

Review of Vapour Compression Heat Pumps for High Temperature Heating using Natural Working Fluids

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Highlights

- Review of recent studies on heat delivery above 80 °C using vapour compression heat pumps
- Recent advances in natural fluids as high temperature working fluids
- Component development for high temperature heat pump operation
- Proposed fluid mixtures, cycle variations, system design in high temperature domain

Abstract

The use of High Temperature Heat Pumps (HTHPs) operating with natural fluids have been shown to be a potential environmentally friendly solution to increase energy efficiency in industrial processes. Industrial processes release a significant amount of energy as low quality waste heat to the environment. This paper reviews the research and development of efficient and cost effective HTHP technology that can utilize this waste heat. Natural fluids are of focus with consideration given to the comparable technologies using synthetic fluids. This review reveals the different challenges from fluid selection, component development to system optimization. The various innovative solutions to these challenges and promising technologies for further studies are discussed. The purpose of this paper is to serve as a start point for research by bringing together ideas, simulations and experimental results as a resource or reference tool for future development in HTHP using natural working fluids.

Keywords: Process heat integration, Heat pump technology, Energy efficiency, Waste heat

Nomenclature

COP	Coefficient of Performance
GHG	Greenhouse Gas
GWP	Global Warming Potential
h	Enthalpy
HACHP	Hybrid Absorption Compression Heat Pump
HTC	High Temperature Cycle
HTHP	High Temperature Heat Pump
HX	Heat exchanger
IHP	Industrial Heat Pump
MVR	Mechanical Vapour Recompression
P	Pressure
ODP	Ozone Depletion Potential
SDT	Saturation Dew Temperature
VCC	Vapour Compression Cycle

1. Introduction

Several reports have documented the negative impact of Greenhouse Gas (GHG) emissions on climate change (Bates *et al.*, 2008; Gitay *et al.*, 2002). It is now globally accepted that to achieve a future of environmentally friendly, cheap and sustainable energy systems, there is a need to increase energy efficiency of industrial processes and to reduce direct emissions of GHG, e.g. from burning fossil fuels. Industrial processes that utilize heat in different forms, either in production of cement, chemicals or metals and also power plants, discharge a large part of this energy at a low temperature to the environment (Kulcar *et al.*, 2008; L. Zhang & Akiyama, 2009). It is estimated that about 60 % of this heat is low temperature heat with little direct thermal and economic value. This low temperature heat is however, in large quantities which makes it profitable for research into its use. Depending on the industry, the waste heat could range from 20 - 51 % of total process heat used in metals and non-metallic industry as well as in cement production factories (Johnson *et al.*, 2008; Sogut *et al.*, 2010). This is clearly a significant amount of energy, such that if recovered, could serve as a method to increase energy efficiency and lower GHG emissions.

High Temperature Heat Pump (HTHP) technology provides a way to utilize low temperature waste heat by its conversion to useful high temperature heat. This heat can be used in steam production, district heating or re-integrated into the industrial process thereby increasing the efficiency of the system (Chua *et al.*, 2010). Other methods to utilize waste heat for electricity generation in heat engines will require the waste heat at temperatures higher than 100 °C to be competitive (Van de Bor *et al.*, 2015). Kleefkens and Spoelstra (2014) have reported current research and development on industrial heat pumps, with focus on waste heat reuse and high temperature delivery. IEA (2014) released a report on industrial heat pumps. The report summarized the markets, the barriers as well as the technology and application of industrial heat pumps. It also discusses the challenges associated with HTHP and its integration into existing process systems.

There have been lots of advancements in heat pump technology at lower heat delivery temperature but fewer at high temperatures above 80 °C. Many countries such as the United States of America, countries in Europe and in Japan have implemented heat pump technology as a policy for energy savings. These are close to room temperature heat pumps. They are widely used in both industries and low capacity commercial applications (S. J. Liu *et al.*, 2009). There is already numerous research into heat pumps operating at temperatures below 80 °C (Arpagaus *et al.*, 2016; Jung *et al.*, 2000; M. H. Kim *et al.*, 2004; Liebenberg & Meyer, 1998; Y. Liu *et al.*, 2009; Miyara *et al.*, 1992; Nakatani *et al.*, 1990; Neksa *et al.*, 1998; Parise & Cartwright, 1988) just to mention a few. This is hardly useful for high temperature industrial heating applications that require steam production or other high temperature heating demand.

There are various technological concepts for the conversion of low temperature heat to high temperature heat. A comprehensive review of these concepts is presented by Chua *et al.* (2010), J. Zhang *et al.* (2016) and others. Each concept has its advantages and area of application. The vapour compression cycle (VCC) can be said to be the most widely used heat pump concept (Ammar *et al.*, 2012; S. J. Liu *et al.*, 2009; Tuan *et al.*, 2012). The main characteristics of this technology is the phase change of the working fluid in a closed circuit.

The availability of waste heat coupled with a high demand for heat at higher temperatures in industrial processes makes it profitable for research and development into HTHP technology. Analysis of the European markets by Nellissen and Wolf (2014) shows a possible 2000 TWh of heat demand across different industries. About 174 TWh of this heat is reachable by industrial heat pumps and 74.8 TWh is high temperature (80 °C - 150 °C). Fig. 1a shows the distribution of industrial heat usage and the temperature across different European industries. Fig. 1b shows how much heat can be supplied by

existing heat pump technology and the potential for HTHPs. Heating demand between 80 °C and 150 °C is argued to be reachable in practice for HTHPs.

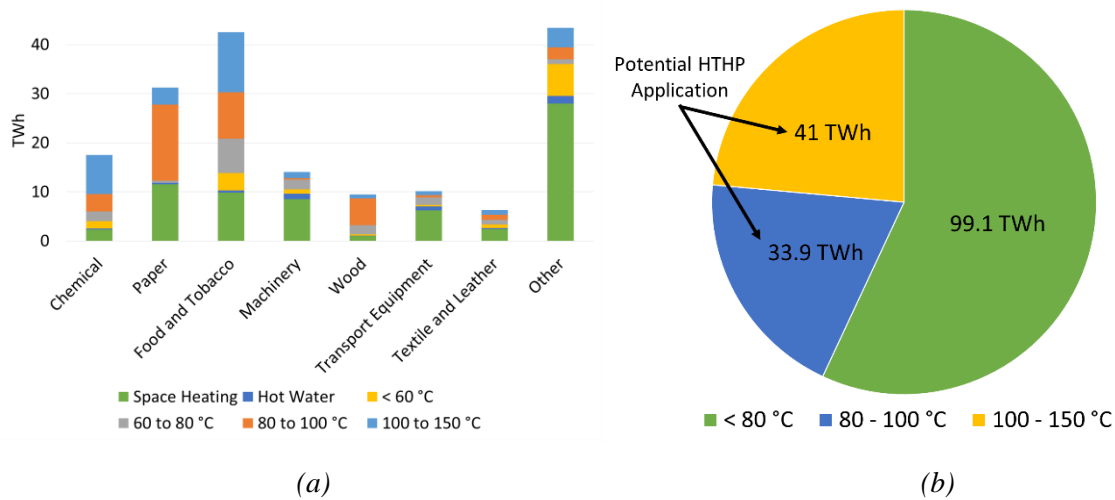


Figure 1a: Heat demand quality and quantity in European Markets by Industry. 1b: Distribution of heat by temperature and potential quantity of heat demand that can be covered by HTHPs (Nellissen & Wolf, 2014)

