

Assessment of Blends of CO₂ with Hydrocarbons as a Zeotropic Refrigerant for HTHPs

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Abstract -The increasing need for energy-efficient and sustainable high-temperature heat pump systems (HTHPs) has led to extensive research into working fluids with optimal thermodynamic performance. Among various refrigerants, carbon dioxide is a promising candidate due to its favourable effects on the environment, good thermophysical properties, and economic feasibility. However, its low critical temperature and high operating pressure pose significant efficiency challenges. One of the methods to explore the use of CO₂ as a refrigerant is to mix it with other hydrocarbons and form zeotropic refrigerant mixtures. Thus, the present study investigates the performance of CO₂-based zeotropic refrigerant mixtures with six hydrocarbons. Key performance indicators, including coefficient of performance (COP), sink outlet temperature, Lorenz efficiency, and condensation heat transfer coefficient, were evaluated for the selected mixtures at different source inlet temperatures. The results indicated that at a source inlet temperature of 90°C, a CO₂/butane mixture delivers a sink outlet temperature of 147.3°C with a COP of 5.73, making it a strong candidate for moderate temperature applications. Additionally, CO₂/butane exhibits the lowest pressure ratio and highest Lorenz efficiency of 77.7% at 90°C source inlet temperature, exhibits reduced compressor workload and improving overall efficiency. For high-temperature applications exceeding 150°C, CO₂/acetone emerges as the most suitable mixture. At a source inlet temperature of 130°C, it achieves a sink outlet temperature of 188.76°C with a highest COP of 6.41 among all tested mixtures. Additionally, CO₂/acetone exhibits a high condensation heat transfer coefficient (1706.9 W/m²K at the same source inlet temperature) leading to lower exergy destruction and enhanced thermal efficiency. Those findings highlight the potential of CO₂-based zeotropic mixtures to enhance HTHP performance by reducing exergy destruction and improving heat exchanger thermal matching without the need for complex system modifications.

Keywords: Carbon dioxide, Hydrocarbons, Lorenz efficiency, zeotropic mixture, heat transfer coefficient, heat pump.

1. Introduction

The growing demand for energy-efficient and sustainable heating solutions has driven extensive research into HTHPs. These systems play a critical role in industrial applications such as food processing, chemical production, and district heating. Among various working fluids, CO₂ has gained attention due to its excellent thermophysical and transport properties, non-toxic, non-flammable, readily available, as well as zero ozone depletion potential (ODP) and limited GWP [1]. Additionally, CO₂ has several advantages over other refrigerants, such as compatibility with normal lubricants and common machine construction materials, low compression ratio, high volumetric heating capacity [2]. Moreover, the cost of CO₂ refrigerant per unit mass is around three times cheaper than that of HFC blends (R404A and R407A) [3]. Despite those advantages, it is challenging to use CO₂ as a refrigerant, primarily due to its low critical temperature (31.1 °C) and high critical pressure (7.38 MPa), which result in high operating pressure and significant performance reduction [5]. This low critical temperature leads to trans-critical conditions on the high-pressure side of the cycle in many applications [6]. The trans critical CO₂ driven HPs have been shown to have high irreversibility caused by throttling losses and superheated vapor horns, which results in low COP [7].

Under trans-critical conditions, condensation heat transfer does not occur at a constant temperature. Thus, the pressure is not determined by the constant condensing temperature, as it varies and can also be optimized. This high optimal pressure results in substantial losses at the throttle valve, which reduces the overall efficiency of the system [6]. To address these issues, many advanced technologies have been introduced, like ejectors, parallel compression, two stage compression, mechanical sub cooling, dedicated mechanical sub cooling. However, the introduction of improved technology requires

additional equipment to modify the system configuration which increases the initial capital cost and makes the system configuration more complex.

To enhance the system energy efficiency without adding additional equipment, mixing CO₂ with other refrigerants to form zeotropic refrigerant mixture is one of the solutions to achieve a higher critical point, lower working pressures and low GWP. This method extends the subcritical operation of pure CO₂, minimizing the compressor work and the high throttling losses. Moreover, the zeotropic temperature glide effect allows a better matching between the refrigerant and the secondary fluid and hence reduces the irreversibility during the heat exchange process.

