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State of the art and working fluids for high temperature heat pumps

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Abstract. In the current framework of the European policy that pushes toward the ecological transition by promoting the use of low GWP refrigerants and the system electrification, high temperature heat pumps (HTHPs) can be considered as an important technology with huge applicative potential. Their capacity to boost the heat quality from lower to higher temperatures, in fact, makes these machines very interesting across numerous domains. On this regard, this paper presents a comprehensive critical review of the state of the art for applications and working fluids related to high temperature heat pumps. The focus is on the analysis of the heat pump thermodynamic cycles and performance, possible suitable refrigerants, operating source and sink temperatures, potential applications and related technical challenges. More than 25 scientific papers are reviewed, showing large application potential in the food, paper, metal and chemical industries, together with the residential sector.

1. Introduction

According to the IEA, industrial heat accounts for nearly two-thirds of industrial energy demand and one-fifth of global energy consumption [1]. As highlighted in [2], industrial heat demand is expected to grow by about 16% in the period 2023-2028, and only one-third of the additional industrial heat demand is expected to be met by renewable sources, despite a 50% increase in consumption.

The amount of renewable heat used in industrial processes is expected to slowly increase in the coming years, with an expected growth from 12% to 15% between 2022 to 2028. Renewable electricity will be the main contributor to this growth due to its application in process heat [2]. HTHPs can effectively recover low or medium temperature waste heat from various industrial processes and elevate its temperature using electricity instead of fossil fuels as energy input.

Within the current framework of progressive electrification of energy demand, as planned by the European Commission through the adoption of the European Green Deal [3], High Temperature Heat Pumps, HTHPs, offer a promising opportunity to decarbonize the heating demand of industrial sectors since they can potentially replace fossil fuels boiler and significantly contribute to achieve the Net Zero Emission (NZE) scenario by 2050, which requires an annual reduction of 3% in industrial CO_2 emissions [4].

The main features of HTHPs include the breadth and diversity of their application domains. In fact, they can be utilized for process heat generation in the food, chemical and pharmaceutical industries, as well as for residential applications such as integration into district heating networks or energy storage in CHEST systems.

However, since they operate at significantly different temperature levels compared to the traditional vapor compression systems [5], their critical issues and characteristics are still under investigation. In fact, in the recent years, HTHPs have gained significant scientific interest, as evidenced by the substantial increase in published papers addressing various technological and thermodynamic aspects aimed at improving their performance.

Therefore, this paper aims to summarize the latest challenges associated with this technology, focusing primarily on potential applications, cycle configurations and suitable working fluids.

2. High temperature heat pumps: fundamentals and applications

2.1 Basic thermodynamic cycle configuration and typical components

HPs are devices that extract heat from a heat source through an evaporation process and raise its temperature through a compression process. At this point, the refrigerant condenses due to thermal interaction with the heat sink and subsequently its pressure drops to the evaporation pressure due to the flashing process in the expansion valve.

A schematic representation of the main components and their transformations into P-h diagram is provided in the Figure 1. The thermodynamic performance of a HP is expressed by the Coefficient of Performance (COP), defined as the ratio between the thermal power supplied to the sink and the electrical power required by the compressor:

$$COP_{HP} = \frac{Thermal\ Power\ Supplied\ to\ the\ Sink}{Electrical\ Power\ Required\ by\ the\ Compressor} \quad (1)$$

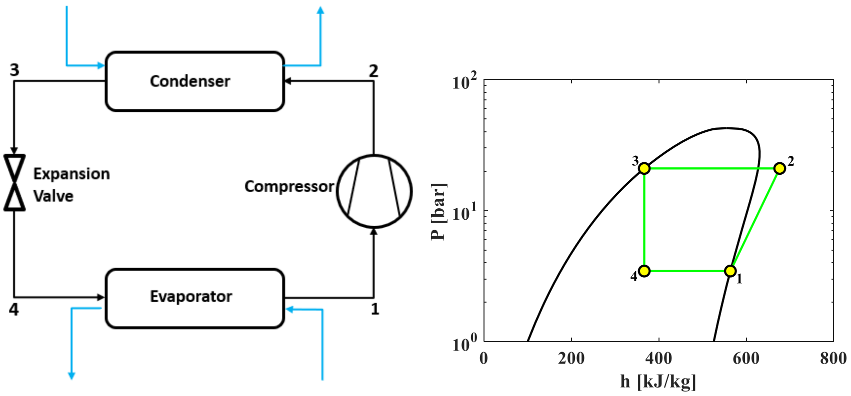

Figure 1. Schematic representation of the components of a basic cycle configuration and a thermodynamic cycle on a P-h diagram.

