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Hydrofluoroolefin-based novel mixed refrigerant for energy efficient and ecological LNG production

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ABSTRACT

To satisfy the worldwide demand for energy, the liquefied natural gas (LNG) industry has grown significantly in the past three decades owing to its low CO_2 emissions and high thermal efficiency compared to the other available energy resources. However, the process of natural gas liquefaction is generally considered to be energy-intensive. In this context, a novel hydrofluoroolefin (HFO-1234yf)-based mixed refrigerant, with the advantages of zero ozone depletion and minimal global warming potential, is proposed to liquefy natural gas in an ecological and energy-efficient manner. A new liquefaction cycle using the HFO-based mixed refrigerant is developed to fully utilize its potential. The results reveal that the overall energy requirement for natural gas liquefaction can be reduced by 46.4% compared with a single mixed refrigerant process, 42.5% compared with a dual mixed refrigerant process, and 36.3% compared with the Linde–single mixed refrigerant process. Economic analysis based on the capacity parameters of each equipment is also performed to emphasize the commercial feasibility of the proposed LNG process. The proposed HFO-based mixed refrigerant system provides an innovative solution to improve the ecological aspects and energy efficiency of natural gas liquefaction processes.

1. Introduction

As global societies continue to expand their energy mix, a single source natural gas is becoming increasingly important. This is mainly due to its high ecological nature compared to the other available fossil fuels. However, the cost of natural gas for storage and transportation depends entirely on the location of natural gas reserves, which are mostly located in remote areas. Liquefaction is considered the most feasible and economic approach for storing and transporting natural gas [1]. Therefore, several new liquified natural gas (LNG) plants will be established in 2018, and SHELL [2] reported that the LNG trade will grow by 50% through 2020. It is expected that the demand for LNG will grow steadily over the next few decades, as part of an overall increasing demand for clean and sustainable energy. LNG production facilities are expanding into new natural gas reserves across the globe [3]. However, natural gas liquefaction is generally considered to be an energy-intensive process, with the refrigeration and liquefaction facilities normally accounting for ~40–50% of the total LNG project (supply chain) cost [4,5], although this cost depends on the site ambient conditions [6,7] and the type of LNG process technology involved.

In recent studies [6,8–13], design optimization of LNG processes has been considered as an alternative approach to improve the energy efficiency to some extent without altering the process configuration. On the other hand, researchers [14–16] have also analyzed the exergy efficiency of each equipment associated with the LNG processes and identified the avoidable and unavoidable exergy loss. For example, Mehrpooya and Ansarinasab [14] performed advanced exergoeconomic analysis of two single mixed refrigerant-based LNG processes. They concluded that the energy efficiency of a LNG process is lowered mainly due to unavoidable exergy destruction in heat exchangers and air-coolers. Most recently, Mehrpooya et al. [17] performed advanced exergoeconomic analysis for a novel integrated LNG-NRU process configuration. They concluded that the cost of exergy destruction in air-coolers and cryogenic heat exchangers is unavoidable. The exergy loss of LNG plants can also be reduced by improving or replacing the high-exergy-loss component of refrigeration cycle units with minimal exergy loss equipment. For example, Fahmy et al. [18] enhanced the energy efficiency of the open-cycle Phillips optimized Cascade natural gas liquefaction process by improving the expansion device of the refrigeration cycle. Mehrpooya et al.

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[19] improved the energy efficiency of a mixed fluid cascade LNG process by replacing the vapor compression cycle with absorption refrigeration cycles. Most recently, Qyyum et al. [20] have improved the energy efficiency of the SMR process by replacing the JT-valve with hydraulic turbines (also known as cryogenic liquid turbines) followed by a modified coordinate descent (MCD) optimization approach. They concluded that the overall energy efficiency of LNG processes can be improved significantly by applying both process retrofitting and design optimization. Furthermore, the energy efficiency of LNG plants has been improved by developing new integrated configurations. For example, Ghorbani et al. [21] presented a mixed fluid cascade process integrated with natural gas liquid recovery and nitrogen rejection units in order to minimize the overall exergy losses.

To date, mixed refrigerant-based LNG processes have higher energy efficiency compared to nitrogen expander-based LNG processes, but at the expense of a high degree of complexity, safety concerns, and greater capital investment [22]. The energy requirement for LNG production through mixed refrigerant-based liquefaction processes is significantly higher than the minimum required energy, although, the selection of the most suitable and appropriate liquefaction process does not depend only on the energy efficiency of any specific liquefaction process. Several other factors such as degree of complexity (how simple is the design?), capacity, start-up, shutdown, safety concerns, and environmental impacts are relevant. In this context, so far, the major issues associated with LNG plants are the capital cost, complexity, and energy efficiency. Hence, there is a substantial industrial need to develop an innovative and eco-friendly LNG process with improved energy efficiency, lower capital investment, and less complexity.

We propose a new mixed refrigerant that consists of hydrofluoroolefin (HFO-1234yf), methane, ethane, propane, n-butane, and nitrogen. To achieve the maximum potential benefits of the proposed mixed refrigerant, a new liquefaction cycle is also proposed, which enables LNG with a high energy efficiency, lower capital costs, and a lower degree of complexity compared with the existing LNG processes. The proposed liquefaction process is also optimized using a newly proposed hybrid optimization algorithm to utilize its full potential. An economic evaluation is also performed to highlight the practical feasibility of the proposed LNG process and emphasize the validity of the proposed liquefaction process.

