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Research paper

Hydrogen liquefaction process with Brayton refrigeration cycle to utilize the cold energy of LNG

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ABSTRACT

A thermodynamic process is investigated and designed for hydrogen liquefaction system to utilize the cold energy of liquefied natural gas (LNG). This study is an initial effort of newly launched five-year governmental project in Korea, aiming at efficient hydrogen liquefiers. Since Korea is a major LNG import country, the cold energy is abundantly available and could be useful in reducing the liquefaction cost. Hydrogen gas at ambient temperature is pre-cooled by LNG and then fed into a closed-cycle Brayton refrigerator. Rigorous thermodynamic analysis is carried out on the process with standard or modified Brayton cycles for the optimal condition to minimize the power consumption. It is revealed that LNG at atmospheric pressure is much more effective in pre-cooling than pressurized LNG (for pipeline distribution), because of the temperature pinch problem in heat exchanger. By taking into consideration the efficiency and other factors such as safety, compactness, and simplicity of operation, 2-stage expansion cycle with LNG pre-cooling is identified as most suitable for the pilot system with a capacity of 0.5 ton/day. Full details of liquefaction process are presented with the optional use of catalysts for ortho-para conversion.

1. Introduction

Hydrogen is emerging as new energy carrier for various applications to take advantage of carbon-free energy system. As liquid hydrogen is used for high-density storage and transfer [1–3], a variety of hydrogen liquefiers [4–8] will be widely furnished in near future. In preparation for the infrastructure of hydrogen supply, the Korean government launched a five-year project in 2019 for the development of efficient liquefaction technology under the funding by the Ministry of Land, Infrastructure, and Transportation (MOLIT). An immediate goal of this project is to design, construct, and demonstrate a pilot system of hydrogen liquefier with a capacity of 0.5 ton/day, which can utilize the cold energy of liquefied natural gas (LNG).

From thermodynamic point of view, the cold energy is an exergy (or availability) added by the input power in the liquefaction process of natural gas [9–11]. Since Korea is one of the major LNG import countries in the world, the cold energy is abundantly available and could be useful in reducing the liquefaction cost. While there have been numerous efforts to utilize the cold energy of LNG in different areas [12–14], this is the first systematic study to apply it for hydrogen liquefaction, as far as the authors are aware.

In practice, the cold energy of LNG is available at two distinct pressure levels, as schematically shown in Fig. 1. Large portion of LNG is pressurized (typically, up to 7 MPa) and then re-gasified at the vaporizers for pipeline distribution to various users. This primary source of cold energy will be called HP (high-pressure) LNG in this paper. On the other hand, some LNG is re-gasified at much lower pressure (at or just above atmospheric pressure) for local use or for smaller-scale applications by truck delivery. This secondary source of cold energy will be called LP (low-pressure) LNG.

The re-gasification process of LNG is thermodynamically complicated, depending upon the pressure level [10,15], because natural gas is a mixture of several hydrocarbons and minor gases. For natural gas with a typical composition, some isobars are drawn on temperature-entropy diagram in Fig. 2(a), and the specific heat is plotted as a function of temperature at the corresponding pressures in Fig. 2(b). Two isobars (7 MPa and 0.1 MPa) are highlighted by bold curves, representing the HP LNG and the LP LNG, respectively. Even though the actual pressure of LP LNG may vary between 0.1 and 0.3 MPa, its lower limit (0.1 MPa) is primarily considered.

The re-gasification of LP LNG consists of two processes: evaporation (the phase change from liquid to vapor) and super-heating of vapor. On the contrary, the re-gasification of HP LNG consists of three processes: warm-up of sub-cooled liquid, evaporation, and super-heating of vapor.

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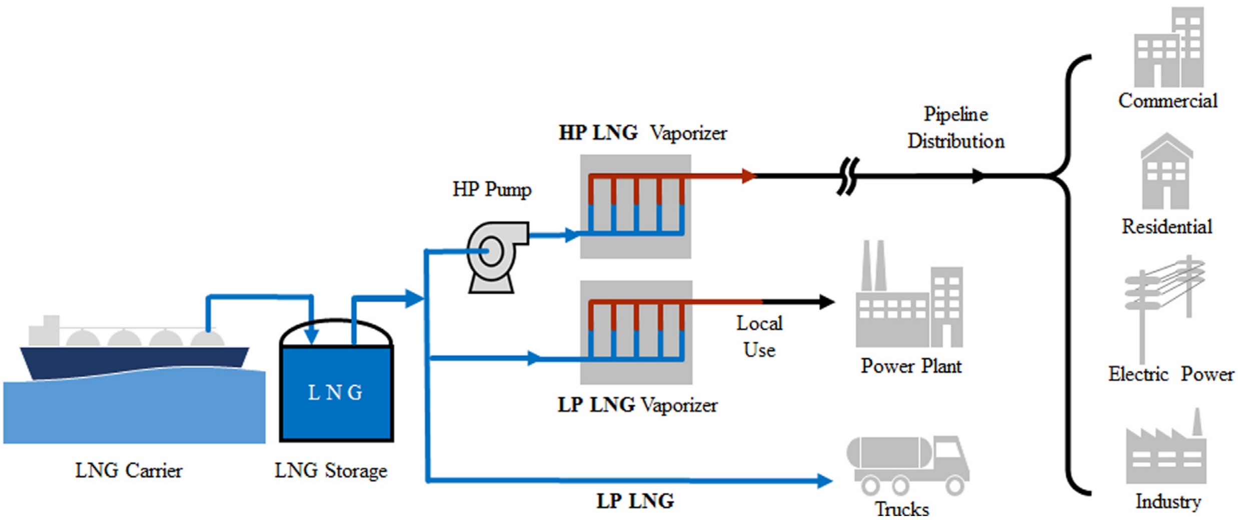
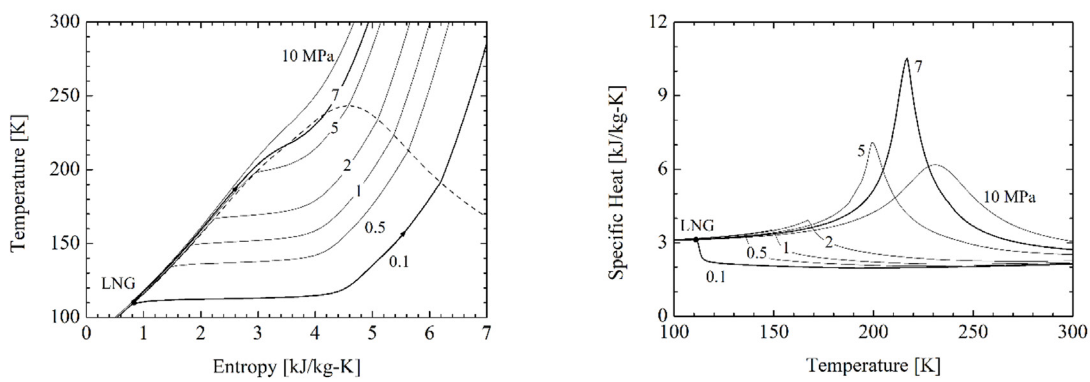


