where the solids remain fixed in beds. Fluids flow through bed in one direction to produce hydrogen. The solid beds are then regenerated with other gases. This hinders the efficiency and output of the system. The particular solids involved in the process also undergo structural changes at the microscopic level, which makes them difficult to physically support in the reactor. In spite of these challenges, the Ca-Br process shows significant promise, and several potential solutions to these challenges have been proposed through the NERI work.

Thermochemical cycles are expected to be a cost and energy efficient way to produce large amounts of hydrogen. The economics strongly depend on the cycle and temperature used. Production efficiency is one factor that helps determine economics and is often used to compare processes; production efficiency is defined as the ratio of the energy content of the hydrogen produced to the energy expended to produce the hydrogen. For thermochemical approaches such as the sulfur-iodine process, an overall efficiency greater than 50% is expected. For comparison, the only commercially available process, electrolysis, is typically 25-35% efficient because of the inefficient generation of electricity.

Common to all thermochemical cycles are insufficient chemical process characterization data and materials issues. Significant research will be necessary to fully characterize cycles to realistically estimate cost and efficiency, demonstrate the feasibility of the processes to produce significant amounts of hydrogen, and understand tradeoffs between different thermochemical cycles. There is also a broad range of materials issues such as developing materials for process equipment, membranes, and catalysts that are stable in a variety of environments, including in high temperatures and strong acids.