Verification of KAERI-DySCo for a Dynamic Simulation of VHTR-based SI Hydrogen Production Facilities 1: Sulfuric Acid Multistage Distillation Column Module

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1. Introduction

The VHTR-based sulfur-iodine (SI) process used to produce hydrogen from water requires a multistage distillation column to concentrate a sulfuric acid solution. To design a concentration process of a sulfuric acid solution that can be applied to the process, its static and dynamic simulation is essentially demanded. According to this necessity, KAERI has developed a dynamic simulation code (KAERI-DySCo) to analyze the start-up behaviors of the SI process components [1]. On the other hand, a 50 NL·H_2/h scale SI test facility to be operated under a pressurized environment has been constructed by the scientific research partners of KIER, KIST, and POSCO. This study focuses on the verification of a simulation module for the sulfuric acid multi-stage distillation column (SAMDC) in the KAERI-DySCo. To verify the SAMDC, a comparison of the results calculated by the SAMDC with experimental data obtained from the operation of the 50 NL·H_2/h scale SI test facility by KIST has been carried out in this work.

2. An outline of distillation column

A schematic diagram of the sulfuric acid multi-stage distillation column is shown in Fig. 1. The column consists of a main column with glass-lined carbon steel, a reboiler with SiC, and a condenser with glass-lined carbon steel [2]. The main column with a 0.05m inside diameter and a 1m length was filled with ceramic Raschig rings of a 0.006m diameter. The reboiler with a 0.22m inside diameter and a 0.6m length was electrically heated by a 0.442kW Kanthal wire.

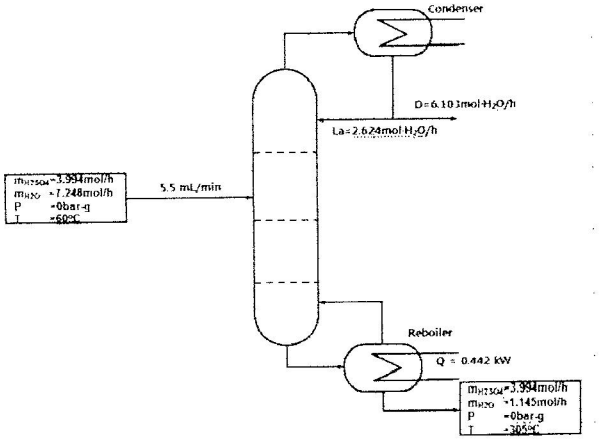

Fig. 1. Schematic diagram of the sulfuric acid distillation column for a 50NL•H_2/h SI test facility.

The main column and reboiler were thermally insulated using a ceramic fiber sheath. The glass-lined cooling coil with a 0.05m^2 cooling area was installed inside the condenser. A sulfuric acid solution of 75 weight % and 60°C flows into a reboiler of as long as $3.25x10^{-4}$ m^3 initially. The reboiler is electrically heated until reaching a boiling point of a 75 weight % sulfuric acid solution at 1bar. When the boiling status of the sulfuric acid solution at the reboiler is confirmed, the sulfuric acid solution of 75 weight % at 60°C is continuously fed through a feed line of as long as $5.5x10^{-6}$ m^3/min. A concentrated sulfuric acid solution is simultaneously discharged from the reboiler to maintain a constant liquid level of the sulfuric acid solution in the reboiler. At the same time, the condensed water is also discharged from the condenser.

3. Simulation model

The total mass and component balances, as well as the heat balance, in the SAMDC are applied to simulate the dynamic behavior of the H_2SO_4/H_2O binary system distillation column, which are the most common balance equations of a staged countercurrent separation system. The liquid (L_n) flows down over the surface of the solids packed into the column, and is exposed to the vapor (V_n), which flows upward through the open channels not filled by packing or liquid. The approach adopted for defining the dynamic mathematical model for the column is to establish a model for a single stage to provide equilibration of liquid and vapor and to duplicate it in a computer for all stages in the column, also incorporating any exceptional parts such as the feed plate, reboiler, and condenser. The following balance equations can be easily obtained for a general stage with a simple binary chemical system, without any chemical reaction.

Total Mass balance:

$$dM_n/dt=V_{n-1}+L_{n-1}-V_n-L_n \quad (1)$$

Component balance:

$$dM_nx_{n,i}/dt=V_{n-1}y_{n-1,i}+L_{n+1}X_{n+1,i}-V_ny_{n,i}-L_nx_{n,i} \quad (2)$$

Heat balance:

$$d(M_nH_n^L)/dt=V_{n-1}H_{n-1}^V+L_{n+1}H_{n+1}^L-V_nH_n^V-L_nH_n^L \quad (3)$$

where M_n (mol) is a holdup, L_n (mol s^{-1}) is the flow rate of liquid leaving stage n, V_n (mol s^{-1}) is the flow rate of the vapor leaving stage n. $x_{n,i}$ is the mole fraction of component i in the liquid phase leaving stage n, and $y_{n,i}$ is the mole fraction of component i in the vapor phase leaving stage n. In addition, H_n^L (kcal mol^{-1}) is the enthalpy of liquid leaving stage n, and H_n^V (kcal mol^{-1}) is the enthalpy of vapor leaving stage n.

