Thermodynamic Design of a Movable Small Scale Non-flammable Mixed-refrigerant Air/Oxygen Liquefier

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Abstract. The thermodynamic design of a small scale air/oxygen liquefier is presented in this paper, which could be a low-cost choice under remote and field conditions. Feed gas is liquefied by a dual mixed-refrigerant (DMR) J-T process driven by single-stage compressors. Low pressure (<8.0 bar) gas sources could be adopted in the system, such as small commercial air compressors and normal PSA oxygen generators. All the components of mixed-refrigerants are non-flammable, which are safe for the liquefaction of air and O₂. Component selection, process configuration design and performance analysis are studied. Ne-N₂-Ar-Freon mixtures are employed as the refrigerant. For air liquefaction, simulated specific power consumption (SPC) of 0.73 kWh L⁻¹ and figure of merit (FOM) of 24.76% are achieved. For O₂ liquefaction, simulated SPC of 0.71 kWh L⁻¹ and FOM of 27.90% are reached.

1. Introduction

Mixed-refrigerant J-T (MRJT) refrigerators could be satisfying cooling sources for air and nitrogen liquefaction. However, as O₂ is a main component of air (21%), it could not be safe when air is liquefied by flammable mixed-refrigerants (normally N₂-HC mixtures). Thus a nonflammable secondary refrigerant might be necessary to deliver cooling capacity from flammable MRJT to feed gas, as processes analyzed by Wang et al. [1]. As a contrast, nonflammable MRJT refrigerator could directly liquefy air even O₂ more safely. Ne, N₂, Ar and hydrofluorocarbon are ideal components of nonflammable refrigerants. The high triple points of hydrofluorocarbon could lead to freezing and clogging at the cold end, which is a critical problem in the application of nonflammable mixed-refrigerants (NFMR). In the patent of Podtcherneniaev et al. [2], a NFMR could be used in a Kleemenko cycle at 105 K without freezing, which consists of Ne, N₂, Ar, R14, R23 and R125, even containing high-boiling components of R134a and R236fa. Boiarski et al. [3] compared the performance of flammable and nonflammable mixtures those based on [2], ranging from 120-210 K. In the nonflammable MRJT of Khatri et al. [4] at 80-150 K, Ne, N₂, Ar, R14 and some HFCs are
selected as the component. The life test of nonflammable MRJT could last for more than one year. Skye et al. [5] developed a mixed-refrigerant cryoprobe with cold tip temperature of 140-180 K, which is precooled by a R22 vapor compression cycle. The NFMR consists of Ar, Kr, R14, R23, R116, R32 and R125. The mixture components are simplified to Ar, R14 and R23 in the modified cryoprobe operating at 163-255 K [6], while the precooling cycle is changed to R410A. Lee et al. [7] designed a nonflammable MRJT cooler with the mixture of N₂, Ar, R14 and C₂F₆ R218, reaching a Carnot efficiency of 40% at 105 K in the simulation. The visualized solid–liquid equilibria experiment by Lee et al. [8] showed that the Ar-R14-R218 mixture with a large mole fraction (> 0.4) of R14 could remain nonfreezing at 77 K, much lower than the triple point of R218 (125.45 K). Because of the low triple point of Ne, N₂ and O₂. Closed Ne-N₂ cycle [9] and Ne-N₂-O₂ cycle [10-11] with an MRJT precooling cycle are also used at 60-70 K for cooling high temperature superconductor, etc. However, the strong oxidizability of O₂ should be considered in a system driven by oil lubricant compressor.

The thermodynamic design of a small scale air/oxygen liquefier is presented in this paper which could be a low-cost choice for remote and field users. The liquefier is based on a dual mixed-refrigerant (DMR) J-T process driven by single-stage compressors. All the components of the mixed-refrigerants are non-flammable, which are safe for the liquefaction of oxygen-containing gases. Low pressure (<8.0 bar) gas sources could be adopted in the system. Component selection, process configuration design and performance analysis are studied in this paper.

2. Process configuration and component selection

2.1. Component selection of nonflammable mixed-refrigerant (NFMR)

The component selection of NFMR is a key problem for air/O₂ liquefiers. For a typical 100 K MRJT, Ne-N₂-HC mixture could be a favorable mixed-refrigerant, as illustrated by Wang et al [12, 13]. The low triple points \( T_{\text{triple}} \) and solid dissolution of the components could avoid clogging at the cold end. However, Ne-N₂-HC mixtures are flammable, which are not safe in air or O₂ liquefiers. NFMR could be a favorable choice to liquefy air and O₂ directly, free of another cycle for cooling capacity delivery.

