THERMODYNAMIC PERFORMANCE OF AMMONIA IN LIQUEFIED NATURAL GAS PRECOOLING CYCLE

by

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Original scientific paper
https://doi.org/10.2298/TSCI201227072S

The selection of proper refrigerants for natural gas liquefaction processes play a key role in cycle's efficiency. Mixed refrigerants have been proven to improve cycle's exergy efficiency over single pure refrigerant. However, the future of some of these refrigerants with higher global warming potential index are unknown due to the continuous restriction being enforced by the energy and environmental agencies over the past few decades. This study examines the benefits and drawbacks of mixing ammonia, a refrigerant with zero global warming potential index and a high occupational safety characteristic, with lighter hydrocarbon refrigerants such as methane and ethane as a mixed refrigerant in a natural gas liquefaction's precooling cycle. Results showed, presence of ammonia in mixed refrigerant not only saved in capital cost due to the smaller footprint of plant and smaller cold box, it also lowers the plants precooling operation expense by reducing the required compression power needed for the precooling cycle up to 16.2%. The results of exergy analyses showed that by reducing the molar concentration of more pollutant refrigerant methane and replacing it with ammonia enhanced the cycle's efficiency by 4.3% and lowered the heat exchanger total exergy loss up to 47.9 kW.

Key words: *liquefied natural gas, precooling cycle, ammonia, mixed refrigerant, exergy*

Introduction

The liquefaction process of natural gas takes tremendous amount of energy and it is mainly due to the compression power of the refrigerant required by the compressors. The liquefied natural gas (LNG) liquefaction process uses about 5-8% of the feed gas to the LNG plants depending on the size of the plant and it is mainly used to power the compressors [1]. Therefore, any process improvement to reduce the amount of energy being used would result in lower energy consumption and lower CO_2 emission into the atmosphere [2]. Such a high amount of compression power is required due to large temperature gradient in the heat exchangers (HTX) and cryogenic side of the cold box [2]. To liquefy natural gas, the gas goes through three main phases of cooling or also known as precooling, liquefaction and subcooling. The key to finding an energy efficient process is to design a pure or mixed refrigerant (MR) cycle whose composite boiling curve slope is very similar to the slope of the composite cooling curve of natural gas in all three phases [3]. Minimum temperature approach (MTA) is a common technique to achieve this goal, and to find a suitable and energy efficient refrigerant for the HTX [3].

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Figure 1(a) demonstrates both hot and cold streams composite curves, natural gas (hot) – 1, and MR (cold) – 2.

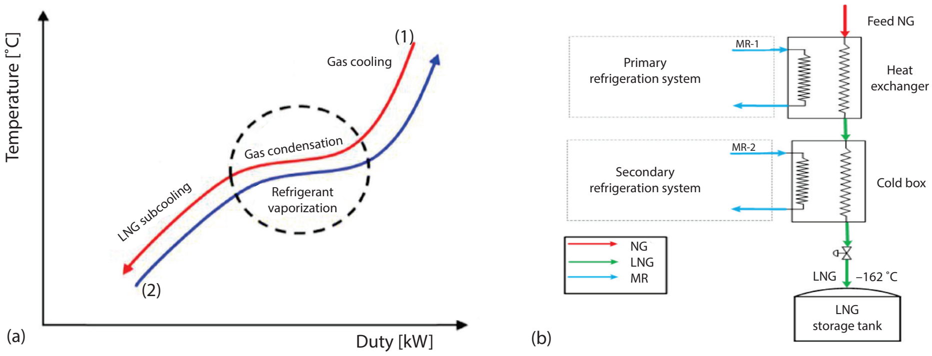

Figure 1. (a) Composite curves of natural gas and MR in LNG liquefaction process [4] and (b) the LNG liquefaction cycle with primary and secondary refrigeration system

All three processes of turning natural gas to LNG typically take place in cold box. However, large LNG plants take the precooling process out of the cold box and set a separate refrigeration cycle. The precooling process of lowering the natural gas temperature moderately before it enters the cold box allows it to downsize the cold box size which leads to capital cost saving and it provides opportunities to better control each phase of LNG liquefaction process. Most large LNG export plants incorporated a precooling cycle to lower both overall liquefaction energy consumption and operation cost [5]. Precooling equipment cost are relatively lower than subcooling equipment because it does not require specially alloy to withstand extremely low temperature of cryogenic process [6]. More than 80% LNG plants employed precooling cycle with using single pure refrigerant for the cycle such as propane. Recently, dual MR and mixed fluid cascade processes have been implemented using MR [7]. Figure 1(b) exhibits two separate refrigeration system where the primary refrigeration system is responsible for the precooling process and lowering the natural gas temperature to moderate level of –30 °C to –50 °C through one or series of HTX. To fully liquefy the natural gas to LNG and lower its temperature to –162 °C, it needs a secondary refrigeration system to take the precooled natural gas to the desired cryogenic temperature in which such a process takes place in a highly insulated enclosure called cold box. Castillo *et al.* [8] investigated the performance of precooling cycle using a single component refrigerant and they were able to lower the natural gas temperature up to –30 °C using kettle type HTX in series, and for the remaining subcooling process, MR was applied. Pillarella *at al.* [9] in a C3MR process found out single refrigerant propane for the precooling consumed 20% of the liquefaction cycle power and the remaining 80% was consumed by the MR process.

Most common precooling cycles are capable of lowering the natural gas temperature from ambient temperature to anywhere between –20 °C to –50 °C depending on the type of refrigerant being used [6]. Most common single refrigerants being widely used for precooling cycle are, propane, CO_2 and some limited number of azeotropic blend of hydrofluorocarbons [7]. While propane is a great choice for the precooling process, but it is a highly flammable gas and its storage cost puts it in a disadvantage. Also, with most plants migrating to the lean natural gas locations for processing natural gas with higher CH_4 content and not being able to extract enough heavier component such as propane as a primary source of cooling for the refrigeration cycle, makes propane a costly option due to the complex delivery logistics to the remote locations [8]. The MR system are highly efficient compared to single pure refrigerant. Ait-Ali [10] used numerical techniques for a two-stage MR cycle, along with Duvedi and Achenie [11] who applied non-linear programing for the most suitable MR composition. Also, Lee *et al.* [12] applied similar non-linear programing techniques on MR to determine the minimum pinch point using the best composite curve for the fluid being cooled. However, in a practical LNG plant setting, such solutions are especially challenging to be effectively implemented and monitored to main the efficiency of the cycle. Qyyum *et al.* [13] enhanced the exergy efficiency of the single MR process by 11% by replacing the conventional Thompson valve with hydraulic turbine.

