Numerical simulation of H_2SO_4 thermal decomposer for a bench-scale nuclear hydrogen production test facility

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1. Introduction

A VHTR-based method of generating hydrogen from the Sulfur-Iodine (SI) cycle is one of the promising approaches to produce massively hydrogen shown in Fig. 1.
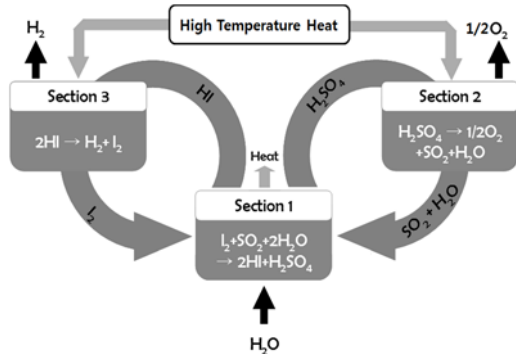

Fig. 1. SI hydrogen production cycle.

The SI cycle offers the potential of highly efficient production of hydrogen from water, but most studies have only been concerned with evaluating its thermal efficiency [1-4] and small scale atmospheric operation test of the SI process [5]. A study was done by Yamawaki et al. on application of nuclear energy to the SI cycle for hydrogen production [6].

The current technical issue of the SI process is to reach steady state operation and then achieve long-term closed-loop operation of the SI integrated test facility without any additional feeding of recycled reagents such as iodine and sulfur dioxide other than water. In this case, the molar ratio of oxygen and hydrogen generated from Section 2 and 3 in Fig. 1 is 0.5/1 which should be maintained. A study on the start-up and static behaviors of a H_2SO_4 thermal decomposer and HI thermal decomposer, which are key components in Sections 2 and 3, is thus important.

This study focused on the H_2SO_4 thermal decomposer (SATD-50L), which are the key component of the bench-scale SI test facility. The SATD-50L was designed by the Korea Institute of Science and Technology (KIST). Based on the design specification and test operation results, numerical calculations for the SATD-50L were done to evaluate the start-up and static behaviors. The numerical simulation was performed at the operational condition to produce 50 NL/h of hydrogen, based on the mass balance of the SI integrated process.

2. Description of SATD-50L and operating condition

Similar to the bayonet type decomposer of the SNL, the SATD-50L for the 50 NL-H_2/h scale SI test facility was designed by the KIST, shown in Fig. 2. The SATD-50L was prepared using a silicon carbide (SiC) tube with a hemispheric end. The single SiC tube equipped with a quartz pipe inside the SiC tube has the following multiple-functions: evaporation of sulfuric acid, primary thermal decomposition of sulfuric acid, and secondary catalytic thermal decomposition of SO_3 consecutively generated from the primary thermal decomposition of sulfuric acid. The height of the electrical heating region is about 1,023.5 mm, and the height of the catalyst-packed region, which is at the top of the inner quartz pipe, is about 150 mm. The outer SiC tube of the decomposer is heated by three electrical heaters individually.

The three heating compartments are adiabatically maintained at constant temperatures of 475, 715, and 915 ºC controlled with a temperature controller.
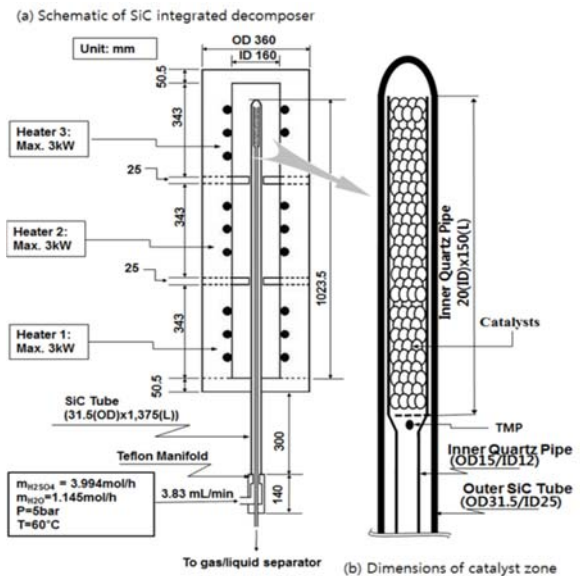

Fig. 2. Schematic of the SATD-50L.

