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Fundamentals and applications of cryogen as a thermal energy carrier: A critical assessment

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ABSTRACT

This paper reviews and assesses the current status of the use of cryogen as an energy carrier, with a focus on the thermodynamic aspects and cryogenic energy extraction. Cryogen as an energy carrier is different from normal heat storage media in that the energy storage in a cryogen occurs through decreasing its internal energy while increasing its exergy. It is shown that cryogens have a higher energy density than other commonly used thermal energy storage media, and cryogen can be efficient working media for recovering low grade heat due to their low critical temperatures. If there are high grade heat sources, a combination of the direct expansion with a Brayton cycle is shown to be the most efficient method to extract the cryogenic exergy for most cryogens. This, however, is not true for hydrogen as its latent heat accounts for only a small portion of the released cold and a simple Brayton cycle is more suitable for the exergy recovery. If there is only ambient and/or a low grade heat source, a combination of direct expansion and a Rankine cycle is more attractive due to its low power consumption in the compression process, and this appears to be more promising when carbon dioxide capture is considered.

1. Introduction

Thermal Energy Storage (TES) may refer to a number of technologies that store energy in a thermal storage medium for later uses (time shifting). Such technologies are often employed to balance energy demands between peak hours (e.g. day time) and off-peak hours (e.g. night time), providing an opportunity to optimize the supply operations based on the demand. The technologies could also be used as a demand side management (DSM) tool for electric and/or heat loads, as well as a supply side management (SSM) tool for efficient and economic power production; see Fig. 1 for a schematic diagram of exemplar applications of TES [1,2].

Applications of the TES technologies in the DSM are mainly associated with low temperature space heating/cooling or domestic hot water services, especially for buildings where heating or cooling demands significantly contribute to high demand charges [3]. For this type of applications, low grade heat/cold is produced from off-peak electricity, solar radiation or industrial waste heat sources, and is stored in thermal storage media in either or both of sensible heat and latent heat, where the latent heat often involves the use of a phase change material. The temperature of the storage media is mostly within −10–100 °C. A number of reviews have been published on the thermal properties and capacities of the storage materials; see for example Refs. [4–9]. These reviews suggest that water is the most popular storage medium though other media such as oils, rock and metals should not be excluded especially for large scale storage applications [10,11]. Applications of the TES technologies in the SSM often involve the use of a working temperature of the storage media that deviates significantly from the ambient environment. For example, high grade heat can be generated by solar energy to produce steam at 250–300 °C [12–14]. Another example is the Archimedes project, where a binary mixture of molten salts (40% KNO_3, 60% $NaNO_3$) is used as a sensible heat storage medium, which is the world's first solar energy system integrated with a gas-fired combined cycle power plant and the working temperature ranges from 290 to 550 °C [15].

This paper aims to review and assess the current status of the use of cryogen as a mean to store energy – the so-called cryogen based energy carrier. Such an energy carrier has attracted lots of attention recently due to its potential for the SSM applications [16–20]. The use of cryogen as an energy carrier is different from normal heat storage in that the energy is stored in a cryogen through decreasing its internal energy while increasing its exergy. In addition, the fundamental aspects associated with cryogen as an energy storage medium will be discussed and various technologies for exploiting the cryogenic energy are analyzed and compared. In the comparison, exergy analysis rather than energy analysis is adopted as the former provides a more accurate representation in terms of power generation.

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Nomenclature

C_p	specific heat (kJ kg^{-1} K^{-1})
E	exergy (kJ kg^{-1})
H	enthalpy (kJ kg^{-1})
P	pressure (MPa)
Q	heat flux (kJ kg^{-1})
S	entropy (kJ kg^{-1} K^{-1})
T	temperature (°C)
W	power flux (kJ kg^{-1})
$\bar{A}$	normalised parameter of A
$\lvert A\rvert$	modulus of A
ΔA	difference of A
δA	discrete element of A
dA	differential element of A

Subscripts

a	ambient
b	boiling point
l	liquid state
P	pump
h	high temperature side

Greek letters

η	percentage or efficiency (%)

Abbreviations

CCGT	combined cycle gas turbine
DSM	demand side management
LNG	liquefied natural gas
MGT	mirror gas turbine
SEM	scanning electron microscope
SSM	supply side management
TEM	transmission electron microscopy
TES	thermal energy storage

2. Fundamental aspects of cryogen as an energy carrier

A cryogen is normally defined as a liquid (liquefied gas) that boils at a temperature below about −150 °C [20]. Examples of the cryogen include liquid nitrogen, liquid oxygen, liquid hydrogen, liquid helium and liquefied natural gas. Cryogenic engineering, a discipline dealing with production, storage and utilization of cryogen, went through a rapid development since 1940s when large scale air and helium liquefaction processes became practical. The cryogenic engineering enables rapid developments in numerous scientific fields including physics (superconducting), chemistry (cryogenic synthesis), biology (long terms storage of biological cells), analytic sciences (Cryo-TEM and SEM), and instrumentation (thermocouple calibration). In the energy field, liquefied natural gas (LNG) has become popular for large scale storage of natural gas and its transportation from the production sites to countries and cities thousands miles away [17]. It is anticipated that similar operations would occur for liquid hydrogen if the hydrogen economy become a reality [18]. Over the past decade or so, liquid nitrogen/air as a combustion free and non-polluting 'fuel' has attracted lots of attention [21]. In the following, fundamental aspects associated with cryogen as an energy carrier will be discussed and compared using liquefied nature gas, liquid hydrogen and liquid nitrogen as examples.

