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PII: S0011-2275(17)30429-0

DOI: <https://doi.org/10.1016/j.cryogenics.2018.02.007>

Reference: JCRY 2788

To appear in: *Cryogenics*

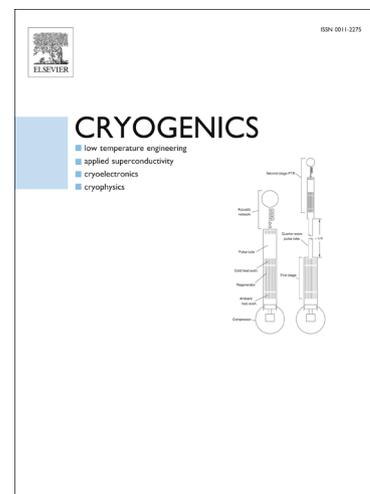
Received Date: 13 December 2017

Revised Date: 6 February 2018

Accepted Date: 22 February 2018

Please cite this article as: Chang, H-M., Nam Ryu, K., Hoon Baik, J., Thermodynamic design of hydrogen liquefaction systems with helium or neon Brayton refrigerator, *Cryogenics* (2018), doi: <https://doi.org/10.1016/j.cryogenics.2018.02.007>

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Thermodynamic design of hydrogen liquefaction systems with helium or neon Brayton refrigerator

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Abstract

A thermodynamic study is carried out for the design of hydrogen liquefaction systems with helium (He) or neon (Ne) Brayton refrigerator. This effort is motivated by our immediate goal to develop a small-capacity (100 L/h) liquefier for domestic use in Korea. Eight different cycles are proposed and their thermodynamic performance is investigated in comparison with the existing liquefaction systems. The proposed cycles include the standard and modified versions of He Brayton refrigerators whose lowest temperature is below 20 K. The Brayton refrigerator is in direct thermal contact with the hydrogen flow at atmospheric pressure from ambient-temperature gas to cryogenic liquid. The Linde-Hampson system pre-cooled by a Ne Brayton refrigerator is also considered. Full cycle analysis is performed with the real properties of fluids to estimate the figure of merit (*FOM*) under an optimized operation condition. It is concluded that He Brayton refrigerators are feasible for this small-scale liquefaction, because a reasonably high efficiency can be achieved with simple and safe (low-pressure) operation. The complete cycles with He Brayton refrigerator are presented for the development of a prototype, including the ortho-to-para conversion.

Keywords hydrogen, liquefaction, thermodynamics, Brayton refrigerator

Nomenclature

			Subscripts or legend
<i>FOM</i>	figure of merit		
<i>h</i>	specific enthalpy	<i>0</i>	ambient
<i>m</i>	mass flow rate	<i>AC</i>	after-cooler
\dot{Q}	heat transfer rate	<i>C</i>	compressor
<i>s</i>	specific entropy	<i>E</i>	expander
\dot{S}_{gen}	entropy generation rate	<i>f</i>	liquid
<i>T</i>	temperature	<i>g</i>	vapor
\dot{W}	power or work rate	<i>HX</i>	heat exchanger
		<i>JT</i>	Joule-Thomson valve
		<i>L</i>	low temperature

1. Introduction

Hydrogen liquefaction is an important thermodynamic process that has been fully developed for large-scale cryogenic applications [1][2]. Over decades, a notable quantity of liquid hydrogen has been consumed as the propellant of rocket engines and space launch vehicles [2]. The hydrogen bubble chamber uses liquid hydrogen in the detection and study of high-energy particles [1]. The spallation neutron source also uses liquid hydrogen for removing the huge amount of dissipated energy from neutron moderators at 20 K or lower temperatures [3]. Recently, new large-scale applications have been proposed and explored, such as a hybrid energy transfer of liquid hydrogen through superconducting power cables [4], and an ocean-going transport of liquid hydrogen for international energy trade [5].

In order to meet these needs, the hydrogen liquefiers with capacity of 500~3,000 L/h are supplied by major gas companies [6][7]. Since the large-scale system has been installed at some limited locations, liquid hydrogen may not be locally available for smaller-scale application in many other regions. In Korea, for example, liquid hydrogen is not commercially available, although a potential market is now emerging for the car or truck fueling station [8] and the power package of unmanned air vehicles or drones [9].

This thermodynamic study is motivated by our immediate goal to design and construct a 100 L/h liquefier for domestic use in Korea. The most suitable thermodynamic cycle for smaller-capacity liquefaction may be different from that of the full-capacity liquefiers, taking into consideration not only the energy efficiency and economic factors, but also the practical issues like the safety and simplicity in operation. As a beginning step of the development program, a variety of refrigeration cycles for liquefaction are proposed and their feasibility is investigated in comparison with the existing liquefaction systems.

Figure 1 compares schematically the thermodynamic structure of refrigerator, liquefier, and refrigerator for liquefaction [10]. A refrigerator operates in closed cycle, receiving the thermal load at cryogenic temperature and rejecting the heat to ambient. On the other hand, a liquefier operates in open cycle, where gas is fed at ambient temperature and liquid is delivered at cryogenic temperature. In most cases, the feed gas itself is the working fluid that undergoes compression and expansion. A refrigerator for liquefaction operates in closed cycle, but the thermal load is distributed over the liquefaction stream from gas at ambient temperature to liquid at cryogenic temperature.

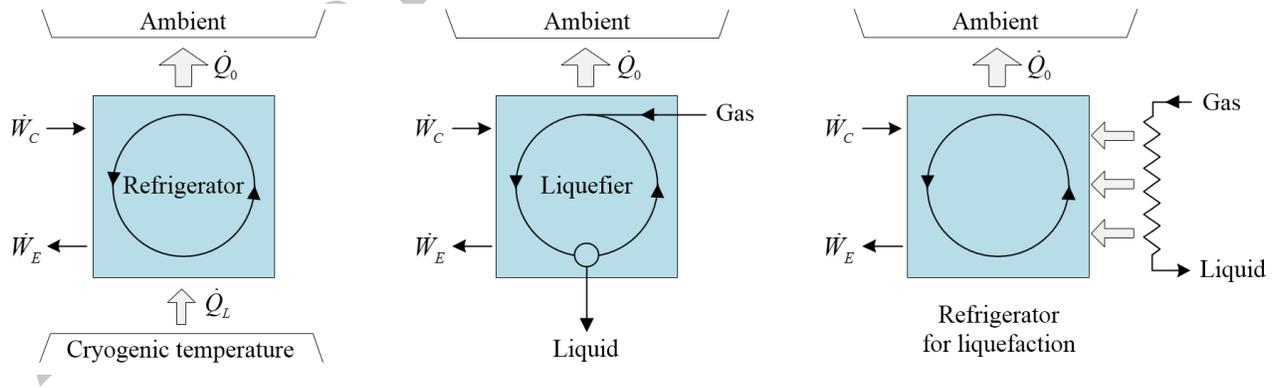


Fig. 1. Thermodynamic structure of refrigerator (left), liquefier (center), and refrigerator for liquefaction (right).

There are various options in selecting the refrigeration cycle for hydrogen liquefaction, as far as the cold temperature is lower than 20 K. A simple and convenient method is to employ a Gifford-McMahon (GM) or pulse tube cryocooler, whose cold-head temperature is below 20 K. It was recently reported that a small rate of liquefaction (1 L/h) was achieved with a single-stage GM cooler and liquid-nitrogen (LN₂) pre-cooling [11]. Because of the limit in refrigeration capacity, these regenerative cryocoolers are not virtually applicable to 100 L/h liquefaction.

