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Analysis of natural refrigerant for different applications in heat pumps above 100ºC

Kenneth Hoffmann[a], Jan Gerritsen[b]

[a]GEA Heating and Refrigeration Technologies, Unit 9, Conqueror Court, Sittingbourne, Kent, ME10 5BH, United Kingdom
[b]GEA Heating and Refrigeration Technologies, De Beverspijken 7c, 5221 EE `s-Hertogenbosch, Netherlands

Abstract

Analysing suitable natural refrigerant for use in high temperature heat pumps for heating demand requiring temperatures between 100ºC to 200ºC. Carbon Dioxide (CO_2), Pentane and Steam have been identified as suitable natural refrigerant. Each refrigerant have their weakness and strength which makes them most suitable for different applications. It has been identified that CO_2 can deliver up to 130ºC, but only when the heat sink inlet temperature is less than 30ºC is the efficiency high enough to make it an interesting option. Pentane is a flammable refrigerant and is not suitable for all environments. Pentane operate sub atmospheric pressure below 36ºC saturated temperature, to minimise the risk of air entering the refrigerant circuit and creating a potential explosive mixture, a pentane heat pump should not operate below 36ºC saturated temperature. Pentane has a low volumetric evaporation energy at low temperature so preferable the suction pressure should not be less than 80ºC to make pentane heat pumps economically attractive. Pentane heat pumps are most suitable for pressurized hot water systems where there is a temperature difference between inlet and outlet of the heat sink. Steam has a very low density below 100ºC which will require 4 – 8 times larger compressor and heat exchangers per kW than traditional refrigerants like ammonia. To minimize compressor and heat exchanger sizes heat lifts below 80ºC should be done with traditional heat pumps and steam compression should only do the last lift from 80ºC to the desired steam pressure. Steam compression is best suited for application requiring steam especially if the steam can be used directly without additional heat exchanger.

Keywords: Heat Pump; Carbon Dioxide; HydroCarbon, Ammonia; Water; Energy Efficiency

1. Introduction

Industrial heat recovery from refrigeration plants started to take off in the late 20th Century. Many plants started to be installed with heat recovery from superheated discharge gas and heat recovery from oil cooling. The energy was normally used for pre-heating of incoming water to 30 - 35ºC. With a low investment cost and a little extra pipework and additional heat exchanger it was possible to achieve an energy and running cost saving. In the beginning of the 2000s the industry started to request higher grade heat as there only were limited gains with pure low grade heat recovery. This lead to the first high temperature heat pumps being installed for recovering the condenser heat and boost it up to higher temperatures. The market started quickly to evolve with add-on heat pumps being able to recover the heat from the refrigeration plant at 25 - 35ºC and delivering hot water at up to 85ºC. This opened up a large new market for heat recovery from the refrigeration system as it was not only the energy in the superheated gas and oil cooling which could be recovered but all the waste energy from the refrigeration plant could now be recovered. Although temperatures up to 85ºC at the time was possible, most installation were for much lower temperatures, around 55 - 65ºC. At these temperatures it was possible to achieve a heating COP of 7 – 10 which resulted in a very short payback of the installation, which was the main driver for the investment decision. In the 2020's the situation changed again, now we see that the industry demand higher temperatures of 80 - 95ºC. Most ammonia heat pump manufacturer are now able to offer heat pump solutions for heat recovery from the refrigeration plant and supplying up to 95ºC hot water. For these higher temperature heat pump the heating COP is around 3 – 4. The lower efficiency extend the payback period of the installation, but with increasing carbon tax and other incentives to electrify the industry there is a general trend for industry to try and cover all heating demands below 95ºC with ammonia heat pumps. This trend is now spreading outside the traditional food and beverage industry which already have an industrial ammonia refrigeration system, this creates new challenges to find the best heat source when there is no waste heat from the refrigeration plant to tab into. The industry is also requiring even higher temperatures, above 100ºC. For these higher temperatures there is not field tested solution with ammonia heat pumps as manufacturers commercial portfolio all ends around 95ºC. For temperatures above 100ºC the focus is on using different refrigerant. Whereas ammonia offer a very high efficiency for all applications between - 40ºC and + 95ºC, it is not the same picture for temperature above 100ºC[1]. There is not one refrigerant which is the best choice for all applications above 100ºC. The different natural refrigerant available offer different benefits which makes them most suitable for specific applications. Carbon Dioxide, Pentane and Water will be evaluated in this paper to determine the most suitable application for the different refrigerant.