Table 1. Properties of some candidates for the nonflammable mixed-refrigerant.

| Refrigerant          | Formula | \( T_{\text{ab}} \) (K) | \( T_i \) (K) | \( p_0 \) (MPa) | \( T_{\text{triple}} \) (K) | Safety |
|----------------------|---------|------------------------|--------------|----------------|-------------------------|--------|
| Neon (R720)          | Ne      | 27.104                 | 44.492       | 2.6786         | 24.556                  | A1     |
| Nitrogen (R728)      | N₂      | 77.355                 | 126.19       | 3.3958         | 63.151                  | A1     |
| Argon (R740)         | Ar      | 87.302                 | 150.69       | 4.863          | 83.806                  | A1     |
| Tetrafluoromethane (R14) | CF₄   | 145.1                  | 227.51       | 3.75           | 89.54                   | A1     |
| Trifluoromethane (R23) | CHF₃  | 191.13                 | 299.29       | 4.832          | 118.02                  | A1     |
| Carbon dioxide (R744) | CO₂    | 194.69                 | 304.13       | 7.3737         | 216.59                  | A1     |
| Hexafluoroethane (R116) | C₂F₆  | 195.06                 | 293.03       | 3.048          | 173.1                   | A1     |
| Sulfur hexafluoride  | SF₆     | 204.9                  | 318.72       | 3.755          | 223.56                  | A1     |
| Pentfluoroethane (R125) | C₂HF₅ | 225.06                 | 339.17       | 3.6177         | 172.52                  | A1     |
| Chlorodifluoromethane (R22) | CHClF₂ | 232.34                 | 369.3        | 4.99           | 115.73                  | A1     |
| Octafluoro propane (R218) | C₂F₈  | 236.36                 | 345.02       | 2.64           | 125.45                  | A1     |
| 1,1,1,2-Tetrafluoroethane (R134a) | CH₂FCF₃ | 247.08                 | 374.21       | 4.0593         | 169.85                  | A1     |
| Trifluoriodomethane (R1311) | CF₃I  | 251.3                  | 396.44       | 3.953          | 120                     | A1     |
| 1,3,3,3-tetrafluoro-1-propene (R1234zeE) | C₃H₇F₄ | 254.2                  | 382.52       | 3.6363         | 168.62                  | A1     |
| 1,1,1,2,3,3,3-Heptafluoropropane (R227ea) | CF₃CHFCF₃ | 256.81                 | 374.9        | 2.925          | 146.35                  | A1     |
| Component                        | Molecular Formula | Normal Boiling Point (K) | Triplet Point (K) | Flammability Classification |
|---------------------------------|------------------|--------------------------|------------------|----------------------------|
| 2-chloro-1,1,2-tetrafluoroethane (R124) | CF₃CHFCl         | 261.19                   | 395.43           | 3.6243                     | 74  A1                       |
| Octafluorocyclobutane (RC318)    | C₈F₈             | 267.18                   | 388.38           | 2.7775                     | 233.35 A1                   |
| Decafluorobutane                 | C₁₀F₁₀           | 271.06                   | 386.33           | 2.3234                     | 145 A1                      |
| 1,1,1,3,3,3-Hexafluoropropane (R236fa) | C₃H₆F₆         | 271.71                   | 398.07           | 3.2                        | 179.52 B1                   |
| 1,1,1,2,3,3-Hexafluoropropane (R236ea) | C₃H₆F₆         | 279.34                   | 412.44           | 3.502                      | 170 A1                      |
| Dichlorofluoromethane (R21)     | CHCl₂F           | 282.01                   | 451.48           | 5.1812                     | 142.8 B1                    |
| 1,1,1,3,3,3-Pentafluoropropane (R245fa) | C₃H₃F₅        | 288.29                   | 427.16           | 3.651                      | 171.05 B1                   |
| 1,1,2,2,3-Pentafluoropropane (R245ca) | C₃H₃F₅        | 298.28                   | 447.57           | 3.925                      | 191.5 A1                    |
| 2,2-Dichloro-1,1,1-trifluoroethane (R123) | C₂HCl₂F₃        | 300.97                   | 456.83           | 3.6618                     | 166 B1                      |
| Perfluoroneopentane             | C₅F₁₂            | 302.9                    | 420.56           | 2.045                      | 148.36 A1                   |

