THERMOCHEMICAL IODINE SULFUR PROCESS FOR HYDROGEN PRODUCTION

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INTRODUCTION

One can think about using methane reforming as a source of hydrogen, and using wind, solar and nuclear processes as energy sources to what is an inherently energy intensive process. However, this still releases to the environment the carbon contained in methane in the form of carbon dioxide. Achieving the advantage of a hydrogen economy should entail using water as a source of hydrogen instead of hydrocarbons like methane. This has to be set as the goal of hydrogenation, even though the system may be initially started up using methane as a source of hydrogen.

HIGH TEMPERATURE PROCESSES

To use water as a source of hydrogen several high temperature thermochemical processes have been suggested. The leading processes are those using sulfuric acid as a catalyst:

1. The hydrogen sulfide process,
2. The iodine sulfur process,
3. The sulfuric acid methanol process.

High temperature around 900 ^oC is needed to ensure fast chemical kinetics, resulting in high thermal efficiencies, small plant sizes and low capital costs.

LOW TEMPERATURE PRODUCTS

Alternatively, less efficient processes around 700 ^oC can be used for the production of:

1. Methanol

Can be used for addition to gasoline, similar to ethanol:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad (1)$$

2. Dimethyl Ether, CH_3OCH_3

For mixing with diesel fuel. The simplest ether, it produces minimal amount s of NO_x and CO gases and can be used as a clean fuel.

It is used as a substitute for propane and used as fuel in households and industry, as well as a propellant in aerosol canisters, as a solvent, refrigerant and as a treatment for warts.

It has a high cetane number of 55 compared with diesel fuel as 40-53. It is a promising fuel for use in diesel engines, internal combustion engines and gas turbines, with low sulfur emissions.

It can be manufactured from lingo-cellulosic biomass. It is relatively non-toxic, but highly flammable.

3. Ammonia, NH_3

Ammonia can be used in internal combustion and in rocket engines. It has been used during World War II to power buses in Belgium, and in engine and solar energy applications prior to 1900. Liquid ammonia was used as the fuel of the rocket airplane, the X-15.

The calorific value of ammonia is 22.5 MJ/kg or 9690 BTU/lb; 1/2 that of diesel fuel. However, it is considered as less efficient than chemical batteries.

Ammonia has been produced from water electrolysis for the production of fertilizer.

