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Performance evaluation of water as a heat pump fluid using calculations and its fundamental properties

H. Gijs Schimmel[a,*], Michel van der Pal[b], Cordin Arpagaus[c]

[a]Standard Fasel, Utrecht, The Netherlands
[b]TNO, Energy & Materials Transition Unit, Petten, The Netherlands
[c]OST - Eastern Switzerland University of Applied Sciences, Institute for Energy Systems (IES), Buchs, Switzerland

Abstract

Industrial processes require a significant amount of heat, which can be supplied by high-temperature heat pumps (HTHP) enabling a carbon-neutral operation. The best working fluid (i.e. refrigerant) for these heat pumps has been addressed earlier by many authors, both experimentally and through simulation. The results do not always coincide and show anomalous behaviour for water. This work assesses the performance of various natural refrigerants (i.e., water, methanol, acetone, heptane, hexane, pentane, butane, and ammonia) based on model calculations and explains the results from fundamental theoretical considerations. A standard heat pump vapor compression cycle was modelled, and the coefficient of performance (COP) was used as the key performance indicator. These calculations have been performed for superheating taken at the exit of the evaporator, as usual, and at the exit of the compressor. Next, building on a theoretical expression for COP, the characteristics of the refrigerants were analysed. The sources of irreversibility of the cycle were analysed for its dependence on the fundamental characteristics of a medium. The results reproduce literature results that water is the best performing refrigerant at heat delivery temperatures above 160 °C. A new finding is that water is also the best performing refrigerant at lower temperatures, provided that wet compression is used, which is standard industrial practice. Further, the theoretical analysis shows that the performance of a refrigerant is connected to the ratio of the specific heat capacity and the heat of evaporation. Among all known natural refrigerants, this ratio is lowest for water. Therefore, this conclusion is fundamental.

Keywords: High Temperature Heat Pumps; Steam; Water; Coefficient of Performance; Wet compression; Refrigerants; Heat Pump Media

1. Introduction

Process heat at 110 °C to 160 °C is used in various industrial processes, such as heating, humidification, cleaning, and sterilization [1]. Today, most of this process heat is generated by fossil fuels or electricity and is often transferred using steam as an energy carrier. Water vapor is a convenient fluid for heating purposes due to its high heat capacity and heat transfer properties. This allows for reasonable flow rates and piping diameters compared to other heating fluids, such as air [2].

As a natural refrigerant, water is readily available, environmentally friendly, non-toxic, non-flammable, low-cost, and has good security and stability, with a large latent heat of vaporization, [1], [2], [3], [4], [5]. Steam is by far the most used heat transport medium and heat pumps using water integrate seamless into these existing steam systems. Extensive experience and well-developed technology eco systems exist for steam around the world. Existing boilers or full-electric boilers can be used as back-up and start-up systems. For electrification of high temperature industrial heat via heat pumps it is the only option at delivery temperatures above 160 °C [6]. However, the physical properties of water, such as its large specific volume and very large heat of evaporation, lead to high-volume flow rates and large compression ratios.

* Corresponding author. Tel.: +31 6 4311 3101
E-mail address: gschimmel@standardfasel.nl

Currently, water vapor compressors are mainly centrifugal, screw, and roots compressors [3]. Multistage centrifugal water-vapor compressors offer higher volume flow rates, screw and roots water-vapor compressors have the advantages of fewer vibration components, a simple structure, good stability and a larger compression ratio. Today, all compressor types can utilize wet compression. With the new water-injected compressor and sealing technology, the heat supply temperature of HTHPs increased over time to 120-180 °C [3] or even over 200 °C with MVR technology and several compression stages [4]. Bless et al. (2017) [2] theoretically analysed various methods for producing saturated steam at 3 bar(a), including vapor compression, direct electrical heating, gas heating, heat pumps with waste heat use, and combinations thereof. In conclusion, HTHP technology was cost-competitive depending on the availability of waste heat and the electricity-to-gas price ratio. Later, Bertsch et al. (2018) [1] identified the need to develop oil-free turbo compressors with water as a refrigerant to further increase HTHP efficiency. While most cycles show a similar performance, the open cycle with liquid injection seems to be a viable solution whenever steam can be used directly [1]. Pachai et al. (2023) [4] presented a way for selecting the optimal refrigerant for HTHP applications and discussed selection criteria for natural working fluids, including molecular mass, triple point, boiling point, and critical point. Wu et al. (2020) [7] compared the performance of HTHP among R718 (i.e. water) and other refrigerants and showed that water performed best above 100 °C heat supply temperature. Wu and Hu (2023) [5] analysed the performance of water across different HTHP configurations and highlighted the advantages of a two-stage cycle with an integrated flash tank in terms of COP and exergy efficiency. Wu et al. (2020) [8] investigated the performance experimentally in a very high-temperature heat pump prototype using a twin-screw compressor with water injection. A COP of about 6.1 was achieved with a heating capacity of 285 kW at 85 °C evaporation and 117 °C condensation temperature. The highest condensation temperature reached 150 °C with a COP of 1.96. Finally, Ramirez et al. [9] tested a heat pump using steam as the medium and showed temperature lifts up to 90 °C and condensation temperatures up to 160 °C.

