Dynamic Optimization Study for Cryogenic Distillation in Hydrogen Isotope Separation System [*]

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Abstract: This paper presents a dynamic optimization study on a cryogenic distillation unit in hydrogen isotope separation system. A packed distillation column with an equilibrator is considered. The packed column was modeled as a theoretical equilibrium-based stage column. The equilibrator was placed to enhance separation performance. An optimal control problem was formulated to minimize the tritium holdup under two product quality constraints, in a situation where feed flowrate is periodically fluctuated. An optimal control policy was obtained for two manipulating variables, namely distillate flowrate and reboiler heat duty. The optimal control policy was analyzed by examining the operating variable profiles of the column.

Keywords: Hydrogen Isotope Separation System, Dynamic Optimization, Cryogenic Distillation

1. INTRODUCTION

In hydrogen isotope separation system (ISS), minimizing the amount of tritium in the system is one of the most important objectives. In dynamic operation of ISS, periodic fluctuations in feed flowrate is a possible scenario to be considered with importance. Change in feed flowrate can result in violation of the inventory regulations and product qualities can be deteriorated below the product quality limits. Therefore, it is important to employ necessary control actions to fulfill the requirements in need.

For this reason, several studies have been made on dynamic simulation of a cryogenic distillation column for ISS. Works of Busigin and Sood (1995); Cristescu et al. (2005); Bhattacharyya et al. (2016); Draghia et al. (2016); Niculescu et al. (2017); Ovcharov et al. (2020) are the main contributions made on the study of dynamic simulation of a cryogenic distillation column or a process for ISS.

There exist only one dynamic optimization study for a cryogenic distillation column in ISS. In Park et al. (2021), an optimal control policy was derived for a packed distillation column. The optimal control problem was given as the minimization of tritium inventory while satisfying a quality constraint for the tritium product, under a scenario where feed flowrate is changed. Two constraints were imposed on operational variables. First, the flowrate of bottoms was fixed proportional to the feed flowrate. Second,

the time derivative of reboiler duty was constrained by a small arbitrary limit. The resulting optimal control policy yielded an operational strategy consisted of two phases. In the first phase, when feed is provided, tritium inventory is minimized and product quality is deteriorated until the constrained limit. In the second phase, when feed is not provided, total reflux operation is employed and product quality is recovered.

In this work, the optimal control problem is defined similar to that of described in Park et al. (2021). The objective is identical which is to minimize the tritium holdup in the distillation column. However, rather than considering a product quality constraint on the bottoms, another product quality on the distillate was added in this work. This is required since we have added distillate flowrate as a manipulating variable. If not considered, the optimal control policy would result in unrealistic small flowrate of the bottoms. Other main differences are the consideration of an equilibrator and the modeling of reboiler and condenser as sieve trays.

The remainder of this paper is organized as follows. The thermodynamic model, models employed for the distillation column, and equilibrator model used in this work are described in Section 2. In Section 3, an optimal control problem is defined and the optimal control policy obtained is presented.

2. METHODS

2.1 Thermodynamic model

The virial equation of state (EOS) model is employed from the work of Park et al. (2021), to calculate the molar enthalpy and fugacities of mixtures. There exist works of employing Peng-Robinson EOS (PR-EOS) Noh et al. (2017); Urm et al. (2021). PR-EOS with Twu alpha function has advantage of accurately estimating the thermodynamic properties in the range between the triple point and the critical point Twu et al. (1995). To be implemented in an optimization framework, the model requires imposition of additional derivative constraints suggested by Kamath et al. (2010) to calculate the roots of the cubic equations for the corresponding liquid and vapor phases. For better convergence in solving our dynamic optimization problem, we adopted virial-EOS model instead of PR-EOS model.