In the case of selecting proper refrigerants for the refrigeration cycle, it is critical to comply with the current standards and regulation enforced nationally and globally. Due to the continuous restriction being imposed by the Department of Energy and other international energy agencies to reduce the amount of hydrocarbon (HC) gases in MR, a less pollutant and environmentally friendly compound such as ammonia has gained global interest for its unique thermodynamic characteristics in the refrigeration cycle [4, 14]. The HC such as C1, C2,… C5, have been the most common refrigerants being used for LNG liquefaction cycle for decades. The reason for that is that such gases for the refrigeration cycle is due to the similarity of cooling composite curve with the hot stream natural gas composite curve which results in enhancing HTX efficiency [15]. However, some of these components are relatively more pollutant compared to the others. Each gas has a specific rate of absorbing energy and escaping the atmosphere which leads to environmental pollution and that is measured by global warming potential index (GWPI). In which, GWPI allows comparisons of the amount of energy the emissions of 1 ton of a gas will absorb over a given time period, usually a 100 year averaging time, compared with the emissions of 1 ton of CO_2 [16]. Following tab. 1 present the GWPI for most common HC refrigerants as well as ammonia. For example, propane which is one of the most common components used for precooling has a GWPI of 4, which means propane pollutes the environment four times higher than CO_2. This table shows CH_4 has the highest GWPI and ammonia has a GWPI of zero showing that it is the most environmentally friendly refrigerant among HC refrigerants [17-19].

Table 1. The GWPI of refrigerants [16]

Refrigerant	GWPI
Methane	28
Ethane	6
Propane	4
Butane	5
Pentane	11
Ammonia	0

Ammonia is a proven refrigerant with high efficiency and it has been used as a single refrigerant for precooling process and it has a capability of lowering natural gas temperature up to –25 °C [20]. Ammonia is lighter than air and tends to disperse more readily which helps some of the safety concerns of gas being trapped if it leaks out from storage vessels or other equipment.

Magnolia LNG plant uses ammonia for the precooling process and it has been operating since 2016. They were able to use a smaller footprint for the plant by replacing propane precooling process and instead implementing ammonia which led to a reduction in cost of equipment [20]. The 200-metric-tpd Maitland LNG plant in Karratha, Western Australia uses an ammonia precooled SMR liquefaction process and has been in operation since 2007 [20]. Other single refrigerant such as ethane and CO_2 are also capable of precooling natural gas up to –70 °C. However, such cycles have low efficiency due to the required higher compression power [21]. Gnanedran and Baghuley [20] completed a study and compared propane precooled cycle *vs.* ammonia and found out, the using propane precooling cycle would require 2.3 times higher condenser size due to higher heat transfer coefficient compared to ammonia, and propane compression power are 15% higher than ammonia's required compression power.

Many of the recent studies use either a single refrigerant which has low cycle efficiency or four to five refrigerants, combination of light and heavy HC, to find the optimal molar composition of MR for every step of the liquefaction cycle. While results of these studies can be beneficial to minimize the exergy loss in the cycle, it is not the most practical method due to the high cost of storage of many refrigerants, complex shipping logistic to the remote LNG plant sites, and the sophisticated control system to sustain the desired variable molar composition of such MR. The objective of this paper is to investigate the performance of a natural gas precooling cycle employing environmentally friendly MR through a practical approach with using ammonia and the lighter HC refrigerants available at the lean LNG plant, CH_4 and ethane. The purpose of adding ammonia to the MR is to reduce the concentration of more pollutant refrigerant with relatively high GWPI, CH_4. Furthermore, this paper examines ammonia's thermodynamic performance through exergy analysis in key mechanical equipment such as HTX and compressor for the proposed natural gas liquefaction precooling cycle.

System description

Proposed precooling cycle and mixed refrigerant

Figure 2 illustrates the proposed precooling cycle with working fluid of MR which is composed of ammonia, and lighter HC CH_4 (C1) and ethane (C2). The reason for choosing only lighter HC for the MR is that most LNG plants are built near lean natural gas revoir where 95% of natural gas composition is mainly CH_4 and ethane. Therefore, LNG plant can produce the amount of the lighter HC refrigerant needed for the liquefaction cycle through the separation process. Besides, if there is a noticeable amount of heavier HC components such as C3, C4, and C5 and heavier ones are found, they are typically separated and sold as iquefied petroleum gas (LPG) due their higher market values.

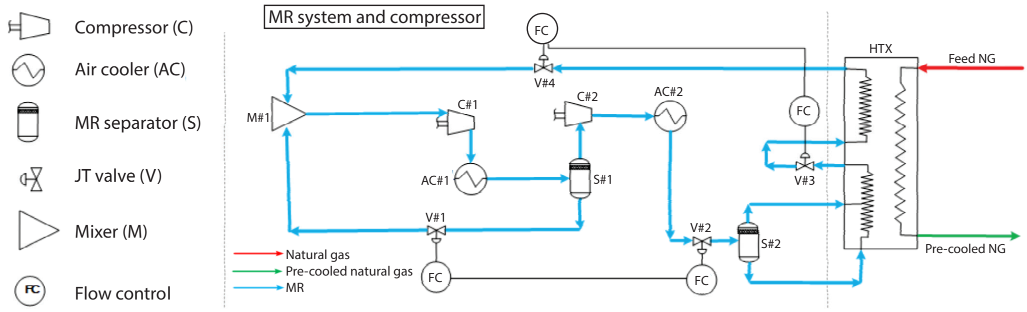

Figure 2. Natural gas liquefaction's precooling cycle

In order to get the working fluid to reach the desired cooling load, it needs to be compressed to a target pressure through a two-stage low and high pressure compressors [22]. These compressors are driven by gas turbines. Each time the MR is being compressed, its temperature elevates above ambient temperature. To lower its temperature, air coolers are being used to bring its temperature down. Using an air cooler may not be the most optimal way to lower the MR temperature, but the cost of the equipment and its operation is very low compared to having a secondary refrigeration system. Air coolers use free source of ambient air and its fan motor does not consume much power relatively, which makes it the most economical choice for lowering the hot compressed MR temperature. The main disadvantage of the air cooler is that its efficiency fluctuates as the ambient temperature changes [23]. Next, the MR goes through one or a series of Joule-Thompson valves to lower its temperature further drops to a target value of approximately –40 °C right before it enters the HTX. Meanwhile, hot fluid, natural gas, enters the HTX at ambient temperature and a pressure of 50 bar. The goal is to lower natural gas temperature close to MR inlet temperature. The pressure drop of both hot and cold fluids are negligible and it is considered to be 0.5 bar for the purpose of this study. The detail specification of MR system and compressors are listed in tab. 2.

