High Temperature Heat Pump using HFO and HCFO refrigerants – system design and experimental results

C. Arpagaus, R. Kuster, M. Prinzing, F. Bless, M. Uhlmann, E. Büchel, S. Frei, S.S. Bertsch, NTB Buchs

J. Schiffmann, EPFL Neuchâtel

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Interstate University of Applied Sciences of Technology Buchs
University of Applied Sciences of Eastern Switzerland

ICR 2019, The 25th IIR International Congress of Refrigeration, Montréal, Québec, Canada
August 24-30, 2019

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Content

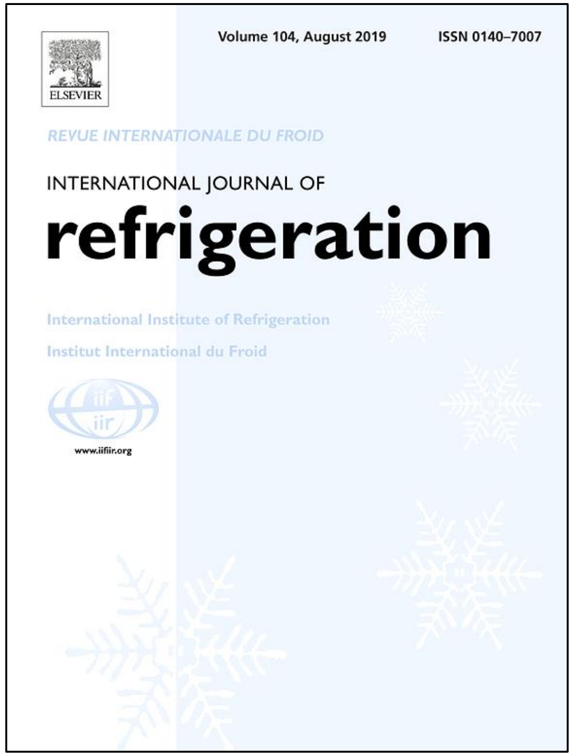
- Introduction to high temperature heat pumps (HTHP)
- Suitable HFOs and HCFOs for HTHPs
- System design of the laboratory scale HTHP at NTB Buchs
- Experimental results with R1336mzz(Z) and R1233zd(E)
- Conclusions

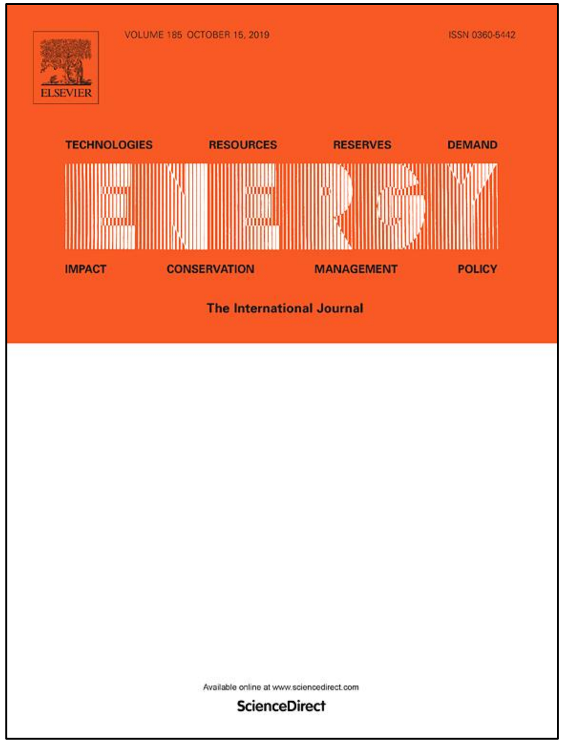
Introduction to high temperature heat pumps (HTHP)

Review Papers

Arpagaus C., Bless F., Schiffmann J., Bertsch S.S.: **Multi-temperature heat pumps: A literature review**, International Journal of Refrigeration, 2016, 69, 437–465.

Arpagaus C., Bless F., Uhlmann M., Schiffmann J., Bertsch S.S.: **Review - High temperature heat pumps: Market overview, state of the art, research status, refrigerants, and application potentials**, Energy, 2018, 152, 985-1010





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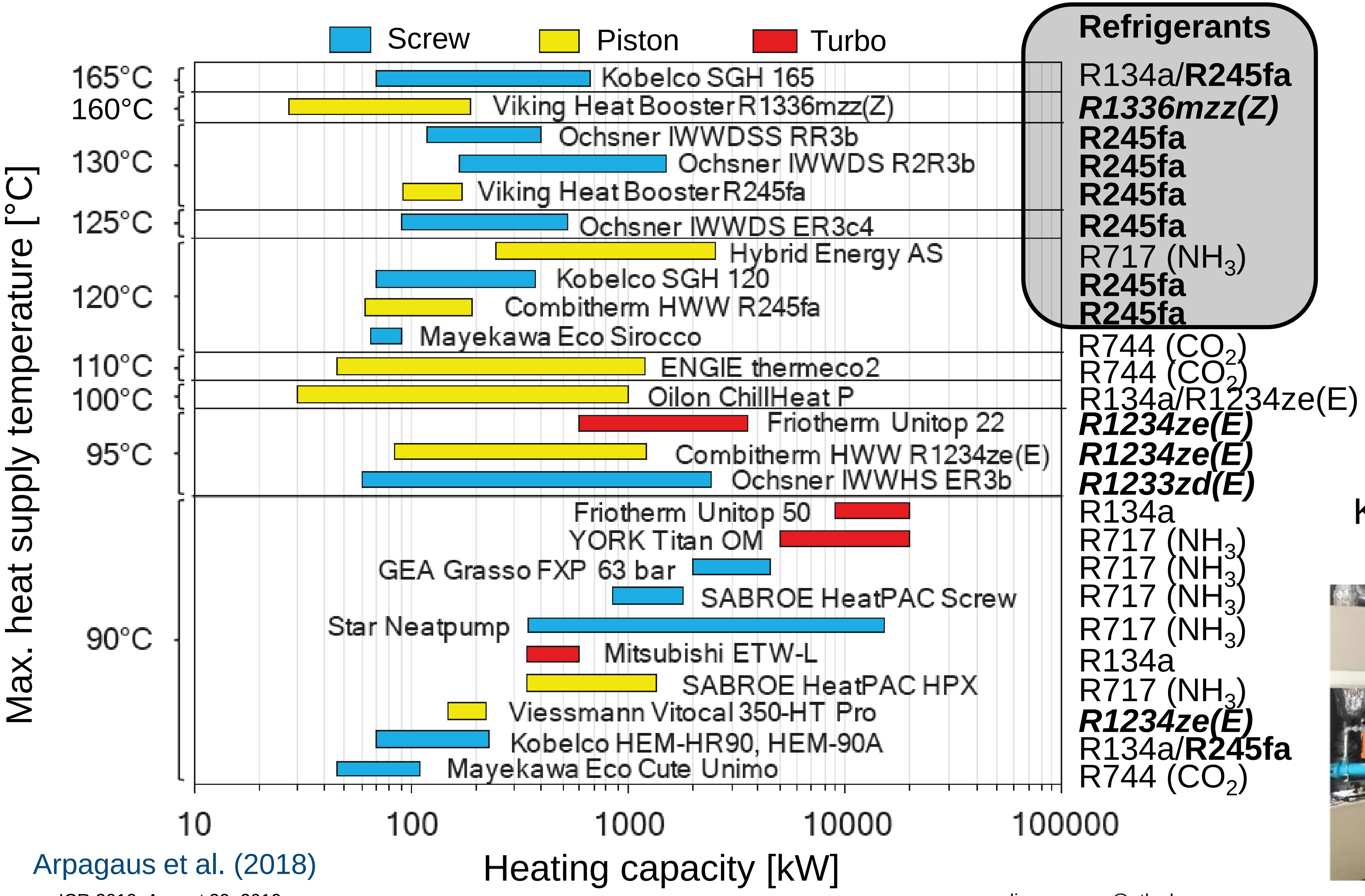
R245fa is predominantly used in industrial HTHP … but has a high GWP of 858



