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High Temperature Heat Pumps: Market Overview, State of the Art, Research Status, Refrigerants, and Application Potentials

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High Temperature Heat Pumps: Market Overview, State of the Art, Research Status, Refrigerants, and Application Potentials

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ABSTRACT

This study reviews the current state of the art of high temperature heat pumps (HTHPs) with heat sink temperatures of 90 to 160°C. The focus is on the analysis of heat pump cycles, suitable refrigerants, and the operating ranges of commercially available HTHPs and heat pumps at the research status.

More than 20 HTHP models from 13 manufacturers have been identified on the market that are able to provide heat sink temperatures of at least 90°C. Only a few heat pump suppliers have already managed to exceed 120°C. Large application potentials have been recognized particularly in the food, paper, metal, and chemical industries, especially in drying, pasteurizing, sterilizing, evaporation, and distillation processes.

The heating capacities range from about 20 kW to 20 MW. The refrigerants used are mainly R245fa, R717, R744, R134a, and R1234ze(E). Most circuits are single-stage and differ primarily in the applied refrigerant and compressor type. Internal heat exchangers (IHX) are used to ensure sufficient superheating. Process optimization is achieved with economizer cycles or two-stage turbo compressors with intermediate vapor injection. Two-stage cascade cycles or open flash economizers are also applied in commercial HTHPs. The COP values range from about 1.6 to 5.8 at temperature lifts of 130 to 40 K, respectively.

Several research projects push the limits of the achievable COPs and heat sink temperatures to higher levels. Research groups in Austria, Germany, France, Norway, The Netherlands, Switzerland, Japan, Korea, and China are active in the experimental research of HTHPs. Several laboratory scale HTHPs have been built to demonstrate the technical feasibility of sink temperatures above 120°C. The heat pump cycles examined are mainly single-stage and in some cases contain an IHX for superheating or an economizer for vapor injection into the compressor. The investigated refrigerants are R1336mzz(Z), R718, R245fa, R1234ze(Z), R600, and R601. R1336mzz(Z) enables exceptionally high heat sink temperatures of up to 160°C. The experimentally obtained COPs at 120°C heat sink temperature vary between about 5.7 and 6.5 at 30 K temperature lift and 2.2 and 2.8 at 70 K lift. New environmental friendly refrigerants with low GWP and improved components lead to a need for research on optimized cycles.

The high level of research activity and the large number of demonstration R&D projects indicate that HTHPs with a heat sink temperature of 160°C will reach market maturity in the next few years. However, despite the great application potential, other competing heating technologies and most importantly low prices for fossil fuels are still hindering the wider spread of HTHPs in industry.

Keywords: high temperature heat pump, market overview, state of the art, research status, COP, refrigerant

1. INTRODUCTION

High temperature heat pumps (HTHPs) are suitable systems for waste heat recovery in various industrial processes such as drying, sterilization, papermaking, or food preparation (Arpagaus *et al.*, 2017a, 2017b). Low-temperature waste heat can be upgraded efficiently into usable high temperature heat. In addition, multi temperature heat pumps using multiple heat sources at different temperature levels are appropriate devices to increase efficiency when waste heat from several heat sources is available (Arpagaus *et al.*, 2016).

The screening of the open literature revealed that there is a limited number of studies comparing different vapor compression HTHP systems. Most of the research studies focus on one specific vapor compression HTHP system only. There is a lack of a comprehensive comparison of those studies. Hence, the objectives of this review paper are:

(1) A thorough state of the art review of commercially available HTHPs on the market focusing on suitable cycle concepts, applied refrigerants, and current limits of operation.
(2) A systematic comparison of experimental studies on HTHPs in R&D status with an evaluation of the heat pump cycles, operating ranges, refrigerants, achieved heat sink temperatures, and COPs.
(3) Identification of suitable refrigerants for HTHP applications with heat sink temperatures above 120°C, discussion of their selection criteria with general focus on the examination of possible heat pump cycles, and suggestions for future research areas.

This review study assumes 90°C as a boundary level of the heat sink temperature for classifying a HTHP. Focus is on electrically driven closed-cycle vapor compression heat pumps, as this type is most widely used and available in a large variety of sizes for different applications. Thermally driven sorption cycles or hybrid absorption-compression heat pumps are other relevant technologies for high temperature heat supply in industrial applications, especially if high temperature glides in the sink and source are available. An extended version of this review study has been published recently by Arpagaus *et al.* (2018) in the International Journal of Energy.