THERMOCHEMICAL HYDROGEN PRODUCTION: THE IODINE SULFUR (IS) PROCESS

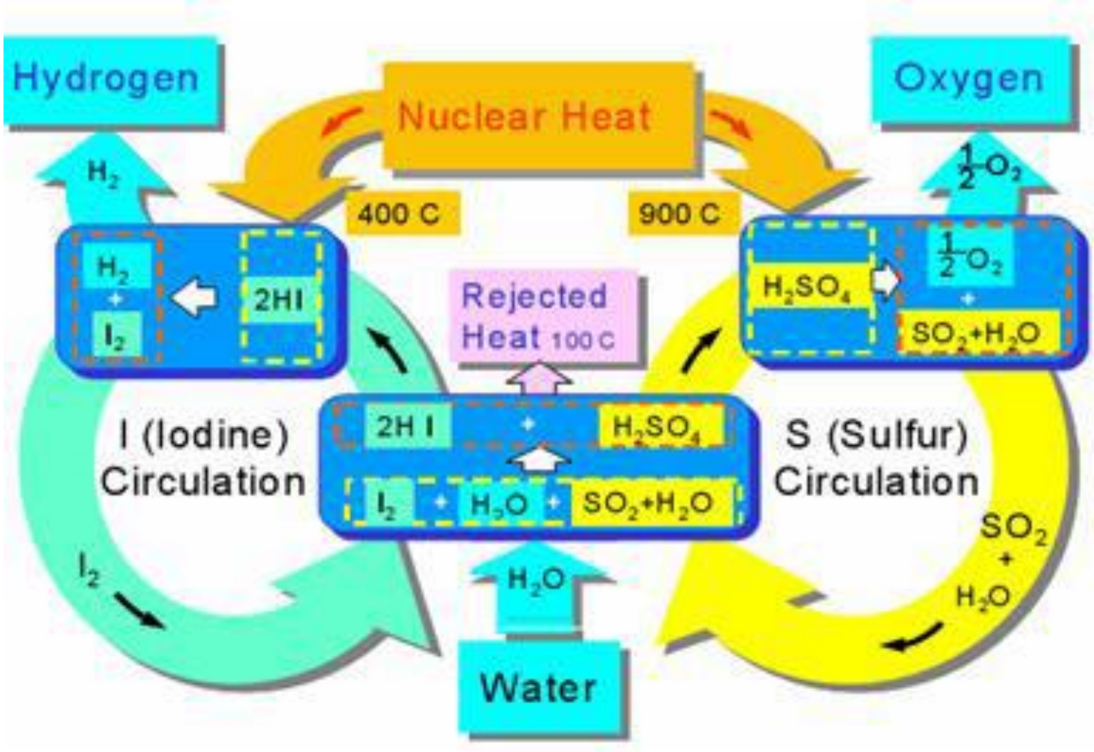

Figure 1. Sulfur Iodine process for hydrogen production operates at 900 degrees C.

In the three processes using sulfuric acid as a catalyst, a high temperature low pressure endothermic process involves the decomposition of sulfuric acid to produces water, oxygen and sulfur dioxide:

$$2H_2SO_4 \rightarrow 2H_2O + 2SO_2 + O_2 \quad (1)$$

The last reaction is carried out at about 800-1,000 degrees Celsius for efficient hydrogen production. The oxygen is separated and low and intermediate temperature steps follow.

In the Iodine Sulfur (IS) process, iodine is added in addition to water at low temperature to the sulfur dioxide after removing the oxygen:

$$2I_2 + 2SO_2 + 4H_2O \rightarrow 4HI + 2H_2SO_4 \quad (2)$$

This is followed by an intermediate temperature hydrogen-producing step as:

$$4HI \rightarrow 2H_2 + 2I_2 \quad (3)$$

If we add Eqns.1-3, we obtain the overall hydrogen producing reaction as:

$$2H_2O \rightarrow 2H_2 + O_2 \quad (4)$$

This identifies sulfuric acid and iodine as catalysts since they appear on both sides of the equations but do not appear in the final overall equation.

PROCESS EFFICIENCY

Research in Japan at the Japan Atomic Energy Research Institute is demonstrating the production of hydrogen at their High Temperature engineering Test Reactor (HTTR), using steam reforming of methane gas. The iodine sulfur process is under development to be tied up ultimately to the HTTR. Similar research is taking place in the USA.

Currently, thermo chemical hydrogen production processes are favored to water electrolysis which surprisingly has an efficiency of about 80 percent:

$$\eta_{electrolysis} = 0.80 \quad (5)$$

The argument that is presented is that it has to be coupled to a thermal process for the production of electrical energy that would be used in electrolyzing the water. These thermal processes have efficiencies for existing light water reactors of about 34 percent, to 50 percent for advanced gas cooled systems. Thus:

$$\eta_{electricity} = 0.34 - 0.50 \quad (6)$$

The overall hydrogen production efficiency is surmised to be the product of the two efficiencies in Eqns. 5 and 6 as:

$$\eta_{hydrogen} = \eta_{electrolysis}\eta_{electricity} = 0.242 - 0.40, \quad (7)$$

implying an overall hydrogen production efficiency of 24.2-40 percent. So unless the electrical production electricity is increased, thermo chemical processes remain the more efficient process at a projected efficiency of 50 percent. Some suggestions have been advanced of combined cycle hydrogen and electricity plants reaching an efficiency of 60 percent [3].

