

Simulation Study for Determining Optimal Operation Window of Iodine Excess for SI Thermochemical Cycle for Hydrogen Production

Dr. Satchidanand R Satpute*

Associate Professor, Department of Chemical Engineering, College of Engineering, Bharati Vidyapeeth University, Dhanakwadi, Pune

Dr. Shripad T Revankar

Professor of Nuclear Engineering, School of Nuclear Engineering, Purdue University West Lafayette, IN 47907-1290, USA.

Dr. Prakash V Chavan

Professor and Head, Dept. of Chemical Engineering, College of Engineering, Bharati Vidyapeeth University, Dhanakwadi, Pune

Abstract --Energy sustainability issue has driven technology for selecting hydrogen as viable future energy source. The SI(Sulfur iodide) cycle was found to be one of the best cycle for large scale hydrogen production. The Bunsen reaction and phase separation forms important parts of SI thermochemical cycle and were considered for study in the paper. HI/H₂SO₄/I₂/H₂O of 2/1/n/12 was used in accordance with recent literature data.

Effect of iodine on reduction of components in HIx phase was studied. The optimal operating range was obtained from the study. Iodine excess of 4-6 was obtained as optimal range for operation whereas water excess was fixed at 12. The optimal range found was 305-320 K.

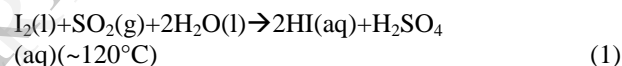
Keywords: Bunsen reaction, liquid-liquid equilibrium, phase separation, hydrogen production, SI cycle.

INTRODUCTION

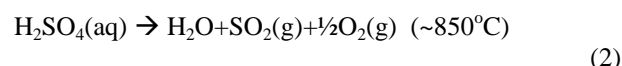
Energy security for the future has driven research to find reliable and sustainable source of energy that is renewable. Hydrogen is found to be promising energy carrier for a sustainable energy system in the future and can be produced through variety of methods. Numbers of cycles were studied for this purpose. The team of General Atomics (GA), Sandia National Laboratories (SNL) and the University of Kentucky (UK) studied available literature in view of evaluating thermo chemical processes that offer potential for efficient, cost effective, large scale production of hydrogen

from water, in which primary heat input is high temperature from Advanced nuclear reactor. Their evaluation concluded Sulfur-Iodide thermochemical water splitting cycle to be the best, for large scale hydrogen production using high temperature heat from nuclear reactor. A well established sulfur-iodine (SI) process was developed at General Atomics (GA)[1-4]. The SI process consists of three chemical processes, which sum to the dissociation of water as shown in Figure 1. These processes are as follows:

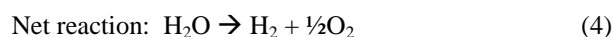
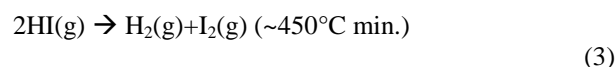
Bunsen reaction (Section I) :



Sulfuric acid decomposition.(Section II):



Hydric 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[3], there are several issues with Bunsen reaction and hence improvements are being considered. Here in this work the effect of iodine is studied for Bunsen reaction and phase separation section in SI cycle.

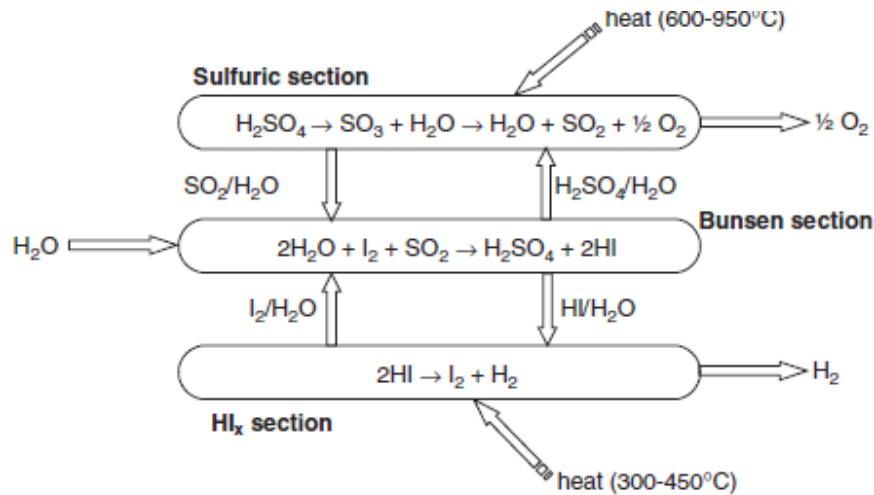
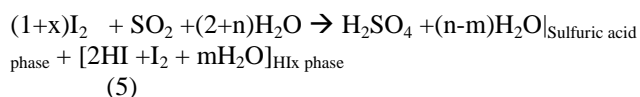


Figure 1: SI thermochemical cycle schematic

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 produce 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 (SA phase) in which HI exhibits low solubility, and a hydrogen iodide phase (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.

