Increasing the COP of a refrigeration cycle in natural gas liquefaction process using refrigerant blends of Propane-NH$_3$, Propane-SO$_2$ and Propane-CO$_2$

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ABSTRACT

This paper investigates the feasibility of using inexpensive techniques to enhance the coefficient of performance (COP) of the refrigeration cycle used in the liquefaction of natural gas. The effect of mixing the propane refrigerant with ammonia, sulfur dioxide and carbon dioxide on the performance and the work of the compressor is studied. It is shown that the mixture of ammonia-propane and sulfur dioxide-propane enhances the overall COP by 7% and 9%, respectively. The addition of ammonia and sulfur dioxide to the propane refrigerant reduces the overall compressor work by reducing the overall mass flowrate required to absorb a constant heat from the natural gas. On the other hand, the mixture of carbon dioxide-propane degrades the overall COP by 70%. The addition of carbon dioxide increases the overall mass flowrate required to absorb a constant heat from the natural gas. Interestingly, the proposed method requires small capital and running costs.

1. Introduction

Natural Gas is a preferred energy source because of its low emission and efficient combustion. To reduce the risks related to harmful energy sources like nuclear energy, natural gas has become an important energy source used in electrical power generation plants [1]. The increasing desire for natural gas led to enhancements of natural gas technologies. Technology enhancements focused on the main natural gas processes including but not limited to gas extraction, treatment, preparation for transport, and transportation to the desired destination. The preparation to transport involves storing natural gas in containers by either compressing it or liquefying it [2]. Liquefaction is an important process in the natural gas transport as it is considered to have a lower overseas transportation cost compared to other transportation forms [2].

1.1. Existing liquefaction technologies

There are many technologies available for liquefaction of natural gas. Current technologies include i) single refrigerant processes (cascade [3]), ii) mixed refrigerant processes (DMR [3], Linde [3]) and iii) combined refrigerant processes (APCI [3]). The efficiency of these liquefaction processes generally depends on the working fluid, the arrangement of the refrigeration cycles, and the number of elements used in the cycle. The working principle of each one of these liquefaction processes is different. The cascade processes use a single refrigerant (single working fluid) in multi-stage refrigeration cycles connected in series. Each refrigeration cycle has a single refrigerant and cools the natural gas partially until the natural gas liquefies at -160 °C. DMR/Linde processes use mixed refrigerants in the refrigeration cycles to have a better fit with the cooling curve of natural gas, and hence, reduce the compressors’ energy consumption. The APCI liquefaction processes, the mostly used worldwide, use a combination of a single refrigerant refrigeration cycle (using propane) to pre-cool the natural gas. The natural gas is then refrigerated further down to -160 °C using a mixed refrigerant cycle. Due to their simpler propane pre-cooling cycle, the APCI liquefaction processes offer a higher liquefaction performance (i.e. high coefficient of performance (COP)) with lower running cost compared to the DMR/Linde processes. APCI allows the natural gas to pass through three levels of cooling [3]. The primary cooling level consists of reducing natural gas temperature down to 1.7 °C using propane as a refrigerant. This cooling step takes place after natural gas is cooled from 38 °C to 15.5 °C using air and water chillers. In the second APCI cooling level, natural gas is fed to a
two-staged heat exchanger tower. The first stage consists of a mixture of heavy propane with butane as refrigerants to reduce the natural gas temperature to -50 °C. The secondary cooling stage consists of reducing natural gas temperature down to -160 °C by spraying light gases mixture (such as methane, ethane and nitrogen) over the natural gas tubing. Additional refrigerants, such as nitrogen, may be added to the APGI cycle to enhance its performance. This cycle is known as AP-X cycle.

