

Experimental results of HFO/HCFO refrigerants in a laboratory scale HTHP with up to 150 °C supply temperature

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Extended Abstract

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1. Introduction

The range of electrically driven high temperature heat pumps (HTHP) for industrial applications has grown steadily in recent years. At least 26 industrial HTHP products are commercially available, capable of delivering heat at sink temperatures from 90 to 160 °C [1–4]. Heat pumps of this type are available in a wide range of heat outputs (20 kW to 20 MW) and the technology will be further commercialised in the coming years to play a key role in the decarbonisation of the industrial sector. Several presentations at the industrial heat pumps sessions at the ICR 2019 conference in Montréal confirmed this trend. By switching from fossil fuels to renewable energies and increasing energy and resource efficiency, the CO₂ footprint can be significantly reduced.

The use of industrial HTHPs is particularly interesting for heat recovery applications and various industrial processes, such as drying, steam generation, sterilisation, paper production or food preparation. From a research perspective, HTHP technology is being further developed and the limits of heat supply temperatures and performance figures are further explored. Various experimental R&D projects are currently running on an international level to push HTHPs from the laboratory scale towards industry. The main research objectives are (1) extending the limits of heat source and sink temperatures to higher levels, (2) improvement of heat pump efficiency (COP) by multi-stage cycles and oil-free compressors, (3) development of temperature-resistant components, such as valves and compressors, and (4) developing and testing of new synthetic environmentally friendly refrigerants with low GWP.

The choice of the optimal refrigerant is subject of much debate. The partially fluorinated hydrocarbons (HFC) R134a, R245fa and R365mfc have a greenhouse effect (GWP of 1'300, 858 and 804 [5]) and are experiencing a phase-down (i.e. production and consumption) in most industrialised countries. In Europe, the F-Gas regulation prohibits the use and reduces the market availability of greenhouse refrigerants. Consequently, only refrigerants with a GWP < 150 may be used in new commercial heat pumps starting from 2022. In Switzerland, the legal basis for refrigerants is regulated in the Chemicals Risk Reduction Ordinance (ChemRRV) [6] and industrial heat pumps with heat source capacity >600 kW are affected by the HFC ban.

Beside natural refrigerants, such as water (R718), CO₂ (R744), ammonia (R717), butane (R600), propane (R290), and pentane (R601), the application of the 4th generation of new synthetic hydrofluoroolefin (HFO) and hydrochlorofluoroolefin (HCFO) refrigerants with low environmental impact is becoming increasingly important as drop-in replacements for HFC in future HTHPs. Even though HCFOs contain a chlorine atom in their structure and do not comply with the legal requirements

of the Montreal Protocol (ODP of zero) there are national regulations, like the ChemRRV [6] that allow the use of HCFO refrigerants with an OPD < 0.0005.

At NTB Buchs a laboratory scale HTHP has been developed as part of the SCCER-EIP project [7]. The developed HTHP is single-stage, operates with a variable-speed reciprocating compressor, and contains a continuously adjustable internal heat exchanger (IHX) for superheating control. A viscous POE oil (173 mm²/s at 40 °C) was used to achieve sufficient lubrication at high temperatures with the refrigerants. The basic functionality of the HTHP and first experimental results with R1233zd(E) and R1336mzz(Z) have already been published in previous papers by Arpagaus et al. [8–12].

This paper examines the performance of R1336mzz(Z) (Opteon™MZ from Chemours), R1233zd(E) (Solstice®zd from Honeywell), and R1224yd(Z) (AGC Chemicals) in the same laboratory HTHP in a drop-in test. A parameter study was carried out to investigate the COP as a function of the temperature lift between heat source temperatures of 30 to 80 °C and heat sink temperatures of 80 to 150 °C.

2. Investigated HFO/HCFO refrigerants

Table 1 lists the thermodynamic, environmental and safety properties of the investigated refrigerants.

Table 1: Thermophysical, environmental, and safety properties of the tested HFO/HCFO refrigerants.

Refrigerant	R1233zd(E)	R1224yd(Z)	R1336mzz(Z)	R245fa
Brand (manufacturer)	Solstice®zd (Honeywell) Forane®HTS 1233zd (ARKEMA)	AMOLEA®1224yd (AGC Chemicals) [13]	Opteon™MZ (Chemours)	Genetron®245fa (Honeywell)
Molecular formula	E-CF ₃ -CH=CHCl	Z-CF ₃ -CF=CHCl	Z-CF ₃ -CH=CH-CF ₃	CHF ₂ CH ₂ CF ₃
Molecular weight [kg/kmol]	130.5	148.62	164.06	134.05
Critical temperature [°C]	165.6	155.5	171.3	154.0
Critical pressure [bar]	35.7	33.4	29.0	36.5
Normal boiling point [°C]	18.0	14.6	33.4	14.9
ODP (CFC-11=1) [-]	0.00034 [5], 0.00030 [14]	0.00023 [15]	0	0
GWP (CO ₂ =1, 100 years) [5] [-]	1 [5], <5 [14]	0.88 [15]	2 [5]	858
Atmospheric lifetime [days]	~14 [16], 26 [5], 36 [14], 40.4 [17]	20 [15]	22 [5]	7.7 years [18]
LC50 (rat, 4 h) [ppm v/v]	120*000	>213*000	102*900	>203*000
Occupational exposure limit (OEL) [ppm v/v]	800	1*000	500	300
Safety classification (ASHRAE)	A1	A1	A1	B1
Final degradation products in the atmosphere [19]	CO ₂ , HF, HCl	similar structure like R1234yf with potential for degradation to TFA	CO ₂ , HF	CO ₂ , HF
TFA molar yield from degradation	~ 2% [14]		< 20 % [20]	< 10 % [18]