Pachai et al. (2023) [4] presented a way for selecting the optimal refrigerant for HTHP applications and discussed selection criteria for natural working fluids, including molecular mass, triple point, boiling point, and critical point. Zini et al. [6] presented an evaluation of different refrigerants for high temperature heat pumps, highlighting the importance of natural refrigerants. Andersen et al. [10] found that natural refrigerants provide the highest COP for most industrial applications.

Standard Fasel delivers industrial HTHPs and has extensive experience with steam. The motivation for this work was to investigate the performance of water as a heat pump medium, especially regarding its COP. In a business case for a heat pump it is often compared against either a fossil-fuel fired or a full-electric solution. Such a business case has a threshold in COP, below which no pay-back is achieved. Therefore the COP that can be realized is a dominant factor in final investment decision making for industrial heat pumps. For water, the authors initially found a mismatch between COP values derived from theory [11] and simulated COP values [4], [6], [10]. This paper aims to understand the reason why the COP varies between different media. A second goal is to bridge the gap between theory and simulation that the authors perceived in literature.

The performance and characteristics of water as a refrigerant for HTHPs are studied. Special attention is given to explanations for the difference between refrigerants. The group of refrigerants that is studied is on purpose limited to natural refrigerants. Simulations are used to study the performance of different refrigerants to reproduce literature results. Simulations are also used to investigate the effect superheating at the inlet versus the outlet of a compressor. The latter involves wet compression for non-skewed media and its effect on the performance is discussed. A theoretical analysis on the performance of different media is then performed to provide further insight. Implications for industrial heat pumps are discussed and conclusions drawn.

1.1. Natural refrigerants

An extensive evaluation on refrigerant media for HTHPs by Zini et al. [6] concludes that, depending on the condensation temperature, the natural media ammonia, methanol and water are optimal fluid choices. Natural refrigerants are the group of substances that are abundant in nature, such as water, CO_2, ammonia and hydrocarbons. They possess the following characteristics:

(1) their use as refrigerants will contribute negligibly to their natural concentrations,
(2) they show negligible ozone depletion potential, and
(3) they possess global warming potentials below 10.

Increasingly more companies are committed to the exclusive use of natural refrigerants. This paper has limited the choice of refrigerants to those suitable for use in a standard vapor compression cycle with heat delivery temperatures above 100 °C. This excludes refrigerants with a critical temperature below 100 °C such as CO_2. Nowadays alkanes are widely proposed as heat pump refrigerants. In this work, we selected the normal isomers of butane, pentane and hexane to represent this group. The second group contains substances showing hydrogen bonding such as water, methanol and ammonia. The refrigerants analysed in this paper are thus: water, methanol, ammonia, butane, pentane and hexane. For clarity of figures this list is not exhaustive. Results in this work can be extended to other refrigerants with relative ease.

1.2. COP: the performance indicator for heat pumps

The performance of a heat pump is best described by its Coefficient of Performance (COP). This COP is defined as the ratio between the *Heat delivered* Q_H delivered to a sink at T_H and the *Work input* w:

$$COP = \frac{Q_H}{w}. \tag{1}$$

The well-known expression due to S. Carnot [12] for the maximum COP of a heat pump uses the source temperature T_L and is:

$$\mathrm{COP}_{\mathrm{Carnot}} = \frac{T_H}{T_H - T_L}, \tag{2}$$

which assumes that the heat sources and sinks are at constant temperatures. When this is not the case, the COP shall be expressed using entropic mean temperatures that are defined by:

$$\bar{T} = \frac{Q}{\Delta S}, \tag{3}$$

which reduces to logarithmic mean temperatures for sources and sinks with a constant heat capacity [13]. The maximum possible COP using these mean temperatures, known as the Lorenz COP, becomes

$$\mathrm{COP}_{\mathrm{Lorenz}} = \frac{\bar{T}_H}{\bar{T}_H - \bar{T}_L}, \tag{4}$$

which is equal to $\mathrm{COP}_{\mathrm{Carnot}}$ when temperatures of the source and sink are constant.

1.3. Working principle of a basic one-stage heat pump

A general subcritical evaporation-condensation heat pump cycle is shown in Fig. 1 (A) [7].