Table 2. Precooling cycle MR system and compressors specifications

Items	Values
1st compressor outlet pressure [bar]	20
2nd compressor outlet pressure [bar]	70-80
HTX inlet temperature [°C]	20
HTX outlet temperature [°C]	–40±2
HTX inlet pressure [bar]	10±1
HTX outlet pressure drop [bar]	0.5
Compressors' efficiency	85%

Case study

Total of eight cases are being developed to study the performance of ammonia while is mixed with C1 and C2. In first four cases, MR of ammonia, C1 and C2, at various compositions being tested against lean natural gas with higher CH_4 concentration of 90%. Following four Cases, cased 5 through 8, same MR being applied to the precooling cycle, but this time the natural gas CH_4 concentration is 80% and it is considered rich natural gas due to higher amount of heavier HC. The purpose of testing proposed MR against rich natural gas is to evaluate the robustness and adoptability of the proposed precooling cycle against various natural gas feed condition. The strategy of developing these eight cases is to gradually drop the amount of refrigerant with highest GWPI, CH_4, in MR and replace that with higher concentration of more environmentally friendly gas, ammonia which has a zero GWPI. The detail molar composition of MR for each case is listed in tab. 3.

Table 3. The MR molar composition of eight study cases

Items	NH_3 %	C1 %	C2 %
Cases 1 and 5	25	50	25
Cases 2 and 6	30	40	30
Cases 3 and 7	35	30	35
Cases 4 and 8	40	20	40

Molar composition of each case were chosen in such a way where MR in each case is capable of providing desired cooling load. Also, such molar composition of MR must be capable of reaching approximately –40 [°C] when its pressure dropped through the Joule-Thompson valve. Lowering molar concentration of C1 than listed in tab. 3 in the MR further would increase the gap between two composite curves in HTX which leads to increase in exergy loss and the compressions power which results in lower cycle efficiency. Table 4 lists the detail molar composition of lean and rich natural gas being used for this study in addition other natural gas specification needed for the exergy analyses.

Methodology and governing equations

Exergy analysis

The liquefaction process consumes a high amount of energy and it is very costly. LNG plants are constantly seeking improvements in the liquefaction process to lower the cost of production and enhance the cycle's efficiency [24]. Exergy analysis are being employed here as a tool to identify the components with high energy consumption and higher exergy loss and improve the overall efficiency of the process. The exergy loss can be found in each component of the cycle from compressor, HTX, Joule-Thompson valves and, *etc.* The main source of the exergy loss that most LNG plants concern about are typically the HTX and compressors. The reason most LNG plants put such high emphasis on these two equipment are, the compressors consume a large amount of power which contributes to higher operation cost and the other one is the HTX which is costly and it increases the capital cost of the plant [25]. To develop an energy efficient precooling process, it would require to minimize the exergy loss in the HTX. This can be achieved by reducing the gap between the two hot and cold composite curves. The gap between two composite curves represent the entropy generation in the HTX [26]. The goal here is to find a balance where proper mixture of refrigerants listed in tab. 1 allows to reduce the GPWI without impacting the precooling cycle's performance and reduce the exergy loss in HTX. Studies shows MR has greater exergy efficiency compared to single refrigerant cycle [27]. Typically with sudden increase or decrease of temperature of working fluid in the HTX, it can cause higher entropy generation which leads to greater exergy loss. For example, low exergy efficiency in the N_2 expander LNG precooling process is a results of noticeable difference between the boiling temperature of N_2 (boiling point of −195 °C) and natural gas (inlet temperature of 30 °C) [28].

Table 4. Natural gas specification for the proposed precooling cycle

Items	Lean natural gas Cases 1-4	Rich natural gas Cases 5-8
Methane [%]	90	80
Ethane [%]	8	16
Propane [%]	1	2
Butane [%]	0.3	0.6
Pentane [%]	0.2	0.4
Nitrogen [%]	0.5	3
HTX inlet pressure [bar]	50	50
HTX outlet pressure drop [bar]	0.5	0.5
HTX inlet temperature [°C]	20	20
HTX outlet temperature [°C]	–40±2	–40±2

Exergy loss of individual equipment

Exergy is defined as the minimum theoretical work required to bring a quantity of matter formed in the environment to a specific thermodynamic state reversibly, which can be determined from the enthalpy and entropy changes. The flow exergy values for each hot and cold streams of liquefaction cycle are evaluated [29]:

$$e_{\mathrm{f}} = h - h_0 - T_0\left(s - s_0\right) \tag{1}$$

where e_{f} [kJkg^{-1}] is the flow exergy, h [kJkg^{-1}] – the specific enthalpy, and s [kJkg^{-1}K^{-1}] – the specific entropy, h_0 and s_0 represent specific enthalpy and specific entropy at dead state of T_0 and P_0. The reason exergy is critical even when pinch analysis is performed on the HTX, is attributable to the MTA alone cannot optimize the mixed refrigeration cycle. Lee [30] has conducted many studies in this area and placed emphasis on the importance of exergy analysis and how friction in the valve, compressor, and HTX can be so critical to a plant's operation performance. Due to the nature of the liquefaction processes and inevitable irreversibilities, some exergy will be destroyed during the heat transfer process between the MR and natural gas in HTX and the compression power provided to drive the compressors. The rate of exergy loss can be due to rate of entropy generation, $\dot{S}_{\mathrm{gen}}$, by the Gouy-Stodola theorem [29]:

$$\dot{E}_{\mathrm{d}} = T_0 \dot{S}_{\mathrm{gen}} \tag{2}$$

Exergy loss in HTX

In accordance with the Second law of thermodynamics, the exergy destruction is present within the system during the process and vanishes in the limiting case where there are no irreversibilities. Most of the irreversibility in the LNG liquefaction process is caused by energy losses in the compressor and HTX [29]. To evaluate the rate of exergy loss for the HTX and compressors shown in fig. 2 at a steady-state, the energy balance must be developed:

$$\frac{\mathrm{d}E_{\mathrm{cv}}}{\mathrm{d}t} = \sum_{\mathrm{j}}\left(1-\frac{T_0}{T_{\mathrm{j}}}\right)\dot{Q}_{\mathrm{j}} - \left(\dot{W}_{\mathrm{cv}}\right) + \sum_{\mathrm{i}}\left(\dot{m}_{\mathrm{i}}e_{\mathrm{f,i}}\right) - \sum_{\mathrm{o}}\left(\dot{m}_{\mathrm{o}}e_{\mathrm{f,o}}\right) - \dot{E}_{\mathrm{d}} \tag{3}$$

At a steady-state, $\mathrm{d}E_{\mathrm{cv}}/\mathrm{d}t$ is equal to zero. For the cold box, considering it is well insulated ($\dot{Q}_{\mathrm{i}} = 0$), and no external work is being done on the system, nor is any work being generated by the HTX ($\dot{W}_{\mathrm{cv}} = 0$). Therefore, the previous equation is simplified [29]:

$$\dot{E}_{\mathrm{d,HTX}} = \sum_{\mathrm{i}}\left(\dot{m}_{\mathrm{i}}e_{\mathrm{f,i}}\right) - \sum_{\mathrm{o}}\left(\dot{m}_{\mathrm{o}}e_{\mathrm{f,o}}\right) \tag{4}$$

where $\dot{E}_{\mathrm{d,HTX}}$, $e_{\mathrm{f,i}}$ and $e_{\mathrm{f,o}}$ are the total exergy loss of the HTX, the flow exergy of inlet stream, and flow exergy of outlet stream per unit mass, respectively, $\dot{m}$ [kgs^{-1}], i, and o – the mass-flow rate of the fluid, the inlet streams and outlet streams, respectively.

Exergy loss in compressor

To evaluate the exergy loss in compressors, the same energy balance as listed in previous eq. (3) is applied at steady-state. Considering the negligible heat transfer for the compressors, the rate of exergy loss can be described [29]:

$$\dot{E}_{\mathrm{d,comp}} = (\dot{m}_{\mathrm{i}}e_{\mathrm{f,i}}) - (\dot{m}_{\mathrm{o}}e_{\mathrm{f,o}}) - \dot{W}_{\mathrm{comp}} \tag{5}$$

This equation represents the minimum amount of power to be added from inlet state to outlet state when there is an increase in internal energy and enthalpy due to changes in working fluid experiences. Due to the presence of inevitable irreversibilities, the amount of required power must be more than what is actually needed for the system. The actual power needed can be calculated using the First law of thermodynamics. In this study, the optimal process is being targeted through MTA, which can affect the amount of power required for the compressors.

Exergy loss in Joule-Thompson valve

Joule-Thompson valves are used in the refrigeration cycle to lower the pressure of the MR which leads to lowering the MR temperature. The Joule-Thompson valve is a low cost and it is a simpler approach compared to using turbo-expanders for the refrigeration cycle. Most LNG plants prefer using series of Joule-Thompson valves for the liquefaction process rather than improving cycle efficiency slightly by investing considerable amount of capital, pricey operation cost and maintenance cost on turbo-expanders. Nevertheless, the Joule-Thompson valve has lower thermodynamic efficiency, which impacts the performance of the liquefaction process. Thermodynamically, an isenthalpic expansion takes place when high pressure refrigerant goes through the Joule-Thompson valve. A Joule-Thompson expansion valve associated with the refrigeration cycle has a low energy efficiency owing to entropy generation during isenthalpic expansion which the exergy loss through the valve can be evaluated:

$$\dot{E}_{\mathrm{d,JT}} = (\dot{m}_{\mathrm{i}}e_{\mathrm{f,i}}) - (\dot{m}_{\mathrm{o}}e_{\mathrm{f,o}}) \tag{6}$$

Exergy efficiency of cycle

Exergy efficiency known as the Second law of efficiency of the cycle is utilized in this study to evaluate the effectiveness of the engineering measures taken to potentially improve the performance of the pre-cooling cycle. To evaluate the thermal performance of a cycle in a practical setting, exergy efficiency is a more suitable criterion for the assessment of thermodynamic performance compared to thermal efficiency. To determine the performance of such a MR system and the degree of its reversibility, evaluation of the exergy efficiency of the whole precooling cycle as opposed to evaluating the exergy efficiency of each equipment individually must be performed. This is calculated by taking the ratio of the minimum power required for the liquefaction cycle per compressor power input, rather, calculating the difference of flow exergy of inlet natural gas and outlet LNG per total required rate of shaft work as defined [31]:

$$\varepsilon_{\text{sys}} = \frac{\left(\dot{m}_{\text{h,i}} e_{\text{fh,i}}\right) - \left(\dot{m}_{\text{h,o}} e_{\text{fh}}\right)}{\sum \dot{W}_{\text{compressor}}} \tag{7}$$

where $e_{\text{fh,i}}$ and $e_{\text{fh,o}}$ are the natural gas and precooled natural gas flow exergy, respectively. The compression power listed in the denominator is the total power required from both compressors shown in fig. 2. While individual mechanical component exergy analysis for compressors and HTX can be useful to determine the source and magnitude of the exergy loss, it is not the most suitable analysis to improve the efficiency of the whole liquefaction cycle, as each individual mechanical equipment may suggest an approach to change the working parameters where it may not be beneficial to performance of another equipment in the cycle. Therefore, exergy efficiency of the entire cycle must be performed to better assess whether the proposed solution can be reliable. The thermophysical properties needed for the analysis are computed using REFPROP [32] in conjunction with MATLAB software.