R1233zd(E) has a critical temperature of 165.6 °C and a critical pressure of 36.2 bar and is available as Solstice®zd from Honeywell or as Forane®HTS 1233zd from ARKEMA. Although R1233zd(E) contains a chlorine atom that potentially can participate in the catalytic destruction of the ozone layer, its atmospheric lifetime is sufficiently low (~14 days [16], 40.4 days [17]) so that the compound will not reach the stratosphere and thus not participate in ozone depletion (ODP is 0.00034 [5]). So far, there is a limited investigation on the use of R1233zd(E) for HTHP applications [21]. First experimental results could be presented at the DKV conference 2018 [10] and ICR 2019 [8] with the developed laboratory HTHP system at NTB Buchs. Compared to a basic cycle the integration of an IHX led to approx. 15% COP increase at W60/W110 conditions [8]. The maximum heat sink temperature tested was 150 °C, whereby a COP of 2.1 was achieved with a heat source of 80 °C (70 K lift). At Ulster University another HTHP test facility is being developed to test R1233zd(E) as a part of the CHESTER project [21,22]. Simulation results of Shah et al. [21] showed an up to 8% higher COP with R1233zd(E) compared to R245fa. Further investigation is ongoing to test R1233zd(E) and oil miscibility.

R1224yd(Z) is another HCFO refrigerant designed for use in heat pumps for waste heat recovery and centrifugal chillers. AGC Chemicals (Asahi Glass) markets it as Amolea™1224yd [23]. The physical properties are close to R245fa. Its critical temperature is 155.5 °C and the saturated vapour pressure slightly lower (about 13% smaller at 120 °C) [24]. With an ODP of almost zero (0.00023, atmospheric lifetime of 20 days) and a GWP of 0.88 it has a low environmental impact [15]. The toxicity is indicated with a value of 1'000 ppm of OEL was provided as a maximum value for organic compounds [25]. In addition, AMOLEA™ 1224yd is classified as A1, which indicates non-flammability and low-toxicity.

At the ICR 2019 conference, Kaida et al. [24] presented first experimental results of R1224yd(Z) in a commercial SGH165 heat pump (with economizer and IHX) developed by KOBELCO and the Japanese electric utilities. Drop-in tests at an operating point W50/W95 (45 K temperature lift) revealed a 3% higher heating capacity and 12 % higher COP compared to R245fa. The performance improvements were attributed to increased refrigerant mass flow rate, decreased viscosity, and decreased required pressure ratio (higher adiabatic compressor efficiency). The chemical stability and compatibility with PAG oil, O-rings, and motor insulation material was comparable with R245fa. Overall, R1224yd(Z) was suggested as suitable R245fa alternative for HTHPs.

R1336mzz(Z) has a higher critical temperature of 171.3 °C at a feasible pressure of 29 bar. Chemours commercialized R1336mzz(Z) under the brand Opteon™MZ. R1336mzz(Z) is safety class A1, has a GWP of 2, an ODP of 0, and an atmospheric life of only 22 days [5]. Polyolester oil (POE) is recommended as lubricant, as it is fully miscible over wide ranges of temperatures and compositions [26,27].

Apart from GWP and ODP, the degradation products of refrigerants in the atmosphere and their effects on human health and the environment are a hot topic repeatedly featured in the recent open public [28]. The atmospheric degradation of HCFCs, HCFCs and HFOs is initiated by reaction with OH radicals leading to the formation of halogenated carbonyl compounds which are further oxidised to hydrofluoric acid (HF), hydrochloric acid (HCl), formic acid (HC(O)OH), CO₂ and in some cases trifluoroacetic acid (TFA, CF₃C(O)OH) [14,18–20,29]. For comparison, the >C=C< double bond in HFOs reacts two orders of magnitude faster with OH radicals than R134a [19]. For example, the molar yield of R134a to decompose into TFA is 7 to 21%, while for R245fa it is <10% [18]. As a result of their long atmospheric lifetimes (13.4, 7.7 years [18]), the gaseous TFA can be widely distributed in the atmosphere, descends via rainfall to earth and accumulates in various water bodies, including rivers, streams, lakes and wetlands, as well as “terminal sinks” like salt lakes, playas and oceans [28,29]. HF and HCl neutralize quickly due to the buffer capacity of surface water [19].