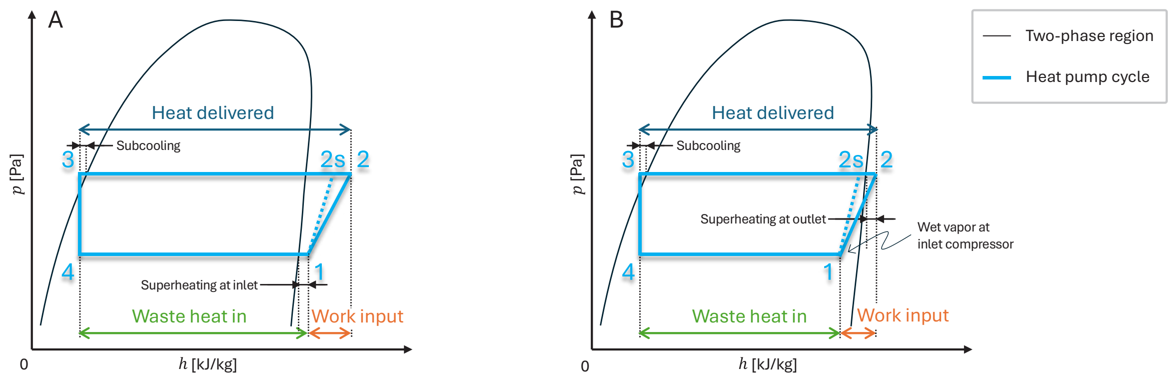

Figure 1. Pressure-enthalpy diagrams showing a heat pump cycle for water. The area within the black line (known as the vapor dome) is the two-phase region, where liquid and vapor coexist. (A) The refrigerant is superheated at the inlet of the compressor to avoid a liquid fraction at the outlet of the compressor. (B) Superheating at the outlet of the compressor. For refrigerants with a "non-skewed" domes, this typically means that compression starts in the two-phase regime, as is standard practice for water. For refrigerants with "skewed" domes, this approach makes sure that a liquid fraction is avoided during compression.

Such a heat pump takes a medium at the exit of an evaporator (point 1) at a low pressure, compresses the gas and brings it to the inlet of a condenser (point 2) where it condenses at a higher pressure delivering heat at a corresponding higher temperature (point 3), under an isobaric process. Finally, the liquid returns to the evaporator inlet (point 4) by flowing through an expansion valve, which is an isenthalpic process. In the evaporator, the liquid is evaporated at a constant lower pressure and corresponding lower temperature, which is an isobaric process.

2. COP estimates from simulations

The COP of heat pumps using different media described above were calculated. The analysis assumes heat exchange at a single temperature level in the condenser. This means that any superheating present in the vapor that enters the condenser is delivered to the heat sink at the condensation temperature. An example of such an arrangement is a pentane heat pump that produces steam through a re-boiling heat exchanger. Another example is a heat pump that uses steam as refrigerant and delivers steam to an industrial process. In both case the enthalpy contained in the superheating is used, but the temperature at which heat is exchanged is governed by the condensation temperature. This means that some heat is exchanged with a larger temperature difference, which in turn produces additional entropy and decreases the performance of the heat pump. The temperature difference in heat exchangers at the source and sink side of the heat pump have been neglected. Actual COPs will therefore be somewhat lower than the values presented here.

The simulations are performed for three cases. The first two cases are aimed to reproduce literature results, while the last case represents some the experience of the authors on industrial heat pumps. Given the goal to compare simulations and theoretical considerations, a simplified vapor compression cycle has been chosen. The heat loss from the cycle is neglected as well as the pressure loss within the cycle. The isentropic compression efficiency is chosen to be independent on the medium and on the temperature.

2.1. Characteristics of basic, detailed and industrial cases

The three cases are defined as follows:

- a basic case without superheating and subcooling and
- a detailed case where superheating (to ensure dry compression) and subcooling (to increase performance) are considered.
- an industrial case which uses a large temperature lift of 80 K, without superheating or subcooling.

The sets of assumptions also differ in the temperature lift, 40 K, 60 K and 80 K. The case parameters are summarized in Table 1. The basic case is chosen close to the case reported in [6]. The detailed case enables a comparison with results reported in [4]. The industrial case has large temperature lifts that are often encountered in industrial practice. For all cases an isentropic efficiency of 70% is assumed, which is again chosen to reproduce literature results. This efficiency depends on the compression technology and size of the compressor. We calculate the *Work input* and the *Heat delivered* to the process by means of a Python script using Coolprop [14]. For water we use the recommended IAWPS-95 formulation [15]. The references for the equations of state for methanol, ammonia, butane, pentane and hexane can be found in [16], [17], [18], [19] and [20] respectively.

Table 1. Parameters for the basic, detailed and industrial cases. The required superheating was imposed at the compressor inlet. In a second instance the cases were also analysed when superheating was imposed at the outlet rather than the inlet.

Case	basic	detailed	industrial
Superheating degree	0 K	15 K	0 K
Subcooling degree	0 K	10 K	0 K
Isentropic compressor efficiency	70%	70%	70%
Temperature lift	40 K	60 K	80 K

2.2. Simulation results, controlling superheating at the compressor inlet

The results shown in Fig. 2 reproduce curves published in literature [6], [4] and [7]. Though some differences exist (which we have not analysed further), these results all demonstrate that water is the most efficient refrigerant for delivery temperatures above about 160 °C (corresponding to a steam pressure of around 6 bar(a)). Further, what is present in all estimations is the peculiar behaviour of water when compared to the other media. Water shows very high COPs at high temperatures but possesses a steeper slope leading to lower COP values at lower temperatures. Water does not follow the convergence to a common COP at lower temperature as do other refrigerants. Why is water special as a medium?