2.2 Cryogenic distillation unit

The cryogenic distillation unit is composed of a packed column and an equilibrator. Hydrogen isotopes are separated by the difference in boiling points. With the appropriate displacement of sidestream to the equilibrator, the unpreferred hydrogen isotopologues HD, HT, and DT can be converted to the preferred isotopologues H_2, D_2, and T_2. The converted isotopologues are recycled as feed to the column at the sidestream location, and in result, product qualities can be improved.
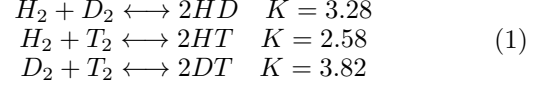
Distillation column In this work, the packed columns are modeled as a theoretical stage column with the adoption of fixed value of height equivalent to theoretical plates (HETP). Specifically, the equilibrium-stage based model is used from the works of of Park et al. (2021) and Urm et al. (2021). A difference of the model used in this work is that the complementarity constraints are not imposed. Complementarity constraints are used to model single-phase regions Kamath et al. (2010). However, in the scope of this work, all theoretical stages are assumed to be in phase equilibrium. Therefore, the complementarity constraints are not required.

We employ hydrodynamic model from the work of Stichlmair et al. (1989). The parameters of the hydrodynamic model for ISS are retrieved from the work of Park et al. (2021). The model calculates the liquid holdup and the pressure drop in the packed region of the distillation column. However, the non-flooding constraints on each theoretical stage was not taken in account, since flooding can be avoided by setting an appropriate operating range of reboiler heat duty. Additionally, the reboiler and condenser are modeled as sieve trays in our work.

For the models employed in this work, we use the following set notations. The number of theoretical stages is noted as N. The set NT $= \{1, \ldots, N\}$ represents the set of numbered theoretical stages. The stages are numbered from condenser to reboiler, such that index 1 represents the condenser, and index N represents the reboiler. Subscript j refers to the quantity associated with the jth stage. The set NC $= \{H_2, HD, HT, D_2, DT, T_2\}$ denotes set of hydrogen isotopologues, which are in ascending order of it's boiling

point. Superscript i refers to the quantity associated with the component $i \in$ NC.

Equilibrator Three equilibrium reactions are considered in the equilibrator, where equilibrium is assumed to be instantaneously established. The equilibrators are assumed to be operated at 300 K. The equilibrium constants are retrieved from Souers (1986).

$$
\begin{array}{ll}
H_2 + D_2 \longleftrightarrow 2HD & K = 3.28 \\
H_2 + T_2 \longleftrightarrow 2HT & K = 2.58 \\
D_2 + T_2 \longleftrightarrow 2DT & K = 3.82
\end{array} \tag{1}
$$

Holdup is not considered in the equilibrator.

3. OPTIMAL CONTROL PROBLEM OF A CRYOGENIC DISTILLATION UNIT

3.1 Problem definition

Fig. 1 describes the schematic diagram of the cryogenic distillation unit, consisting of a distillation column and an equilibrator. The feed is fed in the middle of the distillation column. A sidestream product of the column is fed to the equilibrator in liquid phase. The product stream of the equilibrator is fed back to the same theoretical stage.
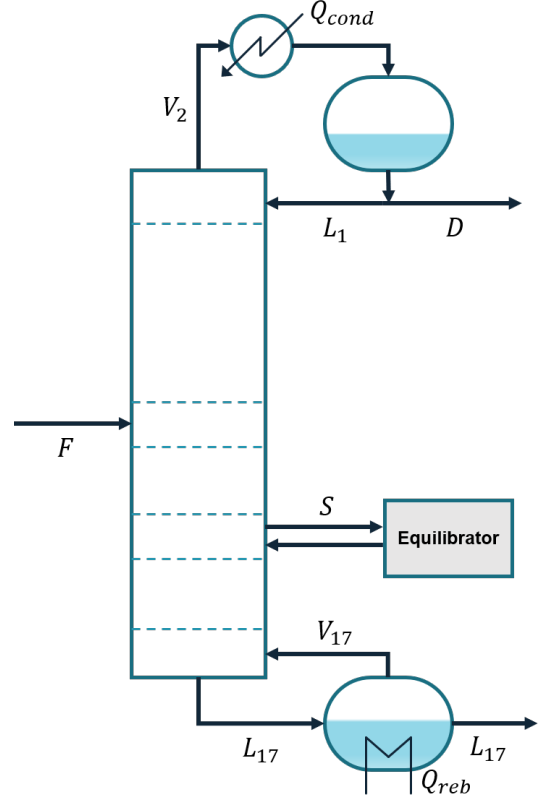

