Review

A thermodynamic review of cryogenic refrigeration cycles for liquefaction of natural gas

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ABSTRACT

A thermodynamic review is presented on cryogenic refrigeration cycles for the liquefaction process of natural gas. The main purpose of this review is to examine the thermodynamic structure of various cycles and provide a theoretical basis for selecting a cycle in accordance with different needs and design criteria. Based on existing or proposed liquefaction processes, sixteen ideal cycles are selected and the optimal conditions to achieve their best thermodynamic performance are investigated. The selected cycles include standard and modified versions of Joule–Thomson (JT) cycle, Brayton cycle, and their combined cycle with pure refrigerants (PR) or mixed refrigerants (MR). Full details of the cycles are presented and discussed in terms of FOM (figure of merit) and thermodynamic irreversibility. In addition, a new method of nomenclature is proposed to clearly identify the structure of cycles by abbreviation.

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Contents

1. Introduction

Liquefaction of natural gas is one of the most important thermodynamic processes in cryogenic gas industry. For the purpose of high-density storage and long-distance transport, natural gas is liquefied to cryogenic liquid called LNG (liquefied natural gas) in a large based-load plant near gas reservoir. The liquefaction of natural gas is different in thermodynamic structure from that of other cryogenic gases, such as air (nitrogen and oxygen), hydrogen, or helium [1,2], as illustrated in Fig. 1. In general, a refrigeration system is used to remove a thermal load ($\dot{Q}_L$) from

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Nomenclature

FOM	figure of merit
h	specific enthalpy
$\dot{m}$	mass flow rate
$\dot{Q}$	heat transfer rate
s	specific entropy
$\dot{S}_{gen}$	entropy generation rate
T	temperature
U	overall heat transfer coefficient
$\dot{W}$	power or work rate

Greek letters

ε	heat exchanger effectiveness

Subscripts

0	ambient
1, 2, 3, …	location in refrigeration cycle
AC	after-cooler
C	compressor
E	expander
F	natural gas feed
HX	heat exchanger
JT	JT valve
L	LNG or liquefied natural gas
max	maximum
min	minimum
MIX	mixing device

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low-temperature source, and it works in a closed cycle, as shown in Fig. 1(a). The refrigeration requires a cost of net input power ($\dot{W}_C - \dot{W}_E$), and heat ($\dot{Q}_0$) must be rejected to ambient. A liquefaction system is used to receive gas at ambient temperature and deliver liquid at cryogenic temperature, and it works in an "open" cycle (strictly speaking, not a complete cycle), as shown in Fig. 1 (b). In most cases, the gas itself is the working fluid that undergoes the process of compression and expansion. The liquefaction also requires a cost of input power, and heat must be rejected to ambient. On the other hand, a natural gas liquefaction system works basically like a closed refrigeration cycle, but the thermal load is distributed over a temperature range of the natural gas (NG) flow from ambient to cryogenic LNG temperature, as shown in Fig. 1 (c). In order to clarify this structural difference, this review is titled with the term, "refrigeration cycles for liquefaction of natural gas."

Natural gas (NG) is a mixture of different hydrocarbons and minor gases. Along the flow of liquefaction, its specific heat varies significantly over temperature, depending on the pressure and composition. Fig. 2 shows the temperature–entropy (*T*–*s*) diagram and the specific heat (at constant pressure) as a function of temperature for NG with a composition of 1% nitrogen, 91% methane, 5% ethane, 2% propane, 0.6% n-butane, and 0.4% i-butane (on mole basis). As the isobar of 5 MPa is indicated by bold curve, for example, the liquefaction flow of NG can be divided into three regions by the phase: pre-cooling (vapor), condensation (phase change), and sub-cooling (liquid). The specific heat has a sharp peak around 200 K, which makes the cooling load uneven along the NG flow. In order to achieve a high thermodynamic efficiency, it is crucial to minimize the entropy generation due to the temperature difference between the refrigeration cycle and the NG flow.

A variety of liquefaction processes have been developed and patented over the past half century, and further effort still continues for improving the processes in efficiency, capacity, or reliability. Out of the numerous liquefaction processes, however, only a few are under operation in practice, and one dominant process (widely called C3-MR or propane-precooled mixed-refrigerant process) has been considered the reasonable choice for large-scale liquefaction. It was only several years ago that many plant engineers began to look for different options in refrigeration cycles, because the most suitable process may be different for smaller-scale liquefaction or under particular conditions, such as peak-shaving plants, offshore or floating plants, re-liquefaction of boil-off gas, and biogas/waste application. In accordance with the recent needs, a few monographs and review articles have been published up to date to compare various LNG processes under operation or for future development [3–12]. This paper is another review with the same motivation, but has been prepared with unique features in the following three aspects.

First, the main objective of this review is to examine the structure of cryogenic refrigeration cycles from a thermodynamic point of view. As thermodynamics is "the science of energy and entropy" aiming at efficient energy conversion [13,14], it is intended to describe how efficiently a variety of refrigeration cycles work with different refrigerants. The refrigeration cycles include possible modifications and proposals as well as fully developed and proven ones. Thermodynamic efficiency (to be defined as FOM) is the major index to evaluate the cycles, and the loss of thermodynamic availability (called the irreversibility) is itemized by the contribution of each component in the cycle. Other technical issues involved in practical liquefaction process (such as the
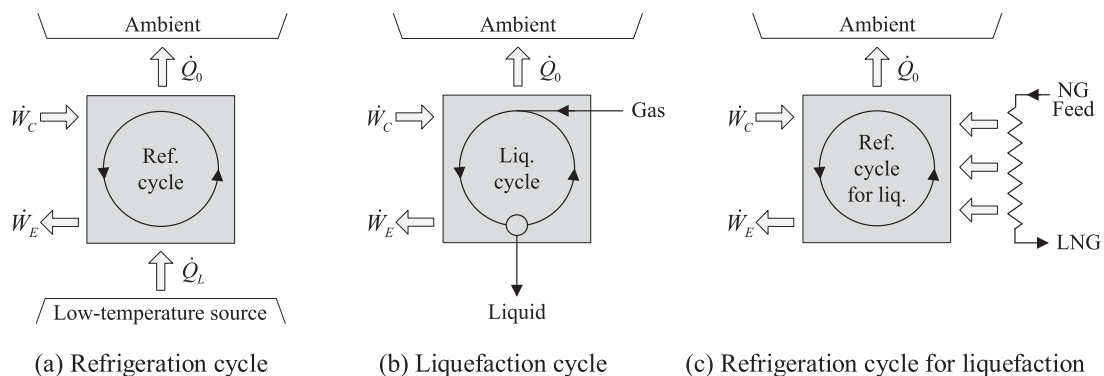

(a) Refrigeration cycle   (b) Liquefaction cycle   (c) Refrigeration cycle for liquefaction

Fig. 1. Energy and mass flow in cryogenic refrigeration and liquefaction cycles.
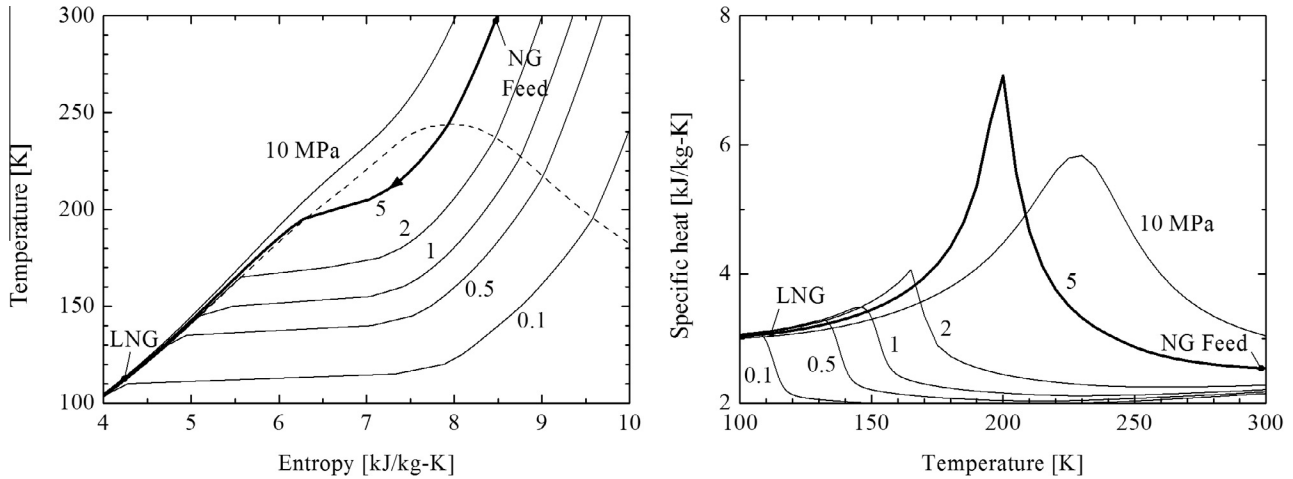
Fig. 2. Temperature–entropy (*T*–*s*) diagram and specific heat as a function of temperature for NG with a composition of 1% nitrogen, 91% methane, 5% ethane, 2% propane, 0.6% n-butane, and 0.4% i-butane.

pre-treatment of natural gas, the power supply to compressors, or the separation or recovery of gases or liquids) are not directly considered.

Second, the "ideal" refrigeration cycles are the major focus of thermodynamic analysis. In theory, there exists an absolute (and unique) minimum in the input power to liquefy a unit mass of natural gas. A real liquefaction system needs more power input than the theoretical minimum for many different reasons. These reasons can be sorted into two groups: the reasons from the refrigeration cycle itself and the reasons from the imperfect performance of components in the cycle. The former is intrinsic to the selected thermodynamic cycle and refrigerants, while the latter is about the technical issue associated with economic factors. In engineering education on thermal design, it is common to introduce an ideal cycle first and then consider the deviation of practical cycles with the effect of components [13,14]. An ideal cycle here means that every component in the cycle is perfect, and the second group of reasons is excluded. Specifically, it will be assumed that the effectiveness of all heat exchangers is 100% (or the minimum temperature approach is zero), the pressure drop in all flow components is zero, and the adiabatic efficiency of all compressors and expanders is 100% (or the process is isentropic).

Thirdly, the cryogenic refrigeration cycles are systematically classified, and a new method of nomenclature is proposed in accordance with the thermodynamic classification. Over decades, many liquefaction processes have been called by their refrigerant or key component (e.g. C3-MR or Nitrogen-Expander process), by technical terms (e.g. Single MR, Dual MR, Optimized Cascade, or MFC), or even by proper nouns (e.g. PRICO, AP-X, or LIQUEFIN). The systematic classification with new nomenclature will be able to clearly identify the structure of refrigeration cycles and simply name the cycle with abbreviated characters and symbols.

2. Definition and performance index

For the entire liquefaction system shown in Fig. 1(c), including the refrigeration cycle and the NG stream from ambient temperature (subscript 0) to the LNG temperature (subscript *L*), the first law or the energy balance equation is written as:

$$\dot{m}_F(h_0 - h_L) = \dot{Q}_0 - (\dot{W}_C - \dot{W}_E) \tag{1}$$

where $\dot{m}_F$ and h are the mass flow rate and specific enthalpy of NG feed, respectively, and $\dot{Q}_0$ and $(\dot{W}_C - \dot{W}_E)$ are the heat rejected to ambient and the work input (the compressor work minus the expander work), respectively. The expander work $\dot{W}_E$ is applicable only to the cycles that have work-producing expanders such as a turbine. In practice, the expander work may be used for compressing the refrigerant or simply dissipated with a braking device, but $(\dot{W}_C - \dot{W}_E)$ is considered as the input. A liquefaction system is usually evaluated in terms of the work per unit mass of liquefied gas, $(\dot{W}_C - \dot{W}_E)/\dot{m}_F$. For thermodynamic evaluation, however, a dimensionless parameter (valued between 0 and 1) should be adopted, and the FOM (figure of merit) is such a performance index defined by the combined first and second laws.