HFO and HCFO decompose much faster into their final products, which means they can occur locally at the point of emission and have direct effects. The molar yields of TFA formation from the degradation depends on the refrigerant [8]. For example, the degradation of R1234yf leads to a 100% molar yield of TFA. Interestingly, the HFO and HCFO refrigerants suitable for HTHP show little or no TFA and therefore have a negligible impact on the environment, which seems to be promising. R1233zd(E) decomposes to max. 2% TFA [14], whereas the yield for R1336mzz(Z) (containing two CF₃-CH= groups) is expected to be < 20% [20]. As R1224yd(Z) has a similar molecular structure like R1234yf there is potential for degradation to TFA.

On the other hand, over 200 million tons of TFA are already naturally present in the oceans from natural sources such as undersea vents and volcanic activity. In a worst case scenario of unregulated use of HCFCs, HCFCs and HFOs by 2050, Solomon et al. [29] estimated a total additional contribution of TFA to the oceans of <7.5% of the approx. 200 ng acid equivalents/L present at the start of the millennium, which was judged to be a negligible risk on the aquatic organisms.

3. Experimental Results and Discussion

After heating up the HTHP to the desired heat source and heat sink temperatures, the water flow rates in the two hydraulic circuits were adjusted by the pumps to receive constant temperature differences of 3 K at the heat source (ΔT_{Source}) and 5 K at the heat sink (ΔT_{Sink}). Mean values of at least five minutes were used for the data analysis. The heating COP was determined from the measured heating capacity (\dot{Q}_{Sink}) and the electrical power consumption of the compressor (P_{el}). Table 1 and Figure 2 (A to D) summarize the results of the parameter studies with the refrigerants R1224yd(Z), R1233zd(E) and R1336mzz(Z).

Table 2: Operating conditions and performance parameters of the experimental runs with refrigerants R1224yd(Z), R1233zd(E), and R1336mzz(Z) in the laboratory HTHP (1-stage cycle with IHX).