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 (iii) carrying out the Bunsen process in an electrochemical cell with membranes [14].

3. SIMULATION METHODOLOGY

In present work, simulation of Bunsen reaction and separator in SI cycle were investigated. The study was aimed at studying the effect of iodine in feed on phase separation i.e HI_x phase and SA phase. Figure 2 shows the ASPEN model used for liquid-liquid separation. Thermodynamic model used was ELECNRTL. I₂/HI mixture from step 1 was mixed with sulfuric acid at room temperature. Residual water with was added to separator. Two phase separation (SA phase and HI_x phase occurs in decanter (SEP2). The temperature range used was 290-400K. water excess used was 12 mole excess whereas it was based on H₂SO₄ moles. The iodine excess was varied from 1 to 12 mole excess. So feed composition chosen were HI/H₂SO₄/I₂/H₂O=2/1/n/12, where n varied from 1-12.

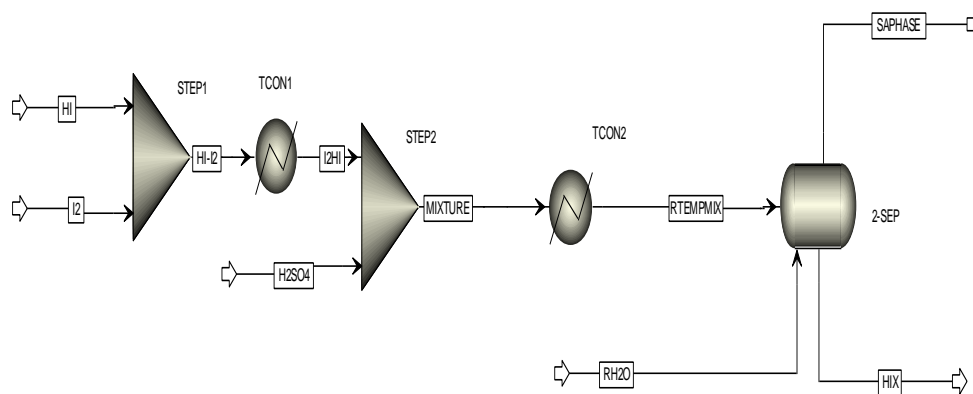


Figure 2: Model for Bunsen reaction with separation

4. RESULT AND DISCUSSION

Last decade many researcher [5-15] have studied Bunsen reaction and phase separation experimentally that forms the important part of SI thermo chemical cycle. The effect of Iodine and water excess on Bunsen reaction and

phase separation were studied. The contaminations in Sulfuric acid (SA) phase and Hydriodic acid(HA) phase were observed to reduce with increase of iodine concentration in feed. Present work study the effect of iodine on phase separation.