Fig. 1. Schematic of a cryogenic distillation unit consisted of a packed distillation column and an equilibrator. The packed distillation column is modeled as a theoretical stage column with the adoption of HETP. A sidestream product of the column is fed to the equilibrator and returned to the same theoretical stage.

Feeding scenario Feed flowrate profile is retrieved from Park et al. (2021) and reproduced in Fig. 2. The composition of feed is assumed to be constant over time. Feed stream specification is presented in Table 1.
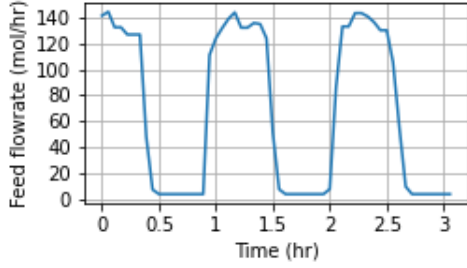

Fig. 2. Feed profile reconstructed from Park et al. (2021)

Table 1. Feed stream specification used in this study

Parameter		Value
Feed composition	H_2	0.0033
	HD	0.0493
	HT	0.0441
	D_2	0.2271
	DT	0.4464
	T_2	0.2297
Temperature		24 K
Pressure		1.45 kPa
Flowrate	Min	3.6 mol/hr
	Max	144.4 mol/hr

Column design specification The design specification of the column are summarized in Table 2. Feed stage is selected at a location that of the middle of the column, where separation efficiency can be maximized. The sidestream stage is selected at a position where quality of bottoms can be improved. The condenser is set as a total condenser, which implies (2).

$$V_1 = 0 \qquad (2)$$

where V_j is the interstage molar flowrate of vapor leaving jth stage.

Table 2. Column design specification

Parameter	Value
Packed height	0.75 m
Diameter	0.08 m
Type of packing	Metal gauze packing
HETP	0.05 m
Number of equivalent stages	17 (15+2)
Feed stage	8
Sidestream stage	13
Condenser type	Total condenser

Sidestream and equilibrator specification During operation, the sidestream ratio, S/L_{13}, is assumed constant as the value of that in the initial steady-state, as in (3).

$$S/L_{13} = S^{ss}/L_{13}^{ss} \qquad (3)$$

where S is the sidestream flowrate; and L_j is the interstage molar flowrate of liquid leaving jth stage.

The output stream of the equilibrator is assumed to be cooled to 24 K before it is fed to the distillation column. The pressure of the output stream is assumed to be pressurized to 1.45 kPa, which is higher than the pressure

of the theoretical stage it is fed. Since holdup is not considered in the equilibrator, the flowrate of the output stream is given equal to that of the input stream, at all time.

Optimal control problem The optimal control problem is given in (4). The optimal control problem is given to minimize the tritium holdup, INV^T, during operation, while the atomic fractions of tritium in the distillate and bottoms are constrained to be below 0.35 and abobe 0.75, respectively. The manipulating variables during column operation are distillate flowrate, D, and the reboiler heat duty, Q_{reb}. In order to solve the optimization problem with differential and algebraic equations, initial conditions are provided for the component molar holdups, M_j^i, and the internal energy of the holdups, U_j. The initial values of the manipulating variables are also fixed.

