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Simulation of Bunsen Reaction with Electro-dialysis for Efficient Phase Separation

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1. Introduction

Among the Thermochemical Cycles, a well established sulfur-iodine (SI) process developed at General Atomics (GA) and first described in the mid 1970's [1,2] has been considered for hydrogen production using high temperature heat from a nuclear reactor in the France, Japan, Korea, China and US. The SI process consists of three chemical processes, which sum to the dissociation of water. These processes are as follows:

Bunsen reaction (Section I) :
$I_2(l)+SO_2(g)+2H_2O(l) \rightarrow 2HI(aq)+H_2SO_4(aq)$(~120°C)
Sulfuric acid decomposition.) (Section II):
$H_2SO_4(aq) \rightarrow H_2O+SO_2(g)+½O_2(g)$ (~850°C)
Hydridic acid decomposition (Section III):
$2HI(g) \rightarrow H_2(g)+I_2(g)$ (~450°C min.)
Net reaction: $H_2O \rightarrow H_2 + ½O_2$

For Section I (Bunsen Process), GA modified the earlier flowsheet [3], since the previous thermodynamic model was insufficient to perform a strictly thermodynamic model. This restricted their ability to fully optimize the flowsheet. The earlier flowsheet for Section I was modified by changing the flow rates to match the modified versions of Sections II and III. In particular, temperatures and liquid compositions were kept the same as the earlier flowsheet to maintain constant activities of each species in the liquid phases and the total pressure was modified as necessary to maintain the same SO_2 partial pressure. As explained in section 2, there are several issues with Bunsen reaction and hence improvements are being considered. Here in this work implementation of electro-dialysis in Bunsen process is being studied to improve efficiency in Bunsen process.

2. Issues with Bunsen Reaction

Section I Bunsen reaction, is exothermic and it is carried out in liquid phase at 120 C. In this reaction, water reacts with I_2 and SO_2 to produces H_2SO_4 and HI, in two immiscible aqueous phases. Bunsen process, is typically operated in liquid water media with a large excess of iodine to avoid side processes between iodine and sulfur compounds, and to segregate the two product acids into two corresponding liquid phases: a sulfuric acid phase (about 50 wt% H_2SO_4) in which HI exhibits low solubility, and a hydrogen iodide phase (namely the ''HIx phase'') containing almost all of the excess iodine and in which H_2SO_4 is only slightly soluble. Hence, the reaction stoichiometry and mass balance of this process can be described as follows:

$$(1+x)I_2 + SO_2 +(2+n)H_2O \rightarrow H_2SO_4 +(n-m)H_2O|_{\text{Sulfuric acid phase}} + [2HI +I_2 + mH_2O]_{\text{HIx phase}}$$

where x and n are the iodine and water molar excess quantities, respectively, and m is the molar quantity of the excess water, n, that ends up in the HI_x phase. Although the excess water in the Bunsen process helps to make this process thermodynamically favorable, the exothermic processes at low temperature and the high irreversibility due to the large negative change in the Gibbs free energy lead to a significant energy loss, because the heat released at low temperature cannot be effectively recovered, and the irreversible process reduces the cycle efficiency.

Other alternative methods to segregate the acids have been recently suggested in the Bunsen process. These include (i) adjustment of the process solvent to segregate the acid products by the use of a solvent other than water, (ii) a novel route involving the addition of a precipitating agent to separate iodide from sulfate by means of solid salt formation by ion exchange processes, and (ii) carrying out the Bunsen process in an electrochemical cell with membranes. (Gokul et al 2011).

3. Benchmark

The objective of this task was to develop a simulation model for the GA SI cycle flowsheet, which is considered as a baseline flowsheet for the current work, and benchmark the model with the GA flowsheet simulation results. The GA flowsheet [1] is shown in Fig.2 A similar flowsheet was developed in ASPEN PLUS using recent thermodynamic data. The results were compared with GA results and the agreement was good. The temperature dependence study in Bunsen process was carried out by General Atomics (GA) with flowsheet. GA flowsheet was reproduced by ASPEN modeling with temperature study as shown in Fig. 2. Figure 2 shows H_2SO_4 generation rate variation depending on the temperature. The optimum operation temperature was 393K since the H_2SO_4 generation was the highest at 393 K. The result exactly matched to GA's result.

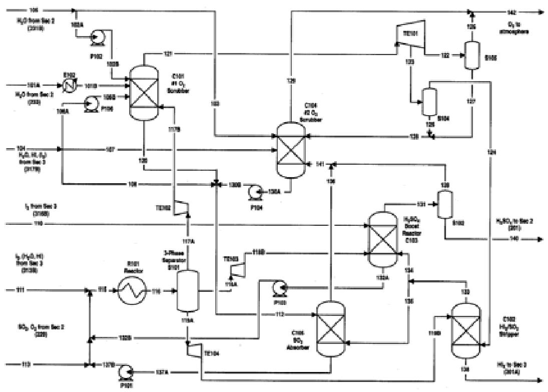

Fig. 2 Flowsheet for Bunsen reaction [1]

4. Improvement

The objective of this task is to investigate and implement the recent advances in Bunsen process to enhance efficiency of the process. Use of membrane electrolysis techniques for the Bunsen process is considered to improve process efficiency and to reduce cost of hydrogen production. In the past study, SO_2 dissolved in dilute solution of H_2SO_4 and iodine dissolved in dilute solution of HI acid were, respectively, used as anolyte and catholyte [4]. Implementation of the electro-dialysis technique will reduce the role of excess iodine, eliminate liquid-liquid separation step, and increase the thermal efficiency. 93% the amount of excess I_2 and 69 % the amount of water that is recycled in the cycle were reduce. Taking advantage of reducing recycling agent and eliminating step reduced the capital by about 20%.

Membrane techniques suggested for the reduction of the recycling agents such as the electro-dialysis, electrochemical cell, and hydrogen permselective membrane reactor methods are reviewed and the relevant data are collected. The design of the Bunsen process flowsheet adapted for the membrane techniques is carried out based on the available literature and data. The simulation models for the membrane and process components are developed and analyzed. The effects on the process efficiency and cost reduction for each membrane technique are estimated, if any.

5. Conclusion

ASPEN benchmark study against GA flowsheet was studied with comparison in temperature dependence data, and the optimum temperature was converged. The implementation of electro-dialysis in ASPEN Bunsen modeling is studied to improve the efficiency.

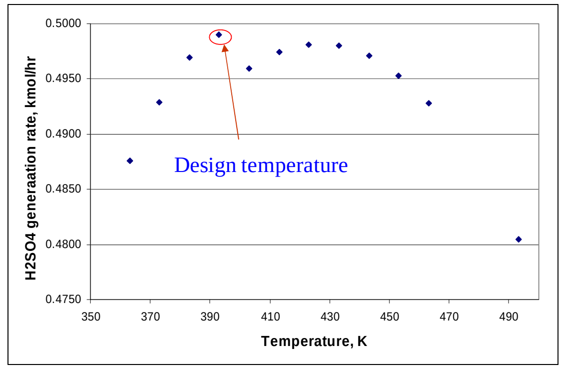

Figure 1. Temperature dependence in Bunsen Process

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