

## A STUDY ON A CLOSED-CYCLE HYDROGEN PRODUCTION BY THERMOCHEMICAL WATER-SPLITTING IS PROCESS

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Thermochemical hydrogen production process produces hydrogen from water by absorbing high temperature nuclear heat supplied by High Temperature Gas-cooled Reactors. This paper presents a result of a laboratory-scale demonstration experiment of the thermochemical hydrogen production by IS (Iodine-Sulfur) process. Hydrogen and Oxygen could be produced with stable rate and with molar ratio of 2 to 1, the stoichiometric ratio of water splitting. Also, the fluctuation of the composition of the process solution could be controlled to be lower than 3%.

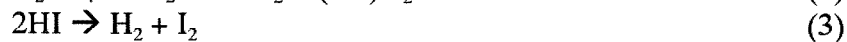
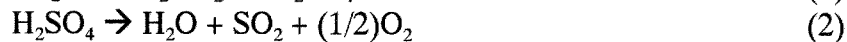
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### 1 INTRODUCTION

Hydrogen has ideal characteristics as an energy carrier. It can be transported for long-distance with less transportation loss than electricity. It can be stored in the forms of compressed gas, liquid, or hydrogenated compounds using hydrogen-absorbing alloys. It can not only be used as a fuel in a wide variety of industrial sectors, but also be transformed into electricity by fuel cells. Also, it is very clean in the sense that water is the only waste material after burning. Therefore, hydrogen is a promising candidate of alternative energy carriers in our future energy system [1].

Hydrogen can be produced by a variety of methods. At present, most of the hydrogen used in industry comes from fossil resources. However, because of the growing concern on the global environmental issues and the potential problem of the energy resources depletion, it is desirable to produce hydrogen from water. Thermochemical water-splitting cycle, the concept of which was proposed by Funk and Reinstrom [2], offers a method for the large-scale production of hydrogen. The cycle is composed of plural chemical reactions and the net chemical change of the cycle is the water decomposition. The cycle works like a chemical engine to produce hydrogen by absorbing high temperature heat through endothermic chemical reactions and exposing waste heat through low temperature exothermic chemical reactions. By utilizing high temperature nuclear heat supplied by High Temperature Gas-cooled Reactors, the cycle works as an energy converter from nuclear energy to chemical energy of hydrogen.

Based on these backgrounds, JAERI has been conducted a study on a thermochemical cycle composed of the following three chemical reactions.



The cycle is named IS process after the elements used in the process, iodine and sulfur. It has attractive features such that all the chemicals are used in the fluid phase and the endothermic sulfuric acid decomposition reaction proceeds stoichiometrically with large entropy change. The process was proposed and studied by General Atomic Co. [3] and has been studied also in Germany [4], Canada [5], and Japan [6].

The purpose of the present study is to demonstrate the laboratory-scale continuous hydrogen production by IS process [7]. The emphasis is given to produce hydrogen and oxygen with the stoichiometric ratio of water decomposition reaction and to maintain the process solution in a stable composition, since these are the basic requisites of the so-called "closed-loop operation". The close-loop operation means that the process materials other than  $\text{H}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{O}_2$  circulate in the process without loss, and is an important and a valuable characteristic of the thermochemical cycle. This paper presents recent achievements of the demonstration study.

## 2 EXPERIMENTAL APPARATUS

A scheme of the laboratory-scale experimental apparatus is shown in **Fig.1**. It was designed to produce several liters of hydrogen per hour and was made of glass and Teflon. The apparatus includes the every fundamental reactors and separators of IS process. A brief description of the unit operations is as follows.

In **R1**, the  $\text{SO}_2$  gas is chemically absorbed by aqueous solution of HI,  $\text{I}_2$ ,  $\text{H}_2\text{SO}_4$  producing HI and  $\text{H}_2\text{SO}_4$ , where the reaction (1), the so-called Bunsen Reaction, takes place. The acids are then separated spontaneously into two liquid phases. The heavier phase is mainly composed of HI,  $\text{I}_2$  and  $\text{H}_2\text{O}$  (hereafter called as HI phase). The lighter phase is mainly composed of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$  (hereafter called as sulfuric acid phase). The two solutions are separated in **S1**. The residual sulfuric acid in the HI phase is completely separated in **F2**, where the reverse reaction of the Bunsen Reaction takes place and the sulfur compounds are separated as gaseous  $\text{SO}_2$  and recycled to **R1**. The purified HI- $\text{I}_2$  aqueous solution is fed to a distillation column, **DS**, where the hydriodic acid (HI- $\text{H}_2\text{O}$  solution) is separated from iodine. Then, the hydriodic acid is fed to **R3**, where it is vaporized and decomposed using Pt catalyst. The sulfuric acid phase is similarly purified, concentrated, vaporized and decomposed in **F1** and **R2**. The decomposition reaction is carried out with Pt catalyst.