From the second law, the entropy balance equation for the system is written as:

$$\dot{m}_F(s_0 - s_L) + \dot{S}_{gen} = \frac{\dot{Q}_0}{T_0} \tag{2}$$

where s is the specific entropy of NG feed, and T_0 is the ambient temperature where $\dot{Q}_0$ is rejected. The entropy generation rate, $\dot{S}_{gen}$, is zero in a reversible system, but has a positive value in practical systems. By eliminating $\dot{Q}_0$ from Eqs. (1) and (2), the work input is expressed as:

$$\dot{W}_C - \dot{W}_E = \dot{m}_F[(h_L - h_0) - T_0(s_L - s_0)] + T_0\dot{S}_{gen} \tag{3}$$

Since $\dot{S}_{gen}$ is non-negative, the minimum work required for the liquefaction is

$$\dot{W}_{min} = \dot{m}_F[(h_L - h_0) - T_0(s_L - s_0)] \tag{4}$$

which is the absolute minimum given by the thermodynamic limit. The bracket in Eq. (4) is the flow availability or exergy of LNG. The FOM of a liquefaction system is defined as the ratio of the minimum work to the actual work.

$$FOM = \frac{\dot{W}_{min}}{\dot{W}_C - \dot{W}_E} = \frac{(h_L - h_0) - T_0(s_L - s_0)}{(\dot{W}_C - \dot{W}_E)/\dot{m}_F} \tag{5}$$

The difference between the actual and minimum works is the entropy generation rate multiplied by the ambient temperature

$$(\dot{W}_C - \dot{W}_E) - \dot{W}_{min} = T_0\dot{S}_{gen} \tag{6}$$

which is called the irreversibility or the loss of availability (exergy). In Eq. (3), the entropy generation rate can be itemized by the contribution of each component involved in the system.

$$\dot{S}_{gen} = \sum_{HX}(\dot{S}_{gen})_{HX} + \sum_{JT}(\dot{S}_{gen})_{JT} + \sum_{MIX}(\dot{S}_{gen})_{MIX} + \sum_{AC}(\dot{S}_{gen})_{AC} \tag{7}$$

where HX, JT, MIX, and AC denote heat exchangers, *JT* valves, mixing devices, and after-coolers, respectively. It is noted that there is no entropy generation in ideal compressors (*C*) and expanders (*E*).

3. Classification and proposed nomenclature of refrigeration cycles

The refrigeration cycles for NG liquefaction are classified in two different ways – by the principle of expansion processes to produce low temperatures and by the type of working fluids (refrigerants) used in the cycles. Table 1 lists the refrigeration cycles in a two-dimensional way in accordance with this classification.

3.1. Cycles by expansion process

Two distinct expansion processes are used in cryogenic refrigeration – JT (Joule–Thomson) expansion and adiabatic expansion [1]. The JT expansion is a throttling process through flow resistance, such as a valve or a porous plug. Since neither heat nor work is transferred, the enthalpy of fluid remains the same so that this expansion process is modeled as isenthalpic. The JT expansion is an irreversible process, where the cooling effect is strongly dependent on the thermodynamic property of refrigerant. A refrigeration cycle with JT expansion is called "JT cycle", whose standard structure for liquefaction is shown in Fig. 3(a). High-pressure refrigerant is cooled in a counter-flow heat exchanger (HX) to liquid, and then expanded through a JT valve typically into "two-phase" region for the return flow of cold refrigerant at low pressure. The cold HX at the bottom may or may not be used, depending on the thermodynamic property of refrigerant.

On the contrary, the adiabatic expansion is a working-producing process with expanders, such as a turbine or an expansion engine. In an ideal case, the expansion is reversible and adiabatic so that this expansion is modeled as isentropic. In general, the adiabatic expansion is thermodynamically more efficient than the JT expansion, but the cryogenic expanders are costly and difficult to operate. A refrigeration cycle composed of isentropic and isobaric processes is called "(reversed) Brayton cycle", whose standard structure for liquefaction is shown in Fig. 3(b). In order to safely produce work in the expander, it is important that the refrigerant should remain in "gas phase" (or at least "vapor-rich" saturated state) throughout the cycle.

Both JT and adiabatic expansions can be used in a refrigeration system, and "Claude cycle" is one of the examples, whose standard structure is shown in Fig. 3(c). High-pressure refrigerant is branched into two streams, and then one is expanded through an expander in gas phase and the other is further cooled-down to liquid and finally expanded through a JT valve to the cold end. Alternatively, one or more JT cycles and Brayton cycles may be combined in many different ways.

3.2. Cycles by type of refrigerant

Refrigeration cycles can be classified by the type of refrigerants used in the cycles – pure refrigerant (PR) and mixed refrigerant (MR). The PR cycles use a single-component fluid, such as propane or nitrogen. The MR cycles use a mixture of multi-component fluids, for example, a mixture of nitrogen, methane, ethane, and propane. During the phase change (evaporation or condensation) along an isobar, temperature is constant for PR, but varies continuously for MR.

In general, the PR cycles are simple and easy to operate, but require multi-staged refrigeration to achieve a high efficiency by reducing the temperature difference between the NG feed and PR in HX's, as explained later. On the contrary, the MR cycles could be thermodynamically more efficient with a small number of components, but requires a sophisticated engineering in the design and operation of cycles. In many cases, a liquefaction system is composed of two or more separate cycles, which can be a combination of PR and MR cycles to take advantage of the two cycles at the same time.

3.3. Proposed nomenclature of refrigeration cycles

In accordance with the classification, a new method of nomenclature is proposed to clearly and simply identify the structure of

Table 1
Classification of sixteen refrigeration cycles with proposed nomenclature.

	Pure refrigerants (PR)		Mixed refrigerants (MR)		Pure and mixed refrigerants (PR + MR)	
JT (Joule–Thomson) cycles	(1)	p3J + e'3J + m3J	(2)	M1J	(7)	p4J + M2J
			(3)	M2J	(8)	b1J/e1J + M2J
			(4)	M1J + M1J		
			(5)	M1J + M2J		
			(6)	M2J + M2J		
Brayton cycles	(9)	n1B	(13)	M1B		
	(10)	n2B				
	(11)	n1B + n1B				
	(12)	m1B + n1B				
Combined or Claude cycles	(14)	p3J + e'3J + n1B	(15)	M1C	(16)	p4J + M1J + n1B

(1)	3-stage propane JT, 3-stage ethylene JT, and 3-stage methane JT cycles	p3J + e'3J + m3J	Cascade
(2)	1-stage MR JT cycle	M1J	SMR
(3)	2-stage MR JT cycle	M2J	SMR with PS
(4)	Dual 1-stage MR JT cycles	M1J + M1J	PRICO
(5)	1-stage MR JT, 2-stage MR JT cycles	M1J + M2J	DMR-1
(6)	Dual 2-stage MR JT cycles	M2J + M2J	DMR-2
(7)	4-stage propane JT, and 2-stage MR JT cycles	p4J + M2J	C3-MR
(8)	Parallel 1-stage butane JT, 1-stage ethane JT, and 2-stage MR JT cycles	b1J/e1J + M2J	
(9)	1-stage nitrogen Brayton cycle	n1B	N turbine
(10)	2-stage nitrogen Brayton cycle	n2B	
(11)	Dual 1-stage nitrogen Brayton cycles	n1B + n1B	Dual N turbine
(12)	1-stage methane Brayton, and 1-stage nitrogen Brayton cycles	m1B + n1B	
(13)	1-stage MR Brayton cycle	M1B	
(14)	3-stage propane JT, 3-stage ethylene JT, and 1-stage nitrogen Brayton cycles	p3J + e'3J + n1B	C3–C2–N2
(15)	1-stage MR Claude cycle	M1C	NG Claude
(16)	4-stage propane JT, 1-stage MR JT, and 1-stage nitrogen Brayton cycles	p4J + M1J + n1B	AP-X
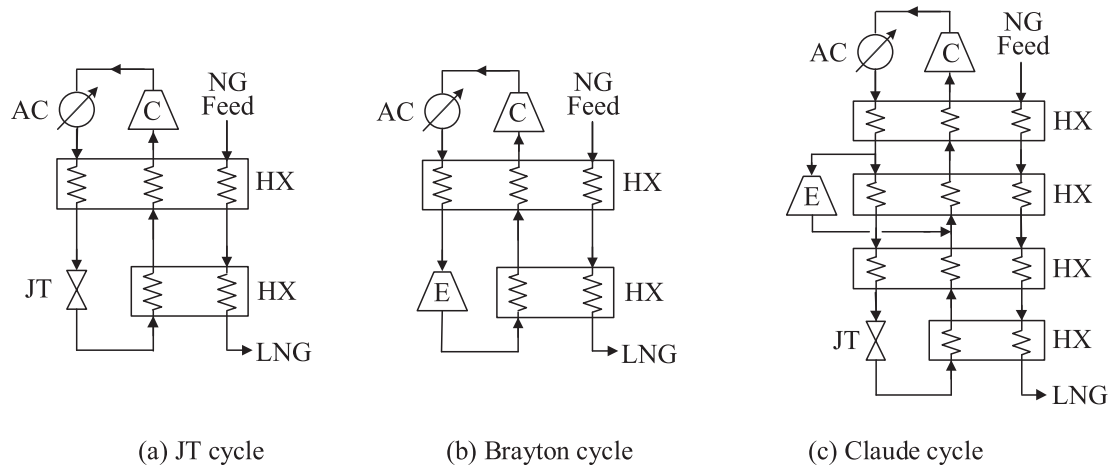
Fig. 3. Standard JT, Brayton, and Claude cycles for liquefaction of natural gas (*C*: compressor, AC: after-cooler, HX: heat exchangers, JT: Joule–Thomson valve, *E*: expander).
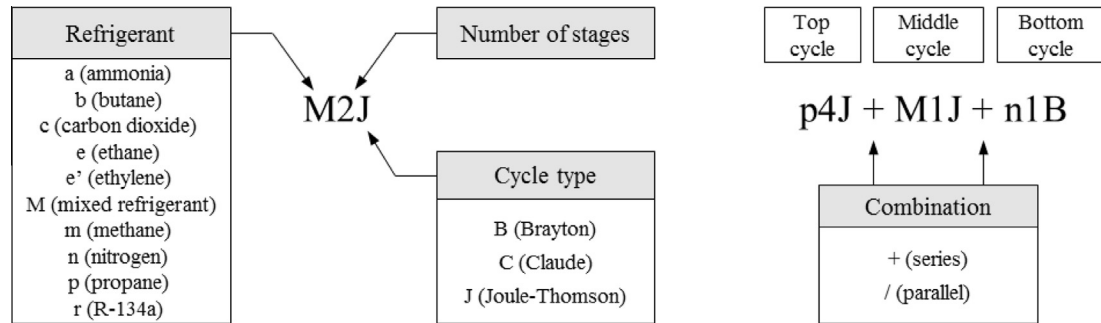
Fig. 4. Examples to illustrate the proposed nomenclature of refrigeration cycles.

cycles. As illustrated in Fig. 4, a refrigeration cycle is denoted by three characters listed in order of an alphabet, a number, and another alphabet, which denote the refrigerant, the number of stages, and the cycle type, respectively.