HTHPs are not different from conventional heat pumps below 80 °C in terms of its mode of operation. The principal components and thermodynamic cycle are the same. The main difference is the temperature of heat delivery which is higher and as such some changes have to be made to the system design to accommodate for this, while of course taking in consideration the environmental impact (Parise & Cartwright, 1988). Operating at high temperatures will require modifications in most if not all of the equipment in conventional heat pumps. New types of working fluids will have to be evaluated with expanded working domains. As noted by Yu *et al.* (2014), the most important parameter for practical HTHP is finding a suitable working fluid with good performance. A good way of doing that is to perform a thermodynamic screening of the refrigerants similar to what Devotta and Pendyala (1994) did for HTHP with condensing temperature between 80 - 120 °C. T. X. Li *et al.* (2002), N. X. Liu *et al.* (2005) and S. Zhang *et al.* (2010) also performed experiments to determine the best refrigerant for a given cycle, though mostly below the 90 °C condensing temperature range.

When implementing HTHP in industrial processes, it is important to evaluate the technology and refrigerant in a holistic way including energy and cost efficiency, but also Global Warming Potential (GWP) and possible future environmental impacts. Natural working fluids have under the above mentioned criteria's a significant advantage compared to synthetic refrigerants, which first need to be developed and tailor-designed to the working temperatures of the HTHP. Working fluid selection should be primarily based on natural fluids and its mixtures or any form of synthetic refrigerant with little or no GWP and Ozone Depletion Potential (ODP). The equipment design has to minimize all forms of losses as much as possible, reduce energy consumption and of course be a cost effective alternative to existing technology.

The definition of what constitutes “high temperature” in a HTHP varies across literature. The focus of this paper will be on HTHP capable of producing heat at 80 °C and above, with the use of a VCC, its variations and comparable technologies. This paper will review the current state of the art in HTHP, the research and development and the technological principles of existing market solutions. Classification will be based on natural working fluids, optimization, cycle configurations and VCC variations. It will highlight recent successes and the challenges of developing a HTHP.

2. State of the art of HTHP designs

2.1. The Suitable Working Fluid

Certain thermodynamic properties (some of which are listed in Table 1) of working fluids tend to negate its ability to give suitable performance for certain HTHP operating conditions, while others favour good performance. There are also the important characteristics of environmental impact, which make synthesized working fluids less applicable. As in most engineering solutions, a compromise is made for the working fluid with the least undesirable properties, for both thermo-physical characteristics and its impact on the environment.

Table 1: Common natural working fluids and their properties

Ashrae Number	IUPAC Name	ODP	net GWP 100-yr	Molar mass g/mol	Normal Boiling Point(s) °C	Critical Temp. °C	Critical Pressure (absolute) kPa
R-290	Propane	0	3.3	44.1	-42.1	96.7	4,248
R-600	Butane	0	4.0	58.1	0.0	152.0	3,796
R-600a	Isobutane	0	3.0	58.1	-11.7	134.7	3,640
R-601	Pentane	0	4.0	72.1	36.1	196.6	3,358
R-601a	Isopentane	0	4.0	72.1	27.7	187.8	3,378
R-717	Ammonia	0	0.0	17.0	-33.3	132.4	11,280
R-718	Water/Steam	0	0.2	18.0	100.0	373.9	22,060
R-744	Carbon dioxide	0	1.0	44.0	-78.0	31.0	7,380

Many researchers have tried to evaluate different working fluid suitability to HTHP (Bertinat, 1986; Brunin *et al.*, 1997; Devotta & Pendyala, 1994; Goktun, 1995; Narodoslawsky *et al.*, 1988; Tamura *et al.*, 1997). These studies also revealed a better understanding of the influence of physical properties on heat pump performance. They derived correlations between the performance parameters and deduced the required basic properties for selection of working fluid for HTHP. Based on the theoretical study, they concluded that a good HTHP working fluid would have a high critical temperature to have a high COP (except in trans-critical operation). It will have a low boiling point temperature to have a small volumetric flow for a reasonable sized compressor.

They evaluated multiple working fluids based on criteria such as; environmental influence with relation to ODP and GWP, safety of the working fluid, its toxicity, flammability. They also considered properties like material compatibility, oil solubility, leak detection (Goktun, 1995). Hardly any working fluid can satisfy these selection criteria with mostly favourable properties. Different operating conditions would require a different working fluid. The purpose is to find the most suitable working fluid that works within a specific operating condition.

The use of natural refrigerants and their mixtures as a working fluid solves the question of direct environmental impact. This is when we do not take into consideration the indirect consequence of a possible lower Coefficient of Performance (COP), which can increase emissions depending on the energy mix of the electricity production. The following sections will discuss different working fluids and the state of the art technology for its application to HTHPs.

2.2. Ammonia (NH₃)

Ammonia has been widely used for heating and cooling applications, especially for large capacity energy requirements. It has GWP and ODP of zero. Stene (2008) discussed the characteristics of ammonia for these applications. Palm (2008b) has investigated the possibility of using ammonia as working fluid for low capacity domestic hot water heat pumps. In both of these researches and as with others (Huang & Yuan, 2013; Korfitsen & Kristensen, 1998; Palm, 2008a), the discharge temperature

of the heat sink is below 80 °C. The high compressor discharge temperature of ammonia coupled with a high pressure of 60 bar for a condensation temperature of 97.5 °C limits the application of ammonia for HTHPs. Further development to ammonia system design appears to show good potential as a HTHP working fluid. The desire to have the condensation temperature significantly higher than the heat sink target outlet temperature may not be required. As the condensation temperature increases, depending on the suction temperature, the percentage of heat in the de-superheating region contributes more to the heating capacity of the heat pump. Ammonia, unlike other working fluids has a significantly high compressor discharge temperature compared to its saturation temperature at a given discharge pressure, as shown in Fig. 2b.