2. Main Section

Carbon Dioxide, Pentane and Water have very different thermodynamic characteristic when operating at temperature above 100ºC. Carbon Dioxide is in the transcritical area as the critical point is 31.32ºC. When delivering heat energy above this temperature Carbon Dioxide will not be condensing, but it will be gas cooling without a phase change. Pentane is flammable and have a low heat of vaporization (268 kJ/kg at 120ºC), so it is necessary to circulate a large mass flow per kW. Water on the other hand have a very high heat of vaporization (2202.2 kJ/kg at 120ºC), so only a small mass flow is required per kW capacity, but when designing heat pumps and refrigeration plant the most important is the volumetric evaporation energy as this determines the compressor size needed for heat pump. Solutions which require large compressors and heat exchanger sizes per kW of heating can become economically unattractive. It is predicted that many new technologies will enter the high temperature heat pump market over the coming years and CAPEX and OPEX will be the key driver for the investment in decarbonisation with heat pumps.

All calculations in this study is based on 100% isentropic efficiency of the compressors. Different refrigerants are most suitable for different compression technologies and as the study is focused on refrigerants only and not on compression technologies, we have chosen to use the same standard for all refrigerants as this gives the most fair comparison although the actual performance figure for each refrigerant will differ from real life measurements. There can be large differences between the isentropic efficiency of different compression technologies varying from 30% to 90%, so choosing the right compression technology is also very important, but this topic is not covered in this paper.

Table 1. Physical properties of high temperature refrigerants

**R744 (CO_2) will not be boiling at atmospheric pressure as it will be in solid state (dry ice).*

Refrigerant	R601	R718	R744
Molecular structure	CH3-3(CH2)-CH3	H2O	CO2
Molar weight	72.15	18.0	44.0
Boiling point at 1.013 bar (°C)	36.1	100.0	-78.51*
Critical temperature (°C)	196.6	373.9	31.0
Critical Pressure (bar)	33.7	22.1	73.8
Heat of vaporization @ 120°C (kJ/kg)	268	2202.2	-
Volumetric evaporation energy @ 120°C (kJ/m^3)	6630	2471	-
Volumetric evaporation energy @ 85°C (kJ/m^3)	3588	812	-
GWP_{100} (CO_2=1)	11	0	1
Safety group (ASHRAE 34)	A3	A1	A1

2.1. Transcritical Carbon Dioxide (CO_2) heat pump up to 130ºC

There are heat pumps available on the market for delivering heating water at up to 130ºC according to IEA Annex 58 using CO_2 as refrigerant. As the heating is done by gas cooling the 130ºC is achieved by having a discharge gas of the CO_2 of up to 160ºC. To achieve this high discharge temperature it is necessary to superheat the refrigerant before compression. This can be done with an internal heat exchanger between the gas outlet of the gas cooler and the refrigerant outlet from the evaporator. The internal heat exchanger helps achieving higher discharge temperature but is also helps improving the efficiency of the heat pump. For a reasonable performance of the CO_2 heat pump it is necessary to cool the gas to below the critical point (T = 31.03ºC, h = 335.7kJ/kg) on the saturation curve, otherwise it is mainly flash gas after the expansion valve and a minor part liquid. Flash gas flows straight to the compressor without absorbing any energy from the heat source and it is critical for the efficiency of the heat pump that most of the energy comes from the heat source and not from the electrical energy used to compress the gas. All the energy used for compressing gas which does not work as energy uptake from the heat source is wasted energy, so it is important to have as little flash gas as possible after the expansion valve. To cool the CO_2 gas to less than 31.03ºC on the saturation curve it is required that the heat sink enters the gas cooler at lower temperature. If the incoming heat sink water is warmer an internal heat exchanger can help cooling the gas to below 31.03ºC. This helps reducing the flash gas, but for CO_2 the additional superheat before compression reduces the density of the gas (this is similar to ammonia where superheat also have detrimental effect in the compressor efficiency), which leads to less mass flow through the compressor. Due to the 2 effects working against each other, there is a small efficiency improvement by adding internal heat exchanger to CO_2 heat pumps. The range of commercial CO_2 compressor that are available on the market has a maximum suction pressure of 25ºC (65 bar). This limits the available heat sources for this type of heat pump[2]. For high temperature application it is a benefit to have the highest possible heat source temperature as this gives the best efficiency but due to compressor suction pressure limitations there is a limit to what is possible with CO_2 heat pumps.