The refrigerant is represented by its first lower-case letter, such as propane by ⟨p⟩, and nitrogen by ⟨n⟩. A prime is added over the alphabet, if a hydrocarbon is unsaturated, such as ⟨e′⟩ for ethylene to distinguish from ⟨e⟩ for ethane. The only exceptional use of a capital letter is ⟨M⟩, which stands for mixed refrigerant to distinguish from ⟨m⟩ for methane. The third capital letter represents the cycle by the type of expansion, which has three options: ⟨B⟩ for Brayton cycle, ⟨C⟩ for Claude cycle, and ⟨J⟩ for Joule–Thomson cycle. The cycle type here includes all standard or modified cycles. It is recalled that a JT cycle contains JT expansion only, a Brayton cycle contains adiabatic expansion only, and a Claude cycle contains both JT and adiabatic expansions. For example, M2J stands for 2-stage MR JT cycle, which has the same structure as MR process with a phase separator, as described later.

When two or more separate cycles are involved, their combinations are indicated by either + (series) or/(parallel). The top (i.e. warm) cycle comes first, and then the bottom (i.e. colder) cycles follow. For example, p4J + M1J + n1B stands for a series combination of 4-stage propane JT cycle, 1-stage MR JT cycle, and 1-stage nitrogen Brayton cycle, which is known as the AP-X process under operation at the largest-capacity plants. In some cases, the refrigerant of bottom cycle is pre-cooled by the top cycle, which can be optionally indicated by grouping the cycles with (parenthesis). For example, (p4J + M1J) + n1B means that the MR of M1J cycle is pre-cooled by p4J cycle, but n1B cycle works independently from two JT cycles on the top. A series combination of 3-stage propane,

3-stage ethylene, and 3-stage methane JT cycles is denoted by p3J + e′3J + m3J, and more specifically by (p3J + (e′3J) + m3J), meaning that the ethylene of e′3J is pre-cooled by P3J and the methane of m3J is pre-cooled by e′3J, which is the structure of conventional cascade liquefaction process described later.

Sixteen refrigeration cycles were selected and listed in Table 1 for detailed examination. As described below, the selected cycles represent the simplified version of existing or proposed liquefaction processes. Among the numerous proposed cycles, only a limited number of cycles were selected mainly to examine how the modified structure affects the thermodynamic performance. The primary modification under consideration here includes the multi-staged refrigeration and the combination of multiple cycles. The effect of different refrigerants is also examined, but only a few limited choices are included and other feasible ones are briefly mentioned in the text as necessary or appropriate. It is recalled that this review focuses on the thermodynamic nature of cycles, instead of technical issues in practical liquefaction processes. In Table 1, the sixteen cycles are classified two-dimensionally by the expansion process (as JT, Brayton, and combined or Claude cycles) and by the type of refrigerants (as PR, MR, and both). The full thermodynamic names for each cycle are footnoted with the commercial or conventional terms of corresponding or closely related processes.

4. Thermodynamic performance of ideal cycles

Details of thermodynamic performance are presented for the sixteen cycles listed in Table 1. As mentioned above, only ideal cycles are considered in order to focus on the thermodynamic

		1	2	3	4	5	6
Temperature [K]		298.0	271.4	271.4	271.4	249.3	249.3
Pressure [MPa]		0.949	0.949	0.448	0.448	0.949	0.212
Vapor fraction		0.000	0.000	0.000	1.000	0.000	0.001
Flow rate [kg/s]		4.044	4.044	1.165	1.165	2.879	0.702
7	8	9	10	11	12	13	14
249.3	230.7	230.7	230.7	298.0	271.4	249.3	230.7
0.212	0.949	0.100	0.100	1.347	1.347	1.347	1.347
1.000	0.000	0.002	1.000	1.000	1.000	1.000	0.000
0.702	2.176	2.176	2.176	1.926	1.926	1.926	1.926
15	16	17	18	19	20	21	22
205.4	205.4	205.4	185.3	185.3	185.3	205.4	168.8
1.347	0.566	0.566	1.347	0.238	0.238	0.238	1.347
0.000	0.001	1.000	0.000	0.002	1.000	1.000	0.000
1.926	0.644	0.644	1.282	0.634	0.634	0.634	0.647
23	24	25	26	27	28	29	30
168.8	168.8	185.3	205.4	224.4	205.4	185.3	168.8
0.100	0.100	0.100	0.100	2.261	2.261	2.261	2.261
0.003	1.000	1.000	1.000	1.000	1.000	1.000	0.000
0.647	0.647	0.647	0.647	0.571	0.571	0.571	0.571
31	32	33	34	35	36	37	38
144.2	144.2	144.2	125.7	125.7	125.7	144.2	113.0
2.261	0.800	0.800	2.261	0.283	0.283	0.283	2.261
0.000	0.000	1.000	0.000	0.004	1.000	1.000	0.000
0.571	0.331	0.331	0.240	0.155	0.155	0.155	0.085
39	40	41	42	0	43	44	45
113.0	113.0	125.7	144.2	298.0	271.4	249.3	230.7
0.114	0.114	0.114	0.114	5.000	5.000	5.000	5.000
0.005	1.000	1.000	1.000	1.000	1.000	1.000	0.975
0.085	0.085	0.085	0.085	1.000	1.000	1.000	1.000
46	47	48	49	50	51		
205.4	185.3	168.8	144.2	125.7	113.0		
5.000	5.000	5.000	5.000	5.000	5.000		
0.760	0.000	0.000	0.000	0.000	0.000		
1.000	1.000	1.000	1.000	1.000	1.000		

Fig. 5. 3-stage propane JT, 3-stage ethylene JT, and 3-stage methane JT cycles (p3J + e′3J + m3J).

Fig. 6. FOM of propane–ethylene–methane (p + e′ + m) JT cycles with different number of stages.

structure and properties of refrigerants. The following assumptions are made for cycle analysis.

- The ambient temperature is 298 K.
- The natural gas (NG) feed has a constant composition (1% nitrogen, 91% methane, 5% ethane, 2% propane, 0.6% n-butane, and 0.4% i-butane on mole basis) at 5 MPa, and the inlet and exit temperatures are 298 K and 113 K, respectively.
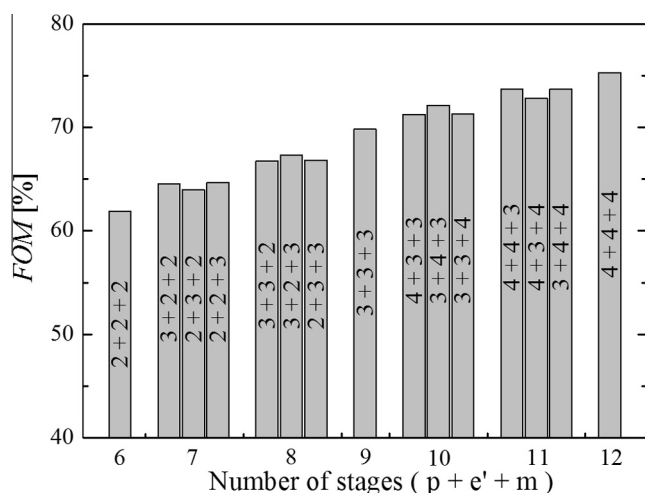- The mass flow rate of NG (that is, the liquefaction rate) is 1 kg/s.
- The pressure drop in all heat exchangers (HX), after-coolers (AC), separators, and mixing devices (MIX) is zero.
- The effectiveness of all HX's is 100%, or the minimum temperature approach between the hot and cold streams is 0 K.
- The adiabatic efficiency of all compressors (C) and expanders (E) is 100%.
- The maximum and minimum pressures of refrigerants are limited to 10 MPa and 0.1 MPa, respectively.
- The number of compression stages is determined such that the pressure ratio at each stage is 2–3, and an AC is placed at each compression stage whose exit temperature is above 298 K.
- The exit condition of pure refrigerants (PR) is saturated vapor in all evaporating HX's.

The cycle analysis is performed with a process simulator (Aspen HYSYS Version 8). The thermodynamic properties of refrigerants and NG are calculated with the Peng–Robinson equation of state (EOS) linked to the simulator. For each cycle, the results are presented as a table of thermodynamic states and graphically in temperature–entropy diagram (excluding the compression and after-cooling processes), temperature profiles in HX's, and exergy expenditure (i.e. the composition of FOM and irreversibility ratio by components). The temperature profiles in multi-stream HX's are the composite curves of hot and cold streams.

4.1. JT cycles with pure refrigerants (PR)

The JT cycles with PR involve a constant-temperature cooling process by evaporating refrigerant. For efficient liquefaction, the NG feed should be refrigerated by a series of multiple JT cycles, and each cycle is composed of multiple stages [15–21], as commonly called "cascade". Typical refrigerants are propane, ethylene (or ethane), and methane in the top, middle, and bottom cycles, respectively. Either ethylene or ethane may be used in the middle

cycle, but ethylene is superior to ethane because of its lower boiling temperature.

Fig. 5 shows an example of 3-stage propane JT, 3-stage ethylene JT, and 3-stage methane JT cycles (p3J + e′3J + m3J). At each cooling stage, propane is directly fed into compressors, but ethylene and methane are super-heated before entering the compressors. As noted in T–s diagram and temperature profiles in HX's, the cooling temperature at each stage is determined by the corresponding saturation pressure in each JT cycle. Since the highest and lowest pressures are fixed, two intermediate pressures are optimized. The maximum FOM is 69.8% for p3J + e′3J + m3J with optimized intermediate pressures. The major portion of irreversibility occurs in HX's due to the stepwise temperature profile.

The number of stages in each JT cycle is largely an economic consideration. Fig. 6 shows how the FOM increases as the total number of stages increases from 6 (=2 + 2 + 2) to 12 (=4 + 4 + 4), assuming that the ambient temperature is fixed at 298 K. The three numbers inside the column (in format of p + e′ + m) indicate the number of stages in the top (p), middle (e′), and bottom (m) cycles, respectively. As the total number of stages increases, the FOM increases more or less linearly, but the number of required components should increase accordingly. Depending on the operating and capital costs, the number of stages is determined typically as 3 in each JT cycle, but 10 (=4 + 3 + 3) stages are used in tropical climate.

4.2. JT cycles with mixed refrigerants (MR)

The structure of JT refrigeration cycle can be significantly simplified by using mixed refrigerants (MR). Fig. 7 shows the simplest 1-stage MR JT cycle (M1J), as used in the SMR process [22]. The performance of M1J is strongly dependent on the composition and pressure levels of MR. There have been a great number of reports to find the optimal conditions that maximize the FOM. Basically, the optimization needs an empirical and iterative procedure, but a somewhat robust approach has been developed, such as the sequential quadratic programming (SQP) [3,23] or the nonlinear programming (NLP) [24–26]. Recently, a generic algorithm (GA) [27–29] and knowledge-based optimization (KBO) [30] are introduced to considerably reduce the number of iterations.

The maximum FOM is 57.1% for M1J with the optimized pressure and composition of MR. The minimum temperature approach (0 K) is found at an intermediate temperature as well as two ends. The optimized composition (n + m + e + p) of MR is constant over the cycle, as listed at the bottom of thermodynamic table. The temperature difference in HX is quite small in the low-temperature region, but the irreversibility in HX is large due to the temperature mismatch near the warm end of HX.

In order to improve the thermodynamic performance, there are several schemes to modify the MR JT cycle. An important modification is to arrange the cycle for 2-stage refrigeration with a phase separator (symbolized by a small circle) as shown in Fig. 8 [31,32], which will be called 2-stage MR JT cycle (M2J). From the phase separator, liquid with heavy components is expanded at an intermediate temperature, and vapor with lighter components is expanded at the cold end. It is noted that two cooling streams are at the same pressure level, but the compositions of MR are different each other, as they are determined by the phase separation at ambient temperature. The pressure levels and composition of MR are optimized.