Arpagaus et al. (2018)

HeatBooster S4 (Viking Heating Engines AS)

Kobelco SGH 120/165 (Steam Grow HP)

Research gaps in High Temperature Heat Pumps

- Application of natural refrigerants, such as hydrocarbons (R600, R601), CO_2 or water
- Extending heat source/sink to higher temperatures
- Improving heat pump efficiency (COP)
(e.g. by multi-stage cycles, oil-free compressors)
- Development of temperature-resistant components (e.g. valves, compressors)
- New control strategies for higher temperatures
- Scale-up of functional models to industrial scale
- **Testing of new environmentally friendly synthetic refrigerants for HTHPs (e.g. HFOs and HCFOs)**

Suitable HFOs and HCFOs for HTHPs

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The 4th generation of synthetic low GWP refrigerants for chiller, ORC, and HTHP applications

Montréal Protocol (1987)

CFC (R113)

Ozone layer depletion

Regulation (2037/2000)

HCFC (R123)

Kyoto Protocol (1997)

HFC (R245fa)

Global warming geeenhouse gases

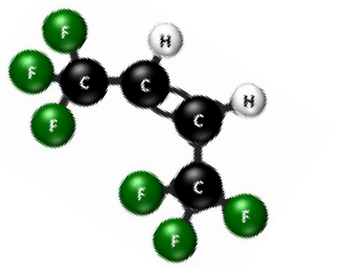
EU F-Gas Regulation (517/2014)

Paris Agreement (2015)

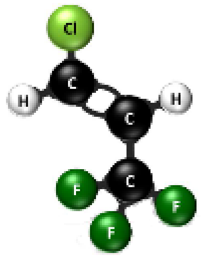
Kigali Amendment (2019)

Cost increase

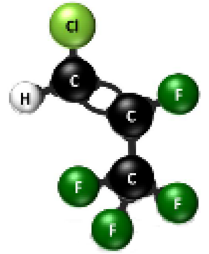
HFO (R1336mzz(Z)) HCFO (R1233zd(E), R1224yd(Z))



R1336mzz(Z)



R1233zd(E)



R1224yd(Z)

Criteria :

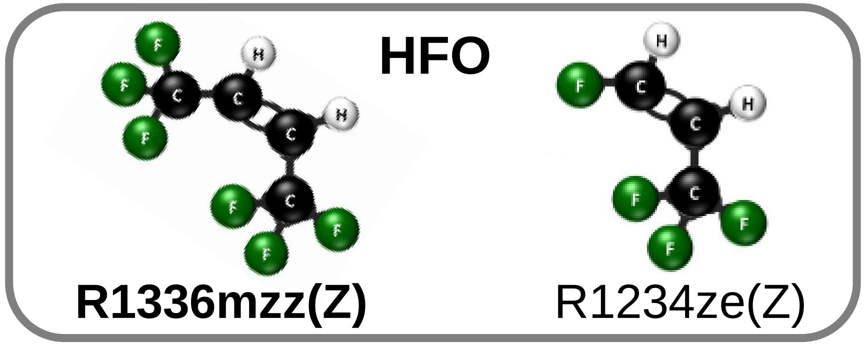
- low GWP
- short atm. lifetime
- zero/low ODP
- low flammability
- high efficiency
- high T_{crit}

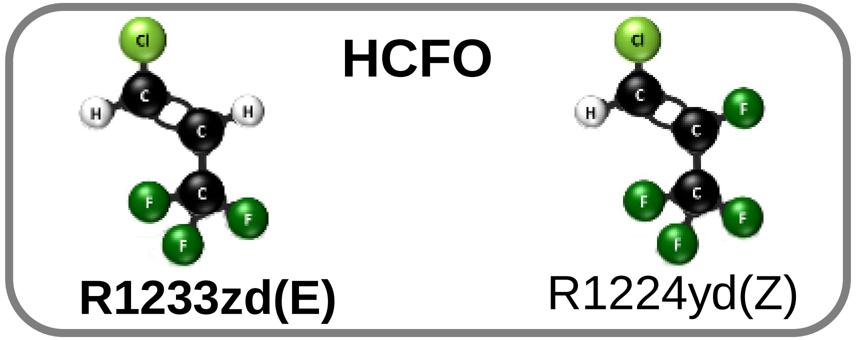
CFC: fully halogenated chlorofluorocarbons
HCFC: partially halogenated chlorofluorocarbons
HFC: hydrofluorocarbons
HFO: hydrofluoroolefins
HCFO: hydrochlorofluoroolefins

Properties of suitable HFO and HCFO refrigerants for HTHPs

Tested in this study (R1336mzz(Z), R1233zd(E))