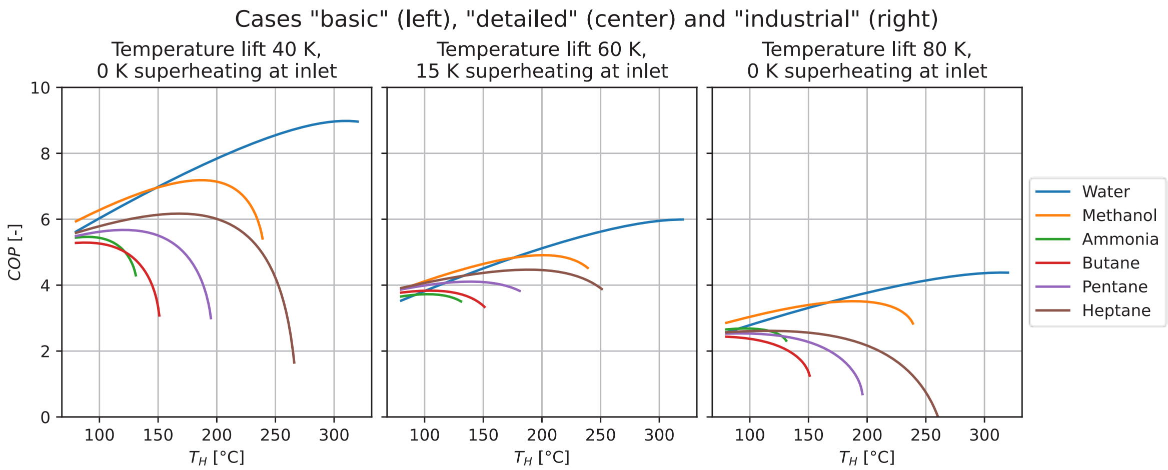

Figure 2. COP as a function of T_H of a heat pump for three cases and multiple refrigerants. The reader is referred to Table 1 for the parameters used for each case. Water is the best refrigerant medium above T_H = 160 °C. On closer inspection, especially water does not follow convergence of its COP towards low temperatures as do the other refrigerants.

The answer to this question lies in the fact that it is common practice to avoid any liquid fraction at both the inlet and the outlet of the compressor. A compression process that does not involve any liquid fraction during the whole process is described as "dry compression". Dry compression is used to prevent liquid hammer in the compressor. When an isentropic compression process of a saturated vapor at a low pressure to a higher pressure ends in the two-phase regime, the medium possesses a "skewed" vapor dome in the T-s diagram. For these media, the vapor at the inlet of a compressor needs to be superheated to achieve dry compression throughout the whole compression process.

However, media that have a non-skewed vapor dome, such as water vapor and methanol, starting with saturated vapor at the inlet means that the whole compression process is dry. Dry compression with water vapor results in massive superheating at the outlet of a compressor, even with very efficient compressors. As discussed above, a high degree of superheating at the outlet is thermodynamically not favourable as it increases the average temperature at which heat is delivered, resulting in a lower COP. In industrial water vapor compressors, liquid water is therefore injected at the inlet such that the water vapor at the exit of the compressor is only slightly superheated. This process is described as wet compression and is illustrated in Fig. 1 (B). It is therefore expected that wet compression increases COP, specifically for media with non-skewed domes.

2.3. Simulation results, controlling superheating at the compressor outlet

To enable wet compression, the simulation procedure is adjusted. Instead of controlling the degree superheating at the compressor inlet, it is now controlled at the compressor outlet. Refrigerants with a skewed dome will still follow a dry compression path. On the other hand, refrigerants with a non-skewed dome follow a partly wet compression path, starting in the two-phase region. The simulations for different refrigerants are comparable in the sense that the amount of superheating at the exit of the compressor is kept constant. This means that the negative effect of superheating at the inlet of the condenser on the COP is now similar, though not exactly equal. It shall be noted that the degree of superheating at the source becomes dependent on the refrigerant.

Referring to Fig. 1 (B), the procedure outlined here means that point 2 is known and point 1 is reversely calculated using the isentropic efficiency of the compressor. The results when superheating is controlled at the compressor outlet are shown in Fig. 3. It can be observed that water shows COP results that are about 10% higher for temperatures below 150 °C. By allowing wet compression, water is consistently the best refrigerant analysed here. Small improvements are also visible for several other refrigerants, which is connected to the observation that the degree of superheating at the outlet of the compressor is mostly lower with wet compression compared to dry compression. In the next section a theoretical analysis is presented regarding the factors that influence the COP, which are then evaluated for different media.