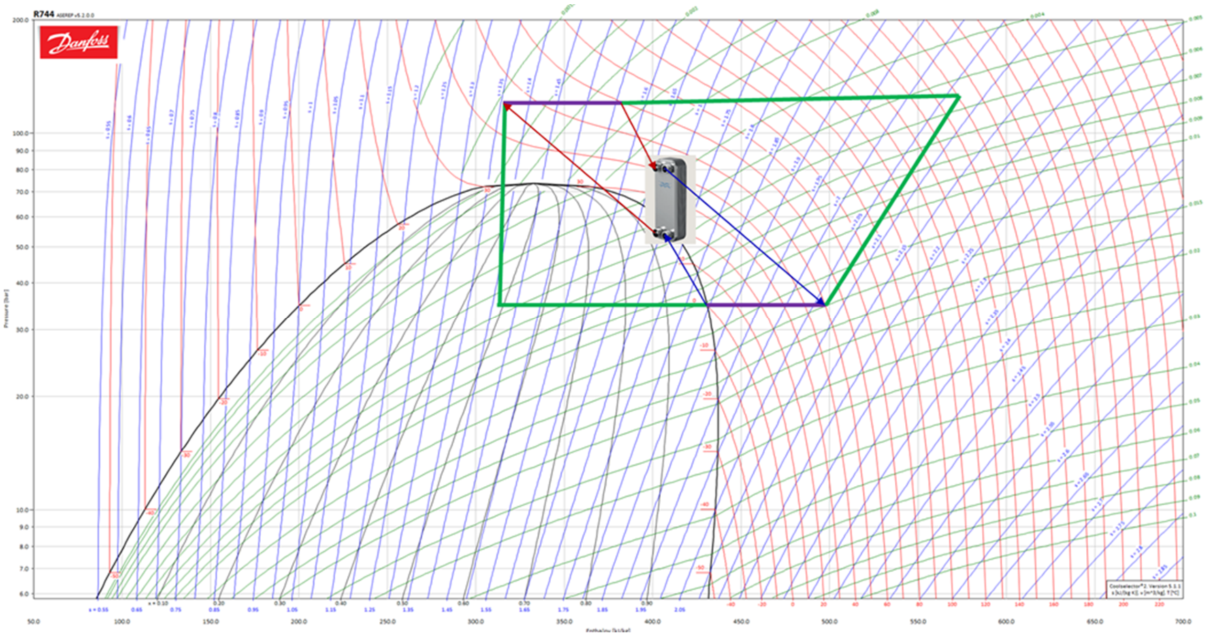


Figure 1. R744 (CO_2) heat pump in logP-h diagram

The graph in figure 1 shows an example of a CO_2 transcritical heat pump, the graph is based on an evaporation temperature of 0ºC and a discharge pressure of 110 bar. The graph also shows the effect of an internal heat exchanger, cooling the gas after the gas cooler and superheat the gas before compression.

Table 2. Operation condition and efficiency of CO_2 transcritical heat pump
Evaporation temperature 0ºC, condensing pressure 110 bar.