Several researchers have shown the importance of CO₂-based zeotropic mixtures to significantly enhance the performance and efficiency of heat pump systems. Sarkar and Bhattacharyya (8) explored CO₂/R600 and CO₂/R600a (0.5/0.5) mixtures for medium and high-temperature heat pumps, The result indicates that refrigerant mixtures of CO₂/ R600a have more than twice the COP than that of R600. R600a mixtures also enable the elimination of the extremely high-pressure requirements of CO₂ systems, making it the best alternative working fluid for CO₂ heating. Ju et al. [9] also tested CO₂-propane mixtures for high sink temperature lift, identifying an optimal mass fraction of 12%/88%. This mixture was proposed as an alternative to R22, showing increased COP and better heating capacity. Koyama et al. [10] on the other hand, tested a mixture of CO₂ with 10% dimethyl ester (DME) and found no significant differences in COP but a notable reduction in optimal discharge pressure by 2 MPa and 1.9 MPa for heating and cooling mode, respectively. A recent study by Gomez et al., [11] showed that a mixture of 5% CO₂ and 95% Acetone achieves a COP of 5.66 for industry scale HTHPs at the target sink outlet temperature of 200 °C. Onaka et al. [12] also investigated the evaporation heat transfer of CO₂/DME mixtures in a horizontal tube and observed a reduction in the heat transfer coefficient by 20% for a 10% CO₂ mixture and by 48% for a 25% CO₂ mixture.

Thus, the present study investigates the performance of blends of CO₂ with six different hydrocarbons namely butane, pentane, isopentane, diethyl ether (DEE), methanol and acetone for HTHPs. It also examines condensation heat transfer characterization of these CO₂ based zeotropic refrigerants. The performance of HTHPs is significantly influenced by the thermodynamic properties of the working fluid. These proposed zeotropic refrigerant mixtures, characterized by temperature glide during phase change, can offer improved thermal performance by better matching the temperature profiles of heat exchangers. This approach can lead to increased COP, reduced exergy destruction, and increased overall system efficiency.

2. Method

This section presents the heat pump layout and assumptions used for modelling the HTHPs, along with performance and condensation analysis of the working fluid. In the present study DW-Therm HT (heat transfer fluid) is used as a heat source with inlet temperature range 50-130 °C, and water is used as a heat sink. The source inlet temperature was the main input parameter for the entire system at constant lift temperature that influences the system's performance. REFPROP software version 10.1 [13] was linked to excel to obtain properties of the fluid and for further system analysis.

2.1. Heat pump layout

Figure 1 shows a HTHPs layout for zeotropic refrigerants, a layout similar to standard heat pumps but with the incorporation of two internal heat exchangers, IHX1 and IHX2. IHX1 ensures dry compression. Following compression to state 2, the zeotropic nature of the CO₂/HC mixture necessitates the identification of state 3, which signifies the onset of condensation. Due to the temperature glide occurring during the phase change, saturated vapour is identified at state 3 within the condenser. State 4 then exchanges heat with the outlet fluid from the evaporator at state 9 before exiting IHX1 and entering IHX2. Finally, within IHX2, heat is transferred from state 6 to the low-pressure stream, transitioning it from state 7 to state 8, after which state 6 undergoes a throttling process.