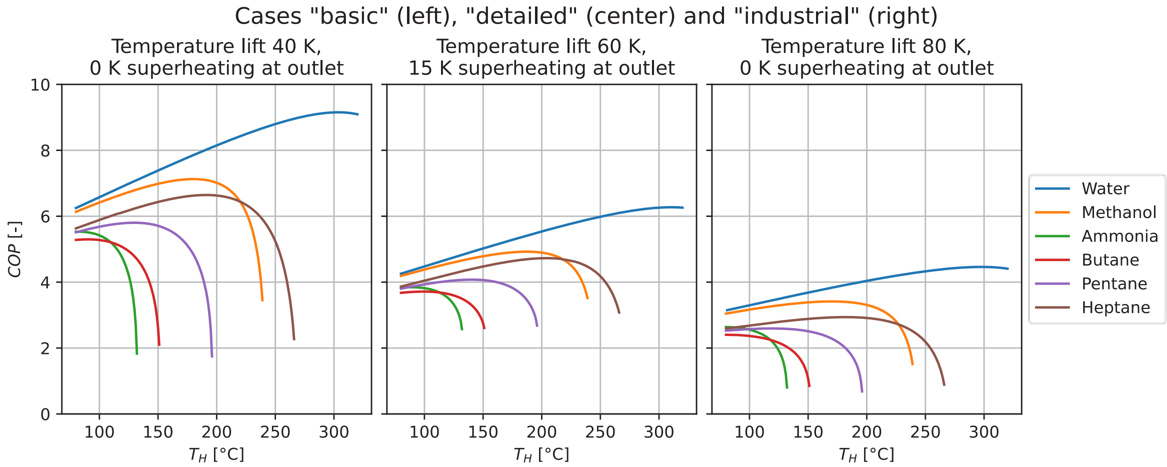

Figure 3. COP as a function of T_H of a heat pump for three cases and multiple refrigerants. The reader is referred to Table 1 for the parameters used for each case. The degree of superheating is taken at the outlet of the compressor rather than the inlet. For media like water this means that the compression starts in the two-phase regime.

3. Theoretical analysis

Above, it was investigated how different refrigerants perform for three different cases. In this section, a theoretical foundation for the difference between different refrigerants will be derived. The theoretical analysis will be limited to the same cycle as used in the simulations presented above, thus a subcritical evaporation-condensation heat pump cycle. Further, in this analysis, heat is delivered to the heat sink via condensation only, thus no superheating at the outlet of the compressor is present. Also, heat is absorbed from the heat source by evaporation only.

3.1. Theoretical considerations

Our aim is to find a theoretical explanation for the dependency of the COP on the heat pump medium, rather than just simulating them and compare. Jensen et al. (2018) [11] derived an expression for the COP of an actual heat pump cycle which uses a throttling valve to expand the medium from high to low pressure. The cycle is a subcritical evaporation-condensation heat pump cycle, similar to the one we have used in the simulations. We present Jensen's expression in the following form:

$$\mathrm{COP} = \mathrm{COP}_{\mathrm{Lorenz}}\, g(\mathbb{T})\, \eta_{is,c} \left(1 + \frac{w_{is,e}}{w_{is,c}}\right) + \left[1 - \eta_{is,c} - f\right]. \tag{5}$$

In this paper we have opted to use a strict sign convention meaning that work being done *on* the medium is negative. Therefore, the sign before the ratio $w_{is,e}$ over $w_{is,c}$ is positive rather than negative. For readability we have gathered all terms involving temperatures and temperature differences at the evaporator and condenser in a function $g(\mathbb{T})$.

Let us start by discussing the first term, $\mathrm{COP}_{Lorenz}\, g(\mathbb{T})\, \eta_{is,c}(1 + \mathrm{w}_{\mathrm{is,e}}/w_{is,c})$. This term can be thought of as describing the heat pump action. The theoretical maximum coefficient of performance, COP_{Lorenz}, is dependent on the source and sink temperatures only. The factor $g(\mathbb{T})$ depends on the temperature glides and the temperature difference over the pinch in the heat exchangers, relative to the sink temperature and the temperature lift. This factor is close to 1 since this paper neglects the temperature differences in source and sink. This factor is in good approximation not dependent on the refrigerant properties, specifically since we assume a subcritical evaporation-condensation heat pump, thus no glides are present. Next, the isentropic compressor efficiency, $\eta_{is,c}$, depends on the compressor technology and does not significantly depend on the refrigerant medium [21]. Thus, none of the factors discussed till now introduce a significant dependency of the COP on the refrigerant type.

The last factor, $(1 + w_{is,e}/w_{is,c})$, contains $w_{is,e}$ which is the isentropic work that can be extracted from the condensed liquid flowing from high to low pressure in the heat pump. Further it contains $w_{is,c}$, the isentropic work needed to compress the gaseous medium from low to high pressure. Both works are a function of the pressure difference between evaporator and condenser and are determined by the characteristics of the refrigerant. The ratio between these works is always negative. This term thus describes that the actual COP is lower than the theoretical COP when a throttle valve is used instead of extracting work. From a thermodynamic perspective, this makes the cycle less reversible.

Finally, we discuss the group $[1 - \eta_{is,c} - f]$. The fraction of the power used for compression is $\eta_{is,c}$. Consequently, the fraction of power that is directly converted to heat in the compressor is therefore $1 - \eta_{is,c}$. With a correction for heat loss from the system, f, the expression above results. In the following $f = 0$, since in the experience of the authors the heat loss can be made negligible for industrial-scale compressors.

The analysis presented here shows that the dependency of COP on the refrigerant only scales with the ratio between the isentropic work for compression and expansion, $w_{is,e}/w_{is,c}$. The aforementioned aim to find a theoretical explanation for the dependency of COP on refrigerant can now be narrowed to finding a theoretical expression for this ratio.

3.2. Approach

First, an expression for the isentropic work needed to compress an amount of a medium from low to high pressure is determined. By definition an isentropic process is reversible. This means that the isentropic work produced by expansion of the same amount of gaseous medium between high and low pressure equals the work needed for compression. The expansion work for an actual liquid that is expanded is then calculated by taking into account how much vapor is present at each point during the expansion process. Note that throughout this analysis work and heat are expressed per amount of refrigerant (for instance per kilogram).

