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Thermochemical Water Splitting for Hydrogen Production Utilizing Nuclear Heat from an HTGR*

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Abstract: A very promising technology to achieve a carbon free energy system is to produce hydrogen from water, rather than from fossil fuels. Iodine-sulfur (IS) thermochemical water decomposition is one promising process. The IS process can be used to efficiently produce hydrogen using the high temperature gas-cooled reactor (HTGR) as the energy source supplying gas at 1000℃. This paper describes that demonstration experiment for hydrogen production was carried out by an IS process at a laboratory scale. The results confirmed the feasibility of the closed-loop operation for recycling all the reactants besides the water, H_2, and O_2. Then the membrane technology was developed to enhance the decomposition efficiency. The maximum attainable one-pass conversion rate of HI exceeds 90% by membrane technology, whereas the equilibrium rate is about 20%.

Key words: high temperature gas-cooled reactor; hydrogen production; thermochemical; water splitting

Introduction

The oil crisis in the 1970s emphasized the need for new energy sources which are now even more urgent due to the global environmental issues widely recognized in the world in recent years. Nuclear and hydrogen energy sources are promising candidates for new primary and secondary energy sources[1].

Hydrogen is a flexible energy carrier which can be stored in a variety of ways and transported over long distances with low transportation costs. Hydrogen can be used as a fuel in a wide variety of industrial applications and can be transformed into electricity in fuel cells. Hydrogen is very clean in the sense that water is the only product after burning. Therefore, it will play an important role in future clean energy systems[2].

Among the various kinds of nuclear reactors, the high temperature gas-cooled reactor (HTGR) provides especially high-temperature heat at about 1000℃ with inherent safety. HTGRs will be used not only to supply a large amount of future electricity generation but also to supply energy in non-electrical fields. One potential application of the HTGR is for hydrogen production, which is regarded as one of the leading nuclear heat utilization applications in non-electrical fields. There are several potential hydrogen production processes that can use nuclear heat. The final goal of the hydrogen production system using HTGR is to produce hydrogen without CO_2 emissions. Hydrogen production from water, rather than from fossil fuels, will result in a carbon free energy system. With certain endothermic and exothermic chemical reactions, water can be split at lower temperatures than that required for direct thermal decomposition. However, the reactions must be carefully selected so that the process results in water splitting. The process works like a chemical engine to produce hydrogen while absorbing high-temperature

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heat and discharging low-temperature waste heat. The iodine-sulfur (IS) thermochemical water decomposition process is one promising method[3] that can efficiently and cleanly produce hydrogen with the high temperature gas-cooled reactor as the heat source supplying gas at 1000℃. The system offers a novel and promising means for large-scale hydrogen production from water.

1 Iodine-Sulfur Process Principles

The IS process consists of three chemical reactions[4].

$$xI_2+SO_2+2H_2O=2HI_x+H_2SO_4 \tag{1}$$

$$2HI=I_2+H_2 \tag{2}$$

$$2H_2SO_4=2H_2O+2SO_2+O_2 \tag{3}$$

The principles for the IS process are illustrated in Fig. 1. The so-called Bunsen reaction, Eq. (1), is an exothermic sulfur dioxide (SO_2) gas absorbing reaction, which proceeds spontaneously in the liquid phase at 20-100℃. Gaseous sulfur dioxide reacts with iodine and water producing an aqueous solution of hydriodic acid and sulfuric acid. The two kinds of acids are separated by liquid-liquid phase separation in the presence of excess iodine. The hydrogen iodide (HI) decomposition reaction, Eq. (2) , produces hydrogen with a low endothermic heat of reaction at 300-500℃ in the gas phase. It can also be carried out in the liquid phase. The sulfuric acid (H_2SO_4) decomposition reaction, Eq. (3), is an endothermic oxygen producing reaction, which proceeds in two stages. First, gaseous H_2SO_4 decomposes spontaneously into H_2O and SO_3 at 400-500℃ and then SO_3 decomposes into SO_2 and O_2 at about 800°C in the presence of a solid catalyst. By carrying out these three reactions sequentially, the net result is that the water is decomposed into hydrogen and oxygen. The process has the attractive characteristics that all the chemicals circulate in the process as fluids and the sulfuric acid decomposition proceeds stoichiometrically with a high conversion ratio and large entropy change at temperatures suitable for utilizing the nuclear heat supplied by an HTGR.

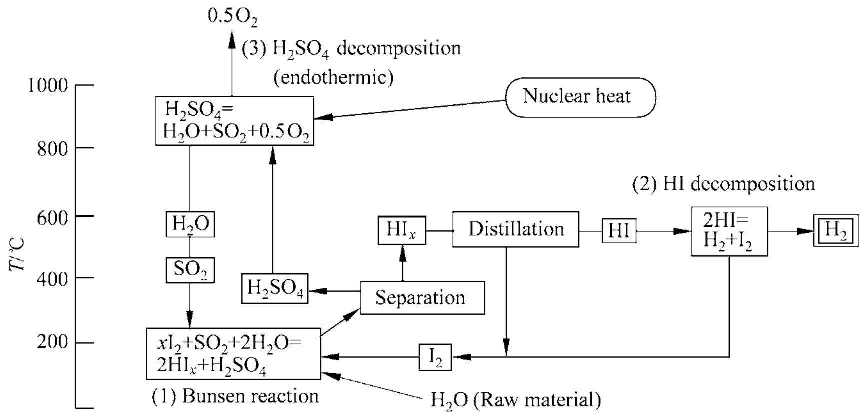

Fig. 1 IS process concept

Since the thermochemical process is an energy conversion process, the energy conversion efficiency is an important factor. The efficiency is usually defined as the ratio of the higher heating value of hydrogen to the net external heat input to the process and is referred to as the "thermal efficiency"[5].

Based on the higher heating value of hydrogen, the IS process thermal efficiency, assuming maximum heat recovery, should be more than 45% for optimum operating conditions, which is expected to be competitive with the conventional water-splitting cycle[1].

R&D on the IS process has been carried out intensively at the Japan Atomic Energy Research Institute (JAERI) since the beginning of the 1980s. The IS process research has focused on three fields[6]: a) development of a closed-loop system, b) improvement of the process to attain high thermal efficiency, and c) development of construction materials.

Closed-loop operation means that the process materials other than water, hydrogen, and oxygen circulate in the process without loss, which is an important advantage of the thermochemical cycle. The aim of the research on the closed-loop operation was to demonstrate the chemical feasibility of continuous hydrogen production in a laboratory-scale IS process. The closed-loop tests sought to produce hydrogen and