	No.	$T_{Source,in}$ °C	$T_{Sink,out}$ °C	ΔT_{Lift} K	ΔT_{Source} K	ΔT_{Sink} K	$T_{Suction}$ °C	$T_{Discharge}$ °C	ΔT_{SC} K	ΔT_{SH} K	p_{Cond} bar	p_{Evap} bar	p_{ratio} -	P_{Comp} kW	\dot{Q}_{Sink} kW	\dot{Q}_{Source} kW	\dot{Q}_{Loss} kW	η_{2nd} %	COP -
R1224yd(Z)	A1	30	70	40	3.0	4.9	57	101	22	5	5.7	1.5	3.8	1.2	4.0	3.5	0.6	40%	3.4
	A2	30	89	59	3.0	5.0	68	121	30	5	9.2	1.5	6.1	1.3	3.2	2.9	0.9	41%	2.5
	A3	40	70	30	3.1	5.0	60	100	17	5	5.9	2.1	2.9	1.3	5.5	5.0	0.8	38%	4.3
	A4	40	89	49	3.0	5.0	73	122	27	5	9.4	2.1	4.5	1.5	4.7	4.0	0.8	42%	3.1
	A5	40	110	70	3.0	5.0	86	143	36	5	14.3	2.1	6.9	1.7	3.7	3.2	1.2	40%	2.2
	A6	50	89	39	3.1	5.0	75	116	21	5	9.5	2.8	3.4	1.7	6.7	7.6	2.6	42%	3.9
	A7	50	109	59	3.0	5.0	90	141	31	5	14.4	2.8	5.2	2.0	5.3	4.7	1.5	41%	2.6
	A8	60	90	30	3.8	5.0	78	115	17	5	9.7	3.5	2.8	1.9	8.4	9.3	2.8	37%	4.5
	A9 Ref	60	110	50	3.2	5.0	92	142	26	5	14.7	3.7	4.0	2.3	7.5	7.8	2.6	42%	3.2
	A10	60	130	70	3.1	5.2	107	161	34	5	21.5	3.8	5.7	2.7	5.9	5.9	2.7	38%	2.2
	A11	70	100	30	4.4	4.9	88	126	17	5	12.2	4.5	2.7	2.3	9.8	10.6	3.1	35%	4.3
	A12	70	110	40	4.2	5.0	95	137	21	5	14.9	4.7	3.2	2.6	9.3	10.1	3.4	38%	3.6
	A13	70	130	60	3.5	5.0	109	162	29	5	21.8	4.9	4.4	3.1	8.0	8.6	3.7	38%	2.6
	A14	70	139	69	3.1	5.0	115	175	31	5	25.2	5.0	5.1	3.3	7.3	7.3	3.3	37%	2.2
	A15	79	120	40	4.8	5.1	104	148	20	5	18.0	5.9	3.1	3.1	10.9	11.6	3.7	36%	3.5
	A16	80	130	50	4.4	4.9	111	161	24	5	22.0	6.1	3.6	3.5	10.0	10.7	4.1	36%	2.9
	A17	80	140	60	3.6	5.0	120	172	21	5	25.4	6.3	4.0	3.8	8.3	8.6	4.1	32%	2.2
	A18	80	150	70	3.1	5.1	130	185	9	5	28.7	6.4	4.5	4.1	5.7	5.0	3.3	23%	1.4
R1233zd(E)	B1	30	69	39	2.9	5.1	56	94	23	5	5.1	1.3	3.9	1.1	3.5	3.3	0.9	37%	3.3
	B2	30	89	59	2.9	5.0	64	118	29	5	8.3	1.3	6.3	1.2	2.8	2.5	0.9	38%	2.3
	B3	40	70	30	3.0	5.1	59	101	18	5	5.2	1.8	2.9	1.2	4.8	4.2	0.5	36%	4.1
	B4	40	89	49	3.0	5.0	74	128	27	5	8.3	1.8	4.6	1.4	4.3	3.6	0.6	43%	3.1
	B5	40	109	69	3.0	5.0	84	143	35	5	12.9	1.8	7.2	1.5	3.3	2.9	1.1	39%	2.2
	B6	50	91	41	3.1	5.0	76	119	23	5	8.7	2.4	3.6	1.6	5.8	5.5	1.4	41%	3.7
	B7	50	109	59	3.0	4.9	90	143	32	5	12.9	2.4	5.3	1.8	4.9	4.3	1.3	41%	2.7
	B8	60	89	29	3.4	5.0	78	115	17	5	8.5	3.2	2.6	1.7	7.8	8.4	2.2	37%	4.7
	B9 Ref	60	111	51	3.0	5.0	93	141	27	5	13.5	3.3	4.1	2.1	6.5	6.7	2.3	41%	3.1
	B10	60	130	70	3.0	5.0	107	167	36	5	19.3	3.3	5.9	2.4	5.5	4.9	1.9	39%	2.3
	B11	70	110	40	3.8	5.0	95	139	22	5	13.4	4.2	3.2	2.3	8.6	9.2	2.9	39%	3.7
	B12	70	130	60	3.4	6.1	110	159	30	5	19.6	4.3	4.6	2.8	7.3	7.4	2.9	39%	2.6
	B13	78	110	32	4.5	5.0	97	141	18	5	13.5	4.9	2.8	2.5	10.3	10.8	2.9	36%	4.2
	B14	80	130	50	3.0	5.0	112	161	25	5	19.7	5.6	3.5	3.2	9.9	10.3	3.6	38%	3.1
	B15	80	149	69	3.3	5.1	126	185	31	5	27.5	5.7	4.8	3.7	7.6	7.9	3.9	34%	2.1
R1336mzz(Z)	C1	30	69	39	3.0	5.0	50	91	20	5	3.2	0.7	4.5	0.8	1.9	1.8	0.6	29%	2.5
	C2	40	70	30	3.0	5.0	58	94	18	5	3.2	1.0	3.1	0.9	3.0	2.6	0.5	30%	3.5
	C3	40	90	50	3.1	5.1	68	113	26	5	5.5	1.0	5.4	0.9	2.4	2.2	0.7	35%	2.6
	C4	40	108	68	3.1	4.8	75	126	30	5	8.5	1.0	8.3	1.0	1.9	1.7	0.7	34%	1.9
	C5	50	90	40	3.0	5.0	75	110	23	5	5.6	1.5	3.8	1.1	3.7	3.4	0.8	36%	3.3
	C6	60	90	30	3.0	5.0	78	108	17	5	5.7	2.0	2.8	1.2	5.2	5.1	1.1	34%	4.2
	C7 Ref	60	110	50	3.0	4.9	91	128	28	5	9.0	2.0	4.4	1.5	4.3	4.1	1.3	38%	3.0
	C8	60	129	69	3.1	5.0	105	148	38	5	13.5	2.0	6.7	1.6	3.3	3.2	1.5	36%	2.1
	C9	70	110	40	3.0	5.0	94	127	22	5	9.1	2.8	3.3	1.7	6.0	6.4	2.0	38%	3.6
	C10	80	111	31	3.7	5.1	98	128	18	5	9.4	3.5	2.7	1.8	7.8	8.6	2.6	34%	4.3
	C11	80	130	50	3.0	5.1	111	149	27	5	14.0	3.7	3.8	2.2	6.7	7.3	2.9	38%	3.0
	C12	80	150	70	3.0	5.1	125	172	36	5	20.4	3.7	5.5	2.5	4.6	4.9	2.8	30%	1.8