The bayonet type decomposer is initially filled with a nitrogen gas which is thermally equilibrated with the heating compartment temperature under 5 bar. The start-up operation of the decomposer is initiated by feeding a 95 % H_2SO_4 solution at 230 mL/h at 60 ºC. The flow path of the sulfuric acid aqueous solution inside the decomposer is designed such that the concentrated acid enters the Teflon manifold inlet and flows up along the outer annulus between the SiC tube and quartz pipe. At the bottom of this annular region, heat is recuperated from the process gas flow downward along the inner quartz pipe, and the combined heat from the recuperation and electrical heater vaporizes the incoming sulfuric acid solution. Afterward, the vaporized sulfuric acid is superheated in the outer annulus and decomposed to SO_3 and H_2O prior to reaching the catalyst region packed with spherical SiC-

supported Pt catalysts. It is expected that the maximum temperature of the process gas stream will be revealed just before entering downward into the catalyst region of the inner quartz pipe. The sulfur trioxide, SO_3, is decomposed to SO_2 and O_2 at the catalyst region. The decomposed gas mixture continuously flows down. As the heat is recuperated, the down-flowing stream temperature drops.

3. Simulation results

The SATD-50L for the 50NL-H_2/h scale SI test facility was designed to carry out multiple functions of the vaporization and decomposition of the sulfuric acid in a single SiC tube. Therefore, the first matter of concern is to predict the start-up behavior of the sulfuric acid liquid level inside the SiC tube. As the start-up operation of the decomposer is initiated by feeding a 95 % H_2SO_4 solution at 3.83 ml/min at 60 °C, the sulfuric acid solution heats up and its interface is continuously raised until reaching the boiling point, 372.6 °C, at 5 bar.

Fig. 3 shows a locus of the interface during start-up. The interface level of the sulfuric acid solution exhibits oscillated motion due to the combined heat from the recuperater and electrical heater and then, reaches a steady level of 280 mm from the inside bottom of the electrical heating furnace. Based on this calculation result, it is expected that the primary dissociation of the sulfuric acid takes place in the region of 280 mm to 1023.5 mm from the inside bottom of the electrical heating furnace.
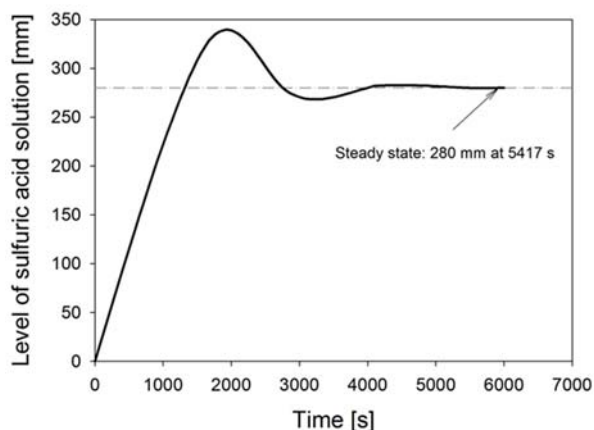

Fig. 3. Predicted start-up dynamic behavior of the level of sulfuric acid solution in the SATD-50L.

The second matter of concern is to predict the process stream temperature at the temperature measuring point (TMP) in Fig 2, in which the secondary decomposed gas mixture is only discharged from the catalyst-packed region of the quartz pipe. Fig. 4 shows the predicted temperature at the TMP as a function of the operation time. A steady temperature of 824.6 °C at TMP is revealed at a start-up operation time of 2,765 s. When compared with the approaching times to the steady state of the interface level of the sulfuric acid solution and process stream temperature at the TMP, it is anticipated that the approaching time to the steady

interface level will require a longer time than that to the steady temperature at the TMP. It is also expected that the decomposition yield of H_2SO_4 in the superheating region of the outer SiC annulus is nearly 100 % at a steady state.
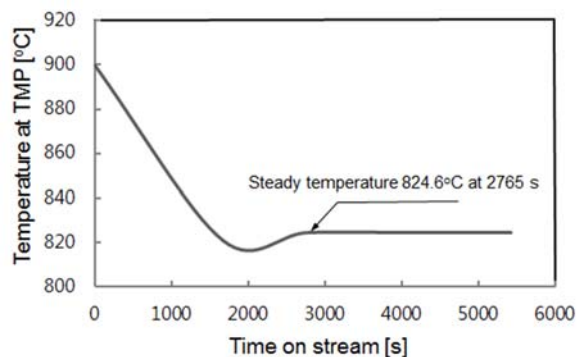

Fig. 4. Predicted start-up dynamic behavior at the temperature measuring point (TMP) in the SATD-50L.