Fig. 1. Schematic illustration of LNG supply process where the cold energy is utilized at two pressure levels: high-pressure (HP) for pipeline distribution and low-pressure (LP) for local use or truck delivery.



(a) Temperature-entropy diagram (b) Specific heat as a function of temperature

Fig. 2. Thermodynamic properties of typical LNG (with a composition of 91% methane, 5% ethane, 2% propane, 1% butane, and 1% nitrogen on mole basis) at different pressure levels.

As shown in Fig. 2(b), the specific heat at 7 MPa has a sharp peak around the pseudo-critical point of mixture. This radical variation of specific heat has a very significant implication for the nature of cold energy, as discussed later.

Recently Chang et al. [8] published a comprehensive thermodynamic work on the selection of suitable cycle for smaller-capacity liquefaction, taking into account the efficiency and the low-pressure operation for safety. In their work, the concept of refrigerator for liquefaction was presented in comparison with refrigerator or liquefier, as schematically shown in Fig. 3. A closed-cycle Brayton refrigerator in Fig. 3(a) takes the thermal load (Q_L) at low temperature and release the heat to ambient (Q_O). An open-cycle Claude liquefier in Fig. 3(b) receives gas at ambient temperature and delivers cryogenic liquid. In most liquefiers, the gas itself is the working fluid of the open cycle. A Brayton refrigerator for liquefaction in Fig. 3(c) is a combination of them, since the refrigerator works in a closed cycle, but the refrigeration load is distributed over the stream from gas to cryogenic liquid.

It was reported in [8] that the open-cycle Claude liquefier is dominant in thermodynamic efficiency, as widely used in full-scale hydrogen liquefiers. For small-scale liquefaction, on the other hand, the closed-cycle Brayton refrigerators for liquefaction can take advantage of easier operation and no need of high-purity gas. It was also reported that reasonably high efficiency can be achieved with Brayton refrigerators operating at considerably lower pressures. Specifically, standard Brayton cycle with liquid-nitrogen pre-cooling and 2-stage expansion Brayton cycle without pre-cooling were preferably recommended for 100 L/h liquefaction.

This study is a design effort to investigate the similar Brayton refrigeration cycles for hydrogen liquefaction, but with a focus on the effect of pre-cooling with LNG. A major issue is to estimate how much input power can be reduced by the cold energy of LNG and to identify the most suitable cycle for small or medium scale liquefaction with LNG pre-cooling. The national institute hosting this governmental project has set a thermodynamic goal in terms of required work per unit liquid mass at 51.5 MJ/kg (14.3 kWh/kg), assuming that the cold energy is provided with no cost. This goal is based on the performance of commercial products with similar capacity [5,6]. It is also intended in this study to examine the effect of two distinct pressure levels of LNG on the thermodynamic performance. Upon the results of thermodynamic study, the details of process design will be carried out towards the pilot system with a capacity of 0.5 ton/day (294 L/h).

2. Brayton refrigeration cycles for liquefaction

Standard and two modified Brayton refrigeration cycles with LNG pre-cooling are shown in Fig. 4. In all cycles, helium is the working fluid, and the compressors (C) and the after-coolers (AC) are located at ambient temperature. The compression may be multi-staged as

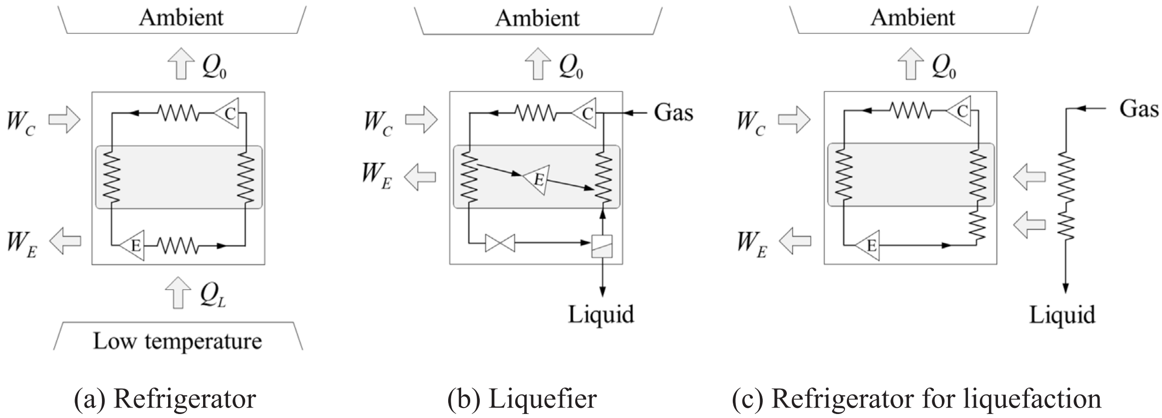


Fig. 3. Comparison of thermodynamic cycles for refrigeration and liquefaction: (a) closed-cycle Brayton refrigerator, (b) open-cycle Claude liquefier, and (c) closed-cycle Brayton refrigerator for liquefaction.