The high compressor discharge temperature, if properly integrated with an intercooler/de-superheater using multiple streams, can be used to achieve a 90 °C or above hot water delivery as done in the hot water production for district heating in Drammen (Hoffmann & Pearson, 2011).

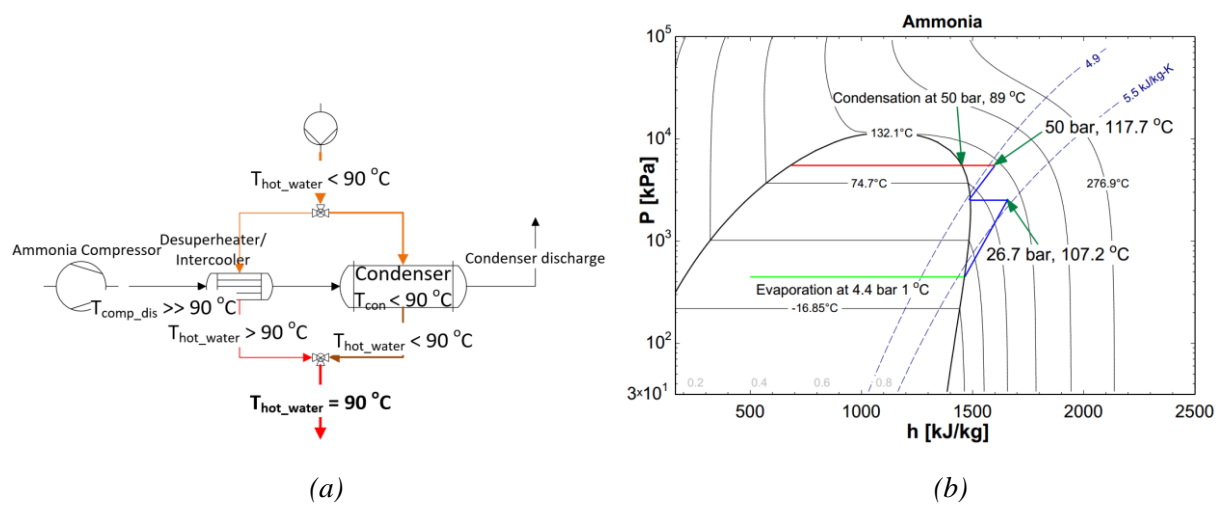


Figure 2a: Simplified principle of Drammen district heating heat pump schematics. 2b: P-h diagram of ammonia showing high compressor discharge temperature optimized for heating.

Fig. 2a shows the basic principle of water flow through the NH₃ heat pump installed in Drammen, Norway. Using multiple water streams, with a condensation temperature slightly lower than 90 °C, the circuit combination of de-superheating, heat of condensation and intercooler heat is able to bring the final delivery temperature to 90 °C (Hoffmann & Pearson, 2011). The system is optimized to ensure all the available heat is made useful. This ammonia system consist of 3 two-stage single screw compressor. Using piston type compressors, Fukano *et al.* (2011) reports on the development of an ammonia heat pump with heat delivery of maximum 85 °C. The heat source for this system was an existing cooling plant.

Aside the high compressor discharge temperature and pressure, ammonia also has challenges in the type of materials used in the system as ammonia reacts with copper in the presence of water. This limits the material type selection available for ammonia heat pumps, though over the years components have been developed with compatible materials for ammonia. Improvement in compressor technology recently has made pressure up to 60 bar possible in ammonia compressors at higher discharge temperature. The toxicity of ammonia also prevents its direct use in applications where leakage is considered high risk. Introducing a secondary cycle reduces the outlet temperature possible in the heat sink. These problems are not unique to HTHPs and are equally challenging at lower temperatures. However, for a HTHP with possible high temperature lift, and operating at technological boundaries of the system components, minimizing all losses in efficiency becomes even more important.

2.3. Carbon dioxide (CO₂)

With the re-introduction of CO₂ as a competitive working fluid (Lorentzen, 1994), the use of CO₂ for HTHPs has been successfully tested and demonstrated by Neksa *et al.* (1998) and others. Delivery temperature above 80 °C is achievable in a trans-critical CO₂ cycle. CO₂ trans-critical systems take advantage of the large temperature glide at constant pressure, matching it with the heat sink temperature glide to minimize exergy destruction in the gas cooler. This is particularly beneficial for high heat sink temperature difference application like hot water production. The thermodynamic principle required for the optimization of a CO₂ trans-critical system has been shown to be largely dependent on gas cooler exit temperature (or heat sink inlet temperature) (Cecchinato *et al.*, 2005; Neksa, 2002).

Consequently, research into different possible ways to improve the gas cooler exit temperature and/or minimize the expansion losses are ongoing. Some authors (Fronk & Garimella, 2011; Hwang & Radermacher, 1998; Neksa *et al.*, 2005; Pettersen *et al.*, 1998; Sarkar *et al.*, 2004; Sarkar *et al.*, 2005) through theoretical analysis and experimental studies have suggested improvement to the gas cooler heat exchanger. The research focus ranged from heat exchanger type, exergy analysis, forced or natural convection, use of micro-channels and others.

There has also been numerous research work on improving overall system performance through multiple stage compression, different methods of inter-stage cooling and economizer, and comparisons of heat source systems (Cavallini *et al.*, 2005; Cecchinato *et al.*, 2009; Cho *et al.*, 2009; Hafner *et al.*, 2014b; Hu *et al.*, 2016; Jin *et al.*, 2016; Sarkar & Agrawal, 2010; Zha *et al.*, 2008). Finally, developments in the expansion device is equally important as the high-pressure gas cooler needs to be kept constant for best performance. Research by some authors (Agrawal & Bhattacharyya, 2007, 2008; Banasiak *et al.*, 2012; Banasiak *et al.*, 2015; Banasiak *et al.*, 2014; Chen & Gu, 2005a; Deng *et al.*, 2007; Elbel & Hrnjak, 2008; Hafner *et al.*, 2014a; Haida *et al.*, 2016; H. J. Kim *et al.*, 2008; D. Li & Groll, 2005; Madsen *et al.*, 2005; Nickl *et al.*, 2005; J. L. Yang *et al.*, 2005) focused on different expansion devices such as capillary tube, expanders and ejectors as a way to improve the performance of a CO₂ heat pump.

