Estimation of the Thermal Efficiency of Hybrid Sulfur Cycle for Hydrogen Generation using Gas Cooled Reactor

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1. Introduction

There are three major ways to generate hydrogen from water. These are pure electrolysis, pure thermochemical methods and hybrid methods. Pure electrolysis splits water molecules into hydrogen and oxygen using electrical energy. A pure thermochemical method is a series of chemical reactions to split water at high temperature [1], but much lower temperatures than that of direct dissociation of water (4000 ^{o}C). The hybrid cycle is a combination of electrolysis and thermochemical cycle. The hybrid sulfur cycle (often called the Westinghouse Cycle) has two steps for decomposing water into hydrogen and oxygen. Hydrogen and sulfuric acid are produced by electrolysis of a sulfur dioxide and water mixture at low temperature. The sulfuric acid is decomposed into sulfur trioxide and steam and the sulfur trioxide is decomposed into sulfur dioxide and oxygen at high temperature (~1100 K). The sulfur dioxide is supplied to the electrolyzer [2,3].

In this study, we develop detailed flow sheets for the hybrid sulfur cycle and estimate the overall efficiency of the hydrogen production process.

2. Hybrid Sulfur Cycle

The hybrid sulfur cycle has two steps of reaction [2]:

$$H_2SO_4 \rightarrow H_2O + SO_3 \rightarrow SO_2 + ½O_2 + H_2O$$
(thermal decomposition, ~850 ^{o}C) (1)
and
$$2H_2O + SO_2 \rightarrow H_2SO_4 + H_2$$
(electrolysis, 87 ^{o}C) (2)

The first step is the decomposition of sulfuric acid into sulfur dioxide and oxygen, and this is the same chemical decomposition step used in the SI cycle [1]. The second step is electrolysis of water with sulfur dioxide. The theoretical voltage to decompose pure water is 1.23 V, with many conventional electrolyzers needing 2.0 V or higher. The theoretical potential required for electrolysis with sulfur dioxide is 0.17 V.

The original hybrid sulfur cycle was proposed by Westinghouse [1,2]. Workers at Westinghouse had assessed the cycle efficiency and found some optimal conditions for their cycle [3].

There is room for further development and improvement beyond Westinghouse's work. The available schematics do not include a detailed flow sheet. Also, the analysis used theoretical electrode potential and work of separation which tends to exaggerate the efficiency of the real process.

In this study we developed a detailed flow sheet model and estimated cycle efficiency using experimental data for electrode potential and appropriate estimating work of separation. The details are discussed in the following sections.

3. Developed Flow Sheet

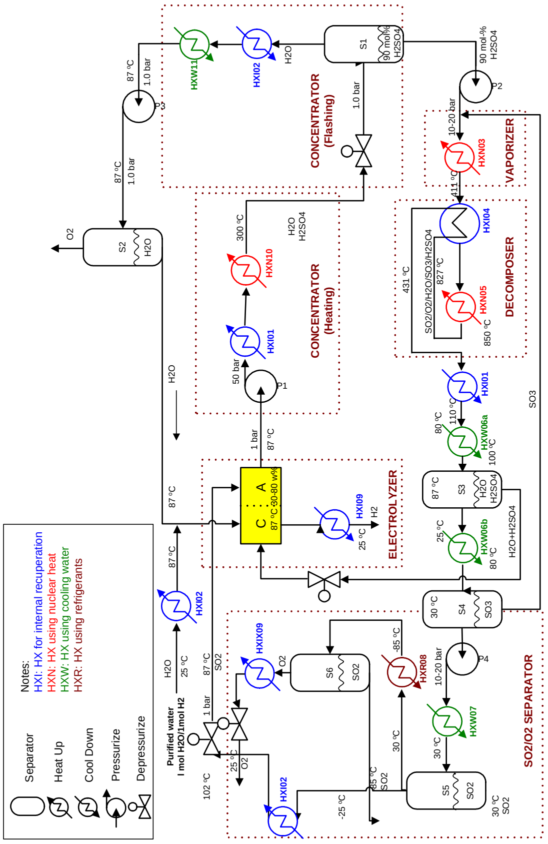

Figure 1 developed flow sheet

Figure 1 depicts the details of the developed flow sheet. There are four major sub-systems in the cycle: concentrator, decomposer, separator and electrolyzer.

The cycle efficiency is defined as:

$$\eta_{H_2} = \frac{Q_{H_2,LHV}}{Q_{electrolyzer} + Q_{concentrator} + Q_{decomposer} - Q_{recuperators}} \quad (3)$$

4. Results and Discussion

We have estimated the cycle efficiency under a variety of operating conditions using the software CHEMKIN [4] and CANARY [5], and the maximum efficiency is about 47.0 % under the conditions of 10 bar and 1200 K for the decomposer.