A dominant choice is to use a helium (He) Brayton refrigerator, in the similar way as nitrogen (N_2) Brayton refrigerators are widely utilized for the liquefaction of natural gas [10] or methane [12]. Recently, Chang et al. [13] published a paper on standard or modified versions of He Brayton refrigeration cycle for liquid hydrogen below 20 K in the neutron moderators under construction at European Spallation Source [3]. It was reported that the thermodynamic performance of standard Brayton cycle could be significantly improved by employing two turbo-expanders in series or in parallel. The similar modifications could be effective in hydrogen liquefaction as well. Another choice is to use a neon (Ne) Brayton refrigerator as pre-cooler of Linde-Hampson system. Since the normal boiling temperature of Ne is 27 K, the Ne Brayton refrigerator is not capable of liquefying hydrogen by itself, but may be useful for pre-cooling the hydrogen flow to Joule-Thomson (JT) valve. Lately, a major gas company has successfully developed Ne Brayton refrigerators with a capacity of 2~10 kW at 60~70 K [14][15], which could be shortly modified for this application. The objective of this thermodynamic study is to identify the most feasible cycles for small-scale hydrogen liquefaction and determine the key parameters of a 100 L/h liquefier for prototype construction.

2. Existing and Proposed Cycles

2.1 Existing cycles

The Linde-Hampson system is obviously desirable for small-scale liquefaction, because of its simplicity. For hydrogen liquefaction, however, a pre-cooling is required, because the maximum inversion temperature is lower than ambient temperature [1]. The LN_2 pre-cooled Linde-Hampson system for hydrogen liquefaction is shown in Figure 2(a). In general, this system requires a very high pressure of hydrogen, because the production of cryogenic liquid relies only on the Joule-Thomson (JT) process. It is noted that the LN_2 heat exchanger (HX1) in Figure 2(a) has three streams.

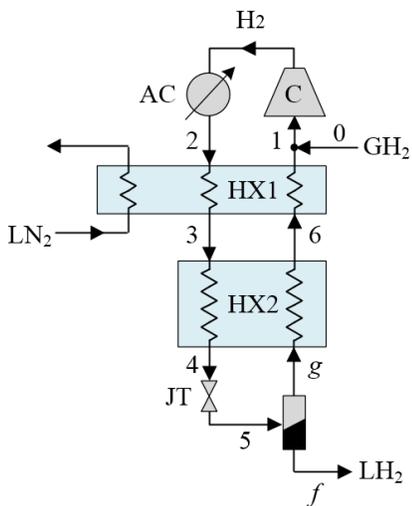
Many industrial hydrogen liquefiers are based on Claude cycle [1]. Figure 2(b) shows the standard Claude system for hydrogen liquefaction. The high-pressure gas is diverted from the main stream, expanded through a turbo-expander (E), and reunited with the low-pressure stream. The stream to be liquefied continues to a JT valve at the cold end. The turbo-expander is a key component, where the adiabatic expansion is effectively used for the production of low temperature. Figure 2(c) shows the Claude system with LN_2 pre-cooling.

2.2 Proposed cycles

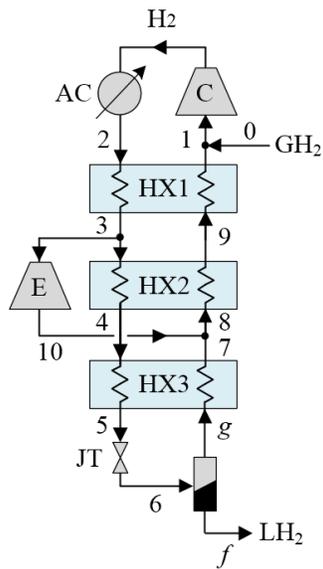
Standard and modified He Brayton cycles are proposed for hydrogen liquefaction. The standard He Brayton refrigerator is shown in Figure 2(d), and the He Brayton refrigerator with LN_2 pre-cooling is shown in Figure 2(e). While the Linde-Hampson and Claude systems are classified as a liquefier in Figure 1, the He Brayton systems are classified as a refrigerator for liquefaction. The lowest temperature of He gas at the exit of turbo-expander (E) must be lower than 20 K, and the liquefaction flow of hydrogen may be at atmospheric pressure. It is noted that the HX's have multiple (three or four) streams in these systems.

In order to improve the thermodynamic performance, the He Brayton cycle is modified by employing two turbo-expanders in different ways [13]. Figure 2(f) shows 2-stage He Brayton refrigerator, where two expanders are arranged in series. Alternatively, Figure 2(h) shows dual-turbine He Brayton refrigerator, where two expanders are arranged in parallel. Figures 2(g) and 2(i) show the 2-stage He refrigerator with LN_2 pre-cooling and the dual-turbine He refrigerator with LN_2 pre-cooling, respectively. In 2-stage systems, two turbines have the same flow rate, but different pressure ratios. In dual-turbine systems, on the contrary, two turbines have the same pressure ratio, but different flow rates.

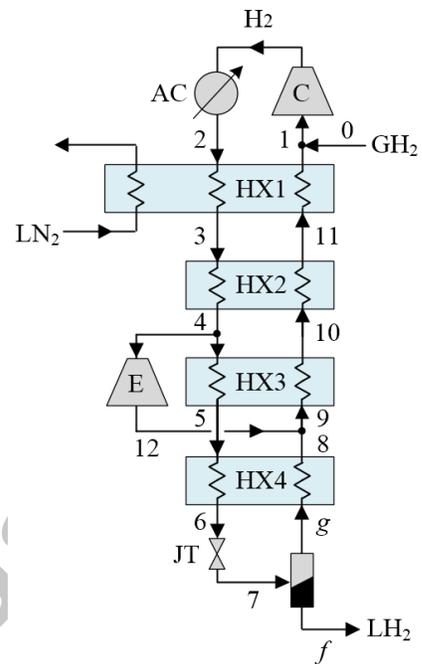
Figure 2(j) shows the Linde-Hampson system pre-cooled by Ne Brayton refrigerator, and Figure 2(k) shows the Linde-Hampson system pre-cooled by LN_2 and Ne Brayton refrigerator. These systems are more complicated in a sense that two separate cycles (Ne refrigeration cycle and H_2 liquefaction cycle) are combined.