The maximum FOM is 53.3% for optimized M2 J. The minimum temperature approach (0 K) is found at two ends and an intermediate temperature. The FOM of M2J may be usually lower than that of M1J, because the mismatch in temperature profiles is even larger near the warm end. In spite of the shortcoming in FOM, this 2-stage cycle has advantages in practical operation, such as a smaller flow rate of MR (which may result in a smaller size of heat

	1	2	3	4	0	5
Temperature [K]	298.0	113.0	113.0	298.0	298.0	113.0
Pressure [MPa]	5.300	5.300	0.400	0.400	5.000	5.000
Vapor fraction	0.564	0.000	0.045	1.000	1.000	0.000
Flow rate [kg/s]	3.968	3.968	3.968	3.968	1.000	1.000
n + m + e + p [%]	8.6 + 30.1 + 24.3 + 37.0					

Fig. 7. 1-stage MR JT cycle (M1J).

	1	2	3	4	5	6
Temperature [K]	298.0	240.0	215.5	222.2	298.0	298.0
Pressure [MPa]	4.000	4.000	0.300	0.300	0.300	4.000
Vapor fraction	0.000	0.000	0.220	0.687	1.000	1.000
Flow rate [kg/s]	1.892	1.892	1.829	4.257	4.257	4.257
n + m + e + p [%]	1.1 + 11.3 + 30.3 + 57.3			8.6 + 30.1 + 24.3 + 37.0		
7	**8**	**9**	**10**	**11**	**0**	**12**	**13**
298.0	240.0	113.0	111.8	225.8	298.0	240.0	113.0
4.000	4.000	4.000	0.300	0.300	5.000	5.000	5.000
1.000	0.312	0.000	0.045	0.974	1.000	0.974	0.000
2.365	2.365	2.365	2.365	2.365	1.000	1.000	1.000
7.7 + 36.1 + 31.0 + 25.2							

Fig. 8. 2-stage MR JT cycle (M2J).

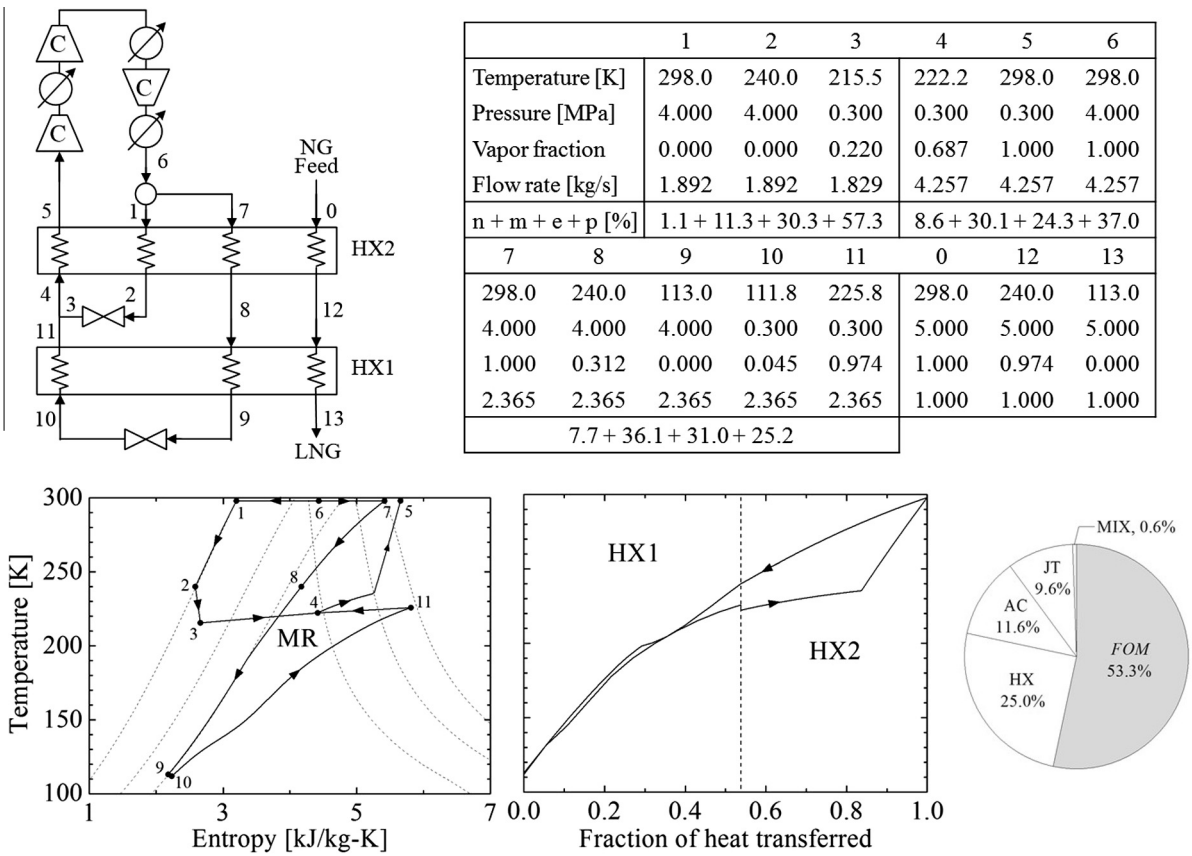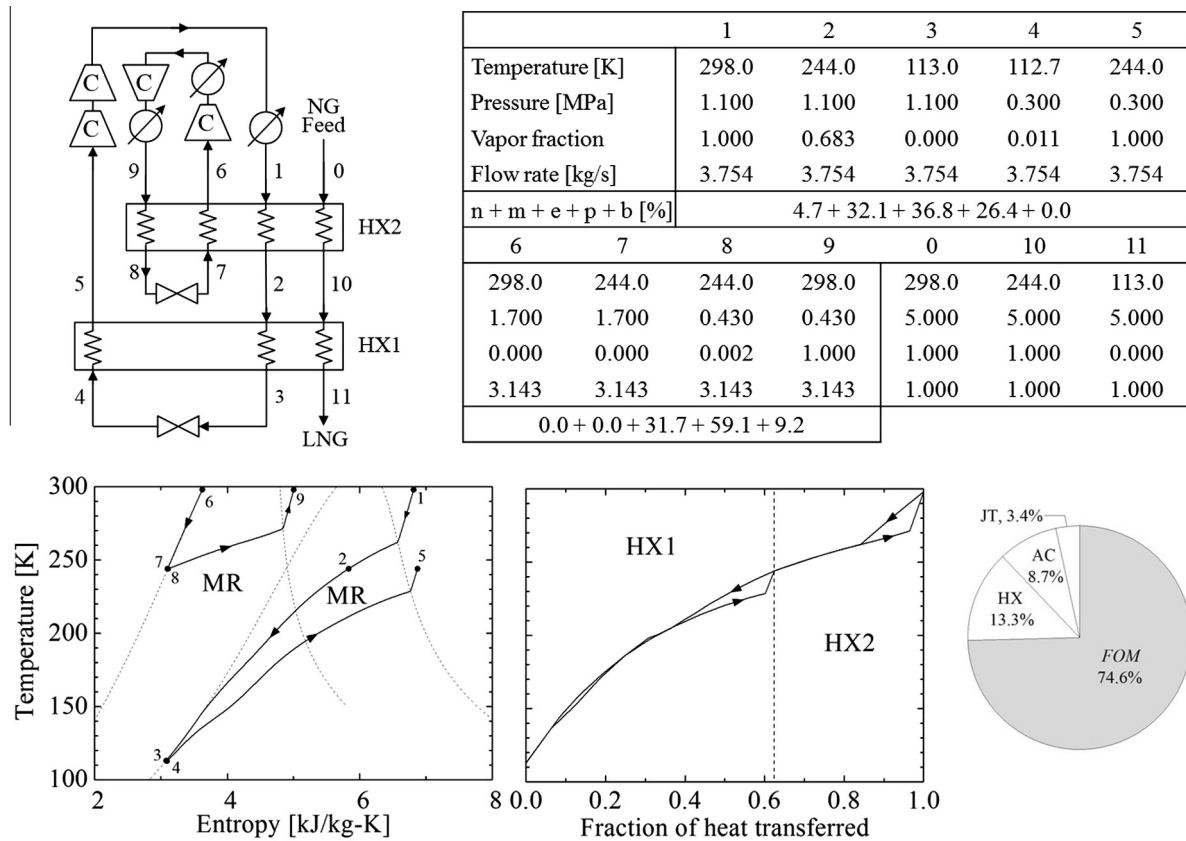|	1	2	3	4	5
Temperature [K]	298.0	244.0	113.0	112.7	244.0
Pressure [MPa]	1.100	1.100	1.100	0.300	0.300
Vapor fraction	1.000	0.683	0.000	0.011	1.000
Flow rate [kg/s]	3.754	3.754	3.754	3.754	3.754
$n + m + e + p + b$ [%]	4.7 + 32.1 + 36.8 + 26.4 + 0.0				
	6	7	8	9	0	10	11
	298.0	244.0	244.0	298.0	298.0	244.0	113.0
	1.700	1.700	0.430	0.430	5.000	5.000	5.000
	0.000	0.000	0.002	1.000	1.000	1.000	0.000
	3.143	3.143	3.143	3.143	1.000	1.000	1.000
	0.0 + 0.0 + 31.7 + 59.1 + 9.2						

Fig. 9. Dual 1-stage MR JT cycles (M1J + M1J).

exchangers), and less possibility of freezing of heavy components at the cold end [3].

The FOM of MR JT cycles can be considerably improved, if two separate cycles are employed in series. Out of a variety of combinations, three cycles are presented here – dual 1-stage MR JT cycles (M1J + M1J), 1-stage MR JT and 2-stage MR JT cycles (M1J + M2J), and dual 2-stage MR JT cycles (M2J + M2J), as shown in Fig. 9, Fig. 10, and Fig. 11, respectively. The structure of M1J + M1J is close to the PRICO process [33], and M1J + M2J and M2J + M2J are simplified versions of the DMR (dual mixed-refrigerant) processes [34–37].

The pressure levels and composition of MR are optimized in two-dimensional way for each MR JT cycle. The maximum FOM is 74.8%, 78.2%, and 78.6% for optimized M1J + M1J, M1J + M2J, and M2J + M2J respectively. These values are well above those for M1J and M2J, mainly because the temperature profiles get closer each other and the irreversibility in HX's is reduced. On the other hand, the irreversibility at JT and MIX is slightly added due to the increased number of stages.

Numerous combinations of MR JT cycles have been designed and developed, even though the details of cycles are not included in this review. An MR process under recent development in Korea, called the KSMR process [35], is similar to M2J in structure, but the two cooling stages are configured at different pressure levels and the overall compression work is minimized with a sophisticated arrangement of multiple compressors and phase separators at ambient temperature. In some cases of dual M2J cycles (M2J + M2J), the evaporating pressure in top M2J cycle can be arranged as two-stage as well [3]. The multi-pressure evaporation could be effective in reducing the temperature differences near the warm end, but may also cause more irreversibility due to the mixing of streams [37]. 3-stage MR JT cycles (M3J) have been also designed earlier by using two phase separators, as used in KLEEMENKO or TEALARC processes [38,39].

More complex structures with three separate MR JT cycles in series have been developed as well. The MFC (multi-fluid cascade) process [40] is based on 2-stage MR JT (at top) and dual 1-stage MR JT cycles (in bottom) in series (M2J + M1J + M1J). The top 2-stage MR-JT cycle works as a pre-cooling cycle for the NG feed as well as the MR streams of two bottom JT cycles. The LIQUEFIN process [41] is also composed of three MR JT cycles in series, but the two top cycles are 1-stage MR JT cycles and the bottom cycle is 2-stage MR JT cycle (M1J + M1J + M2J). Since the multiple cycles are basically independently each other, much more efforts are needed to find the optimal conditions, even though the FOM may reach an even higher value once every cycle is optimized. Another advantage of multiple MR cycles is that the performance is less sensitive to the conditions of NG feed and ambient climate [3].

