Effectiveness analysis of pre-cooling methods on hydrogen liquefaction process

Yejun Yang, Taejin Park, Dohoon Kwon[*], Lingxue Jin, and Sangkwon Jeong

Cryogenic Engineering Laboratory, Korea Advanced Institute of Science and Technology, Daejeon, Republic of Korea

Abstract

The purpose of this analytic study is to design and examine an efficient hydrogen liquefaction cycle by using a pre-cooler. The liquefaction cycle is primarily comprised of a pre-cooler and a refrigerator. The fed hydrogen gas is cooled down from ambient temperature (300 K) to the pre-cooling coolant temperature (either 77 K or 120 K approximately) through the pre-cooler. There are two pre-cooling methods: a single pre-coolant pre-cooler and a cascade pre-cooler which uses two levels of pre-coolants. After heat exchanging with the pre-cooler, the hydrogen gas is further cooled and finally liquefied through the refrigerator. The working fluids of the potential pre-cooling cycle are selected as liquid nitrogen and liquefied natural gas. A commercial software Aspen HYSYS is utilized to perform the numerical simulation of the proposed liquefaction cycle. Efficiency is compared with respect to the various conditions of the heat exchanging part of the pre-cooler. The analysis results show that the cascade method is more efficient, and the heat exchanging part of the pre-coolers should have specific UA ratios to maximize both spatial and energy efficiencies. This paper presents the quantitative performance of the pre-cooler in the hydrogen liquefaction cycle in detail, which shall be useful for designing an energy-efficient liquefaction system.

Keywords: pre-cooling, hydrogen liquefaction, LN_2, LNG, cold exergy

1. INTRODUCTION

To cope with global environmental problems, such as global warming and air pollution, many countries have adopted corresponding measures. As a method of reducing CO_2 emission, the demand for hydrogen as an energy carrier is emerging. Among the efficient methods for utilizing hydrogen, the liquefied hydrogen is an attractive way to utilize hydrogen due to the high energy density. To expand the hydrogen economy, it is essential to develop an efficient hydrogen liquefier. One of the strategies for accomplishing the efficiency enhancement is equipping an efficient pre-cooling apparatus in the liquefier.

In general, the pre-cooling method is categorized by the type of the pre-coolant: liquid-nitrogen (LN_2) pre-cooling, helium (He) pre-cooling, and mixed-refrigerant (MR) pre-cooling. LN_2 is generally selected as a pre-coolant due to its low normal boiling temperature (77 K), inexpensiveness and eco-friendliness.

LN_2 precooling method has been studied in many research groups. Figure of merit (FOM) of the hydrogen liquefaction was analyzed for several cycles according to whether the LN_2 pre-cooling is added or not by Chang [1]. The results show that the performance of the liquefier is improved by about 12 % when the LN_2 pre-cooling is added for the helium Brayton cycle. C. Lee et al. [2] suggested the method of achieving 67 K by utilizing sub-atmospheric devices, such as cold compressor and vacuum pump. Besides LN_2, MR [3] and LNG [4] have also been considered as the pre-coolants.

* Corresponding author: dhoon417@kaist.ac.kr

In this study, we aim to find an effective pre-cooling method on hydrogen liquefaction process. Required works for liquefying the hydrogen are numerically calculated under various conditions of the pre-cooler and the results are discussed. The pre-cooling is assumed to be accomplished by feeding the warm hydrogen gas through a copper coil that is submerged into a pre-coolant bath. The fed gas exchanges heat with both liquid and vaporized pre-coolant to recycle the cold exergy of the vented vapor from the pre-coolant bath and reduce the consumption of the pre-coolant. The benefit of pre-cooling is studied by only one pre-coolant or by in the cascaded manner two pre-coolants.

2. ANALYTICAL METHOD

In this study, the efficiency changes of hydrogen liquefaction cycle according to the pre-cooling method and the level of cold exergy reutilization are analyzed. The detailed process analysis is conducted by a commercial analyzer, Aspen HYSYS. The physical properties of fluids are calculated by Peng-Robinson equation of state. The properties of methane (CH_4) are utilized to simulate LNG for simplicity.