In order to aid the stable steady-state operation, some equipments were added to the apparatus. To transport the iodine rich solution from **DS** to **R1** at temperatures higher than  $120^\circ\text{C}$ , a new pumping system was devised [8]. Also, two buffer tanks were set around **R3** to control the feed flows to **R3** and **S1**.

The products, hydrogen and oxygen, were transferred by nitrogen carrier gas from the reactors to analysis sections, where the compositions and the flow rates were measured and then the production rates were computed. The flow rates were measured by thermal mass flow meters (Hastings, ST500M). The compositions were measured by a thermal conductivity detector (Ohkura, R5037) and a concentration cell featuring YSZ electrolyte (Toray, LC700H)

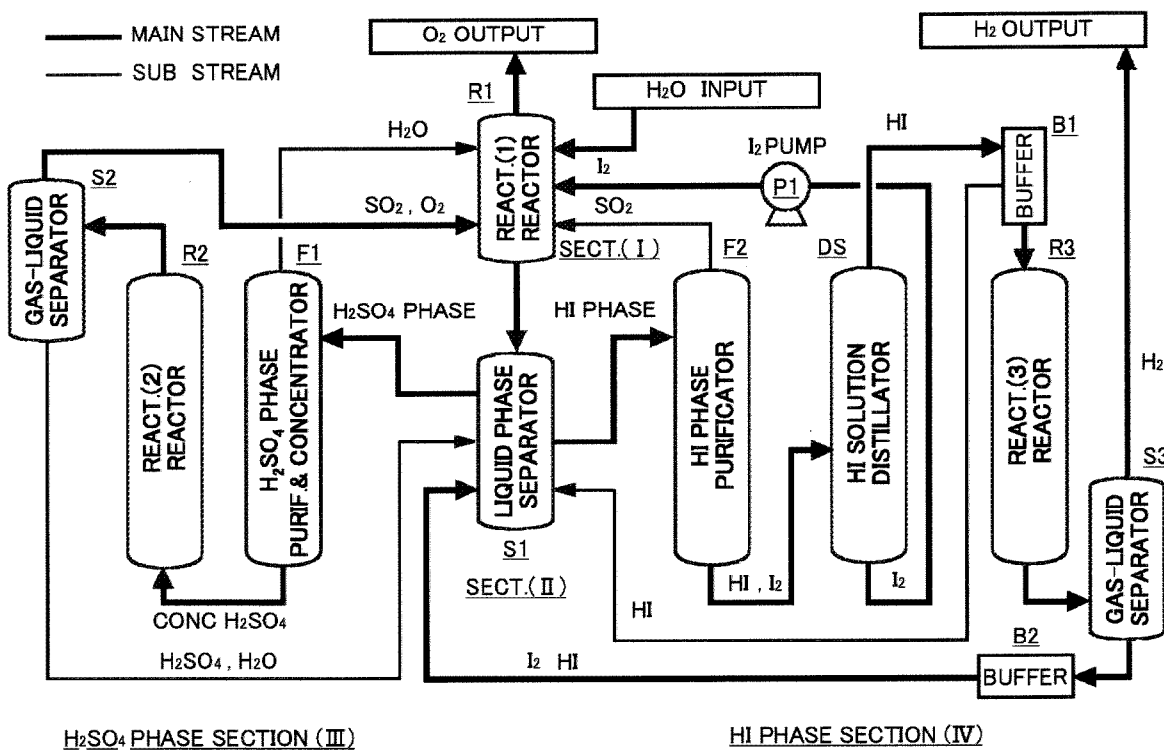


Fig. 1 Flowsheet of the laboratory-scale demonstration apparatus (schematic)