$$
\min_{D, Q_{reb}} \int_{t_0}^{t_f} \left(\sum_{j \in NT} INV_j^T \right) dt
$$

$$
\begin{aligned}
\text{s.t.} \quad & x_1^{H_2} + \frac{1}{2} x_1^{HD} + \frac{1}{2} x_1^{HT} \leq 0.35 \\
& x_{17}^{T_2} + \frac{1}{2} x_{17}^{HT} + \frac{1}{2} x_{17}^{DT} \geq 0.75 \\
& M_j^i(0) = (M_j^i)^{ss}, \quad j \in NT, i \in NC \\
& U_j(0) = U_j^{ss}, \quad j \in NT \\
& D(0) = D^{ss} \\
& Q_{reb}(0) = Q_{reb}^{ss} \\
& INV_j^T = \frac{1}{2} M_j^{HT} + \frac{1}{2} M_j^{DT} + M_j^{T_2}, \quad j \in NT
\end{aligned}
$$

$$(4)$$

where x_j^i is the component molar fraction.

The manipulating variables are bounded as in (5).

$$
\begin{aligned}
0 &\leq D \\
0 &\leq Q_{reb} \leq 1000
\end{aligned}
\qquad (5)
$$

3.2 Results and Discussion

The problem was implemented in a framework of an optimization modeling language, Pyomo (Hart et al., 2011), and solved with a nonlinear programming solver IPOPT (Wächter and Biegler, 2006). The problem was solved on a 3.6 GHz Intel i9-9900K processor.

Initial operating condition The initial operating condition was obtained by solving a steady-state simulation. In Table 3, the column specification for the initial operating condition is presented and the obtained result is summa-

Table 3. Column specification for the initial operating condition and overall result

Parameter	Value
Feed flowrate	141.29 mol/hr
Reboiler heat duty	550 W
Distillate flowrate	90 mol/hr
Top pressure	1400 kPa
Sidestream flowrate	50 mol/hr
Condenser heat duty	-544.51 W
Total tritium holdup	5.380 mol
Protium atomic fraction in distillate	0.309
Tritium atomic fraction in bottoms	0.767
Total pressure drop	16.28 Pa

rized. The solution was obtained in 34 iterations and 3.83 CPU seconds.
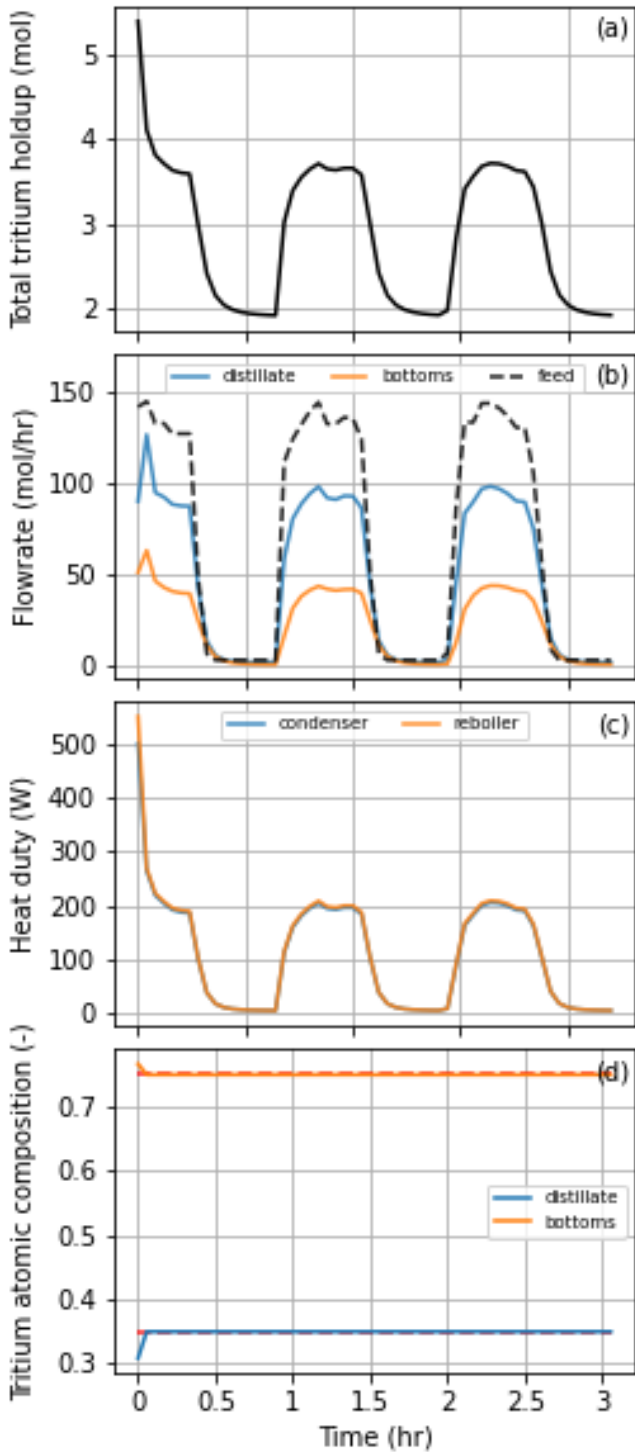