The component selection for NFMR is conducted by the following four principles. Firstly, the flammability safety classification of each component should be Group A1 according to ANSI/ASHRAE Standard 34-2007 [14]. Hydrocarbons, RE170, A2 class (R41, R32, R152a, R142b, R143a, etc.), CO, H₂S and COS are not accepted for the flammability. O₂ and N₂O are not suitable for their strong oxidizability. Secondly, the triple point (T triple) should be low enough to avoid cold clogging. The substances with T triple higher than 120 K are not accepted. The candidate with the lowest T triple in a certain temperature zone is a priority. Thirdly, the poisonousness and environmental protection features are considered. Thus CO, F₃N, H₂S, COS and SO₂ are excluded for the poisonousness. R11, R12, R13, R113, R114, R115, R12B1 and R13B1 are excluded for the high ODP (ozone depletion potential). Fourthly, the cost and source are significant. Kr and Xe are much more expensive than normal refrigerants, which are only reported in some patents. Some nonflammable candidates with normal boiling points (T nb) ranging from 27-300 K are listed in Table 1 and Fig. 1.

As shown in Fig. 1, the T triple of most nonflammable candidates are relatively high, especially in middle and high temperature zone. Since the MRJT would be completely unworkable with cold clogging, the candidates with the lowest T triple are adopted preferentially to avoid solid formation at cold end. For low-boiling components, Ne, N₂ and Ar are the only choices. The T nb gap between Ar and R14 is large, as well as the gap of isothermal throttling effect (ΔhT) distribution, as illustrated in Fig. 2. For middle-boiling components, R14, R23 and R22 are selected for their low T triple. R218 (ODP=0) could be an environmental-friendly alternate for R22 (ODP=0.05). Although the T triple of R124 (74 K) is low enough, it is unsuitable for its excessive large viscosity and glassy state at low temperatures. R13I₁ could be considered as a high-boiling component. Thus the series of Ne, N₂, Ar, R14, R23 and R22 is employed as the components of NFMR in this paper. However, detailed liquid-solid equilibria experiments are still necessary in further investigation.
2.2. Liquefaction process configuration

Because of the absence of suitable high-boiling components, the $\Delta h_T$ of NFMR in high temperature zone is relatively small. Although excessive inferior-high-boiling components like R22 could partly make up this absence, it is still not feasible to add too much R22 in the NFMR. As the $T_{\text{triple}}$ of R22 is relatively high, excessive R22 might result in cold clogging. In order to avoid a small minimum $\Delta h_T$ at warm end, the recuperator warm end inlet temperature of main MRJT ($T_{\text{h,in,main}}$) is required to be low enough, which is also the precooling temperature. However, the precooling temperature is beyond the suitable range of single-stage vapor compression refrigeration cycles. Thus, a mixed-refrigerant precooling cycle is employed to precool the high pressure warm main mixed-refrigerant and feed gas to 235 K (240 K in O$_2$ liquefier). A dual mixed-refrigerant (DMR) process is proposed.

The DMR air/O$_2$ liquefier consists of a main MRJT cycle, a precooling MRJT cycle and an open gas cycle, as shown in Fig. 3. The main MRJT is an auto-cascade cycle with a phase separator. The separator is employed to remove the lubricant and some high-boiling components to avoid clogging at cold end. After being cooled by the precooling cycle in the precooling heat exchanger (HX1), the feed gas and high pressure warm mixed-refrigerant are cooled down by the low pressure cold mixed-refrigerant in recuperative heat exchangers (HX2, HX3). The liquefied air and O$_2$ are throttled to ambient pressure and sent to Dewar.

The process is designed to be driven by commercial single-stage oil lubricant compressors for normal refrigeration. The maximum operating pressures in each cycle are below 20 bar (all pressures in this paper are absolute pressure value) with pressure ratios less than 6. Low pressure gas sources are adopted in this paper. Commercial oil-free small air compressor could be employed to supply compressed air for liquefaction or for PSA (pressure swing adsorption) O$_2$ generator. The liquefiers are designed with gas inlet pressure of 7.0 bar.