2. Eco-friendly HFO-based mixed refrigerant

Natural gas liquefaction processes require tremendous amounts of energy for the shaft work in the compression units of the refrigeration cycle. This shaft work strongly depends on the temperature gradients in the main cryogenic LNG exchanger [23]. Thermodynamically, the LNG process can be categorized into three main steps: cooling, liquefaction, and sub-cooling. Entropy generation causes an exergy loss or increment in the shaft work requirement owing to a sudden increase or decrease in temperature during the LNG process. For instance, the low energy efficiency in the N_2-expander LNG process is due to a large difference between the boiling temperature of N_2 (boiling point $-195\,^{\circ}C$) and natural gas (inlet temperature $26\,^{\circ}C$) to make subcooled LNG. This process ignores the cooling step and only accounts for sudden liquefaction and sub-cooling, that according to the third law of thermodynamics causes entropy generation (or exergy loss). In the conventional C3MR-based LNG process, propane (boiling point $-42.04\,^{\circ}C$) is used to precool the natural gas to its boiling point, which causes low entropy generation. The entropy generation can be further minimized by adding one or more ecological components as an intermediate with a boiling point between the propane boiling point and the natural gas inlet temperature. Fig. 1a shows the typical composite curve plot based on a conventional mixed refrigerant (nitrogen, methane, ethane, and propane) taken from the optimization study by Khan and Lee [13]. The triangular area ABC in Fig. 1a indicates the large interval between the natural gas temperature and the boiling point of propane, which leads to entropy generation in the cooling zone.

There is room for improvement in the triangular region ABC. Adding n-butane (boiling point $-0.5\,^{\circ}C$) as an additional refrigerant component to the conventional mixed refrigerant can reduce this area. Fig. 1b shows the composite curve plot of added n-butane. The reduced triangular area DEF in Fig. 1b demonstrates the effect of n-butane. This gap could be reduced even further by adding a refrigerant with a boiling point between propane and butane. Several refrigerants are available that satisfy the thermodynamic properties of an ideal mixed refrigerant with a low compression power requirement. These refrigerants have extraordinary thermodynamic properties and can improve the energy efficiency of LNG plants with a low capital cost. However, the critical issue is that these refrigerants are not environment friendly. For example, HFC (hydrofluorocarbons), carbon dioxide gas, halocarbons, nitrous oxide gas, and non-soot aerosol particles are pollutants implicated in global warming and ozone depletion, despite having the properties to generate a superior refrigeration effect. Furthermore, ozone depletion potential (ODP) and global warming potential (GWP) are limitations of many refrigerants. For example, 1,1,1,2-tetrafluoroethane (boiling point $-26\,^{\circ}C$) can be used as an intermediate but has a GWP of 1430 in 100 years [24,25]. While modern HFC refrigerants can have zero ODP, they are still banned in many countries owing to their high GWP.

2,3,3,3-tetrafluoropropene (HFO-1234yf) and n-butane are the best candidates to reduce this exergy loss during cooling of natural gas, because n-butane and HFO-1234yf (boiling point $-29\,^{\circ}C$) as the intermediate components will reduce the boiling point difference between propane and the natural gas inlet temperature. The coefficient of performance (COP) of n-butane is 2.8% higher than that of iso-butane, which is defined by the ratio of useful cooling provided to required compression power [26]. Globally, the use of HFO-1234yf has grown, as it is an eco-friendly fourth-generation refrigerant used in air conditioning systems and vehicles [27]. HFO-1234yf has been reported in several studies [28–30] to have a zero ODP and low GWP (i.e., less than or equal to 4 in 100 years). A mixed refrigerant using HFO-1234yf in combination with nitrogen, methane, ethane, propane, and n-butane was proposed in this study to achieve the potential benefits of the LNG process. The proposed HFO-based mixed refrigerant (HFO-MR) is ecologically favorable concerning ODP and GWP. Table 1 shows the characteristic thermodynamic and environmental properties of each component in the proposed HFO-MR LNG process.

3. HFO-MR natural gas liquefaction process

3.1. Process simulation

A well-proven commercial simulator Aspen Hysys® V9 with the database Aspen Plus® V9 was used to simulate the initial and base case of the proposed LNG process. The new refrigerant HFO-1234yf is still not available in the database of Aspen Hysys V9; therefore, the database of Aspen Plus was used. The simulation basis and feed conditions are summarized in Table 2.

The following assumptions were used for the simulation of the proposed LNG process.

- The thermodynamic properties were calculated using the Peng-Robinson thermodynamic fluid package.

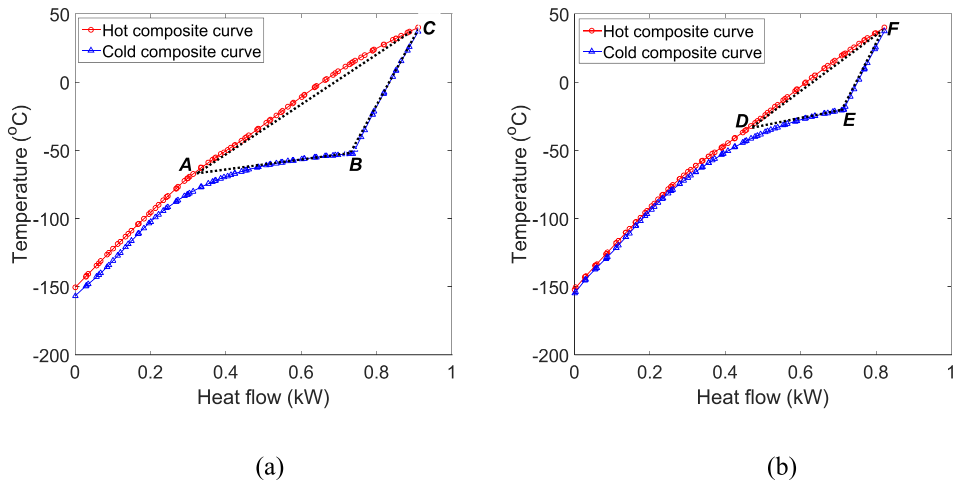

Fig. 1. Composite curves of a) conventional mixed refrigerant; b) with the addition of n-butane.

Table 1
Properties of the HFO-MR components.