2. APPLICATION POTENTIALS

The major process heat demand in industry occurs in the production, the processing, and the finishing of products. Generally, process heat is supplied above 80°C, which is about the starting temperature for applications of HTHPs. The theoretical application potential for the use of heat pumps in industrial processes can be estimated by evaluating the heat demand of each industrial subsector and the temperature levels of the applied processes.

Figure 1 illustrates the distribution of the industrial heat demand in Europe and the U.S. by industrial subsector and temperature level. For the European heat pump market, Nellissen & Wolf (2015) evaluated a technical heat potential of about 626 PJ at temperatures of up to 150°C, which would be accessible with heat pumps. About 116 PJ or 19% of that potential lies between 100 and 150°C and is argued to be particularly reachable by industrial HTHPs. The temperature range above 150°C remains inaccessible for vapor compression heat pump technology for the time being. Major technical potential of HTHP applications between 100 and 150°C is found in the food and tobacco, the chemical, and the paper industries (see black shaded bars in Figure 1, left). The theoretical market potential of process heat in Europe would be larger, but for practical reasons it is often not possible to fully exploit it. Overall, great application potential for HTHPs is identified in drying processes, as well as in pasteurizing, sterilizing, evaporation, and distillation.

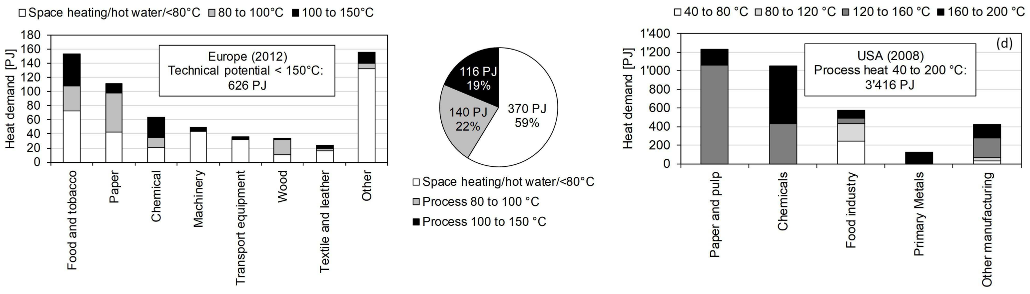


Figure 1: Left: Technical market potential of process heat in Europe accessible with industrial heat pumps distributed by temperature and industrial subsectors (based on Eurostat data from 2012 of 33 countries, data adapted from Nellissen & Wolf, 2015). Right: Theoretical potential of HTHPs in the U.S derived from the industrial process heat demand in 2008 below 200°C (data adapted from Fox *et al.*, 2011).

Fox *et al.* (2011) investigated the industrial energy consumption in the U.S. for 2008 where process steam below 260°C is heavily used. The analysis revealed a total process heat demand of 3’416 PJ between a temperature of 40 to 200°C. The major potentials for process heat were identified in the paper and pulp, chemical, food, and metal industries, which is in line with the major main natural gas consumers. All industrial subsectors use steam in temperature ranges suitable for HTHP application. It is assumed that the data presented for Europe and the U.S. are representative for the corresponding industrial subsectors around the world. However, in order to assess the worldwide potential for HTHPs in industrial processes, more data of the global industrial heat demand with proportions of the temperature levels and the final end-use are required.

3. MARKET OVERVIEW

The range of heat pump models on the market with high heat sink temperatures has grown steadily in the recent years. Over 20 heat pump models from 13 manufacturers have been identified (Arpagaus *et al.*, 2017a, 2017b, 2018) (Table 1). The companies Kobe Steel (Japan), Viking Heat Engine SA (Norway), Ochsner Energie Technik GmbH (Austria), Mayekawa (Japan), Hybrid Energy AS (Norway), Combitherm (Germany), Dürr Thermea GmbH (Germany), and Friotherm (Switzerland) show pioneering developments with their HTHPs in industrial scale providing heat sink temperatures above 110°C. Some heat pumps already supply 130 to 165°C of heat. The heating capacity range goes from about 20 kW up to 20 MW. Still there are significant limitations in use due to sometimes very particular application with large temperature glides on the heat sink and the use of refrigerants, which will soon be phased out due to environmental and regulation reasons. In particular, HFCs like R134A, R245fa, or R365mfc are targeted by the European F-gas regulation by a phase down reduction in the use of 79% for 2030. Highly promising for HTHPs are HFOs, like R1336mzz(Z) or R1233zd(E) with low toxicity, no flame propagation, and low GWP. R1336mzz(Z) is about to be commercialized by Chemours under the brand name Opteon™ MZ. Honeywell proposes Solstice®ze (R1234ze(E)) and Solstice®zd (R1233zd) as refrigerants for HTHP applications. HFO working fluids are authorized without restriction by the regulations, as are natural refrigerants (e.g. R601, R600), but there is still a lack of research on these refrigerants.