Fig. 3. Resulting optimal control policy: (a) total tritium holdup, (b) flowrate of distillate, bottoms, feed and reflux, (c) heat duty of condenser and reboiler, (d) atomic fraction of tritium in distillate and bottoms.

Optimal control policy   The optimal control problem was discretized over 56 elements using backward finite difference method. All variables were initialized with the corresponding value at the initial operating condition. The

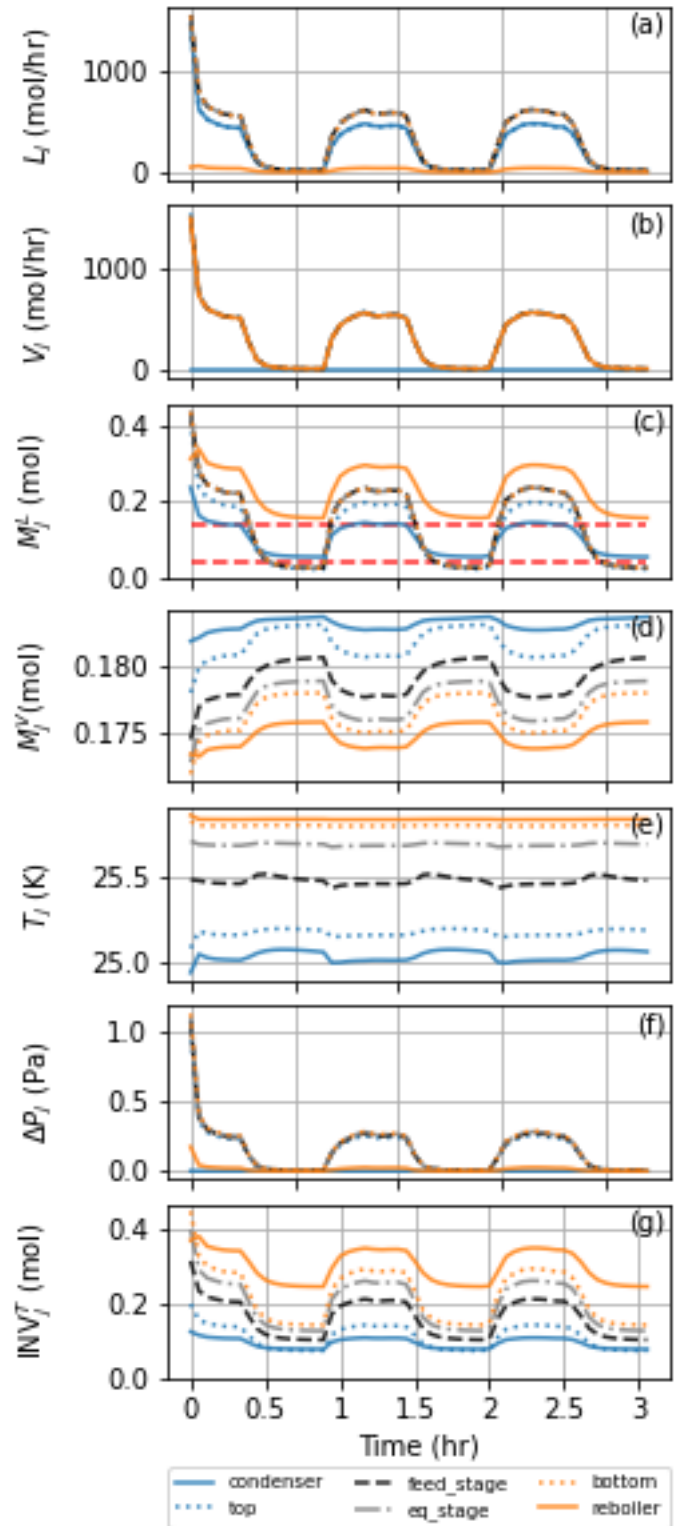optimal solution was found after 1424 iterations and 2.52 CPU hours.

