



**Master's Thesis of Engineering** 

# Analysis of electric power consumptionby LNG utilizationin hydrogen liquefaction process수소 액화 공정에서 LNG 활용에 따른전력 사용량 분석

February 2023 Graduate School of Engineering Seoul National University Electrical and Computer Engineering Major

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#### Analysis of electric power consumption by LNG utilization in hydrogen liquefaction process

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February 2023

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#### Abstract

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In response to the climate change crisis, realizing hydrogen economy society that has a higher interest in constructing hydrogen liquefaction plants for efficient storage and transportation is emerging. However, the higher liquefaction cost of hydrogen is a barrier to realizing a hydrogen economy society. Among several methods to resolve the drawback of hydrogen liquefaction, adopting cold energy of liquefied natural gas (LNG) in the hydrogen precooling process and nitrogen re-liquefaction process after the hydrogen precooling is one of the approaches to reducing the cost of hydrogen liquefaction. The Republic of Korea demanded an LNG quantity of 33 Mtons in 2020, driven by power generation, heating, and in the vaporization process, 0.85 Mtoe of cold energy of LNG was meaninglessly dissipated into the sea. This study introduced the 30 TPD large-scaled hydrogen liquefaction plant-based hydrogen precooling that uses nitrogen only and hydrogen precooling that uses not only nitrogen but also cold energy of LNG and analyzed the three types of nitrogen re-liquefaction cycle (Claude, Linde-Hampson, Dual-pressure Linde-Hampson cycle) that applied first two hydrogen precooling. In addition, economic analysis was conducted based on a total of six case studies. Analysis of total usage of liquid nitrogen and cold energy of LNG shows that the case with hydrogen precooling using not only nitrogen but also cold energy of LNG and application of Linde-Hampson cycle for nitrogen re-liquefaction and the case with hydrogen precooling using not only nitrogen but also cold energy of LNG and application of Dual-pressure Linde-Hampson cycle for nitrogen re-liquefaction maximize the utilization of cold energy of LNG and minimize the liquid nitrogen usage. In terms of net power consumption, the latter case shows the lowest power consumption at 2109.46 kW, and its annual electrical cost was calculated as 1.57 MUSD (85 ¢/kW). In conclusion, in the utilization of cold energy of LNG, the case with hydrogen precooling using not only nitrogen but also cold energy of LNG and application of Dual-pressure Linde-Hampson cycle for nitrogen re-liquefaction has 66% lower net power consumption compared to the case with hydrogen precooling using nitrogen and the application of Claude cycle for nitrogen re-liquefaction.

**Keyword:** Hydrogen liquefaction, Hydrogen precooling, Liquefied natural gas (LNG), Ortho-Para hydrogen conversion (OPHC), Nitrogen (N2) re-liquefaction **Student Number:** 2020-24830

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#### **Chapter 1. Introduction**

#### 1.1 Necessity and Background

As the climate change crisis is encountered, there are global aims to reach carbon neutrality by 2050, and the world is gathering its capability in increasing renewable power generation [1]. Whilst facing this crisis, renewable energy has its own problems, such as being intermittent in nature, having a large varying power output and having a low operating rate [2, 3]. Although the problems with intermittency and varying power output may be inevitable, the operation stoppage caused by the difference in supply and demand of the renewable power and the power grid could be resolved by storing energy using Energy Storage System (ESS) which stores and supply electrical energy when power is needed[4, 18]. Nonetheless, poor storage safety with relatively high capital cost is a drawback of ESS [5, 19]. For the efficient operation of a renewable energy-based power system, a water electrolysis that produces and stores energy in the form of hydrogen is one of the alternative methods [6]. To realize a hydrogen economy society, more concentration on producing green hydrogen through a water electrolysis process using renewable energy resources is required [7]. Typically, hydrogen can be stored in the form of gaseous hydrogen and liquid hydrogen. Gaseous hydrogen has low energy density per volume and its stability is low since gaseous hydrogen is highly-compressed with 700 bar, on the other hand, liquid nitrogen can be stored with low risk since it is stored with normal pressure (10 bar) and its volume is reduced by more than 800 times compared to gaseous hydrogen. Therefore hydrogen liquefaction is required to store and transport hydrogen efficiently [8].

However, high liquefaction cost is the drawback of liquid hydrogen. In order to overcome high liquefaction cost, many studies have increased their scrutiny of hydrogen liquefaction efficiency and cost reduction [9, 10, 11, 13, 15, 16, 20, 21, 22, 23]. In general, there are three ways of reducing the liquefaction cost. The first is increasing the plant's capacity [8, 10, 11], the second is improving the efficiency of the refrigeration cycle [11, 13, 17], and the last is adopting cold energy of liquefied natural gas (LNG) for hydrogen liquefaction process [17, 20, 21, 22, 23].

#### 1.1.1 Characteristic of hydrogen

Hydrogen consists of two forms, ortho-hydrogen and para-hydrogen. These two are determined according to the direction of the nuclear spin of each atom of the hydrogen molecule. If two hydrogen atoms rotate in the same direction, it is called ortho-hydrogen, and it is entitled as para-hydrogen when each atom rotates in the opposite direction.



Figure 1. Ortho-Para hydrogen overview

As shown in Fig.1, at 300K, the fraction of ortho and para-hydrogen is 75:25, at 77K, the fraction becomes 50:50 and ortho-hydrogen to para-hydrogen fraction ratio turns into 0.2:99.8 at 20.3K before liquefaction begins at 1 atm. In the process of ortho-para hydrogen conversion, the heat of 527.138 kJ/kg is generated, and this heat is greater than the latent heat of hydrogen, which is 448.71 kJ/kg [24, 25]. Therefore, it is essential to convert it into para-hydrogen before liquefaction using an ortho-para hydrogen converter (OPHC), and liquefy it for long-term storage purpose [26]. Fig.2 shows the overview of para-hydrogen. It represents the theoretical exothermic heat and the actual exothermic heat of para-hydrogen according to temperature. Theoretically, the exothermic heat which is 27.562 kJ/kg at 300K is the heat that already released into the air. Thus, it is unnecessary to account for the hydrogen liquefaction process. The real exothermic heat that represented as blue line is calculated according to the mathematical expression (1).