Table 1: Industrial HTHPs with heat sink temperatures above 90°C
(adapted from Arpagaus *et al.*, 2017a, 2017b, 2018).

Manufacturer	Product	Refrigerant	Max. heat sink temperature	Heating capacity	Compressor type
Kobe Steel (Kobelco steam grow heat pump)	SGH 165	R134a/R245fa	165°C	70 to 660 kW	Twin screw
	SGH 120	R245fa	120°C	70 to 370 kW	
	HEM-HR90, -90A	R134a/R245fa	90°C	70 to 230 kW	
Vicking Heating Engines AS	HeatBooster S4	R1336mzz(Z) R245fa	150°C	28 to 188 kW	Piston
Ochsner Energie Technik GmbH	IWWDSS R2R3b	R134a/ÖKO1	130°C	170 to 750 kW	Screw
	IWWDS ER3b	ÖKO (R245fa)	130°C	170 to 750 kW	
	IWWHS ER3b	ÖKO (R245fa)	95°C	60 to 850 kW	
Hybrid Energy	Hybrid Heat Pump	R717/R718 (NH_3/H_2O)	120°C	0.25 to 2.5 MW	Piston
Mayekawa	Eco Sirocco	R744 (CO_2)	120°C	65 to 90 kW	Screw
	Eco Cute Unimo	R744 (CO_2)	90°C	45 to 110 kW	
Combitherm	HWW 245fa	R245fa	120°C	62 to 252 kW	Piston
	HWW R1234ze	R1234ze(E)	95°C	85 to 1’301 kW	
Dürr thermea GmbH	thermeco$_2$	R744 (CO_2)	110°C	51 to 2’200 kW	Piston (up to 6 in parallel)
Friotherm	Unitop 22	R1234ze(E)	95°C	0.6 to 3.6 MW	Turbo (two-stage)
	Unitop 50	R134a	90°C	9 to 20 MW	
Star Refrigeration	Neatpump	R717 (NH_3)	90°C	0.35 to 15 MW	Screw (Vilter VSSH 76 bar)
GEA Refrigeration	GEA Grasso FX P 63 bar	R717 (NH_3)	90°C	2 to 4.5 MW	Twin screw (63 bar)
Johnson Controls	HeatPAC HPX	R717 (NH_3)	90°C	326 to 1’324 kW	Piston (60 bar)
	HeatPAC Screw	R717 (NH_3)	90°C	230 to 1’315 kW	Screw
	Titan OM	R134a	90°C	5 to 20 MW	Turbo
Mitsubishi	ETW-L	R134a	90°C	340 to 600 kW	Turbo (two-stage)
Viessmann	Vitocal 350-HT Pro	R1234ze(E)	90°C	148 to 390 kW	Piston (2 to 3 in parallel)

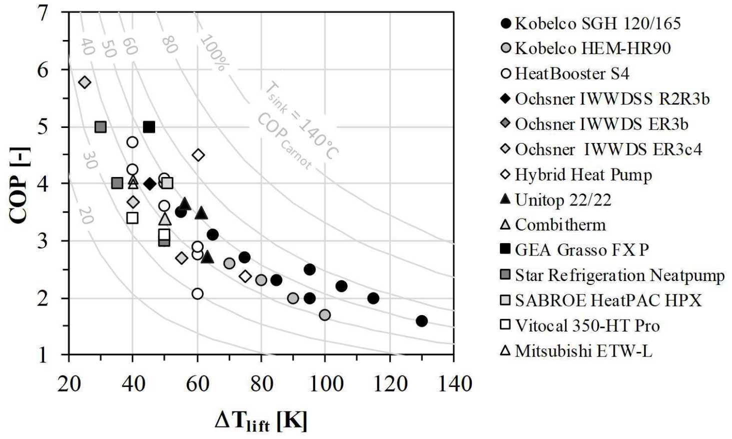


Figure 2: COP as a function of the temperature lift for various industrial HTHPs (adapted from Arpagaus *et al.*, 2017a, 2017b, 2018).