Properties	Nitrogen	Methane	Ethane	Propane	HFO-1234yf	n-butane
Mol. wt. [31]	28.01	16.04	28.05	42.08	114	58.12
NBP [31] (°C)	−195.806	−161.49	−88.6	−42.04	−29	−0.5
Tc (°C) [31]	−146.95	−82.586	32.17	96.97	94.7	151.97
Pc (bar) [31]	34	45.99	48.72	42.48	33.82	37.96
SG at 60 °F	0.3	0.3	0.3564	0.5077	1.09302	0.5844
[a]ODP [32]	0	<0	0	0	0	0
[b]GWP [33]	0	25	6	3	4	4

[a] Ozone depletion potential of R-11 i.e., 1.
[b] Global warming potential (100 year), $CO_2 = 1$.

Table 2
Operating conditions and assumptions for process simulation.

	Conditions
Natural gas (Stream-20) [34]	
Temperature (°C)	26.0
Pressure (bar)	80.0
Flow rate (kg/h)	1.0
Composition	**Mole fraction**
Nitrogen	0.0055
Methane	0.9318
Ethane	0.0505
Propane	0.0109
Iso-butane	0.0008
n-butane	0.0005
Pressure drops across LNG-exchangers [34]	
LNG-exchanger 1 (CHX-01)	
Stream-20 to Stream-21 (bar)	4.5
Stream-8 to Stream-9 (bar)	4.5
Stream-14 to Stream-15 (bar)	4.5
Stream-10 to Stream-11 (bar)	0.1
LNG-exchanger 2 (CHX-02)	
Stream-21 to Stream-22 (bar)	5.5
Stream-15 to Stream-16 (bar)	5.5
Stream-17 to Stream-18 (bar)	0.1

- The enthalpies and entropies for all streams were determined by selecting the Lee-Kesler model.
- There were negligible heat losses to the environment
- The isentropic efficiency of each compressor was 83%
- Each after-cooler outlet temperature was 26.0 °C
- The pressure drop across each inter-stage cooler was negligible
- The pressure of the end flash gas drum was set at 1.25 bars
- The end flash gas vapor fraction was 8.0%
- The minimum internal temperature approach (MITA) inside the cryogenic heat exchangers was set as 3 °C.

3.2. Process description

The flow diagram of the proposed HFO-MR LNG process is shown in Fig. 2, with all streams designated as 'stream-x'($x = 1, 2, 3, 4, \ldots.$). The mixed refrigerant (stream-1) was compressed to a high pressure 'P_2' (pressure of stream-13) through four compressor stages equipped with after-coolers. To avoid a high compression power and reduce the reversibility of the process, the compression ratio was chosen in the practical range of 1:3. Cooler-3 cooled the compressed mixed gas refrigerant (stream-6) to 26 °C, where an almost 30–35% liquid fraction could be obtained (stream-7). This was due to the presence of components such as propane, HFO-1234yf, and n-butane having a higher critical temperature in the proposed mixed refrigerant (see Table 1). A phase separator was installed after stream-7 to separate the liquid (stream-8) and vapor (stream-12). The vapor stream was introduced into K-4, while the liquid stream was introduced into the first cryogenic heat exchanger CHX-01 to precool the high-pressure stream-14 and feed natural gas stream-20. In CHX-01, stream-10 was completely vaporized by taking the latent heat of vaporization from stream-20 and stream-14 and exits from CHX-01 as a superheated stream-11. Subsequently, the second cryogenic exchanger was used to liquefy the precooled natural gas (stream-21) by exchanging the latent heat with stream-17. The pressure of the mixed refrigerant was lowered using JTV-2, and stream-17 was vaporized inside the heat exchanger and obtained with all vapor fractions as stream-18. Stream-18 and stream-11 were mixed at the same pressure and

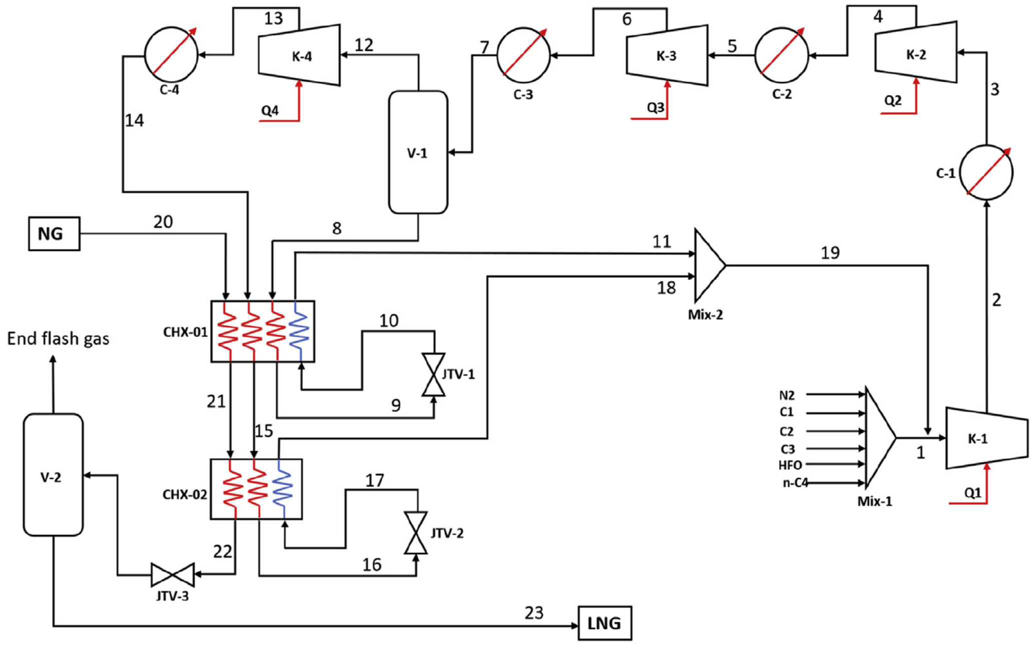

Fig. 2. Process flow diagram of HFO-MR natural gas liquefaction process.

then recycled as stream-19. Both cryogenic LNG exchangers were used with a MITA value of 3 °C. LNG cryogenic exchangers transferred the heat with a MITA as small as 1–3 °C [35]. To satisfy the fluid dynamics in mixer-2, the pressures of stream-11 and stream-18 were adjusted to the same optimum value of 2.96 bar. Natural gas obtained as subcooled liquid (stream-22) was flashed through the expansion valve (JTV-3) to a pressure slightly higher than the atmospheric pressure and then liquefied completely as an LNG product (stream-23).