Heating water	Discharge temperature	CO_2 temperature after gascooler	Suction superheat	Flash gas	Heating COP
55ºC to 90ºC	100ºC	60ºC	0 K	65%	2
35ºC to 90ºC	100ºC	40ºC	0 K	34%	3.5
5ºC to 90ºC	100ºC	10ºC	0 K	3%	5
55ºC to 130ºC	160ºC	60ºC	22 K	50%	2.5
25ºC to 130ºC	160ºC	30ºC	22 K	23%	4.0

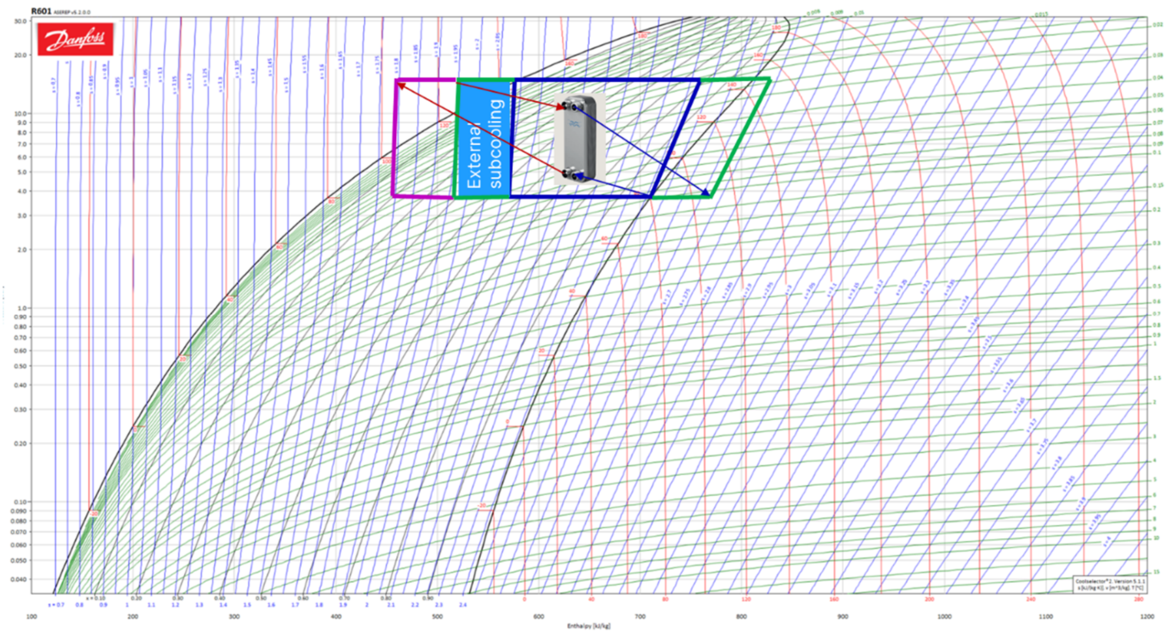
Based on the process showed in the graph in figure 1, we have calculated the theoretical performance of a CO_2 heat pump at different flow and return temperature of the heating water, with or without superheating the gas before compression. The calculations in Table 2 is theoretical calculation. In the first 2 rows are assumed 0K superheat, this would not be possible with the commercial range of semi hermetic CO_2 compressor on the market as there is a requirement of minimum 10K superheat for safeguarding of the compressor. The table shows that without an internal heat exchanger to superheat the gas before compression it is only possible to achieve discharge temperature of 100ºC, which is not sufficient to reach 130ºC hot water. When just looking at the 3 top rows of the table, we see that the incoming heat sink water temperature have big influence on the amount of flash gas after the expansion valve and subsequently the efficiency of the heat pump. Heating water from 5ºC to 90ºC (COPh = 5) is 2.5 times more efficient than heating the water from 55ºC to 90ºC (COPh = 2). For each degree of additional gas cooling from 60ºC down to 10ºC (first three rows in table 2) the efficiency improves with 3%. By adding an internal heat exchanger to pre-heat the CO_2 before compression with 22K, it is possible to achieve 160ºC and thereby 130ºC hot water temperature. The additional superheat of the CO_2 before compression gives a small amount of efficiency gain, but the most important is that it makes it possible to get to the higher water temperature.

Based on the findings in this study we concluded that CO_2 transcritcal heat pumps are particularly suited for applications like boiler make-up water, drying or de-humidification processes where there is a large temperature difference between inlet and outlet of the heat sink and a low heat source temperature.