Most heat pump circuits are single-stage and differ in the used refrigerant and compressor type. Internal heat exchangers (Mayekawa, Ochsner, Viking) are applied to ensure sufficient superheating. Optimizations are achieved with economizer cycles (Mitsubishi), turbo compressors with intermediate injection (Friotherm), parallel-connected piston compressors (Viessmann, Dürr thermea), and 2-stage cascade cycles (Ochsner).

Figure 2 shows the COP values for the various industrial HTHPs listed in Table 1 as a function of the respective temperature lift. The COP values range between about 1.6 and 5.8 with a temperature lift of 130 to 25 K, respectively. The mean COP of this data composition is about 3.3 at an average temperature lift of 61 K. Also plotted are the COP Carnot curves at 140°C sink temperature. Most experimental data range between 40 to 60% Carnot efficiency (Second Law efficiency).

Despite the great ecological potential, there are still some market barriers to the wider spread of industrial HTHPs:

- Lack of available refrigerants in the high temperature range with low GWP
- Lack in the understanding of the HTHP technology (low level of awareness of the technical possibilities among users, consultants, investors, plant designers, producers, and installers)
- Lack of knowledge about the integration of HTHPs in industrial processes
- Cost-intensive integration into existing processes due to tailor-made designs (leads to payback periods larger than for gas or oil fired boilers)
- Lack of suitable and approved compressors
- Competing heat-producing technologies generating high temperature using fossil fuels
- Low fossil energy prices (low gas to electricity price ratio)
- Lack of pilot and demonstration systems
- Lack of training and events additionally supporting the spread of HTHP knowledge.

A big hurdle to accelerated market diffusion of HTHP technology in the industrial sector can be found in the economic efficiency. Typically, large heat pumps are individual and specially designed, or products, which are manufactured in small lot sizes. Larger lot sizes would increase productivity due to the economy of scale. One possible way would be to make heat pumps modular, so that parts of the heat pump circuit or the hydraulic integration could be produced in larger quantities. If sufficient installation space is available at the customer site, several standard HTHPs could also be connected to a large heat pump system. Another hurdle lies in the lack of available compressors and refrigerants, which again increases prices. On this topic, increased research effort has started worldwide over the last few years. Finally, it is not always easy to implement a heat pump into an existing plant, since it needs well thought out integration on the heat sink and heat source side. In order to overcome this hurdle, successful integrations need to be demonstrated and published. Another option is to integrate the heat pump already into a production machine instead of the plant allowing for multiple benefits at the same time.

In order to address the above-mentioned barriers, the International Energy Agency (IEA) has already conducted several programs on the subject of industrial heat pumps. Currently, the IEA Annex 48 from 2016 to 2019 on Industrial Heat Pumps (Second Phase) is trying to overcome existing difficulties and barriers for the larger scale market introduction of industrial heat pumps.

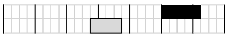
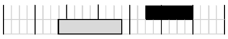
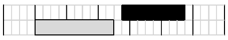
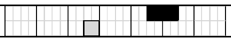
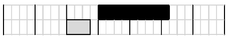
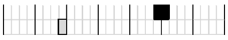
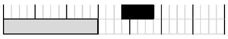
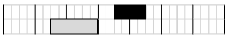
4. RESEARCH STATUS

There is a high level of research activity in the area of HTHP technology development. Various R&D projects are currently running on an international level showing the will to develop the domain of HTHPs and to push the transfer towards the industrial sector. The main research goals are improving heat pump efficiency, testing new environmental-friendly refrigerants, and achieving high heat sink temperatures of above 100°C to produce low-pressure steam.

Table 2 gives an overview of the most relevant experimental research projects sorted according to the maximum achieved heat sink temperatures. Further information is given on the project partners, the heat pump cycle, the compressor type, the refrigerant, and the heating capacity. Research groups in Austria, France, Germany, Norway, The Netherlands, Switzerland, Japan, Korea, and China are mainly driving the experimental research on HTHPs. The heating capacities of the laboratory functional models range from about 1.8 to 12 kW. Larger prototypes are capable of producing several 100 kW of heat. Piston compressors are mainly used in laboratory systems. Most of the studied cycles are single-stage and partly contain an IHX and/or an economizer with intermediate vapor injection into the compressor. There are a few experimental studies on two-stage cycles and studies with additional subcoolers for combined water heating. The refrigerants investigated are mainly R1336mzz(Z), R718, R245fa, R1234ze(Z), R600, and R601, as well as fluids with no further published information on the chemical composition, such as LG6, ÖKO1 (contains R245fa), ECO3, HT125, BY-4, or BY-5. The highest heat sink temperature of almost 160°C was achieved using a single-stage cycle with an IHX and the HFO refrigerant R1336mzz(Z).