described later, even though only single-stage is drawn for simplicity. Hydrogen gas (GH_2) at ambient temperature enters the pre-cooling heat exchanger (PHX), and then is fed into the main heat exchangers of refrigeration cycle. PHX is a counter-flow heat exchanger that may play the role of an LNG vaporizer (as shown in Fig. 1) at the same time. The first heat exchanger (HX1) has two streams, but next heat exchangers (HX2, HX3, HX4) have three (i.e. one cold and two warm) streams. The coldest heat exchanger is called liquefying heat exchanger (LHX) for liquid delivery.

The standard Brayton cycle has one turbine (E) at the cold end, as shown in Fig. 4(a). The helium temperature at the exit of turbine is lower than liquid hydrogen temperature (20 K). In order to achieve a higher efficiency, the standard cycle can be modified by employing two turbines. In Fig. 4(b), two turbines are arranged in series, as called 2-stage (expansion) cycle [17]. In Fig. 4(c), on the contrary, two turbines are arranged in parallel, as called dual-turbine cycle [17]. The flow rate is same for two turbines in 2-stage cycle, while the pressure levels are same for two turbines in dual-turbine cycle.

Since the pre-cooling behavior is quite different by the pressure level of LNG, both HP LNG and LP LNG are considered in each cycle. Consequently, three different cycles are analyzed with two different LNG pressure levels so that the total number of cycles to analyze and optimize will be six. In order to examine the effect of LNG pre-cooling, three corresponding cycles without pre-cooling will be compared as well.

3. Analysis and thermodynamic optimization

3.1. Performance index and assumptions

Thermodynamic performance of a liquefaction system can be evaluated by the required work per unit mass of liquid [4].

$$\frac{W}{\dot{m}_f} = \frac{W_C - W_E}{\dot{m}_f} \tag{1}$$

where W_C and W_E are the power input to compressors and the power output from expanders or turbines, respectively, and $\dot{m}_f$ is the mass flow rate of liquid. The turbine power may be actually used for compressing gas or may be electro-mechanically dissipated. In this paper, the "net" power input is counted as performance index. As the LNG cold energy is utilized, the exergy or flow availability of LNG can be considered as additional input power, but is not counted here, because the cold energy is regarded as being free.

For the purpose of cycle analysis and optimization, the simplifying

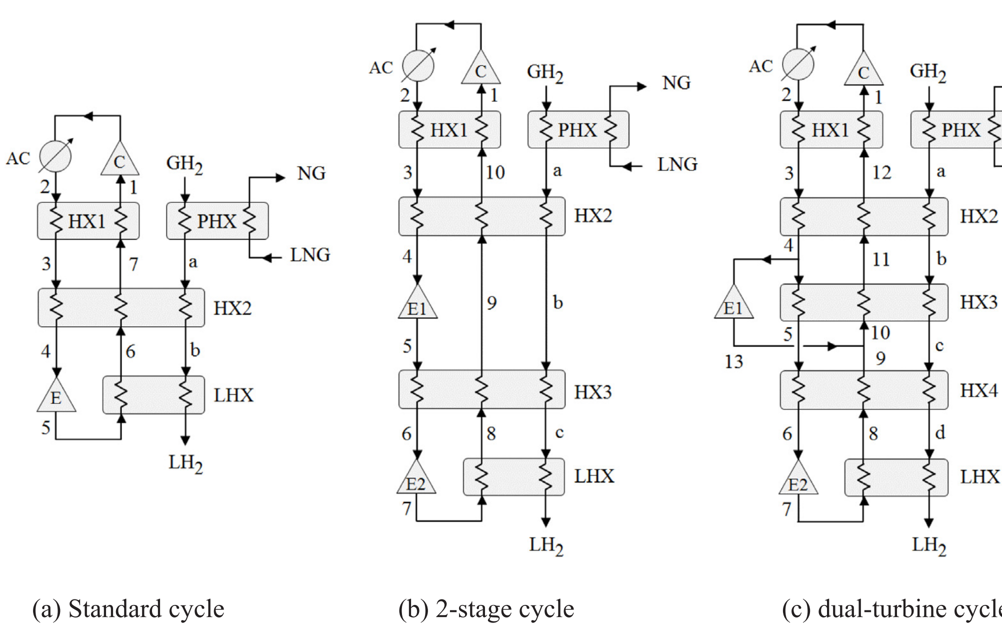


Fig. 4. Standard and two modified Brayton refrigeration cycles for liquefaction with LNG pre-cooling.

assumptions are made:

① The ambient (hydrogen feed and after-cooling) temperature is 300 K.
② Hydrogen at the exit is saturated liquid at 20 K and the flow rate is 5.79 g/s (0.5 ton/day).
③ LNG temperature is 111 K, and LNG pressure is 7 MPa for HP LNG and 0.11 MPa for LP LNG.
④ The composition of LNG is 91% methane, 5% ethane, 2% propane, 1% butane, and 1% nitrogen on mole basis.
⑤ The minimum temperature approach is 1.5 K for PHX and HX1, and 1.5% of the absolute temperature of hot stream for other heat exchangers (HX2, HX3, HX4, LHX).
⑥ In all heat exchangers, the pressure drop of each stream is 10 kPa.
⑦ In refrigeration cycles, the upper and lower limits of pressure are 1 MPa and 0.1 MPa, respectively.
⑧ The adiabatic (isentropic) efficiency of all compressors (C) is 75%, and the compression is multi-staged with a pressure ratio of 1.6 ~ 2 at each stage.
⑨ The adiabatic (isentropic) efficiency of all turbines (E) is 70%.