Refrigerant	Brand (manufacturer)	T_{crit} [°C]	p_{crit} [bar]	ODP [-]	GWP_{100} [-]	Lifetime [days]	SG	NBP [°C]
R1336mzz(Z)	**Opteon™ MZ (Chemours)**	**171.3**	**29.0**	**0**	**2[a]**	**22[a]**	**A1**	**33.4**
R1234ze(Z)[b]	Not yet available	150.1	35.3	0	<1[a]	10[a], 18[b]	A2L	9.8
R1233zd(E)	**Solstice®zd (Honeywell)** Forane®HTS 1233zd (ARKEMA)	**165.6**	**35.7**	**0.00034[d], 0.00030[e]**	**1[a], <5[e]**	**26[a], 40.4[d], 36[e]**	**A1**	**18.0**
R1224yd(Z)	AMOLEA®1224yd (AGC Chemicals)	155.5	33.3	0.00023[c]	0.88[c]	20[c]	A1	14.0
R365mfc	Solkane®365mfc (Solvay)	186.9	32.7	0	804[a]	8.7 years[a]	A2	40.2
R245fa	Genetron® 245fa (Honeywell)	154.0	36.5	0	858[a]	7.7 years[a]	B1	14.9





References:
T_{crit} and p_{crit} (EES F-Chart Software, V10.643, 2019), ODP basis R11=1.0 (UNEP, 2017), GWP_{100} (100-year time horizon, CO_2=1.0), SG: Safety group classification (ASHRAE 34, 2016), [a]Myhre et al. (2013), IPCC 5th assessment report, [b]Fukuda et al. (2014), [c]Tokuhashi et al. (2018), [d]Patten and Wuebbles (2010), [e]Sulbaek Andersen et al. (2018) (3D global model)

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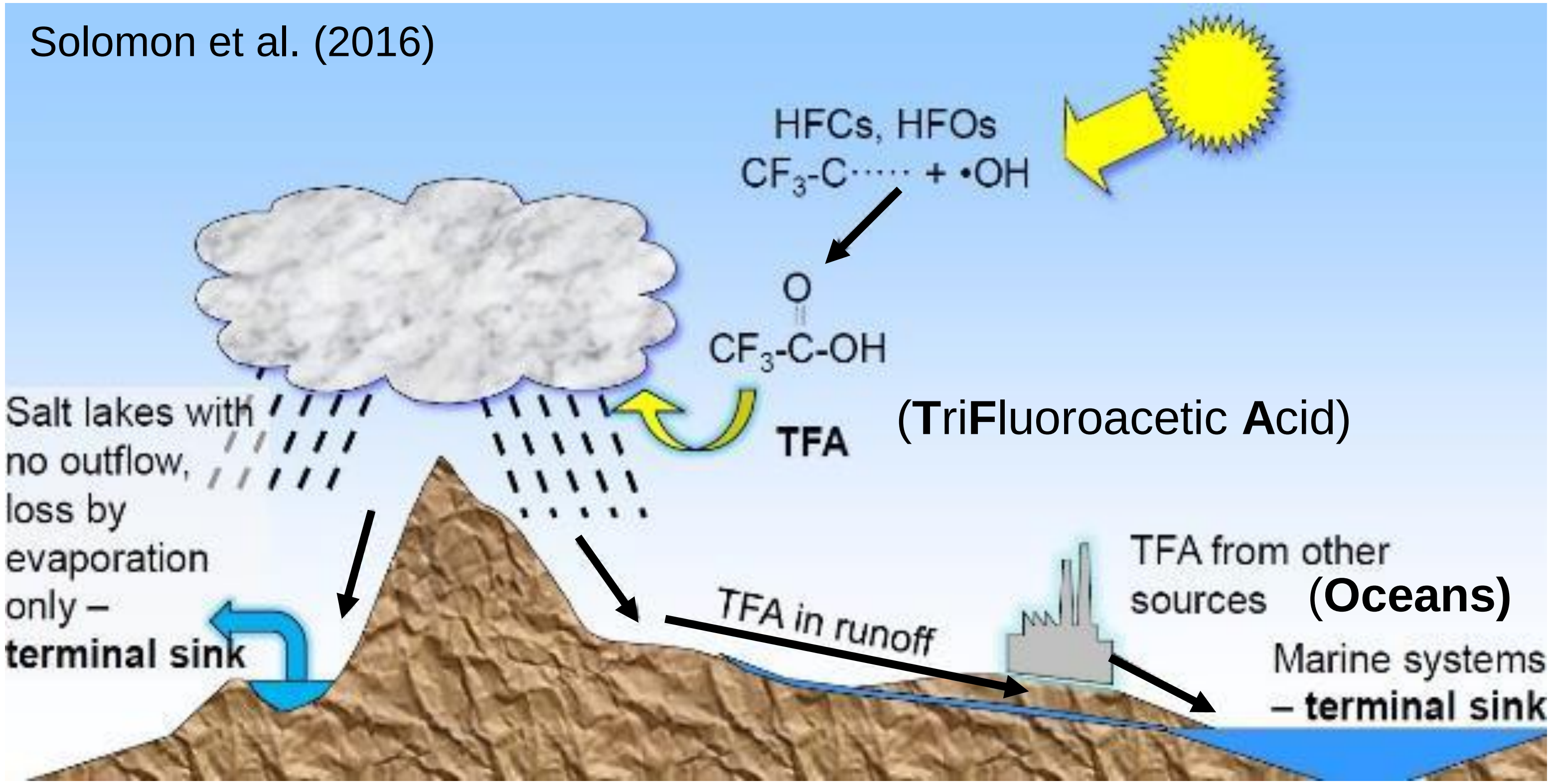
Environmental fate of TFA (trifluoroacetic acid, $CF_3C(O)OH$)



- **268 million tons TFA are present in the oceans, i.e. non-anthropogenic**
- 200 ng/L average TFA concentration in oceans (Frank et al., 2002)

Upper range scenario:

- **Total TFA yield from 1990 up to 2050 = 20.625 million tons TFA** (Solomon et al., 2016)

: 1.34×10^{21} L oceans water

Total additional contribution of TFA form HFCs and HFOs to the oceans is 15.3 ng/L* or <7.5% of the naturally present TFA

Negligible risk for aquatic organisms and human health

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FHO Fachhochschule Ostschweiz

Atmospheric degradation products of HFOs and molar yields of TFA formation (Trifluoroacetic acid, $CF_3C(O)OH$)