2.1. Efficiency Enhancement by Reutilizing Cold Exergy of Boil-off Pre-coolant

Fig. 1 shows the schematics of the pre-cooler applied to hydrogen liquefaction cycles. For efficient hydrogen liquefaction, the supplied hydrogen is pre-cooled by boil-off vapor as well as the liquid as shown in the figure. The heat exchangers in the equivalent schematics represent the
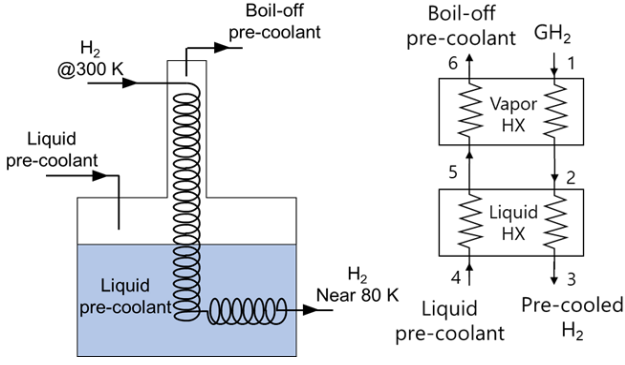
Fig. 1. Schematics of pre-cooler which reutilizes the cold exergy of boil-off pre-coolant (left) and equivalent schematic composed of heat exchangers (right).

heat exchange of hydrogen gas with the vapor and the liquid pre-coolant separately in the pre-cooler. This configuration is considered just for realistic manufacturability. Based on this illustration, the numerical analysis is conducted to confirm the effect of reutilizing the cold exergy of boil-off pre-coolant.

The equivalent schematic at the right side of Fig. 1 is analyzed under the following assumptions.

➢ The inlet pressures of all streams are fixed as 1 bar, and the pressure drop in heat exchanger is neglected.
➢ The temperatures of the supplied hydrogen from the feedstock and the supplied pre-coolant from the pre-cooling bath are set to the ambient temperature (300 K) and the saturated temperature (77 K for LN_2 or 120 K for LNG), respectively.
➢ The minimum temperature approach inside the heat exchangers is set as 3 K.
➢ When the hydrogen is pre-cooled, conversion heat is generated due to ortho to para conversion. The conversion heat, however, is not considered in this study for the simplicity.

The temperature of Point 2 in the configuration indicates the effectiveness of the cold exergy reutilization by vapor. By varying this temperature, we calculated and compared the UA of each heat exchanging part and the amount of the pre-coolant that are required for pre-cooling 1 kg of H_2 per second, where U is the overall heat transfer coefficient, and A is the area of the heat exchanger. The analysis is conducted using two different pre-coolants, LNG (CH_4) and LN_2.

2.2. Efficiency Enhancement by Pre-cooling Method

There are three types of pre-cooling methods, which are pre-cooling with LN_2, LNG, and with both pre-coolants (cascade method, LNG+LN_2). As shown in Fig. 2, hydrogen gas is pre-cooled by the pre-cooler first and then liquefied by a cryogenic refrigerator. The ideal liquefaction work, W, is calculated by following Eq. (1),

$$W = h - h_0 - T_0(s - s_0) \qquad (1)$$

where W is the actual liquefaction work; h is the enthalpy at saturated liquid condition; s is the entropy at saturated

liquid condition; T is the temperature; h_0, T_0 and s_0 indicate the properties at the ambient temperature (300 K) condition.

The FOM for calculating the required pre-coolant liquefaction work and ideal liquefaction work are referred to Ref. [5]. The FOMs for LNG and LN_2 liquefaction cycles are selected as 0.276 and 0.115, respectively. The required work for pre-coolant production, therefore, is calculated with Eq. (1) and the FOM values.

The coefficient of performance (COP) of the refrigerator is approximated by Eq. (2) [6].

$$\eta = 0.3 \times \left(\frac{T_L}{T_H}\right)^{0.881} \qquad (2)$$

where η is the percent Carnot efficiency; refrigerator cold end's temperature, T_L, is set to the hydrogen liquefaction temperature, 20 K; the warm end temperature of the refrigerator, T_H, is set to the ambient temperature, 300 K. The required work for liquefying the pre-cooled hydrogen can be calculated with Eq. (2) as a result.

The pre-cooled gas hydrogen enters the liquefying stage in a superheated state. The liquefying refrigerator, therefore, has to absorb not only the latent heat of the hydrogen but also the sensible heat of it. In this work, however, T_L is assumed to be constant as 20 K for simplicity. This assumption may result in the overestimation of the required work of the liquefying refrigerator because as shown in Eq. (2), the COP of the refrigerator is proportional to the cold end temperature. In practical application of the refrigerators, the cold end temperature is set to close to the temperature of the cooling target because big temperature difference between them will lead to large entropy generation as a result.