Assumptions ③ and ④ are the same LNG conditions as Fig. 2. Assumption ⑤ means that the heat exchangers are sufficiently effective and optimized [8,14], as discussed later. Assumption ⑥ is a fairly simplified one, since the pressure drop is actually dependent on the capacity or size of heat exchangers. But it is also true in plate-fin heat exchangers (to be used in pilot system) that most of pressure drop occurs at the inlet and the exit. Assumption ⑦ is a safety constraint in accordance with the gas regulations. The component performance in Assumptions ⑧ and ⑨ is rather conservative in order to simulate the pilot system under construction.

Cycle analysis is carried out with a general purpose process simulator (Aspen Technology HYSYS), and the standard database is incorporated for the thermodynamic properties of helium, hydrogen [18,19], and natural gas mixture. Hydrogen feed is assumed to be normal hydrogen (i.e. 25% para-hydrogen) in the cycle analysis and optimization, and the catalysts for ortho–para conversion will be considered later in the process design.

3.2. Pre-cooling heat exchanger (PHX)

In PHX, the temperature distribution of two counter-flows (hydrogen and natural gas) is calculated and plotted in Fig. 5(a) and (b) for HP LNG and LP LNG, respectively. In both cases, two inlet temperatures are same (300 K and 111 K), and the minimum temperature approach is set at the same value (1.5 K). The temperature profile is notably different, mainly because of the location of pinch point (the point of minimum temperature difference). As indicated by arrows, the pinch point is located at two ends of heat exchanger in case of LP LNG, but at a point in the middle of heat exchanger and the warm end in case of HP LNG. As a result, the exit temperature of hydrogen is sufficiently low (112.5 K) with LP LNG, but is considerably higher (129.6 K) with HP LNG.

An obvious reason for the contrasting behavior is found in the variable specific heat of LNG shown in Fig. 2. Specifically, the local peak of specific heat is a detrimental obstacle to pre-cool by HP LNG [20], however highly effective the heat exchanger may be. It can be shortly confirmed by the simulation that the lowest possible pre-cooling temperature would be 111 K with LP LNG, but as high as 127.5 K with HP LNG, if the PHX were infinitely large or the minimum temperature approach were zero. The key point here is that LP LNG is far superior to HP LNG as pre-coolant, even though their temperature may be same.

3.3. Standard cycle with LNG pre-cooling

In the analysis of LNG pre-cooled standard cycle shown in Fig. 4(a) (excluding the PHX), there are two independent variables, as the number of unknowns is 17 (7 temperatures, 9 pressures, 1 flow rate) and the number of given conditions is 15 (7 HX, 7 ΔP, 1 Turbine). The cycle is completed if two variables are given, for example, the high pressure (P_H) and the low pressure (P_L). The calculated work per unit liquid mass is plotted in Fig. 6 as a function of P_L, when P_H = 1 MPa. There exists an optimal P_L to minimize the work per liquid mass, which is 0.17 MPa for HP LNG and 0.18 MPa for LP LNG. In the optimized conditions (indicated by dots in Fig. 6), the minimum work per unit liquid mass is 72.9 MJ/kg for HP LNG and 65.0 MJ/kg LP LNG.

The optimization presented above is repeated with lower values of P_H. Noting that the liquefaction process is based on Brayton cycle, a dominant design parameter is the pressure ratio (P_H /P_L) [4]. In other words, the thermodynamic performance is determined principally by the ratio and is independent of pressure values in ideal Brayton cycle. In practical cycle based on the given assumptions, however, it can be readily shown that as the pressure level decreases (for a given pressure ratio), the effect of pressure drop becomes more detrimental, thus the work per liquid mass increases [16]. The final decision on operating pressures is made with P_H = 1 MPa and the optimized P_L, as given above.

3.4. Two-stage expansion cycle with LNG pre-cooling

In the analysis of LNG pre-cooled 2-stage cycle shown in Fig. 4(b) (excluding the PHX), there are three independent variables, as the number of unknowns is 25 (11 temperatures, 13 pressures, 1 flow rates) and the number of given conditions is 22 (10 HX, 10 ΔP, 2 turbines). The cycle is completed if three variables are given, for example, the high pressure (P_H), the intermediate pressure (P_I), and the low pressure

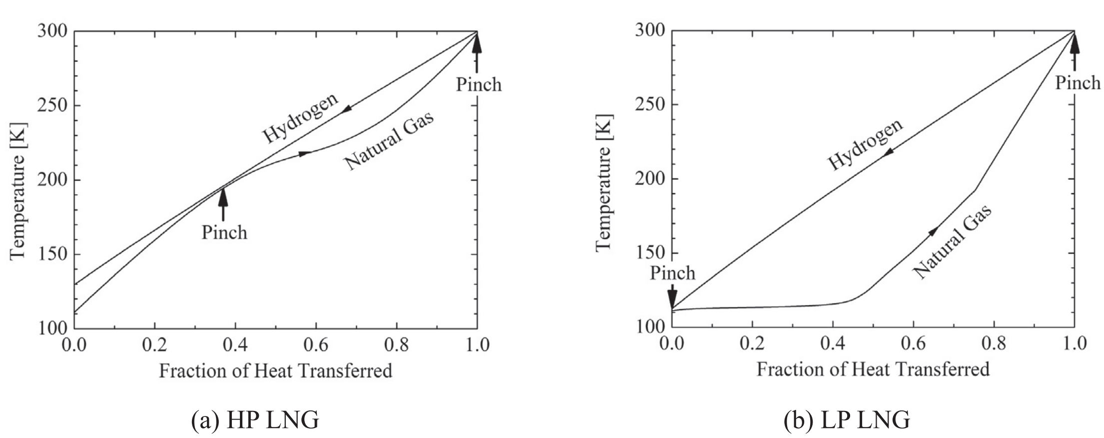


Fig. 5. Comparison of temperature profile in pre-cooling heat exchanger (PHX) with HP LNG and LP LNG.