3.3. Optimization of the proposed LNG process

For the optimization of the proposed LNG process, the minimization of specific compression energy in the proposed HFO-MR liquefaction process was chosen as the objective function. The flow rate of individual refrigerants and operating pressures were significant to the energy requirement (objective function) and irreversibility of the process. These variables were chosen as the key decision variables in the optimization of HFO-MR liquefaction process. These decision variables are listed with lower and upper bounds in Table 3. The condensation pressures for CHX-01 and CHX-02 were designated as 'P_1' and 'P_2' respectively. P_1 depends on P_2, because P_2 was a decision variable and constrained with a MITA of 3 °C in both cryogenic exchangers.

Mathematically, the optimization problem of HFO-MR liquefaction process was formulated as:

$$\text{Min}\, f(X) = \text{Min.}\left(\sum_{i=1}^{n} W_i/m_{LNG}\right) \tag{1}$$

subjected to:

$$\Delta T_{1(min)}(X) \geq 3;\ \Delta T_{2(min)}(X) \geq 3 \tag{2}$$

$$BOG\,(X) < 0.1 \tag{3}$$

$$1.018 \leq P_{LNG}(X) \leq 1.8 \tag{4}$$

$$T_{19}(X) > T_{19,Dew}(X) \tag{5}$$

where X is the vector of decision variables, $X = (P_2, P_O, T_{21}, m_{N2}, m_{C1}, m_{C2}, m_{C3}, m_{HFO}, m_{C4})$.

3.4. Base case for optimization

By using the conditions listed in Table 4, the base case of the HFO-MR liquefaction process was simulated as a benchmark for the optimization studies of the proposed LNG process. A knowledge-

Table 3
Decision variables and bounds.

Decision Variables	Lower bound	Upper bound
High pressure of MR (stream-13), P_2 (bar)	45.0	65.0
Evaporation Pressure (stream-19), P_o (bar)	1.1	3.5
Temperature of NG (stream-21), T_{21} (°C)	−40	5.0
Flow rate of nitrogen, m_{N2} (kg/h)	0.1	0.75
Flow rate of methane, m_{C1} (kg/h)	0.15	0.85
Flow rate of Ethane, m_{C2} (kg/h)	0.45	1.15
Flow rate of Propane, m_{C3} (kg/h)	0.60	1.45
Flow rate of HFO-1234yf, m_{HFO} (kg/h)	0.20	0.95
Flow rate of n-butane, m_{C4} (kg/h)	0.55	1.2

Table 4
Simulation condition for the base case of HFO-MR liquefaction process.

Variables	Base case condition
High pressure of MR (stream-13), P_2 (bar)	60.0
Evaporation Pressure (stream-19), P_o (bar)	2.18
Temperature of NG (stream-21), T_{21} (°C)	−13
Flow rate of nitrogen, m_{N2} (kg/h)	0.2815
Flow rate of methane, m_{C1} (kg/h)	0.5525
Flow rate of ethane, m_{C2} (kg/h)	0.9250
Flow rate of propane, m_{C3} (kg/h)	1.35
Flow rate of HFO-1234yf, m_{HFO} (kg/h)	0.45
Flow rate of n-butane, m_{C4} (kg/h)	0.95
Specific compression power (kW)	**0.3041**

based optimization algorithm was used to establish a base case for the proposed LNG process. The main simulation conditions and overall specific compression power are listed in Table 4.

3.5. Hybrid optimization algorithm

The optimization approach was selected or proposed based on the following parameters.

- Optimization problem type (constrained or unconstrained, etc.)
- Objective function type (continue or discontinue, etc.)
- Optimization approach should be gradient free
- Ability to avoid trapping in local minima
- Complexity of objective function (dimensions of optimization problem)
- Initial estimation of design variables
- Distribution of design variables