2.1. *Exergy density*

Cryogens carry high grade cold energy, which according to the second law of thermodynamics, is a more valuable energy source than heat. The appropriate parameter to quantify the energy in terms of usefulness is exergy, which is defined as the maximum theoretical work obtainable by bringing the fluid into equilibrium with the environment. Assuming heat/cold is stored in a material with a constant specific heat, C_p, an increase or a decrease in its temperature by ΔT from the ambient temperature, T_a, will lead to an amount of heat, ΔQ, being charged or discharged into the material:

$$\Delta Q = C_p \Delta T \tag{1}$$

In a reversibly infinitesimal heat transfer process the exergy change of the material could be calculated as:

$$dE = dH - T_a \cdot \frac{\delta Q}{T} \tag{2}$$

The exergy, ΔE, stored in the material therefore could be obtained by integrating Equation (2) from T_a to $(T_a + \Delta T)$:

$$\Delta E = C_p \left(\Delta T - T_a \cdot \ln \left(\frac{T_a + \Delta T}{T_a} \right) \right) \tag{3}$$

Combining Equations (1) and (3) gives the percentage of the available energy stored in the material (η):

$$\eta = \frac{\Delta E}{|\Delta Q|} = \frac{\Delta T - T_a \cdot \ln \left(\frac{T_a + \Delta T}{T_a} \right)}{|\Delta T|} \tag{4}$$

Equation (4) is illustrated in Fig. 2 where the ambient temperature is assumed to be 25 °C. One can see from Fig. 2 that, given a temperature difference, the stored cold is more valuable than the stored heat particularly at large temperature differences.

The energy stored in a cryogen is in the form of both sensible and latent heat. Table 1 compares the specific heat, latent heat and

Fig. 1. Application of TES.

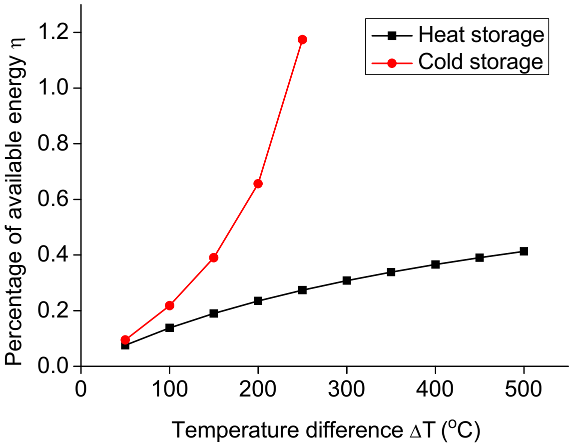

Fig. 2. Exergy percentage as a function of temperature difference for heat and cold storage.

exergy density of the three typical cryogens with some commonly used heat storage media. One can see that, although the specific heat and phase change heat of the cryogens are of similar order of magnitude to those of the heat storage materials, the exergy density of cryogens is much greater. Among the cryogens listed, liquefied hydrogen has the highest exergy density (about an order of magnitude higher than the other materials). Liquid nitrogen has the lowest exergy density among the cryogens listed, but it is still much higher than high temperature thermal energy storage media. Note that the high exergy densities of methane and hydrogen are mainly due to their chemical exergies see Section 2.2 for more discussion.

2.2. Chemical and physical (thermal) exergy of cryogens and their storage and delivery

As mentioned above, cryogens can contain both physical (thermal) and chemical exergies. Table 2 shows a comparison among the three cryogens listed in Table 1. One can see that the densities of the chemical exergy of liquid hydrogen and liquid methane are respectively ~10 times and 48 times their physical exergies. Liquid nitrogen does not have chemical exergy.

Cryogens are in liquid form, which are much easier to store and transport particularly when there are no pipelines. For example, for a given mass, liquefied methane (main component of natural gas) takes about 1/643 the volume of the gaseous methane at the ambient condition, whereas liquefied hydrogen takes about 1/860 the volume of gaseous hydrogen. It is anticipated that storage and transportation of liquid hydrogen will play a crucial role in the use of renewable energy to produce the energy carrier.

Although liquid nitrogen contains no chemical exergy, its thermal exergy density is still highly competitive to the current battery technologies [16]. Therefore liquid nitrogen is regarded not only as an energy storage medium [19] but also as a potential combustion free fuel for transportation [21].