Fig. 4. Internal profiles on each theoretical stage: (a) liquid flowrate, (b) vapor flowrate, (c) liquid holdup, (d) vapor holdup, (e) temperature, (f) pressure drop, (g) tritium holdup.

The resulting optimal control policy is presented in Fig. 3. It is found that, in the time interval of 0 - 200 s, the total tritium holdup is reduced (Fig. 3a) by 23.8 % compared to the initial condition. The flowrate of both distillate and bottoms are increased (Fig. 3b), which reduces the amount of tritium holdup inside the column. In the same time interval, the reboiler heat duty (Fig. 3c) is reduced until the quality constraint on the distillate and that on the bottoms are satisfied (Fig. 3d) at the bound. Consequently, the tritium atomic fraction is decreased inside the column, which in turn reduced the amount of tritium holdup. In Fig. 3b, the optimal distillate flowrate profile is shown. The profiles of feed flowrate, flowrate of reflux stream and flowrate of bottoms are shown together. Both flowrate profile of the distillate and the bottoms show similar behavior with the feed flowrate profile. However, the ratio of distillate flowrate to bottoms flowrate varies in the range of 1.11 to 3.52.

In Fig. 3c, the optimal reboiler heat duty profile is shown together with the heat duty profile of the condenser. The optimal control policy implies that when feed is provided, heat should be provided to the reboiler to keep the temperature of the reboiler above a value. As a result, the atomic fraction of tritium in the bottoms will always satisfy the purity constraint (Fig. 3d). Note that the condenser heat duty is a dependent variable.

In Fig. 3d, the atomic fraction profiles of tritium in the distillate and bottoms are shown. Both atomic fraction profiles show that the imposed purity constraints are satisfied at the solution.

In Fig. 4, the internal profiles of the liquid flowrate, vapor flowrate, liquid holdup, vapor holdup, temperature, pressure drop, and tritium holdup are shown for six characteristic theoretical stages. Specifically, the condenser, top theoretical stage, feed stage, sidestream stage, bottom theoretical stage, and the reboiler were chosen for illustration.

In Figs. 4a and 4b, the profiles of liquid flowrate and vapor flowrate in each stage are shown. The increased heat duty of the condenser and reboiler resulted in a higher flowrate of internal liquid flow and vapor flow. Note that the liquid flowrate of the condenser is the reflux flowrate, and the liquid flowrate of the reboiler is the bottoms flowrate.

In Figs. 4c and 4d, the profiles of liquid holdup and vapor holdup in each stage are shown. The optimal control policy resulted the liquid holdup in the condenser and reboiler to be reached near the minimum holdup required in order to have a liquid flow. When the heat duties are decreased, the ratio of the liquid holdup in the packed tower to the liquid holdup in the condenser and reboiler changed. In detail, comparatively less amount of liquid holdup remained in the packed tower. Note that such a trend is only valid in our problem where specific packing parameters and hydraulic parameters are assumed.