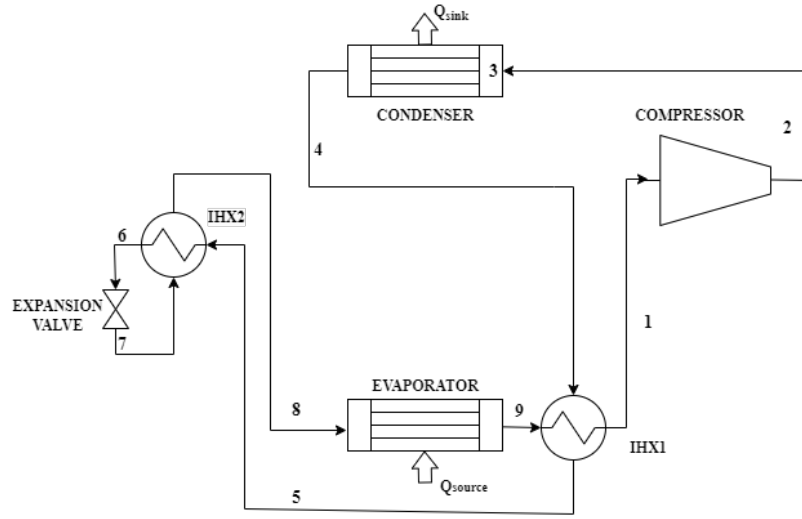


Figure 1: Heat pump layout for proposed CO₂ based zeotropic mixtures.

The entire system has been modeled based on the energy balance of individual components, leading to the derivation of the conservation equations. Steady-flow energy equations, in accordance with the first law of thermodynamics, have been applied to each component. The following assumptions were made for the theoretical analysis:

- Heat losses to the surrounding are neglected.
- The refrigerant is assumed to be in a saturated state at the outlet of the evaporator.
- $\Delta T_{IHX1} = 5\text{ K} = T_5 - T_9$, $\Delta T_{sink\ pinch} = \Delta T_{source\ pinch} = 2.5\text{ K}$
- The compressor functions with a constant isentropic efficiency (η_{is}) of 0.8

2.2. Performance Analysis

The evaluation of HTHPs relies on several critical performance indicators. The sink outlet temperature is one of performance parameter which quantifies the system's ability to deliver thermal energy at high temperature levels required for specific industrial applications. COP relates the supplied heat Q_{sink} to the consumed electric power of the compressor W_{comp}

$$COP = \frac{Q_{sink}}{W_{comp}} \quad (1)$$

Lorenz efficiency (η_{lorenz}) relates the COP to the maximum achievable COP_{lor} for finite heat reservoirs in terms of a Lorenz cycle [19] and therefore gives an indication about the improvement potentials.

$$\eta_{lorenz} = \frac{COP}{COP_{lor}} \quad (2)$$

$$COP_{lor} = \frac{T_{sink,av}}{T_{sink,av} - T_{source,av}} \quad (3)$$

Where: $T_{sink,av}$ and $T_{source,av}$ are average sink and source temperature of the HTF respectively.

2.3. Condensation Analysis

Condensation of zeotropic refrigerants differs significantly from that of pure fluids due to temperature glide during phase change. The less volatile component condenses at the dew point temperature, while the more volatile component accumulates at the interface of the liquid condensate and vapour [15]. And in this study heat transfer coefficient of zeotropic refrigerant

during condensation were analysed. The model suggested by Silver-Bell-Ghaly [16] was adopted in this study to predict the condensation heat transfer coefficient of zeotropic mixtures h_{wf} defined as,

$$\frac{1}{h_{wf}} = \frac{1}{h_{pure}} + \frac{Z}{h_v} \quad (4)$$

Zhang *et al.*, [17] derived an equation to calculate the convective heat transfer coefficient for pure refrigerant h_{pure} which is given by;

$$h_{pure} = 0.4703 R_{eq}^{0.5221} P_r^{\frac{1}{3}} B_o^{0.1674} \rho^{*0.2126} \left(\frac{K_l}{D_h} \right) \quad (5)$$

Z in equation 3 is the ratio of the sensible heat transfer coefficient of the vapor phase and the total heat transfer coefficient during the condensation and $\frac{Z}{h_v}$ represents the heat transfer resistance caused by the mixture effects. Z is simplified as [18].

$$Z = \frac{\text{sensible heat transfer coefficient of vapor}}{\text{total heat transfer coefficient of condensation}} = X_m C_{pv} \frac{T_{gl}}{h_{lg}} \quad (6)$$

h_v is the heat transfer coefficient of the vapour phase referring to the vapour-liquid interface and can be calculated based on the formula below [19].