2.3. Thermodynamic properties as thermal cycle working fluids

In a power generation system, the working fluid of a thermal cycle, such as water in a Rankine cycle or nitrogen in a Brayton cycle, is normally involved in the energy extraction process from the thermal storage media and the thermal energy storage media work only as the heat/cold sources in the cycle. In the cold energy extraction process, the cryogen, which serves as the cold source, can also be used as the thermal cycle working fluid through direct expansion cycles [21,22]. Thermodynamically, the use of cryogen as the working fluid in thermal cycles can be very efficient in terms of recovering low grade heat. Currently low to medium grade heat is often recovered by steam cycles in which water/steam is the working fluid. For example, such an approach has been widely used to recover waste heat from the Brayton cycle with a combined cycle gas turbine (CCGT) technology. The approach has also been investigated for the use of low grade solar heat [12,15,23]. However, steam is not an idea working fluid for utilizing low grade heat as the critical temperature of water (374 °C) is much higher than the ambient temperature and its critical pressure (22.1 MPa) is extremely high. Therefore in subcritical or even trans-critical cycles great proportion of heat is consumed to gasify the water in phase change processes. In these heat transfer processes a great quantity of exergy is lost due to temperature glide mismatching between the heat source and the working fluid – the so-called pinch limitations [24,25].

To compare the properties of thermal cycle working fluids in using a low grade heat source, a heat exchange process is taken as an example. It is assumed that the working fluids are to be heated from ambient temperature, T_a, to $T_h = 400$ °C. A normalised heat, $\overline{Q}$, is used, which is defined as the ratio of heat load at a certain temperature, T, to the total heat exchange amount during the whole process.

Table 1
Comparison of specific heat, latent heat and exergy density of cryogens and some commonly used heat storage materials [9,15].

Media component	Storage method[a]	Specific heat (kJ/kgK)	Phase-changing/Working temperature (°C)	Fusion/Latent heat (kJ/kg)	Exergy density (kJ/kg)
Rock	S	0.84–0.92	1000	N	455–499
Aluminum	S	0.87	600	N	222
Magnesium	S	1.02	600	N	260
Zinc	S	0.39	400	N	52
N_2 (liquid)	S + L	1.0–1.1	−196	199	762
CH_4 (liquid)	S + L	2.2	−161	511	1081
H_2 (liquid)	S + L	11.3–14.3	−253	449	11987
$NaNO_3$	L	N[b]	307	182	89
KNO_3	L	N	335	191	97
40% KNO_3 + 60% $NaNO_3$	S	1.5	290–550	N	220
KOH	L	N	380	150	82
$MgCl_2$	L	N	714	452	316
NaCl	L	N	801	479	346
Na_2CO_3	L	N	854	276	203
KF	L	N	857	425	313
K_2CO_3	L	N	897	236	176
38.5% MgCl + 61.5% NaCl	L	N	435	328	190

[a] In this description 'S' indicates the thermal is stored in the form of sensible heat while 'L' for latent heat.
[b] 'N' reveals that these data is not available.

Table 2
Comparison of physical and chemical exergies of the cryogens.

Cryogen	Thermal exergy (kJ/kg)	Chemical exergy (kJ/kg)	Gas density (kg/m^3)	Liquid density (kg/m^3)
Liquid H_2	11,987	116,528	0.0824	70.85
Liquid N_2	762	0	1.1452	806.08
Liquid CH_4	1081	51,759	0.6569	422.36

$$\overline{Q}(T) = \frac{H(T) - H(T_a)}{H(T_h) - H(T_a)} \tag{5}$$

where H is the enthalpy. Fig. 3 compares the temperature dependence of the normalised heat of water with the three cryogens, where the ambient temperature is assumed to be 25 °C. One can see that, given a working pressure, the specific heat (the slope of the lines) for the three cryogens (hydrogen, methane and nitrogen) is approximately the same. However, different behavior occurs to water. If the working pressure is lower than its critical value (22.1 MPa), the specific heat of water changes greatly due to phase change. This will lead to inefficient use of the heat source considering that the heat source carriers (hot-side working fluids) are mostly fluids with a constant specific heat (e.g. flue gases or hot air). Although water behaves similarly to the cryogens under supercritical conditions (e.g. the case with pressure of 30.0 MPa in Fig. 3), the high working pressure increases the technical difficulties in realizing the process.