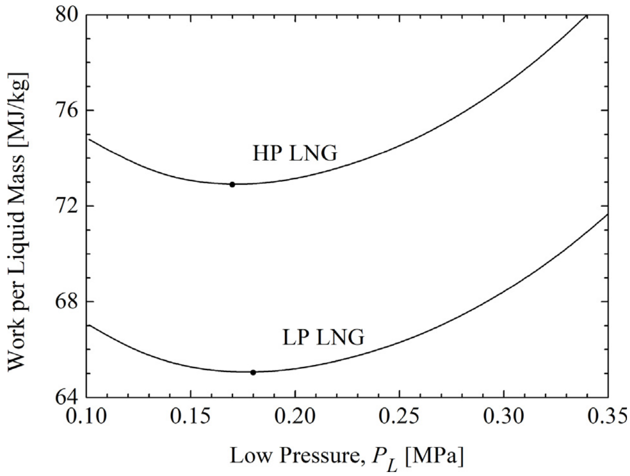


Fig. 6. Work per liquid mass as a function of P_L in LNG pre-cooled standard cycle.

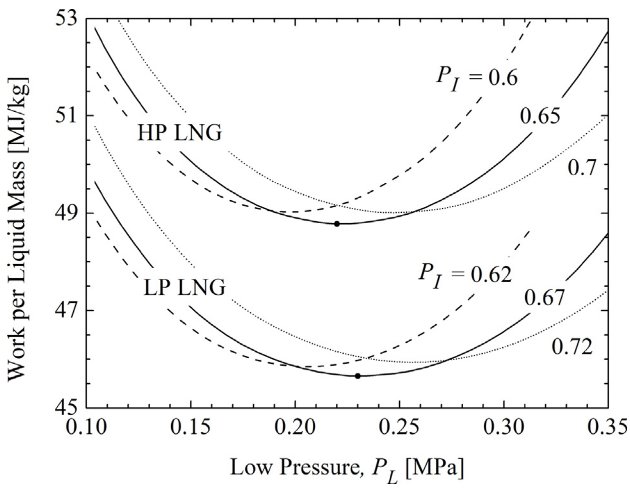


Fig. 7. Work per liquid mass as a function of P_L for various values of P_I in LNG pre-cooled 2-stage cycle.

(P_L). P_I is defined as the exit pressure of first turbine (E1). The calculated work per unit liquid mass is plotted in Fig. 7 as a function of P_L for various values of P_I, when $P_H = 1$ MPa. There exist unique optimal values for P_L and P_I to minimize the work per liquid mass, which are 0.65 MPa and 0.22 MPa for HP LNG, and 0.67 MPa and 0.23 MPa for LP LNG, respectively. In the optimized conditions (indicated by dots in Fig. 7), the minimum work per unit liquid mass is 48.8 MJ/kg for HP LNG and 45.7 MJ/kg LP LNG.

The 2-dimensional optimization demonstrated above is repeated with lower values of P_H. In the same context as standard cycle, it can be readily shown that as the pressure level decreases, the work per liquid mass slightly increases. The final decision on operating pressures is made with $P_H = 1$ MPa and the optimized P_I and P_L given above.

3.5. Dual-turbine cycle with LNG pre-cooling

In the analysis of LNG pre-cooled dual-turbine cycle shown in Fig. 4(c) (excluding the PHX), there are three independent variables, as the number of unknowns is 32 (15 temperatures, 15 pressures, 2 flow rates) and the number of given conditions is 29 (13 HX, 13 ΔP, 2 turbines, 1 mixing). The cycle is completed if three variables are given, for example, the high pressure (P_H), the low pressure (P_L), and the flow ratio of warm turbine (x).

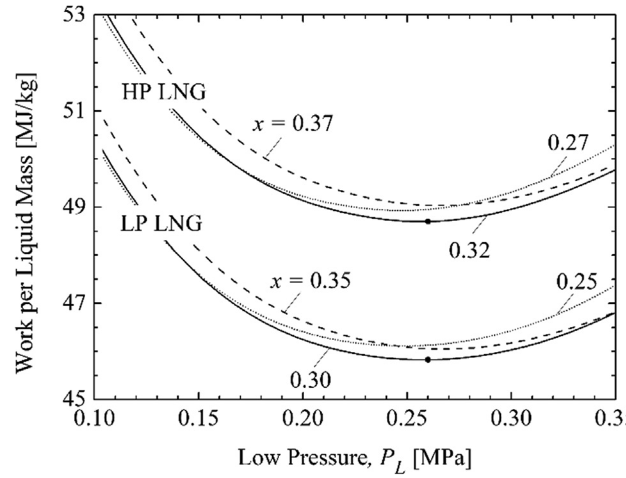


Fig. 8. Work per liquid mass as a function of pressure ratio for LNG pre-cooled dual turbine cycle.

$$x = \frac{\dot{m}_{E1}}{\dot{m}_C} = \frac{\dot{m}_{E1}}{\dot{m}_{E1} + \dot{m}_{E2}} \tag{2}$$

The calculated work per unit liquid mass is plotted in Fig. 8 as a function of P_L for various values of x, when $P_H = 1$ MPa. There exist unique optimal values for P_L and x to minimize the work per liquid mass, which are 0.26 MPa and 0.32 for HP LNG, and 0.26 MPa and 0.30 for LP LNG, respectively. In the optimized conditions (indicated by dots in Fig. 8), the minimum work per unit liquid mass is 48.7 MJ/kg for HP LNG and 45.8 MJ/kg LP LNG.

The 2- dimensional optimization demonstrated above is repeated with lower values of P_H. In the same context as standard cycle, it can be readily shown that as the pressure level decreases for a given pressure ratio, the work per liquid mass increases. The final decision on operating pressures is made with $P_H = 1$ MPa and the optimized P_L and x given above.