1.2. Liquefaction enhancement due to major changes implemented in the plant

The main drawback of the natural gas liquefaction processes is the high power consumption by the compressors and the size of the plant for liquefaction facilities. There are multiple methods to enhance the performance of the LNG plant. One possible way to enhance the performance is by the addition of multistage compressor stations with a multistage turbine, utilizing the partial power obtained from the expansion of the refrigerant to run the compressor. Another possible method is the selection of an appropriate refrigerant blend [4]. For instance, a high boiling point and dense refrigerant blend enhances the absorbed heat and reduces the compression duty, respectively, which both increase the COP of the cycle. The latter method of enhancing the performance of the LNG plant is the focus of this paper. Based on the current designs of the refrigeration cycles, the coefficient of performance (COP) of the cycle increases with the increase in the power consumption (as multiple compression stages required) and adding additional elements such as compressors and turbo-expanders. However, having higher power consumption and adding more elements increase the operating cost. Also, larger and complex plants are not suitable for natural gas liquefaction plants. In recent years, several researchers have focused on COP enhancement of the refrigeration cycle while minimizing the capital and operating costs. The efforts made in this regard can be summarized in two categories: In the first category, major additions (and hence changes) have been implemented in the refrigeration cycles [5]; whereas other groups have focused on applying minor changes resulting in enhancement of the overall efficiency of the cycles. Examples of the attempts in the first category include the work of Barclay and Denton [6] where they showed that liquefaction power consumption may be reduced by pre-cooling propane, CO2, or propylene. Due to its stable nature, CO2 is the most desirable choice in the liquefaction plants. For example, Yuan et al. [7] studied the impact of utilizing CO2 as the refrigerant in the pre-cooling cycle followed by single nitrogen (N2) expansion to cool natural gas. In their study, they proposed compressing nitrogen in two stages using pre-cooled water chillers and CO2 refrigerant. Following this stage, nitrogen is expanded to lower its pressure and temperature. When lower pressure and temperature are achieved, natural gas is cooled down in the heat exchangers. In other words, the combination of CO2 refrigerant to pre-cool the nitrogen refrigeration cycle reduce the overall energy consumption required in the gas liquefaction process. Other innovative cycles proposed include the fuel cell hybrid turbo-expander which has been developed to investigate the effects of available exergy in the natural gas pressure reduction stations [8]. The results showed a 10% improvement in the efficiency of the turbo-expander after the addition of the fuel cell.

1.3. Liquefaction enhancement due to minor changes implemented in the plant

The second category of the efforts made towards enhancement of the liquefaction process includes the work of Rodgers et al. [9] who emphasized that the use of turbo-expanders replacing the Joules Thompson expansion valves enhances the performance of the refrigeration cycle. This is due to the partial power utilization from the turbines that is fed back to the compressors. They also used part of the turbine exhaust waste heat as a regenerative power to the compressor which resulted in a 12% improvement in the cycle's efficiency. Similarly, Mortazavi et al. [10] investigated the effect of replacing expansion valves with two phase expanders, liquid turbines and gas turbines. Their model achieved a 7.07% reduction in power consumption by the expansion work recovery. Khan et al. [11] investigated the enhancement of the Single Mixed Refrigerant (SMR) liquefaction process based on non-linear modeling of exergy. They were able to enhance the process efficiency based on optimum composition of the refrigerant, flowrate, suction pressure and evaporation pressure. In another study, Khan et al. [12] optimized the propane precooling liquefaction process by identifying optimum operating conditions using HYSYS. Their results showed 15.51% COP enhancement and 18.76% exergy enhancement due to lower cooling duty requirement at the intermediate cooling stage. As for their optimal operating conditions, they selected temperatures of 5 °C, 0 °C and -40 °C for the high pressure, intermediate pressure and low pressure evaporator stages, respectively.