3. Extraction of energy from cryogen

Cryogenic energy recovery has been investigated theoretically using the second law of thermodynamics [18,20,26]. Four main methods have been proposed to extract the cold exergy from cryogen for power generation. The first one is the so-called direct expansion method. With such a method, cryogen is pumped to a high pressure and is then heated to the atmospheric temperature by the environmental heat or waste heat, followed by an expansion process to generate power. The second approach uses an indirect heating medium (working fluid) via a Rankine cycle in which the cryogen works as liquid condensate flowing through the condenser where the cryogenic exergy is transferred to the working fluid. The temperature difference between ambient and the cryogen drives the working fluid to generate power in the Rankine cycle. The third method uses a Brayton cycle in which the cryogen cools down the inlet gas of a compressor. The high pressure working gas after the compressor is then heated by the ambient and/or other heat sources and expands through an expander to generate power. Apparently, the lower the temperature of the inlet gas of a compressor, the less work required in the compression process, implying that the use of the cryogenic energy in the Brayton cycle can improve the cycle efficiency. The fourth method is the use of a combination of the three methods. Among the four methods, the direct expansion is the simplest but is also most inefficient as it does not use the cold energy of the cryogen fully and a great deal of cold energy is discarded into the environment, leading to the loss of energy. As a consequence, in the following, attention is paid mainly to the other three methods.

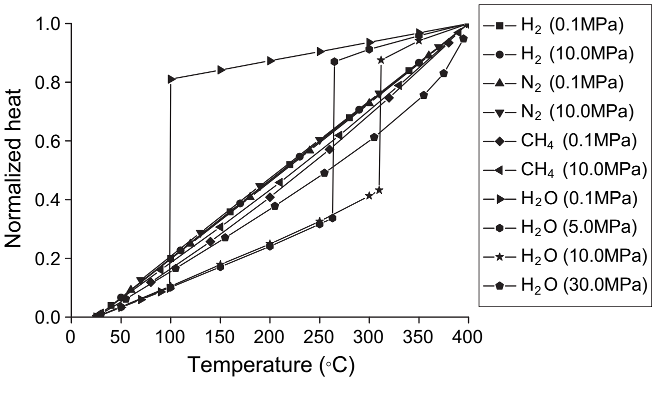

Fig. 3. Normalised heat vs. Temperature diagram of some working fluids.

3.1. Indirect Rankine cycle method

The Rankine cycle is a thermodynamic cycle which converts thermal energy, heat and/or cold to work. Fig. 4 shows three schematic configurations of the Rankine cycle. The heat and cold sources are supplied externally to a closed-loop, which usually uses a phase change material as the working fluid. When used as a heat sink in the Rankine cycle, cryogen is vaporized at a pressure that is at or slightly higher than the ambient pressure. To recover both the latent cold and sensible cold released by the cryogen, a working fluid with a liquefaction/boiling point slightly higher than the cryogen would be an idea working fluid. Propane has a boiling point of −42 °C at the ambient pressure and has been used as the working medium in a simple Rankine cycle to extract the cryogenic exergy of liquefied nature gas (LNG) at industrial scales. Fig. 4(a) shows the schematic diagram of the simple Rankine cycle, where propane is first pumped to a high pressure after liquefied by LNG. The high pressure propane is then heated up by sea water or other waste heat sources and expands in a turbine to generate electricity. Due to the large temperature difference of two the fluids in the condenser and the lack of cold recovery in the evaporator, the overall efficiency is very low [17].

From the thermodynamic point of view, the use of a single fluid in a Rankine cycle is not the best approach to the use of cold exergy. In order to maximise the efficiency, the use of cascading cycles have been proposed [27,28]; see Fig. 4(b). In these cycles lower boiling point materials such as methane and ethene are adopted as a working fluid in the first stage, while propane, water and ethane are used as the working media in the subsequent cycles. In the cascading configuration shown in Fig. 4(b), the cold energy is transferred in the form of latent heat thus the heat exchange occurs under the condition of constant and minimum temperature difference. In such a way, the overall efficiency is enhanced by minimising the exergy loss in the process of heat transfer. However, the cascading configuration greatly increases the system complexity, which can weaken the operation stability. Cryogenic energy can also contribute to carbon dioxide capture. For example, Deng et al. [29] proposed a cogeneration power system using LNG and the concept of oxy-fuel combustion. Fig. 4(c) shows the proposed process, where the cycle is essentially a recuperative Rankine cycle with carbon dioxide as the main working fluid and natural gas is fired in the combustor with pure oxygen. Exhaust gas with a pressure higher than 0.5 MPa from the turbine is cooled and condensed along with the vaporisation process of LNG. Such a cogeneration system is efficient and is regarded as commercially practicable. Table 3 gives a summary of the exergy recovery processes discussed above.