4.3. JT cycles with pure refrigerants (PR) and mixed refrigerants (MR)

The robustness of PR JT cycles and the high efficiency of MR JT cycles can be achieved at the same time, if a PR JT cycle is used at the top and a MR JT cycle is used in the bottom. The most reputed is the combined 4-stage propane JT and 2-stage MR JT cycles (p4J + M2J) shown in Fig. 12, as widely called C3-MR process [42–45]. The propane JT cycle has the same structure as the top cycle of p3J + e′3J + m3J, but the number of stages is 4 in most cases (or can be 3 in cold climates). Since the pre-cooling temperature is determined by the low-pressure of top propane cycle, the bottom MR JT cycle is optimized and operated nearly independently of the top cycle.

The maximum FOM is 80.5% for optimized p4J + M2J. The optimization of p4J + M2J includes the three intermediate pressure
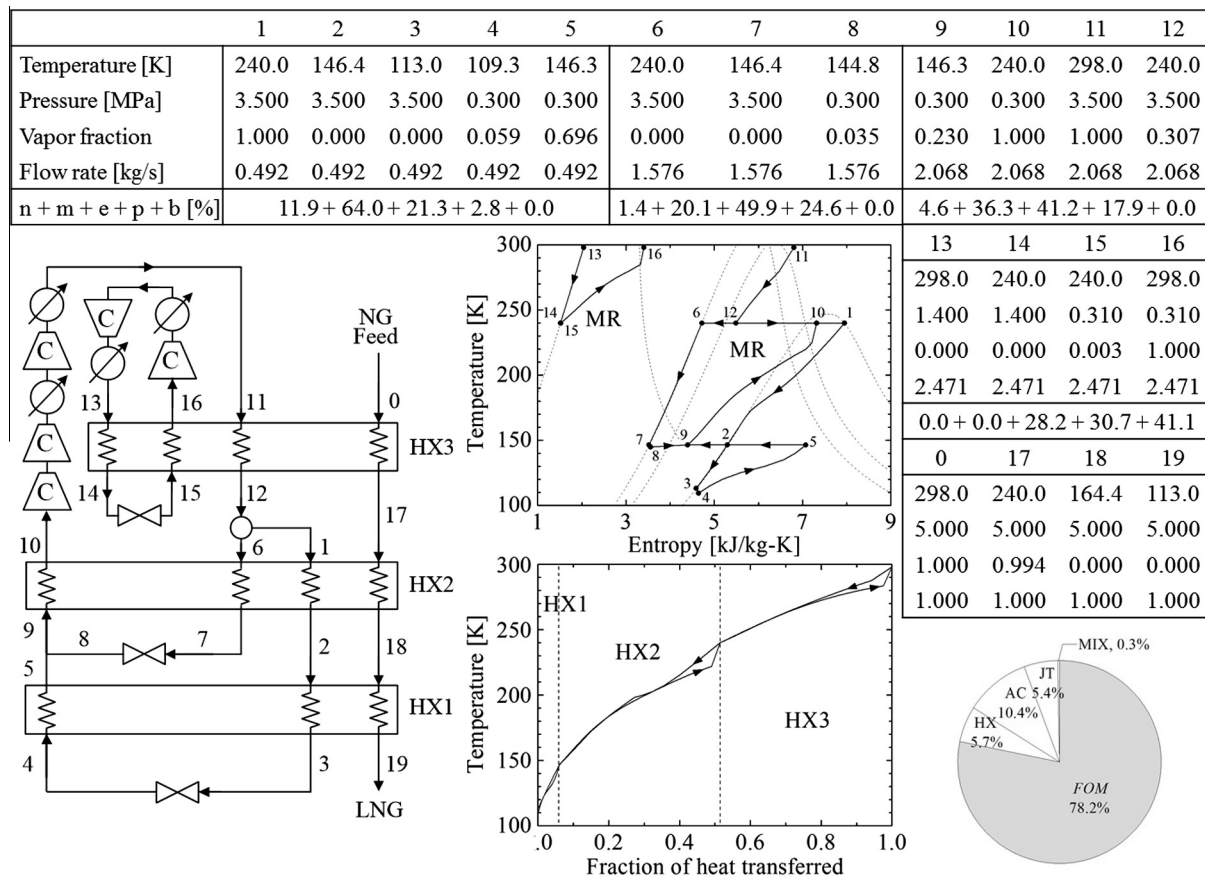
	1	2	3	4	5	6	7	8	9	10	11	12
Temperature [K]	240.0	146.4	113.0	109.3	146.3	240.0	146.4	144.8	146.3	240.0	298.0	240.0
Pressure [MPa]	3.500	3.500	3.500	0.300	0.300	3.500	3.500	0.300	0.300	0.300	3.500	3.500
Vapor fraction	1.000	0.000	0.000	0.059	0.696	0.000	0.000	0.035	0.230	1.000	1.000	0.307
Flow rate [kg/s]	0.492	0.492	0.492	0.492	0.492	1.576	1.576	1.576	2.068	2.068	2.068	2.068
n + m + e + p + b [%]	11.9 + 64.0 + 21.3 + 2.8 + 0.0					1.4 + 20.1 + 49.9 + 24.6 + 0.0			4.6 + 36.3 + 41.2 + 17.9 + 0.0			

	13	14	15	16
Temperature	298.0	240.0	240.0	298.0
Pressure	1.400	1.400	0.310	0.310
Vapor fraction	0.000	0.000	0.003	1.000
Flow rate	2.471	2.471	2.471	2.471
	0.0 + 0.0 + 28.2 + 30.7 + 41.1			

	0	17	18	19
Temperature	298.0	240.0	164.4	113.0
Pressure	5.000	5.000	5.000	5.000
Vapor fraction	1.000	0.994	0.000	0.000
Flow rate	1.000	1.000	1.000	1.000

Fig. 10. 1-stage MR JT and 2-stage MR JT cycles (M1J + M2J).

levels of top p4J, and the pressure levels and composition of M2J. As shown in the diagrams, the temperature profiles of hot and cold streams are very close to each other along the bottom M2J, and the stepwise profile matches reasonably well in the top p4J, too. Indeed the irreversibility in HX and AC is noticeably reduced and the value of FOM is the highest among the cycles presented in this review.

Apart from the practical applicability to base-load plants, there are other options in selecting the PR of top JT cycle. Two examples are ammonia (a) or R-134a (r), since their boiling temperatures are close to that of propane. The structure and thermodynamic characteristics of a4J + M2J and r4J + M2J are nearly identical to Fig. 11. In general, the ammonia JT cycle has a merit of small flow rate because ammonia has the largest value of latent heat of vaporization, and the R-134a JT cycle may take advantage of non-flammable and non-toxic working fluid. The maximum FOM is 78.2% and 79.4% for optimized a4J + M2J and r4J + M2J, respectively. Recently more works were reported on the selection of pre-cooling cycle with different refrigerants (top cycle) for M2J cycle [46,47].

A unique combination of two JT cycles with PR on the top of M2J has been lately proposed and patented [48]. As shown in Fig. 13 and 1-stage butane JT cycle and 1-stage ethane JT cycle are combined in parallel for the pre-cooling of MR and NG feed (b1J/e1J + M2J). The symbol ⟨/⟩ between b1J and e1J denotes their "parallel" combination, as listed in the "combination" box of Fig. 4. As the pressure levels of b1J and e1J cycles are optimally determined, the minimum temperature approach is found not only at two ends of HX3, but also over a wide range in the middle, where the condensing ethane is part of the hot streams and the

evaporating butane is part of the cold streams. It was reported that the parallel JT cycles can take advantage of high FOM and simple structure at the same time. The maximum FOM is 70.2% for b1J/e1J + M2J with the optimized pressure levels and flow rate in both cycles. This can be considered as a relatively high value, by taking into account the simple structure and easy operation with the 1-stage JT cycles with PR.

4.4. Brayton cycles

Turbine-based liquefaction processes are operated on standard or modified Brayton cycles, as used for peaking shaving plants or for recently proposed off-shore application [3,49–57]. While either PR or MR may be used in a Brayton cycle, it is essential for the refrigerants to remain in vapor phase (or at least vapor-rich condition) for the safe operation of turbines. Nitrogen is the most common refrigerant, and the simplest and standard cycle is shown in Fig. 14, as called 1-stage nitrogen Brayton cycle (n1B). In theory, there is no limit in the pressure range, but the optimum conditions for all Brayton cycles are found between 0.1 and 10 MPa according to the assumption.

The maximum FOM is 60.3% for n1B with optimized pressure levels. It is recalled that the output power from expander is subtracted from the input power to compressors in Eq. (5), and the compression is multi-staged with an inter-cooler between the stages from the assumption. The minimum temperature approach is found at two ends and an intermediate point. The major source of irreversibility is the after-coolers (AC) due to the large temperature rise by adiabatic compression and the large flow rate of nitrogen.

	1	2	3	4	5	6	7	8	9	10	11
Temperature [K]	298.0	267.2	240.0	240.0	267.2	267.2	298.0	298.0	298.0	267.2	266.5
Pressure [MPa]	1.100	1.100	1.100	0.509	0.509	0.509	0.509	1.100	1.100	1.100	0.509
Vapor fraction	1.000	0.000	0.000	0.001	0.856	0.337	1.000	0.391	0.000	0.000	0.007
Flow rate [kg/s]	1.303	1.303	1.303	1.303	1.303	3.748	3.748	3.748	2.445	2.445	2.445
$n + m + e + p + b$ [%]	0.0 + 0.0 + 48.5 + 40.9 + 10.6					0.0 + 0.0 + 29.6 + 43.9 + 26.5			0.0 + 0.0 + 17.4 + 45.9 + 36.7		

	12	13	14	15	16	17	18	19
	146.3	240.0	298.0	281.3	240.0	240.0	146.4	144.8
	0.300	0.300	3.500	3.500	3.500	3.500	3.500	0.300
	0.230	1.000	1.000	0.869	0.307	0.000	0.000	0.035
	0.492	0.492	2.068	2.068	2.068	1.576	1.576	1.576
	4.6 + 36.3 + 41.2 + 17.9 + 0.0					1.4 + 20.1 + 49.9 + 24.6 + 0.0		

	20	21	22	23	24
	240.0	146.4	113.0	109.3	146.3
	3.500	3.500	3.500	0.300	0.300
	1.000	0.000	0.000	0.059	0.696
	0.492	0.492	0.492	0.492	0.492
	11.9 + 64.0 + 21.3 + 2.8 + 0.0				

	0	25	26	27	28
	298.0	281.3	240.0	146.4	113.0
	5.000	5.000	5.000	5.000	5.000
	1.000	1.000	0.994	0.000	0.000
	1.000	1.000	1.000	1.000	1.000

Fig. 11. Dual 2-stage MR JT cycles (M2J + M2J).

The thermodynamic performance of Brayton cycles can also be improved by modifying the standard cycle or combining two separate cycles in series. A modified Brayton cycle for 2-stage refrigeration is shown in Fig. 15, as called 2-stage nitrogen Brayton cycle (n2B). The high-pressure nitrogen is expanded in the first expander only to an intermediate pressure, where a branched flow is returned through the warm HX and the other flow is expanded further to the lowest pressure and temperature at the cold end. The pressure levels and flow rates at each stage are optimized.

The maximum FOM is 67.1% for optimized n2B. The minimum temperature approach is found at an intermediate position as well as two ends, and the temperature profiles are closer to each other than those of n1B. It is noticeable in the coldest HX at bottom that the temperature profiles appears to be almost overlapped (or

parallel with a small gap), because the specific heat is nearly constant over this temperature range for both NG and nitrogen. A nitrogen Brayton cycle therefore is an excellent option for the bottom of NC liquefaction, as mentioned below.