1.4. Liquefaction enhancement due to the use of mixed refrigerants

Lately, a special attention has been given to the use of mixed refrigerants as they provide flexibility in matching the cooling properties of natural gas [11] and can replace the high efficient, though ozone depleting, HCFCs. For example, Park et al. [13] studied the effect of mixed refrigerants as a replacement for the HCFC 22 refrigerant in air conditioning units. Their results indicated a 5.7% increase in the COP when they used a refrigerant blend consisting of 45% R1270, 40% R290 and 15% DME [13]. Park et al. [14] measured the thermodynamic performance of R433A (consisting of a blend of 30% propylene and 70% propane) and HCFC 22 in a broadband type heat pump/air conditioner. Their study concluded that R433A enhances COP by 4.9–7.6% as compared to HCFC 22. Rocca and Pano [15] proposed HFC and HC mixed refrigerants as a replacement for R22 HCFC. They compared the COP of the R22 refrigerant with their proposed blended refrigerants including R417A (consisting of a blend of 46.6% R125, 50% R134a and 3.4% R600a), R422A (consisting of a blend of 85.1% R125, 11.5% R134a and 3.4% R600a) and R422D (consisting of a blend of 65.1% R125, 31.5% R134a and 3.4% R600a). Their cycle’s COP showed its highest values when they used R22, and then followed by R417A, R422A and R422D, consecutively. In another study, Aprea et al. [16] investigated a possible alternative for R22 refrigerant. They studied the effect of the blended refrigerants on the reduction of the compressor power consumption. In their analysis, R22 refrigerant showed a COP value of 2.8 at the 30 Hz motor current supply frequency; whereas the second highest COP (2.5 at the same frequency) was achieved using R407C (consisting of a blend of 23% R32, 25% R125 and 52% R134a). In all of the studies conducted for the mixed refrigerants, the percentage of pure elements in the mixed refrigerants is determined in accordance to the ambient temperature of the refrigeration cycle [17]. In a similar study, Alabululkarim et al. [18] used a genetic algorithm to optimize the C3MR cycle. In their study, the MR cycle was enhanced by 13.28% using new mixed refrigerants with mass fractions of 0.1027 nitrogen, 0.218 methane, 0.5306 ethane, and 0.1487 propane. Ding et al. [19] utilized the advantages of the high specific refrigeration effect of methane, and the low boiling temperature of nitrogen to optimize the expansion process using ASPEN HYSYS. They used this mixture in the propane precooled N2–CH4 expansion liquefaction process. This refrigerant mixture produced 36.06% less unit power consumption of 0.411 kWh/kg. Song et al. [22] proposed refrigeration cycles enhancement by reducing the exergy destructions caused by each refrigerant in the mixed refrigerant. Flowrate of the refrigerant (R1) responsible for the increased exergy destruction was increased to reduce
the exergy destruction. In a study focused on the selection refrigerants in single stage refrigeration cycle, Luyben [23] figured that ammonia is one of the few refrigerants that can be utilized in single stage refrigeration cycles for enhanced heat absorptions. Pham et al. [24] suggested that the use of heavy refrigerants impact the heat transfer performance in a refrigeration cycle; hence, it requires lesser compressor energy. In their study, they suggested that refrigeration cycles with i-C5 would not need a natural gas compressor to provide additional energy boost for refrigeration when compared with refrigeration cycles operating with i-C4.

Among all the refrigerants studied in the literature, pure natural fluids (i.e., hydrocarbons, ammonia, carbon dioxide, air, etc.) have potential to be used as pure refrigerants in future LNG plants [25, 26, 27, 28]. Acuna et al. [29], Pearson [30] and Watson [31] indicated the possibility of using the ammonia, sulfur dioxide (R-764) and carbon dioxide as pure refrigerants. In another study, ammonia, carbon dioxide, and mixed refrigerants were among the various refrigerants which have been proposed in the LNG industry [32]. This paper investigates the feasibility of mixing propane, a hydrocarbon used in all C3MR natural gas liquefaction plants [3], with non-hydrocarbon natural fluids. Excluding the CFC’s and HCFC’s due to their potential environmental effects, the most promising gases which would provide an improvement in the overall COP are ammonia (NH3), sulfur dioxide (SO2) and carbon dioxide (CO2). These gases (NH3, SO2 and CO2) are already being used in the industry as pure refrigerants and have boiling temperatures around the operating temperatures in the pre-cooled refrigeration cycle investigated in this study. In order to enhance the refrigeration cycle performance, refrigerant gases must have boiling points below 0 °C in order to prevent condensation inside the refrigerator. Ammonia boils at -33 °C and sulfur dioxide boils at -10 °C. Therefore, these two refrigerants are suitable refrigerants to be mixed with propane for propane refrigeration COP enhancement. By mixing the propane refrigerant with the industrially approved gases, the coefficient of performance (COP) will alter resulting in observing either an increase or a decrease in operating costs. The refrigerant blend has better properties in terms of compressibility (important for the compressor) shown by the enthalpy change across its terminals, and heat absorption due to its high boiling point (important for the evaporator). Both ammonia and sulfur dioxide show higher heat absorption capacities as compared to hydrocarbons. This is mainly because of their higher boiling point temperatures. Despite these advantages, ammonia and sulfur dioxide are both toxic and the latter is also highly corrosive as compared to hydrocarbons. On the other hand, carbon dioxide, alone as a refrigerant, can be used as a pre-cooler to the propane precooling cycle due to its low cost. It is not recommended to mix carbon dioxide with the hydrocarbon as CO2 has lower heat absorption capacity. Given their potential in advancing the refrigeration cycles, NH3, SO2, and CO2 have negative environmental impact. For example, ammonia pollution has a great negative impact on the biodiversity due to nitrogen accumulation on plant species. In addition to its impact on biodiversity, ammonia damages grasslands, heathlands, forests, and lichen and mosses on bog and peatland habitats [33]. Similar to ammonia, sulfur dioxide has a negative environmental impact when released to the atmosphere due to its high acidity. Sulfur dioxide gas is considered one of the main reasons for acid rain creation. Acid rain leads to deforestation, aquatic life deterioration, and leads to respiratory tract infections [34]. Thirdly, carbon dioxide is the number one cause for global warming due to its ability to trap heat [35]. The trapped heat leads to increased earth temperatures. Therefore, it is crucial that the refrigeration systems utilizing these gases be inspected routinely to ensure no gas leakage exists. On the other hand, collecting these gases from the environment and using them as refrigerants will reduce their concentrations in the atmosphere; hence, this reduces their negative impacts on the environment. The goal of this study is to investigate the possibility of improving COP using the refrigerant mixture at low cost to eliminate the need of running a separate refrigeration cycle prior to the propane cycle as studied in literature. A major constraint which could be presented while shifting from one blend to another is the provision of the refrigerant inventory near the plant. This would add to the cost of the plant which includes provision of the new components.