VERY-HIGH-TEMPERATURE REACTOR: VHTR

The USA is considering a new Generation IV innovative reactor design. An amount of $1.1 billion is budgeted for its construction until 2010. The reactor would be ready for demonstration by 2015.

The core would be He cooled using fuel similar to that of the Gas Turbine Modular Helium Reactor (GT-MHR) or a Pebble bed Modular Reactor (PBMR).

The Very High Temperature Reactor or VHTR is a fourth generation gas cooled reactor design that would produce both electricity and hydrogen (Fig. 1). The Idaho National Engineering Laboratory (INL) is sponsoring the development of the project.

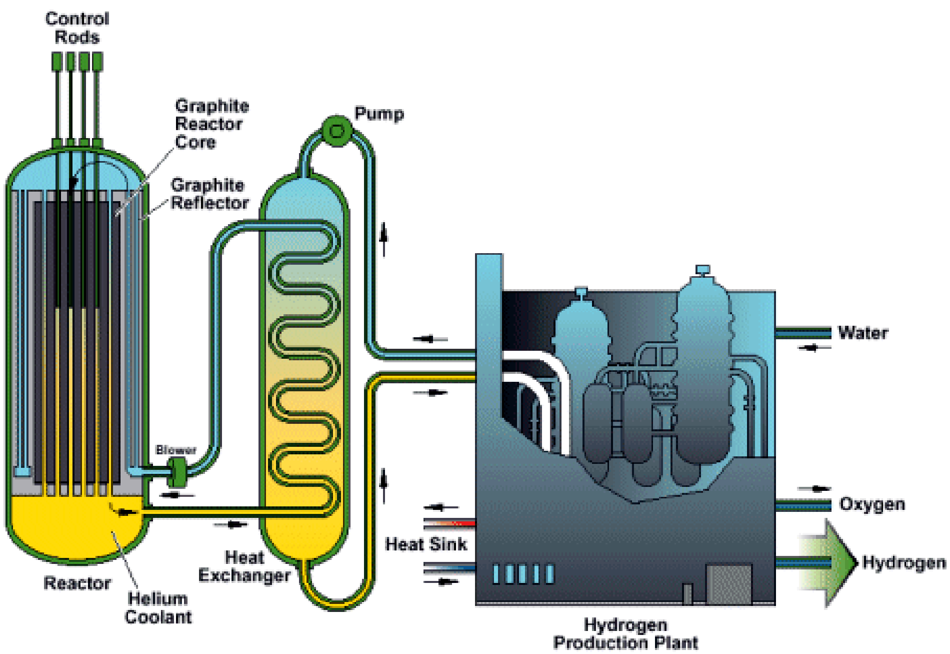

Figure 2. Very High Temperature Hydrogen and Electricity (VHTR) design.

