Exergy and Energy Analysis of Low GWP Refrigerants for Ultra-Low Temperature Applications: Recent Advances and Challenges

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Exergy and Energy Analysis of Low GWP Refrigerants for Ultra-Low Temperature Applications: Recent Advances and Challenges

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Abstract. The quest for environmentally benign refrigerants has intensified due to the detrimental effects of conventional high global warming potential (GWP) fluids on climate change. This study provides recent advances in exergy and energy analysis of several low GWP refrigerants such as R-41, R-1132a, R-1234yf, R-170, and R-1150 in comparison to traditional high GWP refrigerants (R-508A/B and R-23) for ultralow-temperature applications because exergy and energy analysis is crucial in evaluating the efficiency and sustainability of refrigeration systems. The analysis employs thermodynamic principles to evaluate these refrigerants' efficiency and environmental impact under varying operating conditions. Key parameters such as exergy destruction, energy consumption, and coefficient of performance (COP) are assessed for these alternative refrigerants' feasibility, effectiveness, overall performance, and sustainability. This study explores the trade-offs between energy efficiency and environmental impact, aiming to provide insights into optimal refrigerant selection for different low-temperature cooling requirements. Through comprehensive exergy and energy analyses, this research contributes to understanding how low GWP refrigerants can mitigate environmental concerns while maintaining or improving system efficiency for ultralow-temperature refrigeration applications.

Keywords: Energy, Exergy**,** Auto-cascade refrigeration system, Ultra-low temperature, Low GWP refrigerant, Coefficient of performance

1 Introduction

Ultralow temperature is crucial in various applications (scientific, medical, pharmaceutical, food production/ storage, semiconductor manufacturing, chemical, and industrial processes) where precise temperature control at ultralow levels is essential. As to the American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) definition, ultralow-temperature (ULT) refrigeration units are defined as those that function at temperatures ranging from −50 °C and −100 °C. This temperature range is addressed individually since the design and construction issues for systems operating in this range are different from those related to cryogenics (−148.15 °C to −273.15 °C) and industrial refrigeration (−35 °C to −50 °C), which fall between it [1]. Moreover, conventional refrigeration methods, such as the vapor compression method, are frequently employed in home refrigeration systems for various food storage applications limited to −25 °C [2].

In order to achieve ultra-low temperatures both cascade and auto-cascade refrigeration systems are used. Cascade systems use separate cycles with independent refrigerants and separate compressors. These cycles are arranged in such a way that the evaporator of the lower temperature cycle (operating at very low temperatures) serves as the condenser for the higher temperature cycle. Whereas auto-cascade (heat exchange between the refrigerants occurs automatically as they pass through the compressor stages, hence termed as autocascade) refrigeration system is a specific type of cascade system where the heat exchange between the different refrigeration cycles is achieved using a single compressor with multiple stages. Each stage operates with a different refrigerant, typically with different temperature ranges.

Note that, ultralow-temperature (ULT) refrigeration which frequently employs refrigerants with extremely high GWP values, such as R-23 and R-508A/B has not been put into the phase-down list by environmental protection agencies due to a lack of alternative low GWP options and research. However, in recent years, the quest for environment-friendly refrigerants has intensified due to concerns over global warming potential (GWP) and climate change issues. This has led to research efforts focused on identifying alternative refrigerants with low GWP values suitable for ultra-low temperature applications [3]. These refrigerants' exergy and energy analysis plays a crucial role in assessing their thermodynamic performance and overall environmental impact. Therefore, in this study, we delve current state of research, technological advancements, and the key challenges in adopting low-GWP refrigerants for ultralow-temperature applications. This study may contribute to the ongoing dialogue on sustainable refrigeration technologies and their role in mitigating climate change impacts by addressing these issues.

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2 Alternative low GWP refrigerants for ULT applications

The search for alternative low GWP refrigerants suitable for ULT applications has intensified in recent years for ultra-low temperature applications. These refrigerants include (a) Hydrofluoroolefins (HFOs) (b) Hydrocarbons (HCs) (c) Natural refrigerants (d) Blends and mixtures. Alternative low GWP refrigerants for the low-temperature side and high-temperature side of a two-stage cascade refrigeration system (Fig. 1) are listed in Table 1 and Table 2 respectively.