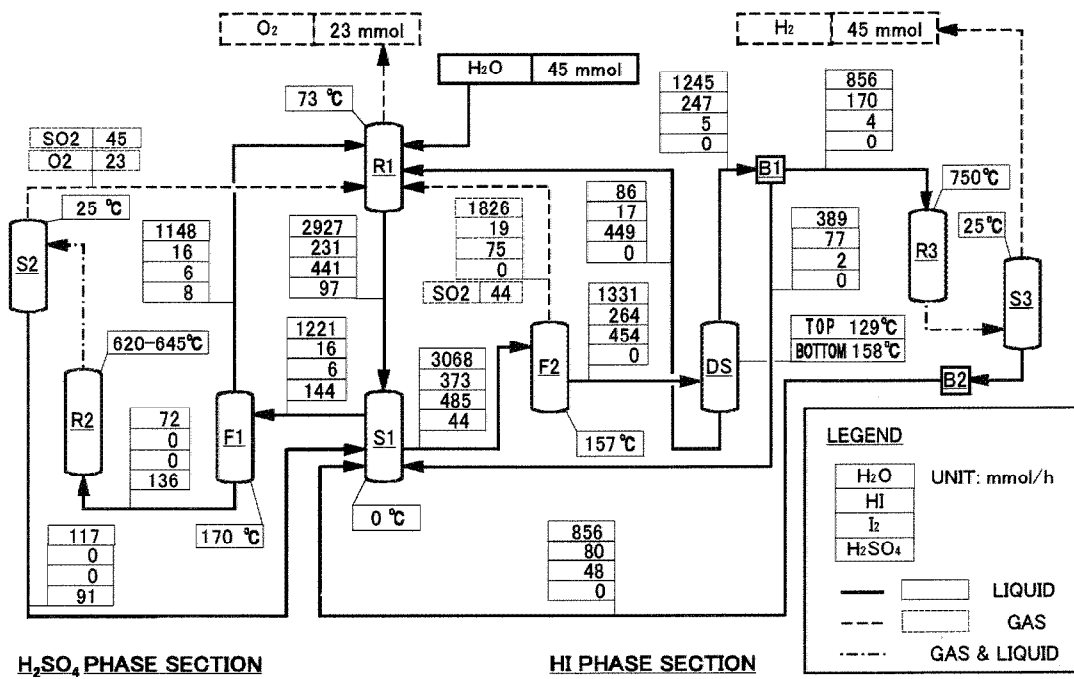


Fig. 2 Mass flow sheet of the demonstration experiment

for the gaseous mixture containing hydrogen and that containing oxygen, respectively. In order to monitor the composition of the representative process solution, the iodine concentration of the sulfuric acid phase in S1 (hereafter denotes as  $f_{I_2}$ ) were continuously measured by a visible spectrophotometer (Hitachi, L-4200H).

The every operation was carried out under atmospheric pressure. A typical mass flow sheet and the representative operating temperatures are shown in **Fig.2**. The key parameters for determining the mass flows are the composition of the Bunsen Reaction product solution, the temperature of the liquid-liquid phase separation and those of the reactions (2) and (3). In the present experiments, these parameters were chosen from the viewpoint of ease of operation considering the limitations arising from the small size of the apparatus. It should be noted here that the HI conversion ratio at R3 shown in the fig. 2 was realized by connecting four reactors in series. By separating only hydrogen from the outlet gas of each reactor by partial condensation, the once-through conversion exceeding the equilibrium one could be attained [9].

### 3 PROCESS CONTROL

Hydrogen and oxygen producing sections were operated with the feed solutions supplied from the liquid phase separator, S1. Therefore, it was the primary requirement for the stable closed-loop operation to maintain the stable composition of the composition of the phase-separated solution. As recognized by the flowsheet, the fluctuations of almost all the reactions, separations and transportation might affect the composition. Practically, however, the distillation column, DS, and the transportation of iodine-rich bottom solution of DS were the key points for the stable operation of the apparatus. The difficulty of controlling the column condition came from its long response time and the high sensitivity to the change of the

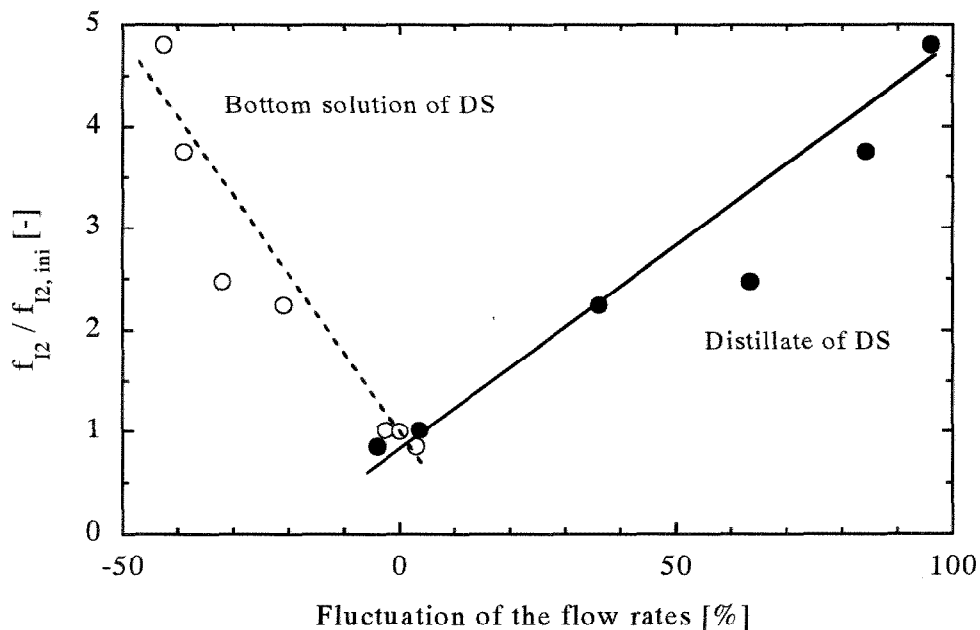


Fig. 3 Effect of the flow rate fluctuation of the distillate and the bottom solution of DS on the iodine concentration of the sulfuric acid phase [10]