3.3. Isentropic work for compression and expansion

We envision a Carnot engine acting between two reservoirs at T_L (the evaporator) and T_H (the condenser). The engine contains a medium that is compressed and expanded between the pressures corresponding to these temperatures. The medium delivers heat to a sink via condensation only, thus excluding the effect of superheating and sub-cooling. The amount of heat L that is released is the heat of evaporation. For a Carnot engine, which is isentropic, the amount of work needed is $w_{is,c}$. The definition of COP can therefore be written as

$$COP = \frac{L}{w_{is,c}}. \tag{6}$$

Combining this equation with Carnot's equation for COP (1) we get:

$$\frac{L}{w_{is,c}} = \frac{T_H}{T_H - T_L}. \tag{7}$$

Rearranging, we find

$$w_{is,c} = L\frac{T_H - T_L}{T_H}. \tag{8}$$

Expansion is the reverse process apart from the fact that expansion work is negative (since performed *on* the medium), which gives:

$$w_{is,e} = -L\frac{T_H - T_L}{T_H}. \tag{9}$$

The work produced by expansion of a liquid is very small due to the high bulk modulus of liquids compared to gases and is neglected here.

3.4. Amount of vapor produced

During compression, some refrigerants undergo wet compression as discussed above. A small fraction of liquid evaporates during this process. In the following, this small fraction is considered negligible and the amount of gas that undergoes compression is considered to be constant. Expansion, on the other hand, starts in the liquid phase, meaning that initially the gas fraction is zero and stays small during the expansion process. During expansion, as the pressure drops, vapor evaporates from the liquid. This is accompanied by a temperature decrease of the liquid. From a heat balance, assuming adiabatic conditions, it is concluded that the heat that is released by the temperature decrease of the liquid is used to evaporate the vapor. The amount of vapor that is produced can be written as a fraction $x(T)$ of the amount of liquid. Consequently the amount of heat used to evaporated the vapor is $x(T)L$, where L is the heat of evaporation, which is assumed a constant in this analysis. As indicated, this heat is equal to the heat released by cooling the liquid. Thus, it is given by the amount of liquid multiplied by its the heat capacity and the temperature difference, $\left(1 - x(T)\right) C_{liq}\ [T_H - T]$. Combining these expressions and using the fact that the vapor fraction $x(T) \ll 1$ gives:

$$x(T) = \frac{C_{liq}}{L}[T_H - T]. \tag{10}$$

3.5. Ratio of isentropic expansion and isentropic compression work

The isentropic work produced during the expansion process can be expressed as a function of the temperature T:

$$w_{is,e}(T) = -L\frac{T_H - T}{T_H}. \tag{11}$$

The total work that is produced depends on the amount of gas that is expanded, for which Eq. (10) is derived. Expansion from temperature T to $T + dT$ produces an amount of work equal to:

$$dw_{is,e} = x(T)\frac{dw_{is,e}(T)}{dT}dT. \tag{12}$$

Eq. (11) can be used to find the derivative of the work with respect to temperature. Integrating this expression from condenser temperature T_H to evaporator temperature T_L gives the expression for the work produced by the mixture of liquid and gas:

$$w_{is,e} = \int_{T_H}^{T_L} x(T)\frac{dw_{is,e}(T)}{dT}dT = \frac{C_{liq}L}{LT_H}\int_{T_H}^{T_L}[T_H - T]dT =$$

$$= \frac{C_{liq}}{T_H}\left[T_H(T_L - T_H) - \frac{1}{2}(T_L^2 - T_H^2)\right] \tag{13}$$

which can be rearranged to:

$$w_{is,e} = -\frac{1}{2}C_{liq}\frac{(T_H - T_L)^2}{T_H}. \tag{14}$$

Recalling that the work for compression from T_L to T_H is given by:

$$w_{is,c} = L\frac{T_H - T_L}{T_H}, \tag{15}$$

the ratio between the work produced by expansion of the mixture of gas and liquid to the work needed for compression becomes:

$$\frac{w_{is,e}}{w_{is,c}} = -\frac{1}{2}\frac{C_{liq}}{L}(T_H - T_L). \tag{16}$$

The determining factor in this expression, C_{liq}/L, as well as the right hand side of equation (16) have been evaluated for the refrigerants selected in this work, see Table 2 for an overview. Comparing the first column with Fig. 3 (at $T_H =$ 100 °C), it is concluded that the ratio of C_{liq}/L evaluated at T_H is a reasonable estimator of the relative performance of different refrigerants. The tabulated values of the COP reduction fraction, which is the right hand term of Eq. (16), confirms the general order in the performance of the refrigerants studied. A calculation of C_{liq}/L for all media available in CoolProp [14] confirmed that water has the lowest value of C_{liq}/L at temperatures of 50, 100, 150 and 200 °C.

Table 2. A theoretical analysis showed that the COP is reduced by a factor that scales with the ratio of heat capacity versus the heat of evaporation. This is shown on the left side of the table. On the right side the factor by which the COP is reduced is shown as a percentage for the three cases studied. All values in the table have been evaluated for $T_H = 100$°C, since at this temperature all refrigerants are well below their critical temperature. The heat capacity of the liquid is the average value between T_L and T_H and the heat of evaporation is taken at the average of T_L and T_H. The last column gives the volumetric heating capacity.