2. Material and methods

The proposed method consists of blending refrigerants with propane. This addition has no running cost and can be added to provide an improvement in the basic refrigeration cycle shown in Figure 1. The industrially used software HYSYS, with Peng Robinson used as the property package, to simulate the refrigeration cycle and to evaluate the enthalpy values in the cycle. To assess the reliability of the software used, an example of an industrially-used refrigerant consisting of a mixture of R-134a and R-125 is analyzed. The COP curve of this mixture is shown in Figure 2. Although pure R-134a is a more efficient refrigerant to be used (with a COP of 2.21 as compared to R-125 COP of 1.657), industry uses the mixture blend of 42% R-134a and 58% of R-125 to obtain a balance between the efficiency and cost (the cost of R-134a is three times that of R-125) [36]. As shown in Figure 2, the 58% mole fraction of R-125 is associated with the cost ratio discussed above.

Using the software package, three gases are blended with propane to study the effectiveness of blend refrigerants in increasing COP of the refrigeration cycle. An increase in the COP of the propane-gas mixed refrigerant will essentially save the capital and running cost of having a separate pure gas component refrigeration cycle prior to the propane cycle.

3. Theory

A refrigerant going through a refrigeration cycle experiences compression, evaporation, expansion and condensation. In the basic refrigeration cycle shown in Figure 1, the compression is caused by the compressor (for the pressure increase), and expansion (for the pressure reduction) is caused by the expansion valve. The equation for the work done by the compressor can be calculated as [37].

\[ W_{in} = m(h_{2in} - h_1), \] (1)

where \( m \) is the mass flowrate of the refrigerant, \( h_{2in} \) is the actual refrigerant enthalpy at the compressor outlet and \( h_1 \) is the refrigerant enthalpy at the compressor inlet. The actual compressor exit enthalpy is calculated as [37].

\[ h_{2out} = \frac{(h_{2in} - h_1)}{\eta_{compressor}} + h_1, \] (2)

where \( h_{2out} \) is the isentropic refrigerant enthalpy at the exit of the compressor and evaluated at the compressor exit pressure and entropy equals to that of the compressor inlet entropy. \( \eta_{compressor} \) is the isentropic efficiency of the compressor.

![Figure 1. A schematic of a basic propane refrigeration cycle.](image)
The equation of the heat absorption from the evaporator is calculated as
\[ Q_{\text{sat}} = m(h_4 - h_1), \] (3)
where \( h_4 \) is the refrigerant enthalpy at the evaporator inlet, \( h_1 \) is the refrigerant enthalpy at the evaporator outlet.

