Verification of KAERI-DySCo for the Dynamic Simulation of VHTR-based SI Hydrogen Production Facilities 2: Hydriodic 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 hydriodic acid solution. To design the concentration process of the hydriodic 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 hydriodic acid multi-stage distillation column (HI_xMDC) in KAERI-DySCo. To verify the HI_xMDC, a comparison of the results calculated by the HI_xMDC with experimental data obtained from the operation of the 50 NL·H_2/h scale SI test facility by KIER has been carried out in this work.

2. Outline of distillation column

In the SI process, a hypoazeotropic HI_x aqueous solution is produced by a Bunsen reaction and separated from a sulfuric acid solution at a phase separator. The hypoazeotropic HI_x aqueous solution is fed into an electrodialysis cell to obtain a hyperazeotropic HI_x solution. The purpose of the HI_xMDC is to generate the most suitable hydriodic acid vapor from the hyperazeotropic HI_x aqueous solution as the top product of the column. This hydriodic acid vapor is fed into an HI thermal decomposer to finally produce hydrogen and iodine. A schematic diagram of the HI_xMDC is shown in Fig. 1. The HI_xMDC consists of a main column with tantalum-lined carbon steel, a reboiler with tantalum-lined carbon steel, and a partial condenser with tantalum-lined carbon steel [2]. The main column with a 0.05m inside diameter and 1.337m length of stripping and rectifying sections was filled with ceramic Raschig rings of 3/8 and 1/4inch diameters, respectively. The HI_x aqueous solution of 14.97mole% HI, 18.15mole% I_2, and 66.88mole% H_2O at 80°C flows into the reboiler for as long as $1.6\times10^{-3}m^3$ initially. The reboiler is heated until the boiling point of the HI_x aqueous solution at 7bar. When the boiling status of the solution at the reboiler is confirmed, the HI_x feed solution at 80°C is continuously fed through a feed line as long as a total flow rate of 668.16mol/h.

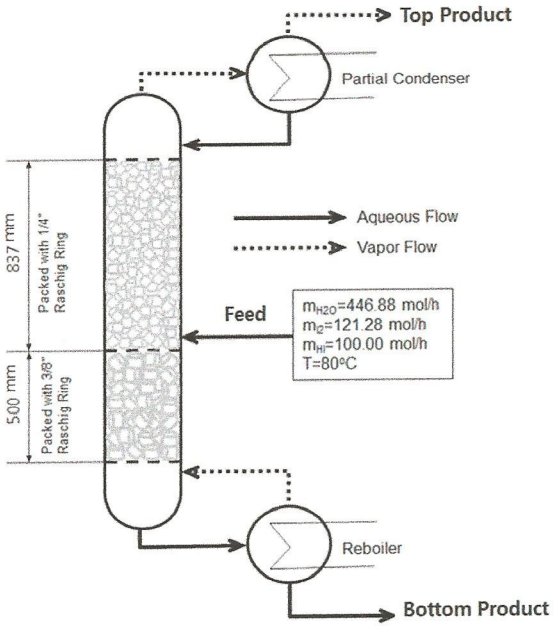

Fig. 1. Schematic diagram of the hydriodic acid distillation column for a 50NL•H_2/h SI test facility.

3. Simulation model

The total mass and component balances and heat balance in the HI_xMDC are applied to simulate the dynamic behavior of the HI_x ternary 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 a 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 the liquid and vapor and to duplicate it in a computer for all stages in the column, and 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 ternary 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, and V_n (mol s^{-1}) is the flow

rate of the vapor leaving stage n. In addition, $x_{n,i}$ 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. Also, 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 HI_x ternary system distillation were obtained by Eq. (4).

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

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. In this work, the ideal gas law was applied for the gas phase and Neumann's modified NRTL model and parameters based on Engel's model for the solvation of HI by H_2O were applied to calculate the activity coefficient in the $HI/I_2/H_2O$ ternary aqueous phase [3].