Two separate Brayton cycles may be combined in series. Fig. 16 shows the dual nitrogen 1-stage Brayton cycles, where nitrogen is used in both the top and bottom cycles (n1B + n1B). Fig. 17 has the same structure, but methane is used in the top Brayton cycle, while nitrogen is used in the bottom Brayton cycle (m1B + n1B). In either case, the pressure levels and flow rate are optimized in the two cycles.

The maximum FOM is 67.1% and 69.7% for optimized n1B + n1B and m1B + n1B, respectively. It is interesting to note that the FOM of n1B + n1B is nearly the same as that of n2B, which means that

	1	2	3	4	5	6	7	8
Temperature [K]	231.0	142.5	113.0	108.8	142.4	231.0	142.5	140.8
Pressure [MPa]	3.500	3.500	3.500	0.300	0.300	3.500	3.500	0.300
Vapor fraction	1.000	0.000	0.000	0.062	0.739	0.000	0.000	0.035
Flow rate [kg/s]	0.392	0.392	0.392	0.392	0.392	1.476	1.476	1.476
n + m + e + p [%]	12.9 + 68.0 + 17.4 + 1.7					1.6 + 28.1 + 49.9 + 20.4		

	9	10	11	12	13	14	15
	142.6	231.0	298.0	277.7	260.0	244.6	231.0
	0.300	0.300	3.500	3.500	3.500	3.500	3.500
	0.217	1.000	1.000	0.889	0.602	0.411	0.273
	1.868	1.868	1.868	1.868	1.868	1.868	1.868
	4.7 + 39.0 + 41.0 + 15.3						

	16	17	18	19	20	21	22
	298.0	277.7	277.7	277.7	260.0	260.0	260.0
	0.949	0.949	0.543	0.543	0.949	0.310	0.310
	0.000	0.000	0.000	1.000	0.000	0.001	1.000
	3.121	3.121	1.030	1.030	2.091	0.990	0.990

	23	24	25	26	27	28
	244.6	244.6	244.6	231.0	231.0	231.0
	0.949	0.177	0.177	0.949	0.101	0.101
	0.000	0.001	1.000	0.000	0.002	1.000
	1.101	0.635	0.635	0.467	0.467	0.467

	0	29	30	31	32	33	34
	298.0	277.0	260.0	244.6	231.0	142.5	113.0
	5.000	5.000	5.000	5.000	5.000	5.000	5.000
	1.000	1.000	1.000	1.000	0.976	0.000	0.000
	1.000	1.000	1.000	1.000	1.000	1.000	1.000

Fig. 12. 4-stage propane and 2-stage MR JT cycles (p4J + M2J).

there is no clear merit in using two separate cycles with the same gas. On the other hand, m1B + n1B is somewhat superior to n2B and n1B + n1B under this specific condition. When compared with n1B + n1B, the pressure levels of m1B + n1B are much lower, but the mass flow rate of methane is larger. In the optimized m1B + n1B, methane remains in vapor phase throughout the cycle.

Mixed refrigerants may be used in a Brayton cycle, but the selection of MR is subject to the constraint that the refrigerants

	1	2	3	4	5
Temperature [K]	231.0	142.5	113.0	108.8	142.4
Pressure [MPa]	3.500	3.500	3.500	0.300	0.300
Vapor fraction	1.000	0.000	0.000	0.062	0.739
Flow rate [kg/s]	0.392	0.392	0.392	0.392	0.392
n + m + e + p [%]	12.9 + 68.0 + 17.4 + 1.7				

6	7	8	9	10	11	12
142.6	231.0	298.0	231.0	231.0	142.5	140.8
0.300	0.300	3.500	3.500	3.500	0.300	0.300
0.217	1.000	1.000	0.273	0.000	0.000	0.035
1.868	1.868	1.868	1.868	1.476	1.476	1.476
4.7 + 39.0 + 41.0 + 15.3				1.6 + 28.1 + 49.9 + 20.4		

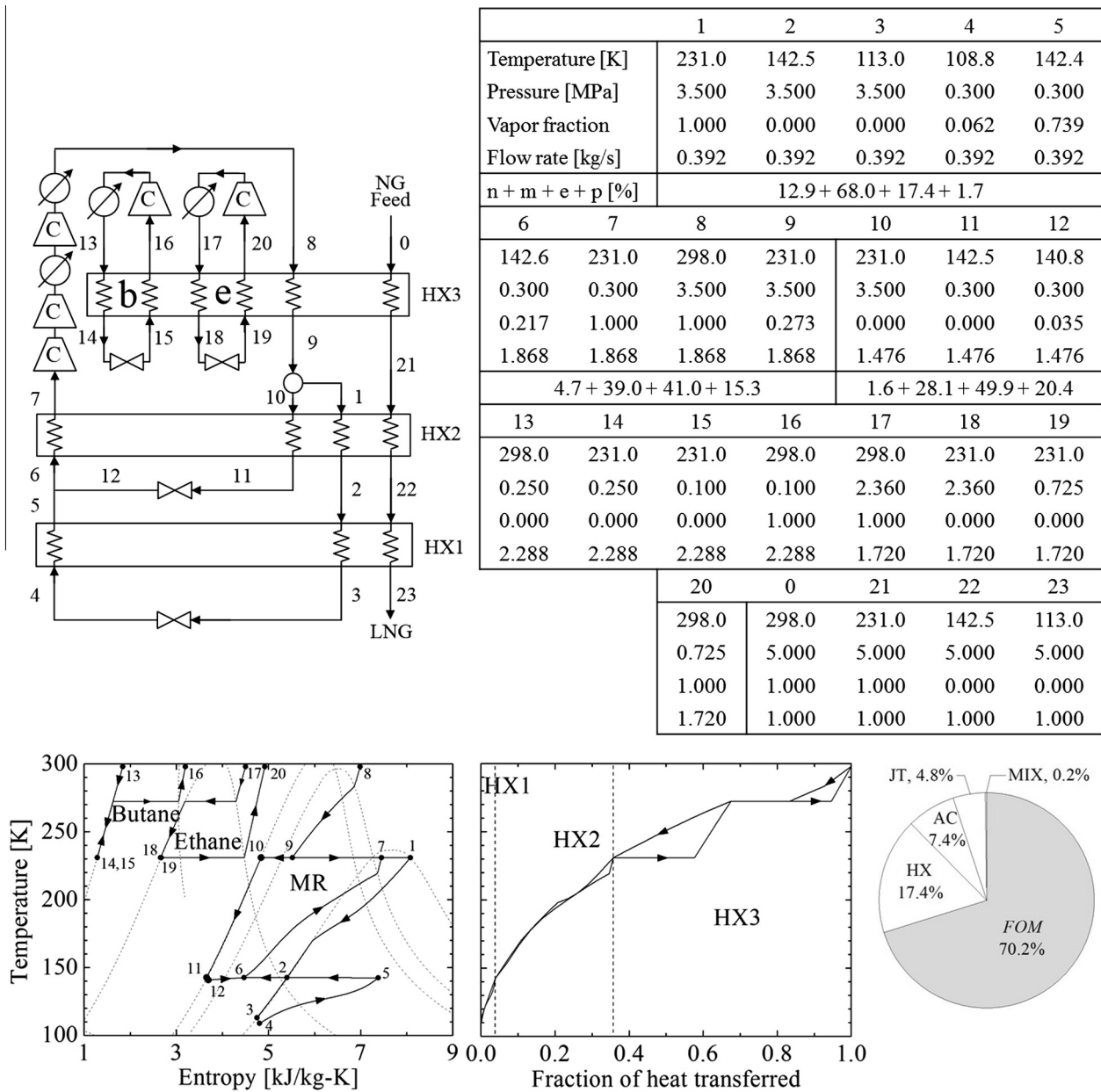| 13	14	15	16	17	18	19
298.0	231.0	231.0	298.0	298.0	231.0	231.0
0.250	0.250	0.100	0.100	2.360	2.360	0.725
0.000	0.000	0.000	1.000	1.000	0.000	0.000
2.288	2.288	2.288	2.288	1.720	1.720	1.720

20	0	21	22	23
298.0	298.0	231.0	142.5	113.0
0.725	5.000	5.000	5.000	5.000
1.000	1.000	1.000	0.000	0.000
1.720	1.000	1.000	1.000	1.000

Fig. 13. Parallel 1-stage butane/1-stage ethane, and 2-stage MR JT cycles (b1J/e1J + M2J).

should be in vapor phase or at least the liquid content should be within a certain limit (for example, less than 10%). One practical choice to satisfy this constraint is a mixture of nitrogen and methane [3], which can be denoted by M1B. The pressure levels and composition of MR are optimized for M1B. As shown in Fig. 18, the maximum FOM is 61.1% for optimized M1B, where the MR is a mixture of 74.0% nitrogen and 26.0% methane on mole basis. When compare with n1B, M1B has minor benefits of a higher FOM and a smaller flow rate.

4.5. Combined and Claude cycles

JT and Brayton cycles can be combined in a variety of ways for efficient liquefaction. Among the PR cycles, a series combination of either Brayton + JT + Brayton ($B + J + B$) cycles or JT + JT + Brayton ($J + J + B$) cycles is an intuitive choice, since the bottom Brayton cycle can efficiently cover the liquid region with a nearly constant specific heat, as mentioned above. Fig. 19 shows a series combination of 3-stage propane JT, 3-stage ethylene JT, and 1-stage nitrogen Brayton cycles ($p3J + e'3J + n1B$) [58]. The top and middle cycles are basically identical to those of $p3J + e'3J + m3J$, but the bottom cycle is replaced by an independent n1B. Alternatively, nitrogen of the bottom n1B cycle may be pre-cooled by the top and/or middle cycles to increase the FOM to an extent. The pressure levels of JT and Brayton cycles are optimized. The maximum FOM is 72.6% for optimized $p3J + e'3J + n1B$, which is evaluated as the highest among all PR cycles under consideration.

