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Low GWP refrigerant options for high temperature heat pump applications for industrial decarbonization

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ABSTRACT

Fossil fuels have been the primary energy source for industrial process heating applications since the onset of the industrial revolution. The use of heat pump vapor compression cycles is one of the prime options to electrify and decarbonize these industrial applications in which low pressure steam is currently being used, produced by traditional boilers. The choice of refrigerants is a critical selection criterium to ensure a reliable and efficient design can be achieved to fulfil application thermal and efficiency requirements. The normal boiling point and critical temperatures among other factors provide an indication of the fluids viability to be used as an efficient heat pump refrigerant. Other properties affect the achievable performance and reliability based on source and sink temperature boundary conditions as well as potential compression end conditions and potential wet compression concerns.

This paper evaluates low GWP refrigerant options and their potential for high temperature heat pump (HTHP) conditions based on their performance and wet compression tendency evaluated by different methodologies.

Keywords: High temperature heat pump, Low GWP, HC, HFO, HCFO, Wet compression

INTRODUCTION

Industrial heating needs have traditionally been addressed by steam generated by traditional fossil fueled boilers since the early days of the industrial revolution. Global climate change needs to reduce man-made carbon emissions have led to a variety of initiatives to reduce direct and indirect impacts over the last few decades. The electrification of heating by using heat pumps is one of the prime solutions to reduce fossil fuel consumption to generate heat based on renewable energy sources. Heat pump vapor compression technology can be differentiated based on the source and sink temperatures that apply to the application conditions. Arpagaus et al. (2018) proposed temperature levels and nomenclature for the heat source from which the energy can be used to the heat sink at which level the heat is rejected and utilized as outlined in Figure 1.

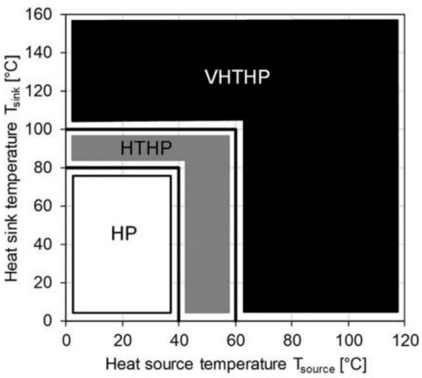

Figure 1. Proposed temperature levels for heat pumps (HP), high temperature HP (HTHP) and very (VHTHP) as described by Arpagaus (2018)

Conventional heat pump (HP) is hereby comfort heating conditions with a source temperature level up to 40°C while the heat rejection up to 80°C. High temperature heat pump (HTHP) extends the source up to 60°C with rejection increasing the temperature to 100°C. Beyond these levels with source temperature up to 120°C and rejection up to 160°C for very high temperature heat pump (VHTHP) which allow for steam generation.

Barmigbetan et al. (2018) investigated refrigerant options for both fluorinated and nonfluorinated options for a sink temperature level of 125°C and found R1233zd(E) and R600 had great potential.

Jiang et al. (2022) compiled a review of HTHP systems described in the literature and summarized refrigerants used as well as system performance and schematics. They have included pure components as well as developmental refrigerant blends as part of their summary and made recommendations for an increase of operating range and improvement of COP for temperature lifts below 40K.

Mairhofer and Stavrou (2022) performed a multi criteria study to investigate optimal refrigerants for HTHP applications. They modeled working fluids using PC-Saft (Perturbed Chain Statistical Associating Fluid Theory) and found that the occurrence of either dry compression or wet compression is highly dependent on fluid properties. This means for wet compression fluids superheating before the compressor suction is needed to avoid entering the two-phase dome during the compression process which will limit efficiency and impact compressor reliability.

This paper evaluates suitable pure, single component refrigerants with critical temperatures above 130°C for their tendency for wet compression as well different approaches to determine if wet compression can be expected.

REFRIGERANT PROPERTIES AND MODELING

The selection of refrigerant options for HTHP applications is dependent on them having a high critical temperature to ensure subcritical operation can be achieved to simplify controls as well as improve heat transfer and maintain large enthalpy differences in the condenser. Table 1 summarizes fluorinated and hydrocarbon refrigerant options with critical temperatures above 130°C. The fluorinated options evaluated are nonflammable with an ASHRAE Standard 34 (2024) flammability classification of 1. Likewise, the hydrocarbon options are highly flammable with a class 3 designation. The options are listed in order of increasing normal boiling point temperature with a GWP below 20. R-245fa has been added as a reference since it has been successfully used in ORC and heat pump applications.