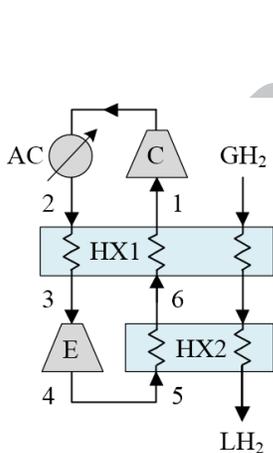
(a) Linde-Hampson with LN₂ pre-cooling



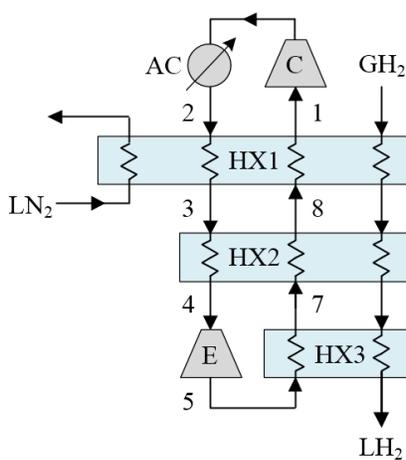
(b) Claude



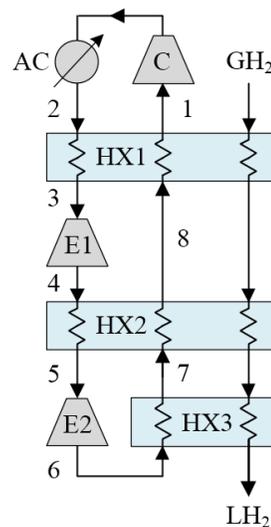
(c) Claude with LN₂ pre-cooling



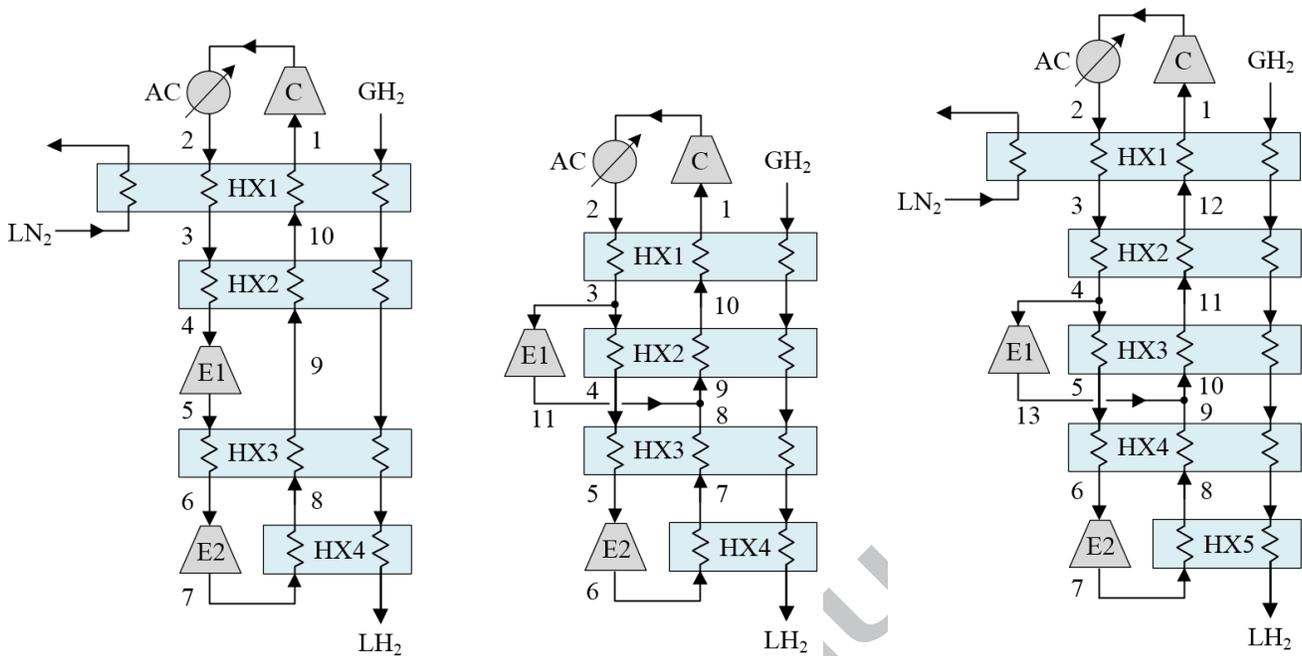
(d) He Brayton



(e) He Brayton with LN₂ pre-cooling



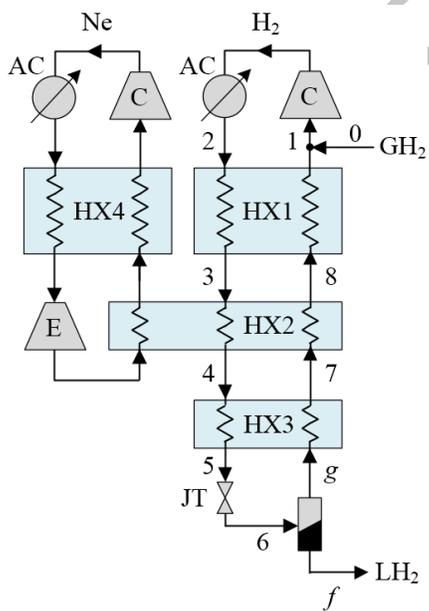
(f) 2-stage He Brayton



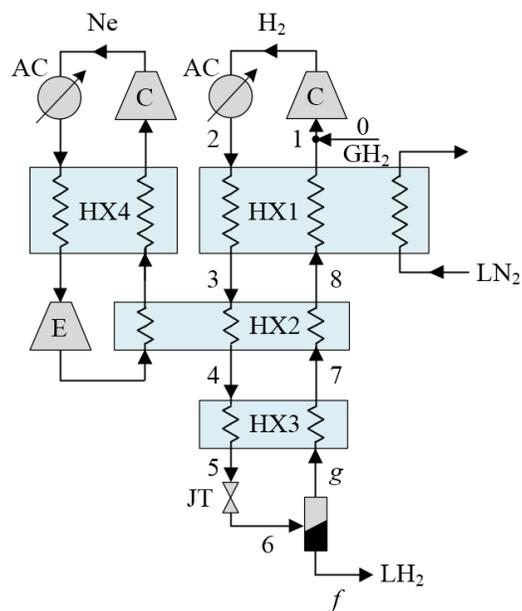
(g) 2-stage He Brayton with LN₂ pre-cooling

(h) Dual-turbine He Brayton

(i) Dual-turbine He Brayton with LN₂ pre-cooling



(j) Linde-Hampson with Ne Brayton pre-cooling



(k) Linde-Hampson with LN₂ and Ne Brayton pre-cooling

Fig. 2. Three existing cycles (a), (b), (c), and eight proposed cycles (d), (e), (f), (g), (h), (i), (j), (k).

3. Thermodynamic analysis and design

3.1 Performance index and assumptions

For a liquefier or a refrigerator of liquefaction in Figure 1, the energy and entropy balance equations are written as

$$\dot{Q}_0 = \dot{m}_f (h_0 - h_f) + (\dot{W}_C - \dot{W}_E) \quad (1)$$

$$\frac{\dot{Q}_0}{T_0} = \dot{m}_f (s_0 - s_f) + \dot{S}_{gen} \quad (2)$$

respectively. In Eq. (1) and (2), h and s are the specific enthalpy and entropy of hydrogen, respectively, and the subscripts 0 and f denote the feed gas at ambient (T_0) and the cryogenic liquid, respectively. By combining Eq. (1) and (2), the input power can be expressed as

$$\dot{W}_C - \dot{W}_E = \dot{m}_f \left[(h_f - h_0) - T_0 (s_f - s_0) \right] + T_0 \dot{S}_{gen} \quad (3)$$

where the bracket is the absolute minimum of liquefaction work per unit mass, and the last term is the additional work (called the irreversibility) due to entropy generation [16]. The total irreversibility can be itemized as the sum of the contribution by each component.