HTHPs face unique challenges that are not encountered by ordinary heat pumps used in air-conditioning sector. Their applications range from the production of pressurized hot water to generation of high-temperature steam or hot air for industrial processes. Additionally, HTHPs can be integrated into heating and cooling networks for residential heating and cooling. Therefore, further research is needed on key aspects such as possible applications, cycle configurations and working fluids.

Depending on the size and application, different types of compressors can be used in HTHPs, such as scroll compressors for small size plants ([6], [7], [8]), reciprocating ([9], [10], [11], [12], [13]) and screw compressors ([9], [14], [15], [16]) for larger size plants.

Regarding the heat exchangers, plate or brazed plate heat exchangers are commonly used in most cases. Additionally, some systems may include an internal heat exchanger (IHX) to allow for a certain degree of superheating at the compressor inlet, which can be necessary for some fluids to ensure a completely dry compression, as it will be explained in Section 3.

As for the expansion device, instead, electronic or hand expansion valves are often used in HTHPs to ensure a better control of the superheating at the compressor inlet.

In addition, the thermodynamic cycle of a heat pump can be either transcritical, where heat transfer to the heat sink occurs above the critical point of the working fluid, or subcritical, where all the thermodynamic processes occur below the critical point of the refrigerant.

By addressing these aspects, the performance and efficiency of the HTHPs can be optimized for various industrial and residential applications.

2.2 HTHPs potential applications

HTHPs could be a useful technology to use waste heat from industrial processes as heat source, raising its temperature and using it in other processes. In almost all the reviewed papers, industrial waste heat is identified as the primary heat source. The most common applications for HTHPs, based on their size and heat sink temperature, are illustrated in Figure 2.

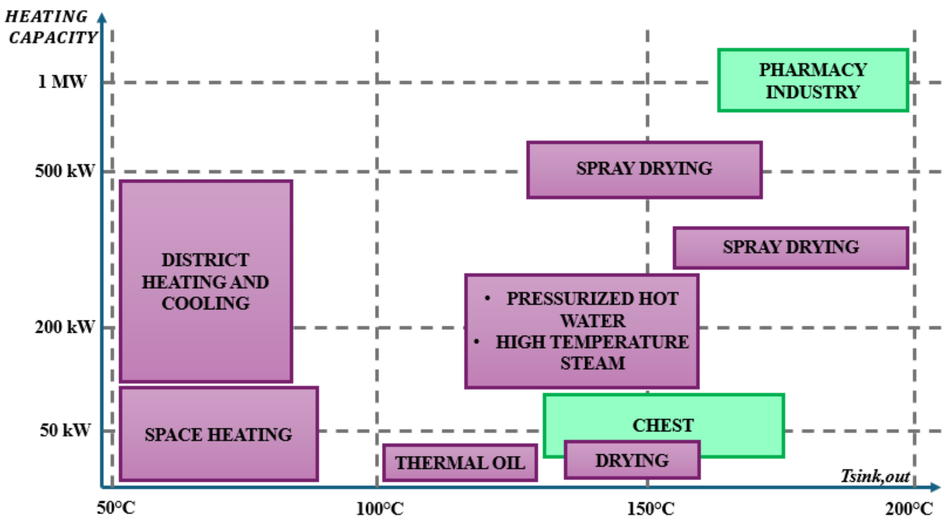

Figure 2. Common applications for HTHPs based on heating capacity and heat sink outlet temperature.