4. Simulation Results

Fig. 2 shows the outlet temperature discharged from the reboiler as a function of the operation time. The start-up time required until approaching a steady state temperature of 199.4°C is about 700s. The predicted temperature dynamic response is rapidly increased with an increase in the operation time until 200s, and then shows slow dynamics to attain a steady state temperature until 700s. The steady state temperature obtained from the start-up dynamic simulation agrees well with the KIER value of 206°C within a ±3.3%

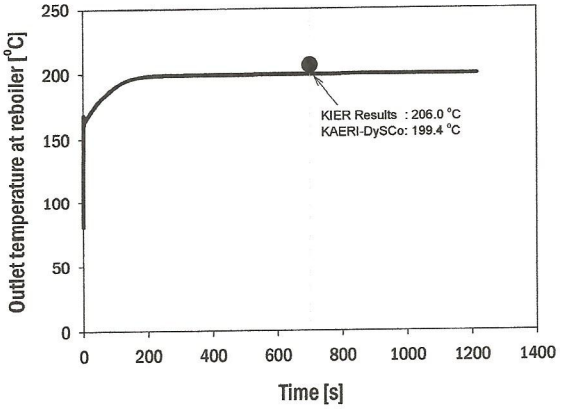

Fig. 2. Predicted start-up dynamic response of the outlet temperature at a reboiler.

The outlet mole fractions of HI, I_2, and H_2O at the reboiler are shown as a function of operation time in Fig. 3. The start- up time approaching the steady state is identical between both cases of the outlet mole fraction and temperature. When comparing the two steady state values obtained from the start-up dynamic simulation results and the KIER data, both values agreed well within ±10% error, as shown in Fig. 3.

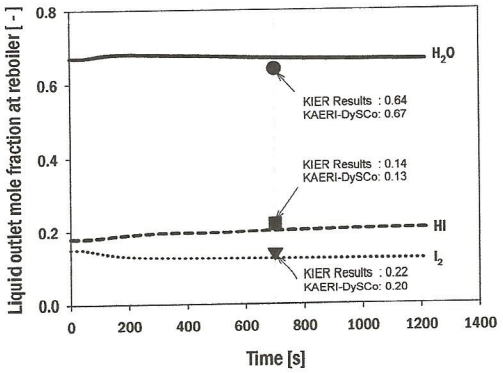

Fig. 3. Predicted start-up dynamic responses of outlet mole fractions of HI, I_2 and H_2O at a reboiler.

Fig. 4 shows the predicted start-up dynamic response of the outlet mole fractions at the condenser. Regarding the vapor composition discharged from the condenser, Fig. 4 shows the predicted start-up dynamic responses of the outlet vapor mole fractions of HI, I_2, and H_2O at the partial condenser. The outlet concentration of hydrogen iodide is rapidly increased to near pure HI vapor at approximately 50s from the start-up of the column, maintains around a 0.99 mole fraction for about 400s, and then advances to the steady state value of a 0.26 mole fraction, while the iodine concentration is monotonously increased with the progress of the operation time until approaching the steady state value of 0.1 mole fraction. A highly pure HI vapor stream "HI overshoot" generated during the start-up operation could lead to an iodine super-saturation condition in the outlet stream of a HI thermal decomposer. The iodine super-saturation condition rigorously requires temperature control and thermal insulation of the process pipe lines to prevent a tube-clogging problem owing to iodine precipitation. Such a tube-clogging problem ultimately gives rise to a fail in the integrated continuous operation of SI hydrogen production facilities. The water vapor discharged from the partial condenser shows a spike-heel of a 0.1 mole fraction at approximately 50s from the start-up of the column owing to the vapor-liquid phase equilibrium calculation, and then advances to the steady state value of a 0.73 mole fraction.

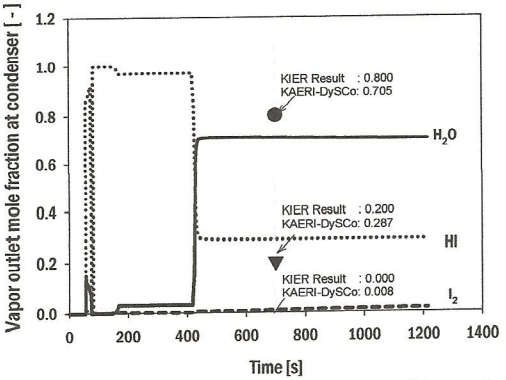

Fig. 4. Predicted start-up dynamic response of the outlet mole fractions at a condenser.

5. Conclusion

In agreement with the steady state values measured experimentally by KIER, it has been finally confirmed that the HI_xMDC, 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 able to calculate the start-up dynamic behavior of the multistage hydriodic acid distillation column.

Acknowledgments

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