Figure 2.Para hydrogen graph overview

$$Q_{ex} = \frac{Para\% - Para\%@300K}{100\% - Para\%@300K} = kJ/kg$$
(1)

Where,

 $Q_{ex}$  = The actual amount of heat to be cooled at the specific temperature

Para% = Para hydrogen fraction at the specific temperature

Para @300K = Para hydrogen fraction at 300K

## 1.1.2 Current state of hydrogen liquefaction plant worldwide



Figure 3. Hydrogen liquefaction cycle per capacity

Fig.3 [27] shows the hydrogen liquefaction cycle depending on the capacity. The hydrogen liquefaction plant uses different refrigeration cycles in accordance with the plant capacity. In most cases, a liquefaction plant of 1~5 TPD or less capacity uses the helium Brayton cycle, and the medium bulk size of 30 TPD or less uses the hydrogen Claude cycle[24, 25]. As shown in Fig.4 [28], capacity of about 30 TPD is the largest plant size among existing hydrogen liquefaction plant.

Continent/Country	Location	Operated by	Capacity (TPD)	Commissioned in	Still in operation
America					
Canada	Sarnia	Air Products	30	1982	Yes
Canada	Montreal	Air Liquide	10	1986	Yes
		Canada Inc.			
Canada	Becancour	Air Liquide	12	1988	Yes
Canada	Magog, Quebec	BOC	15	1989	Yes
Canada	Montreal	BOC	14	1990	Yes
French Guyane	Kourou	Air Liquide	5	1990	Yes
USA	Painsville	Air Products	3ª	1957	No
USA	West Palm Beach	Air Products	3.2ª	1957	No
USA	West Palm Beach	Air Products	27 <sup>a</sup>	1959	No
USA	Mississippi	Air Products	32.7 <sup>a</sup>	1960	No
USA	Ontario	Praxair	20	1962	Yes
USA	Sacramento	Union Carbide,	54ª	1964	No
		Linde Div.			
USA	New Orleans	Air Products	34	1977	Yes
USA	New Orleans	Air Products	34	1978	Yes
USA	Niagara Falls	Praxair	18	1981	Yes
USA	Sacramento	Air Products	6	1986	Yes
USA	Niagara Falls	Praxair	18	1989	Yes
USA	Pace	Air Products	30	1994	Yes
USA	McIntosh	Praxair	24	1995	Yes
USA	East Chicago, IN	Praxair	30	1997	Yes
Subtotal			300		
Europe					
France	Lille	Air Liquide	10	1987	Yes
Germany	lngolstadt	Linde	4.4	1991	Yes
Germany	Leuna	Linde	5	2008	Yes
Netherlands	Rosenburg	Air Products	5	1987	Yes
Subtotal	-		24.4		
Asia					
China	Beijing	CALT	0.6	1995	Yes
India	Mahendragiri	ISRO	0.3	1992	Yes
India	India	Asiatic Oxygen	1.2	-	Yes
India	Saggonda	Andhra Sugars	1.2	2004	Yes
Japan	Amagasaki	Iwatani	1.2ª	1978	No
Japan	Tashiro	MHI	0.6 <sup>a</sup>	1984	No
Japan	Akita Prefecture	Tashiro	0.7	1985	Yes
Japan	Oita	Pacific Hydrogen	1.4	1986	Yes
Japan	Tane-Ga-Shima	Japan Liquid Hydrogen	1.4	1986	Yes
Japan	Minamitane	Japan Liquid Hydrogen	2.2	1987	Yes
Japan	Kimitsu	Air Products	0.3	2003	Yes
Japan	Osaka	Iwatani (Hydro Edge)	11.3	2006	Yes
Japan	Tokyo	Iwatani, built by Linde	10	2008	Yes
Subtotal			30.6		
Worldwide			355		
a Not included in the su	ubtotal of the capacity	for the year 2009.			

Figure 4. Hydrogen liquefaction cycle per capacity

## 1.1.3 Current state of hydrogen liquefaction plant in the republic of Korea

In 2019, Korean government announced a roadmap to activate the hydrogen economy by increasing hydrogen use from 0.2 million tons per year to 3.9 million tons and increasing the clean hydrogen ratio to 50% by 2030 and 100% by 2050, by establishing a million tons of clean hydrogen production system. In the republic of Korea, 0.5 (Korea Institute of Machinery and Materials), 5 (Changwon city + Doosan Enerbility CO., LTD + Air Liquide), 30 (Hyosung + Linde), and 100 TPD (SK E&S) liquefaction plants are currently under construction or in the process of constructing. Changwon city is planning to commercialize the liquid hydrogen from the year of 2023.

## 1.1.4 Current state of LNG usage in the republic of Korea

Based on the data of LNG usage of Korea in 2020, the total quantity demand of LNG for power generation and heating was 32 Mtons per year, and about 1.3 Mtoe of cold energy was dissipated annually[29,30]. Many debates are being conducted harvesting cold energy from LNG to construct a more economical hydrogen liquefaction plant due to cold energy from LNG makes less consumption of liquid nitrogen (LN2).

#### 1.2 Literature review

In several similar conceptual studies using cold energy of LNG in hydrogen liquefaction, Yang et al. [19] found that the usage of a combination of LN2 and cold energy of LNG is more efficient than that of operating separately. Chang et al. [15] investigated thermodynamic effect of precooling using cold energy of LNG with standard and modified Brayton refrigeration cycles for hydrogen liquefaction plant. Cardella et al. [12] analyzed the cost reduction of the overall hydrogen liquefaction process, including the capital and operating costs of the liquefaction plant. Riaz et al. [20] simulated the system that reduced the amount of refrigerant required by 50% using Aspen HYSYS commercial software to remove unnecessary precooling cycles of hydrogen liquefaction using cold energy of LNG, resulting in a 40% reduction in specific energy consumption (SEC). Bian et al. [18] simulated a hydrogen liquefaction process using a dual-pressure Brayton cascaded cycle and precooling of hydrogen required for hydrogen liquefaction using LNG to reduce the energy consumption and capital cost of hydrogen liquefaction. As mentioned above, prior investigations have implemented cold energy of LNG usage in the hydrogen liquefaction plant. However, little research has been conducted to show the advanced application of cold energy of LNG.