HTHPs could be widely used in high temperature steam generation. It is important to note that the temperature lift between the evaporating and condensing temperatures can affect the system performance. Navarro-Esbrì and Mota-Babiloni [6] studied the impact of temperature lift and pressure ratio variation on system performance and internal heat exchanger efficiency, respectively. In addition, the choice of working fluid could also significantly affect the performance of these systems. On this purpose, Arpagaus and Bertsch [17] analyzed the performance of HTHPs using various HFOs and HCFOs as working fluids, evaluating their COP. Similarly, Vieren et al. [18] examined the performance obtained with some natural fluids such as hydrocarbons (HC) and synthetic fluids like HFOs and HCFOs, in both subcritical and transcritical cycles, varying the heat sink temperature glide. Both [6] and [18] performed the same analysis considering a thermal oil heating up to 130°C as application.

The optimal integration of HTHPs in industrial processes may benefit from a pinch analysis, as demonstrated by Arpagaus et al. [19] who investigated their integration in a food industry for for producing hot air for drying and spray drying processes. They also screened potential working fluids for a fixed temperature lift of 117K, considering both subcritical and transcritical operations. Additionally, as highlighted in [20], for a given working fluid and temperature lift, it is crucial to optimize HTHP cycle configuration in order to achieve higher COP values.

HTHPs also show great potential for producing pressurized hot water up to 160°C, as demonstrated in [9]. Due to the high temperature required on the sink side, reasearchers mainly focus on the cycle configuration and the most suitable working fluids. For instance, Ganesan and Eikevik [20] studied the performance of R744/HCs mixtures in both the upper and lower stages of a cascade cycle configuration, conducting a parametric analysis by varying T_{src}, T_{sink}, and the percentage of R744 in the mixtures. A similar study [14] analyzed the performance of an Adsorption-Compression Heat Pump (ACHP) with a R717 and R718 mixture varying T_{src}, ΔT_{lifr} and the mass fraction of R717. Zauner et al. [21] adopted a similar approach in their study on the integration of an HTHP in an extrusion factory

The use of HTHPs in District Heating Networks (DHNs) [22] and Compressed-Heat Energy Storage (CHEST) systems [12] [23] are among the most promising applications. In these cases, the key challenge is to choose the most suitable fluid based on the required sink temperature. In both scenarios, HTHPs can achieve very high performance, with COP reaching values up to 5.7.

The integration of HTHPs in industrial processes could also significantly reduce the equivalent CO_2 emissions, taking into account both direct and indirect contributions: in fact, as highlighted by Mateu-Royo et al. [24] the total equivalent CO_2 emissions reduction is between 19% and 63% compared to conventional heating technologies. According to [7], depending on the energy mix of each country, the total equivalent CO_2 emissions reduction could be estimated between 10% and 90%. However, despite the environmental benefits of this technology in the decarbonization and electrification of the industrial sector, the low degree of standardization and the still few practical examples of applications currently limit the large-scale development and use of HTHPs [19].

A summary of the main applications, along with their respective sizes and temperature levels, is provided in Table 1.

Table 1. Summary of the reviewed papers based on their applications, size, temperature levels and objectives.