The thermodynamic performance of a liquefaction system is evaluated by the *FOM* (figure of merit), defined as the minimum work divided by the actual work [1]:

$$FOM = \frac{\dot{W}_{min}}{\dot{W}_C - \dot{W}_E} = \frac{\dot{m}_f \left[(h_f - h_0) - T_0 (s_f - s_0) \right]}{\dot{W}_C - \dot{W}_E} \quad (4)$$

The minimum work in the bracket is the flow availability (or exergy) of liquid, which is 12.0 kJ/g for normal hydrogen [1], and the actual work is the input to compressors subtracted by the output from expanders. In practice, the output power from expanders may be used for compression or simply dissipated in a braking device, but the net input power (i.e. the difference between compressor work and expander work) is considered in calculating the *FOM*. In the Linde-Hampson cycle in Figure 2(a), the expander work is simply taken as zero.

For the purpose of cycle analysis and design, the following simplifying assumptions are made:

- ① The ambient and after-cooling (and inter-cooling) temperature (T_0) is 300 K.
- ② The low pressure of all cycles is 101 kPa.
- ③ The pressure drop in all heat exchangers (HX) is zero.
- ④ The adiabatic efficiency of all compressors (C) is 80%, and the compression is multi-staged with inter-cooling such that the pressure ratio at each stage is 2~3.
- ⑤ The adiabatic efficiency of all expanders (E) is 75%.
- ⑥ The minimum temperature difference between hot and cold streams in HX's is 1% of the absolute temperature of hot stream.

Assumptions ② and ③ are made to compare the simplified cycles, and should be modified in practical design. Assumption ⑥ means that all HX's have a reasonably high effectiveness in accordance with the optimized condition [13][16], as discussed later. For example, the temperature difference is 3 K, if the hot stream is at 300 K, and 1 K, if the hot stream is 100 K.

A general-purpose process simulator (Aspen HYSYS) is used for the cycle analysis. The thermodynamic properties of hydrogen, helium, and neon are calculated with the standard database [17][18]. Hydrogen is

assumed to be normal hydrogen (composed of 75% ortho-hydrogen and 25% para-hydrogen) for the cycle analysis [1][2], and the required ortho-to-para conversion is considered later in the final design.

3.2 Linde-Hampson and Claude systems

For the analysis of the Linde-Hampson system with LN₂ pre-cooling shown in Figure 2(a), there is only one independent variable, if it is additionally assumed that LN₂ is the saturated liquid at 101 kPa. The variable is selected as the high pressure of hydrogen, whose optimum is determined to maximize the *FOM*. In calculating *FOM* for LN₂ pre-cooled systems, the input power required to supply LN₂ should be added to the actual power in the denominator of Eq. (4). Although the exergy of LN₂ may be considered as its minimum, it is practically more reasonable to take into account the price of LN₂ in comparison with the electricity consumed by compressors. It is thermodynamically assumed that the input power is four times the exergy of LN₂, which means that N₂ gas at ambient temperature is being liquefied to LN₂ with an exergy efficiency of 25%. The results show that the high pressure of hydrogen must be as high as 12.9 MPa in order to maximize the *FOM*. Under the condition, the maximum *FOM* is 14.5% and the liquid yield (the mass fraction of the gas that is liquefied) is 0.168. This tough operational condition is obviously due to the penalty of the simple and inefficient JT process. The temperature-entropy diagram and exergy expenditure of the optimized Linde-Hampson system are presented with the notation (a) in Figures 3 and 4, respectively, along with other cycles discussed below.

In the standard Claude system shown in Figure 2(b), there are two independent variables, which are selected as the high pressure and expander flow ratio (the ratio of mass flow through the expander to total mass compressed). It is a well-known design problem to optimize the expander flow ratio in association with the minimization of entropy generation due to the temperature difference in HX's [1][16][19]. The maximum *FOM* is 20.8%, when the high pressure and expander flow ratio are optimized at 6.0 MPa and 0.70, respectively. This improved performance is the result by the contribution of the efficient adiabatic expansion of turbo-expander.

The liquefaction performance of Claude system can be significantly improved with LN₂ pre-cooling, as shown in Figure 2(c). In the Claude system with LN₂ pre-cooling, there are also two independent variables, as in standard Claude system. The maximum *FOM* is 27.2 %, when the high pressure and the expander flow ratio are optimized at 2.5 MPa and 0.69, respectively. Because of LN₂ pre-cooling, the turbo-expander works at a lower temperature and the operating pressure is lower. As the industrial hydrogen liquefiers are operated under this or similar condition, these values will be a reference in evaluating the proposed cycles.

3.3 He Brayton refrigerators

In the He Brayton cycles shown in Figures 2(d) or 2(e), there is only one independent variable (the high pressure of He), because the low pressure of He and the hydrogen pressure are fixed at 101 kPa. It should be noted in all Brayton cycles that the temperature pinch (i.e. the minimum temperature difference) in the coldest HX is located at the point of saturated vapor of hydrogen, as discussed in [12]. When there is no pre-cooling, the maximum *FOM* is 8.7% with the optimized high pressure at 0.91 MPa, but when the LN₂ pre-cooling added, the maximum *FOM* is 21.1% with the optimized high pressure at 0.32 MPa. Figure 5 shows the effect of LN₂ pre-cooling in standard He Brayton cycles, indicating the point of maximum *FOM* in each cycle by a dot.

In the 2-stage He Brayton cycles shown in Figures 2(f) or 2(g), there are two independent variables (the high pressure and intermediate pressure of He), because two turbines are arranged in series. The maximum *FOM* is 21.5% without pre-cooling, when the high and intermediate pressures are optimized at 0.41 MPa and 0.23 MPa, respectively. It is noticeable that the pressure ratio is almost same for two turbines. With LN₂ pre-cooling, the maximum *FOM* is 24.2%, and the optimized high and intermediate pressures are 0.29 MPa and 0.22 MPa, respectively. The effect of LN₂ pre-cooling, however, is not so significant in 2-stage cycle.