Process improvement and pinch analysis

Pinch analysis provides an effective approach to reduce the exergy loss in the HTX and the compression power on MR. Combination of these two significantly enhance the cycle efficiency. A critical factors that play important roles in the cycle's efficiency are the MR mass-flow rate and pressure. The process improvement is mainly focus on lowering the compression power while constraining the MTA value close to 3 °C in the HTX. Therefore, the objective function is represented:

$$M_{\text{inf}}(x) = \sum_{\text{j}} \left(\frac{\dot{W}_{\text{j}}}{\dot{m}_{\text{LNG}}} \right), \quad \Delta T_{\min}(x) \geq 3 \tag{8}$$

where x is the key design variables such as MR mass-flow rate, composition, condensation and vaporization pressure which has noticeable impact on overall liquefaction process efficiency [4].

Results and discussions

A total of eight cases were tested to evaluate the thermodynamics performance of ammonia in MR in an LNG liquefaction precooling cycle. The eight cases were split in two groups of four where in the first four cases, the proposed MR was examined against lean natural gas with a higher mount of CH_4 concentration of 90% *vs.* the second group of cases with rich natural gas with lower CH_4 concentration of 80%. The objectives were to lower the concentration of more pollutant refrigerant compound, CH_4, and introduce a more environmentally friendly refrigerant, ammonia into the MR.

Compression power and cycle efficiency

Table 5 shows the amount of compression power needed for both low pressure and high pressure, compressor for the proposed LNG precooling cycle. The total compression power to pressurize the MR reduces as ammonia's concentration increases from 25% in Case 1 to 40% in Case 4. However, the mass-flow rate ratio increases slightly by 4.2%, which means Case 4 requires a higher amount of MR compared to Case 1 for the precooling process. The reduction of compression power by 16.2% is attributed to increase of as ammonia's concentration in the MR, which also resulted in increase of cycle's efficiency by 4.3%. Comparing the results of this study with Xu *et al.* [33], it shows the maximum compression power found in this study which is 764 kW is about 21% less compared to 967 kW reported by Xu *et al*. [33] for their proposed MR using five HC refrigerants. Such a noticeable difference in compression power could save significant amount of energy consumption and operation cost. A similar trend of increasing mass-flow rate ratio can be observed, but it is increased at a much higher rate compared to the lean natural gas cases. In addition, the total compression power needed for the rich natural gas cases are much larger compared to lean natural gas which caused the cycle efficiency to drop from 33.7-23.4%. This shows the proposed MR is thermodynamically advantageous for a cycle with a lean feed natural gas than rich natural gas.

Table 5. Compressor power requirement and cycle's exergy efficiency

	Case study	Mass-flow rate ratio [kgMRkgLNG^{-1}]	Low pressure compressor power [kW]	High pressure compressor power [kW]	Total compression power [kW]	Cycle exergy efficiency [%]
Lean natural gas	Case 1	1.41	220.2	209.4	429.6	29.4
	Case 2	1.43	211.2	178.0	389.3	32.1
	Case 3	1.45	202.9	170.8	373.8	33.0
	Case 4	1.47	195.5	164.5	360.0	33.7
Rich natural gas	Case 5	1.78	392.07	372.92	764.99	23.4
	Case 6	1.80	380.83	321.01	701.84	25.5
	Case 7	1.83	370.80	312.11	682.91	26.2
	Case 8	1.85	362.50	305.14	667.64	26.8

Figure 3(a) illustrates the correlation between concentration of ammonia in MR, total compression power and cycle exergy efficiency. This plot shows as ammonia's concentration increases in MR, it enhances the cycle efficiency and lowers the compression power in all eight

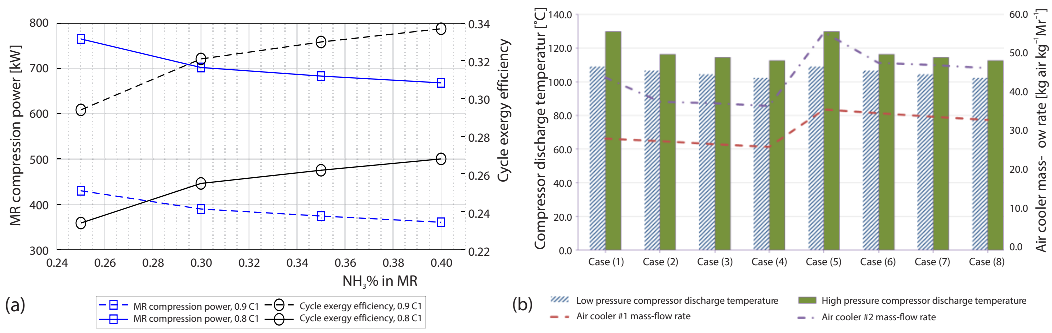

Figure 3. (a) Correlations between ammonia's molar concentration in MR, compression power and cycle's efficiency and (b) correlation between low pressure and high pressure compressors discharge temperature and air coolers mass-flow rate

cases. However, the improvement is more significant for lean natural gas due to the higher cycle efficiency values compared to rich natural gas. Among eight cases, Case 4 has the highest cycle efficiency of 33.7% with lowest compression power of 360 kW. Whereas the best case scenario for the rich natural gas cases has a cycle efficiency of 26.8% with compression power value of 667.64 kW. Such a lower compression power value for lean natural gas case can be highly beneficial to the LNG plant operation cost by lowering energy consumption of the gas turbines. Consequently, it reduces the amount of carbon emission the atmosphere by the gas turbines.

Exergy loss of individual equipment

The exergy loss values are calculated for each individual equipment displayed in the precooling cycle schematics in fig. 2. The detail exergy loss numerical values of the equipment are listed in tab. 6.