Austin and Sumathy (2011) and M. H. Kim *et al.* (2004) have written a comprehensive and critical review on improvements to CO₂ heat pump systems. Both highlighted the development of CO₂ heat pump technology since its re-introduction. However, these researches are not particularly focused on high temperatures. They are rather efforts to improve the CO₂ cycle from a broader perspective. More important to HTHPs is increasing the compressor discharge pressure and temperature to achieve higher heat sink outlet temperature with improved efficiency.

For higher outlet temperatures of heat sink, White *et al.* (2002) constructed a prototype CO₂ heat pump to heat water to temperatures above 65 °C. Using the experiment results, they developed a computer model to simulate performance at 120 °C. They reported a small reduction in heating capacity and heating COP at this temperature. The gas cooler operating pressure of trans-critical CO₂ is often optimized for best performance slightly below 100 bars (Chen & Gu, 2005b). At this pressure, the maximum outlet temperature of the heat sink will be in the range of 80 to 100 °C. Hence, CO₂ systems for heating are often coupled with properly sized hot water storage tanks arranged in series for best effectiveness (Berntsen *et al.*, 2014; Pitarch *et al.*, 2015). A prototype CO₂ heat pump was constructed by Eikevik *et al.* (2005) to investigate drying possibilities of different products under different conditions. This heat pump could operate in various modes with condensation, trans-critical operation and pure gas mode at high temperatures. The operating range was up to 90 °C. They had also investigated the design, energy consumption and drying chamber operation for products such as fish, fruits, vegetables, dairy and heat sensitive materials (Eikevik *et al.*, 2004).

A drawback to CO₂ HTHP is the low critical temperature of 31 °C. Evaporating temperature will always have to be below 31 °C regardless of heat source temperature to keep the system in trans-critical mode. This coupled with the high compressor discharge pressure for high temperature delivery creates a system

with a pressure differential of over 100 bar between high and low sides of the cycle. Fig. 3 highlights the challenges for using CO₂ in HTHP.

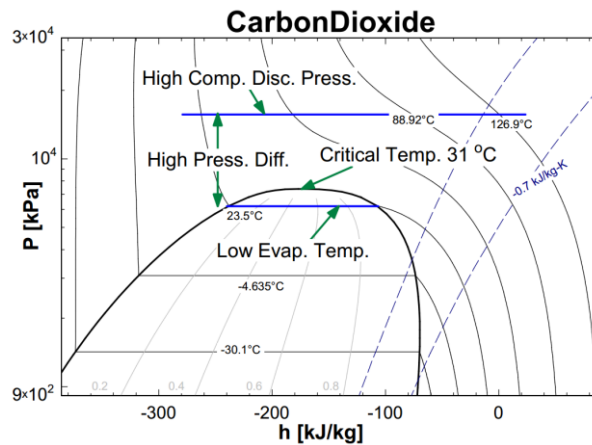


Figure 3: *P-h* diagram showing the thermodynamic challenges of CO₂ for HTHP. Highlights on high discharge pressure and high pressure difference

CO₂ is a promising working fluid for HTHP. However, heat sink outlet temperature above 100 °C will require improvement of component technology to handle relatively high pressure in the compressor, heat exchangers and system piping. Matching of temperature glides in the gas cooler will be important, as low temperature glide in heat sink will not be optimal for CO₂ trans-critical HTHP. HTHP will take advantage of the many research into CO₂ efficiency improvement that is ongoing for lower temperature heat pumps.

2.4. Water (H₂O)

Water is the safest known working fluid in the heat pump and refrigeration industry. It is almost completely free and readily available. It is also very stable with most heat pump materials. The thermodynamic properties of water such as high critical temperature (373.9 °C) at pressure (220 bar) makes it a good fluid for HTHP applications.

However, the boiling temperature at standard normal boiling point conditions (100 °C) is high. This makes water as working fluid, to operate at sub-atmospheric pressure for heat source temperatures below 100 °C. The density of water vapour is relatively low when compared to other working fluids. Therefore, large compressors or high-speed compressors will be required to transfer equivalent mass flow compared to what a smaller compressor would with other working fluids (Bantle *et al.*, 2015). The sub-atmospheric operation and the high flow rate requirements of a heat pump with water vapour are the main challenges to the use of water at HTHPs. Water also has a high compressor discharge temperature for a given pressure lift, which limits the type of compressor, its material and lubricant. These properties are illustrated in the *p-h* diagram in Fig. 4.

Water has for a long time been investigated as a working fluid for HTHPs. The demand for alternative clean energy has further increased research into its use. Eisa *et al.* (1986) investigated the suitability of using water as a HTHP working fluid based on its thermodynamic properties. They found that water becomes more efficient comparatively as the condensing temperature approaches 200 °C with a lift as high as 70 K. Chamoun *et al.* (2013) and Chamoun *et al.* (2014) performed both experimental and numerical investigations into the performance of a new HTHP using water as working fluid. Operating temperature of the condenser was 130 - 145 °C. Their calculations focused on using heat source at a temperature of 80 - 95 °C. They developed a dynamic model of the heat pump using a software application to take into consideration non-condensable gases like air and its purging mechanism. Managing non-condensable gases is important for partly sub-atmospheric operation.

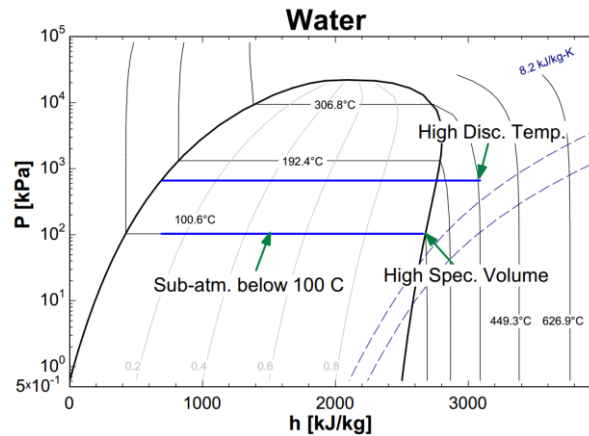


Figure 4: *P-h diagram showing the thermodynamic challenges of water for HTHP. Highlights on high discharge temperature, sub-atmospheric operation and high specific volume*

Madsboell *et al.* (2014) developed a centrifugal water vapour compressor. It is designed to produce heat at a temperature range of 90 - 110 °C for industrial heat pump applications. It has a capacity of 100 - 500 kW with 25-30 °C temperature lift per stage. The principle of this compressor is based on high-speed gear similar to automotive turbochargers. This allows standard electric motors for the driveline instead of a direct drive with expensive high-speed motors. If operated with an open configuration, it can function in drying and concentration applications.