	Refrigerant	Formula	Final degradation products	Molar yields of TFA $CF_3C(O)OH$
HFO	R1234yf	CF_3-CF=CH_2	$CF_3C(O)OH$, CO_2, HF	100%
	R1234ze(E)	E-CF_3-CH=CHF	CO_2, HC(O)OH, HF	<10%, 0%
	R1336mzz(Z)	**Z-CF_3-CH=$CHCF_3$**	**CO_2, HF**	**<20%[a]**
HCFO	**R1233zd(E)**	**E-CF_3-CH=CHCl**	**CO_2, HF, HCl**	**~ 2%[b]**
	R1224yd(Z)	Z-CF_3-CF=CHCl	*similar structure like R1234yf degrading to $CF_3C(O)F$ and hydrolyzing to TFA*	
HFC	R365mfc	CF_3-CH_2-CF_2-CH_3	CO_2, HF	<10%
	R245fa	CHF_2-CH_2-CF_3	CO_2, HF	<10%

TFA formation yield depends on HFO refrigerant

Risk of TFA formation for R1336mzz(Z) and R1233zd(E) is considered to be close to negligible

Products:

$CF_3C(O)OH$	trifluoroacetic acid (TFA)
HC(O)OH	formic acid
CO_2	carbon dioxide
HCl	hydrochloric acid
HF	hydrofluoric acid

References:
Norwegian Environment Agency (2017), WMO (2018), Wallington et al. (2014), Juhasz & Kontomaris (2018), EFCTC (2019), [a]**Henne et. al. (2012), [b]Sulbaek Andersen et al. (2008, 2012, 2018)**, Inoue et al. (2008), ECETOC (2004), Chen et al. (1997)

cordin.arpagaus@ntb.ch

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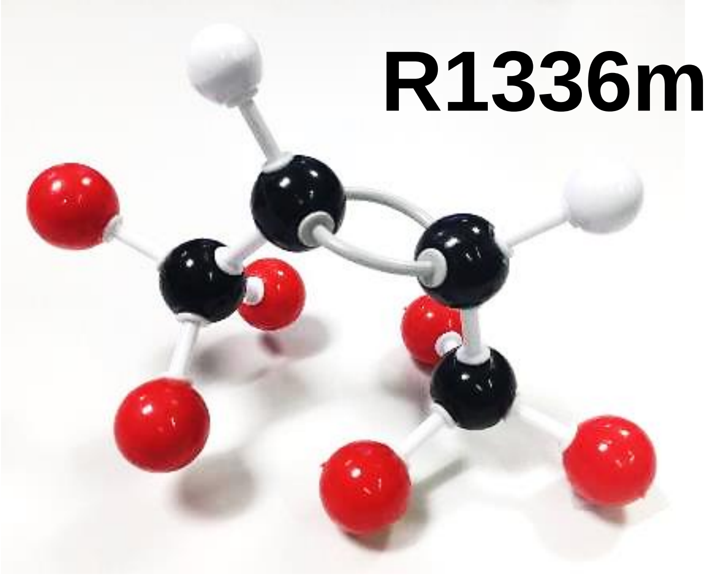
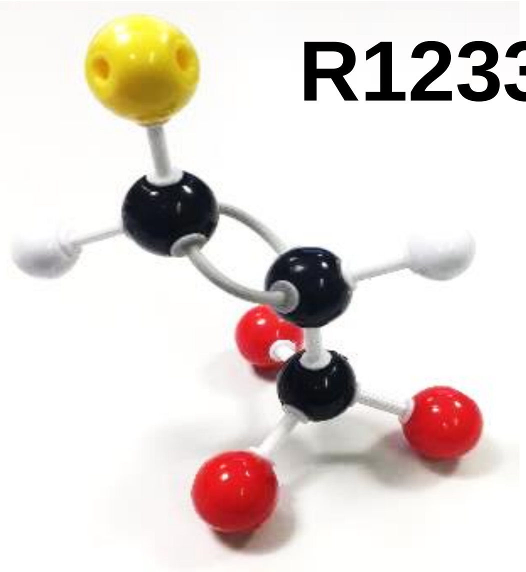
Goals of this study

Objectives:

- **Performance evaluation** of **R1336mzz(Z)** (Opteon^{TM}MZ, Chemours) and **R1233zd(E)** (Solstice®zd, Honeywell) in a laboratory HTHP (**drop-in test**).



R1336mzz(Z)



R1233zd(E)

System design of the laboratory scale HTHP at NTB Buchs

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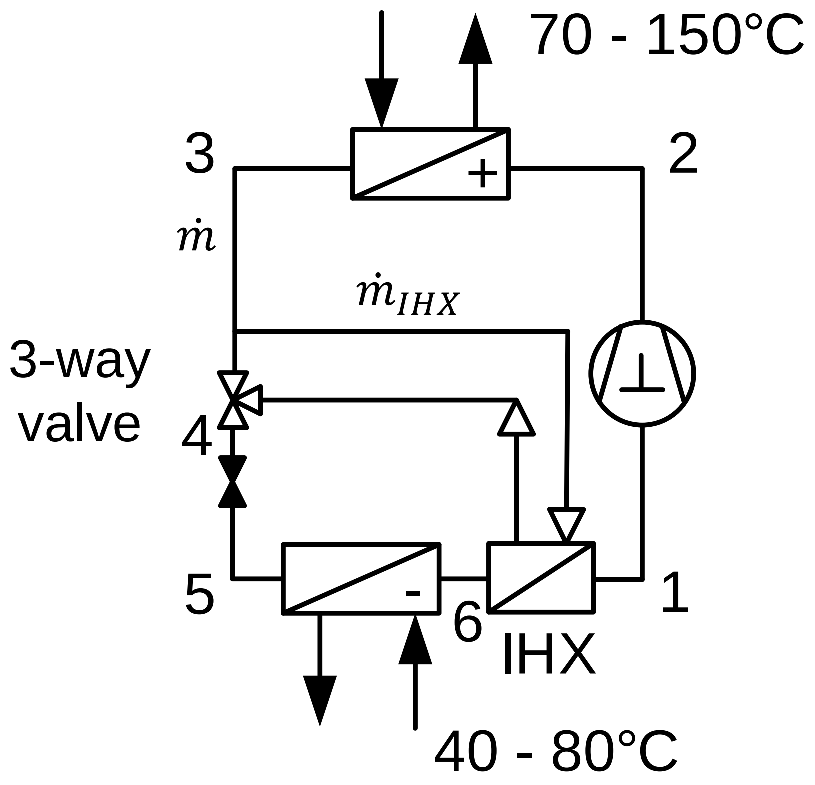
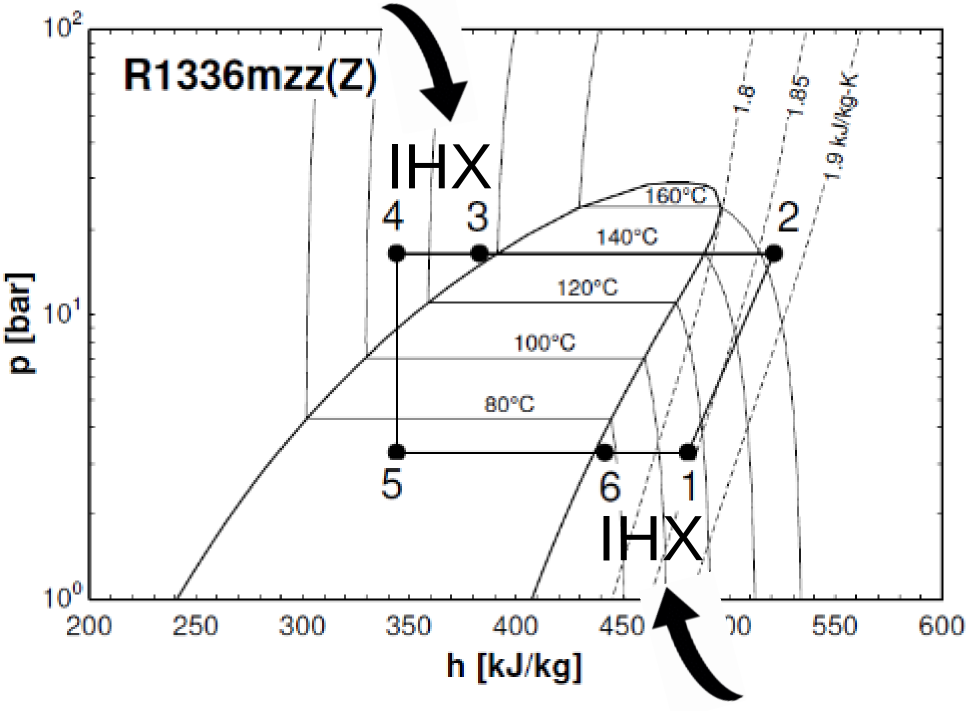
1-stage cycle with internal heat exchanger (IHX) and adjustable 3-way valve