3.2. Indirect Brayton cycle method

The Brayton cycle is a thermodynamic cycle for gas turbines and engines. The main difference between the Brayton cycle and the Rankine cycles lies in that the working fluid in the Brayton cycle is pressurized by a compressor instead of a pump in the Rankine cycle. The working fluid is in the gaseous state throughout the Brayton cycle and the heat or cold transferred to the working fluid is in the form of sensible heat. Therefore the cryogenic energy could only be used to cool the inlet gas of the compressor. Fig. 5(a) shows

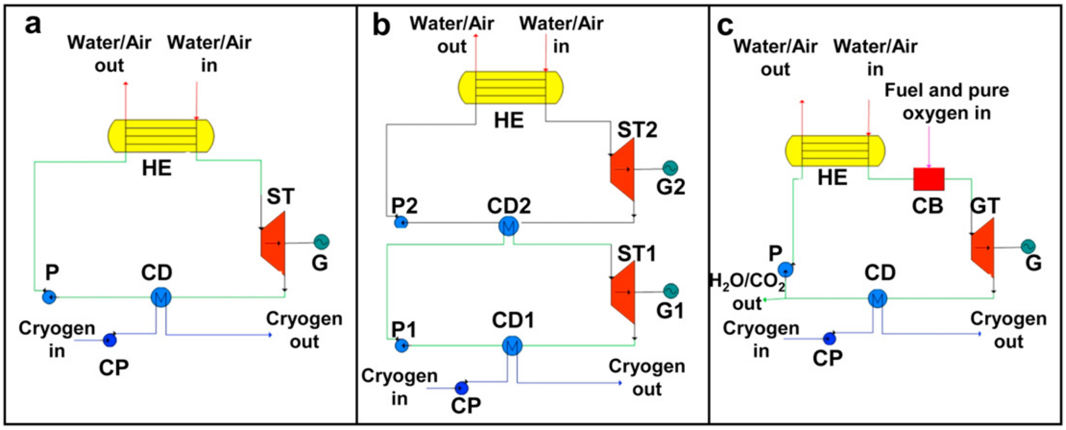

Fig. 4. Schematic configurations of Rankine cycles: (a) simple Rankine cycle, (b) cascading Rankine cycle, and (c) CO_2 capture cycle (CB – Combustion, CD – Condenser, CP – Cryogenic Pump, G – Generator, GT – Gas Turbine, HE – Heat Exchanger, P – Pump, ST – Steam Turbine).

schematically a direct way of using the cold energy to pre-cool the input working fluid in the gas cycle. The feasibility of the use of the cold energy of liquefied natural gas to cool the inlet air has been analyzed by Kim and Ro [30] for gas/steam combined power plants during warm seasons. Air cooling capacity and power augmentation for a combined cycle system are demonstrated as a function of the ambient temperature and humidity in their research, while the corresponding increase in power is larger than 8% on average if the humidity is low enough for warm ambient air and water vapour in the air does not condense.

As a special Brayton cycle the mirror gas turbine (MGT) method is introduced recently to recycle the cold exergy of LNG [31]; see Fig. 5 (b) where the cold released from LNG is used to cool the exhaust gas from a turbine to increase the output work of the turbine and part of the cold exergy from LNG is transformed to decrease the compression work. This is different from the conventional way of cooling only the inlet gas of the compressor. It is reported that seven to twenty percent of exhaust energy can be converted to useful work by introducing three-stage inter-cooling, and the thermal efficiency of the turbine can be improved by over 25% regardless the input of cryogenic exergy [32].

The two Brayton cycles discussed above are open cycles. Closed-loop Brayton cycles have also been investigated; see Fig. 5(c) for a schematic diagram. The closed Brayton cycles can be with or without a combustion process, and not only the air or nitrogen, but also hydrogen and helium can be used as the working fluids. This could decrease the lower temperature of the cycle greatly and hence enhance the cryogenic energy recovery efficiency. Table 4 gives a summary of the work on the cryogenic exergy recovery through Brayton cycles discussed above.

3.3. Combined method

A more efficient approach to the recovery of cryogenic exergy is the combined method, particularly by integrating a Rankine cycle or a Brayton cycle with a direct expansion method. In such a way, part of the thermal exergy is converted to high pressure exergy. In a typical combined method, the cryogen is normally pumped first to a pressure above the critical point of the working fluid before vaporisation, which is followed by direct expansion to form a supercritical open cycle with only sensible heat discharged. Pilot-plant scale work based on the combined method was first established in Japan in 1970s, where closed-loop Rankine cycles were combined with direct expansion cycles in an LNG re-gasification process [33]; see Fig. 6(a) for the flow chart. The process shown in Fig. 6(a) uses propane as the working fluid for the Rankine cycles. Apart from propane, ammonia-water mixtures and Freon have also been used as the working fluids for the combined cycles [34–37]. However, liquefaction of these fluids involves phase change processes and the cold source is in the form of sensible heat, the cryogenic exergy could not be extracted efficiently.

Fig. 6(b) shows a schematic diagram of combining the Brayton cycle with the direct expansion cycle, where the cooling of the working fluid occurs through a sensible heat discharging process, leading to a high performance of the cryogenic exergy recovery. Bisio and Tagliafico used nitrogen as the working fluid in their studies of a combined cycle involving a two-stage compression process with inter-cooling and showed that the system had an overall exergy efficiency of 0.46 [27,28].