$$h_v = f_i h_v^0 \quad (7)$$

Where f_i is the interfacial roughness correction factor, the vapour single-phase heat transfer coefficient h_v^0 is calculated using the well-known Dittus and Boelter correlation [20], which is given by:

$$h_v^0 = 0.023 R_{ev}^{0.8} P_{rv}^{\frac{1}{3}} \left(\frac{k_v}{D_h} \right) \quad (8)$$

The interfacial roughness correction factor f_i can be expressed using the expression given by [21];

$$f_i = 1 + \left(\frac{u_v}{u_l} \right)^{1/2} \left[\frac{(\rho_l - \rho_v) g \delta_{film}}{\sigma} \right]^{0.25} \quad (9)$$

3. RESULT AND DISCUSSION

This section starts with a presentation of the glide temperature with respect to the CO₂ composition of the selected mixtures. Then, the next sections present the results of the performance and condensation analysis of the HTHPs using proposed CO₂ based zeotropic refrigerants. Figure 2 illustrates glide temperature variation of these proposed zeotropic mixture with composition of CO₂ at a pressure of 10 bar.

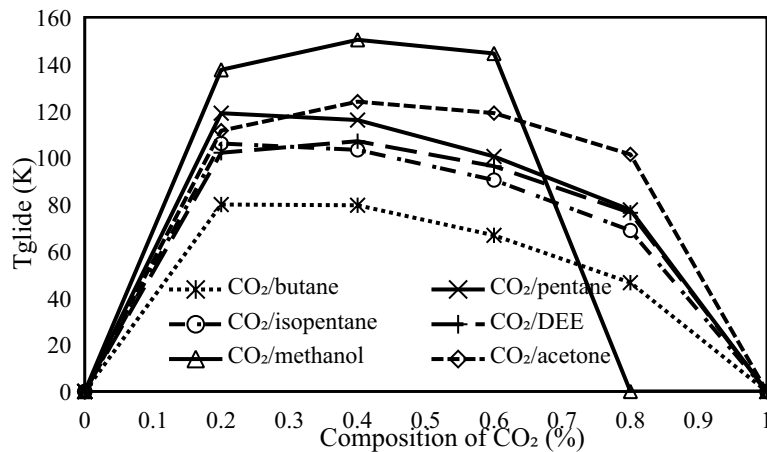


Figure 2: Variation of glide temperature of zeotropic mixtures with percentage composition of CO₂

To calculate the selected performance indicators, the present study considered the temperature lift (ΔT_{lift}) and source glide (ΔT_{source}) of 60K and 10K respectively. The trend of heat sink outlet temperatures of the system for all CO₂ based

zeotropic refrigerant mixtures is represented in Figure 3, which clearly shows the direct relation between the heat source inlet temperature and the heat sink outlet temperature. Heat sink outlet temperature increases with the rise in heat source inlet temperature. The result indicates that all the selected refrigerants deliver moderate and high sink outlet temperatures. At the same source inlet temperature of 90 °C the proposed CO₂ based zeotropic refrigerants deliver sink outlet temperature of CO₂/butane 420.3K, CO₂/pentane 414.9K, CO₂/isopentane 415.3K, CO₂/DEE 416.7K, CO₂/methanol 431.8K, CO₂/acetone 422.37K. Based on this result CO₂/ (methanol, acetone, butane) mixtures delivers better sink outlet temperature than other proposed refrigerants CO₂/methanol have 2.24% increase than CO₂/acetone similarly CO₂/acetone have 0.49% increase than CO₂/butane.

From the proposed CO₂ based zeotropic refrigerants CO₂/ (pentane, DEE, methanol, and acetone) showed applicability to obtain sink outlet temperature above 150 °C at the same source inlet temperature of 130 °C. The maximum sink outlet temperature which is delivered by CO₂/pentane, CO₂/DEE, CO₂/methanol, and CO₂/acetone were found to be 457.88K, 459.17K, 466.7K, and 461.91K respectively. The result also indicated CO₂/methanol has 1.04 percentage increase in maximum sink out let temperature than CO₂/acetone.

