Thermochemical Cycles / HP.2

The Effect of Anolyte Product Acid Concentration on Hybrid Sulfur Cycle Performance

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The Hybrid Sulfur (HyS) cycle (Fig. 1) is one of the simplest, all-fluids thermochemical cycles that has been devised for splitting water with a high-temperature nuclear or solar heat source. It was originally patented by Brecher and Wu in 1975 [1] and extensively developed by Westinghouse in the late 1970s and early 1980s. As its name suggests, the only element used besides hydrogen and oxygen is sulfur, which is cycled between the +4 and +6 oxidation states. HyS comprises two steps. One is the thermochemical (>800°C) decomposition of sulfuric acid (H_2SO_4) to sulfur dioxide (SO_2), oxygen (O_2), and water.

$$H_2SO_4 \;=\; SO_2 + \tfrac{1}{2}\, O_2 + H_2O.$$

The other is the SO_2-depolarized electrolysis of water to H_2SO_4 and hydrogen (H_2),

$$SO_2 + 2\, H_2O \;=\; H_2SO_4 + H_2,\ E° = -0.156\ \text{V}\ [2],$$

explaining the "hybrid" designation. These two steps taken together split water into H_2 and O_2 using heat and electricity.

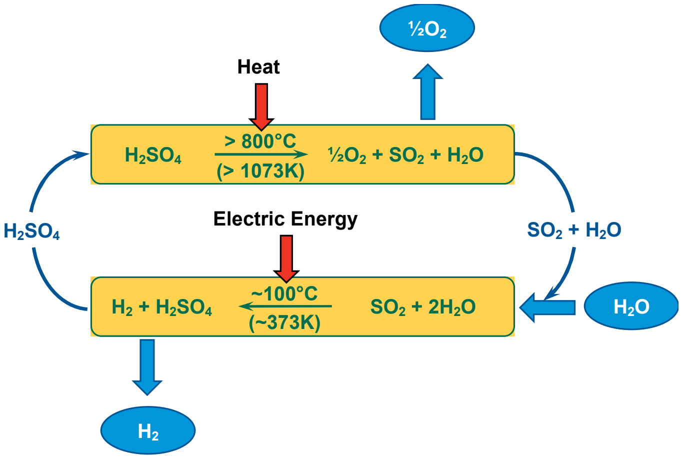

Figure 1. The Hybrid Sulfur cycle

Researchers at the Savannah River National Laboratory (SRNL) and at the University of South Carolina (USC) have successfully demonstrated the use of proton exchange membrane (PEM) electrolyzers (Fig. 2) for the SO_2-depolarized electrolysis (sulfur oxidation) step [3-4], while Sandia National Laboratories (SNL) successfully demonstrated the high-temperature sulfuric acid decomposition (sulfur reduction) step using a bayonet-type reactor (Fig. 3) [5]. This latter work was performed as part of the Sulfur-Iodine (SI) cycle Integrated Laboratory Scale demonstration at General Atomics (GA) [6]. The combination of these two operations results in a simple process that will be more efficient and cost-effective for the massive production of hydrogen than alkaline electrolysis. Recent developments suggest that the use of PEMs other than Nafion will allow sulfuric acid to be produced at higher concentrations (>60 wt%), offering the possibility of net thermal efficiencies around 50% (HHV basis). The effect of operation at higher anolyte concentrations on the flowsheet, and on the net thermal efficiency for a nuclear-heated HyS process, is examined and quantified.