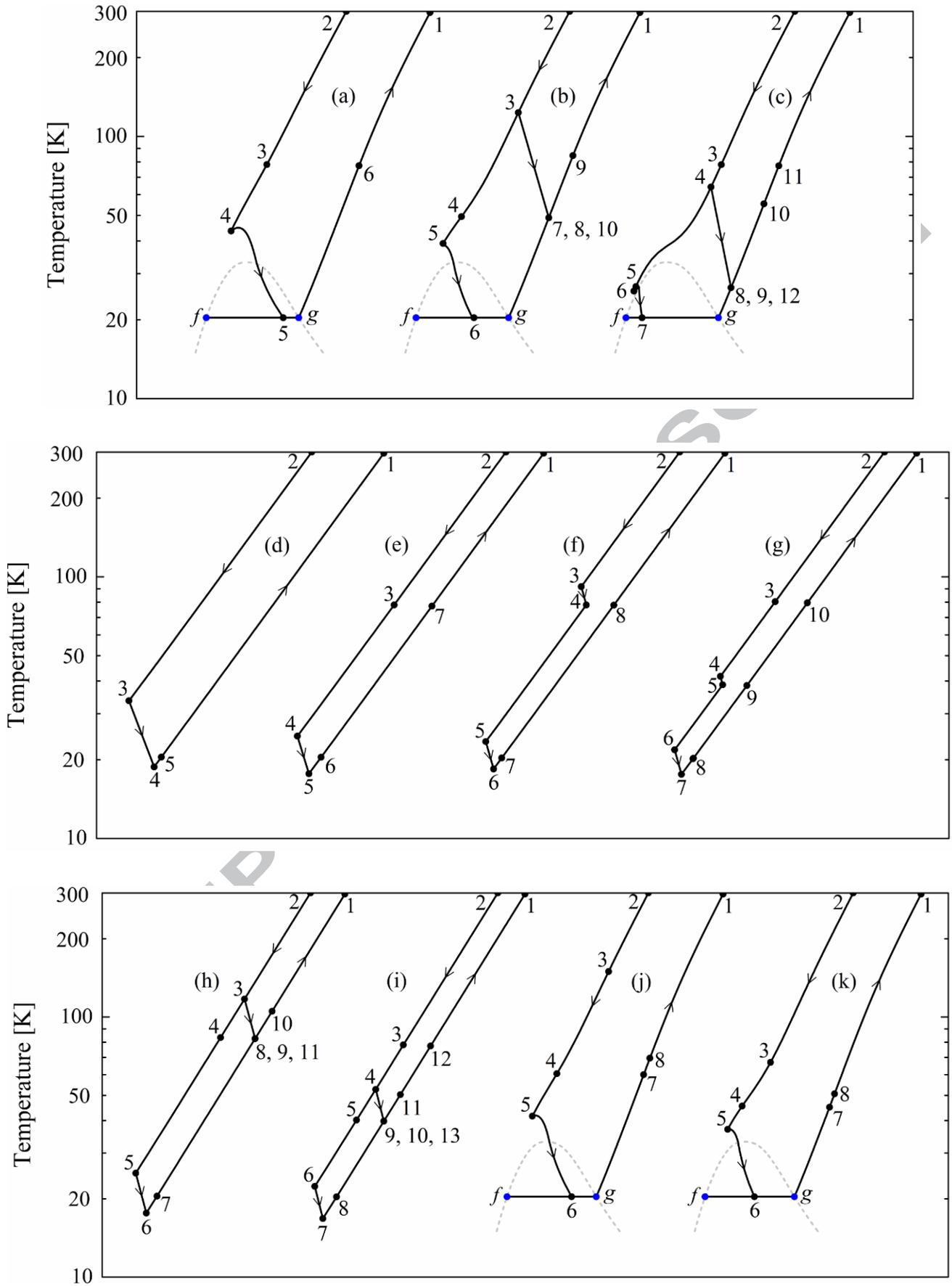


Fig. 3 Temperature-entropy diagram of three existing cycles and eight proposed cycles.

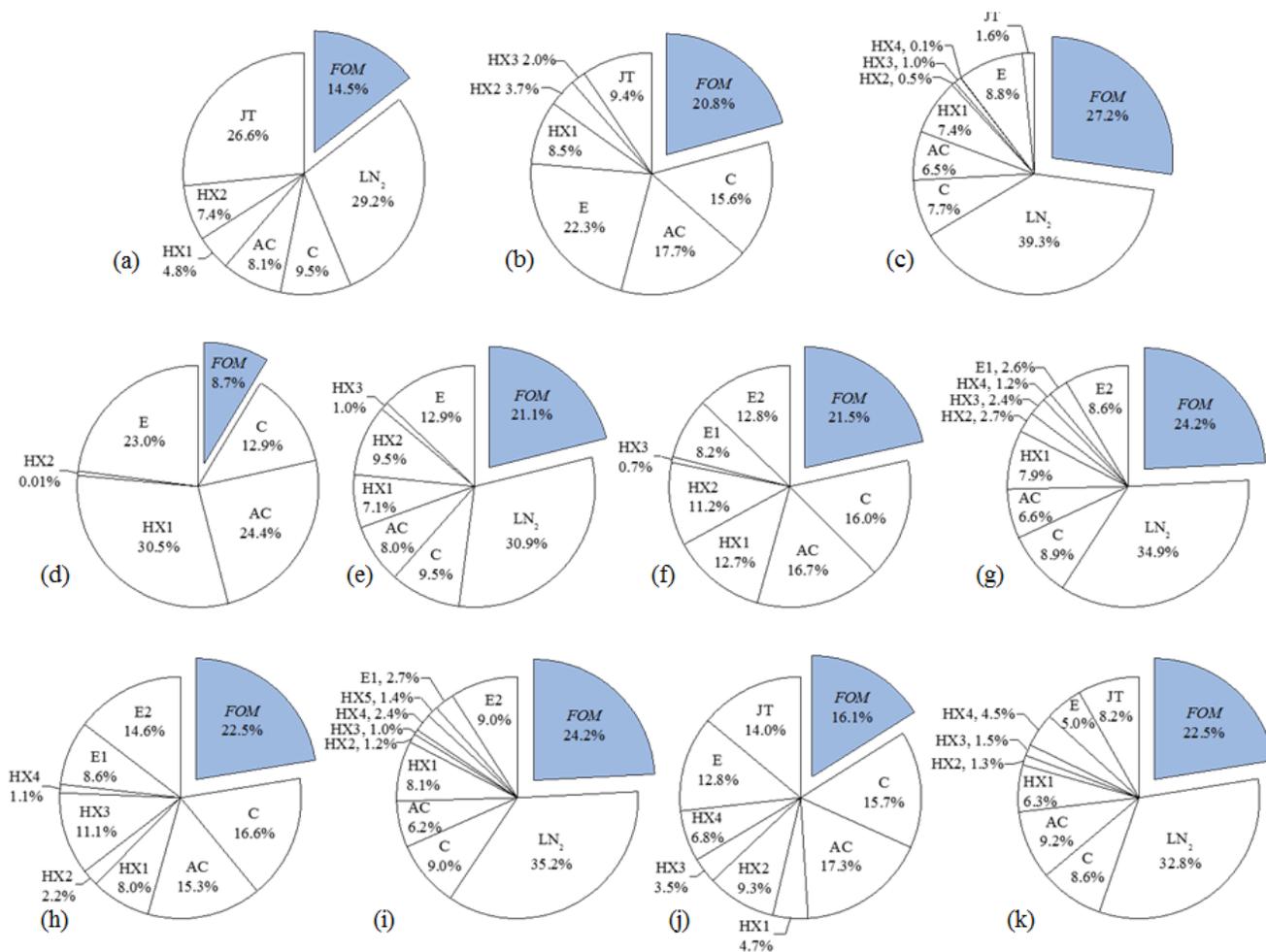


Fig. 4 Exergy expenditure of three existing cycles and eight proposed cycles.