2.2. Pentane heat pumps up to 180ºC

Pentane has a high critical temperature of 196.6ºC, which makes it suitable for high temperature heat pumps. Pentane is in safety category A3, so a highly flammable refrigerant. The refrigerant will be sub atmospheric below 36.1ºC. To avoid air and refrigerant mixture inside the heat pump the pressure should always be kept above 1 bar(a). In contrast to CO_2 heat pumps which cannot operate with suction temperature above 25ºC, Pentane heat pumps should not operate with suction temperature below 36.1ºC[3].

Figure 2: R601 (Pentane) heat pump in logP-h diagram



The graph in figure 2 shows an example of a Pentane (R601) heat pump, the graph is based on an evaporation temperature of 80ºC and a condensing temperature of 145ºC. The graph also shows the effect of adding external subcooler and an internal heat exchanger for superheating the gas before the compression.

Table 3. Operation condition and efficiency of Pentane heat pump

Evaporation temperature 80ºC, condensing temperature 145ºC.	Discharge temperature	Internal subcooling	Flash gas	Heating COP
No superheat	145ºC	0 K	53%	3.9
20 K Superheat	145ºC	14 K	41%	4.4
40 K Superheat	159ºC	28 K	30%	5.1
60 K Superheat	178ºC	42 K	18%	5.4

Based on the process showed in the graph in figure 2, we have calculated the performance of Pentane heat pump, in table 3. In the first row of the table with no superheat before compression, the compression will be into the 2 phase area, this is undesirable for the reliability of the compressor. When operating in the area from 80ºC (evaporation temperature) to 145ºC (condensing temperature) without any subcooling of the refrigerant after condensation we get 53% flash gas after the expansion valve. From the transcritical CO_2 heat pumps we saw that an internal heat exchanger to add subcooling and pre heat the refrigerant before compression have small effect on the efficiency, the opposite is the case for Pentane. We made a series of calculation with different level of superheat from 20K (minimum to avoid 2 phase compression) to 60K. By using an internal heat exchanger the superheat resulted in 14 K to 42 K additional subcooling of the refrigerant which led to a significant drop in the amount of flash gas after the expansion valve. Superheating Pentane before compression have very little influence on the specific volume and does only reduce the volumetric efficiency very little and insignificantly compared to the efficiency gain by increased subcooling. By adding internal heat exchanger it is possible to improve the efficiency from 3.9 to 5.4 at the same operating conditions. For processes where the heat sink has a small temperature difference (less than 10K) or the heat pump is used for evaporation of steam (single temperature level) adding an internal heat exchanger is a good way to improve efficiency. For each degree of additional subcooling achieved with the internal heat exchanger the efficiency improved with 0.6%.

Another way of achieving the additional subcooling is by adding an external subcooler, this require that there is a temperature difference of the heat sink between inlet and outlet. If heating the water from 120ºC to 140ºC it is possible to achieve 20K subcooling by external subcooler and add this energy to the heating water. By adding external subcooler it does not only reduce the amount of flash gas after expansion valve it also have a positive impact on the heat output. From table 4 it is shown how this effect the performance of the heat pump. The first two row is calculated without any superheat of the refrigerant before compression (which lead to 2 phase compression). The external subcooler improves the efficiency from 3.9 to 4.8. When comparing the efficiencies in table 4 with the efficiencies in table 3 we see that for the same amount of flash gas after the expansion valve we get significant better efficiency when adding external subcooler compared to internal subcooler. This is due to the positive energy output of the external subcooler. For each degree of external subcooling we achieve 1.7% better efficiency.

Table 4**.** Operation condition and efficiency of Pentane heat pump with external subcooling
Evaporation temperature 80ºC, condensing temperature 145ºC.

	Discharge temperature	External subcooling	Internal subcooling	Flash gas	Heating COP
No superheat	145ºC	0 K	0 K	53%	3.9
No superheat	145ºC	14 K	0 K	41%	4.8
20 K Superheat	145ºC	14 K	14 K	30%	5.2
20 K Superheat	145ºC	28 K	14 K	18%	6.1

Based on the findings from the analysis of Pentane heat pumps we concluded that they are particularly suited for high pressure hot process water or high temperature district heating where there is a moderate temperature difference of 20 – 40K between inlet and outlet of the heat sink. The heat source needs to be above 40ºC and due to the low density of the gas at low temperature the heat source should preferable be at least 80ºC[4]. For lower heat source temperature an ammonia heat pump can be used as the first stage for best efficiency.