4. Results and discussion

4.1. Selection of refrigeration cycle

In order to identify the most suitable refrigeration cycle for liquefaction process, the optimized cycles are plotted in temperature-entropy diagram (Fig. 9), and also compared in terms of work per liquid mass, pressure ratio, and flow rate (Fig. 10). In Fig. 9, two horizontal dashed lines indicate the temperatures of LNG and liquid hydrogen as reference. In Fig. 10, the white, light grey, and dark grey columns represent the cycles with no pre-cooling, with HP LNG pre-cooling, and with LP LNG pre-cooling, respectively. The work per unit liquid mass is the major economic factor on thermodynamic performance, while the pressure ratio and flow rate are closely related with other factors, such as the operational safety and the compactness of system.

The reduction of power consumption by LNG pre-cooling is estimated at 64–67% for standard cycle, and at 37–41% for two modified (2-stage and dual-turbine) cycles. The effect of pre-cooling is relatively smaller in modified cycles, because the cycle is already composed of two turbines (in series or parallel) and the pre-cooling plays a less important role as third stage [8]. In every cycle, LP LNG pre-cooling is noticeably superior to HP LNG pre-cooling. As the target (51.5 MJ/kg) is indicated by the horizontal dotted line, the standard cycle does not reach the goal in work per liquid mass, but two modified cycles satisfy the requirement. It is noted that both cycles barely meet the criterion with HP LNG, but satisfy it with some margin with LP LNG. Consequently, either 2-stage or dual-turbine cycle could be selected in terms of thermodynamic efficiency.

To compare two modified cycles more closely, the work per liquid

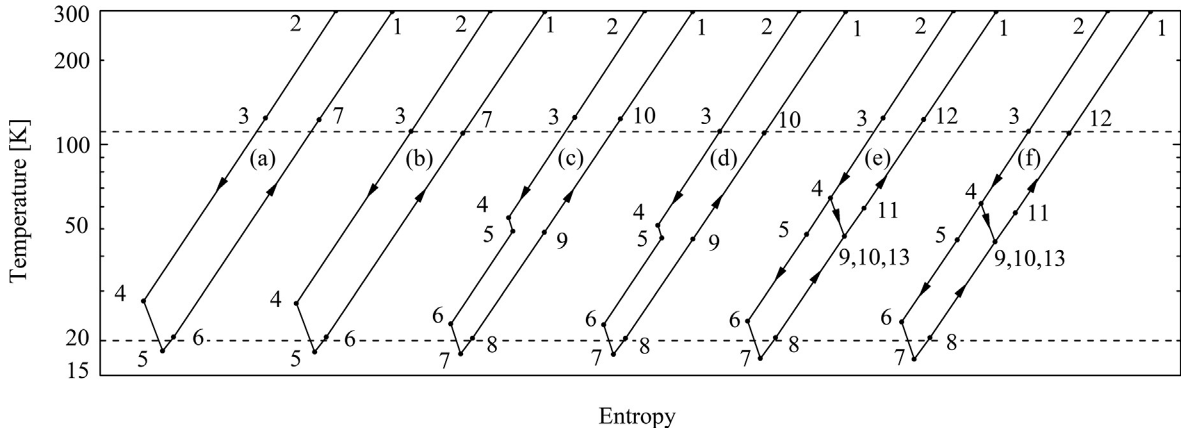


Fig. 9. Temperature-entropy diagram of optimized cycles: (a) standard with HP LNG (b) standard with LP LNG (c) 2-stage with HP LNG (d) 2-stage with LP LNG (e) dual-turbine with HP LNG (f) dual-turbine with LP LNG.

mass is nearly identical, but the pressure ratio is slightly lower in dual-turbine cycle and the flow rate is slightly lower in 2-stage cycle. It can be therefore declared that 2-stage cycle has a potential advantage in compactness. Another factor to consider in the cycle selection is the operational simplicity. In 2-stage cycle, the flow rate is same over the entire single loop, as the turbines are placed in series. In dual-turbine cycle, on the contrary, two flow rates should be optimally controlled for the designed performance, as the turbines are placed in parallel.

In summary, 2-stage expansion Brayton cycle with LNG pre-cooling is selected for the next step of process design, taking into consideration the thermodynamic efficiency and other factors such as safety, compactness, and simplicity. For the pre-cooling of the cycle, LNG at atmospheric pressure is most effective, while the compressed LNG is useful as well with a minor penalty of added input power.

4.2. Optional ortho–para conversion

Hydrogen molecules can exist as either ortho-hydrogen or para-hydrogen. The equilibrium fraction of para-hydrogen is 25% (normal hydrogen) at ambient temperature, but gradually rises to 99.8% as temperature decreases down to 20 K. Since the ortho-para conversion is a slow process, proper catalyst is commonly used in hydrogen liquefier to speed up the conversion [4].

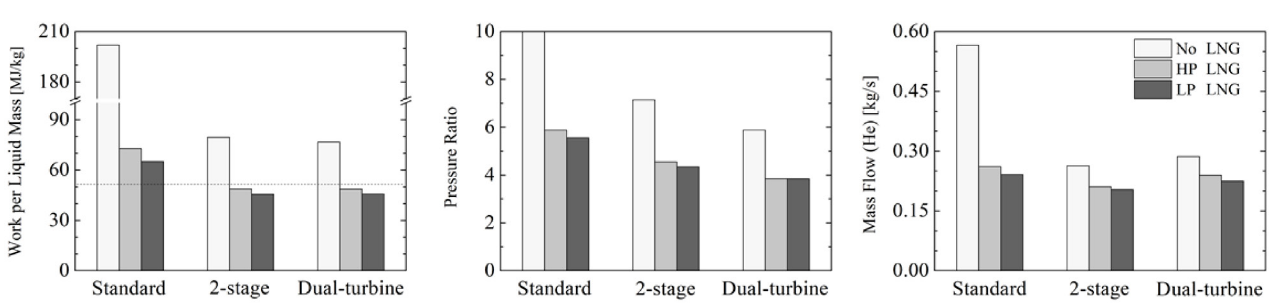
In reality, however, the use of catalytic conversion is optional, depending on how long the liquid will be stored before re-gasification. For example, if the storage period is a few days or shorter, liquid of normal hydrogen is useful enough, because the boil-off by delayed conversion is not so significant. But if the storage period is a month or longer, the catalytic conversion is mandatory to avoid an excessive loss by boil-off. It is proposed in this process design to install the catalyst with a bypass valve for optional use.