#### 1.3 Objectives

In order to liquefy hydrogen, it is essential to precool hydrogen from 300K to about 80K using LN2. This work is to explore the utilization of cold energy from LNG for not only hydrogen precooling but also for liquefying gaseous nitrogen that heat exchanged with hydrogen to reduce the hydrogen liquefaction cost. The capacity of 30 TPD was determined based on the commercialized large-scaled hydrogen liquefaction plant worldwide. This work aims at maximize cold energy of LNG in hydrogen precooling and nitrogen re-liquefaction, less usage of LN2 and less usage of power consumption in nitrogen re-liquefaction showing several case studies. Two hydrogen cooling types such as LN2 as a coolant only and the combination of LN2 and LNG will be carried out primarily to compare the LN2 usage. Subsequently, two hydrogen precooling types with three different cycle for the nitrogen re-liquefaction using Claude, Linde-Hampson cycle, and Dual pressure Linde-Hampson cycle will be conducted. Upon the results of the total 6 case studies, the detail analysis of usage of cold energy of LNG and LN2, and the net power consumption will be carried out towards the capacity of 30 TPD hydrogen liquefaction plant.

#### Chapter 2. Case Overview

CASE	112 mussooling tomo	N2 Re-liquefaction Cycle		
CASE	H2 precooling type	Cycle	N2 precooling type	
CASE 1	LN2	Classific and		
CASE 2	LN2 and LNG	Claude cycle	-	
CASE 3	LN2	T is to TT and a second		
CASE 4	LN2 and LNG	Linde-Hampson cycle	LNG	
CASE 5	LN2	Dual-pressure		
CASE 6	LN2 and LNG	Linde-Hampson cycle	LNG	

Table 1.Simulation case overview

The following is an overview of each case by applying the cold energy of LNG to the hydrogen precooling methods and the re-liquefaction cycles of nitrogen. A total of six case studies are conducted. Hydrogen precooling is divided into two methods such as LN2 only and the mixture of LN2 and the cold energy of LNG. After hydrogen precooling, nitrogen re-liquefaction is conducted, divided into three cycles: Claude, Linde-Hampson, and Dual-pressure Linde-Hampson cycle. In addition, this study tries to compare the general re-liquefaction cycle, which is the Claude cycle, with other advanced cycles that adopt the cold energy of LNG. The following Fig. 5 (a) shows the general process of hydrogen precooling from 300K to 80K using about 80K of LN2 performing OPHC. The boiling point of nitrogen is 77K at atmospheric pressure; however, since the pressure value is 1.3, the temperature changes to 79.53K. Fig. 5 (b) uses the same hydrogen and LN2 value, but the application of the cold energy of LNG is a big difference. From Fig.6 to Fig.8, the application of the nitrogen re-liquefaction cycle will be shown. The reason for re-liquefying nitrogen is that gaseous nitrogen needs to be re-liquefied so that the LN2 cycle can precool hydrogen to 80K. In Fig.6 (a), the LN2 that heat exchanged with hydrogen becomes gaseous nitrogen, a high-pressure, high-temperature state through a compressor. After that, it passes the aftercooler to release heat, and it becomes gaseous nitrogen at 300K with 97 bar. A three-stage heat exchanger and adiabatic JT expansion reached the desired temperature, 79.53 K. In the separator, liquid par is used for hydrogen precooling, and the gaseous part goes back to the three-stage heat exchanger. The gaseous nitrogen is combined before the compressor, and it circulates. The expander in the middle of the heat exchanger reduces the temperature difference between the heat exchanger. Fig.6 (b) uses the same nitrogen re-liquefaction cycle as Fig.6 (a). However, the utilization of cold energy of LNG for hydrogen precooling is the big difference between them. Fig.7 (a), (b) represents the application of the Linde-Hampson cycle in two hydrogen precooling types. Unlike Claude represented in Fig 6. (a), (b), the Linde-Hampson cycle does not use an expander since LNG's cold energy sufficiently lower the nitrogen temperature in the nitrogen re-liquefaction process. Fig.8 (a),(b) shows the application of the Dual-Pressure Linde-Hampson cycle with hydrogen precooling. The feature of the cycle is a dual compressor that reduces the work of the compressor and increases the efficiency of the whole cycle, especially in nitrogen re-liquefaction passes, two compressors, two aftercoolers, two JT valves, and two-phase separators. This cycle is more efficient than the simple Linde-Hampson cycle since its compressor work is reduced.



Figure 5. Simplified diagram of hydrogen precooling

(a) Hydrogen precooling with LN2 only (b) Hydrogen precooling with LN2 and LNG



Figure 6.Simplified diagram of Claude cycle for nitrogen re-liquefaction

(a) Hydrogen precooling with LN2 + Claude cycle

(b) Hydrogen precooling with LN2 and LNG + Claude cycle



Figure 7.Simplified diagram of Linde-Hampson cycle for nitrogen re-liquefaction
(a) Hydrogen precooling with LN2 + Linde-Hampson cycle + N2 precooling with LNG
(b) Hydrogen precooling with LN2 and LNG + Linde-Hampson cycle + N2 precooling with LNG



Figure 8.Simplified diagram of Dual-pressure Linde-Hampson cycle for nitrogen re-liquefaction
(a) Hydrogen precooling with LN2 + Dual-pressure Linde-Hampson cycle + N2 precooling with LNG
(b) Hydrogen precooling with LN2 and LNG + Dual-pressure Linde-Hampson cycle + N2 precooling with LNG

#### Chapter 3. Methodology

#### 3.1 Aspen HYSYS simulation

This study uses a process simulation program for thermodynamic design of hydrogen liquefaction cycle called Aspen HYSYS. Following the flow chart in Fig., nitrogen, hydrogen and methane are chosen for the component list, and RefProp, the property program that invented by NIST is selected as the fluid packages. After the unit setting for the whole simulation process, the stream stetting and the equipment setting need to be decided. Stream setting consists of two streams such as flow stream and energy stream. The composition ratio of the fluid and the thermodynamic state of the fluid are determined in flow stream, and the information about heat and work can be decided in the energy stream. Through the equipment setting, insulation efficiency of the compressor and the expander is determined. Also, the pressure drop on the exchanger is determined.