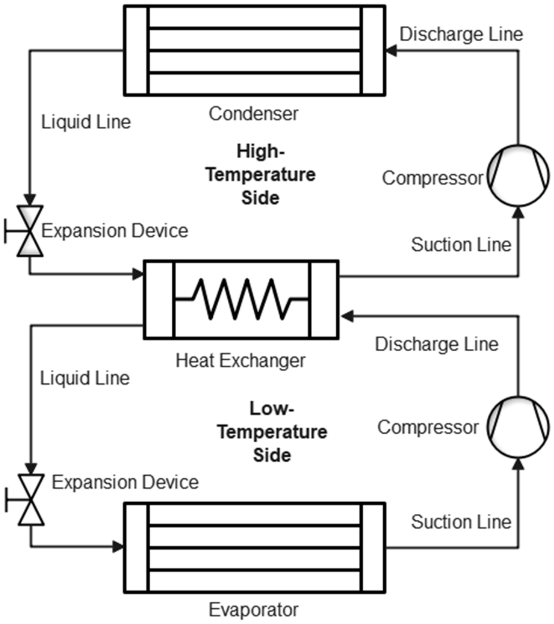

Fig. 1. Schematic of two-stage cascade refrigeration system.

Table 1. Low-temperature side alternative low GWP refrigerants to R-23 (GWP: 12400), R-508A (GWP: 11607), R-508B (GWP: 11698)

Alternative refrigerant	NBP (°C)	GWP$_{100}$ Years	ASHRAE classification
R-14	−128.0	6630	A1
R-41	−78.49	116	N.A.
R-50	−161.48	28	A3
R-1132a	−83.0	<1	A2
R-1150	−103.8	4	A3
R-170	−88.58	5.5	A3
R-744	−78.46	1	A1
R-744A	−90.8	265	A1
R-472A	−84.3	353	A1
R-472B	−66.6	525	A1
R-473A	−87.6	1830	A1
R-469A	−78.5	1357	A1

Table 2. High-temperature side alternative low GWP refrigerants to R-404A (GWP: 3943), R-507A (GWP: 3985), R-134A (GWP: 1300)

Alternative refrigerant	NBP (°C)	GWP	ASHRAE classification
R-717	–33	1	A2
R-1270	–47.6	<1	A3
R-600a	−11.7	<1	A3
R-600	−0.50	20	A3
R-161	−37.5	5	A3
RE-170	−24.78		
R-290	–42.1	11	A3
R-152a	–25	140	A2
R-1234yf	–29.45	<1	A2L
R-1234ze(E)	–18.97	<1	A2L
R-32	–51.65	677	A2L
R-448A	–46.12	1273	A1
R-449A	–44.0	1282	A1
R-407F	–46.06	1824	A1
R-452A	–45.8	1945	A1
R-455A	–52	146	A2L
R-454C	–45.6	148	A2L
R459B	–44.9	145	A2L
R-513A	–28.0	573	A1
R-513B	–29.2	540	A1
R-515B	–18.9	299	A1

3 Recent Advances and Challenges

3.1 Recent Advances

3.1.1 Theoretical study

Qin et al. [4, 5] performed thermodynamic analysis of R-1234yf-blends (R-1234yf/R-744, R-1234yf/R-170, R-1234yf/R-1132a, R-1234yf/R-41, and R-1234yf/R-23 on Joule-Thomson cycle in the evaporator temperature range of −40 °C to −60 °C. Their analysis exhibited that the exergy efficiency, COP, and cooling capacity of all blends are higher than that of R-1234yf/R-41 blend. Moreover, they concluded that R1234yf/R41 has comparable COP and exergy efficiency values as to the R-1234yf/R-1132a, but has a 30% higher cooling capacity. Hence, the R1234yf/R41 blend is more energy-efficient for the LHR system.

Mancuhan [6] performed comparative study for high-temperature side low GWP refrigerants R-290, R-152a, and R-717 in order to replace the high GWP refrigerants R-404A, R-507A, and R-134a in evaporator and condenser temperature range of −40 °C to −10 °C and 45 °C to 10 °C respectively. Their study reveals that R-717, R-152a, and R-290 exhibited the highest COP and exergy efficiency than R-404A, R-507A, and R-134a.