$$IHX: \dot{m}_{IHX}/\dot{m} = 0\% \rightarrow 100\%$$
(Opening degree 3-way-valve)



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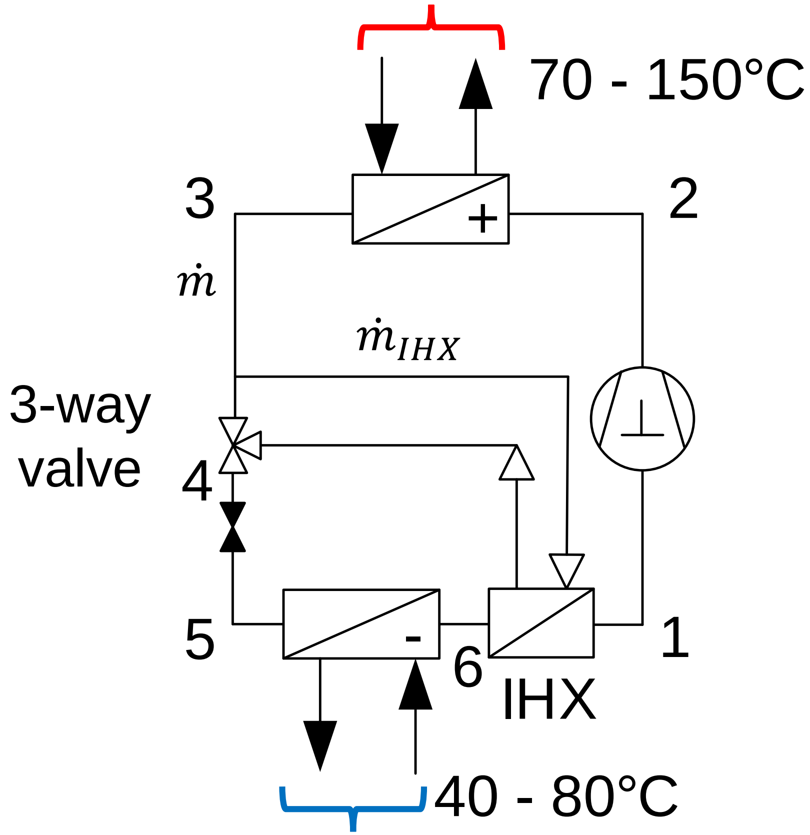
Reference conditions and variation range (water/water heat pump)

ΔT_{Sink} = 5 K (Ref) to 25 K (Temperature glide)