A similar idea was proposed and investigated to combine 1-stage carbon dioxide JT cycle on the top of 1-stage nitrogen Brayton cycle ($c1J + n1B$) [59,60]. Since both refrigerants are inflammable, the combined cycles have an inherent advantage in operational safety. It was reported that the cycles require a smaller footprint area, and may be suitable for offshore or small-scale application.
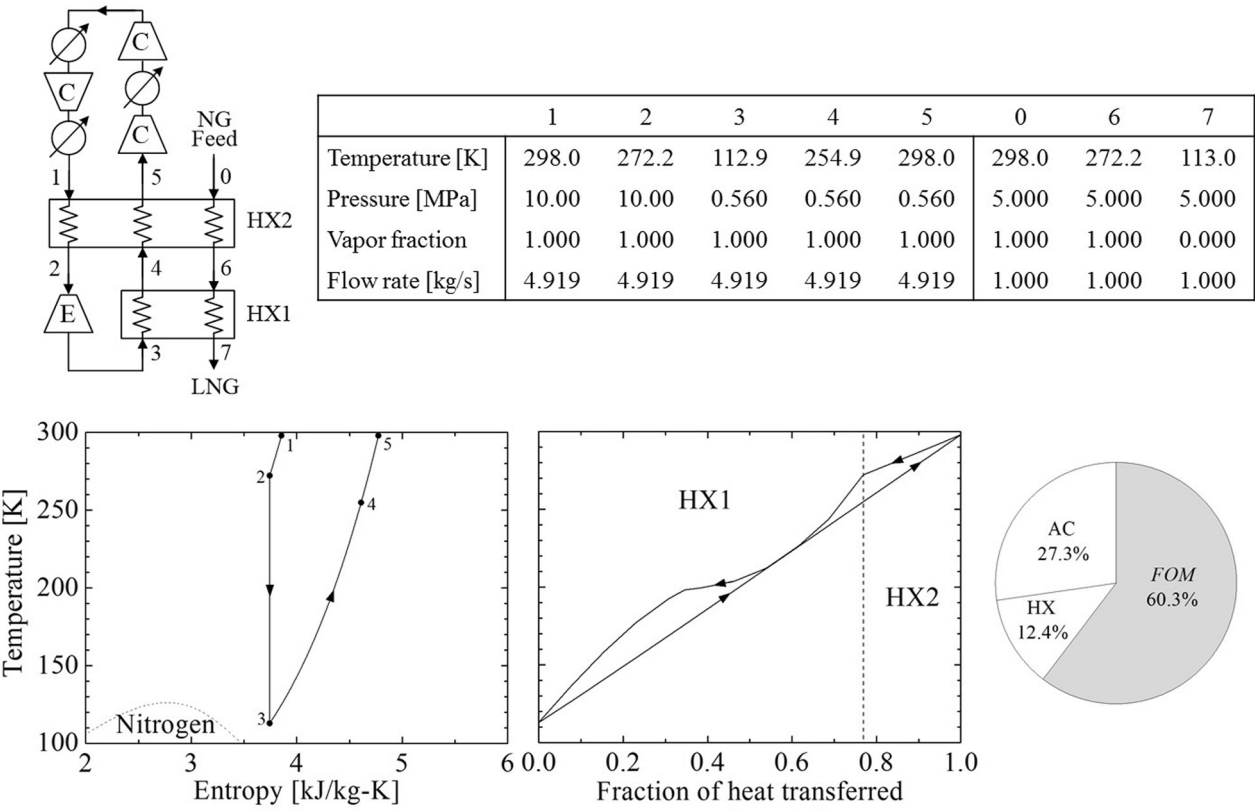
	1	2	3	4	5	0	6	7
Temperature [K]	298.0	272.2	112.9	254.9	298.0	298.0	272.2	113.0
Pressure [MPa]	10.00	10.00	0.560	0.560	0.560	5.000	5.000	5.000
Vapor fraction	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.000
Flow rate [kg/s]	4.919	4.919	4.919	4.919	4.919	1.000	1.000	1.000

Fig. 14. 1-stage nitrogen Brayton cycle (n1B).

	1	2	3	4	5	6
Temperature [K]	298.0	254.0	162.9	113.0	162.9	236.3
Pressure [MPa]	1.800	1.800	0.400	0.120	0.120	0.120
Vapor fraction	1.000	1.000	1.000	1.000	1.000	1.000
Flow rate [kg/s]	6.919	6.919	3.244	3.244	3.244	3.244
	7	8	9	0	10	11	12
298.0	236.3	298.0	298.0	254.0	162.9	113.0
0.120	0.400	0.400	5.000	5.000	5.000	5.000
1.000	1.000	1.000	1.000	1.000	0.000	0.000
3.244	3.675	3.675	1.000	1.000	1.000	1.000

Fig. 15. 2-stage nitrogen Brayton cycle (n2B).

	1	2	3	4	5	6	7
Temperature [K]	298.0	263.6	175.0	247.0	298.0	298.0	263.6
Pressure [MPa]	10.00	10.00	2.340	2.340	2.340	0.600	0.600
Vapor fraction	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Flow rate [kg/s]	3.025	3.025	3.025	3.025	3.025	3.350	3.350
	8	9	10	11	12	0	13	14	15
175.0	113.0	175.0	247.0	298.0	298.0	263.6	175.0	113.0
0.600	0.138	0.138	0.138	0.138	5.000	5.000	5.000	5.000
1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.000	0.000
3.350	3.350	3.350	3.350	3.350	1.000	1.000	1.000	1.000

Fig. 16. Dual 1-stage nitrogen Brayton cycles (n1B + n1B).

	1	2	3	4	5	6	7
Temperature [K]	298.0	239.4	185.0	227.4	298.0	298.0	239.4
Pressure [MPa]	0.300	0.300	0.124	0.124	0.124	0.600	0.600
Vapor fraction	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Flow rate [kg/s]	9.982	9.982	9.982	9.982	9.982	3.493	3.493
	8	9	10	11	12	0	13	14	15
185.0	113.0	185.0	227.4	298.0	298.0	239.4	185.0	113.0
0.600	0.114	0.114	0.114	0.114	5.000	5.000	5.000	5.000
1.000	1.000	1.000	1.000	1.000	1.000	0.993	0.000	0.000
3.493	3.493	3.493	3.493	3.493	1.000	1.000	1.000	1.000

Fig. 17. 1-stage methane and 1-stage nitrogen Brayton cycles (m1B + n1B).

	1	2	3	4	5	0	6	7
Temperature [K]	298.0	270.7	113.0	253.8	298.0	298.0	270.7	113.0
Pressure [MPa]	6.000	6.000	0.300	0.300	0.300	5.000	5.000	5.000
Vapor fraction	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.000
Flow rate [kg/s]	4.271	4.271	4.271	4.271	4.271	1.000	1.000	1.000
n + m [%]	74.0 + 26.0							

Fig. 18. 1-stage MR Brayton cycle (M1B).

5. Discussion

The results presented above are useful primarily for selecting a suitable cycle under any given environments. For each cycle, the thermodynamic performance was indexed by the presented value of FOM in the range of 53.5–80.6%. In addition, the graphic representation of cycles on *T–s* diagram, temperature profiles, and exergy expenditure can provide an intuition on how the structure of cycles works for the liquefaction of natural gas. The listed data on thermodynamic properties at each point of the cycle can also serve as a good starting point for the design of practical liquefaction processes.

In examining the results, it is important to recall that the analysis was performed for ideal cycles with perfect components and optimized condition. The deviation of an actual process from the ideal cycle is estimated by modifying the listed assumptions with proper performance parameters on imperfect components, including the HX effectiveness, the adiabatic efficiency (for compressors and expanders), and the pressure drop. Even though the details on actual cycles may be beyond the scope of this review, a few important comments are made especially about the actual performance of HX's.

There are a few different ways how to incorporate the effect of finite HX size and heat transfer coefficient into the cycle analysis. A common method is to simply specify the value of minimum temperature approach (e.g. ΔT_{min} = 3 K) [3]. This is a convenient way of utilizing the commercial process simulators, but may not be a fair criterion for comparing the cycles with different configurations of HX's. A more reasonable method for fair comparison is to specify the value of HX effectiveness (e.g. ε = 0.98) as a dimensionless parameter. In order to incorporate the value of effectiveness into
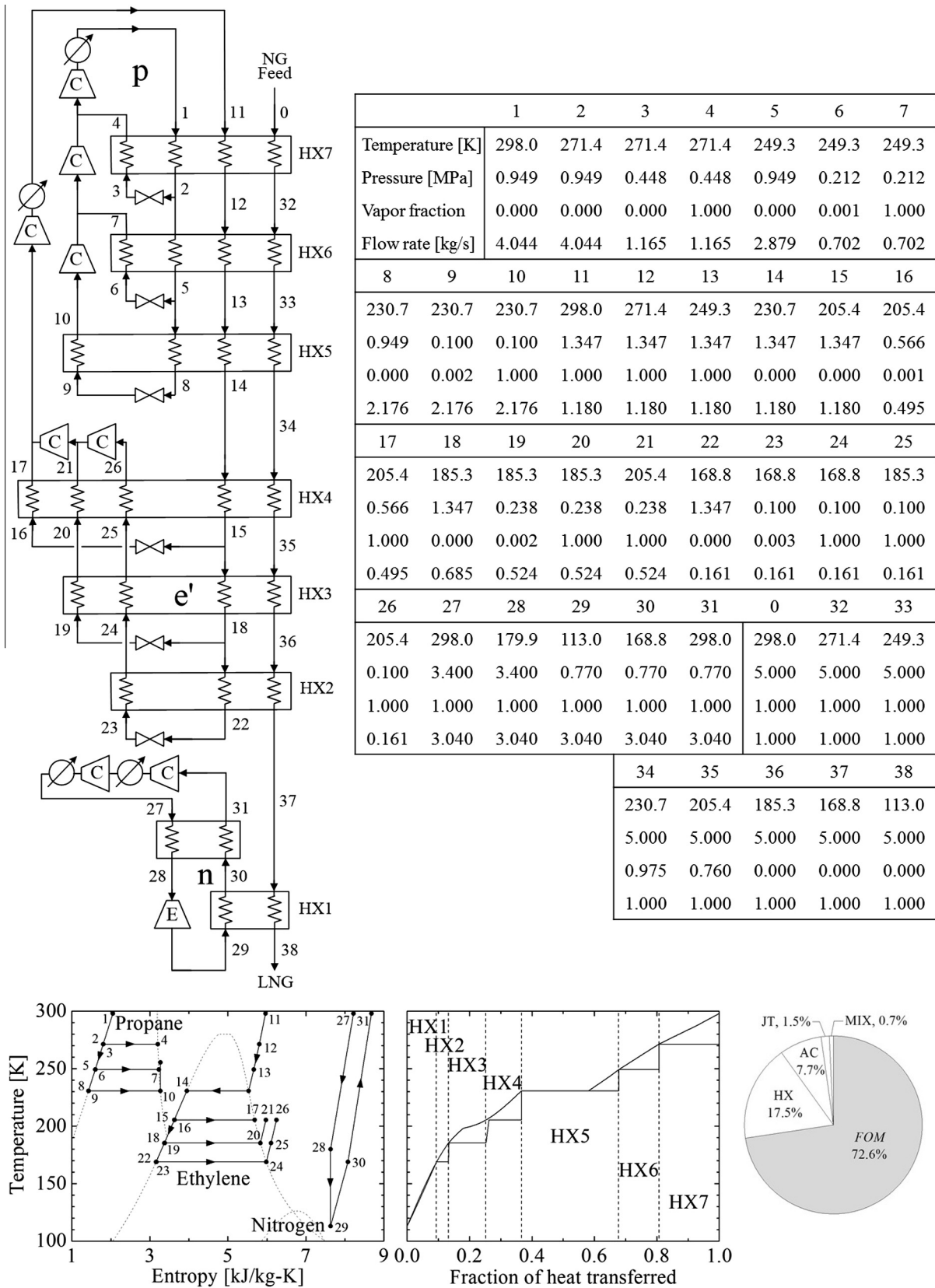
Recently, a closed Claude cycle is proposed to use the natural gas (NG) itself as refrigerant [61], as shown in Fig. 20. This cycle can be termed as 1-stage MR Claude cycle (M1C), since the refrigerant is an MR whose composition is the same as the NG feed. Even though three HX's are used in series above the JT expansion, this cycle is called 1-stage, because a Claude cycle always needs three HX's (in the same context, the Collins cycle used for helium liquefaction or refrigeration [1,2] may be called 2-stage Claude cycle, even though M2C is not considered here). An obvious merit of using the NG itself as refrigerant is that no refrigerant inventory is needed in offshore or floating systems. The pressure levels and expander flow ratio (i.e. the ratio of expander flow to total compressor flow) are optimized.

The maximum FOM is 59.7% for optimized M1C. It is noted in the optimized cycle that the exit condition of expander (*E*) must match exactly with the merging low-pressure stream of MR, as called the "optimally expanded" condition in [61]. In the presented ideal cycle, the vapor fraction of MR is 86.5% at the exit of expander, but should be well above this value in practical cycles, as the adiabatic efficiency of an expander is lower than the unity. A mixture of nitrogen and methane has been investigated for similar Claude cycle [62].