Butt et al. [2] analysed performances of several LT side low GWP refrigerants such as R-41, R-1150, R-1132a, and R-170, and HT side low GWP refrigerants such as R-1270, R-161, R-290, R-1234yf, R-455A, R-459B, and R-454C, to replace the R-23 (LT) and R-404A (HT) respectively, in a cascade refrigeration system (CRS). Their analysis shows that refrigerant pair R-41/R-161 and R-170/R-161 outperform R-23/R-404A in terms of thermodynamic efficiency and GWP. However, if flammability is a key concern, the suggested refrigerant pair is R-1132a/R-1234yf, which is an acceptable option in terms of safety while still maintaining favorable thermodynamic and environmental performance

Faruque et al. [7] investigated the thermodynamic performance of a three-stage cascade refrigeration system (HT side: m-Xylene, MT side: Trans-2butene, Heptane, Cis-2-butene, Toluene, LT side: 1-butene) by combination of 1-butene/Heptane/m-Xylene, 1-butene/Trans-2-butene/m-Xylene, 1-butene/Toluene/m-Xylene and 1-butene/Cis-2-buetene/m-Xylene for 10 kW system in the evaporator temperature range of −120 °C to −90 °C. Their results show that in the evaporator temperature range of −120 °C to −110 °C, 1-butene/Heptane/m-Xylene refrigerant pair outperforms all other pairings. Nevertheless, 1-butene/Toluene/m-Xylene refrigerant duo outperforms other pairs at evaporator temperatures range of −100 °C to −90 °C. At lowest evaporator temperatures (< −120 °C), the cascade heat exchanger may experience higher exergy degradation than the condenser.

He et al. [8] theoretically investigated the performance of a two-stage auto-cascade refrigeration system using LT side refrigerant R-170, R-1150 and HT side R-600a, R-600, and compared with R-23/R-134a in the evaporator temperature range of −60 °C to −35 °C. Their results demonstrated that the COP of R-1150/R-600, R-170/R-600, R-170/R-600a, R-170/R-600, and R-1150/R-600a are superior to R-23/R-134a. Of all the pairs R-170/R-600 shows the best performance. In addition, for the R-23/R-134a and R-170/R-600 systems, the heat exchangers had the highest exergy loss ratios of 56.7% and 52.3%, respectively.

Agari et al. [9] performed exergy and exergoeconomic analysis of auto-cascade refrigeration cycle with R-600. According to their research, the increase in condenser inlet temperature improves the overall avoidable exergy destruction by 88.19%. The increase in compressor inlet mass and evaporator inlet temperature, respectively, increases the overall avoidable investment cost rate by approximately 126.92% and 3.68%, respectively. Additionally, the increase in refrigerator evaporator inlet temperature has a positive impact on the overall avoidable exergy destruction cost rate. In comparison to the base design point, the multi-objective optimization shows gains of 76.78%, 38.66%, and 103.38% in the total avoidable exergy destruction rate, total avoidable investment, and total avoidable exergy destruction cost rates, respectively.

Mota-Babiloni et al. [10] theoretically simulated COP, GWP, cooling capacity (volumetric), and flammability of several pairs of following refrigerants R-32, R-41, R-170, R-290, R-227ea, R-125, R-1150, R-1132a, R-744, R-134a, R-152a, R-1234ze(E), and RE-170 and concluded that mixtures with the least global warming potential and maximum coefficient of performance exhibit considerable flammability, especially at −80 °C evaporator temperature. Moreover. R-170/R-41/R-134a (0.9/0.05/0.05) is a prospective candidate for −50 °C but A3 flammability. R-744/R-41/R-290 (0.7/0.25/0.05) is slightly flammable (A2) for −60 °C, while R744/R-1150 (0.95/0.05) has no flame propagation (A1). For −60 °C, R-744/R-41/R-290 is the most appropriate option by the mass fraction of 0.75/0.2/0.05 and 0.9/0.05/0.05 for slightly flammable and no flame propagation conditions respectively. For evaporation at −80 °C, it is recommended to replace R-290 with R-170.

Liu et al. [11] thermodynamically evaluated the performance of R-600a/R-290/R-170 mixture in auto-cascade refrigeration system for 500 W cooling capacity and concluded that a mixture with a mass fraction of 0.25/0.35/0.40 yields a COP of 0.695 and an exergy efficiency of 0.262 at −66 °C evaporator temperature.