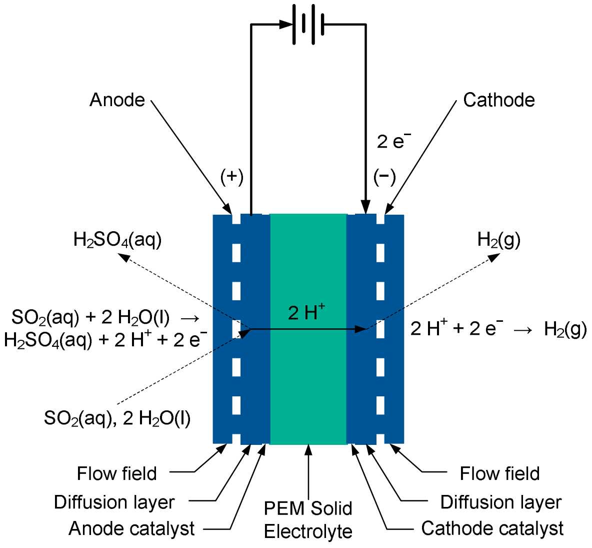

Figure 2. SRNL PEM SO_2-depolarized electrolyzer schematic

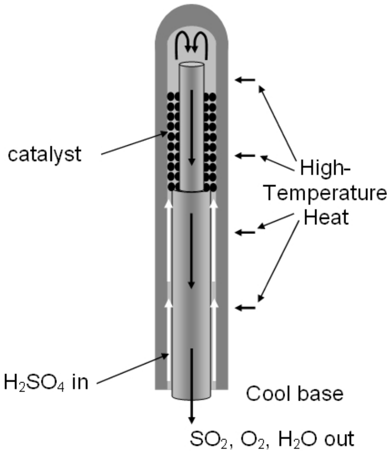

Figure 3. SNL high-temperature bayonet H_2SO_4 decomposer schematic

Problem Statement

The combination of a PEM SO_2-depolarized electrolyzer (SDE) with a bayonet-type high-temperature sulfuric acid decomposition reactor has been described in detail elsewhere [7]. The simplicity of the two key components is an attractive feature and leads to a relatively simple flowsheet. However, there is more to the process than just these two operations, and their integration necessitates that some compromises be made.

The SDE can not operate at high conversion because the cell potential depends on the concentration of SO_2 at the anode. Typically, the SDE is operated with about 40% SO_2 utilization, requiring a fairly large recycle stream and a significant SO_2 concentration in the anolyte effluent. That means unreacted SO_2 needs to be removed and recycled before the sulfuric acid product is fed to the decomposition reactor.

More importantly, the concentration of sulfuric acid in the anolyte is limited by several factors. Higher H_2SO_4 concentration leads to lower SO_2 solubility and higher reversible potential [2]. It can also decrease the conductivity of the PEM separator, increasing the cell potential [8]. Since efficient operation of the SDE is favored by more dilute anolyte, the concentration of the sulfuric acid product also needs to be increased before it is fed to the decomposition reactor.

The decomposition of H_2SO_4 in the bayonet reactor is an equilibrium reaction that is limited by thermodynamics. That means not only does the SO_2 product have to be separated from the O_2 co-product before it can be fed to the SDE, but unreacted H_2SO_4 needs to be removed and recycled as well. The high-temperature heat requirement is governed by the opportunity for recuperation within the bayonet. It has been shown that the heat requirement is minimized by operating the bayonet at the highest possible temperature and pressure, and at a feed concentration of 80.1 wt% H_2SO_4 [9]. Lower concentrations result in more water being vaporized and condensed with incomplete recuperation, so more high-temperature heat is consumed. Feed concentrations below 65 wt% H_2SO_4 result in heating targets in excess of 400 kJ/mol H_2 which, when combined with the other process heat and power needs, affords a net thermal efficiency comparable to that of alkaline electrolysis. Given the greater complexity of the HyS cycle, it will not be more cost-effective than water electrolysis unless it has a significant efficiency advantage. An obvious way to maximize efficiency is to operate the SDE at the highest possible acid concentration without adversely affecting the cell potential.

Approach

As already noted, we have previously proposed a HyS flowsheet that combines a PEM SDE with a bayonet reactor [7]. The anolyte product acid concentration for this flowsheet was limited to 50 wt% H_2SO_4, based on the assumed use of Nafion® as the PEM separator material. Contact with concentrated sulfuric acid decreases the water content of Nafion® and increases its resistivity [8], which has been shown to reach impractical levels as concentrations exceed 50 wt% [10].