$f_{I_2}$ : mole fraction of  $I_2$  in the sulfuric acid phase,  $f_{I_2, ini}$ : initial value of  $f_{I_2}$ .

ambient temperature.

In the present experiments, the information of the  $f_{I_2}$  was utilized for the process control. The information was interpreted owing to the so far obtained knowledge on the liquid-liquid phase equilibrium. With the information of the process conditions thus estimated, the operating conditions were tuned to maintain the steady-state hydrogen production.

**Fig.3** [10] shows the estimated effect of the fluctuation of the distillation column, **DS**, on the  $f_{I_2}$ . Here, the abscissa denotes the flow rate of the distillate and that of the bottom solution, as well. As seen in the figure, the decrease of the bottom solution flow rate and the increase of the distillate flow rate cause the increase of  $f_{I_2}$ . As for the bottom solution flow rate, the new pumping system mentioned in the experimental section was effectively utilized to transport the iodine-rich solution stably. Concerning the distillate flow rate, the effect of its fluctuation on the composition of the phase-separated solution was minimized by tuning the returning flow rate of the distillate from the buffer tank to the phase-separator.

#### 4 DEMONSTRATION RESULTS

The demonstration experiments have been carried out several times so far. In the longest run, the hydrogen production was carried out continuously for 48 hrs, the results of which are summarized in **Fig.4**. It shows the evolution of the produced amounts of hydrogen and oxygen, and that of the fluctuation of the iodine concentration of the sulfuric acid phase. The hydrogen and oxygen could be produced with the production ratio of 2 to 1, which was equal to the stoichiometric ratio of water decomposition reaction. Also, the composition fluctuation of the process solution could be controlled within 3%. These results show that the stable and continuous water splitting by pure thermochemical cycle was demonstrated.

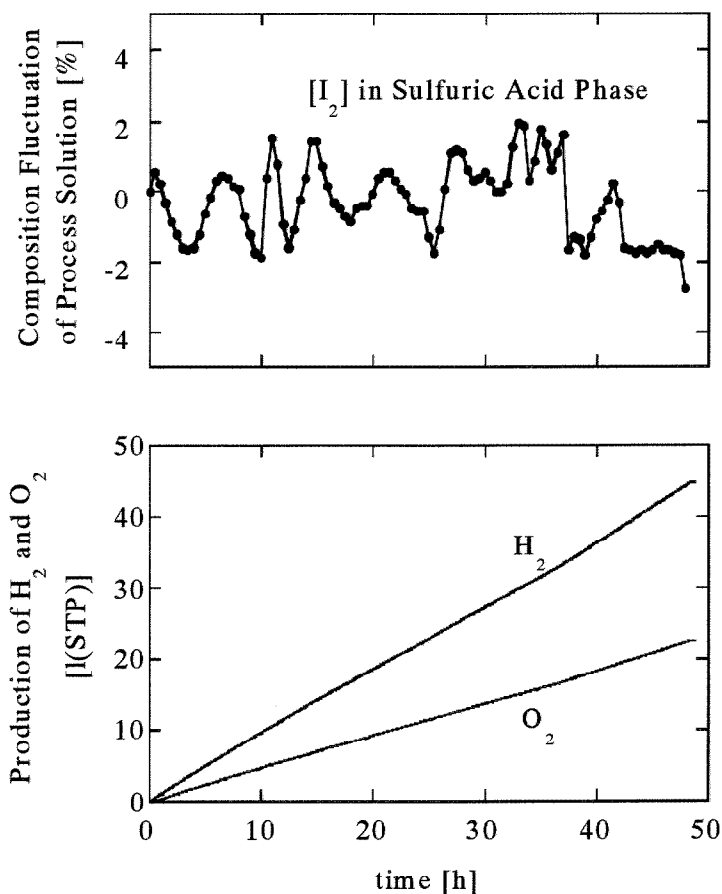


Fig. 4 Results of the demonstration experiment

## 5 CONCLUSIONS

Continuous and stoichiometric production of hydrogen and oxygen by thermochemical IS process was demonstrated in laboratory for 48 hrs. In the next stage, the operation under more efficient process conditions will be carried out such as to use the phase-separated solution with higher iodine concentration at higher operation temperature [6].

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