The maximum temperature of 877.4 °C in the process stream flow path of the SATD-50L is expected at the top of the catalyst-packed region, and as the decomposition of SO_3 takes place in the catalyst-packed region, the temperature of the process stream flow path is decreased due to the endothermic reaction heat.

In the preliminary performance test of the SATD-50L carried out at the KIST, the decomposition percentage of H_2SO_4 to SO_2 was found to be 70±5 % at a feed flow rate of 3.83 ml/min and an operation pressure of 5 bar. The experimental and simulation results at a steady state are shown in Table 1. The simulation results of the temperature at the TMP and the decomposition percentage of the H_2SO_4 to SO_2 are lower than the experimental values, about 5 % to 10 %. The reason for these lower simulation values is that the energy balance equation omitted the temperature increasing effect from the transportation of radiation heat inside the quartz pipe. Generally, it is recommended that the operating pressure should be decreased in the case of volumetric expansion chemical reactions such as H_2SO_4 and SO_3 thermal decompositions.

Table 2. Experimental and simulation results of the SATD-50L

Operation parameters	Feed concentration: 95 wt% H_2SO_4
	Flowrate and temp.:3.83 mL/min, 60°C
	Operation pressure: 5 bar
Measured temp. at TMP	867±6°C
Calculated temp. at TMP	824.6°C
Experimental dissociation %	70±5%
Calculated dissociation %	62.5%

Fig. 5 shows the calculated temperature profiles inside the SiC tube and quartz pipe according to the process stream flows at a steady state. From this result, it can be seen that the boiling region of the 95 % sulfuric acid solution will be located from 162 mm to 280 mm, and the sulfuric acid vapor evaporated in the boiling region is super-heated until 877.4 °C which

flows up to the top of the SiC tube, and the vaporized sulfuric acid decomposes completely to SO_3 and H_2O prior to reaching the catalyst-packed region.

The downstream of the gas mixture of SO_3 and H_2O flows into the catalyst-packed region of 150 mm to decompose to SO_2 and O_2. The temperature of the process stream is continuously decreased to 824.6 °C due to the endothermic heat of the reaction of SO_3 to SO_2 in the catalyst-packed region. The mixed gas of SO_2, SO_3, O_2 and H_2O discharged from the catalyst-packed region is to be recuperated in either the super heater or the boiler or the incoming acid heating zone. As the heat is recuperated, the down-flowing stream temperature drops to 629 °C. Further recuperation occurs to heat the incoming 95 % sulfuric acid solution through the Teflon manifold.
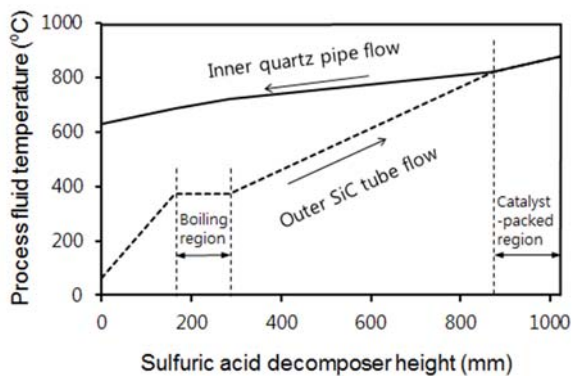

Fig. 5. Simulation results for the temperature profiles of the inner and outer process fluids along the height of the SATD-50L at steady state.

4. Conclusions

Numerical calculations to investigate the start-up and static behaviors of the H_2SO_4 thermal decomposer (SATD-50L) for the 50 NL-H_2/h SI test facility were carried out. The simulations show that the design and operation parameters of the SATD-50L proposed in this study are reasonable to achieve a hydrogen production rate of 50 NL/h. The current prediction indicates that the start-up time to reach a steady state is about 5,417 s, based on the start-up behavior of the interface level of the sulfuric acid solution inside the SATD-50L. The predictions for this interface level and the boiling region of the sulfuric acid solution are very important to prevent damage to the catalyst for SO_3 decomposition in the bayonet-type decomposer which has multiple functions as an evaporator, superheater, and SO_3 decomposer. The simulation results of these two parameters obtained from this research are given as an interface level of 280 mm and a boiling region between 162 mm and 280 mm, from the inside bottom of the electrical heating furnace.

Acknowledgments

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