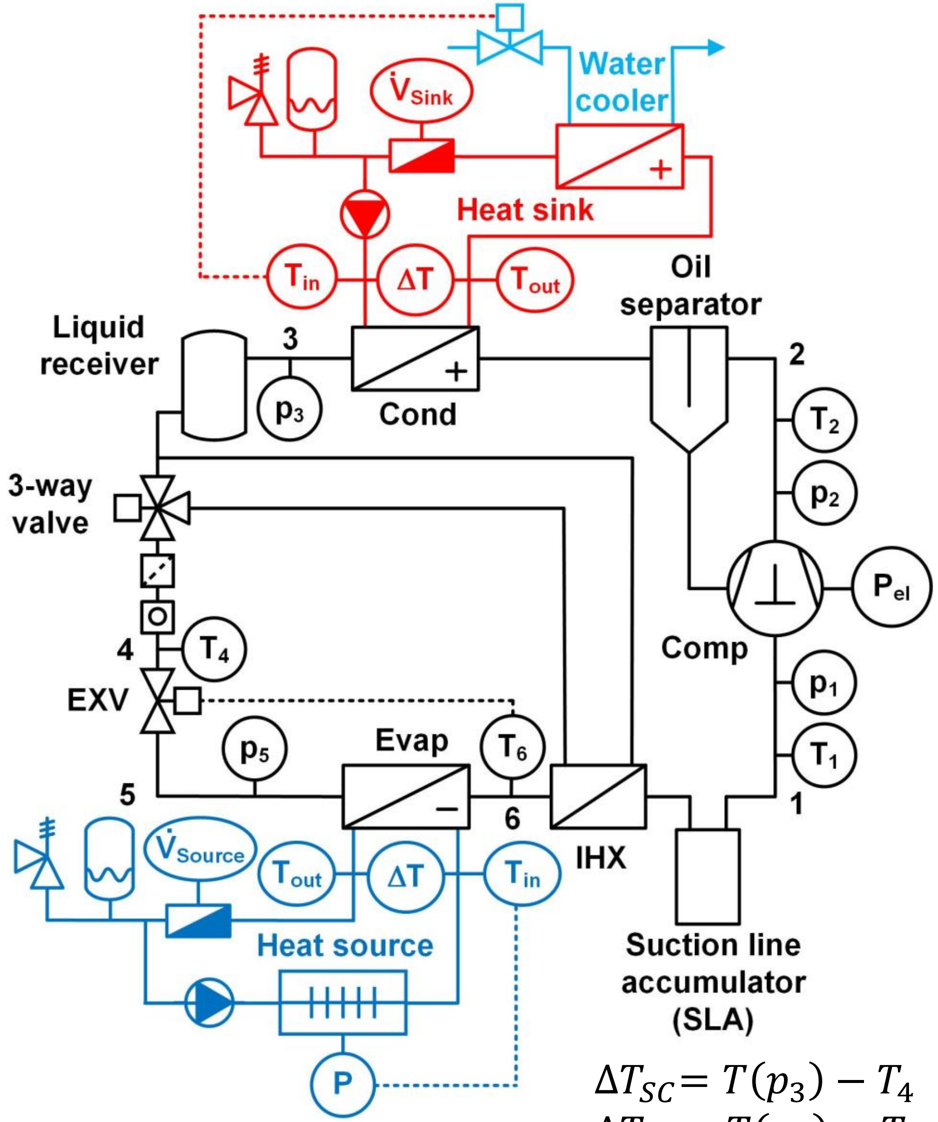


ΔT_{Source} = 3 K (constant)

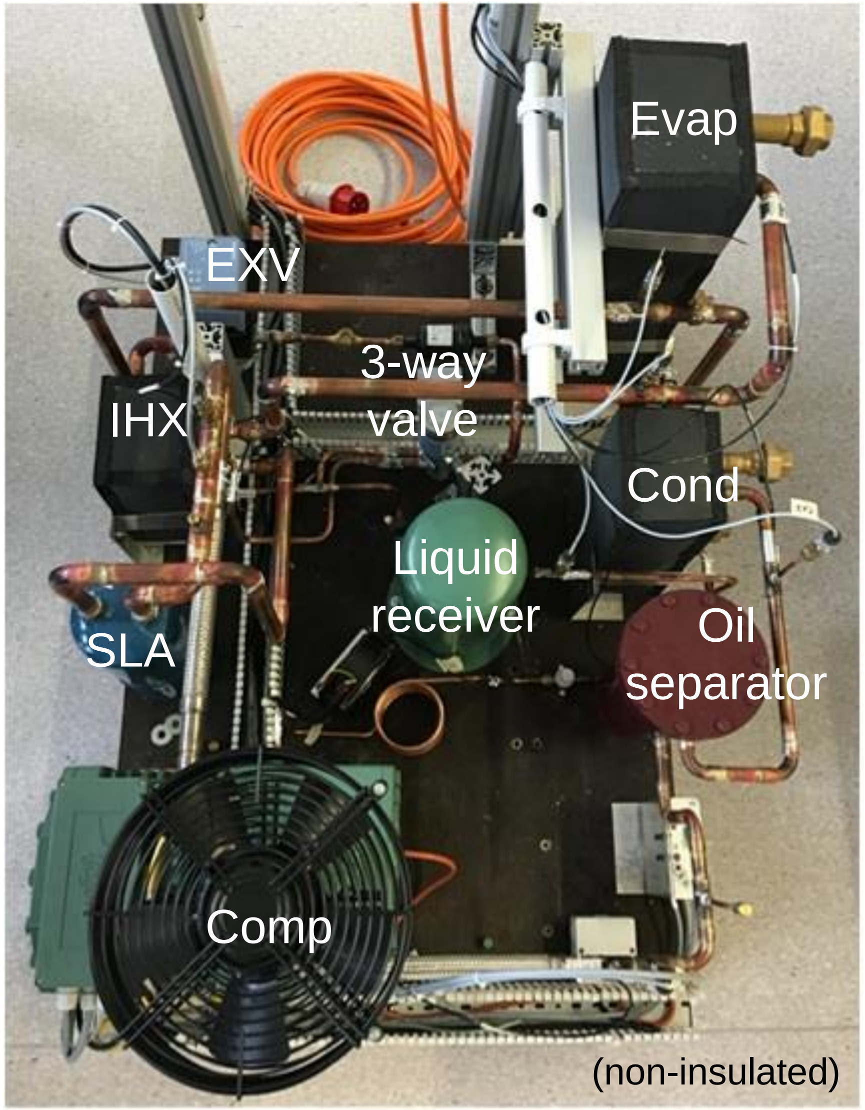
	Reference point (Ref)	Variation range
$T_{Sink,out}$	110 ± 1°C	70 to 150°C
$T_{Source,in}$	60 ± 1°C	40 to 80°C
ΔT_{Lift}	50 K	30 to 70 K
ΔT_{Sink}	5.0 ± 0.1 K	5 to 25 K
ΔT_{Source}	3.0 ± 0.1 K	constant
f_{Komp}	50 Hz	constant
IHX (Opening angle of 3-way-valve)	100%	0 to 100%
$IHX: \dot{m}_{IHX}/\dot{m} = 0\% \rightarrow 100\%$		

Superheating after evaporator:
$\Delta T_{SH} = T_6 - T(p_{Evap}) = 5$ K
IHX generates additional superheating