As shown in Fig. 11, three stages of catalyst are installed along the hydrogen stream. The first is placed at the cold end of PHX to utilize the additional cold energy of LNG, even though the increase of *para*-fraction is so great. The second is placed between HX2 and HX3 in parallel with the first turbine (E1). The third is placed at the cold end of HX4. The first and third conversions are basically isothermal around at 111 K and 20 K, respectively. On the contrary, the second conversion is adiabatic, and the gas temperature will increase by conversion heat.

In order to illustrate the three stages of conversion, the fraction of *para*-hydrogen is plotted as a function of temperature in Fig. 11. It is assumed that the conversion occurs only in the catalysts and the equilibrium fraction is reached at the exit. It is further assumed that the pressure drop is 10 kPa in each stage of catalytic conversion. The dotted curve at top is the equilibrium fraction, and the dashed horizontal line at bottom indicates the simple liquefaction of normal hydrogen (with constant fraction of 25%), when the bypass valves are open. The step-wise graph is the designed process with catalytic conversion, including the first small step of isothermal conversion, the second step of adiabatic conversion (accompanying the temperature increase), and the third step of isothermal conversion nearly at 20 K. The fraction of *para*-hydrogen steps up from 25% to 34.3%, 59.1%, and then 99.6% with LP LNG pre-cooling. Alternatively, the liquid of 34.3% *para*-hydrogen will be obtained, if only the first catalyst is used, and the liquid of 59.1% *para*-hydrogen will be obtained, if the first and second catalysts are used and third bypass valve is open.

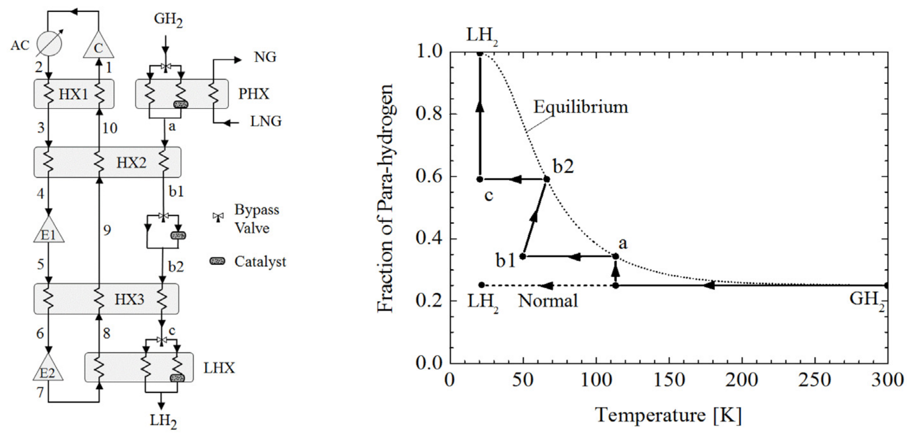
4.3. Plan for pilot system and key components

The liquefaction process for 0.5 ton/day pilot system is summarized as tables in Fig. 11. Two different cases are presented for the liquefaction without or with ortho-para conversion. The detailed values of temperature [K], pressure [MPa], vapor fraction, flow rate [g/s], and *para*-hydrogen fraction are listed at each point of the process. In case of



(a) Work per liquid mass (b) Pressure ratio (c) Flow rate of helium

Fig. 10. Comparison of optimized cycles with or without LNG pre-cooling.



(No conversion)	1	2	3	4	5	6	7	8	9	10	GH2	a	b	c	LH2	LNG	NG
Temperature [K]	298.5	300.0	111.4	51.5	46.4	22.8	17.8	20.4	46.0	109.8	300.0	112.5	51.5	22.8	20.3	111.0	298.5
Pressure [MPa]	0.23	1.00	0.99	0.98	0.67	0.66	0.27	0.26	0.25	0.24	0.14	0.13	0.12	0.11	0.10	0.11	0.10
Vapor fraction	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.00	0.01	1.00
Flow rate [g/s]	204	204	204	204	204	204	204	204	204	204	5.79	5.79	5.79	5.79	5.79	16.7	16.7

(O-P conversion)	1	2	3	4	5	6	7	8	9	10	GH2	a	b1	b2	c	LH2	LNG	NG
Temperature [K]	298.5	300.0	111.8	49.7	44.8	22.5	17.6	20.5	45.1	110.2	300.0	113.4	49.7	66.2	22.5	20.3	111.0	298.5
Pressure [MPa]	0.23	1.00	0.99	0.98	0.67	0.66	0.27	0.26	0.25	0.24	0.17	0.15	0.14	0.13	0.12	0.10	0.11	0.10
Vapor fraction	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.00	0.01	1.00
Flow rate [g/s]	279	279	279	279	279	279	279	279	279	279	5.79	5.79	5.79	5.79	5.79	5.79	17.0	17.0
Para fraction	-	-	-	-	-	-	-	-	-	-	0.250	0.343	0.343	0.591	0.591	0.996	-	-

Fig. 11. Details of hydrogen liquefaction process (0.5 ton/day) with 2-stage expansion Brayton refrigeration cycle pre-cooled by LP LNG and with or without ortho-para conversion.