Numerical analysis is conducted with the same assumptions applied to the analysis in Section 2.1, except the third assumption. In the case of Fig. 2-(c), the temperatures of Point 7 and 10 are assumed to reach the same temperature after heat exchanging with GH_2 for the simple calculation. Furthermore, instead of setting the temperature difference in the heat exchanger, the total UA required for the pre-cooler is fixed from 60 kW/K to 90 kW/K. Additionally, the UA of each heat exchanging part in the pre-cooler is now a variable, while the total UA of them are fixed, for the analysis. Once the UA of each heat exchanger is determined, the required amount of the pre-coolant and the temperature of the hydrogen before entering the liquefying stage (Point 3 in Fig. 2-(a) and (b), or Point 4 in Fig. 2-(c)) are obtained with the set assumptions. Finally, the total required work for hydrogen liquefaction was calculated and compared with the results in different conditions.

3. RESULTS AND DISCUSSION

3.1. Results of Efficiency Enhancement by Reutilizing the Cold Exergy of Boil-off Pre-coolant
Fig. 3 shows the calculation results when LNG (CH_4) and LN_2 are utilized as the pre-coolants. All the values are obtained for pre-cooling 1 kg/s of hydrogen. The two results are numerically analyzed with different pre-coolant,
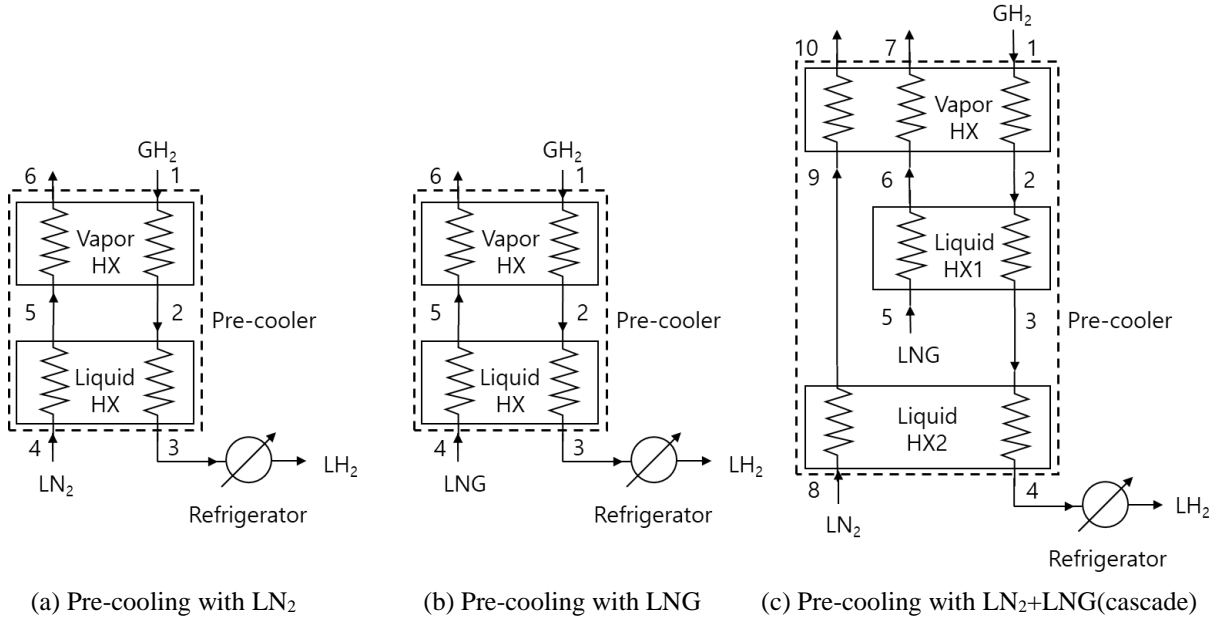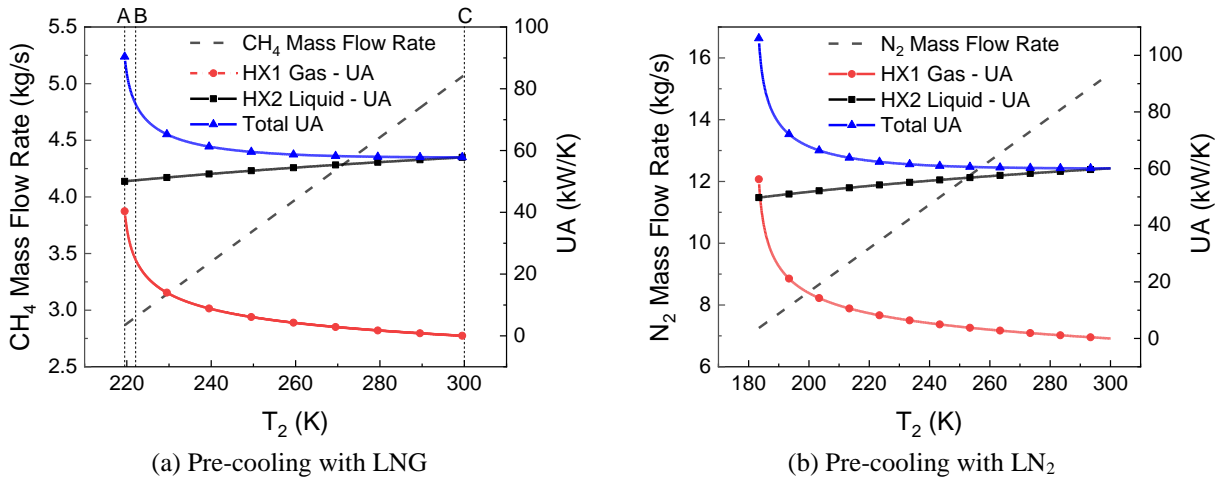
(a) Pre-cooling with LN₂   (b) Pre-cooling with LNG   (c) Pre-cooling with LN₂+LNG(cascade)