Experimental set-up and schematics of the laboratory HTHP



$$\Delta T_{SC} = T(p_3) - T_4$$
$$\Delta T_{SH} = T(p_5) - T_6$$



POE oil SE 170

Variable-speed semi-hermetic piston compressor Bitzer, 2DES-3Y New Ecoline

Motor switch-off temperature ~110 °C

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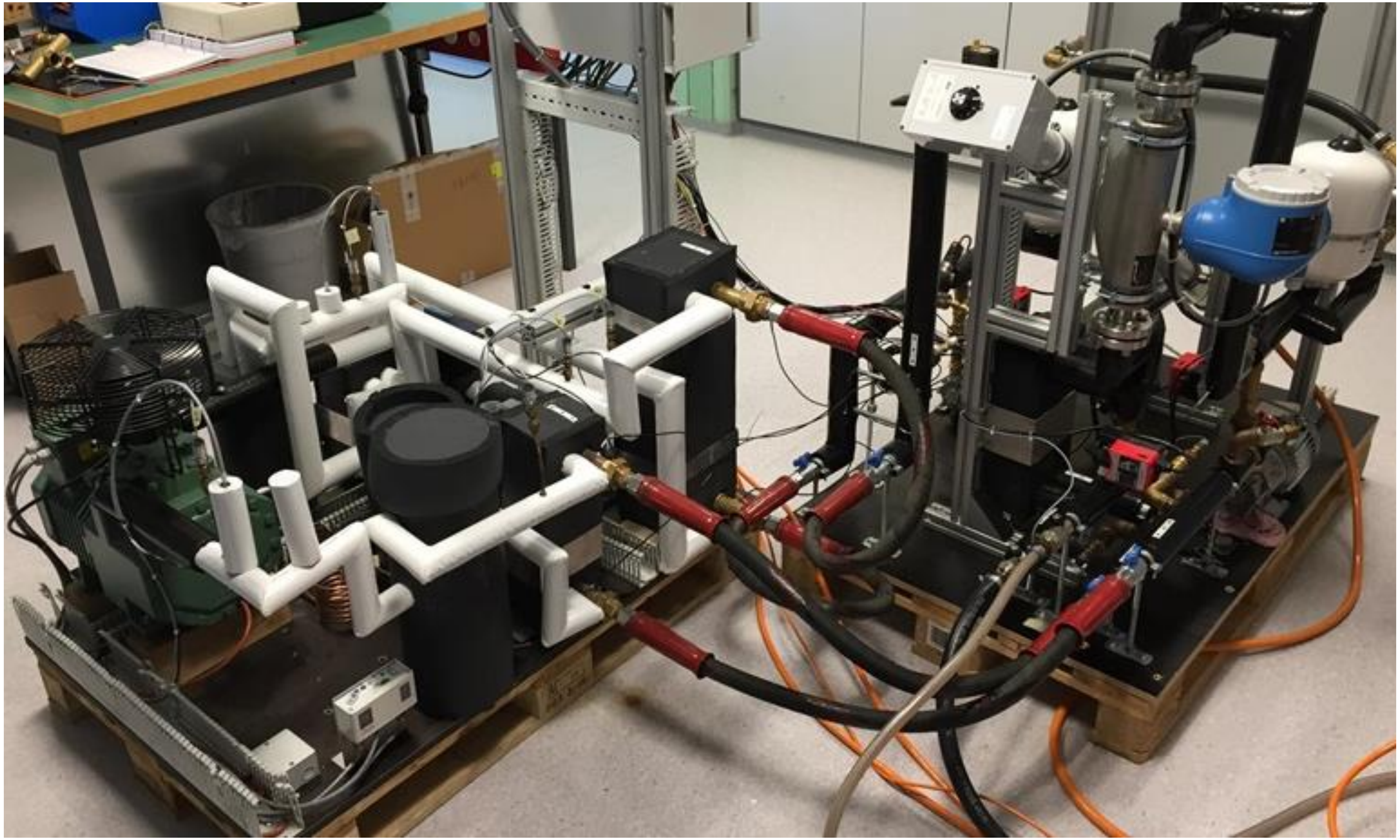
Laboratory HTHP with hydraulic loops for heat source and sink



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Sensors and measurement uncertainties

Measured parameters		Sensor type	Uncertainities
Pressures	$p_{1...6}$	Piezoelectric, 0 to 50 bar, max. 120°C	max. 1.5% of full scale reading
Temperatures	$T_{1...6}$	Thermocouples, type K, class 1	± 1.5 K
Heat sink temp difference	ΔT_{Sink}	Thermocouples, type K, class 1	± 0.1 K
Compressor power	P_{Comp}	Power transmitter, 0 to 15 kW	0.2 % of measuring range + 0.1 % measured value
Heat sink mass flow (water)	$\dot{m}_{H_2O}$	Coriolis, 0 to 1'300 kg/h, max. 180 °C	± 0.05 %

$$COP = \frac{\dot{Q}_{Sink}}{P_{Comp}} = \frac{\dot{m}_{H_2O} \cdot c_{p,H_2O}(T) \cdot \Delta T_{Sink}}{P_{Comp}}$$

$$COP_{Carnot} = \frac{T_{Sink,out}}{T_{Sink,out} - T_{Source,in}}$$

2nd Law efficiency:

$$\eta_{2nd} = \frac{COP_H}{COP_{Carnot}}$$

Error propagation according to RSS method (Root Sum Squares):

$$\Delta COP = \sqrt{\left(\frac{\partial COP}{\partial \dot{m}_{H_2O}} \cdot \Delta \dot{m}_{H_2O}\right)^2 + \left(\underbrace{\frac{\partial COP}{\partial c_{p,H_2O}(T)} \cdot \Delta c_{p,H_2O}(T)}_{\sim 0}\right)^2 + \left(\frac{\partial COP}{\partial \Delta T_{Sink}} \cdot \Delta(\Delta T_{Sink})\right)^2 + \left(\frac{\partial COP}{\partial P_{Comp}} \cdot \Delta P_{Comp}\right)^2}$$

Average uncertainty	R1336mzz(Z)	R1233zd(E)
ΔCOP	**± 0.21 (4.2%)**	**± 0.21 (4.1%)**
$\Delta \dot{Q}_{Sink}$	**± 0.14 kW (3.7%)**	**± 0.22 kW (3.8%)**
ΔP_{Comp}	**± 0.031 kW (2.6%)**	**± 0.032 kW (1.7%)**