Figure 3 shows the experimentally achieved COPs of the different research projects listed in Table 2 as a function of the heat sink temperature and the respective temperature lifts (ΔT_{lift}). The COPs tend to increase with higher sink temperature and lower temperature lift.

Table 2: Research projects with HTHPs sorted by the heat sink temperature. Further information is given on the organization, project partners, heat pump cycle, compressor type, refrigerant, and heating capacity (adapted from Arpagaus *et al.*, 2017a, 2017b, 2018).

Project partners, country	Cycle type	Compressor	Refrigerant	Heat source (grey) and sink (black) temperatures [°C] 20 40 60 80 100 120 140 160	Heating capacity [kW]	References
Austrian Institute of Technology, Vienna, Chemours, Bitzer	Single-stage with IHX	Piston	R1336mzz(Z)		12	(Helminger *et al.*, 2016)
Austrian Institute of Technology, Vienna, Chemours, Bitzer	Single-stage	Piston	R1336mzz(Z)		12	(Fleckl *et al.*, 2015)
PACO, University Lyon, EDF Electricité de France	Flash tank	Twin screw	R718		300	(Chamoun *et al.*, 2014, 2012)
Institute of Air Handling and Refrigeration, Dresden, Germany	Single-stage	Piston	HT 125		12	(Noack, 2016)
Friedrich-Alexander University Erlangen-Nuremberg, Siemens, Germany	Single-stage with IHX	Piston	LG6		10	(Reißner *et al.*, 2013)
Alter ECO, EDF Electricité de France	Single-stage with IHX and subcooler	Twin scroll	ECO3 (R245fa)		50 to 200	(Bobelin *et al.*, 2012)
Tokyo Electric Power Company, Japan	Single-stage	Screw	R601		150 to 400	(Yamazaki & Kubo, 1985)
Austrian Institute of Technology, Vienna, Edtmayer, Ochsner	Single-stage with economizer	Screw	ÖKO1 (R245fa)		250 to 400	(Wilk *et al.*, 2016)
Tianjin University, China	Single-stage	Scroll	BY-5		16 to 19	(Zhang *et al.*, 2017)
Kyushu University, Fukuoka, Japan	Single-stage	Twin rotary	R1234ze(Z)		1.8	(Fukuda *et al.*, 2014)
ECN, SmurfitKappa, IBK, Bronswerk, The Netherlands	Single-stage with IHX and subcooler	Piston	R600		160	(Wemmers *et al.*, 2017)
Korea Institute of Energy Research, Daejeon, South Korea	Single-stage with steam generation	Piston	R245fa/R718		20 to 40	(Lee *et al.*, 2017)
GREE Electric Appliances, Zhuhai, China	Single-stage	Scroll	R245fa		6 to 12	(Huang *et al.*, 2017)
Norwegian University of Science and Technology, SINTEF, Norway	Two-stage cascade	Piston	R600/R290		20 to 30	(Bamigbetan *et al.*, 2017)
Technical University Graz, Austria	Single-stage with IHX	Piston	R600		20 to 40	(Moisi *et al.*, 2017)
Tianjin University, China	Single-stage	Double scroll	BY-4		44 to 141	(Yu *et al.*, 2014)
EDF Electricité de France, Johnson Controls	Single-stage with IHX and economizer	Twin screw, turbo	R245fa		300 to 500 900-1'200	(Assaf *et al.*, 2010) (IEA, 2012, 2014) (Peureux *et al.*, 2014)