There have been reports on the cryogenic energy recovery process for both LNG and liquefied hydrogen [38–41], where the cold energy of the low pressure cryogens is discharged in two stages; see Fig. 6(c). The high grade cold is used to cool the low pressure working fluid before compression and the low grade cold is used to liquefy the working fluid in a Rankine cycle. Therefore this configuration can be regarded as a combination of the Rankine and the Brayton cycles. A particular example for this is the oxy-fuel combustion of LNG, where carbon dioxide could be separated in the condensation process for storage. This makes these technologies much more promising [39,40,42]. The combination of a closed

Table 3
Summary of the cryogenic exergy recovery processes using the Rankine cycle.

Thermal cycle type	Cryogen	Working medium	Heat source	Cryogenic exergy efficiency	System complexity	References
Simple Rankine cycle	LNG	Propane	Sea water/air	<20%	Simple	[17,22,43]
Cascading Rankine cycle	LNG	Propane, methane and water; Ethene and Ethane	Sea water and gas turbine exhaust heat	>60%	Complex	[27,28,44]
CO_2 capture cycle	LNG	CO_2 and water	Nature gas combustion heat	20–60%	Medium	[29,32]

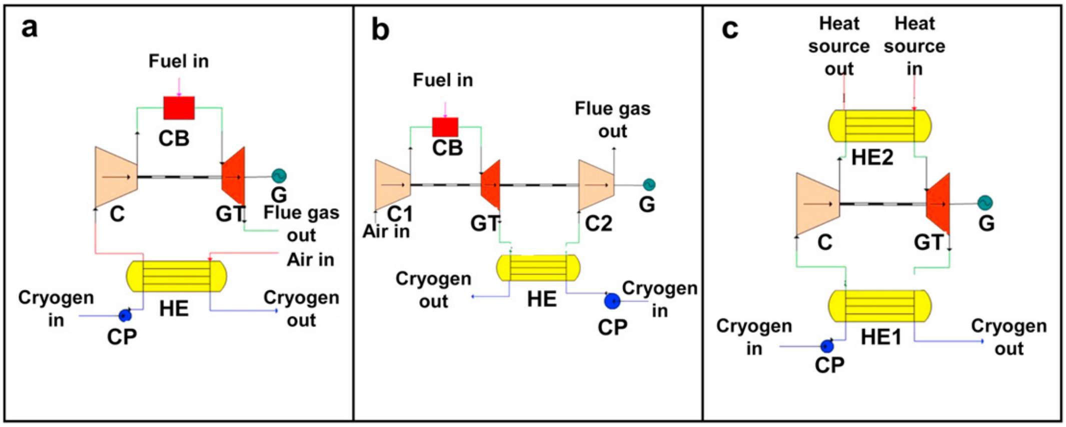

Fig. 5. Schematic diagrams of Brayton cycles: (a) pre-cooling open cycle, (b) post-cooling open cycle, and (c) closed Brayton cycle (C – Compressor, CB – Combustion, CP – Cryogenic Pump, G – Generator, GT – Gas Turbine, HE – Heat Exchanger).

Brayton cycle and a Rankine cycle with direct expansion has also been investigated by Bai and Mang and their aim was to maximise the efficiency [22]; see Fig. 6(d) for a schematic diagram. In their design, the Brayton cycle with nitrogen as the working fluid is employed to recover the high grade cold and the ammonia-water based Rankine cycle is used to recover the low grade cold. From the thermodynamic point of view, the combined cycle proposed by Bai and Mang [22] could also be regarded as a cascading system. Table 5 gives a summary of the work on cryogenic exergy recovery using combined cycles as discussed above.

3.4. Further analyses and discussion

Cryogens contain high grade thermal energy in the form of latent heat and sensible heat. Such valuable energy could only be extracted effectively by selecting an effective thermodynamic method based on the thermodynamic properties and external conditions e. g. heat sources etc. Theoretically, Rankine cycle is an effective method to extract the cryogenic energy if a working medium with a slight higher boiling point than the corresponding cryogen can be found. In addition, the Rankine cycle uses pumps to compress the working fluid, which consumes very small amount of work, so the overall efficiency will not be affected much by the irreversible compression process. However the recovery of the cold released by the working fluid after compression has to be addressed in order to further enhance the efficiency. Although the cascading cycle can be a solution, process optimization is needed to compromise the cycle efficiency and the system complexity.

The Brayton cycle is not an effective method to directly recover the cryogenic energy as the cooling of gas only requires sensible heat. A big loss of cold exergy is therefore inevitable during the heat transfer process involving high grade latent heat although the working fluid (gas) can be cooled to a very low temperature. A more effective way to extract the cryogenic exergy is the use of a method that combines the direct expansion and other cycles.