Kilicarslan and Hosoz [12] performed irreversibility and energy analysis of several pairs of refrigerants, R717/R23, R404A/R23, R507/R-23, R-134a/R-23, R-152a/R-23, and R-290/R-23, and, on cascade refrigeration system for 1 kW cooling capacity, evaporator temperature −40 °C, with 7 °C and 5 °C superheating and subcooling respectively at ambient temperature of 300 K. Their results show that with COP increases with rise in evaporator temperature and polytropic efficiency while irreversibility decreases. Except for a restricted range of polytropic efficiency (50–60%), the refrigerant combination R-717/R-23 has the best COP and lowest irreversibility in every scenario; in contrast, R-507/R-23 has the lowest COP and highest irreversibility. An alternative refrigerant combination to R-717/R-23 is R-152a/R-23. The middle range includes the refrigerant couples R-290/R-23 and R-134a/R-23.

3.1.2 Technological advances

Yan et al. [13] employed an ejector to improve the performance of auto-cascade refrigeration systems for R-134a/R23 refrigerant pair. Their results indicate that ejectors improve COP and exergy efficiency by 8.42-18.02% compared to the basic cycle under the same operating conditions. Furthermore, the compressor has the most exergy destruction, followed by the condenser, cascade condenser, expansion valve, ejector, and evaporator. Chen et al. [14] implemented an ejector to enhance the performance of the cascade refrigeration system and replace R-23 and R-134a with R-170 and R-290, LT and HT side respectively. Their results indicate that the ejector improves the COP and cooling capacity by 40.8% and 60.8% respectively. In addition, an 18.8–40.8% improvement in system exergy efficiency was also observed subjected to system configuration and operating conditions. Udroiu et al. [15] investigated the performance of R-290/R-170 pair a cascade cycle with an ejector on both sides and obtained a 21% higher COP than the standard cascade cycle. Rodríguez-Jara [16] implemented double ejector in the cascade system, first at the outlet of the phase-separator and second at the inlet of the compressor, and analysed the performance of the R-600a/R-1150 pair. The results showed a potential improvement in the COP of 12% for the case of the ejector as an expansion device. However, in comparison to the reference case, the ejector as a pre-compression stage showed no improvement. Liu et al. [17] investigated double ejector-expansion auto-cascade refrigeration cycle using the R-290/R-170 pair and found significant enhancement by 29.6–97.9%, 188.6–334.8%, 36–89% in COP, volumetric refrigeration capacity, and exergy efficiency respectively. Bai et al. [18, 19] reported that the system COP and volumetric refrigeration capacity increased by 19.93% and 28.42%, respectively, upon ejector implementation compared to the traditional auto-cascade system. Moreover, contrary to the findings of the traditional exergy analysis, the advanced exergy analysis indicates that the compressor with the greatest avoidable endogenous exergy destruction has the highest upgrade priority, followed by the condenser, evaporator, and ejector. Souza et al. [20] used Particle Swarm Optimization technique to optimize a two-phase ejector cascade refrigeration system for low GWP refrigerants R-717, R-1234yf, R-290, and R-1234ze(E). The R-1234yf/R-744 pair showed higher exergy destruction, although the R-717/R-744 pair had the highest COP. Feng et al.[21] reported that implementation of ejector in a simple cascade refrigeration system improves the system COP by 17.39–68.37%.

Liu et al. [22] employed an auxiliary separator after the expansion device to collect the enriched vapor in the auto-cascade refrigeration cycle. Their results show 16.1%, 10.23%, and 2.51% improvements in COP, exergy efficiency, and overall cost rate respectively for R-290/R-170.

3.1.3 Experimental study

Llopis et al. [23] experimentally evaluated the performance of R-1150/R-600a by varying the composition (25/75%, 30/70%, and 35/65 %) on auto-cascade refrigeration system in evaporator temperatures between −80 °C to −60 °C and at condenser temperature 25–35 °C. They found that the 30/70% pair is best in terms of COP and energy consumption. The measured experimental coefficient of performance (COP) varied between 0.155 at 25 °C to 0.087 at 35 °C.