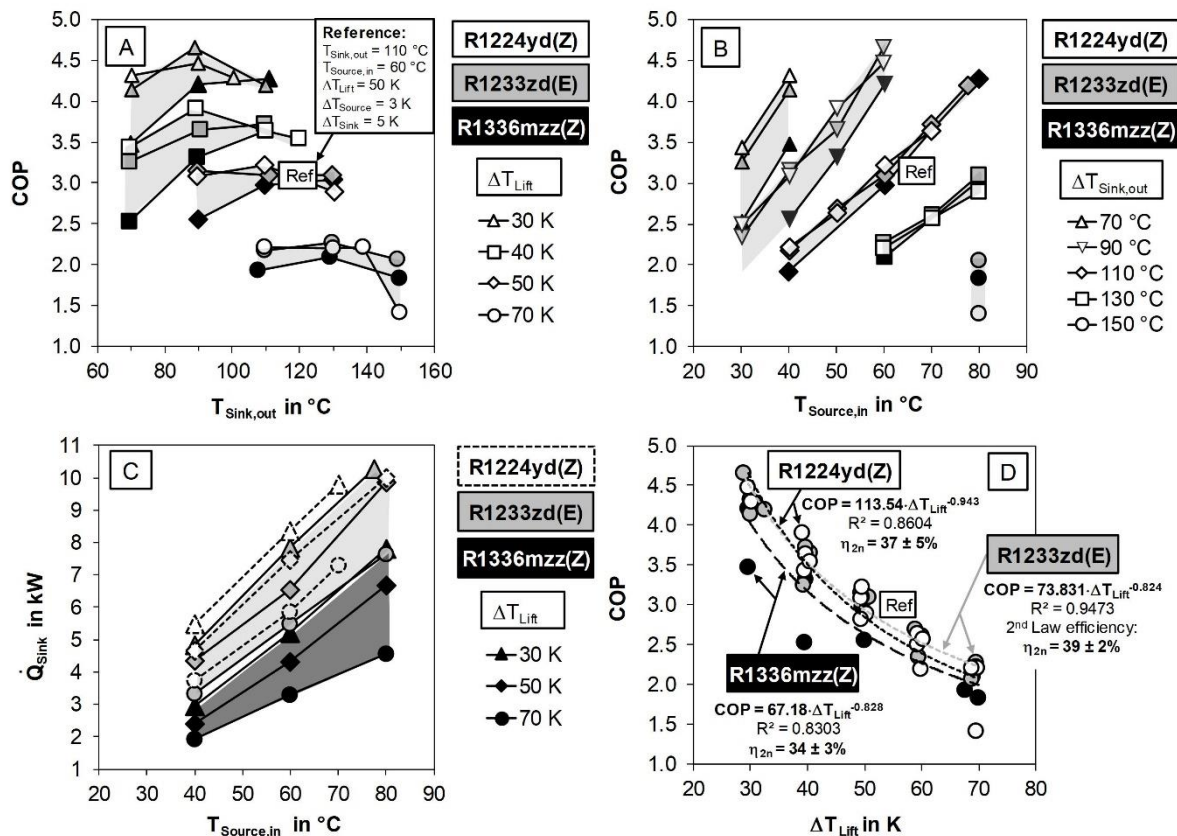


Figure 1: Experimental results of the investigated laboratory HTHP with the refrigerants R1224yd(Z), R1233zd(E), and R1336mzz(Z). (A) COP as a function of the heat sink temperature at different temperature lifts, (B) COP as a function of the heat source at different heat sink temperatures, (C) heating capacity as a function of the heat source temperature at 30, 50 and 70 K temperature lift, and (D) COP fit curves of measurement data with 2nd Law efficiencies.

Figure 1 (A) shows the COP of the HTHP as a function of the heat sink outlet temperature ($T_{Sink,out}$) and various temperature lifts (ΔT_{Lift}). At the reference point conditions (Ref) W60/W110, a heating COP of 3.2, 3.1, and 3.0 was achieved for R1224yd(Z), R1233zd(E), and R1336mzz(Z), respectively.

Up to about 110 $^{\circ}\text{C}$, R1224yd(Z) and R1233zd(E) delivered a slightly higher COP than R1336mzz(Z), which is attributed to the higher heating capacities (see Figure 1, C) and the smaller relative heat losses at the same temperature conditions. Heat losses of about $21 \pm 7\%$ were estimated from an energy balance with the main origin at the compressor. At the higher temperatures, the deviations between the measured COPs were within the measurement uncertainty of about ± 0.2 COP. In this study, the maximal tested heat sink temperature was 150 $^{\circ}\text{C}$. R1336mzz(Z) achieves potentially higher condensing temperatures due to the higher critical temperature of 171.3 $^{\circ}\text{C}$ compared to 166.5 $^{\circ}\text{C}$ of R1233zd(E) and 155.5 $^{\circ}\text{C}$ of R1224yd(Z). In addition, an increase of the temperature glide on the heat sink from 5 to 30 K further increased the COP by 15% [8], which is advantageous in processes with low return temperatures. A larger temperature glide improved the heat transfer in the condenser.

Figure 1 (B) shows the COP as a function of the inlet temperature of the heat source. The increase in efficiency with higher source temperature is evident. The COP data of R1224yd(Z) were comparable to R1233zd(E) except for W80/W150 where the COP decreased due to the narrowing of the two-phase region (in the p-h diagram) near the critical temperature of 155.5 $^{\circ}\text{C}$.