Direct expansion converts part of the thermal energy into the pressure energy through pumping the cryogen to a high pressure. If one defines the pressure exergy, *E(P)*, as the maximum theoretical work obtainable by bringing the fluid to equilibrium with the environmental pressure through an isothermal process at ambient temperature, then

$$E(P) = H(P,T_a) - H(P_a,T_a) - T_a \cdot [S(P,T_a) - S(P_a,T_a)] \tag{6}$$

The proportion of the pressure energy in the cryogenic exergy can then be given as:

$$\eta = \frac{E(P) - W_P}{E_l(P_a) + W_P} \tag{7}$$

where $E_l(P_a)$ is the exergy of liquid cryogen at ambient pressure, and W_P is the pumping power which for an isentropic process can be given by:

$$W_P = [H(P,S_l(P_a,T_b)) - H_l(P_a,T_b)]/\eta_P \tag{8}$$

where η_P is the pump efficiency. The proportion of the pressure exergy is found to increase with increasing pressure, and the increase is very sharp at low pressures of up to ~10 MPa. However, the increase tends to level off at higher pressures; see Fig. 7 for three of the cryogens considered with the pump efficiency taken as 0.7. Considering the rapid increase in the pumping power consumption and the requirements for the turbine inlet pressure, the pumping pressure should be limited to a certain value higher than the critical pressure. From Fig. 7 one can also see that the optimal working pressure for methane is about 20 MPa, while those for nitrogen and hydrogen are slightly higher. The pressure exergy could then be extracted through a direct expansion process.

Table 4
Summary of the cryogenic exergy recovery processes using Brayton cycles.

Thermal cycle type	Cryogen	Working medium	Heat source	Cryogenic exergy efficiency	System complexity	Reference
Open cycle	LNG	Air	Combustion heat	$<$ 20%	Simple	[30,31]
	LNG, LN_2	Nitrogen	Ambient air	$<$ 20%	Simple	[21,27,28,45]
	LNG	Hydrogen	Furnace waste heat	20–60%	Medium	[46]
Closed cycle	LH_2	Helium	Combustion heat	20–60%	Simple	[47]
	LNG	Helium	Combustion heat	20–60%	Simple	[48,49]

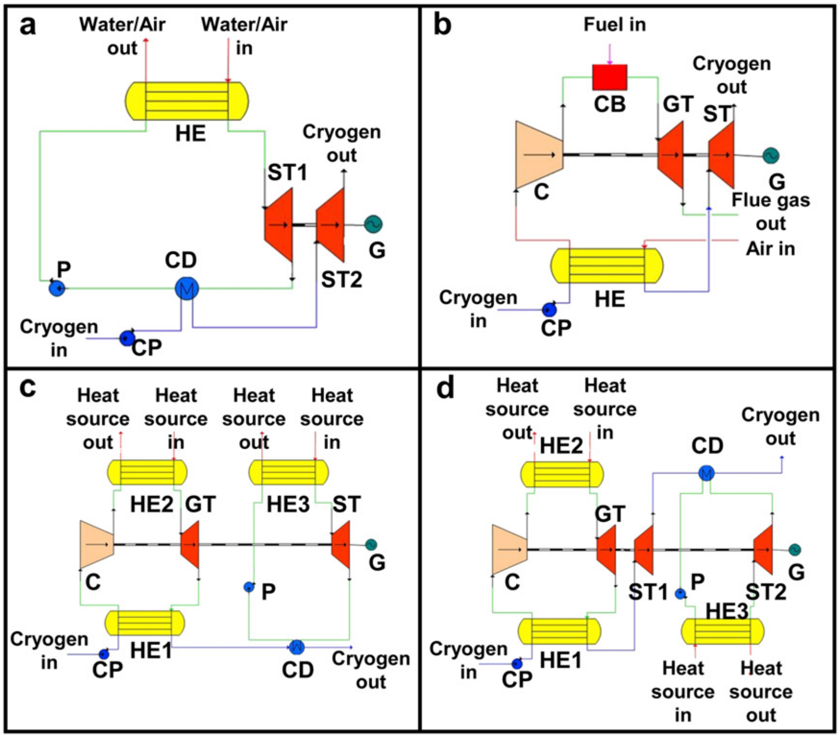

Fig. 6. Schematic diagram of combined cycles: (a) direct expansion-Rankine hybrid cycle, (b) direct expansion-Brayton hybrid cycle, (c) Rankine–Brayton hybrid cycle, and (d) direct expansion-Rankine–Brayton hybrid cycle (C – Compressor, CB – Combustion, CD – Condenser, CP – Cryogenic Pump, G – Generator, GT – Gas Turbine, HE – Heat Exchanger, P – Pump, ST – Steam Turbine).

The remaining exergy exits in the form of sensible thermal cold, which has to be recovered in a thermal cycle, in which the pressure again plays an important role.