The largest-capacity plants under operation are based on a process called AP-X [63,64], which is a series combination of 3-stage propane JT cycle, 1-stage MR JT cycle, and 1-stage nitrogen Brayton cycle (p4J + M1J + n1B), as shown in Fig. 21. It was reported that the capacity limit of efficient p4J + M2J has been successfully overcome with the addition of nitrogen Brayton cycle at the bottom. The pressure levels of three cycles and the composition of MR JT cycle are optimized. The maximum FOM is 76.0% for optimized p4J + M1J + n1B.

	1	2	3	4	5	6	7
Temperature [K]	298.0	271.4	271.4	271.4	249.3	249.3	249.3
Pressure [MPa]	0.949	0.949	0.448	0.448	0.949	0.212	0.212
Vapor fraction	0.000	0.000	0.000	1.000	0.000	0.001	1.000
Flow rate [kg/s]	4.044	4.044	1.165	1.165	2.879	0.702	0.702
8	9	10	11	12	13	14	15	16
230.7	230.7	230.7	298.0	271.4	249.3	230.7	205.4	205.4
0.949	0.100	0.100	1.347	1.347	1.347	1.347	1.347	0.566
0.000	0.002	1.000	1.000	1.000	1.000	0.000	0.000	0.001
2.176	2.176	2.176	1.180	1.180	1.180	1.180	1.180	0.495
17	18	19	20	21	22	23	24	25
205.4	185.3	185.3	185.3	205.4	168.8	168.8	168.8	185.3
0.566	1.347	0.238	0.238	0.238	1.347	0.100	0.100	0.100
1.000	0.000	0.002	1.000	1.000	0.000	0.003	1.000	1.000
0.495	0.685	0.524	0.524	0.524	0.161	0.161	0.161	0.161
26	27	28	29	30	31	0	32	33
205.4	298.0	179.9	113.0	168.8	298.0	298.0	271.4	249.3
0.100	3.400	3.400	0.770	0.770	0.770	5.000	5.000	5.000
1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.161	3.040	3.040	3.040	3.040	3.040	1.000	1.000	1.000
				34	35	36	37	38
				230.7	205.4	185.3	168.8	113.0
				5.000	5.000	5.000	5.000	5.000
				0.975	0.760	0.000	0.000	0.000
				1.000	1.000	1.000	1.000	1.000

Fig. 19. 3-stage propane JT, 3-stage ethylene JT, and 1-stage nitrogen Brayton cycles (p3J + e′3J + n1B).

	1	2	3	4
Temperature [K]	298.0	287.8	122.6	120.0
Pressure [MPa]	10.00	10.00	10.00	10.00
Vapor fraction	1.000	1.000	0.000	0.000
Flow rate [kg/s]	1.950	1.950	0.080	0.080
5	6	7	8	9	10
113.0	115.8	122.6	122.6	276.7	298.0
0.115	0.115	0.115	0.115	0.115	0.115
0.078	0.658	0.865	0.865	1.000	1.000
0.080	0.080	0.080	1.950	1.950	1.950
11	0	12	13	14	15
122.6	298.0	287.8	122.6	120.0	113.0
0.115	5.000	5.000	5.000	5.000	5.000
0.865	1.000	1.000	0.000	0.000	0.000
1.870	1.000	1.000	1.000	1.000	1.000

Fig. 20. 1-stage MR Claude cycle (M1C).

the cycle, the maximum heat must be calculated first (i.e. with 0 K of minimum temperature approach), and then the actual heat is determined by its definition.

$$\varepsilon = \frac{\dot{Q}}{\dot{Q}_{max}} \qquad (8)$$

Another rigorous method is to simultaneously solve the energy equations for all the streams and determine the temperature distribution of respective streams. For this calculation, the values of overall heat transfer coefficient (U) or (dimensionless) the number of transfer unit (NTU) should be specified [65]. This analysis requires huge efforts on the numerical calculation, but the detailed specifications of HX's (e.g. the dimension of plate-fin HX's or spiral wound HX's) can be effectively incorporated.

A thermodynamic optimization theory is cited here with regards to the effect of finite HX sizes, especially when the liquefaction process is composed of multi-stages of HX's in series. It is always true that as any HX area increases, the temperature difference between hot and cold streams in the HX decreases and the FOM of liquefaction increases accordingly. It is an important design strategy, however, how to allocate the HX area to each stage, if the total sum of HX area is fixed. This was formulated with a typical variational problem of minimizing the entropy generation subject to a constraint, and successfully solved by the method of Lagrange multiplier [58]. The results show that the best thermodynamic performance is achieved when the temperature difference is proportional to the absolute temperature of the NG feed.

$$\left(\frac{\Delta T}{T_F} \right)_{opt} \approx \text{constant} \qquad (9)$$

In other words, it is desired is that the temperature difference should be smaller at colder HX.

Finally, the effect of multi-stream HX's should be mentioned. Most of HX's used in the refrigeration cycles for liquefaction have three or more streams. In the cycle analysis presented above, it was assumed that all hot streams have the same temperature and all cold streams have the same temperature at an axial location, as only two composite curves were plotted. It was reported that those temperature profiles are difficult to realize in practice, and the FOM based on the assumption is always an overestimate [65]. Elaboration is needed for proper heat-exchanger design in order to achieve the designated thermodynamic efficiency.
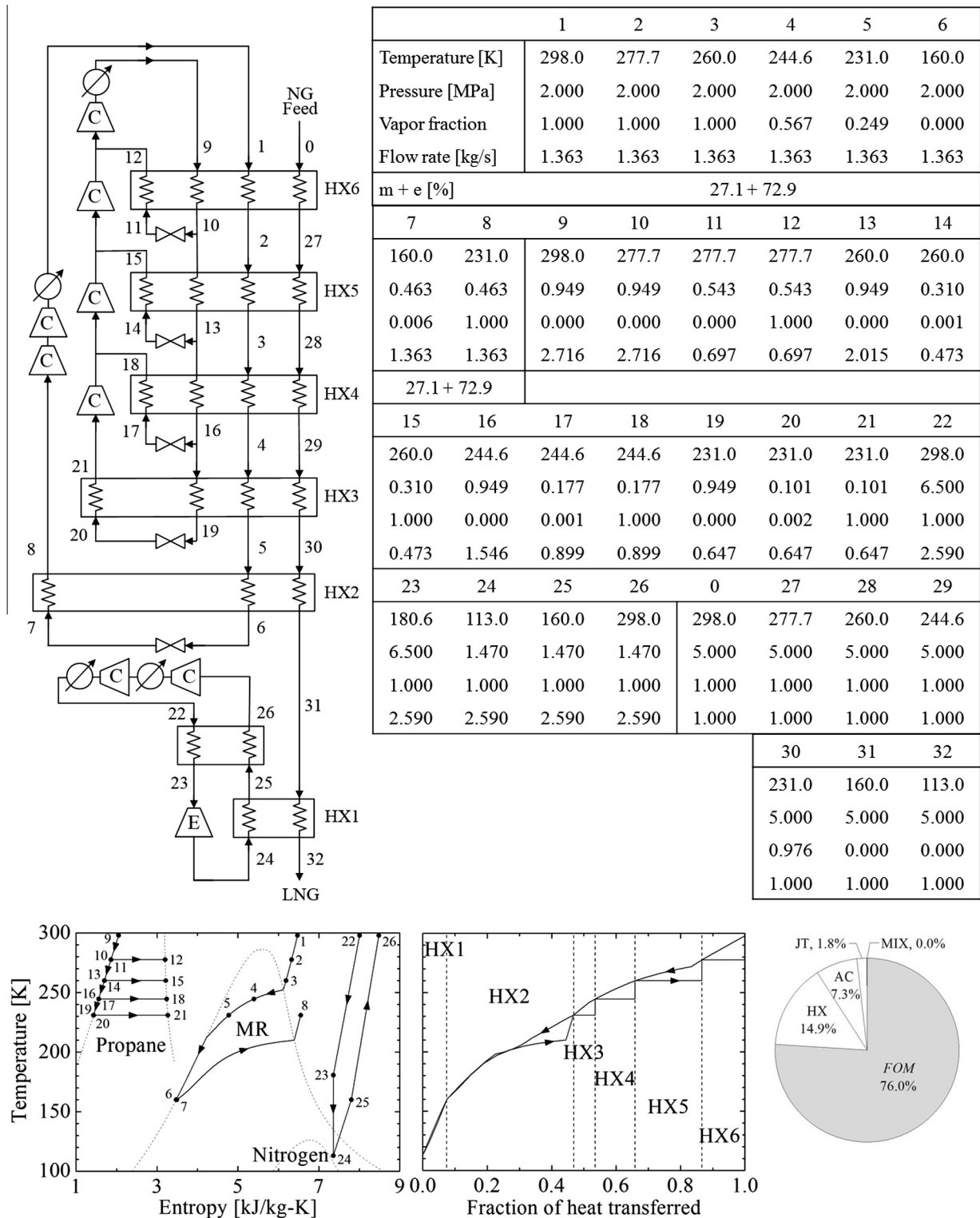
	1	2	3	4	5	6
Temperature [K]	298.0	277.7	260.0	244.6	231.0	160.0
Pressure [MPa]	2.000	2.000	2.000	2.000	2.000	2.000
Vapor fraction	1.000	1.000	1.000	0.567	0.249	0.000
Flow rate [kg/s]	1.363	1.363	1.363	1.363	1.363	1.363
m + e [%]	27.1 + 72.9					
	7	8	9	10	11	12	13	14
	160.0	231.0	298.0	277.7	277.7	277.7	260.0	260.0
	0.463	0.463	0.949	0.949	0.543	0.543	0.949	0.310
	0.006	1.000	0.000	0.000	0.000	1.000	0.000	0.001
	1.363	1.363	2.716	2.716	0.697	0.697	2.015	0.473
	27.1 + 72.9							
	15	16	17	18	19	20	21	22
	260.0	244.6	244.6	244.6	231.0	231.0	231.0	298.0
	0.310	0.949	0.177	0.177	0.949	0.101	0.101	6.500
	1.000	0.000	0.001	1.000	0.000	0.002	1.000	1.000
	0.473	1.546	0.899	0.899	0.647	0.647	0.647	2.590
	23	24	25	26	0	27	28	29
	180.6	113.0	160.0	298.0	298.0	277.7	260.0	244.6
	6.500	1.470	1.470	1.470	5.000	5.000	5.000	5.000
	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
	2.590	2.590	2.590	2.590	1.000	1.000	1.000	1.000
						30	31	32
						231.0	160.0	113.0
						5.000	5.000	5.000
						0.976	0.000	0.000
						1.000	1.000	1.000

Fig. 21. 3-stage propane JT cycle, 1-stage MR JT cycle, and 1-stage nitrogen Brayton cycle (p4J + M1J + n1B).

6. Concluding remarks

It is a difficult but important task to determine which refrigeration cycle is the most suitable for a specific liquefaction system of natural gas, taking a number of practical factors into consideration (such as composition/pressure/amount of natural gas, constraints on size/weight, operation simplicity, safety, statutory requirements, and local climate). This review is prepared with a goal to provide the primary basis of cryogenic refrigeration for liquefaction from thermodynamic point of view. Towards the goal, a variety of refrigeration cycles are classified in systematic way by the type of expansion processes (JT, Brayton, and combined cycles) and by the type of refrigerants (pure and mixed refrigerants). Sixteen standard and modified refrigeration cycles were selected

from the existing and proposed liquefaction processes, and their ideal versions are fully analyzed with the optimal conditions to achieve its utmost thermodynamic performance. Detailed refrigeration cycles are quantitatively presented and compared in terms of FOM (figure of merit) and thermodynamic irreversibility. Hopefully, this review will be helpful in clearly understanding the structure of refrigeration cycles and designing an efficient liquefaction process for future development in accordance with various needs.

Acknowledgments

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