While the trend of liquid holdups shows similar tendency with the heat duties, the trend of vapor holdups exhibits an opposite behavior. This difference is analyzed as a result of a shift in the phase equilibrium in each stage. When heat duties are decreased, the phase equilibrium is established at a relatively higher temperature (Fig. 4e), lower pressure (Fig. 4f), and higher atomic fraction of light components
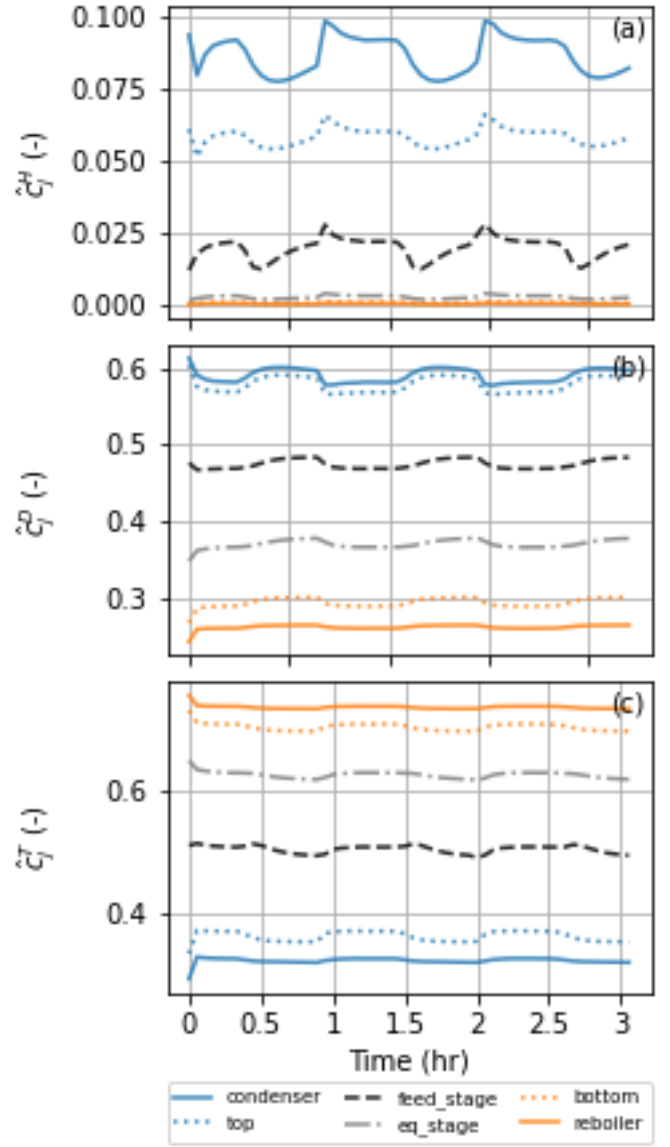

Fig. 5. Profile of atomic composition in each theoretical stage: (a) protium (b) deuterium (c) tritium.

(Figs. 5a and 5b). With a fixed volume given for each theoretical stage, the decrease in liquid holdup volume is another factor.

Fig. 5 shows the profile of atomic composition in the theoretical stages. The atomic fractions are defined as in (6).

$$
\begin{aligned}
\hat{c}_j^H &= \frac{M_j^{H_2} + \frac{1}{2}M_j^{HD} + \frac{1}{2}M_j^{HT}}{\sum_{i \in \mathrm{NC}} M_j^i} \\
\hat{c}_j^D &= \frac{M_j^{D_2} + \frac{1}{2}M_j^{HD} + \frac{1}{2}M_j^{DT}}{\sum_{i \in \mathrm{NC}} M_j^i} \quad j \in \mathrm{NT} \qquad (6) \\
\hat{c}_j^T &= \frac{M_j^{T_2} + \frac{1}{2}M_j^{HT} + \frac{1}{2}M_j^{DT}}{\sum_{i \in \mathrm{NC}} M_j^i}
\end{aligned}
$$

4. CONCLUSIONS

In this paper, we have found the optimal control policy of a cryogenic distillation unit for ISS. The objective was to minimize the amount of tritium in the packed distillation column. Two product quality constraints were imposed. The optimal control policy was obtained, which ensured the product quality constraints to be satisfied at all time. The optimal control policy is, in short, given to manipulate distillate flow rate and reboiler heat duty similarly to the feed flow rate change. Additionally, in the start-up phase, the reboiler duty is shown to decrease and distillate flow rate to increase in a way to decrease the tritium holdup.