AUTHORS	YEAR	APPLICATION	T_{src} [°C]	T_{sink} [°C]	CAPACITY	OBJ.
Navarro-Esbrì et al. [6]	2023	High temperature steam Thermal Oil Heating	83÷117	102÷158	9.2÷12.3 kW	F[c]+ A[a]
Mateu-Royo et al. [7]	2021	Industry (in general)	80	100÷140	N/A	F
Mota Babiloni et al. [8]	2023	N/A	80÷118	102÷158	9.9÷13.4 kW	F
Wilk et al. [9]	2023	Pressurized Hot Water High Temperature Steam Pharmaceutical Industry	60÷80 80 70	up to 160 150 185	300÷375 kW 200 kW 1.7MW	A
Arpagaus et al. [10]	2021	N/A	30÷80	70÷150	10	F
Verdnik et al. [11]	2022	N/A	40÷60	110 160	24.2 kW 30.7 kW	C[b]+F
Hassan et al. [12]	2022	Compressed Heat Energy Storage (CHEST)	80	138	50 kW	F+A
Mateu-Royo et al. [13]	2019	N/A	45÷75	115÷145	N/A	C+F
Ren et al. [14]	2023	Pressurized Hot Water for Food Industry	70	150	150 kW	C+F
Chamoun et al. [15]	2014	Industry (in general)	85	145	300÷330 kW	F
Wu et al [16]	2020	Pressurized Hot Water High Temperature Steam	75÷85	110÷150	285 kW	A+C +F
Arpagaus and Bertsch [17]	2019	High Temperature Steam Drying	30÷80	80÷150	10 kW	F
Vieren et al. [18]	2023	Thermal Oil Heating Drying Spray Drying	N/A	N/A 197 N/A	N/A 297 kW N/A	C+F
Arpagaus et al [19]	2023	Food Industry: Spray Drying Schanpps Distillation	26 23	140 118	597 kW 186 kW	A+C +F
Ganesan and Eikevik [20]	2023	Hot Water	10÷50	110÷150	63÷207 kW	C+F
Zauner et al [21]	2020	Extrusion Factory	50÷80	100÷130	50 kW	A
Mateu-Royo et al. [22]	2020	District Heating Network (DHN)	60÷90	110	N/A	F+A
Hassan et al. [23]	2020	Compressed Heat Energy Storage (CHEST)	40÷100	138 154 183	N/A	F+A
Mateu-Royo et al. [24]	2021	N/A	30÷90	100÷150	N/A	C+F
Mateu-Royo et al. [25]	2018	Industry (in general)	50÷90	110÷150	N/A	C+F
Arpagaus et al. [26]	2019	N/A	40÷90	70÷160	N/A	C+F
Fernandez-Moreno et al. [27]	2022	N/A	70	140	N/A	F
Frate et al. [28]	2019	N/A	50	150	N/A	F

[a] A=Applications; [b] C=Cycle Configuration; [c] F=Fluids.

3. Advancements and Critical Research Challenges in HTHPs

3.1 Cycle modifications

Based on the reviewed papers, eleven different cycle configurations for HTHPs were identified. Among these, one of the most common configurations is the single stage cycle with internal heat exchanger (IHX). As pointed out in [13], the IHX allows an improvement of the COP compared to SS cycle, ensuring a certain degree of superheating at the compressor inlet in order to have a completely dry compression and a certain degree of subcooling at the expansion valve inlet. Furthermore, this cycle configuration allows for a higher discharge temperature at the compressor outlet, increasing the thermal level of heat production and expanding the operating map of the HTHP. Moreover, the needed superheat depends on the working fluid, as described in section 3.2.

Considering the same configuration, as the ΔT_{lift} increases, considering the transcritical operation of the HTHP [11], the control of the pressure in the gas cooler could be beneficial. In this way, it is possible to extend the range of the sink outlet temperature, enabling values up to 200°C (with ΔT_{lift}>100K) on the sink side [18]. Nevertheless, further investigations are necessary and should include more conditions.

In addition to the transcritical cycles, some modifications to the basic cycle configuration could also be considered. In fact, with the increase of the $T_{sink,out}$, two-stage cycle configurations have been investigated. As highlighted in [19], a two-stage cycle with parallel compression allows a reduction of the pressure ratio of each stage, increasing the overall efficiency of the system. Also, the use of an IHX between the evaporator and the low-pressure compressor or an intermediate IHX between the low-pressure compressor and the high pressure compressor gives the opportunity to increase the discharge temperature at the outlet of the high-pressure compressor achieving also an increase of the temperature level of the heat production. However, a comprehensive analysis is required to find the proper system configuration [25].

In Figure 3 some of the most used cycle configurations in HTHPs are shown.