Fig. 2. Three types of pre-cooling method.

(a) Pre-cooling with LNG   (b) Pre-cooling with LN₂

Fig. 3. Variation of required amount of the pre-coolant and UA according to T_2.
(All the values are obtained for 1 kg-H_2/s.)

though, they show similar trends. As previously explained, the required UA of each heat exchanger and the amount of pre-coolant are determined by T_2, the temperature at point 2 in Fig. 2-(a) and (b). Since there is a limit to precooling the hydrogen only by gas enthalpy, UA of Gas HX1 exponentially increases as T_2 decreases. When T_2 increases, the amount of cold exergy from the vapor pre-coolant is required less and the smaller UA for the vapor heat exchanging part is required as a result. At the same time, the liquid heat exchanging part needs to take the larger cooling load from the hydrogen. The UA for the liquid heat exchanging part and the amount of the pre-coolant, thus, are required more. The mass flow rate of the pre-coolant can be seen as an indicator of efficiency. While the mass flow rate decreases linearly, the UA increases exponentially in Fig. 3. The three points A, B and C in Fig. 3-(a) are chosen to explain the results more clearly as following. One is Point A with the total UA of 90.4 kW/K

and the mass flow rate of 2.87 kg-CH_4/s, another is Point B with a total UA of 75.0 kW/K and the mass flow rate of 2.94 kg-CH_4/s, and the other is Point C with a total UA of 57.8 kW/K and the mass flow rate of 5.07 kg-CH_4/s. The preceding two points, A and B, require approximately the same mass flow rate, which is about 70% less than Point C. However, the required UA exponentially increases from B to A. In terms of energy efficiency, it is better to make the total UA of the pre-cooler as large as possible. But, the bigger the UA value, the more disadvantageous it brings in terms of space and economy. Therefore, it is necessary to design a pre-cooler that utilizes the cold exergy of boil-off pre-coolant with proper considerations on both the energy and the space efficiency.

3.2. Results of Efficiency Enhancement by the Pre-cooling Method
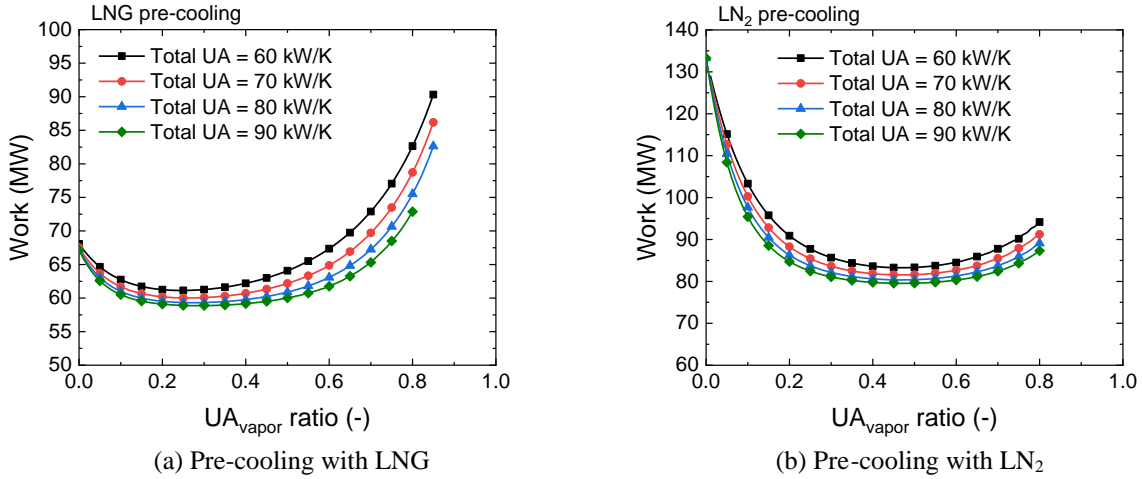In this section, we calculated the total work required to