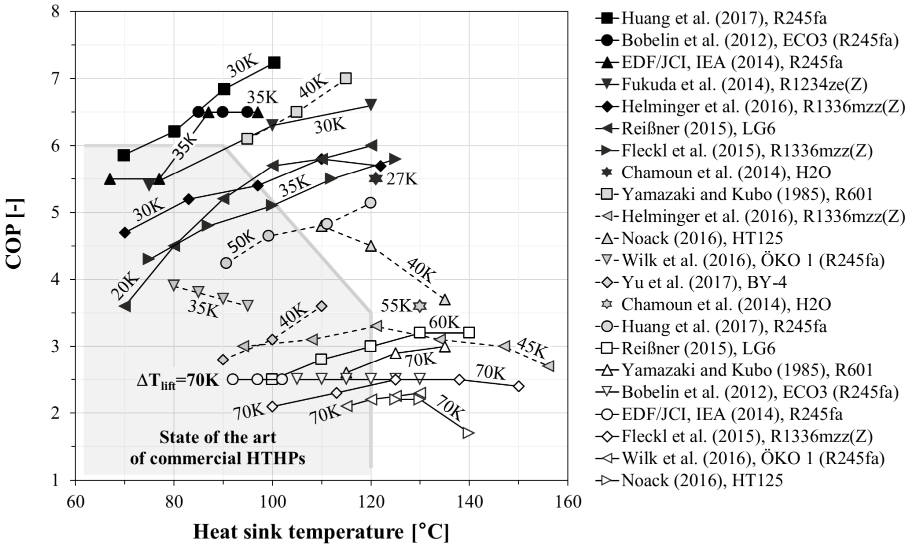


Figure 3: Experimentally achieved COPs of HTHPs in research status as a function of the heat sink temperature at different temperature lifts (ΔT_{lift} from 20 to 70 K). Shaded area: The state of the art of commercial HTHPs with a COP of up to 3.5 at 120°C sink temperature and approximately 6 at 60 to 90°C (adapted from Arpagaus *et al.*, 2017a, 2017b, 2018).

The bandwidths of the COPs of the research studies at 120°C heat sink temperature are in the ranges of about 5.7 to 6.5 at 30 K temperature lift and 2.2 to 2.8 at 70 K, respectively. Helminger *et al.* (2016) achieved the highest sink temperature of 155°C with a COP of 2.7, at a temperature lift of 45 K, and refrigerant R1336mzz(Z). Fleckl *et al.* (2015) reached 150°C with a COP of 2.4 and a considerable temperature lift of 70 K.

Some curves reach a COP maximum and decline slightly with higher heat sink temperature. This phenomenon is related to the situation close to the critical point of the refrigerant, where the condensation enthalpy decreases gradually with higher temperature in relation to the compression enthalpy, whereby the COP decreases. As can be seen, several research projects push the limits of the achievable COPs and heat sink temperatures to higher levels compared to the state of the art results of commercial available HTHPs displayed as shaded area in Figure 3. This area has been determined from data presented in Figure 2. More R&D efforts are dedicated to increase the technological readiness level and efficiency of HTHPs.

5. REFRIGERANTS

The selection of the refrigerant is a key element in the design of HTHPs. The refrigerant must be safe to the environment (zero ODP, very low GWP), future-proof according to regulations (e.g. EU F-Gas regulation No 517/2014), non-toxic, thermodynamically suitable, efficient, and available. In addition, a refrigerant with no or only low flammability (safety groups A1 or A2) reduces the complexity of the safety devices and thus the equipment costs. The upper temperature limit of a heat pump cycle working at subcritical conditions is determined by the critical temperature of the refrigerant. A certain temperature gap (e.g. 10 to 15 K) from the desired condensation temperature has to be maintained to ensure efficient subcritical heat pump operation. The closer the condensation temperature to the critical point, the smaller the condensation enthalpy and the heating COP.

The pressure level of the heat pump system should be kept below a practical limit of about 30 bar, as it determines the material efforts of the equipment. However, there are compressors available for R32 and R410A, which can withstand up to 50 bar. To minimize compressor power the pressure ratio should be as low as possible.

A properly selected oil ensures tightness, lubricity and temperature stability. With today's technology, the compression end temperature e.g. in a piston head should not exceed about 150°C. A too high compressor discharge temperature could pose challenges in the compressor heat management and lead to loss of lubricity and even chemical decomposition and coking of the oil. Moreover, the working fluids need to be chemically compatible (no degradation) with metal materials like aluminum, steel and copper, as well as with polymers.

The achievable COP of a working fluid in a heat pump cycle is one important thermodynamic parameter. The volumetric heating capacity (VHC) is important for the compressor design as it determines its size and cost, and it influences the achievable experimental COP. Other decision criteria for refrigerant selection are the availability on the market and its price. For example, the low GWP refrigerant R1233zd(E) costs about 55 EUR/kg, which is comparable to R245fa (57 EUR/kg) or Novec 649 (59 EUR/kg).

Table 3 compares the properties of a selection of refrigerants suitable for HTHP application. Listed are the chemical composition, the critical pressure and temperature, the ODP, the GWP, the normal boiling point, the safety group classification, the molecular weight, and the current price relative to CO_2.