2.3. Steam compression heat pump up to 200ºC

Steam compression have been used in the process industry for many years, without being defined as heat pumps. Water is the safest refrigerant with no personnel or environmental impact. Below 100ºC it is sub atmospheric and in vapour phase it has a very low density. A high volume flow per kW is required for steam heat pumps. For steam compression turbofan compressors have most commonly been used, they provide a high volume flow and low compression ratio. Lately many other technologies have entered the market for steam compression like screw and piston compressors. In table 1 is shown that at an suction pressure of 80ºC you need more than 4 times the suction volume of a steam compressor compared to a pentane cycle heat pump. At 120ºC suction pressure the difference is reduced to 2.5 times.

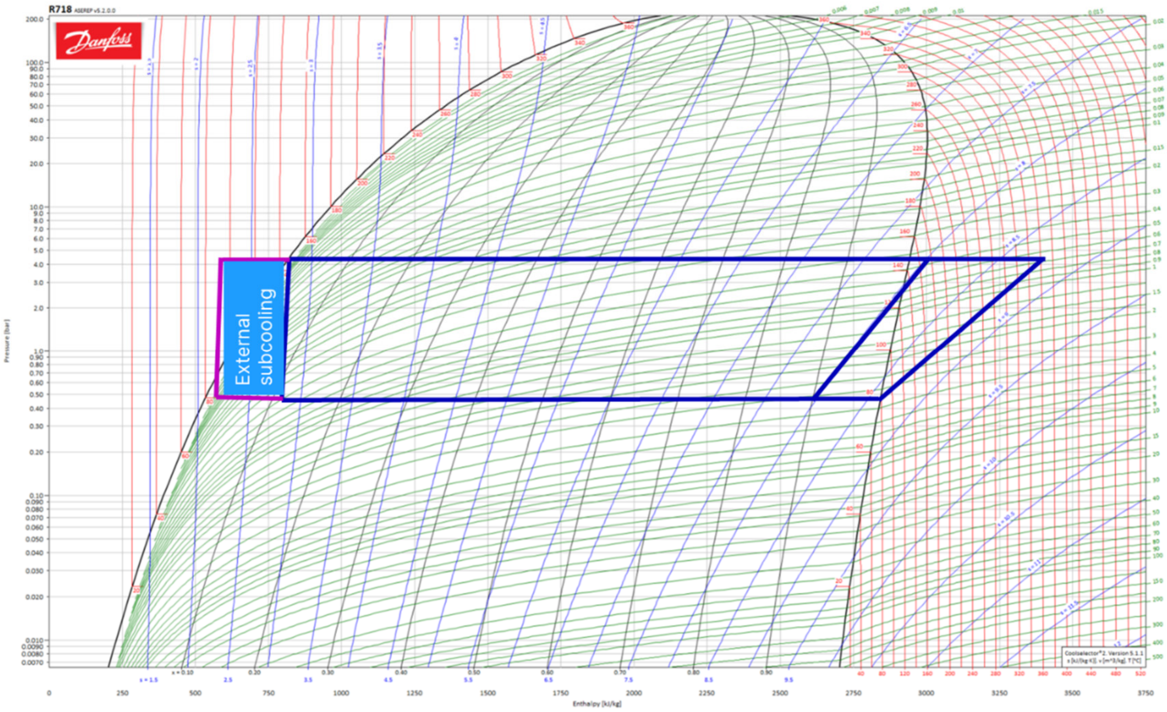


Figure 3. R718 (water) heat pump in logP-h diagram

The Graph in figure 3 shows the operating conditions for a steam compression heat pump, based on water evaporating at 80ºC and condensing at 145ºC. There is shown the traditional refrigeration circuit with compression starting at the saturated gas curve and a second condition where the compression is started before all the liquid have evaporated, with some evaporation happening during the compression process.

Table 5. Operation condition and efficiency of MVR heat pump

Evaporation temperature 80ºC, condensing temperature 145ºC.