Figure 9.Flow chart of Aspen HYSYS

#### 3.2 Conditions and assumptions in HYSYS

The following assumptions and conditions are made for the simulation.

- (a) 30 TPD-based hydrogen liquefaction plant is selected as a plant capacity.
- (b) The pressure mentioned is an absolute pressure
- (c) The pressure drops are set to be 0.3 bar for a liquid-to-gas or gas-to-liquid,0.1 bar for gas-to-gas, 0.5 bar for a liquid-to-liquid, and 0.1 bar for OPHC
- (d) The minimum pressure of gaseous nitrogen after heat exchange is set to 1 bar
- (e) The temperature value and the pressure value of LNG are set to 128K and 75 bar based on the reference from the Korea Gas Corporation (KOGAS)
- (f) The composition of LNG is assumed as 100% of methane.
- (g) The minimum temperature difference of the heat exchanger is set to 1.5% by △T/T.
- (h) REFPROP is chosen for the data on Aspen HYSYS
- (i) Adiabatic efficiency of the compressor and expander is set to 85% based on the general liquid air energy storage (LAES) system
- (j) 4-stage compression and 4-stage aftercooling are done based on the general liquid air energy storage (LAES) system

#### **Chapter 4. Simulation Results**

#### 4.1 H2 precooling

#### 4.1.1 Hydrogen precooling with LN2 only



Figure 10. Simulation result of hydrogen precooling with LN2 only

Case 1 shows the standard hydrogen precooling process. GH2, 1 (2.3 bar, 300K) and LN2 (1.3 bar, 79.53K) exchanged heat in LN2-HEX. The output of GH2 was set to 2.1bar in accordance with the assumption, and the output temperature was determined according to the value of nitrogen temperature. In the OPHC process, duty of 54.82 kW has occurred due to the heat generated by isothermal conversion. In this process, an LN2 of 214.1 tonne/day(TPD) was calculated, which is almost seven times higher than the mass flow rate of the GH2, 1. In the actual liquefaction process, GN2 should go to the nitrogen liquefaction plant. However, this case explains the hydrogen precooling partially. In cases (3), (5), and (6), this partial stage will be applied as hydrogen precooling stage.

#### 4.1.2 Hydrogen precooling with LN2 and LNG



Figure 11.Simulation result of hydrogen precooling with LN2 and LNG

In this case, two-stage heat exchangers, LNG-HEX and LN2-HEX were placed to precool hydrogen. LNG-HEX contains LN2 and LNG and was used to cool down hydrogen from 300K to 135K. The specification of LN2-HEX is the same as the case (1). The output pressure and the temperature of hydrogen became 2 bar, 81.43K. GN2 from LNG-HEX heat exchanged in LNG-HEX once again. As a result, the LN2 consumption became 91.46 TPD and the LNG consumption became 68.11 TPD. By applying LNG heat exchanger, LN2 was reduced by 122.64 TPD compared to case (1). As already mentioned in case (1), GN2 should flow to the nitrogen liquefaction plant. However, this case partially explains the hydrogen precooling that adopting LNG-HEX. In cases (4), (7), and (8), this partial stage will be applied as hydrogen precooling stage.

# 4.2 Claude cycle for nitrogen re-liquefaction4.2.1 Case (1): Hydrogen precooling with LN2 + Claude cycle

The inlet/outlet flow conditions of the LN2 HEX for hydrogen precooling are the same as in case (1). After heat exchange with hydrogen, saturated liquid nitrogen of 1.3 bar becomes a GN2 state of 295.5 K and 1 bar. This nitrogen is combined with 589.3 TPD gas nitrogen with the same temperature pressure of 295.5K from liquefier. It passes GN2 HEX-1 under а а high-temperature-high-pressure state of 300K, 97 bar after four stages of compression and four stages of aftercooler. The high-temperature-high-pressure flow is then divided into GN2 HEX-2 or expanders. The flow to the expander becomes a low-temperature – low-pressure state of 91.04K, 1.2 bar. After that, it is injected into the low-temperature fluid inlet of GN2 HEX-2. The flow that does not pass through the expander heat exchanges with low temperature-low pressure nitrogen at GN2 HEX-2 and GN2 HEX-3 and is injected into the phase separator under a saturated state through the isenthalpic expansion process through the J-T (Joule-Thomson) valve. A liquid in saturated nitrogen in the phase separator is injected into the LN2-HEX of the precooling hydrogen cycle as a low-temperature fluid. In the phase separator, the gas in the saturated nitrogen works as a low-temperature – low-pressure fluid that cool down high-temperature – high-pressure nitrogen in the nitrogen liquefaction cycle. It was calculated that the compression flow rate required to produce liquid nitrogen was 803.4 TPD. The net

power consumption for the entire cycle is 4362.50 kW.