Medium	C_{liq}/L **at 100 °C**	**COP reduction due to throttling** $\frac{1}{2}C_{liq}/L\,(T_H - T_L)$			**VHC** T_H **= 100 °C,** T_L **= 60 °C**
Unit / Case	[1/K]	basic	detailed	industrial	[kJ/m³]
Water	0.0019	4%	5%	7%	294
Methanol	0.0031	6%	8%	10%	1042
Ammonia	0.0098	13%	18%	21%	14,754
Heptane	0.0081	15%	22%	28%	328
Pentane	0.0092	16%	23%	30%	1,795
Butane	0.0120	20%	27%	34%	4,072

4. Discussion

Several articles contain a comparison between several refrigerants for HTHPs, also taking water into account [4], [6], [10]. As indicated in the introduction, the authors found that the results for water cannot be explained by theoretical work [11]. While all refrigerants show convergent behaviour in their COP with decreasing temperature, water does typically follow a different trend. This work studied the reason why. The explanation is that for water a dry compression process gives very high superheating degrees at the outlet of the compressor, leading to lower COP values. When the degree of superheating is taken at the outlet of a compressor rather than the inlet, simulations for the chosen refrigerants show convergent behaviour, also for water. Further, water stands out as the refrigerant with the highest COPs as dictated by theoretical considerations. Controlling the superheating at the outlet of a compressor results in optimal efficiencies for all types of media. In the case of water this is actually standard industrial practice [22].

The theoretical analysis presented here confirms the well-known fact that the expansion work scales with the amount of vapor produced by flashing during expansion of the refrigerant medium from high to low pressure. This production of vapor can be reduced by sub-cooling the high-pressure liquid refrigerant. This provides an explanation for the well-known positive effect of sub-cooling on the performance of a heat pump. This sub-cooling is also achieved when internal heat exchangers (IHX) are used. For cases where all heat is delivered at a fixed temperature, the COP can further be increased by reducing the amount of superheating at the outlet of the compressor. Allowing wet compression and regulating the amount of superheating at the outlet of the compressor is recommended.

Compression technologies for high performance heat pumps shall be able to handle wet vapors at the inlet of the compressor. The volumetric fraction of the liquid is in all cases very small. This means that liquid jamming will only occur when a huge liquid surplus at the inlet is used. Today, thanks to much improved control of the amount of liquid, all compressor types can handle wet compression. Commercial centrifugal compressors commonly inject liquid into the inlet of the compressor and thus allow wet compression. Also screw type compressors can handle liquids at their inlets.

The discussion of the theoretical equation for the COP of a heat pump by Jensen et al. [11] showed that a large negative effect on refrigerant performance is the isentropic work during expansion that is not harvested when a throttling valve is used. This non-ideality is known as the “throttling loss”. The analysis presented in this work found that the reduction in COP for a simple cycle scales with $\mathrm{C_{liq}/L}$, independent on the medium. This can be used as a quick check to assess the potential performance of a refrigerant. However, the outcome is only valid when the refrigerants are used optimally, which means a small and similar degree of superheating at the exit of the compressor. In Fig. (4) the simulations for superheating controlled at the outlet of the compressor are compared to the theoretical expression. This theoretical expression is Eq. (5) for single high and low temperature levels, no temperature differences at the heat exchangers taken into account (meaning $g(\mathbb{T}) = 1$) and negligible heat loss from the cycle (thus $f = 0$):

$$\mathrm{COP} = \frac{T_H}{T_H - T_L}\,\eta_{is,c}\left(1 - \frac{1}{2}\frac{C_{liq}}{L}(T_H - T_L)\right) + \left[1 - \eta_{is,c}\right]. \tag{17}$$

The comparison in Fig. 4 shows that the theory developed by Jensen et al. together with the theoretical work presented here provides a reasonable prediction of the COP for standard vapor compression cycles. Especially closer to the critical point the assumption that the latent heat of evaporation is constant with temperature breaks down leading to larger differences between simulations and theory. The initially observed deviation between theory and simulation in literature has been bridged and can be understood using the concept of wet compression and the theoretical explanation for the performance difference between refrigerants.

Water stands out as the best refrigerant for high temperature heat pumps with respect to performance. Also, for heat delivery temperatures above 160 °C it is the only feasible choice. Water is a very good choice when heat exchanger can be omitted. Well-known examples are open heat pump commonly called mechanical vapour recompression systems, in a published industrial distillation installation operating between about 83 °C and 106 °C [23]. Due to relatively small temperature lift of this case, assuming that heat exchangers would have increased the internal temperature lift by 6K, the COP of an MVR is 26% higher than that of a closed heat pump. A heat exchanger at the outlet can be omitted when steam is delivered to a steam network. This improves the COP of High Temperature Steam Heat Pumps by a few percent, depending on the temperature lift.