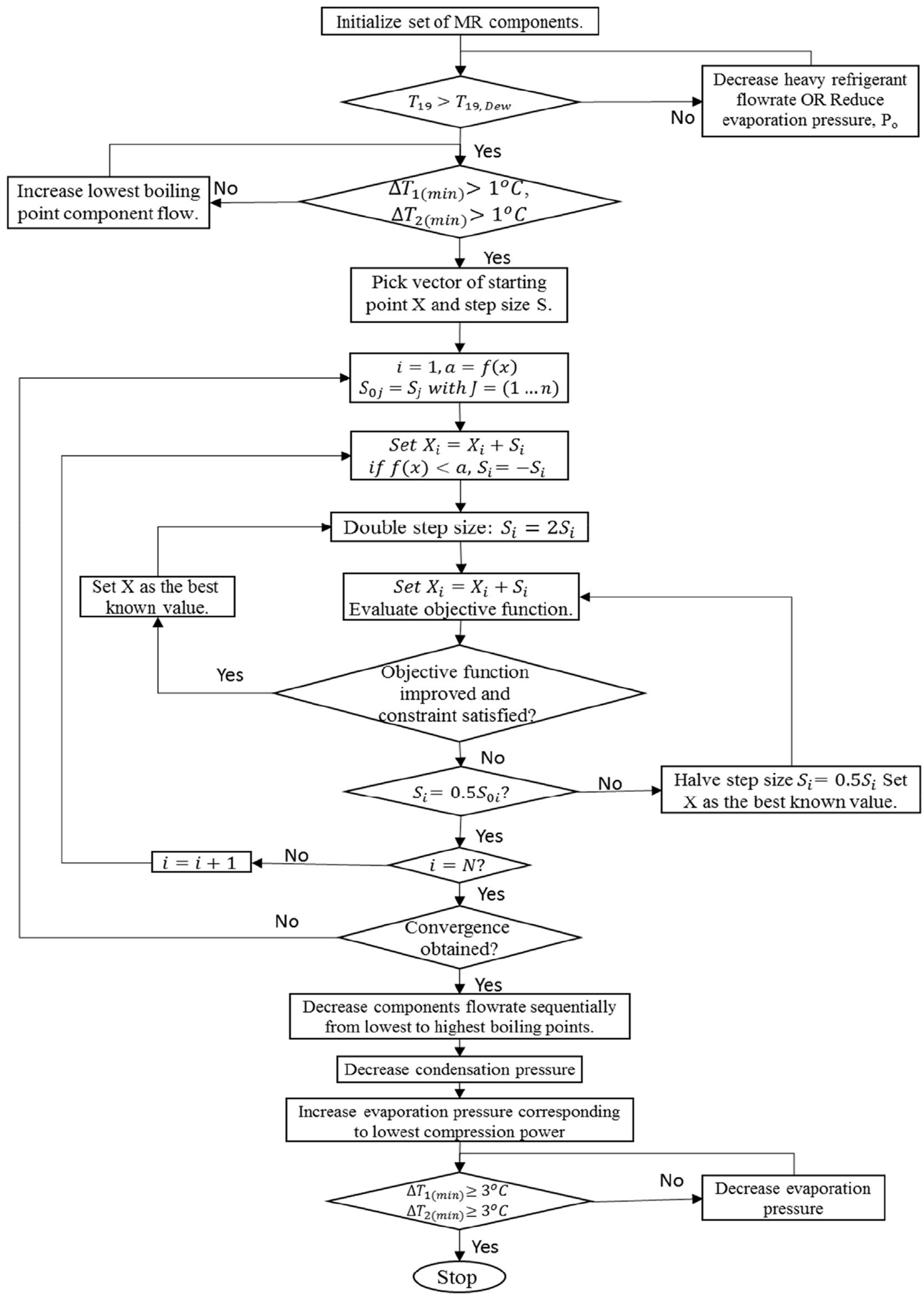

Fig. 3. Proposed hybrid optimization algorithm.

Considering the abovementioned parameters, a hybrid optimization algorithm was proposed, combining the knowledge-based optimization (KBO) [36] and Coggin's [34] optimization algorithms. The proposed optimization approach has two parts: one from KBO and the other from a numerical optimization algorithm, i.e., Coggin's. Usually, numerical optimization algorithms cannot solve issues such as the process limitations and technicalities during the optimization of non-linear and complex thermodynamic problems. In this context, the KBO approach (which works based on process knowledge) is one of the best options, and is simple and reliable. This KBO approach can be integrated with any numerical (single-solution or population-based) optimization approach to achieve rigorous and robust optimization results. The proposed optimization approach addresses the challenges of the many interactions, non-linearity, and thermodynamic irreversibility of the complex natural gas liquefaction process by considering process knowledge. The schematic diagram of the proposed hybrid algorithm is shown in Fig. 3.

Microsoft Visual Studio (MVS) was used to develop an optimizer with a user-friendly interface. The upper and lower range with a step interval and sequence of decision variables could also be manipulated. The proposed hybrid optimization algorithm has three parts: the top and bottom parts based on the knowledge-based optimization algorithm, and a middle part based on Coggin's algorithm. The middle part of the proposed algorithm was coded in the MVS environment and then linked to the Aspen Hysys® V9 using the COM functionality. The coded optimization algorithm was based on a univariate methodology. The local solution of the corresponding variable was strongly dependent on the initial point. The knowledge-based optimization algorithm was used to generate appropriate arbitrary initial points for the optimization by Coggin's algorithm. Coggin's algorithm was used to optimize the HFO-MR liquefaction process such that the vectors of the starting point and step magnitude were chosen from the start of the optimization. In the Coggin's optimization algorithm, a multistage iteration methodology was used to evaluate the objective function. If the objective function was improved (minimization of overall compression power), the search continued in the same direction. Otherwise, it was reversed to identify a new direction for objective function improvement. The optimum value was always upgraded in the optimization procedure according to the algorithm (Fig. 3). Whenever the objective function was improved under design constraints, the step interval was doubled. If no improvement was obtained in the objective function, then the best-known value was chosen as the current variable, and the step size was halved to continue the search. Subsequently, the coded algorithm stopped searching at a constant minimized objective function, and then, according to a hybrid optimization algorithm, the third part of the algorithm was used to refine the optimal results based on the composite curve knowledge.

3.6. Process analysis

The liquefaction of natural gas mainly occurred in the second cryogenic heat exchanger CHX-02. In this exchanger, stream-17 initially took the latent heat of vaporization from stream-15 and natural gas stream-21, which converted natural gas and stream-15 into a liquid. Stream-17 was completely vaporized and exited the CHX-02 at −21 °C as stream-18. Stream-18, which still had some cold energy, was used to reduce the temperature of stream-11 (from CHX-01) in the mixer (mix-2). Finally, stream-19 was obtained as a recycled HFO-MR with superheated temperature −2.5 °C. The temperature of recycled mixed refrigerant (stream-19) should be in the safe region to avoid the liquid fraction at K-1 inlet. At a pressure of 2.96 bar, the dew point of stream-19 was −15.2 °C. In conventional processes, the recycled mixed refrigerant temperature is normally between 20 °C to 38 °C. This temperature was superheated for such a low-boiling-point mixed refrigerant, which generated an entropy increase at the inlet of compressor K-1. In the proposed liquefaction process, the superheated temperature of the recycled mixed refrigerant was decreased to reduce entropy generation at the inlet of K-1, which resulted in low compression power. At a constant inlet pressure, the required energy for compression was directly proportional to the inlet gas temperature, as shown in Fig. 4.