Figure 12.Simulation result of hydrogen precooling with LN2 + Claude cycle

## 4.2.2 Case (2): Hydrogen precooling with LN2 and LNG + Claude cycle

In Figure 9, after heat exchange with hydrogen, saturated liquid nitrogen becomes a GN2 state of 133K and 1.1 bar. Afterward, 295.5K, 1 bar of gaseous nitrogen is combined with 249.4 TPD of the same temperature pressure of 295.5K, which is heat-exchanged with high-temperature-high-pressure nitrogen in a nitrogen liquefier, and passes GN2-HEX 1 under high pressure of 300K, 102 bar through four stages of compression and cooling. High-temperature-high-pressure flow is then divided into GN2-HEX 2 or expanders. The flow passes through the expander and turns into a low-temperature and low-pressure state of 92.27K and 1.3 bar. It is injected into the low-temperature fluid inlet of GN2-HEX 2. The gas that does not pass through the expander heat exchanges with low-temperature low-pressure nitrogen at GN2-HEX 2 and GN2-HEX 3, then injected into the phase separator in a saturated state through the isenthalpic expansion process through the J-T valve. In the phase separator, a liquid in saturated nitrogen is injected as a low-temperature fluid into the LN2-HEX of the hydrogen precooling cycle. The gas of the saturated nitrogen in the phase separator, low-temperature low-pressure fluid, is working as a coolant for cooling high-temperature high-pressure. It was calculated that the compression flow rate required to produce liquid nitrogen was 340.8 TPD. The net power consumption for the entire cycle is 1881.99 kW.



Figure 13.Simulation result of hydrogen precooling with LN2 and LNG + Claude cycle

# 4.3 Linde-Hampson cycle for nitrogen re-liquefaction 4.3.1 Case (3): Hydrogen precooling with LN2 + Linde-Hampson cycle + N2 precooling with LNG

Figure.10 shows that the nitrogen liquefaction cycle of hydrogen precooling by applying a Precooling Linde-Hampson cycle to case (1). Unlike cases (3) and (4) which applied the Claude cycle, 128K of LNG sufficiently cools high-pressurehigh-temperature of nitrogen GN2, 1 (300K, 230 bar) to GN2, 2 (155.2K, 229.9 bar). Unlike Claude cycle, precooling Linde-Hampson cycle does not require expander, and only J-T valve is required. This means that flow rate ratio does not need to be adjusted. Since it does not use an expander, investment costs are reduced. Moreover, efficiency of the system is also better because it uses LNG's cold energy. The conditions of LN2-HEX for hydrogen precooling are the same as in cases (1) and (3). 295.5K, 1 bar of GN2 is combined with the GN2,7 from the nitrogen liquefaction cycle to undergo a four-stage compression and a four-stage after coolers. After the compression/aftercooling stages, the fluid passes through GN2-HEX1 and GN2-HEX 2 to become GN2, 3 (131.2K, 229.8 bar). Then expansion is done with J-T valve and it becomes G/LN2 2, 4 (79.53K, 1.3 bar). This saturated temperature and pressure values are then injected into the phase separator. The gaseous nitrogen from the separator go through GN2-HEX 2 and GN2-HEX 1 to become GN2, 7 and this value is mixed with the nitrogen that precooled hydrogen at LN2-HEX. The net power consumption consumed in this cycle is 4196.29 kW.



Figure 14. Simulation result of hydrogen precooling with LN2 + Linde-Hampson cycle + N2 precooling with LNG

## 4.3.2 Case (4): Hydrogen precooling with LN2 and LNG+ Linde-Hampson cycle + N2 precooling with LNG

Figure 11. shows the modified version of the nitrogen liquefaction cycle of hydrogen precooling by applying a precooling dual pressure Linde-Hampson cycle to the case (1). The conditions of LN2-HEX for hydrogen precooling are the same as in cases (1) and (3). 295.5K, 1 bar of GN2 is combined with the low-temperature-low-pressure from the nitrogen liquefaction cycle to undergo a two-stage compression and a two-stage after coolers. The fluid is mixed with GN2, 7 (295.5K, 13.3 bar) from the cycle and undergoes a two-stage compression and after cooling process again to become 180 bar of GN2 at 300K then operates with high-temperature - high-pressure fluid in GN2 HEX-1. The fluid heat exchanges through GN2-HEX1 and GN2-HEX2 to become GN2, 3, and then injected into the first phase separator as a saturated fluid of 108.6K, 13.5 bar by J-T expansion. The fluid of the first phase separator operates as a low-temperature - medium - pressure fluid and becomes the state of GN2, 7 as described above. The liquid in the first phase separator reaches a saturation of 13.5 bar through adiabatic expansion. The saturated fluid enters the separator 2 and reaches GN2, 12 through GN2 HEX-2 and GN2 HEX-1, and is mixed with nitrogen that precooled with hydrogen for a compression and cooling process again. The LN2 liquefied in the separator 2 enters the LN2-HEX for hydrogen precooling again. The net power consumption consumed in this cycle is 3478.18 kW.



Figure 15. Simulation result of hydrogen precooling with LN2 and LNG + Linde-Hampson cycle + N2 precooling with LNG

## 4.4 Dual-Pressure Linde-Hampson cycle for nitrogen re-liquefaction

4.4.1 Case (5): Hydrogen precooling with LN2 + Dual-Pressure Linde-Hampson cycle + N2 precooling with LNG

The conditions of LN2-HEX for precooling hydrogen are the same as those of cases (2) and (4). In this cycle, precooling Linde-Hampson cycle is applied. 295.5K, 1 bar of GN2 is combined with GN2, 8(295.5K, 1.2 bar) from the nitrogen liquefaction cycle to undergo a four-stage compression and a four-stage aftercooling process. The fluid then becomes GN2.2 (300K, 230 bar) to go through GN2-HEX 1 and GN2-HEX 2. After heat exchange with prior stages, the temperature and the pressure becomes GN2, 4 at 131.4K with 229.8 bar. Then reaches the J-T valve for adiabatic expansion. The nitrogen becomes a saturated value at 80.21 K with 1.4 bar. The gaseous nitrogen from the phase separator flows through GN2-HEX 2 and GN2-HEX to become GN2, 8. The liquid state from the phase separator goes back to the cycle for precooling hydrogen. Through this cycle, 1783.38 kW of net power consumption is calculated.