(a) Pre-cooling with LNG

(b) Pre-cooling with LN₂

Fig. 4. Variation of total required liquefaction work according to UA_{vapor} ratio. (UA_{vapor} ratio is the ratio of the UA of the vapor heat exchanging part to the total UA; All the values are obtained for 1 kg-H2/s.)

liquefy 1 kg/s of hydrogen. The total UA of the pre-cooler was fixed to certain values in order to confirm the effect of the pre-cooling method on the overall efficiency of the hydrogen liquefaction cycle.

Fig. 4. shows the variation of the total work with respect to the UA_{vapor} ratio. UA_{vapor} ratio is defined as the ratio of the UA of the vapor heat exchanging part to the total UA. The total work is the sum of the required work for the pre-coolant production and the required work of the cryogenic refrigerator for liquefying hydrogen.

The results show that liquefaction work decreases as the total UA of the pre- cooler increases. In the constant total UA, the pre-coolant is required less for pre-cooling the hydrogen when the ratio of the UA_{vapor} increases. It leads to the decrease of the required work for pre-coolant production. At the same time, T_3 in Fig. 2-(a) and (b) increases because of the insufficient precooling by the liquid. As a result, the cooling load of the cryogenic refrigerator increases. From these opposite tendencies, the optimal point for achieving the minimum total work exists. When LNG and LN₂ are utilized as the pre-coolants, the optimal UA_{vapor} ratios are 0.27 and 0.47, respectively.

The cascade pre-cooling method is the system which utilized both LNG and LN₂ as the pre-coolants. Fig. 5 shows the required total work according to the UA ratio of 'Liquid HX1', 'Liquid HX2', and 'Vapor HX' in Fig. 2-(c). The results show the trend that the required work decreases as the pre-cooling portion of the LNG increases. When the total UA is 60 kW/K, the minimum required work is found at the ratio of 0.7:0.1:0.2 (LNG: LN₂: vapor HX).

Fig. 6 shows the minimum work for liquefying the 1 kg/s hydrogen at three different pre-cooling methods. The result shows that the efficiency of LNG pre-cooling is higher than that of LN₂ pre-cooling when the total UA of the pre-cooler is fixed. Moreover, the cascade pre-cooling method using both pre-coolants (LNG+LN₂) is the most efficient pre-cooling method. As the total UA increases, the difference of work between the LNG and the cascade precooling method increases.

In the previous discussion, the FOM for pre-coolant production was obtained in the condition of a simple Linde-Hampson cycle where the highest pressure is 200
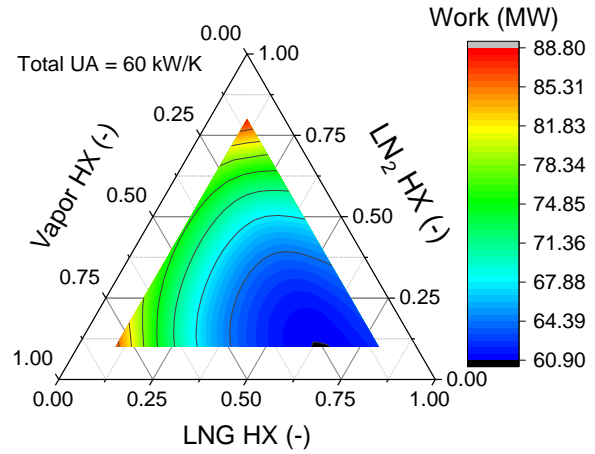