Larminat *et al.* (2014) also considered using water as working fluid. With ammonia and synthetic fluids covering HTHP technology up to 90 °C, water having a high critical point is a good working fluid if the heat source is at a temperature above water boiling temperature at atmospheric pressure. They built and tested a prototype for 700 kW heating capacity operating within 90 and 120 °C heat sink outlet temperature. The challenges involved with water vapour compression were overcome with the use of a centrifugal compressor directly driven by high-speed motor on magnetic bearings. They claimed that the built compressor not only works on closed cycles but also on mechanical vapour recompression systems.

Tolstorebrov *et al.* (2014b) evaluated the energy efficiency of using water vapour as refrigerant for superheated steam drying systems. Their theoretical analysis was based on a steam outlet temperature of 170 °C from three stages of compression. A radial turbo compressor similar to Madsboell *et al.* (2014) was used to meet the volumetric flow requirement of water vapour. The system is also based on mechanical vapour recompression.

Mechanical vapour recompression (MVR) is a variation of the vapour compression cycle. It involves circulation in vapour phase of a fluid (usually water vapour) from a low pressure to higher pressure and temperature using a compressor. Steam MVR has the possibility to use waste heat from the condenser by recovering it in the evaporator thereby increasing its efficiency. MVR applications and researches are common in industrial processes for drying, evaporation and distillation (Cooper & Lyon, 2004; Gao *et al.*, 2015; Tolstorebrov *et al.*, 2014a; J. Yang *et al.*, 2016). It is also being proposed for process energy integration in post-combustion CO₂ capture (Jeong *et al.*, 2015).

The researches above had attempted solution to the two main challenges of water as a working fluid. They have either operated at heat source (close to 100 °C) to avoid sub-atmospheric operation and/or adopted a centrifugal compressor with high flow rate and low-pressure ratio to compensate for the low mass density of water vapour. The high discharge temperature can be used as an advantage. De-superheating and intercooling heat (for multi-staged system) if properly integrated can improve cycle performance.

2.5. Hydrocarbons

Hydrocarbons are emerging as alternative working fluids due to both its environmental friendliness (Zero ODP, Negligible GWP) and its good thermodynamic properties. Research has focused on hydrocarbons such as propane (R290), butane (R600) and iso-butane (R600a) and they are seen to have comparable or better performance to synthetic refrigerant (Bengtsson & Eikevik, 2016; Palm, 2008c). Heavier hydrocarbons are also applicable as HTHP working fluids, with high COP values. However, at low heat source temperatures they operate below atmospheric conditions, which increases the risk of a flammable mixture due to air ingress. Generally, the main challenge for hydrocarbons is the flammability of the fluids. Operating a hydrocarbon fluid at high temperature and pressure further complicates this challenge. The extent to which different hydrocarbon can deliver high temperature heat depends on its properties as seen in Fig. 5. R290 with a relatively low critical temperature of 96.7 °C cannot deliver heat above this temperature at sub-critical operation when compared to R600 with 152 °C critical temperature.

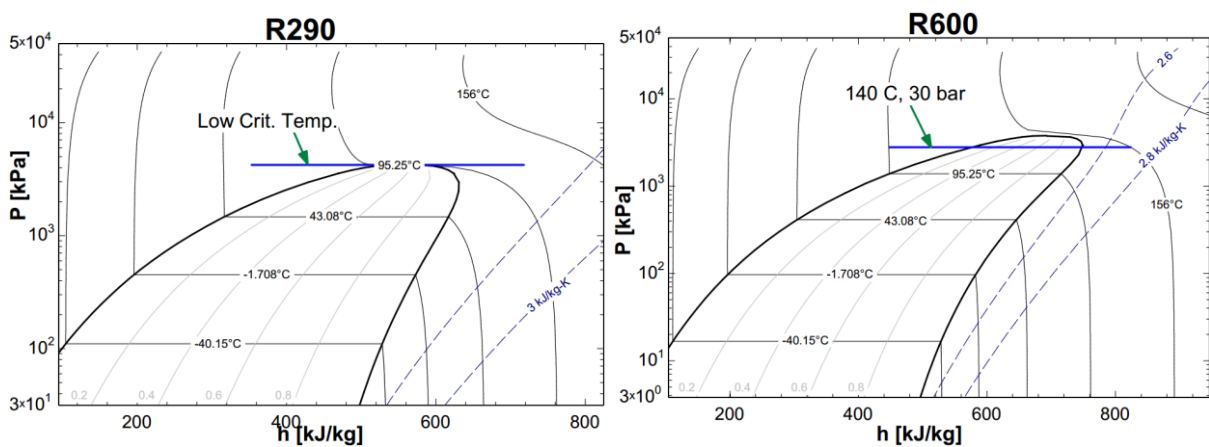


Figure 5: P-h diagram showing the thermodynamic challenges of hydrocarbons R290 and R600 for HTHP. Sub-critical operation for high temperature compared

Stavset *et al.* (2014) analysed a cascade system of propane R290 and butane R600 working fluids for HTHP design to heat water from 95 °C to 115 °C. The numerical analysis compared various evaporating temperatures to find the optimum operating condition for the heat pump. They concluded from their result that with a COP above 60 % of theoretical maximum, the heat pump with R290 and R600 cascade would perform well compared to other heat pump technologies.

As suggested by Stavset *et al.* (2014), coupling hydrocarbons in a cascade system shows good potentials for a HTHP. The low critical temperature of propane is avoided at the high temperature cycle (HTC). A potential improvement to this can be the implementation of a mixture of hydrocarbons in a cascade system. Heating water within suitable temperature glide that matches the glides during condensation will benefit from the zeotropic behaviour of mixtures. So does the potential to have higher evaporating pressure, which reduces compression work. Thermodynamic properties can be favourably adjusted depending on mixture component and mole fractions. These were the conclusions of the paper by Bamigbetan *et al.* (2016) which evaluated suitable natural working fluids for HTHPs. Further elaboration of mixtures are in the next sub-section.

Aside the safety concerns of hydrocarbons in HTHPs, technological constraints exist in finding a suitable compressor. Commercial compressors for hydrocarbons at high temperatures are not readily available. This will require innovative solutions to challenges such as compressor cooling in hermetically sealed compressors.