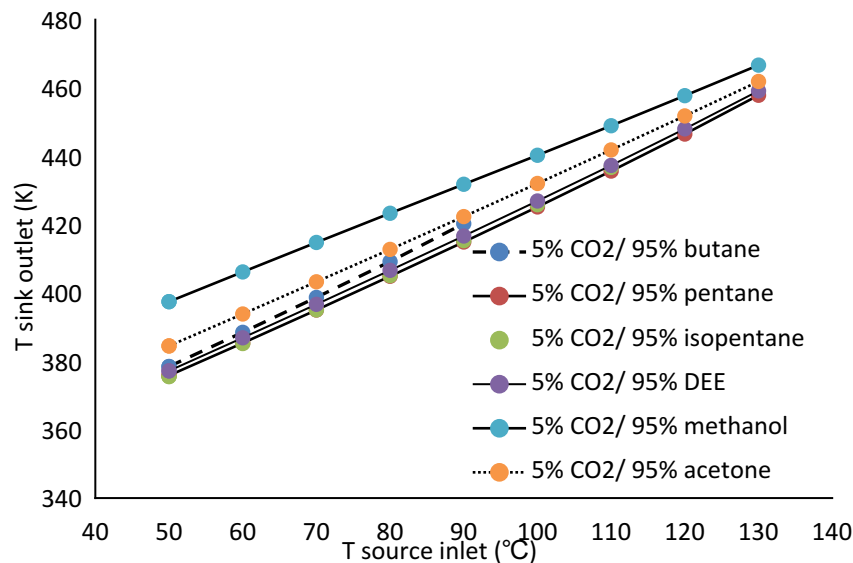


Figure 3: Variation of sink outlet temperature versus source inlet temperature at $\Delta T_{lift} = 60K$.

Figure 4 shows the COP of selected refrigerant mixture for various source inlet temperature. As shown in the result, COP above 5 were observed for all refrigerants even at a minimum source inlet temperature of 50°C. At the same source inlet temperature of 90°C, the proposed CO₂-based zeotropic refrigerants have COPs of: CO₂/butane 5.73, CO₂/pentane 6.07, CO₂/isopentane 6.03, CO₂/DEE 6.08, CO₂/methanol 5.6, and CO₂/acetone 5.99. This result follows the trend in which, at constant source inlet temperatures of 90°C, the CO₂-based zeotropic refrigerants with maximum sink outlet have minimum COP. The higher the sink outlet temperature, the lower the COP [22]. Based on these results, CO₂/ (DEE, pentane, isopentane) mixtures have maximum COP compared to other proposed refrigerants. At the same source inlet temperature of 130°C, the COPs of CO₂/pentane, CO₂/DEE, CO₂/methanol, and CO₂/acetone were 6.28, 6.27, 6.11, and 6.41 respectively.

This result indicates that maximum COP is obtained from the CO₂/acetone zeotropic mixture, which has a 4.92% increment compared to CO₂/methanol. Thus, the outcome of the present model reveals the system is able to deliver high-temperature with high performance using CO₂/ acetone zeotropic refrigerant mixture.