Figure 1 (C) shows the heating capacity (\dot{Q}_{Sink}) as a function of the heat source inlet temperature ($T_{Source,in}$) at constant temperature lifts (ΔT_{Lift}). Overall, the heating capacity of R1336mzz(Z) was about 46 to 76% lower than that of R1233zd(E). This is due to the lower volumetric heating capacity (VHC). A compressor with a larger swept volume would be required to achieve similar heating capacities as R1233zd(E) and R1224yd(Z). R1233zd(E) provided a heating capacity on 5.8 kW at Ref and approx. 10 kW at W80/W110, which corresponded to the capacity limit of the laboratory system. With R1336mzz(Z) a maximum heating capacity of 7.8 kW could be achieved (W80/W111). The drop-in test showed that the heat capacity of R1224yd(Z) was on average 9% higher than that of R1233zd(E). This is consistent with simulation studies by Arpagaus et al. [30] presented at ICR 2019, where VHC values of 1'600 kJ/m³, 2'412 kJ/m³ and 2'639 kJ/m³ for R1336mzz(Z), R1233zd(E) and R1224yd(Z) were calculated in a single-stage cycle with IHX at W60/W110. A compromise between COP and VHC needs to be found depending on the refrigerant.

Figure 1 (D) shows the COP of the measured experimental data as a function of the respective temperature lift. As expected, the COP values decreased with ΔT_{Lift} and followed a fit curve with an average Carnot efficiency (2nd Law efficiency) of 39% for R1233zd(E), 37% for R1224yd(Z), and 34% for R1336mzz(Z). These values are comparable with the results in another HTHP laboratory setup of Helminger et al. [31] using R1336mzz(Z), but lower than with the commercial HeatBooster technology from Viking Heating Engines AS, which achieves approx. 41% at 20 kW [8,32].

Temperature-resistant compressors and stable lubricating oils are decisive components for the further development and commercialization of HTHPs. The measured suction gas temperature ($T_{Suction}$) in the laboratory HTHP exceeded the motor limit temperature of approx. 110 °C at a heat sink outlet temperature of about 130 °C and higher. However, short-term experiments over several minutes at 150 °C were still possible to run.

Finally yet importantly, the acid number (neutralization number) of the POE oils was measured by manual colorimetric titration (in mgKOH/g oil according to DIN 51558-1) as a measure of oil degradation. The POE oils were analysed after about 100 operating hours in the HTHP after each refrigerant test campaign. Fresh oil was also measured for comparison. Visual inspections revealed a slightly yellowish colour of the oils after operation in the HTHP. Overall, hardly any oil degradation was detected. The neutralisation number for fresh POE oil was 0.04, for R1233zd(E) 0.06, for R1336mzz(Z) 0.05 and for R1224yd(Z) 0.25, thus significantly below the 0.5 warning value assumed by the oil supplier FUCHS for HTHP applications. Long-term tests were not the aim of this study.

4. Conclusion

R1336mzz(Z), R1233zd(E) and R1224yd(Z) have been successfully tested in a single stage HTHP with IHX cycle and up to 10 kW heating capacity on a laboratory scale. The operation of the heat pump was demonstrated at 30 to 80 °C heat source and 70 to 150 °C heat sink temperatures (30 to 70 K temperature lifts), for a possible application of waste heat recovery, steam generation or drying. At operating point W60/W110 COPs of 3.2, 3.1 and 3.0 for R1224yd(Z), R1233zd(E) and R1336mzz(Z) were measured. Up to about 110 °C, R1224yd(Z) and R1233zd(E) had a slightly higher COP than R1336mzz(Z) due to higher heating capacities and lower relative heat losses at the same temperature conditions. Due to higher critical temperatures, R1233zd(E) and R1336mzz(Z) were more efficient than R1224yd(Z) at 150 °C heat sink temperature. Otherwise, the differences in COP were within the measurement uncertainty of ± 0.2 COP. The implementation of an IHX increased the COP significantly (approx. 15% for R1233zd(E)) compared to a basic cycle. A further COP increase of approx. 15% was achieved by a higher temperature glide on the heat sink side from 5 to 30 K, which increased subcooling. The very

low GWP, the non-flammability, and the negligible environmental impact (i.e. low TFA formation during atmospheric degradation) indicate a high potential for future use as refrigerant in HTHP applications and retrofit systems. The developed HTHP enables the testing of further alternative HFO and HCFO refrigerants with stabilising additives, HFCs like R245fa or R365mfc for direct comparison or other oils (e.g. POE, PAG) in the future. Further efficiency gains could be achieved by reducing heat losses at high temperatures through better insulation of heat pump components and piping.