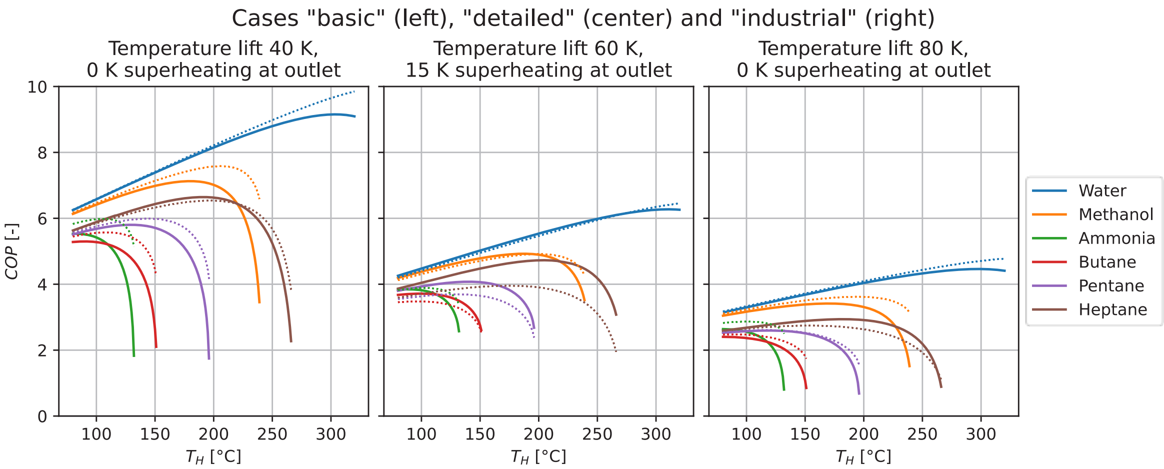

Figure 4. The simulation results shown in Fig 3 with solid lines compared to the theoretical expressions given by Eq. (17) in dotted lines with the same colour.

For lower heat delivery temperatures, the benefit of water becomes increasingly smaller. Water is not expected to be the medium of choice for closed heat pumps at temperatures much below 100 °C due to its low Volumetric Heat Capacity (VHC) [6], [24], the heat of evaporation per unit volume. VHC is commonly defined as the product of the density at the suction side of the compressor times the heat of evaporation:

$$VHC = \rho_{suct}\, L. \tag{18}$$

In Table 2 it is apparent that water has a very low VHC and therefore requires compressors that are capable of high volumetric flows. Also, due to its high heat of evaporation, water requires large pressure ratios. These are factors that drives up the costs. However, for a given process heating demand and a given temperature lift, the amount of electricity fed into a compressor is similar for each medium, be it a bit smaller for water due to its high COP. Therefore, components such as electricity connection, variable frequency drive, drive motor and control system have similar costs between different media. And finally, the well-known fact that the efficiency of heat engines scales with their size means that a good performance can be expected. Given the dominance of the performance of a heat pump in financial decision-making, the authors expect that water will be a dominant medium for high temperature heat pumps. An argument why both heat pumps smaller than 1 MWth and heat pumps larger than 10 MWth may be financially less attractive is contained in a paper submitted by one of the authors [25].

5. Conclusions

Refrigerants are best compared by keeping the degree of superheating constant at the *outlet* of a compressor rather than at the *inlet*. This results in dry compression for media with a skewed vapor dome while reproducing the industrial practice of wet compression for refrigerants that exhibit a non-skewed dome like water. It ensures minimal entropy increase due to superheating at the outlet of the compressor for all media. The theoretical analysis shows that the performance of different media is reduced by a term that scales with the specific heat capacity divided by the heat of evaporation. Both are characteristics of the refrigerant medium, and their ratio can be used to assess the performance of a potential refrigerant medium. It is concluded that water is the best performing refrigerant for high temperature heat pumps. This conclusion is supported by simulations and can be understood from the theoretical analysis presented. The perceived inconsistency in the COP of water as a refrigerant between simulation results and theory in literature disappears when superheating is controlled at the outlet of the compressor. Water's low VHC requires large compressors in terms of volume and its high pressure ratios means a multiple compressor in series. The costs associated with the amount of work input are not increased, therefore the cost increase of a cheat pump using water as the medium is limited. Since performance is a dominant factor in financial decision making, it is expected that water will play an important role as a medium for high temperature heat pumps with heat delivery temperatures above 100 °C.

Nomenclature

Latin symbols and abbreviations

C	heat capacity at constant pressure of the liquid [kJ/(kg K)]
COP	coefficient of performance [-]
f	compressor heat loss ratio [-]
h	enthalpy [kJ/kg]
L	heat of evaporation [kJ/kg]
p	pressure [Pa]
Q	heat flow [kW]
s	entropy [kJ/(kg K)]
T	temperature [K] or [°C]
$\bar{T}$	entropic mean temperature [K]
$g(\mathbb{T})$	factor that takes the effect of temperature differences and glides on the actual COP into account [11]
VHC	volumetric heat capacity [kJ/m^3]
w	work [kW]
x	mass fraction of gas in a gas-liquid mixture [-]

Greek symbols

η	efficiency [-]
ρ	density [kg/m^3]

Subscripts

c	compression
e	expansion
$suct$	suction side of compressor
H	high, indicating the condenser of the cycle
is	isentropic
liq	liquid
L	low, indicating the evaporator of the cycle
$Lorenz$	Lorenz cycle

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