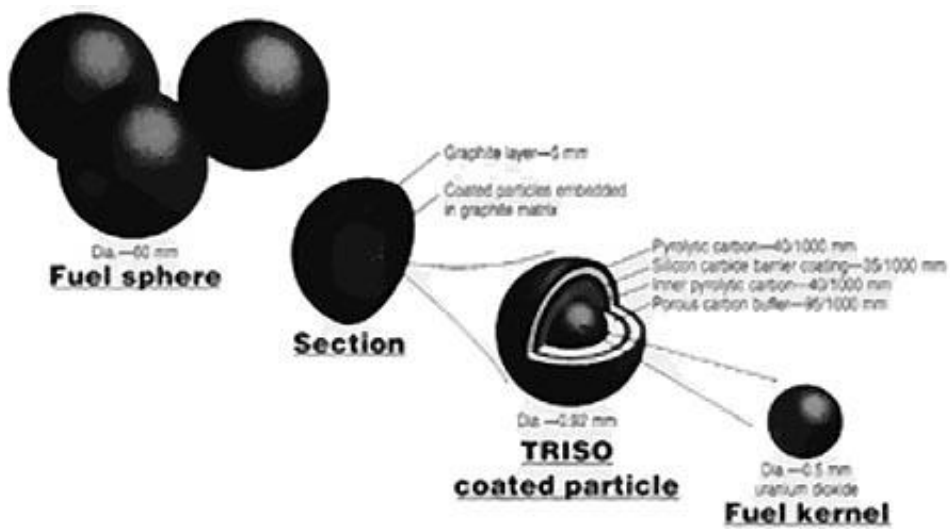

Figure 3. Fuel elements used in the Pebble Bed Modular Reactor (PBMR).

It is a graphite-moderated, He cooled reactor with a once-through uranium fuel cycle, intended for the dual purpose production of electricity and hydrogen. Hydrogen as a nuclear energy carrier is considered for a future nonpolluting energy economy with fuel cells directly producing electricity from hydrogen and releasing steam and water as a product.

The VHTR supplies heat with a He coolant core outlet temperature of 1,000 ^{o}C, which enables applications such as hydrogen production, synthetic fuel production from coal or process heat for the petrochemical industry. The reference pilot reactor is a 600 MWth core connected to an intermediate heat exchanger to deliver process heat. The reactor core can either be a prismatic block core such as the previous USA Fort Saint-Vrain, or the operating Japanese HTTR, or a pebble-bed core such as the operating Chinese HTR-10. For hydrogen production, the system supplies heat that could be used efficiently by a thermochemical iodine-sulfur process.

Figure 4. Experimental Pebble Bed High Temperature Gas Cooled Reactor, HTR-10 at Tsinghua University, China.

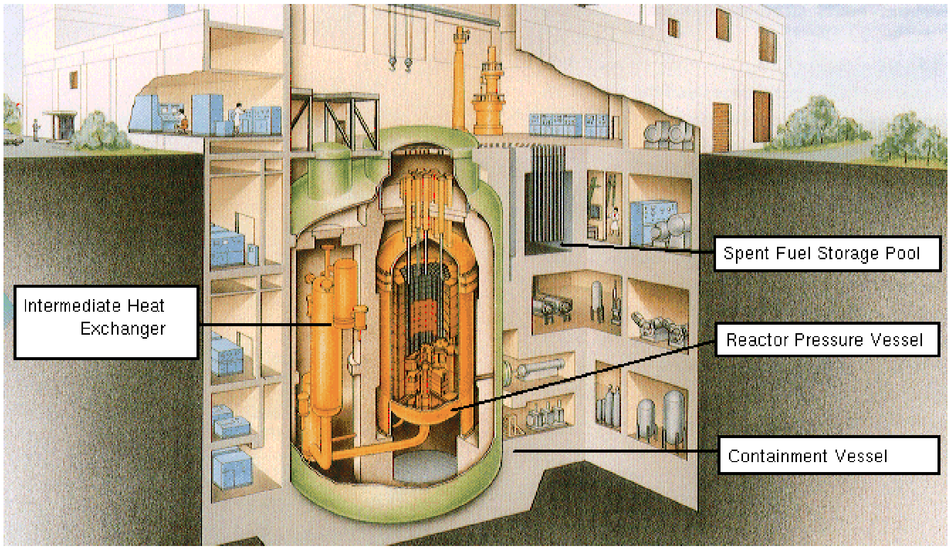

Figure 5. High Temperature Gas Cooler Reactor, HTTR, Japan.