To evaluate the overall cycle coefficient of performance, the COP equation used is
\[ \text{COP} = \frac{Q_{\text{des}}}{W_{\text{compressor}}} \] (4)
\[ \text{COP} = \frac{m(h_4 - h_1)}{m(h_2 - h_1)}. \] (5)

The work of the compressor depends on the change in the outlet and inlet enthalpies and can be estimated as follows:
\[ W_{\text{compressor}} = m(h_4 - h_3). \] (6)

**Boiling Temperature** - It is possible to obtain a high critical temperature and hence high specific refrigeration effect by mixing hydrocarbons with components with high boiling point [4]. The higher the component’s boiling point the faster the evaporation rate and hence the higher the refrigeration capacity. The boiling temperatures of the gases investigated in this study are shown in Table 1. Due to their higher boiling temperature values, \( \text{NH}_3 \) and \( \text{SO}_2 \) are expected to improve components with high boiling point [4]. The higher the component’s boiling point, the faster the evaporation rate and hence the higher the COP [38].

**Critical Temperatures** - Critical temperatures of the refrigerant blend changes according to the mole fraction composition of the two gases due to the change in the boiling temperatures. Therefore, the T-s and P-v diagrams will show changes as the gas composition is altered. Critical temperatures of the gases listed in Table 1 show that the COP of the cycle could be improved for the refrigerant blends of \( \text{NH}_3 \)-propane and propane-SO\(_2\). The higher the critical temperature, the higher the COP [39].

### Table 1. Boiling and critical temperatures of Propane, \( \text{NH}_3 \), \( \text{SO}_2 \) and \( \text{CO}_2 \).

| Gas    | Boiling Temp. (°C) | Critical Temp. (°C) |
|--------|--------------------|---------------------|
| Propane| -42.10             | 96.75               |
| \( \text{NH}_3 \) | -33.45             | 132.40              |
| \( \text{SO}_2 \) | -9.95              | 157.65              |
| \( \text{CO}_2 \) | -78.55             | 30.95               |

**Figure 2.** The COP curve of a basic R-134a refrigeration cycle as a function of the mole fraction of the R-125 refrigerant.

**Mass Flowrate** - According to Eq. (6), the required mass flowrate to achieve the required cooling effect determines the COP of the cycle. Since the mass flowrate term appears at the denominator of the COP equation, it is required to choose a gas blend which provides a low mass flowrate. The blended refrigerants will consist of the combined single element densities and their combined volume flowrates. Both of these properties depend on the pure substances and their blending ratios.

### 4. Results and discussion

The coefficient of performance, \( \text{COP} \), is studied here to evaluate the performance of the refrigeration cycle operating with different blends of refrigerants. The COP of the refrigeration cycle was determined using HYSYS. In this study, a basic refrigeration cycle operating using pure propane was first evaluated. The propane refrigerant is fed to the evaporator to absorb \( 1.5 \times 10^6 \) kJ hr\(^{-1} \) from the natural gas [40], and then it exits the evaporator as saturated vapour with a 5 kPa pressure drop. Propane is then compressed adiabatically with the efficiency of 75%. Inside the condenser, there is a pressure drop of 30 kPa, where propane leaves as a saturated liquid at 45 °C. The propane is throttled using a throttling valve [40]. In Figure 1, propane enters the compressor at the temperature of -15 °C and pressure of 291.1 kPa. The refrigerant then exits the compressor at the temperature of 64.47 °C and pressure of 1569 kPa where it is cooled down by the absorber down to 45 °C. The refrigerant is throttled to cool down to -14.51 °C at the pressure of 296.1 kPa. Compressor isentropic efficiency is selected to be 78% [41]. The COP value obtained for this basic refrigeration cycle is 2.21. The use of different refrigerants has shown different effects on the COP of the cycle [3, 6, 7]: mixed refrigerant such as nitrogen, methane, ethane and propane [42] have shown to improve \( \text{COP} \) while cycles running with nitrogen and carbon dioxide as pure refrigerants have low \( \text{COP} \) [7]. The latter are usually used in liquefaction as they are considered to be safer than hydrocarbon refrigerants. In the following sections, the mixture of three gases (ammonia (\( \text{NH}_3 \)), sulfur dioxide (\( \text{SO}_2 \)) and carbon dioxide (\( \text{CO}_2 \))) with propane is analyzed to study their effect on the COP of the cycle. The operating conditions for each stream are summarized in Table 2.