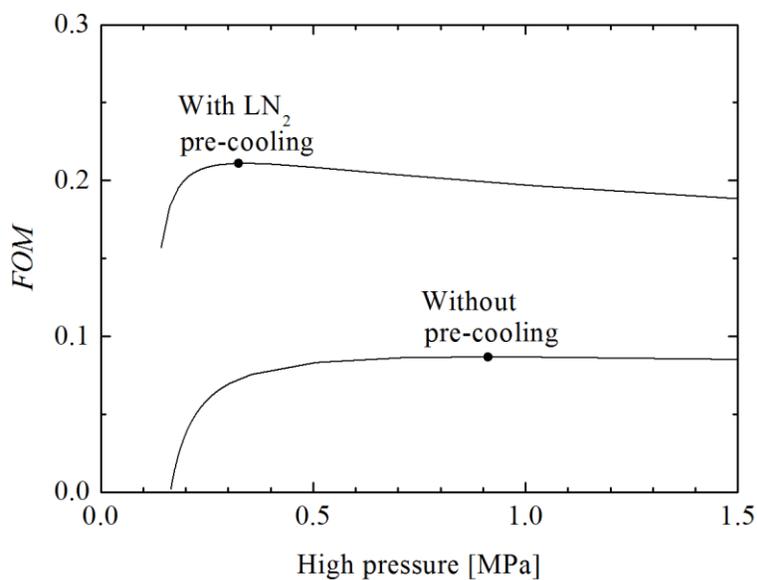


Fig. 5 Effect of LN₂ pre-cooling in standard He Brayton cycle.

In the dual-turbine He Brayton cycles shown in Figures 2(h) or 2(i), there are also two independent variables (the high pressure of He and the mass flow ratio of warm turbo-expander), because two turbines are arranged in parallel. The maximum FOM is 22.5% without pre-cooling, when the high pressure and flow ratio are optimized at 0.35 MPa and 0.37, respectively. With LN_2 pre-cooling, the maximum FOM is 24.2%, when the optimized high pressure and flow ratio is optimized at 0.27 MPa and 0.23, respectively. This small value of flow rate (0.23) means that the flow rate is quite different for two turbo-expanders, even though the pressure ratio is the same. The effect of LN_2 pre-cooling is not so significant in dual-turbine cycle either.

Figure 6 compares the FOM of the standard, 2-stage, and dual-turbine He Brayton cycles as a function of high pressure. The point of maximum FOM at optimized high pressure in each cycle is indicated by a dot. By employing two turbo-expanders, the FOM is considerably increased, and the optimized high pressure is greatly reduced. The arrangement of two expanders (in series or parallel) does not make a remarkable difference in FOM near the optimized condition.

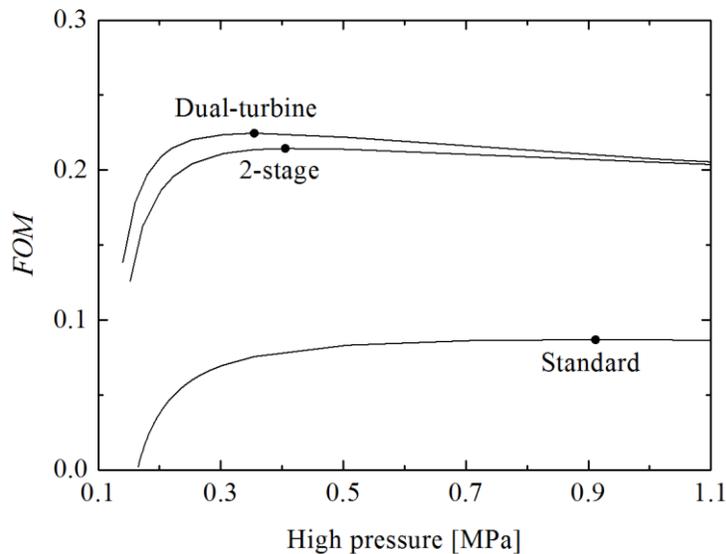


Fig. 6 Comparison of standard, 2-stage, and dual-turbine He Brayton refrigerators

3.4 Ne Brayton refrigerators

The optimization of the Linde-Hampson system pre-cooled by Ne Brayton refrigerator shown in Figure 2(j) is more complicated. There are three independent variables, which are selected as the high pressure of hydrogen (Linde-Hampson), the high pressure of Ne (Brayton), and the lowest temperature of Ne (the exit temperature of expander). It is further assumed that the pressure ratio of Ne Brayton cycle is 2.0, as the Ne refrigerators have been optimally designed and successfully developed [14][15]. After a number of repeated cycle analyses, it is found that there is a unique optimum for the high pressure of hydrogen and lowest temperature of Ne cycle to maximize the overall FOM . The maximum FOM is 16.1%, when the high pressure of hydrogen is 9.0 MPa, and the lowest temperature of Ne cycle is 60 K.

In the Linde-Hampson system pre-cooled by LN_2 and Ne refrigerator shown in Figure 2(k), there are also three independent variables, but it is also assumed that the pressure ratio of Ne Brayton cycle is 2.0. For the optimized cycle, the maximum FOM is 22.5%, when the high pressure of hydrogen is 6.0 MPa and the lowest temperature of Ne is 45 K.

4. Results and discussion

4.1 Comparison of existing and proposed cycles

Figure 7 compares three existing cycles (a), (b), (c), and eight proposed cycles (d), (e), (f), (g), (h), (i), (j), (k) in Figure 1 in terms of FOM and high pressure. The black and grey columns represent the systems without pre-cooling and with LN_2 pre-cooling, respectively. The Linde-Hampson system without pre-cooling is not included in the graphs, as it is not capable of hydrogen liquefaction. The Linde-Hampson system with LN_2 pre-cooling (a) is poor in efficiency and requires an extremely high pressure. It is clearly observed that in all other cases, the LN_2 pre-cooled system has a higher FOM and a lower level of high-pressure than the corresponding system without pre-cooling.

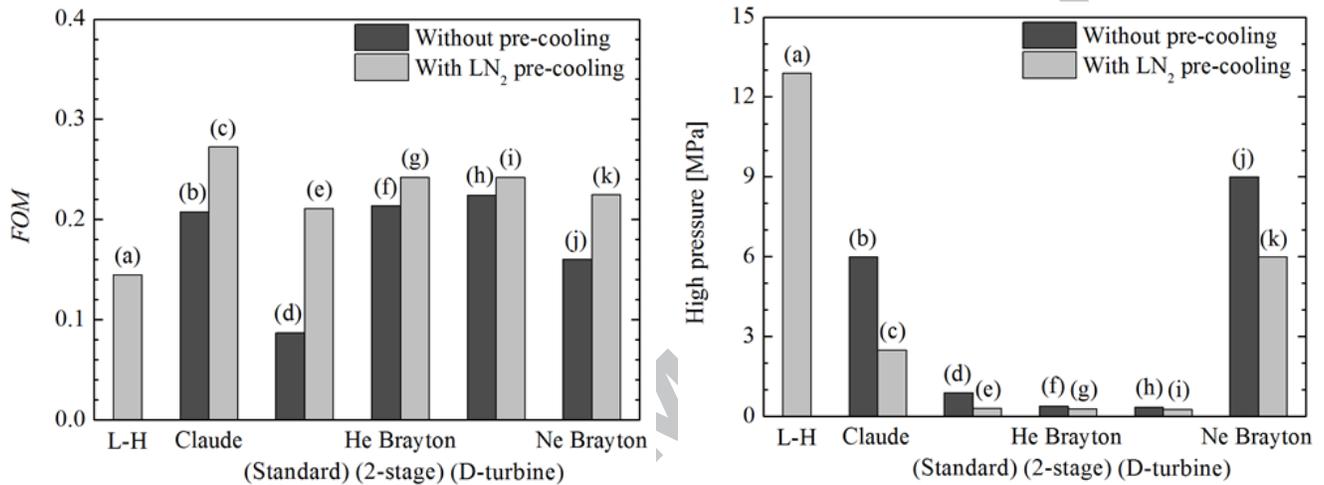


Fig. 7 Comparison of three existing cycles and eight proposed cycles in terms of FOM and high pressure

Above all cycles, the Claude system with LN_2 pre-cooling (c) is most efficient and can operate at a relatively lower level of high pressure than the Linde-Hampson system. The Claude system without pre-cooling (b) is fairly efficient as well, but requires a higher operating pressure. As mentioned above, these values of FOM and high pressure are the reference in evaluating the eight proposed cycles.