3. Thermodynamic analysis methods and conditions

3.1. Analysis model

Thermodynamic design and exergy analysis of the air/O$_2$ liquefiers are conducted by the methods in the research of Wang et al. [1, 12, 13]. Liquid (LAir/LO$_2$) output ($q_{v,\text{liquid}}$), specific power consumption
(SPC) and figure of merit (FOM) are design objectives. \( SPC \) is the ratio of liquid volume flow rate to overall power consumption, as Eqs. (1). \( FOM \) is the ratio of exergy gained by gases to the total power consumption, as Eqs. (2). Exergy gained by gases is the exergy difference between inlet and outlet status.

\[
SPC = \frac{g_{\text{liquid}}}{W_{\text{total}}} = \frac{g_{\text{liquid}}}{W_{\text{CP,main}} + W_{\text{CP,precoolig}}} \tag{1}
\]

\[
FOM = \frac{\text{Minimum liquefaction power}}{W_{\text{total}}} = \frac{m_{\text{liquid}}(e_{\text{liquid, out}} - e_{\text{feed, in}})}{W_{\text{CP,main}} + W_{\text{CP,precoolig}}} \tag{2}
\]

Exergy loss and exergy loss fraction in each component of the liquefier are calculated by Eqs. (3-4).

\[
I_j = \sum E_{\text{in}} - \sum E_{\text{out}} + \sum W_{\text{input}} - \sum W_{\text{output}} - \int_0^Q (T_0/T_\varepsilon - 1)\delta Q_c \tag{3}
\]

\[
\Pi_j = I_j/W_{\text{total}}, \quad \sum \Pi_j + FOM = 1 \tag{4}
\]

3.2. Simulation conditions

According to the operating range of hardware such as single-stage compressors and small air compressors, the simulation is conducted under the following conditions: The minimum approaches in heat exchangers (\( \Delta T_{\text{min}} \)) are 3 K. The maximum compressor discharge temperature is 385.15 K, while liquid in compressor is avoided. The refrigerant outlet temperature of after cooler and feed gas temperature are 308.15 K. The maximum discharge pressure and minimum suction pressure of compressors are 20 bar and 2 bar respectively. The pressure drop of both high and low pressure streams are smaller than 1.0 bar. The adiabatic efficiencies of compressors are 60%. The ambient temperature is 300 K. The mixture composition shift and heat leak are ignored for simplification. The refrigerant and mixture properties \([15]\) are calculated by PR–vdW model \([16-17]\) and the binary interaction coefficients of Vrabec et al. \([18]\). \( FOM \) is the only optimization target in this simulation, as the researches of Wang et al. \([1, 12, 13]\). The precooling cycle is optimized to minimize \( W_{\text{CP,prec}} \).

4. Simulation results and performance analysis

4.1. Operating parameters and mixed-refrigerants

The operating parameters of MRJT refrigerators in air/O\(_2\) liquefier are within the range of commercial single-stage oil-lubricant compressors for normal refrigeration, as listed in Table 2. Since the saturation temperature of O\(_2\) is higher than air, the MRJT refrigerator could supply cooling capacity at higher temperatures in the O\(_2\) liquefier.

| Process                  | Air liquefier | O\(_2\) liquefier |
|--------------------------|--------------|-------------------|
| Compressor suction pressure (bar) | 3.50         | 4.00              |
| Compressor discharge pressure (bar) | 17.00        | 15.00             |
| Temperature before throttling (K) | 98.00        | 235.00            |
| Temperature after throttling (K) | 91.87        | 228.90            |

Table 2. Key operating parameters in air and O\(_2\) liquefiers
The NFMR of main cycle consists of Ne, N\textsubscript{2}, Ar, R14, R23 and R22. The molar fraction of R22 and R23 are restricted at a low level to avoid cold clogging. The NFMR of precooling cycle consists of R14, R23, R22, C\textsubscript{4}F\textsubscript{10} and C\textsubscript{5}F\textsubscript{12}. Comparing with the NFMR in main cycle, the component selection of the NFMR in precooling cycle is much easier. As the refrigeration temperature (235 K or 240 K) is higher than the triple point of most nonflammable candidates, the problem of cold clogging could be ignored. The mixture mole composition is listed in Table 3. As the cold end temperature of O\textsubscript{2} liquefier is higher, less low-boiling components are adopted in its NFMR.