2.6. Mixtures

Improving the performance characteristics of natural working fluids can be achieved by blending fluids of different properties to achieve a compromise between what could appear to be two extremes. A high discharge pressure, flow rate, temperature can be avoided with the right mixture. Mixtures can also benefit from a zeotropic behaviour of the fluid. Matching the heat source and sink to the working fluid can significantly improve performance of a heat pump. By varying mixture composition, the properties can be optimized to fit the requirement.

Zheng *et al.* (2013) conducted a theoretical and an experimental investigation on this topic. They evaluated the behaviour of zeotropic mixtures in a counter-current heat exchanger and conducted their experiment using a mixture of propane and butane R290/R600 (mass fraction of 0.85/0.15) to verify the theory. The results show the influences of system parameters on the temperature differences within the heat exchanger.

Sarkar and Bhattacharyya (2009) proposed a mixture of natural refrigerants CO₂ and Butane (R744/R600), CO₂ and Iso-Butane (R744/R600a) to be used as a working fluid in heat pumps for medium and high temperature heating applications. Their theoretical model and simulations compared the performance indicators for these zeotropic working fluid pairs of various composition against that of pure working fluids. It also compared the mixtures with R114 for high temperature heating (120 °C). They concluded that for high temperature heating, the mixtures showed superior performance in terms of lower compressor pressure ratio, higher volumetric heating effect and higher heating COP. Also due to excessively high side pressure of R744 systems and poor heat transfer properties of R114, the mixtures R744/R600a could serve as a promising alternative.

N. X. Liu *et al.* (2005) evaluated the performance of a ternary mixture of refrigerants (R124/R142b/R600a) named HTR01. They built two model systems of 2.92 kW and 300 kW heat capacity heat pumps and showed that with temperature lift less than 30 K, a COP greater than 3 was achievable. They were able to get condensing temperature to exceed 90 °C applicable for HTHP.

2.7. Synthetic Working Fluids

Synthetic refrigerants are obviously not covered by the term natural refrigerants, but are covered here for reference. Many of these refrigerants are or will be phased out by the Montreal protocol due their ability to deplete the ozone layer. Further phase down of the halocarbons will be done as a consequence of the Kigali amendment to the Montreal Protocol decided for in October 2016. The fourth generation halocarbons, e.g. the unsaturated HFCs, often referred to as HFOs, are not covered by this amendment since their GWP figures are very low. Still, with the history of the unforeseen consequences to the environment for the first three generations of halocarbons, also knowing that most of them are flammable with toxic and other questionable decomposition products, gives good arguments for a precautionary principle to focus on natural working fluids for the future.

Research into synthetic refrigerants, though many of them being phased out, still offer solutions to HTHP. Working fluids like R115, R143, R152, E143 and E245 which can be used for high temperature application have negative environmental impact leading to the focus on natural fluids (Sarkar *et al.*, 2007). Hydrofluorocarbons HFCs, which are the traditional third generation synthetic working fluids, are commonly used in heat pump and refrigeration systems. HFC-134a has a low critical temperature of 122 °C, but when mixed with another synthetic refrigerant such as HFC-245fa, which has a higher critical temperature of 157.5 °C, it can be applied in HTHP. HFC-245fa can also be used as a single working fluid for HTHP (Wu *et al.*, 2015). Oue and Okada (2013) presented the construction and performance of a HTHP design using HFC mixtures. They showed that the zeotropic behaviour of the mixture eliminated the need for multiple compressors and heat exchangers in a cascade system. It achieved a temperature of 90 °C for a heating capacity of 176.2 kW.

Kontomaris (2012) introduced a new working fluid based on Hydrofluoroolefin (unsaturated HFC). The fluid had zero ODP with low GWP of 9.4. Theoretical evaluations of the performance of this working fluid shows a 2.3 % COP improvement when compared with HFC-245fa at 100 °C condensation temperature. With a high critical temperature of 171.3 °C, it was possible to evaluate this working fluid for condensing temperatures of up to 155 °C within a subcritical cycle for industrial process heating requirement. Though compressor technology will have to be improved to operate at such high discharge temperature, the working fluid showed potential for good performance.

Kondou and Koyama (2015) conducted a thermodynamic assessment of unsaturated HFCs for HTHPs. Using operating conditions of heat sink outlet temperature at 160 °C and waste heat available at 80 °C, they compared the performances of R717, R365mfc, R1234ze(E), and R1234ze(Z). The working fluids were evaluated on four different cycle configurations. They concluded that a cascade cycle of R1234ze(Z) and R365mfc results in a relatively high COP.

Fukuda *et al.* (2014) investigated two fluids R1234ze(E) and R1234ze(Z) with low GWP suitable for HTHPs. They accessed their thermodynamic properties through experiments and numerical simulations. They achieved condensation temperature of 105 - 125 °C and concluded there exist capability of the two fluids for industrial heat pumps at high temperatures instead of the usual air conditioners and refrigeration systems. S. J. Zhang *et al.* (2010) and Ma *et al.* (2010) did similar investigations.

The application of synthetic working fluids with high GWP is gradually being phased out due to environmental agreements. Fewer researchers go into its use for HTHP. However, the challenges and results from simulations, experiments and existing prototypes are still relevant to the development of HTHP using natural fluids. Natural fluids such as propane and butane have to an extent performance properties similar to synthetic fluids in heat pumps. The technological transfer of best practices will be important towards the complete phase out of synthetic working fluids.

3. Multiple working fluid evaluations for HTHPs

Ommen *et al.* (2015) considered the technical and economic feasibility of HTHPs. With an upper boundary of 120 °C, they evaluated the Net Present Value of the investment that proves to be profitable. Their comparisons were based on natural working fluids. Their results indicated that R717 performed best for low heat sink temperature glide, R744 was best at high temperature glide at heat sink with a high temperature lift and R600a was most suitable to high temperature applications (90 – 120 °C). The mixture of natural working fluids also serves to improve the performance of a single pure fluid. The availability of temperature glides in the heat exchangers can minimize exergy losses. The benefit from mixtures are however reduced by lower heat transfer coefficients.

Others used the wide array of refrigerants as a starting point towards the development of their own blend of refrigerants. Bobelin *et al.* (2012) performed experiments on industrial HTHPs equipped with scroll compressors to deliver heat at temperatures up to 140 °C. They considered working fluids from natural fluids to HFC and demonstrated the technological feasibility and reliability of a newly developed HTHPs using a new blend of fluids. Their study focused on the French industry where it is estimated that 28% of potential energy savings is linked to waste heat recovery (Berail & Sapora, 2010). Their report showed the achievement of a delivery temperature of up to 125 °C with the system operating at reasonable efficiency. For temperatures up to 140 °C, they suggested further developments in compressor efficiency at high-pressure ratio and expansion valve capable of working at temperature exceeding 120 °C.