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5. References

- [1] C. Arpagaus, F. Bless, M. Uhlmann, J. Schiffmann, S.S. Bertsch, High temperature heat pumps: Market overview, state of the art, research status, refrigerants, and application potentials, *Energy*. 152 (2018) 985–1010. doi:10.1016/j.energy.2018.03.166.
- [2] C. Arpagaus, F. Bless, J. Schiffmann, S.S. Bertsch, Review on High Temperature Heat Pumps – Market Overview and Research Status, in: *Int. Work. High Temp. Heat Pumps*, Sept. 9, 2017, Copenhagen, Denmark, 2017: pp. 1–25.
- [3] C. Arpagaus, F. Bless, M. Uhlmann, J. Schiffmann, S.S. Bertsch, High temperature heat pumps: Market overview, state of the art, research status, refrigerants, and application potentials, in: *17th Int. Refrig. Air Cond. Conf. Purdue*, July 9-12, 2018, 2018: pp. 1–10. doi:10.1016/j.energy.2018.03.166.
- [4] C. Arpagaus, *Hochtemperatur-Wärmepumpen: Marktübersicht, Stand der Technik und Anwendungspotenziale*, 138 Seiten, ISBN 978-3-8007-4550-0 (Print), ISBN 978-3-8007-4551-7 (E-Book), VDE Verlag GmbH, Offenbach, Berlin, 2018.
- [5] G. Myhre, D. Shindell, F.-M. Bréon, W. Collins, J. Fuglestedt, J. Huang, D. Koch, J.-F. Lamarque, D. Lee, B. Mendoza, T. Nakajima, A. Robock, G. Stephens, T. Takemura, H. Zhang, Anthropogenic and natural radiative forcing, in: *Clim. Chang. 2013 Phys. Sci. Basis. Contrib. Work. Gr. I to Fifth Assess. Rep. Intergov. Panel Clim. Chang.*, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2013: pp. 659–740.
- [6] BAFU, *Verordnung zur Reduktion von Risiken beim Umgang mit bestimmten besonders gefährlichen Stoffen, Zubereitungen und Gegenständen (Chemikalien-Risikoreduktions-Verordnung, ChemRRV)*, Stand 9. Juli 2019, 814.81 (2019) 1–31.
- [7] Innosuisse, *SCCER Efficiency of Industrial Processes (SCCER EIP)*, (2019). www.sccer-eip.ch.
- [8] C. Arpagaus, F. Bless, M. Uhlmann, E. Büchel, S. Frei, J. Schiffmann, S.S. Bertsch, High temperature heat pump using HFO and HCFO refrigerants - System design, simulation, and first experimental results, *ICR 2019, 25th IIR Int. Congr. Refrig.* August 24-30, Montréal, Québec, Canada. (2019) 1–9. doi:10.18462/iir.icr.2019.242.
- [9] C. Arpagaus, F. Bless, M. Uhlmann, E. Büchel, S. Frei, J. Schiffmann, S.S. Bertsch, High temperature heat pump using HFO and HCFO refrigerants - System design, simulation, and first experimental results, in: *17th Int. Refrig. Air Cond. Conf. Purdue*, July 9-12, 2018, 2018: pp. 1–10.
- [10] C. Arpagaus, M. Prinzing, F. Bless, M. Uhlmann, E. Büchel, S. Frei, R. Kuster, J. Schiffmann, S.S. Bertsch, *Hochtemperatur Wärmepumpe mit HFO und HCFO Kältemitteln - Systemdesign, Simulation und erste experimentelle Ergebnisse*, in: *Dtsch. Kälte- Und Klimatagung 2018 (DKV-Tagung)*, 21.-23. Nov. 2018, Aachen, 2018.
- [11] C. Arpagaus, F. Bless, S.S. Bertsch, J. Schiffmann, *Wärmepumpen für die Industrie: Eine aktuelle Übersicht*, in: *25. Tagung Des BFE-Forschungsprogramms “Wärmepumpen Und Kälte”*, 26. Juni 2019, BFH Burgdorf, Schweiz, 2019: pp. 1–15.
- [12] C. Arpagaus, M. Prinzing, F. Bless, M. Uhlmann, E. Büchel, S. Frei, R. Kuster, J. Schiffmann, S.S.