Sobieraj [24] experimentally investigated the influence of Experimental Investigation of throttle opening and recuperative heat exchanger on 600a/CO_2 auto-cascade refrigeration system and obtained 20% higher COP. Rodriguez-Criado et al. [25] experimentally investigated the retrofit replacement of R-290 with R-170 in packaged refrigeration unit. Their findings demonstrated that −80 to −65 °C can be achieved with COP ranging from 0.6 to 1.6.

3.2 Challenges

Achieving ultra-low temperatures (−50 to −100 °C) using low refrigerants poses several challenges:

(a) Low normal boiling point: refrigerants suitable for ultra-low temperatures should have boiling points in the range of −50 to −100 °C above the atmospheric pressure to avoid leakage.

(b) Efficiency in expansion: significant cooling is achieved through the Joule-Thomson effect, where the refrigerant's temperature drops drastically as it expands through a throttle valve or an expansion valve. As known, insufficient flash gas separation of zeotropic refrigerant and massive throttling losses are two major causes for the poor performance of auto-cascade system

(c) Limitation of the compression ratio. The cooling capacity needed by ultra-low temperature apparatus cannot be reached economically with a single vapor compression refrigeration cycle due to the constraint of the high compressor pressure ratio.

(d) Non-toxic and non-flammable: Especially important for safety, the refrigerant should be non-toxic and non-flammable to prevent hazards during operation. Handling multiple refrigerants with different properties and temperature ranges requires strict adherence to safety protocols. There may be increased risks associated with refrigerant leaks, compatibility issues, and potential hazards if proper safety measures are not followed.

(e) Refrigerant compatibility with material: auto-cascade/cascade systems utilize multiple refrigerants with different temperature ranges, which must be compatible with each other and with the materials used in the system. Managing these refrigerants involves ensuring proper lubrication, minimizing leaks, and handling any potential interactions between different refrigerants.

(f) Energy efficiency trade-offs: While auto cascade systems can achieve very low temperatures efficiently, the overall energy efficiency can be influenced by factors such as compressor efficiency, heat exchanger design, and the specific properties of the refrigerants used. Achieving optimal energy performance may require careful system design and possibly higher initial costs for energy-efficient components.

4 Conclusions

This study provides a comprehensive overview of low Global Warming Potential (GWP) refrigerants for ultra-low temperature applications through detailed exergy and energy analyses. The key conclusions drawn from the study are:

1. **Performance of Low GWP Refrigerants**: Recent advancements in low GWP refrigerants have demonstrated promising performance in ultra-low temperature applications. The refrigerants evaluated show significant potential in reducing environmental impact while maintaining efficiency and effectiveness in refrigeration cycles. For example, an alternative refrigerant combination to R-717/R-23 is R-152a/R-23. Moreover implementation of ejectors significantly improves the system COP.
2. **Exergy Analysis Insights**: The exergy analysis revealed that while low-GWP refrigerants often have lower exergy destruction compared to traditional high-GWP refrigerants, the performance is highly dependent on the specific operating conditions and system design. Some refrigerants exhibited higher exergy losses in certain temperature ranges, indicating areas where further optimization is necessary.

3. **Energy Efficiency Considerations**: Energy analysis shows that low GWP refrigerants can achieve competitive energy efficiency in ultra-low temperature applications. However, the efficiency gains are influenced by factors such as compressor type, heat exchanger design, and operational parameters. Optimizing these factors is crucial to maximizing the benefits of low GWP refrigerants.
4. **Challenges Identified**: Despite the advances, several challenges remain. The flammability and toxicity are the main obstacles to adopting the low global warming potential alternatives. Additionally, the impact of these refrigerants on system efficiency and reliability, particularly under varying ambient conditions, needs further investigation.
5. **Future Directions**: To address these challenges, future research should focus on the development of new refrigerant blends that optimize both energy efficiency and exergy performance. Enhanced materials and technologies for heat exchangers and compressors that complement the properties of low GWP refrigerants will be essential. Additionally, comprehensive field testing and long-term reliability studies will provide valuable insights into the practical application of these refrigerants.

In summary, while low GWP refrigerants represent a significant step forward in reducing the environmental impact of refrigeration technologies, ongoing research and development are necessary to overcome existing challenges and fully realize their potential in ultra-low temperature applications.

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