Optimization of the Hybrid Sulfur Cycle for Nuclear Hydrogen Production Using UniSim Design

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1. Introduction

The sulfur-based thermochemical cycles are considered as the most promising methods to produce hydrogen. The Hybrid Sulfur (HyS) Cycle is a mixed thermochemical cycle with the sulfur-aided electrolysis as depicted in the Fig. 1. Hydrogen is produced from water by oxidizing sulfur dioxide in the low temperature electrolysis step and the sulfuric acid which is also produced in the electrolyzer proceeds to the high temperature thermochemical step. The sulfuric acid is concentrated in the concentrator first and then decomposed into steam and sulfur trioxide, which is further decomposed into sulfur dioxide and oxygen at high temperature (;1100 K) in the decomposer. After separated with oxygen in the separator, the sulfur dioxide is fed again to the electrolyzer to reduce the required electrode potential far below than that of the typical water electrolysis.

Hydrogen is worth as a future energy carrier when it is produced cost effectively. In that sense, the energy efficiency of the hybrid sulfur cycle is needed to be improved as high as achievable. The flow sheet developed by Westinghouse, the first proposer of the cycle, is not optimized for the cycle efficiency. In the previous work [1], a detailed flow sheet model was developed and also the cycle efficiency of that was roughly estimated using the software CHEMKIN and CANARY based on the experimental data for the electrode potential and appropriate work of separation. The maximum efficiency was found to be 50.5% under the operating conditions of 10 bar and 1200K for decomposer and acid concentration of 60 mol% for decomposer, 60 wt. % for electrolyzer, respectively. In this study, more detailed flow sheet was developed and optimized by using software UniSim Design which is one of the most powerful process design and simulation tools.

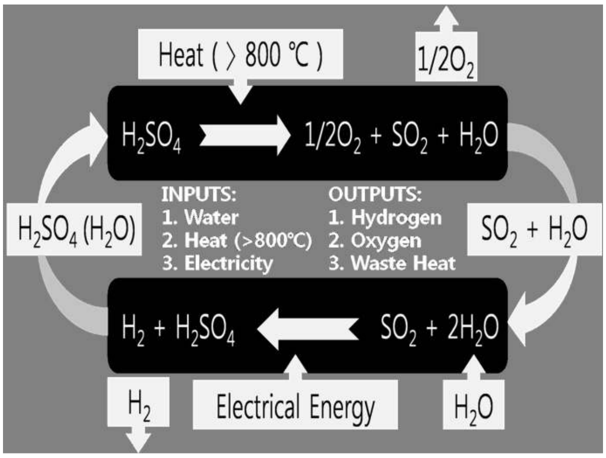

Fig. 1. A simple flow diagram of the Hybrid Sulfur Cycle.

2. Simulation

A simple Hybrid Sulfur Cycle flow sheet was developed and described on the UniSim Design as shown in Fig. 2. PR-Twu equation of state model is selected among the fluid packages provided by basis environment of UniSim Design [3]. Electrolyzer unit is not described. Instead, the experimental data of the required electrode potentials for the various acid concentrations is inputted in the linked spread sheet of the UniSim Design [2]. The thermochemical step: the cycle except the electrolyzer is adjusted to produce 1kgmole/h of sulfur dioxide and this is equivalent to 1kgmole/h of hydrogen from the whole cycle assuming that all the sulfur dioxide are consumed in the electrolyzer. Both unseparated sulfur trioxide and oxygen flowed into the electrolyzer are neglected. Sulfuric acid and sulfur trioxide decomposition are assumed to be isothermal process in the reactor unit defined by decomposition reaction set and k-values from the reference [4]. An internal heat recuperation is maximized for the better heat utilization using 6 heat exchangers and a very low-temperature chiller is added next to the water cooler in the separator to separate sulfur dioxide from oxygen more completely. A chiller (HXR), water coolers (HXW) and nuclear heaters (HXN) are expressed using cooler and heater unit provided by UniSim Design and internal heat recuperators (HXI) are expressed using heat exchanger unit. To complete the cooler and heater units, downstream temperatures are defined instead of thermal duties. For the heat exchanger units, end point model is set as s heat exchanger model and temperatures of 3 out of 4 streams crossing inside of them. Conditions on the geometry, heat leak/loss and pressure drop were disregarded. Adiabatic efficiency of the pump and centrifugal compressor was set to 75% each. Additional sulfuric acid and water are stored then fed continuously and separated oxygen is stored then exhausted or used.

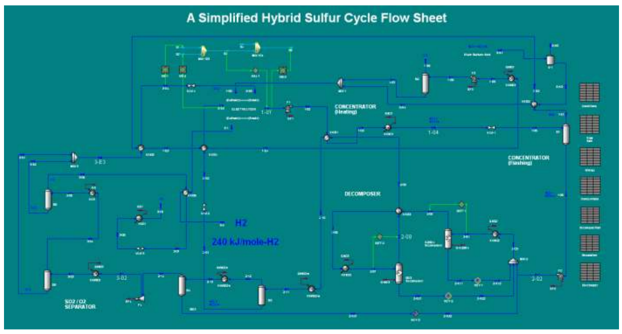

Fig. 2. A developed Hybrid Sulfur Cycle flow sheet described on the UniSim Design.