Table 3. Refrigerants suitable for HTHP application. ODP basis R11=1.0 (UNEP, 2017), GWP_{100} for 100-year time horizon: basis CO_2=1.0, IPCC 5th assessment report from Myhre *et al.* (2013) and F-Gas regulation No 517/2014 (EU, 2014), Safety group (SG) classification according to ASHRAE (2016), NBP: Normal boiling point at 1.013 bar, *M*: molecular weight, Approximate sales price per kg refrigerant relative to CO_2 (9 EUR/kg based on a 10 kg container), n.a.: not yet available but close to market.

Type	Refrigerant	Chemical formula	T_{crit} [°C]	p_{crit} [bar]	ODP [-]	GWP_{100} [-]	SG	NBP [°C]	*M* [g/mol]	Relative price to CO_2 [-]
HFO	R1336mzz(Z)	$CF_3CH=CHCF_3(Z)$	171.3	29.0	0	2	A1	33.4	164.1	n.a.
	R1234ze(Z)	$CF_3CH=CHF(Z)$	150.1	35.3	0	<1	A2L[b]	9.8	114.0	n.a.
HCFO	R1233zd(E)	$CF_3CH=CHCl(E)$	166.5	36.2	0.00034	1	A1	18.0	130.5	6.3
	R1224yd(Z)[d]	$CF_3CF=CHCl(Z)$	155.5	33.3	0.00012	<1	A1	14.0	148.5	n.a.
HC	R601 (pentane)	$CH_3CH_2CH_2CH_2CH_3$	196.6	33.7	0	5	A3	36.1	72.2	4.9
	R600 (butane)	$CH_3CH_2CH_2CH_3$	152.0	38.0	0	4	A3	-0.5	58.1	1.8
CF6	Novec 649[a]	$CF_3CF_2C(O)CF(CF_3)_2$	168.7	18.8	0	<1	n.a.	49.0	316.0	6.8
Natural	R718	H_2O (water)	373.9	220.6	0	0	A1	100.0	18.0	5.6[c]
	R744	CO_2 (carbon dioxide)	31.0	73.8	0	1	A1	-78.5	44.0	1.0

[a] 3M™ Novec™ 649 (3M, 2009), [b] Fukuda *et al.* (2014), [c] Molecular biology reagent quality, [d] AMOLEA® 1224yd from AGC Chemicals (2017).

The HFO refrigerants R1336mzz(Z) and R1234ze(Z) are considered as environmentally friendly alternatives to replace the HFCs R245fa and R365mfc. The advantages of R1336mmz(Z) are the high critical temperature of 171.3°C at a feasible pressure of 29.0 bar. Its safety class is A1, it has a GWP of 2 and an ODP of 0, and an atmospheric life of 22 days (Myhre *et al.*, 2013). Chemours is about to commercialize R1336mzz(Z) under the brand Opteon™ MZ, which can deliver sink temperatures above 160°C. It is stable up to 250°C for organic Rankine cycles, waste heat recovery applications, and steam generation (Kontomaris, 2014). Laboratory tests have shown that the material compatibility relative to copper and steel is similar to those of R245fa. As lubricant, polyol ester oil (POE) with high viscosity is recommended as it is fully miscible over wide ranges of temperatures and compositions.

Relatively little information is available on the isomer R1234ze(Z). Its critical temperature and pressure are 150.1°C and 35.3 bar (Kondou & Koyama, 2014), which allows subcritical cycle operations at high temperatures. Its flammability is rated with A2L (Fukuda *et al.*, 2014) and its thermodynamic properties appear promising. Its GWP is smaller than 1 (Myhre *et al.*, 2013). Therefore, R1234ze(Z) is assessed as a suitable drop-in substitute for R114 in HTHP applications (Brown *et al.*, 2009).

The HCFO R1233zd(E) with a critical temperature of 165.5°C and a critical pressure of 35.7 bar is rated as safety class A1. It is available from Honeywell under the brand name Solstice®zd, and is recommended as a refrigerant for HTHP applications (Honeywell, 2016). Although R1233zd(E) contains chlorine, its ODP is extremely small (0.00034) due to the very short atmospheric lifetime of 40.4 days (Patten & Wuebbles, 2010).