This limitation was removed by assuming the use of an alternative PEM material such as acid-doped poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (PBI) instead of Nafion®. The resistivity of acid-doped PBI membranes, which can operate at much higher temperatures than Nafion®, actually decreases with acid concentration [11]. In fact, the results of preliminary experiments at USC with PBI membranes show that significantly higher acid concentrations, in excess of 65% H2SO4 by weight may be feasible with acid-doped PBI PEM SDEs [12]. We assume, then, that the SDE uses a PEM capable of operation at anolyte H_2SO_4 concentrations of 65 wt% and temperatures of 120 to 140°C. (The reversible cell potential increases with acid concentration and temperature [2], so operation at temperatures or concentrations higher than this may be limited by thermodynamic considerations.)

The existing Aspen Plus flowsheet model of the SRNL HyS process [7, 13] (Fig. 4) was modified to simulate operation of the SDE at 120°C and 65 wt% H_2SO_4 anolyte product concentration. SO_2 conversion was also increased from 40% to 50%, and a cell potential of 0.6 V was imposed. (SDE operation at 0.6 V and 0.5 A/cm^2 is a development target that should be attainable with acid-doped PBI PEMs [12].) Water flux across the membrane was maintained at 1 mol H_2O / mol H_2 product despite the much lower water content of acid-doped PBI (compared to Nafion®). Since a significant water activity gradient will exist between the cathode and anode, it was assumed that the large driving force for water transport would compensate for the reduced water content of the membrane.