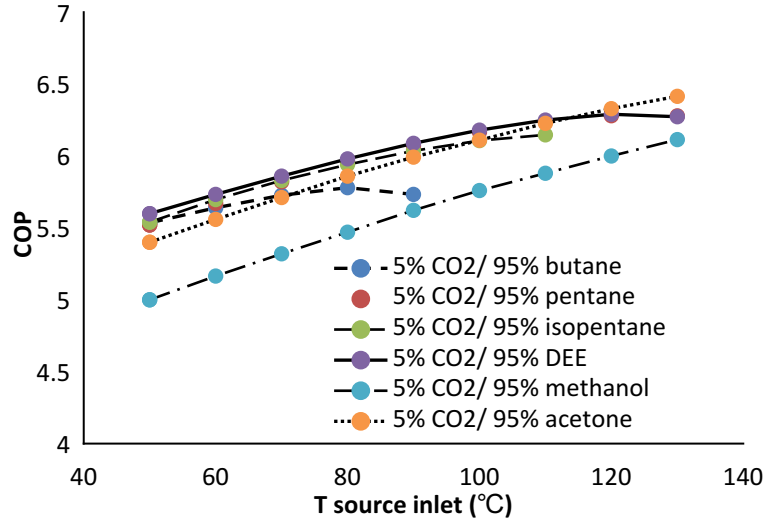


Figure 4: Variation of COP for the proposed CO₂ based zeotropic refrigerants at constant $\Delta T_{lift} = 60 K$.

Figure 5 depicts variation of Lorenz efficiency with source inlet temperature at constant $\Delta T_{lift} = 60 K$. The result indicates that Lorenz efficiency increases as source inlet temperature increases for all proposed CO₂-based zeotropic refrigerants. The results show that CO₂/butane has maximum Lorenz efficiency and CO₂/methanol has minimum Lorenz efficiency for a source inlet temperature ranging from 50-100°C. At 90°C of source inlet temperature, CO₂/butane has a maximum Lorenz efficiency of 77.7%.

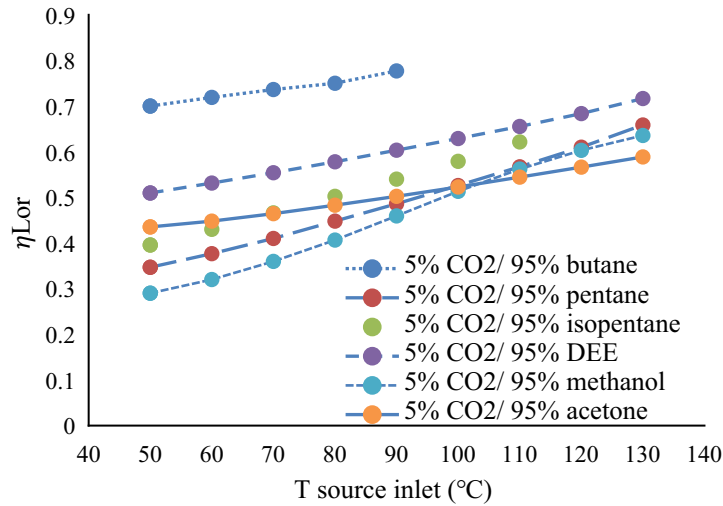


Figure 5: Variation of Lorenz efficiency with source inlet temperature for 5%/95% CO₂/HC zeotropic mixture

Unlike pure refrigerants, zeotropic refrigerants undergo a temperature change during phase change, called glide temperature. As the source inlet temperature of the evaporator increases both the evaporation and condensation pressures increase at a fixed mixture composition, lift and pinch point temperature. This pressure increase leads to a reduction in temperature glide, which results a decrease in the thermal resistance due to the mixture effect (R_{mix}). Despite the decrease in R_{mix} , vapor density increases sharply with rising source inlet temperature, while the liquid density changes relatively little. As a result, the density ratio $\rho^* = \frac{\rho_l}{\rho_v}$ (a critical parameter in the heat transfer correlation for h_{pure}) decreases significantly.

This sharp decline in ρ^* dominates the behaviour of the correlation, leading to a net reduction in h_{pure} . Consequently, the overall heat transfer coefficient of condensation of zeotropic refrigerant mixture h_{wf} also decreases. Figure 6 shows the effect of source inlet temperature on condensation heat transfer coefficient of the proposed CO₂-based zeotropic refrigerants at constant $\Delta T_{lift} = 60\text{ K}$ and $\Delta T_{source} = 10\text{ K}$. The result indicates that the maximum condensation heat transfer coefficient was obtained from CO₂/acetone composition at different source inlet variations. At a source inlet temperature of 130°C, CO₂/acetone mixture has a condensation heat transfer coefficient of 1706.9 W/m²K.