R1224yd(Z) is another A1 non-flammable refrigerant designed mainly for use in centrifugal chillers and waste heat recovery heat pumps. AGC Asahi Glass is going to market the refrigerant as Amolea® 1224yd with commercial production beginning in early 2018 (AGC Chemicals, 2017). With an almost zero ODP (0.00012, atmospheric lifetime of 21 days) and an GWP value under 1, R1244yd(Z) has little impact on the environment. Its physical properties are stated to be very close to R245fa and R1233zd(E). Furthermore, it has also a good compatibility with most commonly used metals, plastics, and elastomers, and it is miscible with POEs.

3M™ Novec™ 649 (3M, 2009) is another refrigerant with favorable thermodynamic properties for use in HTHPs. It has been designed as a replacement for compounds with high ODPs and GWPs, such as sulfur hexafluoride (SF_6) and HFCs like R134a and R245fa. The fluid has a high critical temperature of 168.6 °C and a large molar mass of 316 g/mol. It is an effective heat transfer fluid particularly used for electronics cooling applications.

Natural refrigerants suitable for high temperature applications are especially water (R718), CO_2 (R744), and hydrocarbons (R601, R600). The large latent heat makes water very attractive for temperatures above 150°C. The major part of the heat pump cycle is below atmospheric pressure. Due to the low water vapor density, the required swept volume and pressure ratios are very high. Large compressors or high-speed oil-free turbo compressors with high flow rate are typically used. In order to keep the discharge temperature to a tolerable level, several water vapor recompression stages are required with intermediate cooling (Bless *et al.*, 2017).

CO_2 is feasible as a HTHP fluid if the inlet temperature of the heat sink is not too far above the critical temperature (31°C, 73.6 bar). In such transcritical or supercritical processes, the heat transferred to the heat sink is sensible with a large temperature glide in the gas cooler, which makes R744 particularly suitable for hot water heating and other processes requiring large temperature glides.

A characteristic of especially R601, R1336mzz(Z), Novec 649, and R1224yd(Z)) are the saturated vapor curves with a positive slope (dT/ds>0). To ensure a dry compression with high temperature lifts a sufficiently high superheating is necessary, which depends on the refrigerant, the condensation and evaporation temperatures, and the isentropic compressor efficiency.

6. CONCLUSIONS

High temperature heat pumps (HTHPs) are suitable systems for waste heat recovery in various industrial processes such as drying, sterilization, papermaking, or food preparation. About 20 industrial HTHPs models have been identified on the market, which can provide heat sink temperatures of at least 90°C. Today, only a few commercial available HTHP products manage to exceed 120°C supply temperature using mainly R245fa and R365mfc as refrigerants. The COP values range between about 1.6 and 5.8 with a temperature lift of 130 to 25 K, respectively. Most experimental data range between 40 to 60% Carnot efficiency (Second Law efficiency).

Several R&D projects are currently running on an international level to push the limits of the achievable COPs and sink temperatures to higher levels compared to the state of the art results of commercial available HTHPs. At a sink temperature of 120 °C, the COPs are in the range of about 5.7 to 6.5 at 30 K temperature lift and 2.2 to 2.8 at 70 K, respectively. Highest heat sink temperatures of up to 155°C have been achieved.

There is significant research towards testing new environmental-friendly refrigerants with low GWP for use in HTHPs. Suitable substitutes like R1336mzz(Z), R1234ze(Z), R1233zd(E), R1224yd(Z), and natural refrigerants, such as R718 and R744, and hydrocarbons (e.g. R601, R600) are intensively investigated. In addition, heat pump components are being developed to resist high temperature application, e.g. compressors as the main driving device in a heat pump.

The considerable number of ongoing R&D projects and a quick evolution in the research field provides evidence that HTHPs with heat sink temperatures of up to 160°C will reach market maturity in the coming years. For a wider spread of HTHP technology, the transfer of the research results to applied demonstration projects in industry is very important. Moreover, there is a need for better knowledge in characterization of the waste heat potentials classified by temperature ranges in the industrial sectors.

NOMENCLATURE

CFC	chlorofluorocarbon	p	pressure (bar)
COP	coefficient of performance (–)	POE	polyol ester oil
GWP	global warming potential	SG	safety group classification
HC	hydrocarbon	T	temperature (°C)
HCFC	hydrochlorofluorocarbon	VHC	volumetric heating capacity (kJ/m^3)
HCFO	hydrochlorofluoroolefin		
HFC	hydrofluorocarbon	**Subscripts**	
HFO	hydrofluoroolefin	crit	critical temperature
HTHP	high temperature heat pump	lift	temperature lift
NBP	normal boiling point at 1.013 bar	sink	heat sink
M	molecular weight (g/mol)	source	heat source
ODP	ozone depletion potenial		

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