4. Optimization and Cycle Configuration

The simple theoretical cycle for a heat pump does not necessarily maximize the potential for utilization of both heat source and heat sink combinations, nor does it minimize the required work input. Several changes to the simple cycle can enable a better COP for the same heat source and sink requirement. Some studies have chosen this approach in the development of HTHPs.

Cao *et al.* (2014) conducted performance analyses of different HTHP system configurations for low-grade waste heat recovery using synthetic fluid R152a as working fluid. The analyses were for both thermodynamic performance and the economic quality of the system. The heat source was from oil field waste water at 45 °C. Temperature at the condenser for hot water production was 95 °C. The heat pump system configuration; two-stage with flash tank with/without intercooler showed higher COP and better exergy efficiency. Natural fluids can also benefit from such analysis based on system configurations for HTHP and low grade waste heat recovery

The arrangement of compressors and heat exchangers in a HTHP also affects its performance. The choice of either parallel and series arrangement of both the process cycle and the heat cycle can reflect on the eventual COP of a heat pump. Investigation into this was done by Wang *et al.* (2010). They conducted an analytical and experimental study into performance comparisons of HTHPs among parallel cycles with serial heating on water side, two-stage compression cycle and single-stage compression. The parallel cycle with serial heating was found to have improved COP and giving better average heating capacity.

5. The Hybrid Systems

In order to improve the efficiency of vapour compression cycles, integrating with an internal solution circuit has been shown to be an effective method. Ammonia-Water Hybrid Absorption-Compression Heat Pump (HACHP) utilizes this principle (the Osenbrück Cycle). Pure ammonia condenses at high pressure above 50 bars for high temperature applications. The mixture with water will increase the boiling point temperature of ammonia allowing for higher temperatures to be achieved with lower condensing pressure. The cycle consists of a compressor used to increase the pressure of ammonia rich vapour, and a pump for a weak ammonia solution. Heat rejection occurs at the ‘Absorber’ (the condenser). Here, the weak ammonia solution absorbs the ammonia rich vapour through temperature glide as the solution concentration changes. Systems are designed to take advantage of the temperature glide in order to minimize exergy losses in heat exchangers. The solution expands through a throttle valve and ammonia vapourizes gradually in the ‘desorber’ (the evaporator) where heat is added to the cycle. An ammonia rich vapour and a weak ammonia solution is again formed. A simple illustration of an HACHP is shown in Fig. 6.

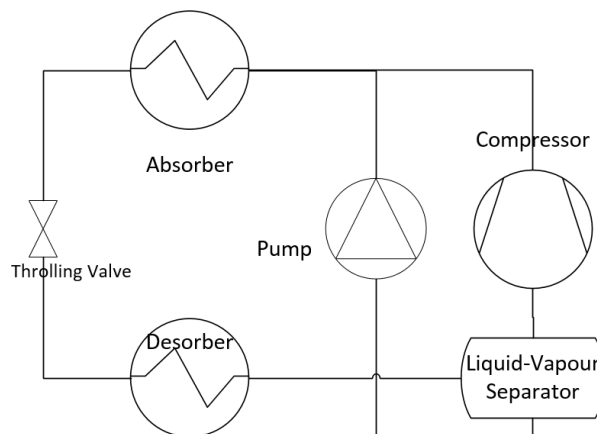


Figure 6: Simple illustration of HACHP

Hewitt *et al.* (2001) examined the possibility of making HTHPs more efficient in an effort to make it financially competitive in the market. They explored alternative fluid mixtures like ammonia-water that can replace R114 for heating water between 60 - 90 °C. Considerations were made to the working fluid compatibility to lubrication, compressor design and heat exchanger design for wide boiling mixtures.

Just like Hewitt *et al.* (2001) had done, Jensen *et al.* (2015b) also evaluated the technical and economic possibilities of an ammonia-water HACHP. They were able to show that at the same operating points, HACHP cost was lower than the conventional vapour compression HTHP. Jensen *et al.* (2015a) theoretically investigated the development of HACHP for even higher temperatures up to 175 °C. They implemented constraints in their design to limit solutions to those economical and technically feasible. They discovered that two parameters, the rich ammonia mass fraction and the circulation ratio, have such high influence on the design that it should be well considered in the development of high temperature HACHP systems.

M. Kim *et al.* (2010) did the application of HACHP to a geothermal water heat source at a temperature of 30 to 50 °C. They investigated the system using a mathematical model in order to validate its applicability. The target is to make a hot water production system for temperatures above 90 °C from a source as low as 20 °C. They went on to investigate experimentally the effect of refrigerant mixtures composition on the operating characteristics of this hybrid heat pump (J. Kim *et al.*, 2013b).

In order to improve the performance of compressors in hybrid systems, Infante Ferreira *et al.* (2006) evaluated the performance of a twin screw oil free wet compressor. Using both theoretical and experimental analysis, they reported on the performance impact of liquid injection process into the compressor. The point of liquid injection, angle of injection, injection flow rate and also labyrinth seal on performance of the compressor were documented. Improvement in compressor technology to allow wet compression will expand the possibilities for HTHPs.

The ammonia-water concentration affects the pressure, density, required mass flow rate and the temperature glide. The concentration therefore is considered an important parameter in defining the application temperature and capacity. Bergland *et al.* (2015) worked on optimizing a HACHP system for high temperatures. Using an ammonia-water absorber model, they achieved a maximum temperature of 171.8 C from a two-stage HACHP system. Other research evaluated the use of HACHP at different operating conditions (J. Kim *et al.*, 2013a). Some other mixtures have been tested for a HACHP by (Bourouis *et al.*, 2000; Tarique & Siddiqui, 1999).

HACHP has found applications in food processing like dairy, slaughterhouses, fish drying to district heating and also industrial applications. There is high potential for the technology in distillation columns as investigated by van de Bor *et al.* (2014). Temperatures of up to 100 °C have been achieved with capacity over 1 MW. The practical limit with existing technology is delivery of heat at 110 °C. Compressor discharge temperature currently limits higher condensation temperatures. The continuous improvement in compressor technology in material, lubrication, wet compression and cooling will be the next phase in the future of HACHP as a HTHP.

6. High Temperature Equipment

Defining the right type of equipment, sizing and operating parameters is perhaps the most difficult aspect of HTHP development. Though there exist many components for natural working fluids in heat pumps, operating at high temperatures will require further or new tests for fluid behaviour with respect to materials, equipment and safety. This implies high cost, and long hours of experiments.