#### 4.1. Propane pre-cooling refrigeration cycle enhancement

**4.1.1. Refrigeration cycle with \( \text{NH}_3 \)-propane mixed refrigerant**

The overall \( \text{COP} \) change of the \( \text{NH}_3 \)-propane mixture as a function of \( \text{NH}_3 \) mole fraction is shown in Figure 3 (a). The added ammonia in the HYSYS analysis ranges between 1% to 100% mole fractions. The \( \text{COP} \) of
Table 2. Streams operating conditions.

| Stream | Temperature (°C) | Pressure (kPa) |
|--------|------------------|----------------|
| Stream 1 | -14.51           | 296.1          |
| Stream 2 | -15              | 291.1          |
| Stream 3 | 64.47            | 1569           |
| Stream 4 | 45               | 1539           |

Figure 3. NH₃-Propane mixture as a function of the NH₃ mole fraction (a) COP curve; (b) Inlet and outlet enthalpy of the compressor; (c) mass flowrate.
the ammonia-propane mixture shows an increasing trend for the mole fraction up to 60%. This increase is due to the combination of i) a small increase in the difference between the compressor inlet and outlet enthalpies, from 106 kJ/kg at 0% ammonia to 423 kJ/kg at 100% ammonia (See Figure 3 (b)), and ii) a large decrease in the mass flowrate, from 6454 kg/h at 0% ammonia to 1433 kg/h at 100% ammonia (See Figure 3 (c)). Since the density of pure ammonia (1.9 kg/m³ obtained from HYSYS) at the given temperature and pressure is lower than that of pure propane (6.48 kg/m³), adding NH₃ to the propane refrigerant was expected to reduce the mass flowrate required to absorb the heat due to the
fact that the mass flowrate of the mixture is directly proportional to its density. On the other hand, the change in the enthalpy depends on the blended refrigerants T-s and P-v diagrams, changing due to the change in the critical point of the refrigerant. For the mole fraction values between 60% and 80%, however, the COP of the cycle decreases. One possible reason for the sudden drop in the COP could be related to the high polarity of NH₃ as opposed to non-polar propane. In essence, the high polarity of ammonia molecules attracts the propane molecules and leads to higher energy requirements to cause condensation and evaporation of the mixed refrigerant; hence, higher compressor work is required to achieve the cooling effect at these ammonia-propane percentages. After the mole fraction of 80%, the COP of the cycle increases which shows the dominant effect of NH₃ which has larger absorption heat compared to that of propane.

Figure 5. CO₂-Propane Propane mixture as a function of the CO₂ mole fraction (a) COP curve; (b) Inlet and outlet enthalpy of the compressor; (c) mass flowrate.
4.1.2. Refrigeration cycle with SO\textsubscript{2}-propane mixed refrigerant

The overall COP change of the SO\textsubscript{2}-propane mixture as a function of SO\textsubscript{2} mole fraction is shown in Figure 4 (a). The added sulfur dioxide in the HYSYS analysis ranges between 1\% to 100\% compositions. The COP of the sulfur dioxide-propane mixture shows an increasing trend for the mole fraction up to 15\%. This increase is due to the combination of a small increase in the difference between the compressor inlet and outlet enthalpies, from 106 kJ/kg at 0\% sulfur dioxide to 123 kJ/kg at 100\% sulfur dioxide (See Figure 4 (b)), with the fast mass flowrate decrease, from 6454 kg/h at 0\% sulfur dioxide to 4808 kg/h at 100\% sulfur dioxide (See Figure 4 (c)). Similar to ammonia, the density of pure sulfur dioxide at the given temperature and pressure (2.46 kg/m\textsuperscript{3}) is lower than that of pure propane (6.48 kg/m\textsuperscript{3}). Thus, adding SO\textsubscript{2} to the propane refrigerant reduces the mass flowrate required to absorb the heat defined in Section 3. On the other hand, the change in the enthalpy depends on the T-s and P-v diagrams of the blended refrigerants. For the mole fraction values between 15\% and 80\%, however, the COP of the cycle decreases. One possible reason for the sudden drop in the COP could be related to the high polarity of SO\textsubscript{2} as opposed to non-polar propane (similar to ammonia). After the mole fraction of 80\%, the COP of the cycle increases which shows the dominant effect of SO\textsubscript{2} which has larger absorption heat compared to that of propane. A special attention is required when using SO\textsubscript{2} as it being corrosive. Therefore, stainless steel pipes would be required in the refrigeration cycle.