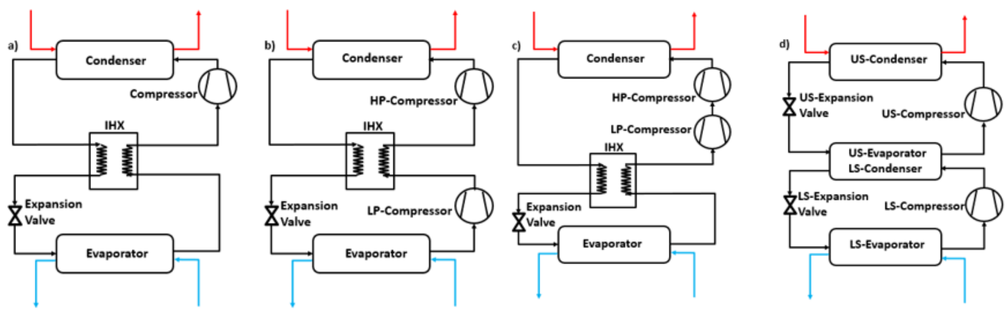

Figure 3. Schematic of some of the most used cycle configurations in HTHPs: a) single-stage with IHX, b) two-stage with intermediate IHX, c) two-stage with IHX and d) cascade

For instance, in this regard Arpagaus et al. [19] examined two case studies: a spray drying process and a schnaps distillation process. In the first one, they compared the subcritical and transcritical operation of an HTHP. Due to a high temperature lift $(\Delta T_{lift} = 117K)$, the transcritical operation allows for a better COP of 2.18 compared to the subcritical COP of 1.77. In the second case study, a two-stage cycle with a COP of 2.34 was chosen for the high temperature lift. In addition, for high ΔT_{lift} cascade cycle can be considered as a further alternative that provides excellent performance, achieving COPs up to 3.84 [20].

As mentioned above, the increase in temperature lift results in higher discharge temperatures at the compressor outlet, which can be dangerous for lubricant dissociation. For these reasons, other cycle modifications can be considered to mitigate the discharge temperature, such as liquid injection in compressor suction line [16], or implementing a two-stage cycle with economizer or flash tank with a vapor injection into the the high pressure compressor suction line [26].

In conclusion, for low ΔT_{lift} values around 30K single-stage configurations with economizer and parallel compression or with internal heat exchanger provide for higher efficiencies [24] while for higher temperature lifts ($\Delta T_{lift} > 70K$) two-stage or cascade cycle configurations allows for higher COP but an optimum temperature must be found in the intermediate heat exchanger for maximizing COP [26].

3.2 Working Fluids

One of the key elements to properly design an HTHP is the choice of the working fluid. In fact, it must be environmentally safe, non-toxic and non or low-flammable in order to reduce the cost of HTHP safety devices. Commonly used fluids for HTHPs include HFC-365mfc and HFC-245fa, but both are high GWP refrigerants and HFC-245fa is also toxic, therefore there is an urgent need to replace these fluids. To address this, many studies have evaluated the properties and performance of low-GWP fluids (HFOs, HCFOs and HCs) in several cycle configurations and working conditions.

In [26], Arpagaus et al. investigated the performance of HFO-1336mzz(Z), HCFO-1224yd(Z), HFO-1234ze(Z), and HCFO-1233zd(E) in various cycle configurations focusing primarily on their COP and volumetric heating capacity (VHC). Due to similar COP and VHC, HFO-1336mzz(Z) is considered the best candidate to replace HFC-365mfc; in fact, because of its low VHC, higher compressor displacement would be required compared to HFC-245fa. Thus, HCFO-1224yd(Z), HFO-1234ze(Z), and HCFO-1233zd(E) are more suitable candidates for replacing HFC-245fa. However, HCFO-1224yd(Z) can potentially cause a higher discharge temperatures at the compressor outlet, requiring a two-stage compressor system with an economizer or a flash tank, that injects vapor into the suction line of the high pressure compressor. Mota Babiloni et al. [8] also agreed that although HFO-1336mzz(Z) can operate at high temperatures thanks to its high critical temperature, its low VHC makes it unsuitable as a replacement of HFC-245fa. Moreover, Hassan et al. [12] do not recommend the use of HFO-1336mzz(Z) in a single stage configuration without IHX, as it requires a high degree of superheat to ensure a dry compression, as suggested in Mateu-Royo et al. [13]. They also highlighted that HCFO-1233zd(E) and HCFO-1224yd(Z) require similar superheat levels as HFC-245fa and, as confirmed in [7], where they showed the potential of HFCO-1224yd(Z) as an alternative to HFC-245fa.