	Discharge temperature	External subcooling	Flash gas	Heating COP
No superheat	312ºC	0 K	11%	5.5
Wet compression	165ºC	0 K	11%	5.4
20 K Subcooling	312ºC	20 K	8%	5.7
40 K Subcooling	312ºC	40 K	4%	5.9
60 k Subcooling	312ºC	60 K	1%	6.1

The theoretical process data shown in table 5 show that when compressing steam at the saturation curve, when all the liquid have evaporated (row 1) that it results in a very high superheat after compression, which is undesirable as this is outside the operating range of many standard component and add additional requirement to the material expansion when in operation. If additional expansion tolerances is needed for the compressors it effect the efficiency. To avoid the high discharge temperature the compressor manufacture start the compression in the wet area by injecting water into the suction flow stream[6]. The injected water evaporate during compression and limits the outlet temperature. In row 2 is shown the effect of wet compression on the outlet temperature, by injecting water into the suction flow stream the outlet temperature have been reduced from 312ºC to 165ºC (at 145ºC condensing temperature).

For steam compression we have not investigated the effect of internal heat exchanger to superheat the suction gas as this has undesirable effect, as it will lead to higher discharge temperature and not less. However we investigated the impact of adding external subcooler. In Table 5, row 3 – 5 the effect on flash gas and efficiency based on different levels of external subcooling is calculated. Without any subcooling we notice that the level of flash gas after the expansion valve is already very low at only 11% and adding 20, 40 or 60K additional subcooling has little effect on the overall efficiency. The efficiency only improves from 5.5 to 6.1 by adding 60 K subcooling, this is only 0.2% per K subcooling which is much less than the effect of 1.7% for external subcooling for a Pentane heat pump.

Based on the findings in the analysis of the steam heat pumps we concluded that they are particularly suited for processes requiring steam as you often can save an additional heat exchanger. It's a clear benefit to make the first temperature from lower temperature heat source (below 80ºC) with another refrigerant, so the suction temperature for the steam heat pump is not less than 80ºC. The very little benefit of additional subcooling and the high volume flow for the steam compressors makes them less attractive for high pressure hot water system.

2.4. Conclusion

Whereas for heat pump applications below 95ºC ammonia have shown to be one of the most efficient option for all applications, there is not the same "one size fits all" for heat pumps above 100ºC. The analysis of 3 different natural refrigerants (CO_2, Pentane, Steam) have shown where they each have their advantages in the market. CO_2 proved to be a good option for applications with low source temperature (<25ºC) and a where the incoming heat sink temperature is low (<30ºC). For applications where pressurized hot water is required there is a benefit of using pentane especially if there is moderate temperature difference of the heat sink which allow for additional heat gain from an external subcooler. Where steam is required the best efficiency can be achieved by direct steam compression, as this can be applied in an open loop compression process. For both Pentane and Steam they should be used in combination with another heat pumps system (For best efficiency ammonia heat pump[7]) if the heat source is less than 80ºC as the heat density of the vapor is very low at lower temperatures.

References

[1] Hoffmann K, Bantle M, Evenmo K, Nilsend V., 2023. Ammonia - Steam cascade heat pump for +100˚C steam generation, IEA Heat Pump Conference, Chicago

[2] Arpagaus C., 2017. Hochtemperature Warmepumpen, Literature study on the state of the art, research, the application potential and refrigerants, NTB Interstate University of Technology Buchs.

[3] Marina A, Smeding S, Wemmers A, Spoelstra S, Kremers P, Eds., 2021. Design and Experimental Results of a Two-Stage Steam Producing Industrial Heat Pump, 13th IEA Heat Pump Conference, Korea

[4] Bless F, Arpagaus C, Bertsch S, Eds., 2021, Theoretical investigation of high temperature heat pump cycles for steam generation, 13th IEA Heat Pump Conference, Korea

[5] Radgen P, Blesl M, Hufendiek K, Eds., 2022. Abwarmepotentiale in der Industrie: Konzepte zur Nutzung im Mittel- und Niedrigtemperaturbereich, 1st ed., Berlin, Wien, Zürich.

[6] GEA, Evaporation Technology using Mechanical Vapour Recompression, Germany

[7] IEA Annex 58, 2023. High temperature heat pumps, GEA Heating and Refrigeration Technologies - GEA CO_2 Heat Pump