Figure 16. Simulation result of hydrogen precooling with LN2 + Dual-pressure Linde-Hampson cycle + N2 precooling with LNG

## 4.4.2 Case (6): Hydrogen precooling with LN2 and LNG + Dual-Pressure Linde-Hampson cycle + N2 precooling with LNG

Case (8) has the same LN2-HEX and LNG-HEX conditions as cases (2) and (4) for precooling hydrogen. The precooling dual pressure Linde-Hampson cycle is applied in this cycle. 295.5K, 1 bar of GN2 is combined with the low-temperaturelow-pressure from the nitrogen liquefaction cycle to go through a two-stage compression and a two-stage aftercooling process. The fluid is mixed with GN2, 8 (295.5K, 13.3 bar) from the cycle and passes a two-stage compression and aftercooling process to become 180 bar and 300K of GN2, 2. The value of GN2, 2 Operates as high-temperature – high-pressure fluid in GN2 HEX-1. The nitrogen acquires cold energy of LNG at GN2 HEX-1, and this flow passes GN2 HEX-2 for further heat exchange and then reaches the J-T valve 1 for adiabatic expansion. The nitrogen becomes a saturated value at 108.8 K with 13.5 bar. The saturated state value of the first phase separator operates as a medium-pressure – low-temperature. The gaseous nitrogen from the first separator goes back to 2-stage compression and 2-stage aftercooling through GN2 HEX-2 and GN2 HEX-1. The liquid state from the first phase separator reaches a 79.53K, 13 bar of saturated value through adiabatic expansion with J-T valve 2. The saturated value enters separator 2, and gaseous nitrogen reaches GN2-12 (295.5K, 1.1 bar) through GN2 HEX-2 and GN2 HEX-1, then mixed with GN2 that precooled hydrogen. The mixed value of GN2 goes back to the compression/aftercooling cycle, and the cycle circulates. The liquid state from separator 2 enters the LN2-HEX for hydrogen precooling.

Through this cycle, 1476.62 kW of net power consumption is calculated.



Figure 17. Simulation result of hydrogen precooling with LN2 and LNG + Dual-pressure Linde-Hampson cycle + N2 precooling with LNG

#### Chapter 4. Discussion

Table 2. Total LN2 and LNG usage

LN2 and LNG consumption								
	CASE 1 CASE 2 CASE 3 CASE 4 CASE 5 CASE							
LN2 [TPD]	803.4	340.8	514.2	218.5	580.7	246.8		
LNG [TPD]	-	68.11	99.16	110.4	100.9	111.1		

Table 3. Total LN2 and LNG usage considering 30% heat loss

LN2 and LNG consumption (30% heat loss consideration)						
	CASE 1	CASE 2	CASE 3	CASE 4	CASE 5	CASE 6
LN2 [TPD]	1044	443	668.5	284.1	754.9	320.8
LNG [TPD]	-	88.54	128.9	143.5	131.2	144.4



Figure.18 Comparison of total LN2 and LNG usage by cases

In order to identify the most economic nitrogen re-liquefaction cycle for the hydrogen liquefaction plant, total usage of LN2 and LNG are compared in table. 2. Table.3 shows the result that takes into account of 30% heat loss. In Fig.18 the grey columns represents the LN2 usage and the grey with line shows the usage of LNG cold energy. Since case 1 does not use the cold energy of LNG, only LN2 usage is represented and it shows the highest consumption of LN2 at 803.4 TPD. Since the purpose of the study is to reduce the usage of LN2 by maximizing the cold energy of LNG, case 4 and case 6 were chosen for the highest cold energy of LNG utilization cases which are at 143.5 and 144.4 TPD respectively. By comparing case 4 and case 6, the most efficient case was determine as case 4 because its LN2 usage are 40 TPD less than case 6.

Cost of electrical energy							
	CASE	CASE	CASE	CASE	CASE	CASE	
	1	2	3	4	5	6	
Net power							
Consumption	6232	2689	5995	2548	4969	2109	
[kW]							
<b>Total Cost</b>	16 M	2 M	4.5 M	1 0 M	37M	16 M	
[USD/yr]	4.0 M	∠ I <b>VI</b>	4.J IVI	1.7 IVI	5.7 IVI	1.0 101	

Table.4 Total cost of electrical energy



Fig.19 Comparison of total cost of electrical energy by cases

<b>Comparison of CASE 4 &amp; CASE 6</b>							
High PressrueMass Flow Rate							
CASE 4	1 bar	-	230 bar	284.05	5 TPD		
CASE 6	1 bar	13.5 bar	180 bar	158.29 TPD	320.84 TPD		

Table.5 Comparison of case 4 and case 6

Table.5 and Fig.19 compare the total cost of electrical energy by cases. As mentioned before, case 4 and case 6 utilized the maximum cold energy of LNG. Even in the total cost analysis, cases 4 and 6 show the lowest net power consumption. However, contrary to the result of LN2 power consumption, case 6 shows the lowest net power consumption than case 4. This explains in Table.5. Since case 4 compressed the gaseous nitrogen from 1 bar to 230 bar at once, but case 6 compressed the gaseous nitrogen from 1 bar to 13.5 bar than 180 bar. Therefore, case 4 required more work than case 6. Comparing case 1, which uses the Claude cycle for nitrogen re-liquefaction and is known as the general liquefaction cycle, with case 6, case 6 saved 66% of net power consumption. To sum up all the analyses, Case 6 is suitable for hydrogen precooling with nitrogen re-liquefaction.