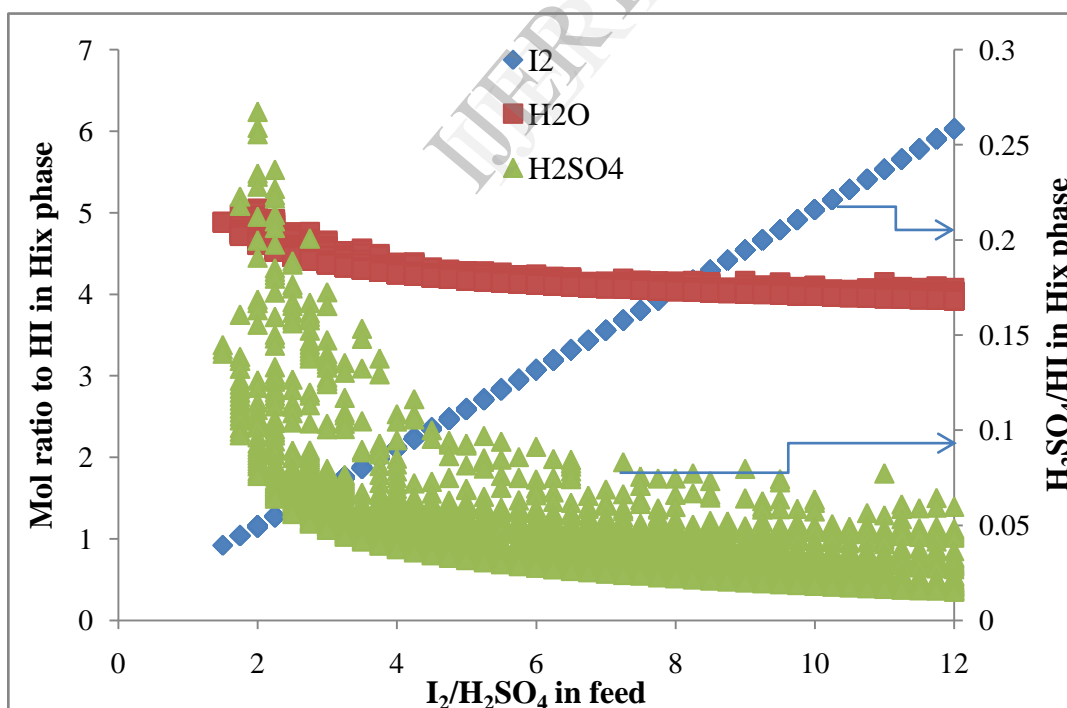


Figure 3: Effect of Iodine on component in HIX phase

4.1 Contamination/distribution of components in phases.

HIx is more important than SA phase being directly involved in hydrogen production. Figure 3 depict the effect of iodine excess in feed on components in HIx phase. H_2SO_4 contamination in HIx phase was observed to reduce drastically as iodine improves from 1 to 4 and

then reduce marginally after 4. The H_2O concentration was also observed to diminish as iodine improves 1-4 and then very gradual decreases. The iodine prefers HIx phase compared to SA phase and hence there is corresponding increase in concentration of iodine in HIx phase with improvement in iodine in feed. This observation coincides with observation with experimental data [6-13].

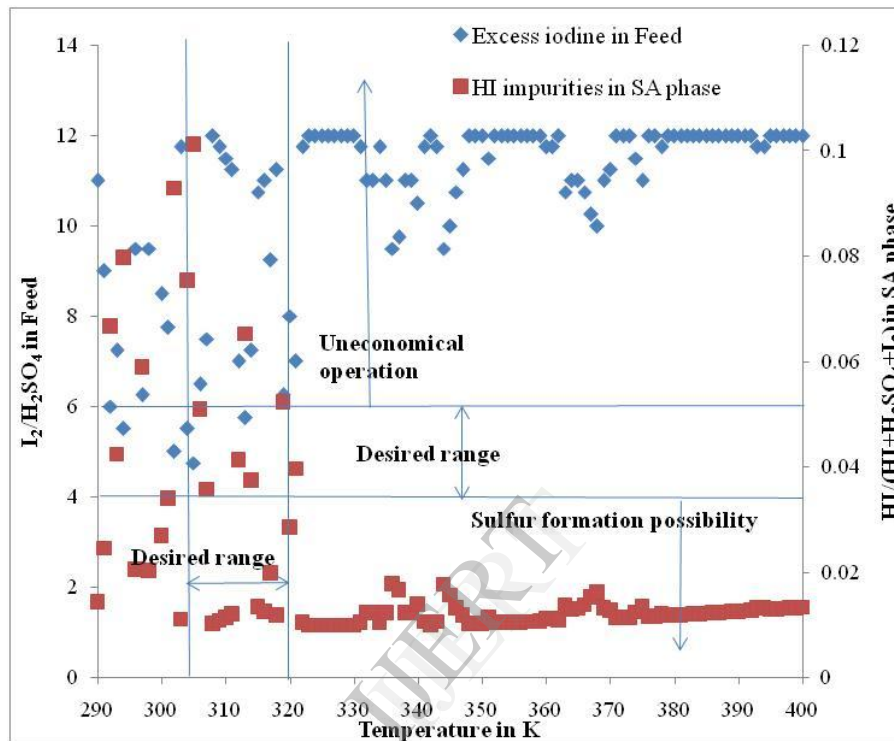


Figure 5: Optimal range study

4.2 Optimal range

The optimal range study is demonstrated in Figure 5. The effect of temperature and iodine excess in feed was studied simultaneously to find out the optimal range of operation. Iodine excess of 4-6 could be concluded as optimal range as minimum contamination points corresponds to that reason and temperature range of 305-320K corresponds to minimum contamination zone.

5. CONCLUSION

Simulation was performed to study the Bunsen reaction and phase separation. Effect of iodine excess in feed on phase separation i.e. reduction of contamination in HIx phase was studied successfully. Simulation results also

matches same trend of reduction as in literature experimental data and has predicted the optimal iodine range.

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