Table 1. Investigated fluids in order of increasing normal boiling point temperature

Refrigerant [-]	GWP [-]	ASHRAE [-]	T_{crit} [°C]	p_{crit} [MPa]	NBP [°C]
R-717	0	B2L	132.4	11.4	-33.3
R-600a	1	A3	134.7	3.6	-11.8
R-600	4	A3	152.0	3.8	-0.4
R-1336mzz(E)	18	A1	130.4	2.8	7.4
R-1234ze(Z)	<1	n/a	150.1	3.6	9.9
R-1224yd(Z)	<1	A1	155.5	3.4	14.6
R-245fa	1030	B1	153.9	3.7	15.0
R-1233zd(E)	1	A1	166.5	3.6	18.3
R-601a	5	A3	187.2	3.4	27.8
R-1336mzz(Z)	2	A1	171.4	2.9	33.5
R-601	5	A3	196.6	3.4	36.1
Cyclopentane	5	A3	238.6	4.6	49.2
Hexane	1	A3	234.7	3.0	68.7
R-718	0	A1	374.0	22.1	100.0

Figure 2 provides a visualization of the refrigerant options based on their critical temperatures and normal boiling point as well as their molecular structure to provide insight into their relationship.

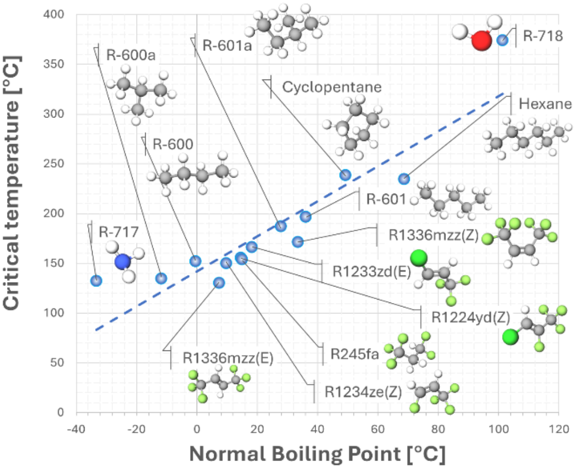

Figure 2. Critical temperature as a function of normal boiling point for investigated refrigerants and their structures

Generally, critical temperature and normal boiling point increase with increasing molecular weight. The relationship of critical temperature and normal boiling point temperature is different between hydrocarbon and halocarbons. For hydrocarbons it can be shown with a range from butane with a four-carbon chain to hexane with a six-carbon chain the critical temperature increases from 152°C to 235°C while the normal boiling point increase by about 70K from -0.4°C to 68.7°C. Depending on the shape of the two-phase dome and the slope of the isentropes a stronger or lesser tendency towards wet compression can be seen that needs to be considered for system design and reliability as described by Mairhofer et al. (2022). Different methods can be used to estimate the tendency of a refrigerant for wet compression based on its properties. Hwang et al. (2025) described an approach to determine the tendency of wet compression of refrigerants depending on the change of enthalpy along the progression of the isentrope for saturated vapor and the change in enthalpy along the saturated vapor line between suction and discharge pressure. An example to visualize the relationship is shown in the pressure- enthalpy and temperature-entropy graph in Figure 3

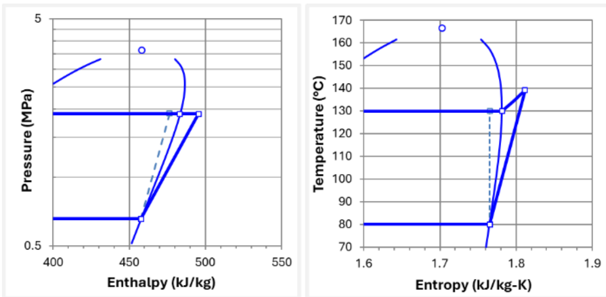

Figure 3. Pressure- Enthalpy and Temperature- Entropy diagram for R1233zd(E) visualizing wet compression tendency definitions

All three visualized compression processes start from saturated vapor at evaporation pressure. The dashed line in Figure 3 represents isentropic compression leading to wet compression. The second line follows the saturated vapor to condensing pressure level while the third line shows an isentropic efficiency of 70% leading to a superheat compressor discharge state.

Hwangs (2025) approach to form a ratio of enthalpy difference along the saturation curve compared to the increase in enthalpy along isentropic compression is defined in equation (1):

$$\lambda = \frac{\Delta h_g}{\Delta h_{is}} \qquad (1)$$

Values greater than 1 indicate a stronger tendency for wet compression while values below 1 would indicate less of a tendency for wet compression. Hwang described a scenario for a 50 K lift from 100°C source to 150°C sink. This consideration was expanded here for a scenario of a source temperature of 80°C and varying sink temperatures between 100°C and 150°C, the ratio of λ was determined for a selection of refrigerants with critical temperatures greater than 150°C as shown in Figure 4.