Table 6. Individual equipment and cycle's total exergy loss rate

	Case study	Air coolers [kW]	Compressors [kW]	Heat exchanger [kW]	Joule-Thompson valves [kW]	Total exergy loss [kW]
Lean natural gas	Case (1)	1125.71	17.25	255.77	77.69	147.41
	Case (2)	1015.88	16.14	255.81	86.72	1374.55
	Case (3)	997.84	15.75	255.85	82.44	1351.87
	Case (4)	977.73	15.51	255.89	81.59	1330.72
Rich natural gas	Case (5)	1417.76	21.72	288.72	97.85	1872.42
	Case (6)	1279.44	20.32	288.78	109.22	1697.76
	Case (7)	1256.72	19.83	288.82	103.83	1669.20
	Case (8)	1231.40	19.54	288.88	102.75	1642.56

The mass-flow rate of air cooler highly depends on the compressors discharge temperature, and it is a critical factor here which determines the size of the air exchanger and the heat exchange duty. Figure 3(b) illustrates the correlation between these two parameters for all eight cases. Results show that the discharge temperatures of the high pressure compressor are relatively higher compared to low pressure compressor, and this is mainly due to higher discharge pressure of the high pressure compressor. The high pressure compressor's discharge temperature range from 112.6-129.9 °C while the low pressure compressor's discharge temperature varies between 102.2-108.9 °C. Furthermore, it can be observed in fig. 3(b) that as the CH_4 concentration reduced from 50% in Case 1 to 20% in Case 4, both high pressure and low pressure compressors discharge temperature are dropped by 13.3% and 6.3%, respectively. As a result, the air coolers mass-flow rates ratio [kgAirkg^{-1}LNG^{-1}] declined from 44.03-36.79 for air cooler #2, and from 28.45-26.32 for air cooler #1. Comparing the results of lean natural gas cases *vs.* rich natural gas cases, the mass-flow rate ratio of air-cooler #2 is larger than air-cooler #2, and that is mainly due to the higher discharge temperature of high pressure compressors compared to low pressure compressors.

The pie charts in fig. 4(b) display the average exergy loss rate of each individual equipment for both groups of higher and low CH_4 feed natural gas cases. Results shows CH_4 concentration of natural gas had minimal impact on percentage of exergy loss by each equipment. The only equipment that have been affected slightly are HTX and air coolers. Lowering the CH_4 concentration of feed natural gas from 90-80% caused the exergy loss of HTX reduced only by 1% and air coolers increased by 1%. The pie charts also indicate that compressors and HTX being the two critical equipment in liquefaction cycle, have combined overall exergy loss rate up to 25%. Such a relatively low exergy loss by these two of the main equipment which impact the cycle's efficiency significantly, makes ammonia an advantageous refrigerant in the mixture for the proposed precooling cycle.

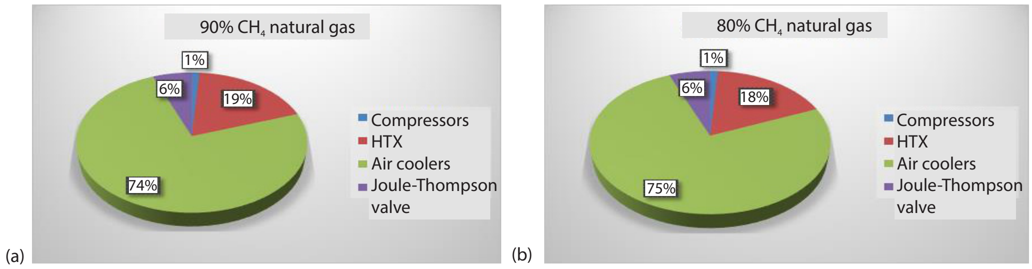

Figure 4. Exergy loss breakdown of individual equipment in precooling cycle for (a) average values of Cases 1-4 and (b) average values of Cases 5-8

HTX exergy analysis through composite curves

The following plots in fig. 5 represent natural gas and MR composite curves and the temperature approach between two composite curves for lean natural gas cases. The composite curves play an important role in liquefaction cycle efficiency. For practical purposes and minimizing the rate of entropy generation in the HTX, the MTA was set to 3 °C [34]. The results show the MTA does not exceed 8 °C. This peak values was noticed on the warmer side of the

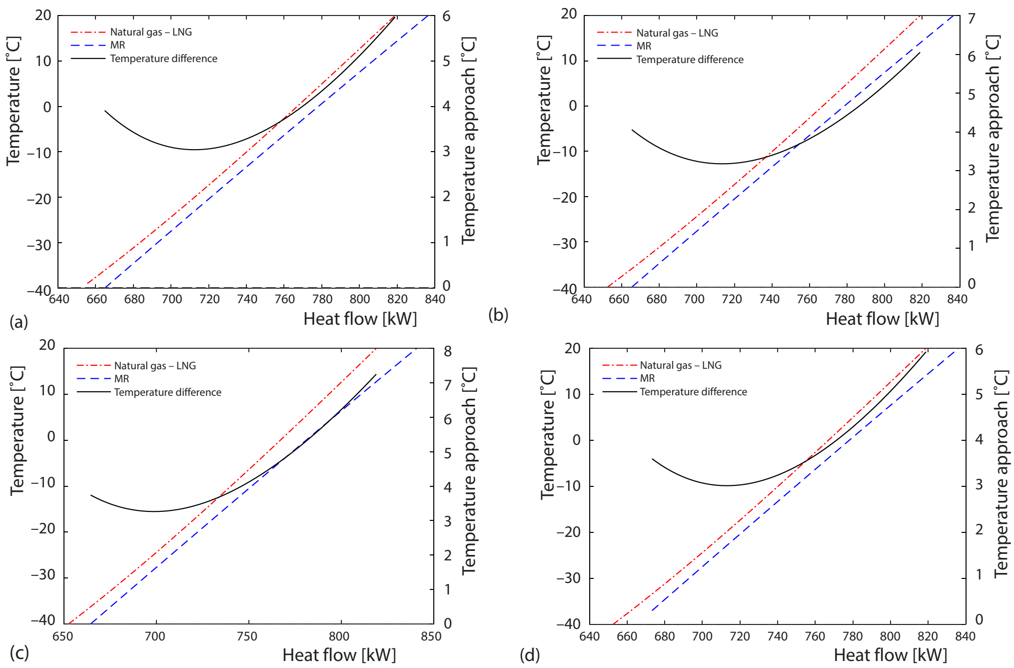

Figure 5. Composite curves of natural gas and MR streams in precooling cycle's HTX for Cases 1-4, lean natural gas with 90% CH_4

HTX. The temperature approach curves show the MTA steadily decreased as the temperature drops from 20 °C to –10 °C but slightly goes back up over range of –10 °C to –40 °C. This phenomenon attributed to presence of ammonia in the MR and keeping the MR in the gaseous phase for the entire precooling process. The small gap between the composite curves is indication of optimal compression power and low exergy in the compressor which can also be observed from the compressor exergy loss values in tab. 6.