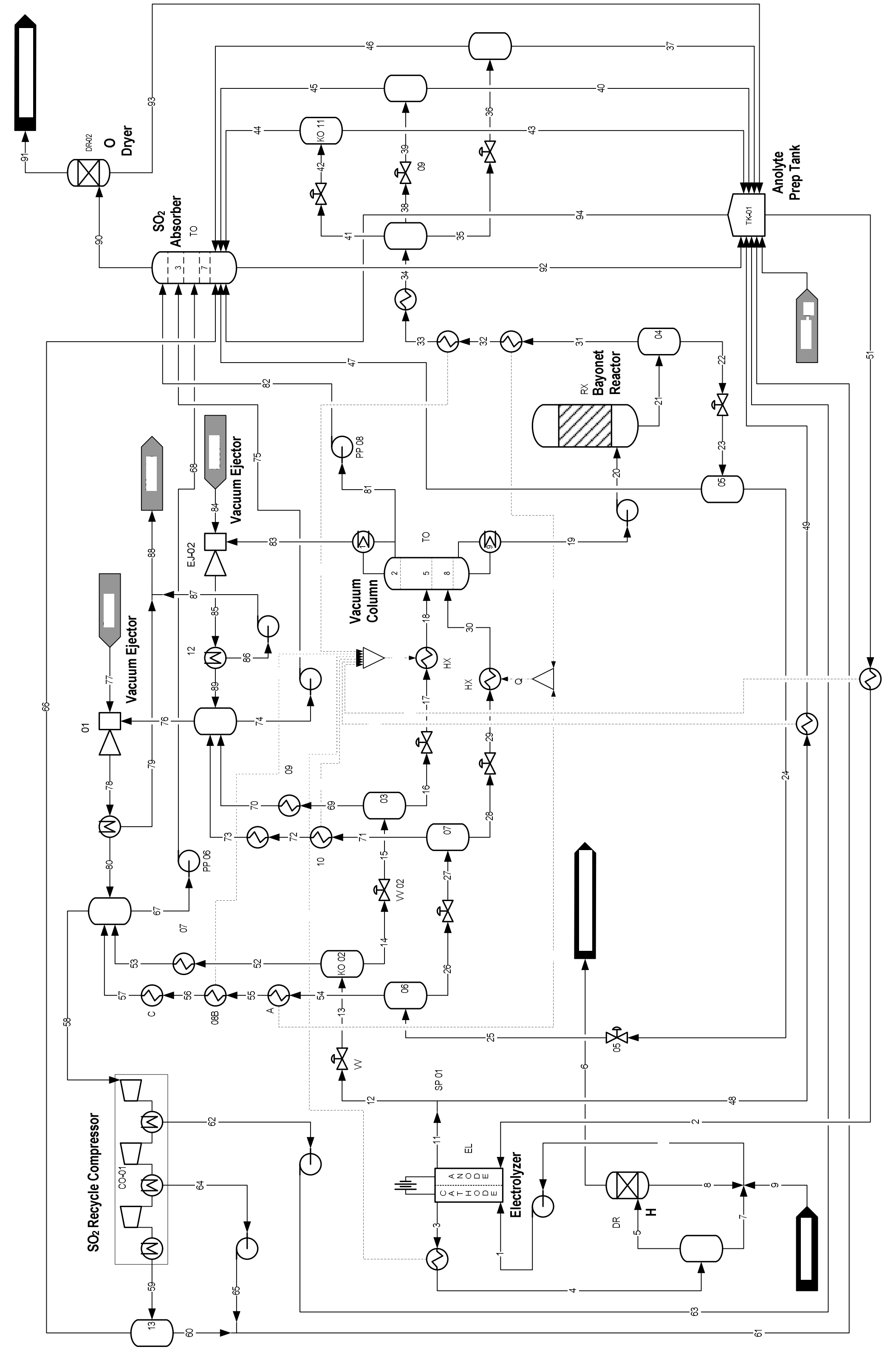

Figure 4. HyS flowsheet using a PEM SDE and a bayonet decomposition reactor [13]

Results

By increasing the anolyte product acid concentration from 50 to 65 wt% H_2SO_4, the quantity of water that has to be removed in the concentration step (in order to increase the acid concentration of the bayonet reactor feed to 75 wt% H_2SO_4) is reduced by roughly two-thirds. This means less than half as much energy is needed to achieve the necessary concentration, so all of the heat input can be provided by recuperation from the SDE and the bayonet reactor. However, the water recovered in the acid concentration step is used to absorb SO_2 from the uncondensed product of the bayonet decomposition reactor. Since less water is available for the O_2/SO_2 separation, a single absorber is no longer sufficient; too much SO_2 would remain in the oxygen product.

We found that the addition of an absorber/stripper combination could reduce the SO_2 content of the oxygen co-product to ≤ 1 ppm using conventional process equipment and without introducing any new reagents. Water is the solvent; the absorber operates at the pressure of the SDE, while the stripper operates at atmospheric pressure, allowing low-pressure steam or recuperation to provide the necessary boil-up. An SO_2 compressor with atmospheric pressure feed is already being used to recycle unconverted SO_2 recovered from the anolyte product, so the overhead from the stripper can simply be added to the recycle compressor feed.

The resulting flowsheet requires two principal energy inputs: 340 kJ/mol H_2 product high-temperature heat for the bayonet reactor (assuming a peak decomposition temperature of 875°C, equivalent to a 950°C primary heat source temperature) and 116 kJ/mol H_2 product electric power for the SDE. Adding the shaft work needed for the recycle compressor and pumps brings the total power requirement to about 125 kJ/mol H_2 product. The atmospheric pressure stripper reboiler operates at around 100°C with a duty of approximately 40 kJ/mol H_2 product. If this heat input can also be provided by recuperation, then the net thermal efficiency of the process will be about 46% on a higher heating value (HHV) basis, assuming a 45% thermal-to-electric energy conversion efficiency. As an alternative, the heat could be supplied by low-pressure steam from the “bottom” of a coupled power conversion cycle.

This work is ongoing; more detailed and up-to-date results will be included in the presentation.

Conclusions

Replacing Nafion® in the SDE with a PEM material that does not rely on high water content for its conductivity (such as acid-doped PBI) will allow the anolyte acid product concentration to be increased beyond 50 wt% H_2SO_4. If the SDE is operated at 65 wt% H_2SO_4, Aspen Plus flowsheet simulation indicates that all of the heat needed to concentrate the bayonet reactor feed can be provided by recuperation from the SDE and from the bayonet product stream. However, the SO_2/O_2 separation can no longer be achieved by selective SO_2 absorption into the recycled water and acid using a single absorber column. The addition of an absorber/stripper combination provides the necessary separation with a minimal low-quality heat input. Net thermal efficiencies of 46% have been calculated to date.

Acknowledgments

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