The effect of decomposer pressure on cycle efficiency is shown in Figs. 2. At 1200 K, 10-20 bar gives the best efficiency.

The compressor work for SO_2/O_2 separator is reduced by increasing the decomposer pressure. But, the saving is not greater than the loss due to low SO_2 yield because of high pressure. As a result, 70-100 bar cases do not show the best efficiency. But, with a high decomposer pressure, the size of equipment can be minimized resulting in saving a portion of initial investment.

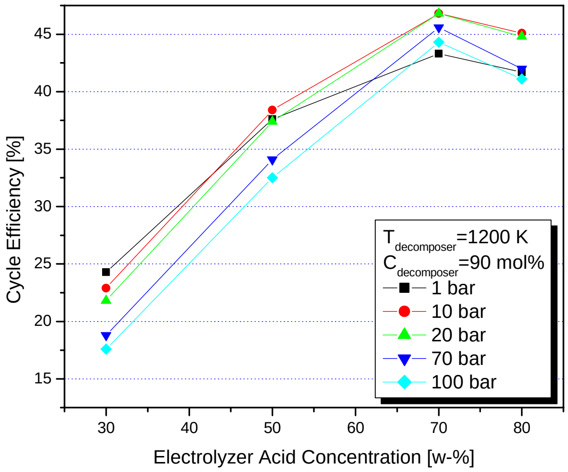

Figure 2. Decomposer pressure and cycle efficiency

The higher temperature always gives a higher efficiency. The maximum temperature of the high temperature gas cooled reactor (HTGR or GT-MHR) would be 850-950 °C (1123-1223 K), and that of the supercritical advanced gas reactor (SCO2-AGR) would be 650-750 °C (923-1023 K). Then the best efficiency with those reactors would be 47.0 % (1200 K) and 37.6 % (1000 K) for HTGR/GT-MHR and SCO2-AGR respectively (assuming thermal to electrical efficiency is 45 %).

The difference between theoretical (~0.17V) and experimental electrode potential (~0.5V) shows that there is room for efficiency enhancement through developing advanced electrolysis methods. For example, for a reduced electrode potential (70 % of original experimental value) by an advanced technology it is predicted to achieve 57 % as cycle efficiency (Fig. 3)

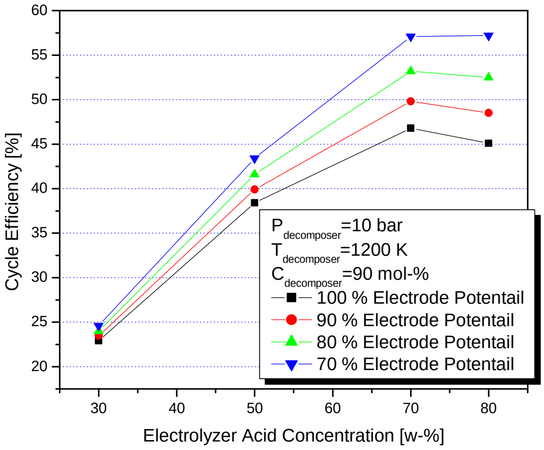

Figure 3. Sensitivity of the electrode potential on cycle efficiency

5. Conclusions

Based on currently available experimental data for the electrode potential, 47.0% (LHV) appears to be the best cycle efficiency (and is attained at 10 bar, 1200 K and 60 mol-% of H_2SO_4 for decomposer, 70 w-% of H_2SO_4 for electrolyzer). But, there is much room of further efficiency enhancement by reducing electrode potential, since the theoretical value is only 15% of the experimental value.

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REFERENCES

1. L.C. Brown et al., “High Efficiency Generation of Hydrogen”, GA–A24285 (2002).
2. L.E. Brecher et al., “The Westinghouse Sulfur Cycle for the Thermochemical Decomposition of Water”, *Int. J. Hydrogen Energy*, **Vol. 2**, pp. 7-15 (1977).
3. R. Carty, K. Cox, J. Funk, M. Soliman, W. Conger, L. Brecher and S. Spewock, “Process Sensitivity Studies of the Westinghouse Sulfur Cycle for Hydrogen Generation”, *Int. J. Hydrogen Energy*, **Vol. 2**, pp. 17-22 (1977).
4. Reaction Design Inc., *http://reactiondesign.com* (2004).
5. Quest Consultants Inc., *http://www.questconsult.com*, (2004).