Figure 6 shows the comparison of the temperature approach curves for both groups of lean and rich natural gas. It can be observed that the temperature approach values are greater for the warmer side of the HTX with higher heat flow values and minimum MTA takes places approximately at 700 kW for all cases. Also, higher concentration of ammonia in MR improved the MTA curve where Case 4 and 8 with the highest concentration of ammonia of 40% have the lowest MTA among other cases. Therefore, it can be concluded that higher concentration of ammonia in the MR reduces the gap between two composite curves and subsequently the rate of exergy loss which leads to enhancing the performance of the HTX. This effects is more noticeable for the rich gas where the rate of exergy loss of HTX at its minimum for Case 8 with 288 [kW], and the highest exergy efficiency among rich natural gas cases. Furthermore, the steady decrease of gap between two composite curves resulted in reduction compression power by 16.2% and 12.6% for lean and rich natural gas, respectively. This proves adaptability of proposed MR with presence of ammonia against various natural gas feed conditions. However, from the cycle exergy efficiency, this impact is more noticeable on a lean natural gas than rich natural gas.

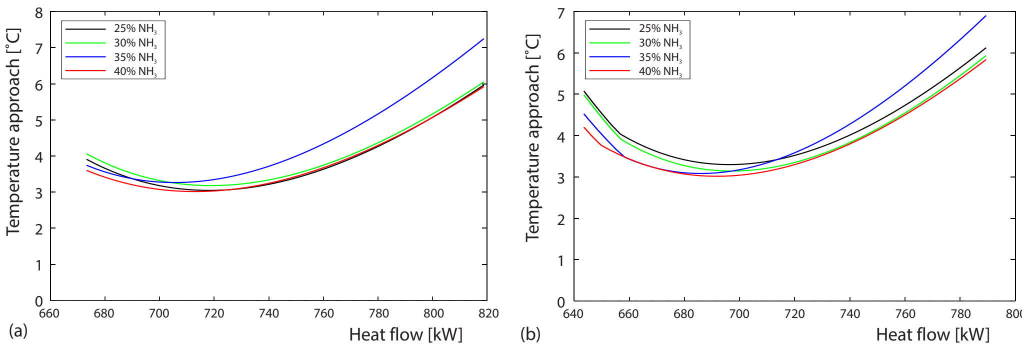

Figure 6. Temperature approach comparison of (a) Cases 1-4, lean natural gas with 90% CH_4 and (b) Cases 5-8, rich natural gas with 80% CH_4

Conclusion

The thermodynamics performance of ammonia was investigated for a natural gas liquefaction precooling cycle. Ammonia with zero GWPI, was utilized in the MR with lighter HC, CH_4 and ethane to reduce the amount of carbon emission the atmosphere by the gas turbine and enhance the precooling cycle's efficiency. The proposed MR precooling cycle was examined against both lean and rich feed natural gas. The results for lean natural gas cases indicated that lowering the concentration of the more pollutant refrigerant, CH_4 with relatively high GWPI, in MR and replacing it with environmentally friendly such as ammonia improved the cycle efficiency by 4.3%. It also reduced the carbon emission and saved cycle's energy consumption through less compression power needed by 16.2%. Exergy analyses results showed that compressors and HTX combined are only responsible for approximately 357 kW on an average which is 25% of the total exergy loss. Such a relatively low exergy loss rate among the major equipment used in precooling cycle is attributed to adding ammonia to the MR and keeping the MR at the gaseous phase for larger temperature range during liquefaction cycle. In summary, presence of ammonia in the MR provided opportunities on saving operation expense by reducing the compression power required by 16.2% and subsequently the carbon emission the atmosphere, lowered molar concentration of high pollutant refrigerant CH_4, enhanced the cycle efficiency by 4.3% and saved on capital cost by downsizing the most critical equipment in liquefaction cycle, cold box, through separating the precooling process from subcooling in the cryogenic HTX.

Acknowledgment

The work presented in this paper supported by mechanical engineering department of UTSA (University of Texas at San Antonio).

Nomenclature

E_d – exergy loss, [kW]
$\dot{E}_d$ – rate of exergy loss, [kW]
e_f – flow exergy, [kJkg^{-1}s^{-1}]
h – enthalpy, [kJkg^{-1}]
h_0 – dead-state enthalpy, [kJkg^{-1}]
$\dot{m}$ – mass-flow rate, [kg^{-1}s^{-1}]
s – entropy, [kJkg^{-1}K^{-1}]
s_0 – dead-state entropy, [kJkg^{-1}K^{-1}]
T – temperature, [°C]
T_0 – dead-state temperature, [K]
T_j – boundary temperature, [K]

Subscripts

cv – control volume
d – destruction
f – flow
gen – generation
i – inlet
j – boundary
o – outlet

Greek symbol

ε – exergy efficiency, [–]

Acronyms

GWPI – global warming potential index
HTX – heat exchanger
LNG – liquid natural gas
MR – mixed refrigerant
MTA – minimum temperature approach

References

[1] Krishnamurthy, G., *et al*., Processing Strategies for Efficient Natural Gas Liquefaction, *Gas Processing & LNG*, Gulf Publishing Holdings, Houston, Tex., USA, 2017, pp. 19-29
[2] Khan, M. S., *et al*., Knowledge Based decision Making Method for the Selection of Mixed Refrigerant Systems for Energy Efficient LNG Processes, *Applied Energy*, *111* (2013), Nov., pp. 1018-1031
[3] Venkatarathnam, G., Srinivasa Murthy, S., 1Effect of Mixture Composition on the Formation of Pinch Points in Condensers and Evaporators for Zeotropic Refrigerant Mixtures, *International Journal of Refrigeration*, *22* (1999), 3, pp. 205-215
[4] Abdul, Q. M., Innovative Propane-Nitrogen Two-Phase Expander Refrigeration Cycle for Energy-Efficient and Low-Global Warming Potential LNG Production, *Applied Thermal Engineering*, *139* (2018), July, pp. 157-165
[5] Zhang, J., *et al*., Technical and Economic Optimization of Expander-Based Small-Scale Natural Gas Liquefaction Processes with Absorption Precooling Cycle, *Energy*, *191* (2020), Jan., pp. 1165-1192
[6] Castillo L, Dorao C., Influence of the Plot Area in an Economical Analysis for Selecting Small Scale LNG Technologies for Remote Gas Production, *Journal Nat Gas Sci. Eng*., *2* (2010), 6, pp. 302-309
[7] Castillo, L., *et al*., Conceptual Analysis of the Precooling Stage for LNG Processes, *Energy Conversion and Management*, *66* (2013), Feb., pp. 41-47
[8] Castillo L., *et al*., Technology Selection for Liquefied Natural Gas (LNG) on Base-Load Plants, *Proceedings*, XIX International Gas Convention, Caracas, Venezuela, 2010
[9] Pillarella M., *et al*., The C3MR Liquefaction Cycle: Versatility for a Gast growing, Ever Changing LNG Industry, *Proceedings*, 15th International Conference on LNG, No. PS2-5, Barcelona, Spain, 2007