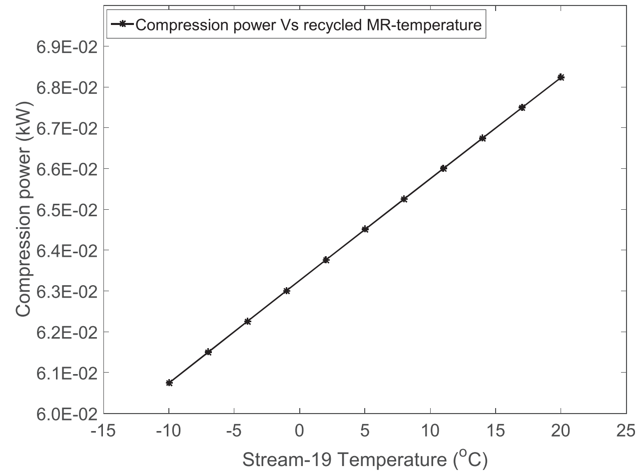

Fig. 4. Relationship between required compression energy and inlet MR temperature.

The minimization of the required overall specific compression power was the objective function in the optimization of HFO-MR liquefaction process. The optimization results are shown in Table 5. Accordingly, the specific compression energy was reduced by up to 25.1% compared with the base case.

Table 6 compares the specific required energy of the HFO-MR process with those of other well-known natural gas liquefaction processes and summarizes the relative energy savings by the proposed HFO-MR process. The results illustrated the superiority of our proposed HFO-MR natural gas liquefaction process as a highly energy-efficient process that enables significant energy savings while satisfying practical and feasible constraints.

3.7. Process analysis in terms of composite curves

The composite curves matching technique is used as a

Table 5
Optimization results of the HFO-MR process.

	Optimized process
Decision variables	
High pressure of MR (stream-13), P_2 (bar)	55.52
Evaporation Pressure (stream-19), P_o (bar)	3.06
Temperature of NG (stream-21), T_{21} (°C)	−18.45
Flow rate of nitrogen, m_{N2} (kg/h)	0.1600
Flow rate of methane, m_{C1} (kg/h)	0.4935
Flow rate of ethane, m_{C2} (kg/h)	0.8655
Flow rate of propane, m_{C3} (kg/h)	1.2700
Flow rate of HFO-1234yf, m_{HFO} (kg/h)	0.2745
Flow rate of n-butane, m_{C4} (kg/h)	0.8720
Constraints	
MITA ($\Delta T_{1(min)}$) for CHX-01(°C)	3.0
MITA ($\Delta T_{2(min)}$) for CHX-02 (°C)	3.0
End flash gas (EFG)	0.08
End flash drum pressure, P_{LNG} (bar)	1.25
Temperature of recycled MR (stream-19)	−2.5
Specific compression power (kW)	**0.2280**

thermodynamic graphical tool to measure the efficiency of any process where cooling and heating are dominant. The entropy generation or exergy losses can be illustrated as a gap between the composite curves. The composite curves will be located far away from each other if there is a large temperature difference between the feed (natural gas) inlet temperature and the boiling point of the refrigerant. This large temperature difference may cause the sudden liquefaction and sub-cooling of natural gas, which will ultimately generate entropy inside the main cryogenic exchanger. Therefore, for an energy-efficient liquefaction process with low specific compression energy, the hot and cold composite curves of the natural gas and mixed refrigerant should be located as closely as possible to each other.

Table 6
Comparison of the HFO-MR process with existing well-known liquefaction processes.

Liquefaction Processes	Specific required energy (kJ/kg-LNG)	[a]Energy savings (%)
Commercial SMR [37]	1485.0	44.8
PRICO by Aspelund et al. [38]	1527.8	46.4
SMR by Khan et al. [13]	1370.0	40.2
DMR by Khan et al. [12]	1426.32	42.5
C3MR by Khan et al. [36]	1001.88	18.1
SMR-Linde [15]	1285.92	36.3
SMR-APCI [15]	1096.56	25.2
MSMR (KSMR) [34]	942.48	13.0
Boosted SMR by Pham et al. [39]	1145.88	30.0
Base case HFO-MR process	1094.76	25.1
Optimized HFO-MR process	**820.80**	

[a] Energy savings improvement of the proposed HFO-MR process compared with the corresponding process.

In the base case of the proposed LNG process, there are huge exergy losses owing to the large temperature gradient inside the main LNG cryogenic exchangers (CHX-01 and CHX-02). The exergy loss inside the main cryogenic exchangers can be analyzed by observing either the peaks of the TDCC (temperature difference composite curve) or the gap between the THCC (temperature enthalpy composite curve). The approach temperature (TDCC) along the length of a multi-stream cryogenic heat exchanger should be low. For efficient and economical heat transfer, the MITA value should be between 1 and 3 °C. In this study, a conservative MITA value of 3 °C was used. The approach temperature (TDCC) inside the precooling cryogenic exchanger CHX-01 and sub-cooling (main liquefier CHX-02) of the base case are shown in Figs. 5a and 6a, respectively. The peak of TDCC inside the precooling cryogenic exchanger CHX-01 and liquefier cryogenic exchanger CHX-02 for the base case was higher in comparison with that of the optimized TDCC, as shown in Figs. 5 and 6. There is a large gap between the hot and cold composite curves in the base case (Figs. 5b and 6(b)) compared with the composite curves of the proposed LNG process, as shown in Figs. 5d and 6(d). From a thermodynamic point of view, if the space between the hot and cold composite curves (THCC) is as small as possible, the liquefaction process can be considered energy efficient.