In future work, we intend to tackle a dynamic optimization problem in a larger scale with an additional objective to reduce variance in product flowrates. Increased number of theoretical stages for producing fuel-grade products will also be considered.

REFERENCES

Bhattacharyya, R., Bhanja, K., and Mohan, S. (2016). Simulation studies of the characteristics of a cryogenic distillation column for hydrogen isotope separation. *International Journal of Hydrogen Energy*, 41(9), 5003–5018.

Busigin, A. and Sood, S. (1995). Steady state and dynamic simulation of the iter hydrogen isotope separation system. *Fusion technology*, 28(3P1), 544–549.

Cristescu, I.R., Dörr, L., Busigin, A., and Murdoch, D. (2005). Iter dynamic tritium inventory modeling code. *Fusion science and technology*, 48(1), 343–348.

Draghia, M.M., Pasca, G., and Porcariu, F. (2016). Software development for the simulation and design of the cryogenic distillation cascade used for hydrogen isotope separation. *Fusion Engineering and Design*, 109, 961–964.

Hart, W.E., Watson, J.P., and Woodruff, D.L. (2011). Pyomo: modeling and solving mathematical programs in python. *Mathematical Programming Computation*, 3(3), 219.

Kamath, R.S., Biegler, L.T., and Grossmann, I.E. (2010). An equation-oriented approach for handling thermodynamics based on cubic equation of state in process optimization. *Computers & Chemical Engineering*, 34(12), 2085–2096.

Niculescu, A., Constantin, T., Ana, G., and Draghia, M. (2017). Dynamic simulation of a multicomponent distillation column for dt separation. *Fusion Engineering and Design*, 124, 752–756.

Noh, J., Fulgueras, A.M., Sebastian, L.J., Lee, H.G., Kim, D.S., and Cho, J. (2017). Estimation of thermodynamic properties of hydrogen isotopes and modeling of hydrogen isotope systems using aspen plus simulator. *Journal of Industrial and Engineering Chemistry*, 46, 1–8.

Ovcharov, A., Szczepanski, R., Kosek, J., Pedrosa, N., Lu, X., Basili, L., Lo Frano, R., and Aquaro, D. (2020). Rigorous dynamic simulation of cryogenic distillation of hydrogen isotopologues in the fuel cycle of a thermonuclear reactor based on uv flash. *Fusion Science and Technology*, 76(3), 179–190.

Park, D., Urm, J.J., Lee, J.U., Chang, M.H., and Lee, J.M. (2021). Dynamic optimization of cryogenic distillation operation for hydrogen isotope separation in fusion power plant. *International Journal of Hydrogen Energy*, 46(47), 24135–24148. doi: https://doi.org/10.1016/j.ijhydene.2021.04.199.

Souers, P.C. (1986). *Hydrogen properties for fusion energy*. Univ of California Press.

Stichlmair, J., Bravo, J., and Fair, J. (1989). General model for prediction of pressure drop and capacity of countercurrent gas/liquid packed columns. *Gas Separation & Purification*, 3(1), 19–28.

Twu, C.H., Coon, J.E., and Cunningham, J.R. (1995). A new generalized alpha function for a cubic equation of state part 1. peng-robinson equation. *Fluid Phase Equilibria*, 105(1), 49–59.

Urm, J.J., Park, D., Lee, J.U., Chang, M.H., and Lee, J.M. (2021). Design study of a cryogenic distillation column for hydrogen isotope separation system. *Fusion Engineering and Design*, 172, 112736. doi: https://doi.org/10.1016/j.fusengdes.2021.112736.

Wächter, A. and Biegler, L.T. (2006). On the implementation of an interior-point filter line-search algorithm for large-scale nonlinear programming. *Mathematical programming*, 106(1), 25–57.