#### Chapter 5. Conclusion

30 TPD hydrogen liquefaction-based hydrogen precooling with nitrogen re-liquefaction using cold energy of LNG was investigated, aiming at less usage of LN2, higher utilization of cold energy of LNG and less power consumption in nitrogen re-liquefaction. Two types of hydrogen precooling, along with ortho-para conversion, were shown initially to compare the usage of LN2 by applying cold energy of LNG in hydrogen precooling. After that, six case studies containing hydrogen precooling with different types of nitrogen re-liquefaction cycles, such as Claude, Linde-Hampson, and dual-pressure Linde-Hampson cycles, were simulated. 30% of the heat loss was considered as the result of LN2, cold energy of LNG, and net power consumption. Compared to the usage of cold energy of LNG and LN2, cases 4 and 6 showed the highest utilization of the cold energy of LNG. By comparing these two, case 4 represented the lowest LN2 usage. Even though the lowest LN2 usage was represented by case 4, which is 284 TPD, surprisingly, case 6 showed the lowest net power consumption, 2109 kW, after considering 30% heat loss. This is because case 4 compressed the 284 TPD of nitrogen from 1 bar to 230 bar at once. Therefore, higher work is required for compression. On the other hand, case 6 compressed 320TPD of nitrogen from 1 bar to 13.5 bar then the final compression was done. This explains the existence of middle pressure, requiring less work than in case 4. Consequently, it is revealed that using the cold energy of LNG for hydrogen precooling and nitrogen re-liquefaction is far superior to that of without using the cold energy of LNG. Also, applying the dual-pressure Linde-Hampson cycle for nitrogen re-liquefaction saved 66% of net power consumption than the general Claude cycle.

#### References

[1] Bouckaert, Stéphanie, et al. Net Zero by 2050: A Roadmap for the Global Energy Sector. 2021.

[2] Notton, Gilles, et al. Intermittent and stochastic character of renewable energy sources: Consequences, cost of intermittence and benefit of forecasting. Renewable and sustainable energy reviews, 2018, 87: 96-105.

[3] Abjard, Saleh Y.; MUSTAFA, Mohammad Wazir; JAMIAN, Jasrul Jamani. Recent approaches of unit commitment in the presence of intermittent renewable energy resources: A review. Renewable and Sustainable Energy Reviews, 2017, 70: 215-223.

[4] Beaudin, Marc, et al. Energy storage for mitigating the variability of renewable electricity sources: An updated review. Energy for sustainable development, 2010, 14.4: 302-314.

[5] Chen, Haisheng, et al. Progress in electrical energy storage system: A critical review. Progress in natural science, 2009, 19.3: 291-312.

[6] Buttler, Alexander; Spliethoff, Hartmut. Current status of water electrolysis for energy storage, grid balancing and sector coupling via power-to-gas and power-to-liquids: A review. Renewable and Sustainable Energy Reviews, 2018, 82: 2440-2454.

[7] Dincer, Ibrahim. Green methods for hydrogen production. International journal of hydrogen energy, 2012, 37.2: 1954-1971.

[8] Cardella, U.; Decker, L.; Klein, H. Roadmap to economically viable

3 8

hydrogen liquefaction. International Journal of Hydrogen Energy, 2017, 42.19: 13329-13338.

[9] Zhang, Jinsong, et al. A review of heat transfer issues in hydrogen storage technologies. 2005.

[10] Yin, Liang; JU, Yonglin. Review on the design and optimization of hydrogen liquefaction processes. Frontiers in Energy, 2020, 14.3: 530-544.

[11] Krasae-in, Songwut; STANG, Jacob H.; NEKSA, Petter. Development of large-scale hydrogen liquefaction processes from 1898 to 2009. International journal of hydrogen energy, 2010, 35.10: 4524-4533.

[12] Cardella, U., et al. Process optimization for large-scale hydrogen liquefaction. International Journal of Hydrogen Energy, 2017, 42.17: 12339-12354.

[13] S.K. Yun, Design and analysis for hydrogen liquefaction process usingLNG cold energy, Journal of the Korean Institute of Gas 15(3) (2011) 1-5.

[14] Y. Yang, T. Park, D. Kwon, L. Jin, S. Jeong, Effectiveness analysis of pre-cooling methods on hydrogen liquefaction process, Progress in Superconductivity and Cryogenics 22(3) (2020) 20-24.

[15] H.M. Chang, B.H. Kim, B. Choi, Hydrogen liquefaction process with Brayton refrigeration cycle to utilize the cold energy of LNG, Cryogenics 108 (2020) 103093.

[16] D. Rosewater, A. Williams, Analyzing system safety in lithium-ion grid energy storage, Journal of Power Sources 300(2015) 460-471.

[17] P. Ribiere, S. Grugeon, M. Morcrette, S. Boyanov, S. Laruellea, G.

Marlair, Investigation on the fire-induces hazards of li-ion battery cells by fire calorimetry, Energy Environ. Sci. 5 (2012) 5271-5280.

[18] Bian, Jiang, et al. Thermodynamic and economic analysis of a novel hydrogen liquefaction process with LNG precooling and dual-pressure Brayton cycle. Energy Conversion and Management, 2021, 250: 114904.

[19] Yang, Jae-Hyeon, et al. Integrated hydrogen liquefaction process with steam methane reforming by using liquefied natural gas cooling system. Applied Energy, 2019, 255: 113840.

[20] Riaz, Amjad, et al. Performance improvement potential of harnessing LNG regasification for hydrogen liquefaction process: Energy and exergy perspectives. Applied Energy, 2021, 301: 117471.

[21] Bae, Ju-Eon, et al. Multi-objective optimization of hydrogen liquefaction process integrated with liquefied natural gas system. Energy Conversion and Management, 2021, 231: 113835.

[22]LindeKrytechnik.HydrogenLiquefier,https://lindekryotechnik.ch/en/references/hydrogen-liquefiers.GoogleScholar

[23] Air Liquide. HYLIAL hydrogen liquefiers. https://advancedtech.airliquide.com/hylial-hydrogen-liquefiers

[24] Mcintosh, G. E. Applications of ortho-para hydrogen catalyst. In: IOP Conference Series: Materials Science and Engineering. IOP Publishing, 2015. p. 012079.

[25] Leachman, Jacob W., et al. Fundamental equations of state for

parahydrogen, normal hydrogen, and orthohydrogen. Journal of Physical and Chemical Reference Data, 2009, 38.3: 721-748.

[26] Hyun Ji Kim, et al. TCD based real-time measurement of Ortho-Para hydrogen fraction. European Hydrogen Energy Conference, 2022.

[27] Dr. Umberto Cardella. Large-scale Liquid Hydrogen Production and Supply Advancing H Mobility and Clean Energy. Perth, September 27th, 2019.