The use of some blends as an alternative to HFC-245fa was investigated by Fernandez Moreno et al. [27] investigated the use of some blends as an alternative to HFC-245fa. When moderate temperatures glides are acceptable the blend R-1233zd(E)/161/601, with a composition of (0.82/0.11/0.07) and a GWP=11.4, is identified as the most promising drop-in replacement of HFC-245fa, showing a COP of 2.64. Instead, for lower temperature glides (of about 2K), the blend R-1233zd(E)/1234ze(Z)/161 with a composition of (0.86/0.12/0.02), GWP=2.7 and COP=2.56 can be considered.

In [17]and [10], the authors demonstrated that for sink temperatures up to 110°C, HFCO-1224yd(Z) and HFCO-1233zd(E) perform better in terms of COP than HFO-1366mzz(Z), which instead showed better results for sink temperatures above 150°C.

Some authors have investigated the potential use of natural fluid such as hydrocarbons (HC) in HTHPs, also comparing them to HFOs and HCFOs.

Mateu-Royo et al. [24] studied the performance of various low-GWP alternatives to HFC-245fa, including HC-601, HC-600, HC-600a, HFO-1336mzz(Z), HFO-1336mzz(E), R514A, HCFO-1233zd(E), HCFO-1224yd(Z), and HFO-1234ze(Z) across different cycle configurations. They noted that although the HC-601, HFO-1336mzz(Z) and R514A exhibited the best COPs, they were not the optimal choice because of their low suction density, which means they would require larger compressors to provide the same heating capacity than other refrigerants with higher suction density. Conversely, HC-600 and HC-600a have higher VHC but also a significant performance decrease. Therefore, HCFO-1233zd(E) and HCFO-1224yd(E) represent a balanced trade-off between COP and VHC, making them comparable to HFC-245fa.

In a previous study, Mateu-Royo et al. [25] analyzed the optimal fluid selection for different temperature lifts and cycle configurations. For both low (40K and 60K) and high (80K and 100K) ΔT_{lift}, in a single-stage cycle with IHX and in a two-stage cycle with IHX, respectively, HC-601 and HFO-1366mzz(Z) provided the best performance, but had too low VHC to replace HFC-245fa. HC-600, with a VHC similar to HFC-245fa, requires smaller compressor but is highly flammable, making HCFO-1233zd€ the most promising replacement.

Arpagaus et al. [19] analyzed the performance of several fluids for transcritical HTHP integration in a spray drying process including HC-600, HC-600a, HC-290, HFO-1234ze(E), HCFO-1224yd(Z) and HCFO-1233zd(E). All of them showed a fairly similar COP of about 2.1 but HC-290 was selected due to its higher VHC, lower pressure ratio and lower cost, although the $T_{sink,out}$ is limited to about 160°C. They also highlighted that the better option for using an HTHP in a schnaps distillation process is a cascade cycle with HFO-1234ze(E) in the lower stage and HCFO-1233zd(E) in the upper stage.

Ganesan and Eikevik [20] also studied a cascade cycle but using a mixture of R744 + HC-601 in the lower stage and R744 + HC-600 in the upper stage, achieving a COP improvement of up to about 25% compared to using only HC-600 and HC-601 in the respective stages. In addition, while increasing the mass fraction of R744 in the blend allows for higher $T_{sink,out}$, it also affects the electrical absorption of the compressor and thus the overall system power consumption.

If the heat sink side glide is such that a transcritical cycle is chosen, Vieren et al. [18] suggest the use of HFO-1336mzz(Z), HFO-1234ze(Z) and HCFO-1233zd(E) as working fluids; for subcritical cycles, acetone, ethanol and methanol are suitable refrigerants, although they are not widely used. If the use of flammable fluids is not allowed, R718 could be a good alternative, although it has low VHC and high pressure ratio and high temperature at compressor discharge.