A theoretical analysis of HTHP cycles shows that the highest amount of irreversible losses occurs for the two main components; the compressor and the heat exchangers. With the compressor having the highest irreversible loss. Apart from advances in water vapour compressors, there has been little development in high temperature compressors for other working fluids. Finding a suitable compressor that can operate at high temperature and at reasonable efficiency will help in HTHP development. For example, Oku *et al.* (2015) developed a scroll compressor for a blended hydrocarbon. Their experiment results showed capability to deliver hot water at 88 °C. More research is needed in high temperature compressor development. However, several studies have focused research on the development of effective heat exchangers.

Working on heat exchangers for zeotropic mixtures, Venkatarathnam *et al.* (1996) and Venkatarathnam and Murthy (1999) studied the effect and behaviours of the heating curves in the formation of pinch point in condenser and evaporators. Z. Y. Liu *et al.* (2012) used the theory proposed by Venkatarathnam, that there is a nonlinear relationship between temperature and enthalpy in the two-phase region for zeotropic mixtures and this can cause pinch points. They studied the effects of this on the performance of HTHP. Their study revealed that in the selection of the composition of zeotropic mixtures, consideration should be taken to check the pinch point occurrence within the condenser and evaporator. Zeotropic mixtures that give smaller temperature difference in the condenser and evaporator will have higher COP if the effect is not diminished due to less efficient heat transfer or compressor efficiency.

Similarly, Zhao *et al.* (2007) and Zhao *et al.* (2013) presented an optimal procedure for designing heat exchangers for HTHPs. Their focus was on heat exchanger type and area optimization. They utilized a dual-stage HTHP to evaluate nine different heat exchanger types, by studying the effect of the heat transfer area. Their procedure showed it is a way to solve component mismatch in HTHP. They were able to achieve reduction in heat exchanger size and number of tubes by this optimal design. Other important parameters for HTHP heat exchangers are the heat transfer coefficient, heat transfer area and the pressure drop which were investigated by Z. J. Li *et al.* (2009) and Longo *et al.* (2014).

Aside the performance characteristics of HTHP equipment, there are many other challenges when operating at high temperatures. Operating the compressor suction at temperatures above atmospheric poses a possibility of liquid entry to the compressor due to condensation. The effectiveness of the expansion valve to maintain a superheat at the evaporator discharge, the installation of an internal heat exchanger for liquid sub-cooling and further superheat of vapour and/or the installation of a suction line accumulator can protect the compressor from liquid entry. Other challenges would involve starting up the system after a long idle period, refrigerant migration after shutdown, mechanical strength of heat exchangers in the de-superheating region, chemical stability of the waste heat source with the evaporator material and compressor lubrication selection and viscosity at high temperature.

Over the years, much research have been documented in literature with solutions to these challenges applicable to heat pumps operating at lower temperatures ($< 80\text{ }^{\circ}\text{C}$). The solutions for HTHP systems would not be significantly different. Existing experimental data at lower temperatures will be useful to predict behaviours of HTHP equipment. Further research on these aspects are expected in the coming years as the industry expands to providing environmentally friendly and cost efficient heating solutions at high temperature. Operational challenges such as start-up or shut-down, material mechanical strength concerns, waste heat source suitability and adaptability and performance of lubricant at these high temperatures will require extensive research which are not available yet in literature.

7. Summary and Conclusion

Ongoing researches, experiments and existing applications has shown the potential of using a VCC and its variations in HTHP for heat delivery above $80\text{ }^{\circ}\text{C}$. Many of the methods suggested in research however, still require technological advancement in certain components to be possible. This technological advancement will have to address both thermodynamic constraints and economic competitiveness. Table 2 summarizes the challenges and possible improvement for the future of HTHP.

Table 2: Challenges and Suggestions for HTHP

Working system	Challenges for HTHP	Existing solutions	Possible improvement
Ammonia	Material compatibility	Steel, and aluminium	Enhanced material properties
	High disch. temp.	Multi-stage, intercooler integration	Cascade system with other fluids
	High disch. press.	60 bar disch. press.	-
	High toxicity	Machine room safety, secondary cycle (glycol)	-
	Compressor cooling	Heat sink integrated as coolant	High temperature lubricant research
	High refrigerant inventory	Plate heat exchangers, machine room, charge mass optimization	-
	Low performance	Flooded type evaporator, multistaging	-
CO₂	High gas cooler exit temp.	Temp. glide matching, HX optimization	Integration with secondary heat sink
	High comp. disch. press.	150 bars comp.	Material, comp. technology improvement
	Expansion device losses	Vapour recompression, expanders, ejectors	Further research in ejectors
	Low performance	Evaporator overfeeding	-
	Low heat sink outlet temp.	Multiple vertical tanks for stratification	-
	Low critical temp.	-	Combined cycle with other working fluid
Water	Sub atmospheric suction press.	Heat source at or above 100 °C	Cascade in HTC with other working fluid
	High disch. temp.	Intercooling between stages	Process integration with intercooler
	Low temp.lift.	Multistaging	-
	High volume flow rate	Turbo compressors, parallel compressors	-
Hydrocarbons	Flammability	Leak detection, ventilation, explosive unit	-
	High disch. press.	-	Comp. technology research
	High dish. Temp.	-	Lubricant, cooling system research, mixture properties
	Charge mass reduction	Multiple units to meet charge requirement	-
	Sub atmospheric suction press.	-	Mixtures properties
HACHP systems	Large heat exchangers	-	Further research in heat transfer
	High discharge temperature	Multi-stage, intercooler integration	-
	Low performance	Internal heat exchangers	Wet compression

This paper has reviewed the current state of art for HTHPs using VCC and its variations. It revealed that in the past 20 years, many have attempted to use the VCC to utilize the large amounts of energy available as waste heat from industrial processes. Different concepts and approach have been done to make the method commercially viable. Pure working fluids have been investigated, mixed fluids have also been evaluated with varying degree of the composition. Performance analysis and economic viability have been carried out on different heat pumps and configurations. Various optimization techniques have been applied to match the selected fluid with the best system cycle. Analyses have been done on the most

effective heat transfer method through sensible heat or latent heat or through the temperature glide of mixed fluids in heat exchangers.

The next step in the development of HTHP will be on compressors that can operate at higher temperatures and pressure. Technological constraints such as compressor cooling, lubrication, and material compatibility will be important for a functional compressor for HTHP. The opportunity for development is there, the positive impact on the environment is substantial and so is the demand for the technology. This review further shows that there are good prospects to find natural working fluids applicable for HTHPs.

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