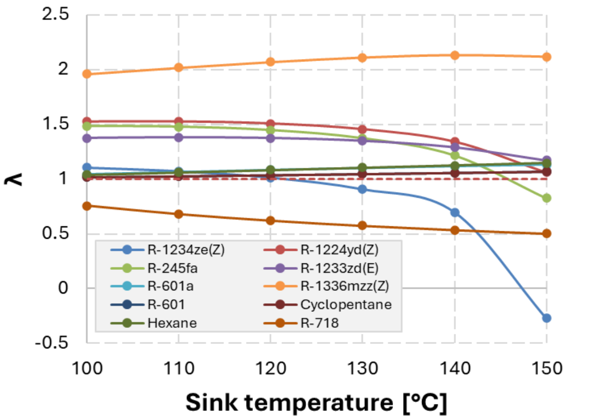

Figure 4. Wet compression tendency factor λ of high critical temperature fluids for varying sink temperatures

Many of the candidates show values close to 1 with no clear indication of wet or dry compression like pentane, cyclopentane and hexane. R-1336mzz(Z) has a positive value for λ across the investigated range indicating wet compression tendency. R-1234ze(Z) as well as R-718 with values lower than 1 have a tendency for dry compression accordingly. Figure 5 demonstrates another way to understand wet compression tendencies by assuming an isentropic efficiency of 70% and determining the resulting compressor discharge superheat (CDSH) on a logarithmic scale from saturated vapor at compression onset.

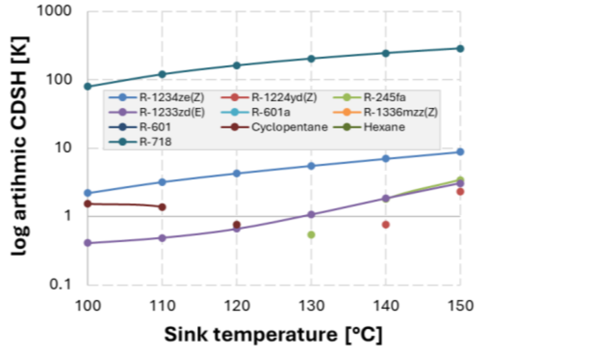

Figure 5. Compressor discharge superheat for 70% isentropic efficiency compression process

This methodology confirms for R-1234ze(Z) dry compression while R-1336mzz(Z) and hydrocarbons with higher critical temperatures have broadly no superheat with cyclopentane being the exception having positive values up to 120°C sink temperature level. R-718 shows the most pronounced level of superheat with values greater than 100K.
The enthalpy change ratio as well as the CDSH confirmation depend on the slope of the two-phase dome of the refrigerant. Therefore, another way of determining the tendency for wet compression is to normalize the entropy change for the target saturated suction temperature representing the source temperature level as shown in Figure 6.
The relative change in entropy confirms the slope of the dome of the investigated refrigerants. A negative slope indicates hereby dry compression tendency while a positive slope represents a tendency for wet compression due to the stronger slope of the dome favoring the compression process to enter the two-phase region. R-718 and R-717 have strongly negative slopes indicating no wet compression potential. All other options are shown in a more detailed view in Figure 6b) and R-1234ze(Z) with a negative slope confirms the dry compression while hexane with a positive slope indicating a stronger tendency to lead to wet compression.

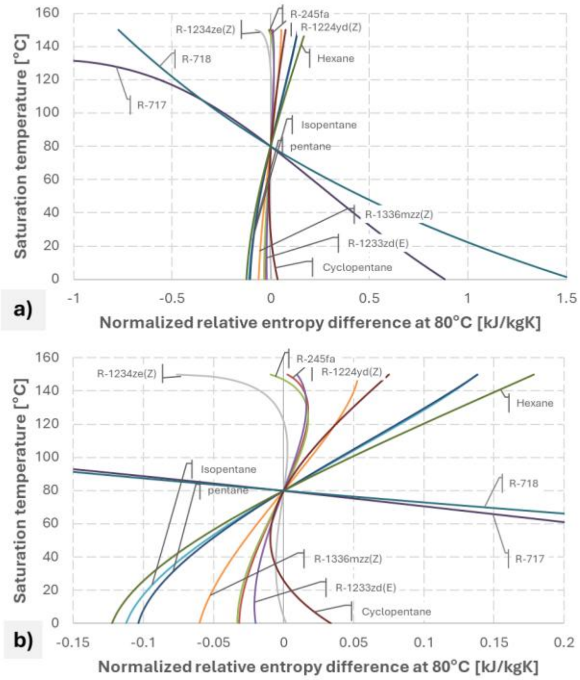

Figure 6. Wet compression tendency evaluation based on relative entropy difference with broad a) and detailed view b)

A simple thermodynamic model was developed to investigate the relative performance of the different evaluated refrigerant options regarding their performance and impact of wet compression potential. The evaluation was performed for a source temperature evaporation level of 80°C with a sink temperature condensing level of 130°C. The evaporator outlet condition is saturated with no subcooling and an isentropic efficiency of 70%. Figure 7 provides a summary of the results for relative COP and capacity as well as compressor discharge superheat.