LNG pre-cooling, the power consumption is 264 kW or 362 kW for the 0.5 ton/day liquefaction of normal hydrogen or equilibrium hydrogen, respectively. The consumption of LP LNG is approximately 1.47 ton/day. In case of HP LNG pre-cooling (not included in the graph and table of Fig. 11), the power consumption is 282 kW or 388 kW for the 0.5 ton/day liquefaction of normal hydrogen or equilibrium hydrogen, respectively. The consumption of HP LNG is approximately 1.45 ton/day.

The key components in the construction of pilot system are compressors, turbines, and heat-exchangers. The detailed component design is beyond the scope of this work, but a few comments are made about their preliminary specifications. As presented above, the specifications of components may vary by the pressure level of LNG and by the optional use of catalysts. Since the pilot system will use LNG delivered by truck, the specifications are taken from the designed process with LP LNG. In regards to ortho-para conversion, the pilot system should be able to demonstrate the liquefaction at various fractions of *para*-hydrogen between 25% and 99.8%.

The helium compressor requires a flow rate of 0.279 kg/s with suction and exhaust pressures of 0.23 MPa and 1.0 MPa, respectively. A single-stage screw compressor or two-stage reciprocating compressors with inter-cooling may be selected. The specifications of two turbines are quite different each other. The inlet temperature is 49.7 K for the first turbine (E1) and 22.5 K for the second turbine (E2), and the pressure ratio and output power are 1.5 and 7.2 kW for E1, and 2.4 and 6.8 kW for E2, respectively. It is interesting that while the pressure ratio of E2 is much greater than that of E1, the output power is no so different each other for two turbines. Typical radial flow-in turbo-expanders may be selected for this application.

Five different heat exchangers are needed in the pilot system, including 3 counter-flow heat exchangers (PHX, HX1, LHX) and 2 multi-stream heat exchangers (HX2, HX3). As commonly used in cryogenic liquefiers, the plate-fin heat exchangers (PFHX) are selected, taking advantage of compactness and design flexibility [20]. It is crucial that every heat exchanger should meet the condition of minimum temperature approach by Assumption ⑤, as being imposed in accordance with the well-known optimization subject to constraints [16,17]. A close attention should be paid to the condensing heat exchanger (LHX), because the pinch point is always located in the middle (at the position of saturated vapor for hydrogen), as previously reported for the methane liquefaction process by cold nitrogen gas [16].

The pressure drop in heat exchangers by Assumption ⑥ should be also carefully checked for validity, since the overall liquefaction performance is significantly affected. As mentioned, the pressure drop in PFHX occurs mainly at inlets and exits, and it is strongly recommended that two or more heat exchangers be combined together in order to reduce the number of inlets and exits [21]. For example, HX2 and HX3 can be manufactured as one piece, as demonstrated in Fig. 12. The flow passage with fin layout is shown for three layers of high-pressure helium (Layer A), low-pressure helium (Layer B), and hydrogen (Layer C). The resulting configuration of PFHX is schematically presented with a stack of A-B-C-B-A. It is noticeable that the low-pressure helium stream in Layer C is straight all the way with one inlet (8) and one exit (10) only.

5. Conclusion

Hydrogen liquefaction process with standard and modified Brayton refrigeration cycles is rigorously studied, aiming at the effective utilization of LNG cold energy. A special attention is paid to two distinct pressure levels of 7 MPa (HP LNG) and 0.1 MPa (LP LNG), at which the cold energy is available in practice. The operating condition is successfully optimized in each cycle to achieve the minimum input power per unit liquid mass. The effect of LNG pre-cooling on the liquefaction performance is quantitatively examined, and three (standard, 2-stage,

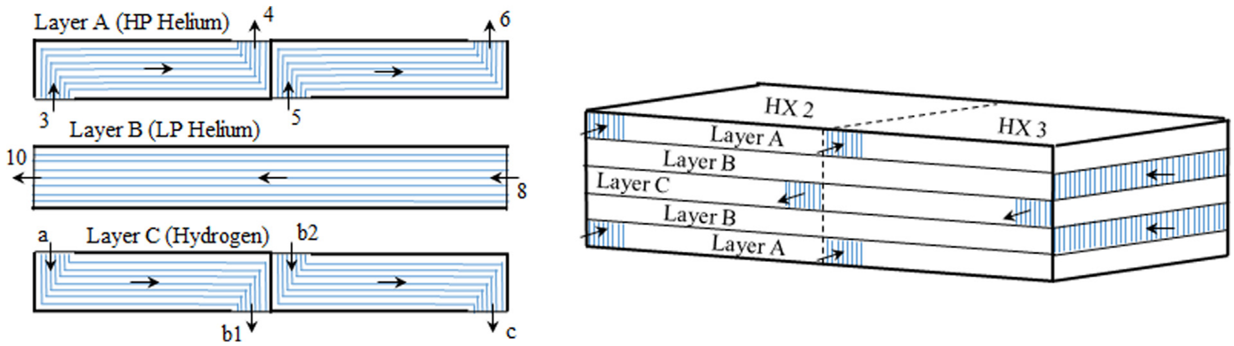


Fig. 12. An example of schematic configuration for plate-fin heat exchanger (PFHX) to combine HX2 and HX3 with three different layers (A, B, C) by A-B-C-B-A stack (not to scale).

and dual-turbine) cycles are compared in terms of power consumption, operating pressure, and flow rate. It is revealed that LP LNG is far superior to HP LNG in pre-cooling of hydrogen, because of the temperature pinch problem in counter-flow heat exchanger. Two-stage expansion Brayton cycle with LP LNG pre-cooling is identified as most feasible, taking into consideration the thermodynamic efficiency and other factors such as safety, compactness, and simplicity in operation. Full details of the liquefaction process with "optional" ortho-para conversion are designed for immediate application to the pilot system with a capacity of 0.5 ton/day.

CRediT authorship contribution statement

Ho-Myung Chang: Supervision, Conceptualization, Writing - original draft. **Bo Hyun Kim:** Data curation, Visualization, Writing - review & editing. **Byungil Choi:** Project administration, Funding acquisition, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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