The most notable is that the high pressure of all Brayton cycles (d) through (i) is lower almost by an order of magnitude, which must be a clear benefit of the gas refrigeration cycle for liquefaction. The standard He Brayton refrigerator without pre-cooling (d) is lowest in thermodynamic efficiency. The main reason is the seriously large irreversibility in HX1, as shown in Figure 4(d). The He Brayton refrigerator with LN_2 pre-cooling (e) has a phenomenally improved efficiency so that the FOM is comparable with the Claude system without pre-cooling (b). Although the dual-turbine cycle without pre-cooling (h) is slightly superior in FOM to the 2-stage cycle without pre-cooling (f), both cycles are sufficiently efficient. A key point here is that the addition of LN_2 pre-cooling makes only a minor improvement in FOM for both cycles. In other words, since these cycles are already composed of two turbo-expanders at the optimized condition (either in series or parallel), the LN_2 pre-cooling plays only a minor role as third stage.

The Linde-Hampson systems pre-cooled by Ne Brayton refrigerator (j)(k) are reasonably efficient with or without LN_2 pre-cooling. The major difficulty, on the other hand, is the level of high pressure of hydrogen in Linde-Hampson system, even though the Ne Brayton refrigerator may operate at low pressures. The pressure level of hydrogen is even higher than that of existing Claude systems (b)(c). If the coldest Ne temperature were

lower, the operating pressure could be lower because of the thermodynamic nature of JT expansion in Linde-Hampson systems, but a serious loss in overall *FOM* should be followed.

In summary, two choices are recommended for the small-capacity (100 L/h) liquefaction. The first is the He Brayton cycle with LN₂ pre-cooling (e). This cycle is an obvious choice from the view point of simple structure and safe operation, taking advantage of the single-loop cycle with only one turbo-expander and without JT valve. A continuous LN₂ supply is indispensable in order to expect the designed performance. The second choice is the 2-stage He Brayton cycle without pre-cooling (f). Among the “dry” systems that do not need the LN₂ supply, this cycle is a compromise between simplicity and efficiency, still taking advantage of the single-loop cycle with two turbo-expanders in series. It should be pointed out that these recommended cycles have various technical merits over the existing Clause system, including the safety (the low pressure operation), the simple operation (no branching flow), and the less contamination problem of hydrogen (no JT valve).

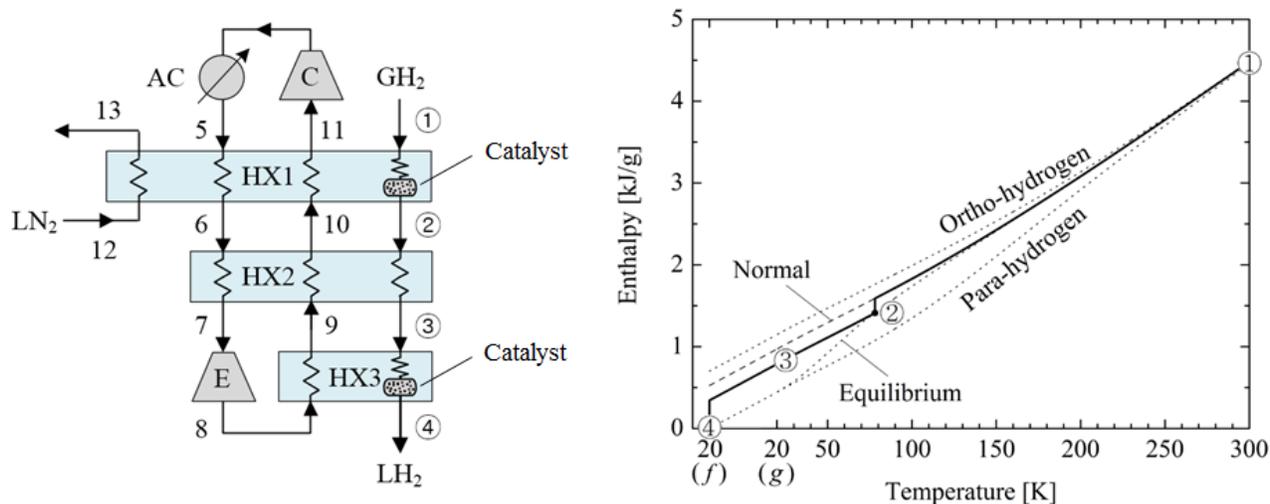
4.2 Ortho-to-para converters

A unique feature of hydrogen liquefaction is the requirement of ortho-to-para conversion, as hydrogen can exist in two different molecular forms (para-hydrogen and ortho-hydrogen). The equilibrium concentration of para-hydrogen is 25% (called the normal hydrogen) at room temperature, but continuously increases up to 99.9% at liquid temperature. Since para-hydrogen has a lower energy level, ortho-hydrogen must be converted to para-hydrogen along the liquefaction process in order to reach the liquid state at stable equilibrium. In practice, since the conversion is a very slow process, proper catalyst is commonly used in hydrogen liquefiers.

Exactly speaking, however, the catalytic converter may or may not be required, depending on the length of storage period as liquid. For example, if the liquid is consumed within a few days, the boil-off caused by slow ortho-to-para conversion is not so severe, and the liquid of normal hydrogen can be just useful as energy carrier. But if the liquid should be stored for a longer period, the catalytic converter is obligatory to avoid the excessive boil-off caused by delayed conversion. Once the catalytic converters are included in a liquefaction system, the thermodynamic cycle should be modified, taking into account the conversion heat.

