

Modeling of Sulfuric Acid Decomposition Process with a Chemical Process Simulator

J. H. Kim, Y. J. Shin, K.Y. Lee, and J. H. Chang

Korea Atomic Energy Research Institute, 150 Dukjin, Yusung, Daejeon , 305-353, jhkim5@kaeri.re.kr

1. Introduction

The S-I (Sulfur - Iodine) cycle, first described in mid 1970s, is a thermo-chemical water splitting cycle. Even though it was rejected by early workers due to severe challenges encountered, nowadays it is considered as a well defined hydrogen production method which consists of three processes pertaining to the chemical reactions described in equations (1)~(3), respectively.

1. $\text{SO}_2 + \text{I}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 2\text{HI}$ (1)
2. $\text{H}_2\text{SO}_4 \rightarrow \text{SO}_2 + \text{H}_2\text{O} + 1/2 \text{O}_2$ (2)
3. $2 \text{HI} \rightarrow \text{I}_2 + \text{H}_2$ (3)

Reaction (2) of the S-I cycle, known as a sulfuric acid decomposition reaction, contains all equipment associated with purification, concentration and decomposition of the sulfuric acid entering from reaction (1). The concentrated solution is transferred to the evaporator where the sulfuric acid is vaporized. The H₂SO₄ vapor is further heated upto 650°C and is transferred to the decomposer. In the decomposer, the sulfuric acid vapor decomposes into the SO₂ and O₂ under the catalyst. The gases are cooled down to 40°C and returned to the H₂SO₄.

The sulfuric acid is concentrated as much as possible to the azeotropic concentration. As the sulfuric acid begins to approach the azeotropic concentration, it is sent to decomposer where it decomposes more and more into SO₃ and H₂O as the temperature is raised. The SO₃ is, according to equilibrium considerations, partially decomposed in the catalytic decomposer to SO₂ and 1/2 O₂ upon further heating. As the hot gas mixture is cooled, undecomposed SO₃ combines with water to go back to H₂SO₄. The SO₂ and O₂ products are returning to reaction (1) process.

In this study, the unit models and flow-sheet models have been developed for the sulfuric acid decomposition process with chemical process simulator. Some sensitivity analysis were done for the equipment such as H₂SO₄ decomposer.

2. Simulation of sulfuric acid decomposition process

2.1 Process description [1]

The simulation flow-sheet has been shown in Figure 1. The sulfuric acid is concentrated prior to decomposition process. The concentrated sulfuric acid is preheated and vaporized during which some of the concentrated sulfuric acid decomposes into H₂O and SO₃ before it enters into the decomposer. In the decomposer, SO₃ decomposes into SO₂ and O₂ only in the presence of catalyst, because the decomposition reaction rate is too slow.

The products from the decomposer are cooled in the recuperator, transferring heat to the decomposer feed.

The products are further cooled by a series of coolers.

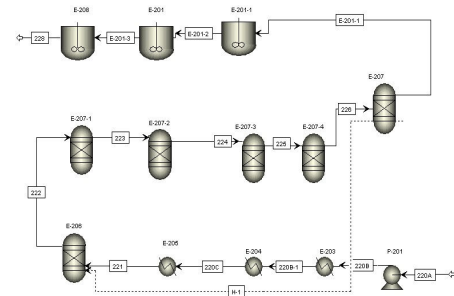


Figure 1. The simulation flow-sheet of the sulfuric acid decomposition process.

2.2 Simulation models

Flow-sheet for the sulfuric acid decomposition process has been developed with unit operation models provided by the chemical process simulator. The sulfuric acid decomposition process is modelled as a series of RGiBBS reactor in the chemical process simulator which is normally used to determine the system of independent reactions and estimate the extent of these reactions based on Gibbs free energy minimization.

The cooling process of reaction (2) products is performed by a cooler. It is simulated as a CSTR(Continuous Stirred Tank Reactor) that can control the reaction kinetics in the aqueous solution.

3. Simulation result

In simulation, the sulfuric acid VLE data at high temperature and pressure (850°C and 35 bar) has been regressed to generate a binary interaction parameters.[2]

The mole fraction of the outlet streams from the decomposer is calculated by chemical process simulator and its result is shown in figure 2 as a function of decomposition temperature. The mole fraction of SO_3 reaches its maximum at 550°C . This means that SO_3 does not decompose under 550°C .

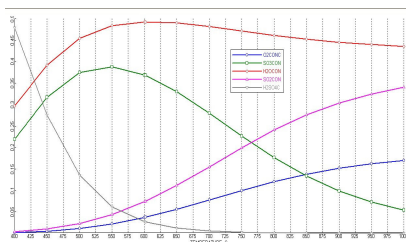


Figure 2. Mole fraction variation of decomposer outlet stream vs. decomposer operating temperature.

The composition of the decomposition process streams is shown in figure 3 in terms of mole fraction. It is understood that some of the sulfuric acid decomposes into SO_3 and water at the entrance and the decomposition reaction proceeds further as the vaporized stream is heated. The sulfuric acid has completely decomposed into SO_3 and water at the entrance to the decomposer.

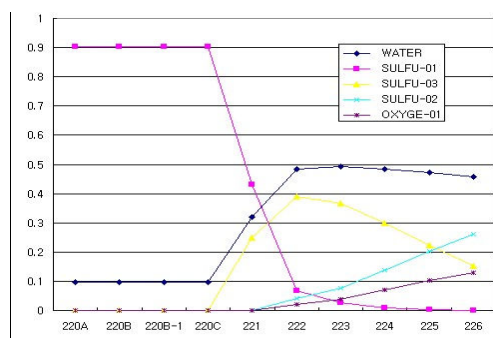


Figure 3. Mole fraction variation of each component in process streams.

4. Conclusion

The flow-sheet for the sulfuric acid decomposition process has been developed based on the S-I cycle. The sulfuric acid VLE data at high temperature and pressure (850°C and 35 bar) has been regressed to generate a binary interaction parameters for sulfuric acid. The binary interaction parameters seem to represent the sulfuric acid decomposition process simulation.

5. References

[1] Norman J. H., Besenbruch G. E., Brown L. C., O'keefe D. R., and Allen C. L., "Thermo-

chemical water-splitting cycle, bench-scale investigations, and process engineering", General Atomic Company, GA-A16713, 1982.

[2] Perry R. H., Green D.W., and Maloney J.O., "Perry's chemical engineers' handbook", McGraw Hill, 1984, pp. 3-65~3-69