[10] Ait-Ali, M. A., Optimal Mixed Refrigerant Liquefaction of Natural Gas, Ph. D. thesis, Mechanical Engineering Department, Stanford University, Stanford, Cal., USA, 1979
[11] Duvedi, A., Achenie, L., On the Design of Environmentally Benign Refrigerant Mixtures: A Mathematical Programming Approach, *Computers and Chemical Engineering*, *21* (1997), 8, pp. 915-923
[12] Lee, G., *et al*., Optimal Synthesis of Mixed-Refrigerant Systems for Low-Temperature Processes, *Industrial and Engineering Chemistry Research*, *41* (2002), 20, pp. 5016-5028
[13] Qyyum, M. A., *et al*., Energy Efficiency Enhancement of a Single Mixed Refrigerant LNG Process Using a Novel Hydraulic Turbine, *Energy*, *144* (2018), Feb., pp. 968-976
[14] Zhu, J. L., *et al*., Offshore Adaptability of the Dual Nitrogen Expander Process with CO_2 pre-Cooling, *Nat. Gas. Ind*., *32* (2012), Apr., pp. 89-95
[15] Castillo, L., Dorao, C. A., On the Conceptual Design of Pre-Cooling Stage of LNG Plants Using Propane or an Ethane/Propane Mixture, *Energy Conversion And Management*, *65* (2013), Jan., pp. 140-146
[16] ***, Ammonia, Webbook.Nist.Gov. Accessed October 17, https://webbook.nist.gov/cgi/cbook.cgi?ID=C7664417&Mask=4&Type=ANTOINE&Plot on, 2020
[17] ***, International Energy Outlook, Eia.Gov. Accessed October 17, https://www.eia.gov/outlooks/ieo/, 2020
[18] ***, Understanding Global Warming Potentials | US EPA, US EPA. Accessed October 17, https://www.epa.gov., 2020
[19] Duvedi, A., Achenie, L., On the Design of Environmentally Benign Refrigerant Mixtures: a Mathematical Programming Approach, *Computers and Chemical Engineering*, *21* (1997), 8, pp. 915-923
[20] Gnanendran, N., Baguley, J., LNG Plant Optimization with Ammonia Precooling, Gas Processing, http://gasprocessingnews.com/, 2018
[21] Baris, Y., *et al*., A Parametric Study On A Subcritical CO_2/NH_3 Cascade Refrigeration System For Low Temperature Applications, *ASME, Journal of Energy Resources Technology*, *140* (2018), 9, 092004
[22] Brown, T. T., Hubbard, J. K., Application of Gas Turbine/Compressors in LNG Plants, *ASME, Journal of Engineering for Power*, *102* (1980), 1, pp. 132-135
[23] Schmidt, W. P., *et al*., Arctic LNG Plant Design: Taking Advantage of the Cold Climate, *Proceedings*, 17th Inte. Conf. and Exhib. on LNG, LNG 17, Houston, Tex., USA, 2013
[24] Ghorbani, B., *et al*., A Novel Energy Efficient LNG/NGL Recovery Process Using Absorption and Mixed Refrigerant Refrigeration Cycles – Economic And Exergy Analyses, *Applied Thermal Engineering*, *132* (2018), Mar., pp. 283-295
[25] Mehrpooya, M., *et al*., Cost And Economic Potential Analysis Of A Cascading Power Cycle With Liquefied Natural Gas Regasification, *Energy Conversion and Management*, *156* (2018), Jan., pp. 68-83
[26] Chang, S., *et al*., Optimization of Mixed Refrigerant System for LNG Processes through Graphically Reducing Exergy Destruction of Cryogenic Heat Exchangers, *Energy*, *168* (2019), Feb., pp. 200-206
[27] Mengyu, W., *et al*., Thermodynamic and Economic Optimization of LNG Mixed Refrigerant Processes, *Energy Conversion and Management*, *88* (2014), Dec., pp. 947-961
[28] Jianlu, Z., *et al*., Offshore Adaptability of the Nitrogen Expander Liquefaction Process with Pre-Cooling, *Applied Thermal Engineering*, *155* (20219), June, pp. 373-385
[29] Khan, N. B., *et al*., A Case Study: Application of Energy and Exergy Analysis for Enhancing the Process Efficiency of a Three-Stage Propane Pre-Cooling Cycle of the Cascade LNG Process, *Journal of Natural Gas Science and Engineering*, *29* (2002), Feb., pp. 125-133
[30] Lee, G.-C., Optimal Design and Analysis of Refrigeration Systems for Low Temperature Processes, Ph. D. thesis, School of Chemical Engineering and Analytical Science, University of Manchester, UMIST, Manchester, UK, 2001
[31] Hasan, M. M. F., *et al*., Optimizing Compressor Operations in an LNG Plant, (Eds. Alfadala, H., *et al*.), *Proceedings*, 1st Annual Gas Processing Symposium, Elsevier, Amsterdam, The Netherland, 2002
[32] ***, Reference Fluid Thermodynamic and Transport Properties, REFPROP Version 10.0, NIST, Gaithersburg, MD, USA, 2018
[33] Xu, X., *et al*., Automatically Varying the Composition of a Mixed Refrigerant Solution for Single Mixed Refrigerant LNG (Liquefied Natural Gas) Process at Changing Working Conditions, Energy, *64* (2014), Jan., pp. 931-941
[34] Hasan, M. M. F., *et al*., Operational Modelling of Multistream Heat Exchangers with Phase Changes, *AIChE J.*, 55 (2009), 1, pp. 150-171

Paper submitted: December 27, 2020
Paper revised: January 16, 2021
Paper accepted: January 19, 2021