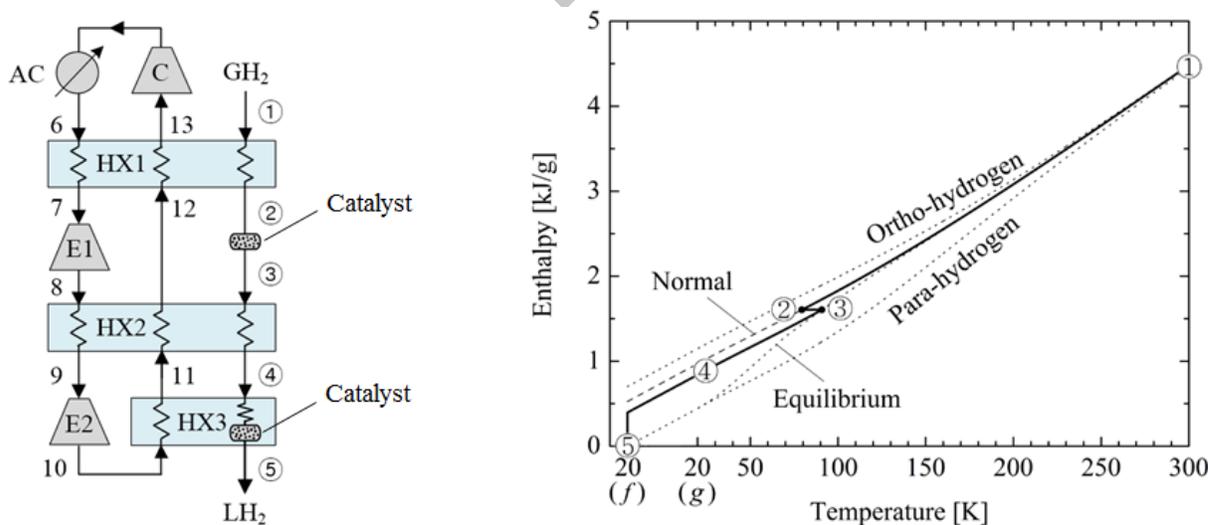
The recommended cycles (He Brayton cycle with LN₂ pre-cooling and 2-stage He Brayton cycle) are designed again with ortho-to-para converters and the results are presented in Figures 8 and 9. In each cycle, two stages of conversion are arranged, as in typical liquefiers [1]. The first catalyst for gas to pass through is located at an intermediate temperature, and the second catalyst is located at the cold end of liquefaction stream. In Figure 8, the first conversion is basically isothermal at LN₂ temperature, assuming that the additional LN₂ supply covers the conversion heat. In Figure 9, on the contrary, the first conversion is an adiabatic process, where the hydrogen temperature increases by conversion heat. In both cycles, the second conversion is isothermal at 20 K, assuming that the He refrigerator covers the additional heat at the cold end.

In order to clarify the difference between isothermal and adiabatic conversion, the liquefaction process is plotted on enthalpy-temperature diagram in Figures 8 and 9. At the left end, the phase change from vapor to liquid (condensation) at 20 K is graphically included. The dotted curves at top and bottom are the enthalpy of ortho-hydrogen and para-hydrogen [1][17][18], respectively, and the dashed curve between them is the enthalpy of normal hydrogen or equilibrium hydrogen. As indicated by the solid curve from right to left, the hydrogen flow has two vertical drops in Figure 8, representing two isothermal conversions, but has a horizontal shift to right and a vertical drop in Figure 9, representing the first adiabatic conversion and the second isothermal conversion, respectively.



	①	②	③	④	5	6	7	8	9	10	11	12	13
Temperature [K]	300.0	78.1	23.7	20.4	300.0	78.1	23.7	17.2	20.3	77.4	297.0	77.4	297.0
Pressure [MPa]	0.101	0.101	0.101	0.101	0.600	0.600	0.600	0.200	0.200	0.200	0.200	0.101	0.101
Vapor fraction	1.000	1.000	1.000	0.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.000	1.000
Flow rate [g/s]	1.967	1.967	1.967	1.967	99.91	99.91	99.91	99.91	99.91	99.91	99.91	16.85	16.85
Para fraction	0.251	0.511	0.511	0.999	(He)	(N ₂)	(N ₂)						

Fig. 8 Recommended He Brayton refrigeration cycle with LN₂ pre-cooling and ortho-to-para converters



	①	②	③	④	⑤	6	7	8	9	10	11	12	13
Temperature [K]	300.0	79.4	90.8	22.6	20.4	300.0	79.4	67.6	22.6	17.7	20.2	67.7	297.0
Pressure [MPa]	0.101	0.101	0.101	0.101	0.101	0.800	0.800	0.460	0.460	0.200	0.200	0.200	0.200
Vapor fraction	1.000	1.000	1.000	1.000	0.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Flow rate [g/s]	1.967	1.967	1.967	1.967	1.967	127.0	127.0	127.0	127.0	127.0	127.0	127.0	127.0
Para fraction	0.251	0.251	0.436	0.436	0.999	(He)							

Fig. 9 Recommended 2-stage He Brayton refrigeration cycle with ortho-to-para converters

4.3 Plan for prototype and heat exchangers

Based on the recommended cycles, the details for 100 L/h (1.97 g/s) liquefaction cycle are presented as a table in Figures 8 and 9, listing the values of temperature, pressure, vapor fraction, flow rate, and para-hydrogen fraction at every point of the cycle. It is recalled that Assumptions ② and ③ are made to compare the simplified cycles, but the operating pressure is determined at a higher level, maintaining the same pressure ratio at its optimum. The additional thermal load for ortho-to-para conversion is included in the design. The hydrogen pressure should be also higher, as the catalytic converters make additional flow resistance. In summary, the He Brayton refrigerator with LN₂ pre-cooling requires 106 kW + 75.5 L/h (16.9 g/s) LN₂, while the 2-stage He Brayton refrigerator requires 158 kW only. These values can be compared with the requirement for the cycles without ortho-to-para conversion; 77 kW + 67.8 L/h (15.2g/s) LN₂ in cycle (d) and 121 kW in cycle (e).

The heat-exchanger (HX) design is a significant next step. Although the details are beyond the scope of this thermodynamic study, a few comments are briefly made. A well-known optimization theory for cryogenic refrigeration is considered in association with the effect of finite HX size, because the system consists of multi-staged HX's. It is always true that as the HX area increases, the entropy generation due to the temperature difference between hot and cold streams decreases. It is an effective design strategy, however, how to allocate the HX area to each stage, if the total sum of the area is fixed. This problem is formulated as an optimization subject to constraints, which is solved by the method of Lagrange multiplier [16][19][20]. As a result, the optimal temperature difference is proportional to the absolute temperature, as already incorporated by Assumption ⑥.

Many HX's in the liquefaction systems have multiple (three or more) streams as shown in Figure 2. Among a few options in HX type, the plate-fin heat exchanger (PFHX) will be selected for the prototype, because of its compactness and design flexibility [21]. As widely used in various cryogenic systems, the multiple layers of aluminum finned-plates can easily create the multi-pass and multi-stream with a very compact structure. It is recalled that in this thermodynamic design, only two composite temperatures were considered, simply assuming that all hot streams have the same temperature and all cold streams have the same temperature. As reported in [22], this assumption is more or less difficult to realize in practice, but can be closely accomplished with an elaborated HX design.

5. Conclusion

Eight different thermodynamic cycles with helium or neon Brayton refrigerator are proposed and rigorously studied for the feasibility of application to small-scale hydrogen liquefaction. A cycle analysis is carried out to determine the optimal operating condition in each cycle, and the proposed cycles are compared with the existing liquefaction systems in terms of thermodynamic efficiency (*FOM*) and operating pressure. It is concluded that a reasonably efficient liquefaction system may well be designed with He Brayton refrigerators operating at much lower pressures. Specifically, the He Brayton cycle with LN₂ pre-cooling and the 2-stage He Brayton cycles are preferably recommended for the next step of development. Full details of the thermodynamic cycles with ortho-to-para conversion are immediately applicable to our prototype construction of 100 L/h liquefier, and should be technically useful as well in the design of other gas refrigeration systems for liquefaction.

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Highlights

- A thermodynamic study is carried out for small-scale hydrogen liquefaction.
- Standard and modified Brayton cycles with helium or neon are investigated.
- Helium Brayton refrigerators are recommended for efficiency and simplicity.
- Detailed design is presented for the prototype development of 100 L/h liquefier.

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