The vapor-liquid equilibrium (VLE) values in the H_2SO_4 distillation have been obtained using the spline-interpolation method [3] with the vapor-liquid equilibrium table presented as functions of sulfuric acid

concentration and total pressure in Perry's Chemical Engineers' Handbook (Edition 7) [4]. The equilibrium relation between the liquid and vapor phases is as follows.

$$\varphi_i y_i P = x_i \gamma_i P_i^{\circ} \quad (4)$$

where P(bar) is the total pressure, φ_i is the fugacity coefficient of component i in the gas phase, y_i is the mole fraction of component i in the gas phase, x_i is the mole fraction of component i in the liquid phase, γ_i is the activity coefficient of component i obtained from the NRTL model, and P_i°(bar) is the saturated vapor pressure of the pure component i. All of the parameters used to calculate the vapor-liquid equilibrium of the sulfuric acid/water binary system using the NRTL model were introduced in 2009 [5].

4. Simulation Results

Fig. 2 shows the outlet temperature discharged from the reboiler as a function of operation time. The start-up time required until approaching a steady state temperature of 306°C is about 30,000s. The predicted temperature dynamic response is rapidly increased with an increase in the operation time until 10,000s, and then shows slow dynamics to attain a steady state temperature until 30,000s. The steady state temperature obtained from the start-up dynamic simulation agrees well with the KIST experimental value of 305°C.

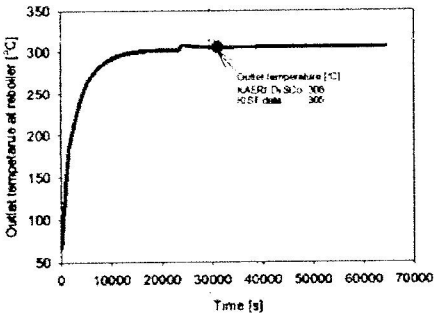

Fig. 2. Predicted start-up dynamic response of the outlet temperature at a reboiler.

Outlet mole flowrates of sulfuric acid and water at the reboiler are shown as a function of operation time in Fig. 3. The outlet mole flowrate of water is rapidly decreased with an increase in the operation time until 10,000s while the sulfuric acid takes almost a constant flow rate regardless of the operation time.

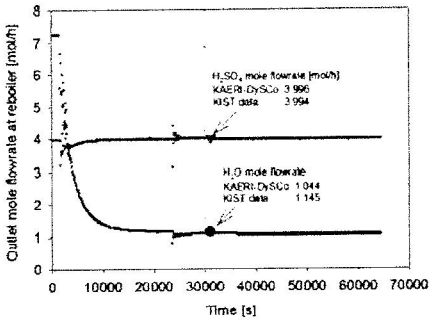

Fig. 3. Predicted start-up dynamic responses of outlet mole flowrates of H_2SO_4 and H_2O at a reboiler.

The concentration of sulfuric acid in the effluent solution discharged from the reboiler reaches a maximum value of 95.4 weight %. The start- up time approaching the steady state is identical between both cases of the outlet mole flowrate and temperature. When mutually comparing two steady state values obtained from the start-up dynamic simulation results and the KIST experimental data, both values are well agreed within a ±8.8% error, as shown in Fig. 3.

Fig. 4 shows the predicted start-up dynamic response of the outlet mole flowrate of water at the condenser.

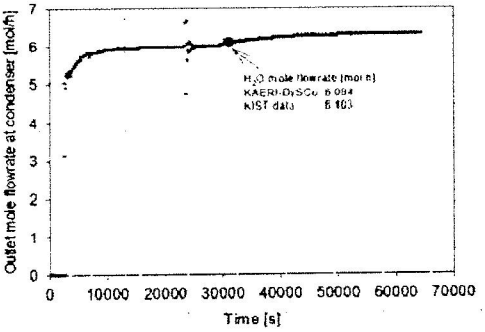

Fig. 4. Predicted start-up dynamic response of the outlet mole flowrate of water at a condenser.

5. Conclusion

In agreement with the steady state values measured experimentally by KIST, it has been finally confirmed that the SAMDC, which is one of the simulation modules in KAERI-DySCo for the dynamic simulation code of VHTR-based SI hydrogen production facilities, is a feasible simulation module for calculating the start-up dynamic behavior of a sulfuric acid multistage distillation column.

Acknowledgments

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