4.1.3. Refrigeration cycle with CO\textsubscript{2}-propane mixed refrigerant

CO\textsubscript{2} is safe to store and available in large quantities in the environment. The overall COP change of the CO\textsubscript{2}-propane mixture as a function of CO\textsubscript{2} mole fraction is shown in Figure 5 (a). The added carbon dioxide in the HYSYS analysis ranges between 1\% to 66\% mole fractions. Exceeding the 66\% mole fraction will cause the CO\textsubscript{2} to reach its critical temperature of the natural gas after the pre-chiller 2 from -15.55 °C to -16.55 °C. Therefore, to cool the natural gas to -35 °C, the conventional second propane refrigeration cycle presented as the pre-chiller 3 in Figure 6 (which uses propane as its refrigerant) will require less duty (the heat duty required to absorb the natural gas heat will be reduced from 2.462 × 10\textsuperscript{7} kJ/h to 2.305 × 10\textsuperscript{7} kJ/h given the same compressor constant). This reduction presents a 6.3\% reduction in the compressor duty in the pre-chiller 3.

4.2. Effect of enhancement in propane pre-cooling refrigeration cycle performance on C3MR performance

As per Krishnamurthy et al. [32], multi-stage precooling configurations are advantageous for LNG train capacities. The proposed COP enhancement is now applied to the first propane refrigeration step, which is the pre-chillers 2 in Figure 6 showing the schematic of a C3MR propane precooling cycle. As a result of this enhancement, the total duty is increased by 7\% (from 1.982 × 10\textsuperscript{7} kJ/h to 2.139 × 10\textsuperscript{7} kJ/h) while keeping the compressor duty constant. This increase reduces the outlet temperature of the natural gas after the pre-chiller 2 from -15.55 °C to -16.55 °C. Therefore, to cool the natural gas to -35 °C, the conventional second propane refrigeration cycle presented as the pre-chiller 3 in Figure 6 (which uses propane as its refrigerant) will require less duty (the heat duty required to absorb the natural gas heat will be reduced from 2.462 × 10\textsuperscript{7} kJ/h to 2.305 × 10\textsuperscript{7} kJ/h given the same compressor constant). This reduction presents a 6.3\% reduction in the compressor duty in the pre-chiller 3.

4.3. Refrigerant blends environmental impact

Given their potential in advancing the refrigeration cycles, NH\textsubscript{3}, SO\textsubscript{2}, and CO\textsubscript{2} may have negative environmental impacts on the Ozone layer depletion as well as on global warming. In order to investigate the environmental impact of the proposed refrigerant mixtures, Table 3 lists the ODP and GWP of the refrigerants in their single state [44]. From Table 3, Eqs. (7) and (8) are utilized to evaluate the environmental impact of the proposed refrigerant mixtures and are shown in Table 4.

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\begin{align*}
\text{ODP}_{\text{Blend}} &= \%mass_{\text{refrig}} \cdot \text{ODP}_{\text{refrig-1}} + \%mass_{\text{refrig}} \cdot \text{ODP}_{\text{refrig-2}} \\
\text{GWP}_{\text{Blend}} &= \%mass_{\text{refrig}} \cdot \text{GWP}_{\text{refrig-1}} + \%mass_{\text{refrig}} \cdot \text{GWP}_{\text{refrig-2}}
\end{align*}

Therefore, the evaluated ODP and GWP of the proposed blends are shown in Table 4.