Frate et al. [28] investigated the performance of various hydrocarbon refrigerants (HCs) in a single-stage system without IHX. They found that cyclopentane and acetone performed well for low source temperatures and high sink temperatures. Additionally, benzene and dichloroethane were identified as the most suitable refrigerants for high sink and source temperatures, and high source temperature with low sink temperatures, respectively. All of these refrigerants are flammable fluids. From a safety perspective, less hazardous alternatives include HFO-1336mzz(Z), HFO-1234ze(Z), HCFO-1233zd(E) e HCFO-1224yd(Z), with HCFO-1233zd(E) demonstrating the best balance in terms of COP and VHC.

Figure 2 presents a summary diagram of the most suitable working fluids for HTHPs based on their critical temperature and potential $T_{sink,out}$.

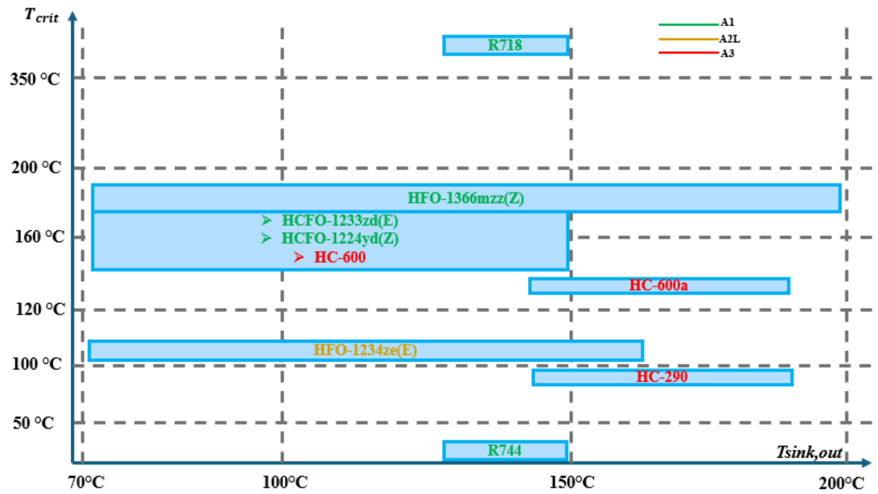

Figure 4. Suitable working fluids based on their critical temperature and $T_{sink,out}$.

3.3 Current Challenges

The large-scale development of HTHPs has the potential to decarbonize industrial processes and residential heating demand. However, to achieve these goals, several challenges associated with HTHPs must be addressed, mainly concerning compressor technology.

Specifically, as mentioned above, HTHPs require higher pressure levels than conventional heat pumps, requiring compressors with much higher compression rations than those currently available commercially. Additionally, there is the need for lubricating oil that are miscible with the refrigerant and capable of protecting and sealing the compressor across the entire temperature range. In this context, oil-free compressors are being increasingly developed, even though they have lower isentropic efficiencies [29].

Furthermore, non-toxic refrigerants that are environmentally safe, non-flammable and chemically stable at temperatures above 200-250°C are also required [30].

4. Conclusions

HTHPs are not yet a well-established technology nor are they commercially mature, but they could play a key role in the environmental transition that will take place in the future. In this review, three main aspects of HTHPs have been considered: potential applications, possible cycle configurations and working fluids.

Despite the potential for HTHPs to be integrated into various industrial processes - such as the production of pressurized hot water, high-temperature steam, hot air for drying and spray drying, and the integration into CHEST systems and DHNs - the low degree of standardization, the limited number of practical application examples, and the need to achieve higher temperatures on the sink side are currently limiting the large-scale development of HTHPs.

Among all the reviewed papers, several cycle configurations have been considered. For small temperature lifts, the most commonly used configurations are the single-stage cycle with an IHX and the single-stage cycle with an economizer and parallel compression. However, as the temperature lift increase, two-stage cycle and cascade cycles exhibit higher efficiencies.

Regarding the working fluids, HFOs, HCFOs, HCs and some blends have been taken into account. HFO-1366mzz(Z) has shown the best COP and VHC as a replacement for HFC-365mfc. Meanwhile, HCFO-1233zd(E) and HFCO-1234ze(Z) exhibit COP and VHC comparable to HFC-245fa.

However, further studies and research are needed to enhance the integration of HTHPs into existing industrial processes and in the residential sector, particularly to achieve higher temperatures on the sink side.

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