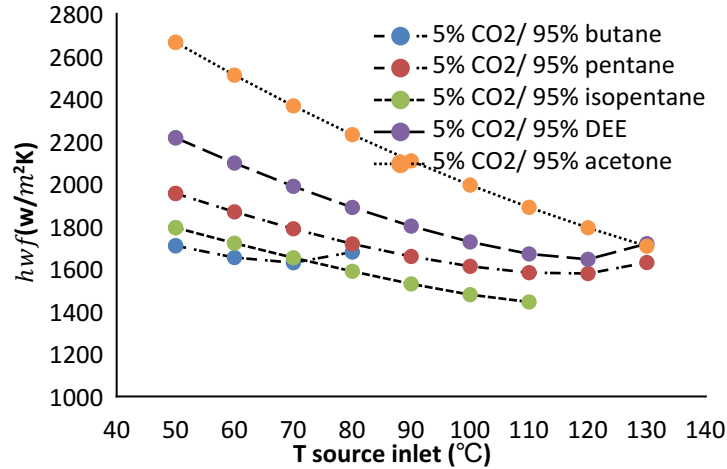


Figure 6: Variation of heat transfer coefficient with source inlet temperature for 5%/95% CO₂/HC zeotropic mixture

4. Conclusion

This study comprehensively evaluated the thermodynamic performance of CO₂-based zeotropic refrigerants for high-temperature heat pump applications. The results demonstrate that the selection of the optimal hydrocarbon based refrigerant mixture significantly influences system efficiency, COP, and heat exchanger performance. From the study the following conclusions were drawn:

- CO₂/butane is recommended for applications requiring sink outlet temperatures up to 140°C, as it offers the highest Lorenz efficiency (77.7% at 90°C source inlet temperature), contributing to enhance system efficiency.
- CO₂/acetone is the preferred mixture for sink outlet temperatures above 150°C due to its superior COP (6.41 at 130°C source inlet temperature), and high condensation heat transfer coefficient (1706.9 W/m²K), making it suitable for industrial high-temperature heating applications.

The implementation of these CO₂-based zeotropic mixtures can significantly improve the energy efficiency and sustainability of HTHPs. Future work should focus on experimental validation and optimization of system configurations to maximize the benefits of these refrigerant blends in real-world applications.