The proposed HFO-MR liquefaction cycle could be further optimized to save more energy. As shown in Fig. 6a, the temperature-enthalpy hot and cold composite curves of the precooling exchanger were still separated. Similarly, for the sub-

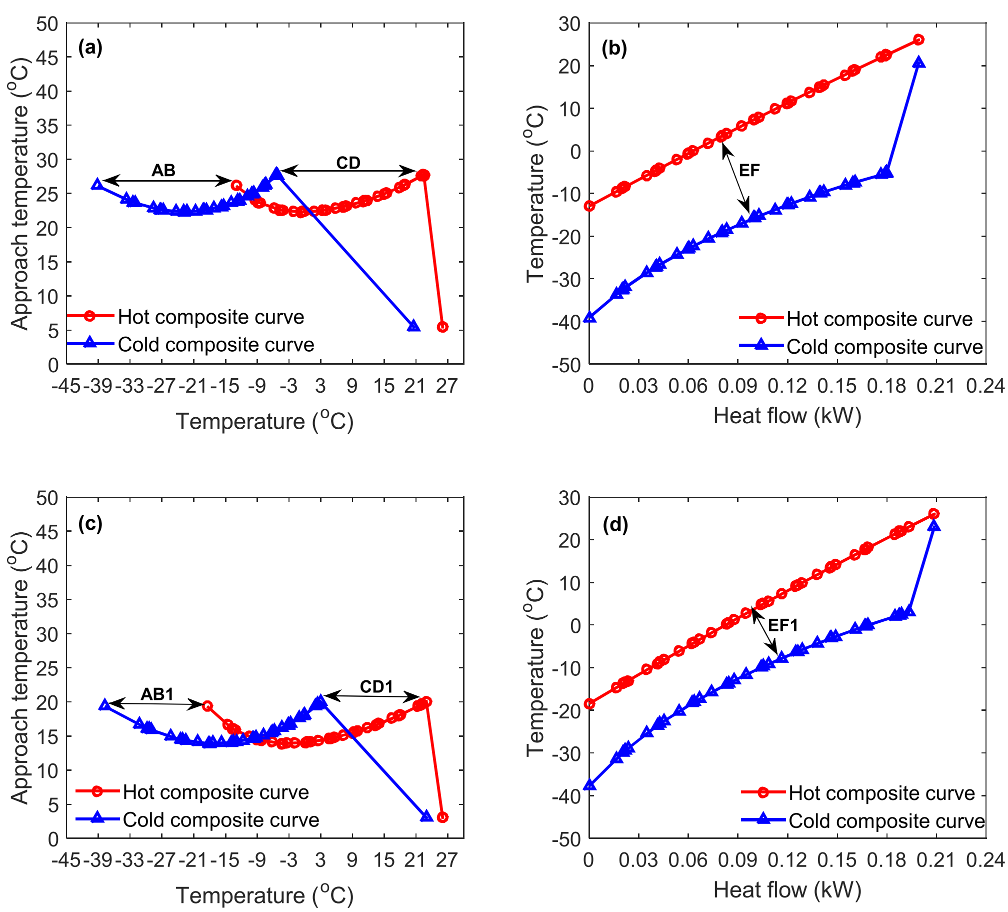

Fig. 5. TDCC and THCC in the precooling exchanger (CHX-01) of the HFO-MR LNG process, without optimization (**a** and **b**) and with optimization (**c** and **d**), respectively.

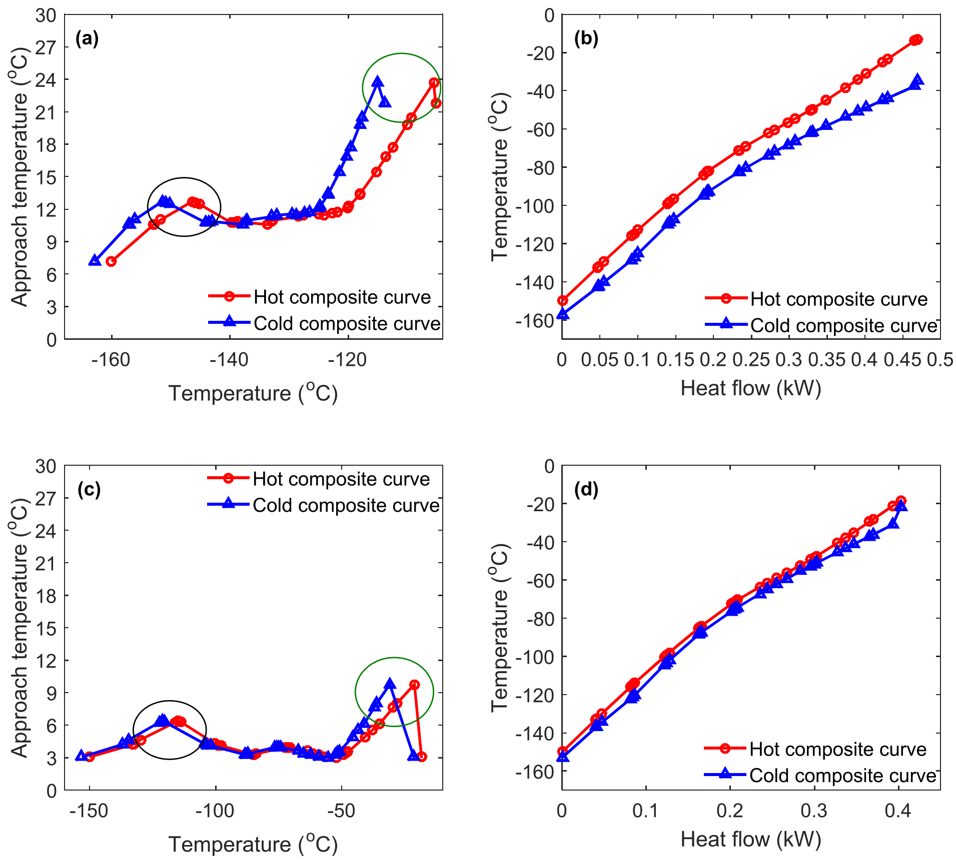

Fig. 6. TDCC and THCC in the main LNG exchanger (CHX-02) of the HFO-MR LNG process, without optimization (**a** and **b**) and with optimization (**c** and **d**), respectively.

cooling heat exchanger, the circled regions have potential for further optimization by other rigorous optimization techniques or by introducing a refrigerant with a boiling point between methane and ethane as well as HFO-1234yf and propane.