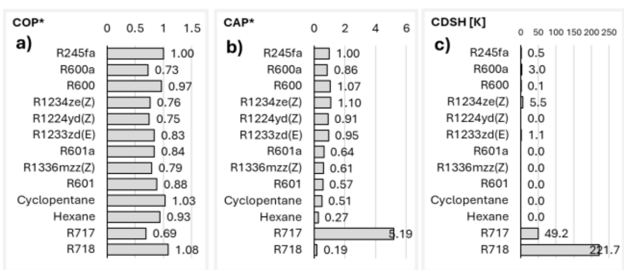

Figure 7. Summary of relative COP* a), relative capacity (CAP*) b) and CDSH c)

The results are compared to the baseline R245fa and show the lack of CDSH for most of the options except R-1234ze(Z), R-600a and R-1233zd(E). Next, conditions are adjusted to achieve CDSH by applying a suction line heat exchanger effectiveness of 50% which transfers heat from the liquid line to the suction line to ensure wet compression is avoided during operation. This leads to an increase in subcooling and therefore lower evaporator inlet quality but at the same time to increased superheat and therefore an increase in compressor power consumption. The results are summarized in Figure 8 and Figure 9.

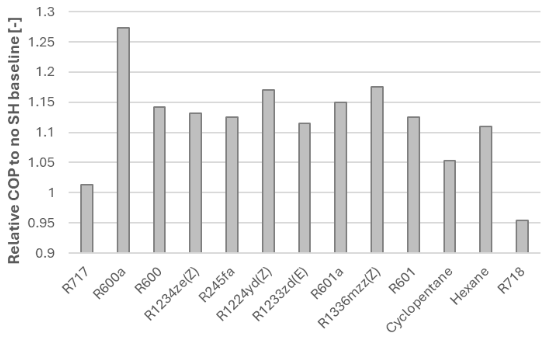

Figure 8. Relative COP of 50% SLHX compared to no SH baseline

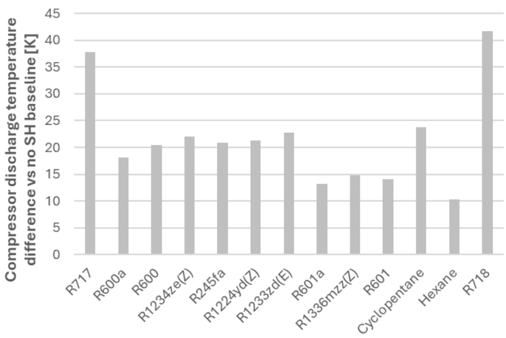

Figure 9. Compressor discharge temperature with 50% SLHX compared to no SH baseline

The relative COP change is more significant for refrigerants with a narrow two-phase dome compared to wider domes as the increase in subcooling is more pronounced compared to fluids that already have a competitive heat of vaporization and condensation. Further the change is more pronounced for fluids that have a stronger tendency for wet compression as more increase is applied compared to fluids that already have superheat in its baseline state.

CONCLUSIONS

This paper investigated HTHP options which can experience challenges due to the potential for wet compression. Different approaches were evaluated to determine the wet compression potential of refrigerants based on operating conditions and fluid properties. Hwang considers the change in enthalpy difference along the saturated vapor curve compared to the isentropic progression. Another method is to evaluate each option for compressor discharge superheat. Finally, the slope of the two-phase dome can be evaluated by characterizing if the slope is negative or having a tendency for dry compression or positive with a tendency for wet compression. Each method can provide insights into the tendency for wet compression that should be avoided for an efficient and reliable system design.

Wet compression is only one parameter when selecting a refrigerant for HTHP. Other factors that have to be considered include limitations on compressor discharge temperature in case lubricated compressor technology is used, suction and discharge pressure levels to avoid vacuum as well as to remain within maximum pressure limitations, to name a few others.

Ultimately, a detailed system model should be considered that includes transport property considerations in the heat exchangers and a more detailed representation of the compressor performance as a function of operating conditions.

NOMENCLATURE

CDSH : Compressor discharge superheat
CDT : Compressor discharge temperature
COP : Coefficient of Performance
GWP : Global Warming Potential
HP : Heat Pump
HTHP : High Temperature Heat Pump
λ : Wet compression indicator enthalpy ratio
PC Saft : Perturbed Chain Statistical Associating Fluid Theory
VHTHP : Very High Temperature Heat Pump
SH : Superheat
SLHX : Suction Line Heat Exchanger

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