Fig. 5. The required work according to UA ratio of each heat exchanging part in cascade pre-cooling method (All the values are obtained for 1 kg-H₂/s.)
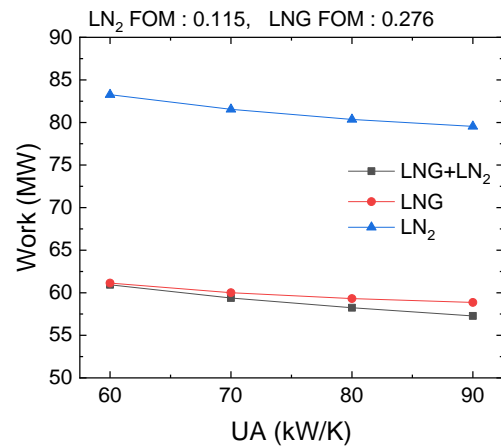

Fig. 6. Minimum required work for each pre-cooling method (All the values are obtained for 1 kg-H₂/s.)

atm [5]. Therefore, the work spent on pre-cooling may have been overrated. We selected the simple pre-coolant production cycle for setting the same condition to each pre-coolant, though, there are more complex cycles which have higher efficiency than the selected cycle. For example, the
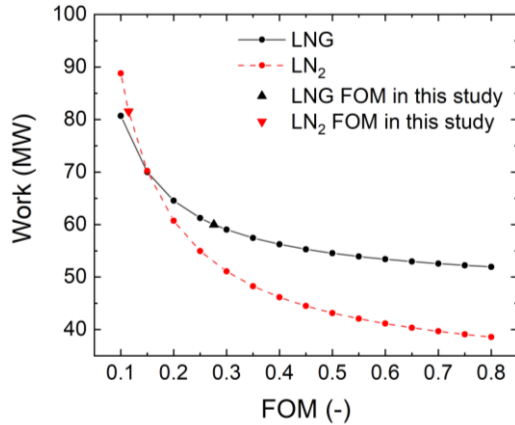
Fig. 7. The minimum required work for hydrogen liquefaction according to FOM for pre-coolant production when total UA is 70 kW/K. (All the values are obtained for 1 kg-H_2/s.)

4-stage propane and 2-stage MR Joule-Thomson cycles that utilized for LNG production can achieve the maximum FOM of 0.805 [7]. Also, the highest FOM of the Kapitza cycle for LN_2 production is approximately 0.78 [8]. It is necessary to confirm the effect of pre-coolant liquefaction FOM on the total hydrogen liquefaction work. The results are shown in Fig. 7.

If the FOM for pre-coolant production changes, the minimum required work for hydrogen liquefaction also changes, and the optimum UA ratio will change as well. That is, we know there is an appropriate UA ratio, but it depends on the conditions. It is definitely necessary to obtain the more detailed actual conditions, such as the FOM of pre-coolant production and the efficiency of the refrigerator.

The results of this study quantitatively show that the efficiency of the hydrogen liquefaction sensitively depends on the pre-cooling conditions and the UA ratio of heat exchanging parts. Therefore, to design the hydrogen liquefaction cycle, the optimum pre-cooling method and UA ratio should be carefully determined according to the conditions, such as the type of pre-coolant and the FOM for pre-coolant production.

4. CONCLUSIONS

Various pre-cooling methods that utilizing LNG and LN_2 as pre-coolants were analyzed to confirm their effects on the hydrogen liquefaction. The conclusions of this study are as follows.

1. The cold exergy of the boil-off pre-coolant was used to improve the pre-cooling efficiency. As a result, reutilizing cold exergy of the boil-off pre-coolant led to efficiency enhancement. Its drawback, however, was the increase of the UA of a pre-cooler. The trade-off between energy efficiency and spatial efficiency should be considered to design pre-cooler.

2. The pre-cooling cycle using each pre-coolant and the cascade pre-cooling cycle using both pre-coolants were compared. In addition, the efficiency changes of the entire cycle according to the UA ratio in the pre-cooler were analyzed. As a result, under the same total UA, the cascade method was the most efficient way among the three different pre-cooling methods for hydrogen liquefaction on our assumptions.

3. When the total UA was fixed, there was a specific UA ratio that maximizes efficiency. Thus, it was important that selecting the optimum portion of the vapor heat exchanging part in the pre-cooler when the total UA of the pre-cooler is limited.

The methodology in this study can be adapted to design the hydrogen liquefaction cycle especially for finding the proper pre-cooling method and the optimum UA ratio inside the pre-cooler.

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