Fig. 8 plots the normalised temperature against the normalised heat at different pressures with the normalised temperature and heat defined respectively as:

$$\overline{T} = \frac{T - T_b}{T_a - T_b} \tag{9}$$

$$\overline{Q} = \frac{H(T) - H_l(T_b)}{H(T_a) - H_l(T_b)} \tag{10}$$

where $H_l(T_b)$ is the enthalpy of liquid cryogen at its boiling point. Note that the definition of $\overline{Q}$ in Equation (9) is similar to that in Equation (5). In Fig. 8, the heat transfer processes are assumed to occur from the boiling point to the ambient temperature at different pressures. For methane and nitrogen, about half of the cold energy is released in the form of latent heat at low pressures. If the fluids are pumped to their supercritical states, the remaining cold will release in the form of sensible heat with approximately constant specific heat. This suggests that the combined direct expansion and Brayton cycle be the most efficient method for fully recovering the cryogenic energy of methane and nitrogen. This, however, does not seem to be held for hydrogen as the latent heat contributes to a very small portion of the released cold. Therefore the simple Brayton cycle would be an efficient method to recover the cryogenic energy of liquid hydrogen, if a suitable working fluid could be found.

It should be noted that the heat source plays a very important role in the selection of the recovery method. If the environmental heat (seawater and air) and other low grade heat sources are available, the Rankine cycle is more suitable whereas the Brayton cycle is more suitable when medium and high grade heat sources are available.

4. Concluding remarks

This paper reviews and assesses the work on the use of cryogen as an energy carrier. It covers both the fundamental thermodynamic aspects associated with cryogen as an energy storage medium and the current status of technologies for cryogenic energy extraction. The following observations are obtained:

Table 5
Summary of the cryogenic exergy recovery using combined cycles.

Thermal cycle type	Cryogen	Working medium	Heat source	Cryogenic exergy efficiency	System complexity	Reference
D + R	LNG	Propane, Ammoina-water, freon	Combustion heat, low temperature waste heat	20–60%	Simple	[22,26,33–37,50]
D + B	LNG	Combustion gas, nitrogen, air	Furnace waste heat	> 60%	Middle	[27,28,31]
R + B	LH_2, LNG	CO_2/water mixture, water/air mixture	Combustion heat	20–60%	Complex	[38–41]
D + R + B	LNG	Nitrogen and ammonia-water	Low level waste heat	>60%	Complex	[22]

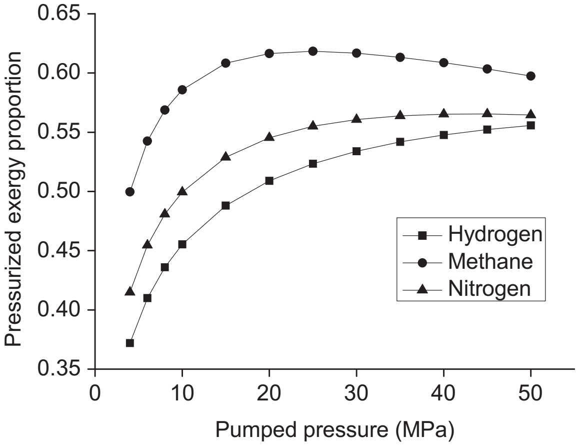

Fig. 7. Exergy conversion of cryogen by pumping.

- Cryogens have a relatively high energy density in comparison with other thermal energy storage media. They can be efficient working media for recovering low grade heat due to their low critical temperature.
- If a high grade heat source is available, the direct expansion - Brayton hybrid system is the most efficient method to extract the cryogenic exergy for most cryogens but not liquid hydrogen. This is because the latent heat of hydrogen only contributes to a small part of the released cold and a simple Brayton cycle would be suitable for the exergy recovery.
- If there is only ambient and/or a low grade heat source, the combination of direct expansion and Rankine cycle is more attractive due to its low power consumption in the compression process. This appears more promising when carbon dioxide capture is considered.

Note that no consideration on the exergetic efficiency of cryogen production has been taken into account in the analyses reported in this work. This is mainly because the manufacturing of cryogen as an energy carrier will involve integration of the cryogen production process and the energy storage system. Such an integrated system is expected to give a higher exegetic efficiency in terms of cryogen production. This is a subject of our current investigation and the results will be reported in the near future.

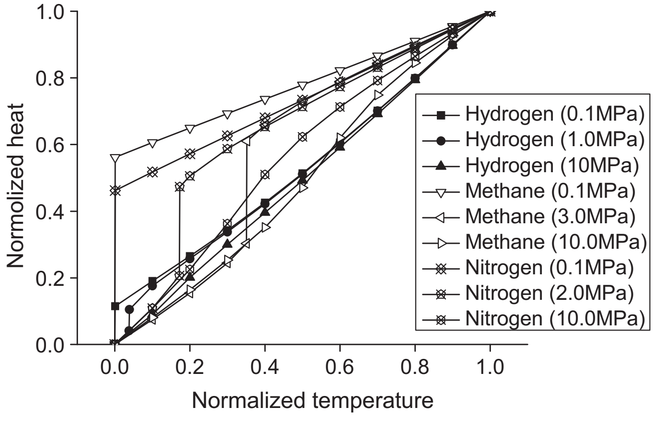

Fig. 8. Normalised heat vs. normalised temperature diagram of cryogens at low temperature range.

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