3.8. Economic evaluation

After optimization, the feasibility of the optimized LNG plant at commercial scale was investigated. The purchased equipment costs and operating costs were the major factors to assess with respect to the preliminary economic performance. There are many existing methods with different degrees of accuracy and complexity that can be used to evaluate the economic efficiency of process plants. The optimized proposed HFO-MR LNG process was evaluated based on equipment capacity. Equation (6) presents the capacity-based correlation [40] that was used to calculate the equipment purchase cost:

$$\log E_{pc} = C_1 + C_2 \log V + C_3 (\log V)^{\,2} \tag{6}$$

where C_1, C_2, and C_3 are the constants of capacity-based correlation (these constants are specific to each type of equipment) and 'V' denotes the capacity parameter (for example, heat transfer area for the cryogenic exchanger, and shaft work for pump and compressors). Table 7 lists the correlation constants used to calculate the equipment purchase costs.

To determine the commercial feasibility of the proposed optimized process, the capacity of the plant was assumed to be 1000 kg/h LNG production. For heat exchangers, the heat transfer area was recognized as a sizing or capacity parameter. Aspen Hysys® did not provide the value of heat transfer area 'A', heat transfer coefficient 'U', or the overall heat transfer coefficient separately; they only provided the product value of 'UA.' Therefore, the value of 'U' was estimated from the literature to be 1200–6000 W/m^{2}K [41–43]. Therefore, in this study, the mean value of this observed range was used to calculate the capacity parameter (heat transfer area) of the main cryogenic LNG exchanger. Subsequently, the capacity parameters of compressors and separators were obtained from the Aspen Hysys® results. Table 8 lists the capacity parameters of the equipment used to produce 1000 kg/h LNG.

It has been shown [10] that LNG processes are energy intensive mainly owing to the huge electricity requirement for the

Table 7
Equipment cost data to be used with equation (6) [40].

Equipment type	Equipment description	C_1	C_2	C_3	Capacity, Units
Compressor	Centrifugal, axial, and reciprocating	2.2897	1.3604	−0.1027	Fluid power, kW
Heat exchanger	Flat plate	4.6656	−0.1557	0.1547	Area, m^2
	Spiral plate	4.6561	−0.2947	0.2207	Area, m^2
	Air cooler	4.0336	0.2341	0.0497	Area, m^2
Separator	Vertical	3.4974	0.4485	0.1074	Volume, m^3

Table 8
Capacity parameters of used equipment for the production of 1000 kg/h LNG.

Equipment	Capacity parameter value
Cryogenic LNG heat exchanger (CHX-01)	3.88 m^2
Cryogenic LNG heat exchanger (CHX-02)	26.38 m^2
Compressors	
K-1	62.10 kW
K-2	66.64 kW
K-3	61.09 kW
K-4	28.20 kW
Separators	
V-1	0.9786 m^3
V-2	0.4128 m^3

Table 9
Economic analysis of the proposed LNG process.

Equipment	Costs (US $)
Total Capital cost ($)	8486870
Total installed cost ($)	156200.0
Total equipment costs ($)	2724400.0
Annualized operating costs ($)	120795.5
Total annualized costs (TAC) ($)	**11488265.5**

compression units involved in the refrigeration and liquefaction operations. Therefore, in this study, only the required specific electricity for the compression units was considered as an objective function of the operating cost. The operating cost in turn was calculated in terms of the annual electricity cost. Air was a negligible utility cost. An electricity cost of $16.8/GJ [40] was used to determine the annual operating cost for compressors, using equation (7) [44].

$$OC = \left(electricty\ cost\,\frac{\$}{kWyr}\right)(specific\ compresion\ power) \tag{7}$$

As a result, the operating cost to produce 1 kg LNG per year was estimated at $120.8. Table 9 lists the total annualized costs to produce 1000 kg/h LNG.

4. Conclusions

The use of a hydrofluoroolefin-based novel mixed refrigerant for energy-efficient and ecological LNG production was demonstrated. To achieve the maximum potential benefits of the proposed novel mixed refrigerant, a new liquefaction process was developed, resulting in a reduction of the required specific compression power. To derive the maximum benefit from this new mixed refrigerant with the proposed liquefaction cycle, a hybrid optimization algorithm was developed and applied. The conclusions drawn can be summarized as follows.

- Based on the optimized results, the specific compression energy was reduced by up to 25.1% compared with the base case.
- Compared to the established liquefaction processes, we illustrated the superior performance of the proposed HFO-MR natural gas liquefaction process.
- The overall energy requirement for natural gas liquefaction can be reduced by 46.4% compared with that of a single mixed refrigerant process, 42.5% compared with a dual mixed refrigerant process, and 36.3% compared with the Linde–single mixed refrigerant process
- It is expected that the eco-friendly fourth-generation refrigerant HFOs, which have grown rapidly for use in air conditioning systems and vehicles, will provide an innovative solution for the improvement of energy-intensive natural gas liquefaction processes from an ecological and energy efficiency perspective.
- An economic analysis of the process was performed in terms of the capacity parameters of the equipment used.

4.1. Future recommendations

- Further improvement in natural gas liquefaction may be possible by introducing an ecological refrigerant with a boiling point between methane and ethane.
- By using other heuristic evolutionary algorithms, further minimization of specific compression power may be possible.
- The accuracy of the economic analysis could be increased using a rigorous economic analyzer and updated cost parameters.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.energy.2018.05.173.

Nomenclature

N2	Nitrogen
C1	Methane
C2	Ethane
C3	Propane
iC4	Iso-butane
nC4	n-butane
iC5	Iso-pentane
MITA	Minimum internal temperature approach
C3MR	Propane precooled mixed refrigerant
DMR	Dual mixed refrigerant
KBO	Knowledge based optimization
NLP	Non-linear programming
GA	Genetic algorithm
PSO	Particle swarm optimization
VSO	Vortex search optimization
SG	Specific gravity
NBP	Normal boiling point
Tc	Critical temperature
Pc	Critical pressure
LNG	Liquefied natural gas
HFO	Hydrofluoroolefin
GWP	Global warming potential
ODP	Ozone depletion potential
ODP	Ozone depletion potential
EFG	End flash gas
OC	Operating cost
TAC	Total annualized cost
MR	Mixed refrigerant
NG	Natural gas
SMR	Single mixed refrigerant
TDCC	Temperature difference between composite curves
THCC	Temperature-Heat flow between composite curves

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