[28] S. Krasae-in, J.H. Stang, P. Neksa. Development of large-scale hydrogen liquefaction processes from 1898 to 2009. Int J Hydrogen Energy, 35 (10) (2010), pp. 4524-4533.

[29] Ministry of Trade, Industry and Energy (Korea Gas Corporation, Korea Customs Service data)

[30] https://www.coldchainnews.kr/news/article.html?no=23361

#### Appendix



T-s diagram of case 1



T-s diagram of case 2



T-s diagram of case 3



T-s diagram of case 4



T-s diagram of case 5



T-s diagram of case 6

#### **Abstract in Korean**

기후변화 위기에 대응하여 수소경제사회를 구축함에 있어서 수소의 효율적인 저장과 우송을 위하여 수소액화 플랜트 건설에 대한 관심이 커지고 있다. 그러나 수소액화 플랜트에서 수소 액화 비용은 수소 경제 사회 구축에 어려움을 준다. 이를 해결하기 위한 여러 방안 중 하나로 수소예냉 단계에서 그리고 수소 예냉 후 질소 재 액화 단계에서 각각 액화천연가스의 냉열에너지를 사용하여 수소액화 비용을 낮추는 방법이 있다. 특히, 우리나라는 발전과 난방 등을 위하여 연간 33 Mtons의 액화천연가스를 사용하고 있으며, 그중 기화과정에서 0.85 Mtoe의 냉열 에너지가 의미 없이 바다로 버려지고 있다. 본 여구는 실제 상용화 된 대형 플랜트인 30 TPD급 수소액화 플랜트의 수소예냉 다계에서 액체질소만을 사용하는 경우와 액체질소와 액화천여가스의 냉열에너지를 동시에 사용한 두 경우를 소개하고, 두 경우의 수소예냉에 세가지 사이클 (클로드, 린데햄슨, 듀얼프레셔 린데햄슨 사이클)을 적용한 질소 재액화 사이클에 대하여 비교 분석하였다. 추가적으로 총 여섯 가지 경우에 대하여 경제성 분석을 하였다. 사이클에 사용된 액체질소와 액화천연가스의 냉열에너지의 총 사용량을 분석한 결과 수소 예냉에 액체질소와 액화천연가스의 냉열에너지를 동시에 사용하고 린데 핵슨 사이클을 적용 경우와 수소 예냉에 액체질소와 액화천연가스의 냉열에너지를 동시에 사용하고 듀얼 프레셔 린데 햄슨 시이클을 적용한 경우가 액화천여가스의 냉열에너지를 최대한으로 활용했고, 액체질소의 사용량이 가장 적었다. 시스템 전체의 소비 동력 측면에서는 수소 예냉에 액체질소와 액화천연가스의 냉열에너지를 동시에 사용하고 듀얼 프레셔 린데 햄슨 사이클을 적용한 경우가 2109.46 kW로 가장 낮았으며 연간 전력 요금은 1.57 MUSD (85 ¢/kW)으로 계산 되었다. 결론적으로 액화천연가스의 냉열을 활용함에 있어서 액체질소와 함께 수소를

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예냉하고, 이때 발생된 기체질소의 재액화 과정에서도 액화천연가스의 냉열에너지를 이용하여 기체질소를 예냉하는 방법이 수소예냉에 액체질소만을 사용한 후 기체질소 재액화에 클로드 사이클을 적용한 경우 보다 66% 소비동력이 낮았다.

주요어: 수소액화, 수소예냉, 액화천연가스, 올쏘-파라 수소 변환, 질소 재액화

학번: 2020-24830

#### Acknowledgement

I would like to take this opportunity to thank those who have supported and encouraged me throughout my time in graduate school. Foremost, I would like to acknowledge and give my warmest thanks to Professor Yong Tae Yoon for giving me a chance to start my master's degree. Thanks to him, I could broaden my vision.

To my research supervisor and life adviser, Doctor Sarng Woo Karng, I would also like to express my deepest appreciation for giving me knowledge in mechanical engineering, strength, life advice, and the opportunity to take part in the clean energy research division at KIST. His guidance helped me in all the time of writing this thesis. The completion of my study could not have been possible without him.

I am also grateful to Professor Seungyong Hahn for his helpful heat and mass transfer lecture. His lecture indeed helped me a lot in writing my thesis. I would also like to thank him for introducing me to a great friend and reviewing my thesis.

My sincere thanks also go to Doctor Youm Huh, who supported me throughout my master's degree. His scholarship helped me complete my study and taught me the meaning of sharing in life. I would like to become a person like him in the future.

There are still so many people I would like to send my sincere appreciation to. I can't thank you enough for what they have done for me. I want to express my sincere gratitude to my KIST colleagues, Bo Hyun Kim, Dae Sung Jang, Anca

Muresan, Myeong-seon Chae, Seong Hoon Kim, Youngkyun Jung, Jisu Park, Young Jae Kim, Cheol Woo Lee, Tae Hyun Kim, Chang Hyun Park for supporting my years of master's degree, helping my thesis, encouraging me mentally and physically.

My most profound appreciation also goes to my SNU friends, Junsu Yun, Heesu Yun, Jeonghoon Woo, Seungsu Lee, and Jihyun Jhun. Thanks to them, my life at SNU was filled with joy and happiness.

My dearest friends, especially Eunjin Choi and her family, Michael Kim and his family, Jai Yun Lee, Shanghai Park, Seunghyun Ha, Yang Geum Shin, Ji Yeon Jun, Haon Oh, Jieun Hong, Manuel Holstein and Hyun Sun Park, I thank them for supporting me continually throughout the whole master's degree and giving me strength to complete the graduate study. They always stood by my side.

I am extremely grateful to my loving, caring, supportive family for their unconditional love and belief in me. It is not exaggerated to say their love, understanding, and prayers make this work. I want to return their kindness for the rest of my life.

Last but not least, I would like to thank god. He was my salvation and waymaker for the past years. He never let me be alone. His words, guidance, and the people he sent me made it possible to complete my master's degree. Thank you, lord.