- Bertsch, Hochtemperatur-Wärmepumpe mit HFO- und HCFO-Kältemitteln, KI Kälte Luft Klimatechnik, 12/2018. (2018) 45–53.
- [13] M. Fukushima, Next Generation Low- GWP Refrigerants AMOLEA, in: JRAIA Int. Symp. 2018, 2018: pp. 1–5.
- [14] M.P. Sulbaek Andersen, J.A. Schmidt, A. Volkova, D.J. Wuebbles, A three-dimensional model of the atmospheric chemistry of E and Z-CF₃CH=CHCl (HCFO-1233(zd) (E/Z)), *Atmos. Environ.* 179 (2018) 250–259. doi:10.1016/j.atmosenv.2018.02.018.
- [15] K. Tokuhashi, T. Uchimaru, K. Takizawa, S. Kondo, Rate Constants for the Reactions of OH Radical with the (E)/(Z) Isomers of CF₃CF=CHCl and CHF₂CF=CHCl, *J. Phys. Chem. A.* 122 (2018) 3120–3127. doi:10.1021/acs.jpca.7b11923.
- [16] L.L. Andersen, F.F. Østerstrøm, M.P. Sulbaek Andersen, O.J. Nielsen, T.J. Wallington, Atmospheric chemistry of cis-CF₃CHCHCl (HCFO-1233zd(Z)): Kinetics of the gas-phase reactions with Cl atoms, OH radicals, and O₃, *Chem. Phys. Lett.* 639 (2015) 289–293. doi:10.1016/j.cplett.2015.09.008.
- [17] K.O. Patten, D.J. Wuebbles, Atmospheric lifetimes and Ozone Depletion Potentials of trans-1-chloro-3,3,3-trifluoropropylene and trans-1,2-dichloroethylene in a three-dimensional model, *Atmos. Chem. Phys.* 10 (2010) 10867–10874. doi:10.5194/acp-10-10867-2010.
- [18] WMO (World Meteorological Organization), Scientific Assessment of Ozone Depletion 2010, Global Ozone Research and Monitoring Project - Report No. 52, Geneva, Switzerland, 2011.
- [19] T.J. Wallington, M.P. Sulbaek Andersen, O.J. Nielsen, Atmospheric chemistry of short-chain haloolefins: Photochemical ozone creation potentials (POCPs), global warming potentials (GWPs), and ozone depletion potentials (ODPs), *Chemosphere.* 129 (2015) 135–141. doi:10.1016/j.chemosphere.2014.06.092.
- [20] S. Henne, D.E. Shallcross, S. Reimann, P. Xiao, S. Boulos, A.C. Gerecke, D. Brunner, Environmental impacts of HFO-1234yf and other HFOs, *ASHRAE/NIST Refrig. Conf. Mov. Toward. Sustain.* (2012) 182–194.
- [21] N.N. Shah, D. Cotter, N.J. Hewitt, Overview on HCFO-R1233ZD(E) use for high temperature heat pump application, in: ICR 2019, 25th IIR Int. Congr. Refrig. August 24-30, Montréal, Québec, Canada, 2019: pp. 1–8. doi:10.18462/iir.icr.2019.
- [22] N.J. Hewitt, D. Cotter, M.J. Huang, N. Shah, Industrial Heat Pumps in the UK Current Constraints and Future Possibilities, in: ICR 2019, 25th IIR Int. Congr. Refrig. August 24-30, Montréal, Québec, Canada, 2019: pp. 1–8. doi:10.18462/iir.icr.2019.
- [23] AGC Chemicals, AMOLEA® 1224yd, Technical Information, ASAHI Glass Co., Ltd., (2017) 1–18.
- [24] T. Kaida, M. Fukushima, K. Iizuka, Application of R1224yd(Z) as R245fa alternative for high temperature heat pump, in: ICR 2019, 25th IIR Int. Congr. Refrig. August 24-30, Montréal, Québec, Canada, 2019: pp. 1–8.
- [25] OARS (Occupational Alliance for Risk Science), Workplace Environmental Exposure Level of HCFO-1224yd(Z), 2017. [https://med.uc.edu/docs/default-source/default-document-library/hcfo-1224yd\(z\)-weel-document-final-2017.pdf?sfvrsn=0](https://med.uc.edu/docs/default-source/default-document-library/hcfo-1224yd(z)-weel-document-final-2017.pdf?sfvrsn=0).
- [26] K. Kontomaris, Zero-ODP, Low-GWP, Nonflammable Working Fluids for High Temperature Heat Pumps, in: ASHRAE Annu. Conf. Seattle, Washington, July 1, 2014, 2014: pp. 1–40.
- [27] K. Kontomaris, HFO-1336mzz-Z: High Temperature Chemical Stability and Use as A Working Fluid in Organic Rankine Cycles, Paper 1525, Int. Refrig. Air Cond. Conf. Purdue, July 14-17, 2014. (2014).
- [28] M. Garry, HFOs - How much is too much? Cover story, *ACCELERATE Magazine*, September 2019, (2019) 30–37.
- [29] K.R. Solomon, G.J.M. Velders, S.R. Wilson, S. Madronich, J. Longstreth, P.J. Aucamp, J.F. Bornman, Sources, fates, toxicity, and risks of trifluoroacetic acid and its salts: Relevance to substances regulated under the Montreal and Kyoto Protocols, *J. Toxicol. Environ. Heal. Part B.* 19 (2016) 289–304. doi:10.1080/10937404.2016.1175981.
- [30] C. Arpagaus, M. Prinzing, R. Kuster, F. Bless, M. Uhlmann, J. Schiffmann, S.S. Bertsch, High temperature heat pumps -Theoretical study on low GWP HFO and HCFO refrigerants, in: ICR 2019, 25th IIR Int. Congr. Refrig. August 24-30, Montréal, Québec, Canada, 2019: pp. 1–8.

2nd Conference on High Temperature Heat Pumps

9th September 2019, Copenhagen, Denmark



doi:10.18462/iir.icr.2019.259.

- [31] F. Helminger, K. Kontomaris, J. Pfaffl, M. Hartl, T. Fleckl, Measured Performance of a High Temperature Heat Pump with HFO-1336mzz-Z as the Working Fluid, in: ASHRAE 2016 Annu. Conf. St. Louis, Missouri, 25-29 June 2016, 2016: pp. 1–8.
- [32] M. Nilsson, H.N. Rislá, K. Kontomaris, Measured performance of a novel high temperature heat pump with HFO-1336mzz-Z as the working fluid, in: 12th IEA Heat Pump Conf. 2017, Rotterdam, 2017: pp. 1–10.