### Table 3. Mixture mole composition of main and precooling cycles in air and O\textsubscript{2} liquefiers

| Mole (%) | Ne   | N\textsubscript{2} | Ar  | R14  | R23  | R22 |
|---------|------|---------------------|-----|------|------|-----|
| Air liquefier, main cycle | 6.81 | 44.16 | 0.00 | 20.19 | 18.83 | 10.00 |
| O\textsubscript{2} liquefier, main cycle | 1.03 | 35.36 | 6.49 | 23.50 | 20.41 | 13.20 |
| Mole (%) | R14  | R23  | R22 | C\textsubscript{4}F\textsubscript{10} | C\textsubscript{5}F\textsubscript{12} |
| Air liquefier, precooling cycle | 5.57 | 47.84 | 2.21 | 28.44 | 15.95 |
| O\textsubscript{2} liquefier, precooling cycle | 1.20 | 51.36 | 5.64 | 23.05 | 18.75 |

4.2. Thermodynamic performances of the air and O\textsubscript{2} liquefier

The overall performances of air and O\textsubscript{2} liquefiers are illustrated in Table 4. The air liquefier achieved a SPC of 0.73 kWh L\textsuperscript{-1} and FOM of 24.76% with feed air compressed to 7.0 bar. For the O\textsubscript{2} liquefier, SPC of 0.71 kWh L\textsuperscript{-1} and FOM of 27.90% are achieved with feed O\textsubscript{2} compressed to 7.0 bar. The air/O\textsubscript{2} compressor power is considered. With a PSA O\textsubscript{2} generator as the gas source (assumed O\textsubscript{2} yield of 30%), the SPC of O\textsubscript{2} liquefier is 1.01 kWh L\textsuperscript{-1}. The corresponding air compressor power consumption is calculated by the method that the O\textsubscript{2} flow rate in liquefier is 30% of the compressed air flow rate.

### Table 4. Overall performances of the air and O\textsubscript{2} liquefiers under designed conditions

| Process | Air liquefier | O\textsubscript{2} liquefier |
|---------|---------------|----------------------------|
| Feed gas and cold box entrance pressure | air, 7.0 bar | O\textsubscript{2}, 7.0 bar |
| Feed gas mass flow rate (g s\textsuperscript{-1}) | 0.68 | 0.82 |
| Liquid output (L h\textsuperscript{-1}) | 2.24 | 2.14 |
| Total power consumption (kW) | 1.63 | 1.53 |
| FOM (%) | 24.76 | 27.90 |
| SPC (kWh L\textsuperscript{-1}) | 0.73 | 0.71 |

The T-Q diagrams in the heat exchangers of the liquefiers are illustrated in Fig. 4. The optimization of mixture composition makes the cold and warm stream match well. However, the absence of proper component between Ar and R14 still results in an unsatisfying match in the corresponding temperature zone. The mixed-refrigerant precooling cycle could improve the heat capacity match and reduce the temperature difference in warm zone effectively, as well as the exergy loss in HX1.
Exergy loss distribution in each component of the liquefiers is calculated by Eqs. (3-4). Obviously the loss in compressors unit takes the largest percentage in overall exergy loss. The exergy loss in the cold stage heat exchanger (HX3) takes the second largest part due to the large \( \text{WLMTD} \) (heat load weighted logarithmic mean temperature difference). Although HX1 undertakes more than 40\% of total recuperator heat load (Fig. 4), the exergy loss in HX1 is relatively small, as analyzed in Section 4.2.

5. Conclusions and discussion

The thermodynamic design of a small scale air/O\(_2\) liquefier is conducted, which could be a low-cost choice under remote and field conditions. Feed gas is liquefied by a dual mixed-refrigerant (DMR) J-T process driven by single-stage compressors. Low pressure (<8.0 bar) gas sources could be adopted in the system, such as small commercial air compressors and normal PSA oxygen generators. All the components of the mixed-refrigerants for main and precooling cycles are non-flammable, which are safe for the liquefaction of oxygen-containing gases. Ne-N\(_2\)-Ar-Freon mixtures are employed as the refrigerant. For air liquefaction, simulated specific power consumption (SPC) of 0.73 kWh L\(^{-1}\) and figure of merit (FOM) of 24.76\% are achieved. For \( \text{O}_2 \) liquefaction, simulated SPC of 0.71 kWh L\(^{-1}\) and FOM of 27.90\% are reached.

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