

Simulation study of water effect for the two phase separation in Bunsen section of SI thermochemical cycle to produce hydrogen utilizing nuclear heat

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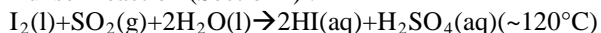
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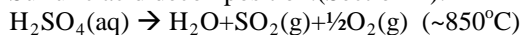
1. Introduction

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:

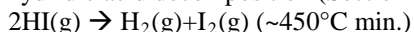
Bunsen reaction (Section I) :



Sulfuric acid decomposition.(Section II):



Hydridic acid decomposition (Section III):

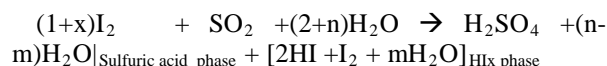


For Section I (Bunsen Process), GA modified the earlier flowsheet [3], since the previous thermodynamic model was insufficient to perform a strictly thermodynamic model. This restricted their ability to fully optimize the flowsheet. The earlier flowsheet for Section I was modified by changing the flow rates to match the modified versions of Sections II and III.. As explained in section 2, there are several issues with Bunsen reaction and hence improvements are being considered. Here in this work the effect of water are studied for Bunsen reaction and phase separation section in SI cycle.

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 I₂ and SO₂ to produces H₂SO₄ 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% H₂SO₄) in which HI exhibits low solubility, and a hydrogen iodide phase (namely the "HI_x phase") containing almost all of the excess iodine and in which H₂SO₄ is only slightly

soluble. Hence, the reaction stoichiometry and mass balance of this process can be described as follows:



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.

There are lot of alternative suggested to overcome this problem viz using alternative solvents, using solid extractant, membrane application[5] but all the method has limitation in term of recovery of solvents and complication because of presence of solid. Immediate best solution would be optimizing the iodine and water excess for SI cycle. Hence this work emphasis on optimizing water excess on Bunsen reaction and phase separation.

3. Simulation Methodology

In the present work, simulation for Bunsen reaction and separation of HI_x, and Sulfuric acid phase were investigated to study the effect of excess water on the separation of two phases. Figure 1 shows ASPEN simulation model to perform liquid-liquid separation. The thermodynamic method in this model was ELECNRTL. I₂/HI mixture from step 1 is mixed with sulfuric acid under room temperature. The residual amount of water, 0.889 mol, is added to the separator. Two phase separation (SA phases and HI_x phase) occurs in the decanter (SEP2).

The temperature range chosen is 290 K to 400 K. Effect of water excess on impurities in both phases HI_x, and SA were analyzed. Feed composition chosen were 1:2:n:1-12 for H₂SO₄:HI:H₂O:I₂. The simulation was carried out for variable H₂O excess at fixed iodine excess. Iodine excess fixed for each was varied from 1 to 12. H₂O excess at fixed iodine was varied from 5 to 22. The effect of contamination in HI_x phase and Sulfuric acid phase was studied at different iodine excess.

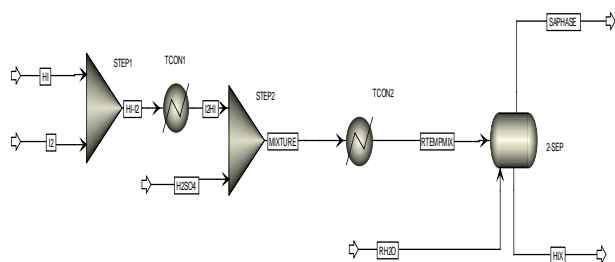


Figure 1. The ASPEN simulation on Liquid-Liquid Separation Test on Bunsen Product.

4. Simulation Result

The reported data here in Figure 2 and Figure 3 considers iodine excess of 6. Figure 2 represents effect of H_2O excess on H_2SO_4 impurities in HIx phase. The H_2SO_4 impurities in HIx phase were observed to improve with increase of H_2O excess. Figure 3 represents effect of water excess on HI impurities in SA phase. The HI impurities in SA phase was observed to reduce with increase in H_2O excess in feed upto 12 remains constant upto 15 and then start rising. Iodine excess plays important role in phase separation. In present simulation, iodine excess was kept constant, so when water excess was less, iodine excess dominate system and cause better phase separation. As water excess increases, causes reduction of effect of iodine excess where water effect dominate over the iodine and hence worsen the separation. H_2SO_4 in HIx phase was observed to improve as excess water prefer HIx phase than SA phase and dominate iodine effect.

5. Conclusion

It can be concluded from the results that low water excess favors the reduction of contamination, which is in agreement with literature experimental published data [4].

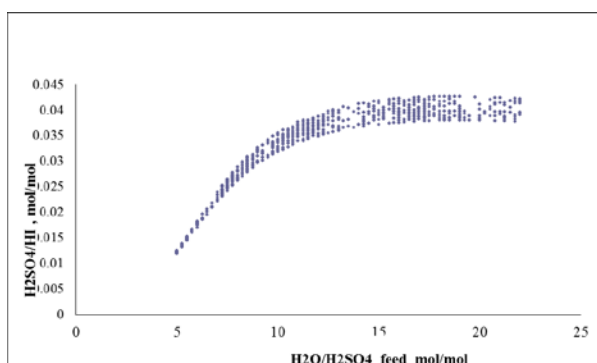


Figure 2. Effect of excess water on H_2SO_4 impurities in HIx phase

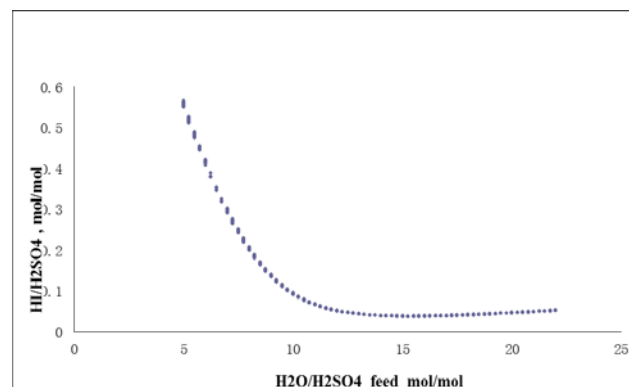


Figure 3. Effect of excess water on impurities in H_2SO_4 phase

ACKNOWLEDGMENT

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