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References

1. Tsamos, K. M., Y. T. Ge, IDewa Santosa, S. A. Tassou, G. Bianchi, and Z. Mylona. "Energy analysis of alternative CO₂ refrigeration system configurations for retail food applications in moderate and warm climates." *Energy Conversion and Management* 150 (2017): 822-829.
2. Sarkar, Jahar, Souvik Bhattacharyya, and M. Ram Gopal. "Transcritical carbon dioxide based heat pumps: Process heat applications." (2004).
3. Bruno, Frank, Martin Belusko, and Edward Halawa. "CO₂ refrigeration and heat pump systems—a comprehensive review." *Energies* 12, no. 15 (2019): 2959.
4. ASHRAE. 15 & 34 Safety Standard for Refrigeration Systems and Designation and Classification of Refrigerants ISO 5149 Mechanical Refrigerating Systems Used for Cooling and Heating—Safety Requirements.
5. Gullo, Paride, Brian Elmegaard, and Giovanni Cortella. "Energy and environmental performance assessment of R744 booster supermarket refrigeration systems operating in warm climates." *International Journal of Refrigeration* 64 (2016): 61-79.
6. Vaccaro, Guglielmo. "Refrigeration with eco-friendly fluids. Development of refrigeration systems with CO₂-based refrigerant mixtures." (2025).
7. Yang, Dongfang, Yulong Song, Feng Cao, Lei Jin, and Xiaolin Wang. "Theoretical and experimental investigation of a combined R134a and transcritical CO₂ heat pump for space heating." *International Journal of Refrigeration* 72 (2016): 156-170.
8. Sarkar, Jahar, and Souvik Bhattacharyya. "Assessment of blends of CO₂ with butane and isobutane as working fluids for heat pump applications." *International Journal of Thermal Sciences* 48, no. 7 (2009): 1460-1465.
9. Ju, Fujun, Xiaowei Fan, Yaping Chen, Huaipu Ouyang, Amin Kuang, Shengfei Ma, and Fang Wang. "Experiment and simulation study on performances of heat pump water heater using blend of R744/R290." *Energy and Buildings* 169 (2018): 148-156.
10. Koyama, S., D. X. Jin, J. Xue, N. Takata, K. Kuwahara, and A. Miyara. "Experimental Study on the Performance of a CO₂/DME System." In *Proceedings*, pp. 1678-1684. 2007.
11. Gómez-Hernández, Jesús, R. O. N. A. N. Grimes, J. V. Briongos, C. Marugán-Cruz, and D. Santana. "Carbon dioxide and acetone mixtures as refrigerants for industry heat pumps to supply temperature in the range 150–220 °C." *Energy* 269 (2023): 126821.
12. Onaka, Yoji, Akio Miyara, and Koutaro Tsubaki. "Experimental study on evaporation heat transfer of CO₂/DME mixture refrigerant in a horizontal smooth tube." *international journal of refrigeration* 33, no. 7 (2010): 1277-1291.
13. Lemmon, Eric W., Ian H. Bell, M. L. Huber, and M. O. McLinden. "NIST standard reference database 23: reference fluid thermodynamic and transport properties-REFPROP, Version 10.0, National Institute of Standards and Technology." *Standard Reference Data Program, Gaithersburg* (2018): 45-46.
14. Illán-Gómez, Fernando, Victor F. Sena-Cuevas, José R. García-Cascales, and Francisco JS Velasco. "Analysis of the optimal gas cooler pressure of a CO₂ heat pump with gas bypass for hot water generation." *Applied Thermal Engineering* 182 (2021): 116110.
15. Huang, Xiaohui, Ji Zhang, and Fredrik Haglind. "Experimental analysis of condensation of zeotropic mixtures from 70° C to 90° C in a plate heat exchanger." *International Journal of Refrigeration* 137 (2022): 166-177.
16. Bell, Kenneth J. "An approximate generalized design method for multicomponent/partial condensers." In *AIChE Symp. Ser.*, vol. 69, pp. 72-79. 1972.
17. Zhang, Ji, Maria E. Mondejar, and Fredrik Haglind. "General heat transfer correlations for flow boiling of zeotropic mixtures in horizontal plain tubes." *Applied Thermal Engineering* 150 (2019): 824-839.
18. Del Col, Davide, Antonio Cavallini, and John R. Thome. "Condensation of zeotropic mixtures in horizontal tubes: new simplified heat transfer model based on flow regimes." *J. Heat Transfer* 127, no. 3 (2005): 221-230.
19. Thome, John R., J. El Hajal, and A. Cavallini. "Condensation in horizontal tubes, part 2: new heat transfer model based on flow regimes." *International journal of heat and mass transfer* 46, no. 18 (2003): 3365-3387.
20. Incropera, Frank P., David P. Dewitt, T. L. Bergman, and A. S. Lavine. "Introduction to Heat Transfer, John Wiley&Sons." *Inc. The United States of America* (1996): 280-284.

21. Zhang, Ji, Brian Elmegaard, and Fredrik Haglind. "Condensation heat transfer and pressure drop characteristics of zeotropic mixtures of R134a/R245fa in plate heat exchangers." *International Journal of Heat and Mass Transfer* 164 (2021): 120577.
22. Navarro-Esbrí, Joaquín, Adrián Fernández-Moreno, and Adrián Mota-Babiloni. "Modelling and evaluation of a high-temperature heat pump two-stage cascade with refrigerant mixtures as a fossil fuel boiler alternative for industry decarbonization." *Energy* 254 (2022): 124308.
23. Zühlsdorf, Benjamin, Jonas Kjær Jensen, Stefano Cignitti, Claus Madsen, and Brian Elmegaard. "Analysis of temperature glide matching of heat pumps with zeotropic working fluid mixtures for different temperature glides." *Energy* 153 (2018): 650-660.