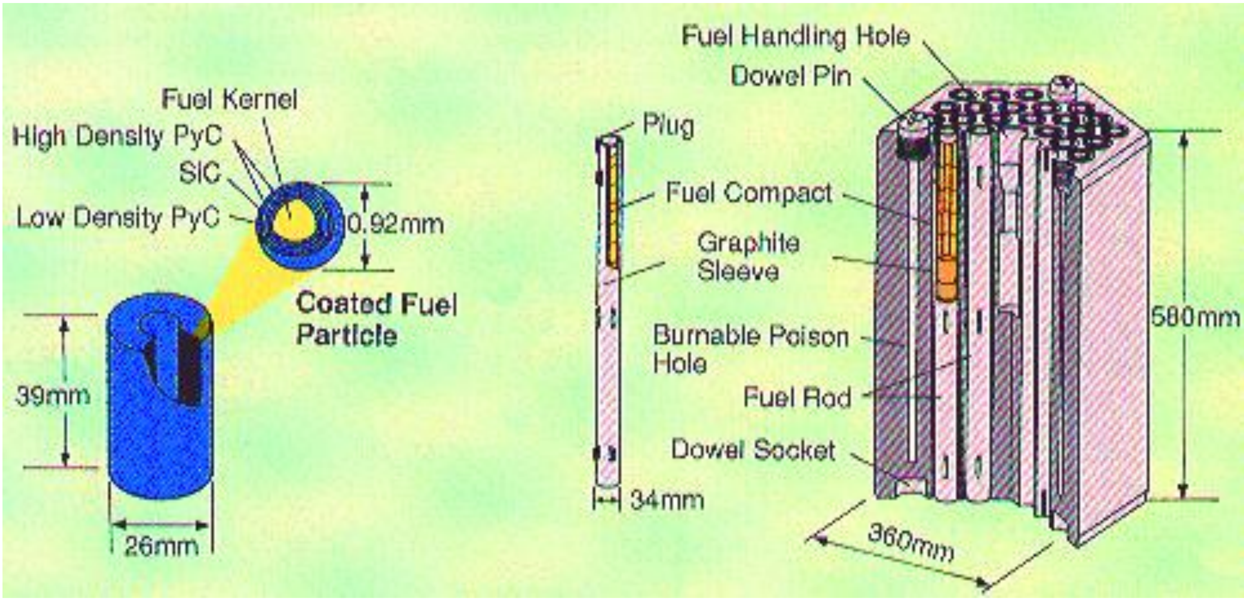

Figure 6. Prismatic graphite fuel assembly in the HTTR.

A safety feature is the reactor heat can be passively radiated through its steel vessel away from the high thermal inertia graphite moderator core without damage to the graphite encased fuel and release of fission products radioactivity. The reactor would be built underground with the earth becoming its ultimate heat sink.

The main circuit releases heat to a steam reformer/steam generator. It is capable to use a U/Pu fuel cycle to manage the actinides waste.

Several goals are aimed at: economical operation, high efficiency comparable to that of combined cycle natural gas plants, minimum waste generation, walk away safety and a proliferation resistant fuel cycle.

The VHTR offers a broad range of process heat applications and an option for high-efficiency electricity production, while retaining the desirable safety characteristics offered by modular high-temperature gas-cooled reactors.

There is a need for developing carbon composites for control rod sheaths. The core internals would need up to ten years of testing for oxidation, post irradiation heat up and fracture behavior of the high temperature materials. Testing for the safety of valves and internal heat exchanger modules will be needed.

The VHTR can be rapidly developed in the years ahead for hydrogen production, or alternatively. It can be used for coal gasification and synthetic fuel production for transportation as a replacement to the depleting liquid hydrocarbon supplies.

Nuclear utilities like Exelon Corp., Dominion Resources Inc. and Entergy Corp., as well as equipment manufacturers like General Electric Co., The Westinghouse Nuclear unit of British Nuclear Fuels Ltd., and the Framatome unit of France’s Areva have shown interest in the VHTR project.

HYDROGENATION OF THE ENERGY SUPPLY

The hydrogenation of the energy supply is expected to restart the construction of a new generation of safe nuclear fission plants, and eventually encourage the development of even safer fusion systems. This will be in addition to whatever other supplies can be provided with wind and solar energy methods.

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