3. Results and Discussion

In this study, to find the optimal operating conditions for the Hybrid Sulfur Cycle, the cycle efficiency was estimated by varying the operating conditions (pressure, temperature, acid concentration in the each component) based on the maximum utilization of internal heat recuperation. Some of the results are shown in Fig. 3., 4.

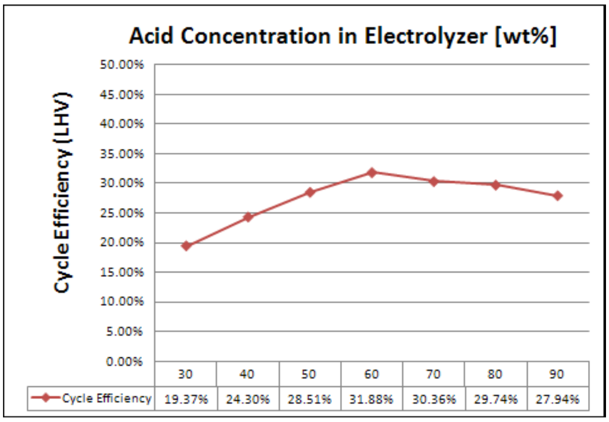

Fig. 3.Effect of electrolyzer acid concentration on efficiency.

Required energy for the electrolyzer increases as increasing acid concentration. However, the energy required to concentrate and decompose the sulfuric acid decreases as increasing acid concentration. As shown in Fig. 3., 60wt% is found to be the optimal electrolyzer acid concentration for the cycle efficiency at a given condition.

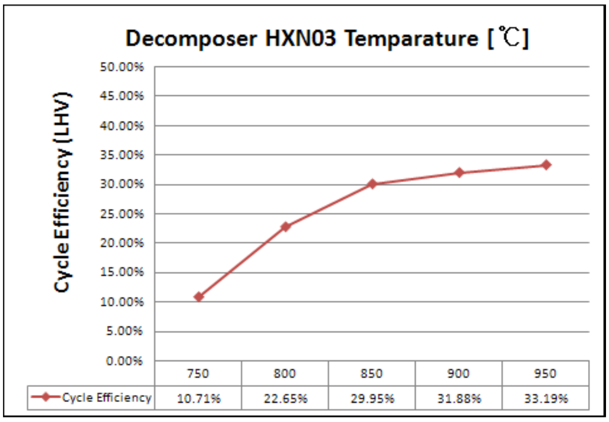

Fig. 4. Effect of decomposer pressure on the cycle efficiency.

It is very clear that the higher temperature in the decomposer always gives a higher efficiency as shown in Fig. 4. Due to higher SO_2 yield, higher temperatures enable higher conversions per pass in the decomposer and reduce the recycle rate in part of the cycle.

On the other hand, at a given temperature, higher pressures bring the lower SO_2 yield while lower compressor power requirements before entering the SO_2/O_2 separator. But, the loss is greater than the saving in this case. The details of pressure and temperature effects on capital cost or feasibility have not been estimated in this study.

4. Conclusions

As a result, about 32% (LHV) appears to be the best cycle efficiency (and is attained at 10bar, 900℃ and 90 mol% for the decomposer, 60 wt% for electrolyzer).

The required energy in the electrolyzer when it is converted to the thermal energy assuming the 45% of W/Q efficiency accounts for a major percentage of all the required energy. However, much portion of this energy comes from the electrode over-potential to overcome energy barriers due to mass transfer, reaction activation, and ohmic resistance limitations [5]. A significant improvement in the cycle efficiency can be realized through the reduction of this electrode over-potential. Therefore, advanced electrolysis materials and configurations are needed to be developed.

Other major factors that can affect the cycle efficiency are high temperature and high acid concentration. Especially for the decomposer which consumes the largest portion of required energy, the higher temperature always a gives higher efficiency. Further researches on the structural materials that can operate in this harsh environment and the effective utilization of high temperature heat from the outlet of advanced gas cooled nuclear reactor should be carried out.

Higher pressure operation for the each component has a different effect on the cycle efficiency while gives an advantage of reducing the component size and minimizing the initial capital cost. Therefore, for the each component, the pressure effect on the capital cost as well as on the cycle efficiency should be evaluated more precisely and accurately.

In the simulation environment, there are many things should be further improved. Above all, more detailed flow sheet including an exact electrolyzer unit or model based on more accurate thermodynamic model is needed to be developed, and also more effective method for the separation of sulfur trioxide and oxygen from sulfur dioxide should be explored and adopted. Finally, to optimize the cycle for the conditions more broadly and specifically, much simpler as well as more realistic data management method for the data to or from the UniSim Design should be established.

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