5. Cost analysis

To evaluate the feasibility of the proposed study, CAPEX and OPEX analysis are provided in this study based on the business approach to small-scale LNG plants presented by Enrique Garcia-Cuerva [45]. In their new business model for small-scale LNG plants (i.e. 4.5 Mtpa), they listed the small-scale LNG plants cost based on several categories as presented in Table 5. The CAPEX allocations are based on the study published by Dominique et al. [46]. Increasing COP reduces the energy consumption by compressors. Since most of the energy consumption by the compressors is represented by the electrical energy, implementing the proposed refrigerant combinations in this study would reduce OPEX by 7\% (with the use of ammonia-propane mixture) and by 9\% (with the use of sulfur dioxide-

Table 3. Single refrigerants environmental impacts.

| Refrigerant   | ASHRAE Number | ODP (equivalent to CPC11) | GWP (relative to CO\textsubscript{2}) |
|---------------|---------------|----------------------------|-------------------------------------|
| Propane       | R-290         | <0 (smog)                  | 3.3                                 |
| Ammonia       | R-717         | 0                          | 0                                   |
| Sulfur Dioxide| R-764         | 1 (AP)\textsuperscript{*}  | NA                                  |
| Carbon Dioxide| R-744         | 0                          | 1                                   |

\textsuperscript{*} Sulfur Dioxide does not have an ODP number; instead, it has an acidification number.
propane mixture). From the economics model presented by Enrique, and assuming 30% of that OPEX is consumed by the LNG compressors, a typical small-scale LNG plant would increase its savings by 0.3 MMUSD/year and 0.4 MMUSD/year by mixing ammonia or sulfur dioxide with propane at the proposed ratios, respectively.

6. Conclusions

Blending propane refrigerant in the propane precooling refrigeration cycle in natural gas liquefaction with ammonia (NH₃), sulfur dioxide (SO₂), and carbon dioxide (CO₂) has been investigated in this paper. Different mole fraction percentages and their effect on the overall COP were studied. It is concluded that NH₃ and SO₂ increase the overall COP when mixed with propane. Therefore, it would be economical to improve the overall COP of the propane precooling refrigeration cycle by at least 7% (or 9%) while simply mixing the propane refrigerant with ammonia or sulfur dioxide. Special material considerations should also be taken into account when SO₂ is used in the refrigeration cycle for its corrosive nature. Although CO₂ is safe to store and used in the refrigeration cycles prior to the propane precooling cycle, it deteriorates the overall COP. Also, Since Propane is less corrosive and toxic than Ammonia, the new mixture (Propane-Ammonia) dilutes the toxicity and corrosion effect of Ammonia. Overall, to expect an increase in the COP of the refrigeration cycle with mixed refrigerants, one should choose a gas that would have a higher boiling point and a lower required mass flow rate.

Table 4. Proposed mixed refrigerants environmental impacts.

| Refrigerant Blend      | Blend ratio by mass | ODP     | GWP     |
|------------------------|---------------------|---------|---------|
| Propane-Ammonia        | 40-60               | 0       | 1.32    |
| Propane-Sulfur Dioxide | 20-80               | 1 (AP)* | 0.66    |
| Propane-Carbon Dioxide | 100-0               | <0 (smog) | 3.3     |

Table 5. CAPEX and OPEX for a small scale LNG plant.

| OPEX | Personnel (35,000 USD/year/person) | 40 operators [45] | 1,400,000 USD/year |
|------|-----------------------------------|-------------------|-------------------|
|      | 8 maintenance staff members [45]  | 280,000 USD/year  |                   |
|      | 9 administrative staff members [45]| 315,000 USD/year  |                   |
|      | **Total OPEX [45]**               | **1094.4 MMUSD**  |                   |
| CAPEX| Consumables                       |                   |                   |
|      | Propane                            | 620 USD/ton [45]  |                   |
|      | SO₂                                | 1600-4800 USD/ton [47] |       |
|      | NH₃                                | 1500-2000 USD/ton [48] |      |
|      | CO₂                                | 70 USD/ton        |                   |
|      | **Electrical [45]**                | **14.96 MMUSD/year** |                |
|      | **Total CAPEX [45]**               | **328.3 MMUSD**   |                   |

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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Declarations

Author contribution statement

Mina Hoorfar, Ali Ahmadi: Analyzed and interpreted the data. Walid Mazyan: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper. Hussain Ahmed: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.