ΔT_{Sink}	5.0 ± 0.1 K
ΔT_{Source}	3.0 ± 0.1 K

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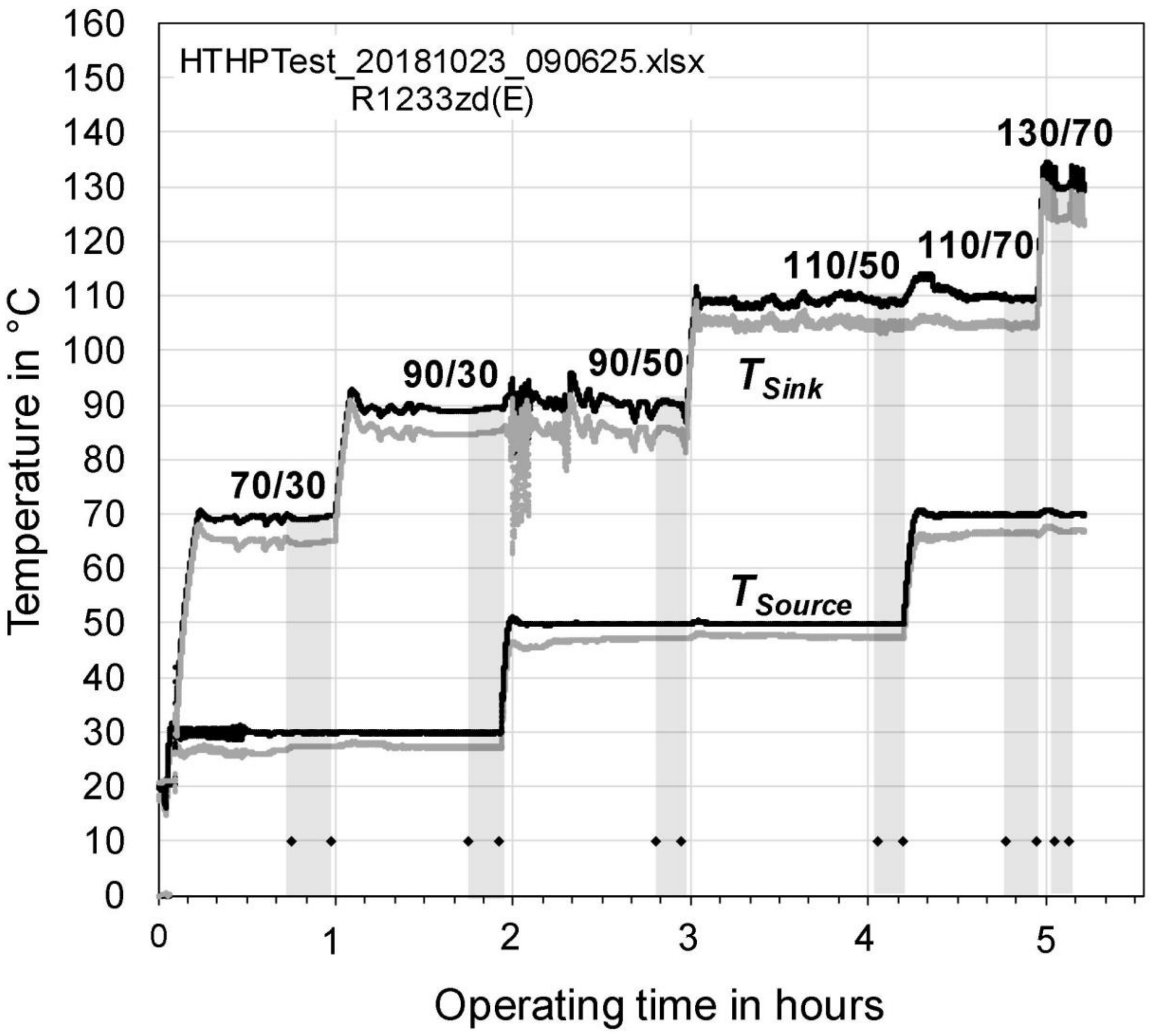
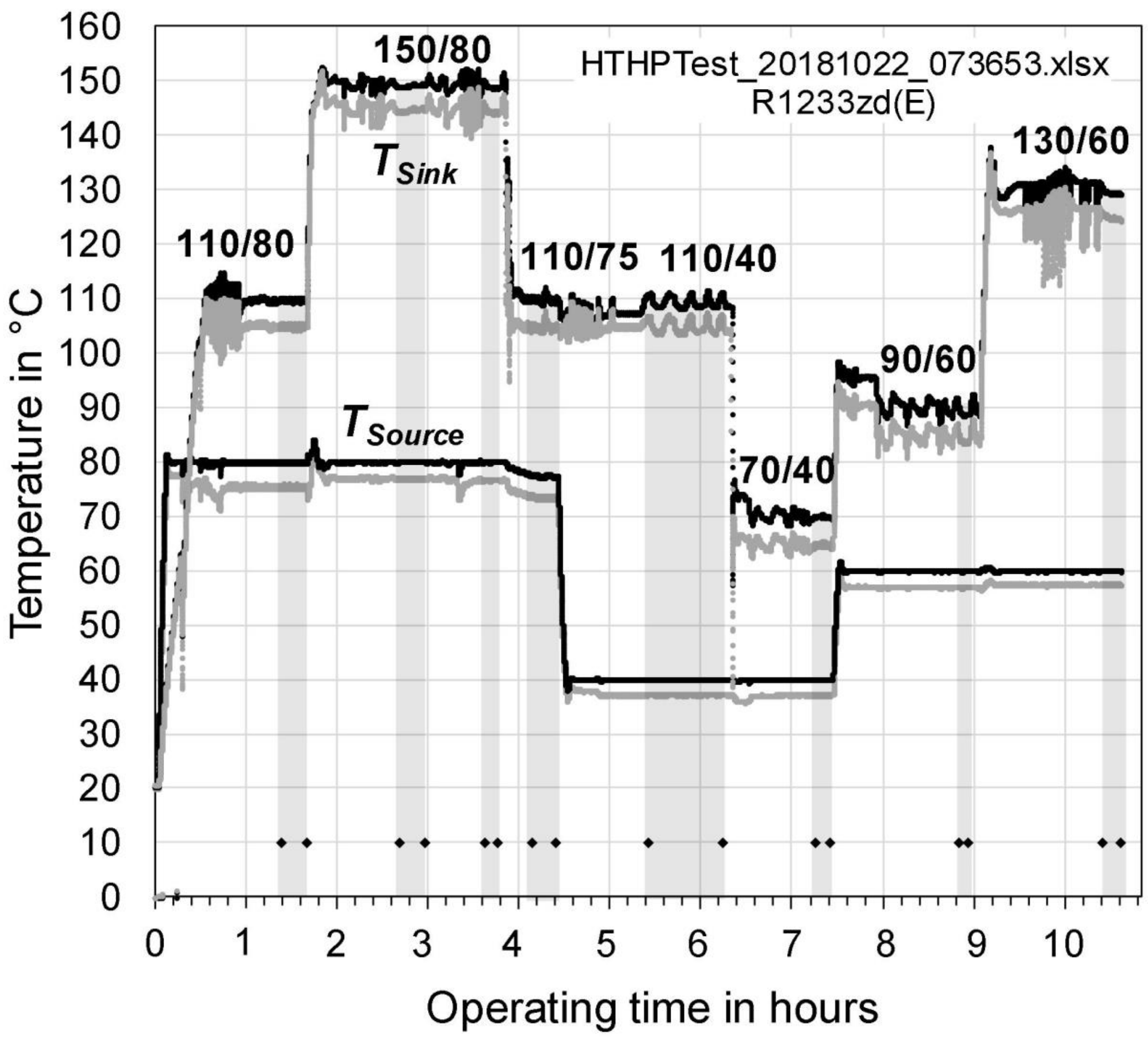
Temperature profiles of experimental runs (at least 5 min stable conditions)





Experimental results with R1336mzz(Z) and R1233zd(E)

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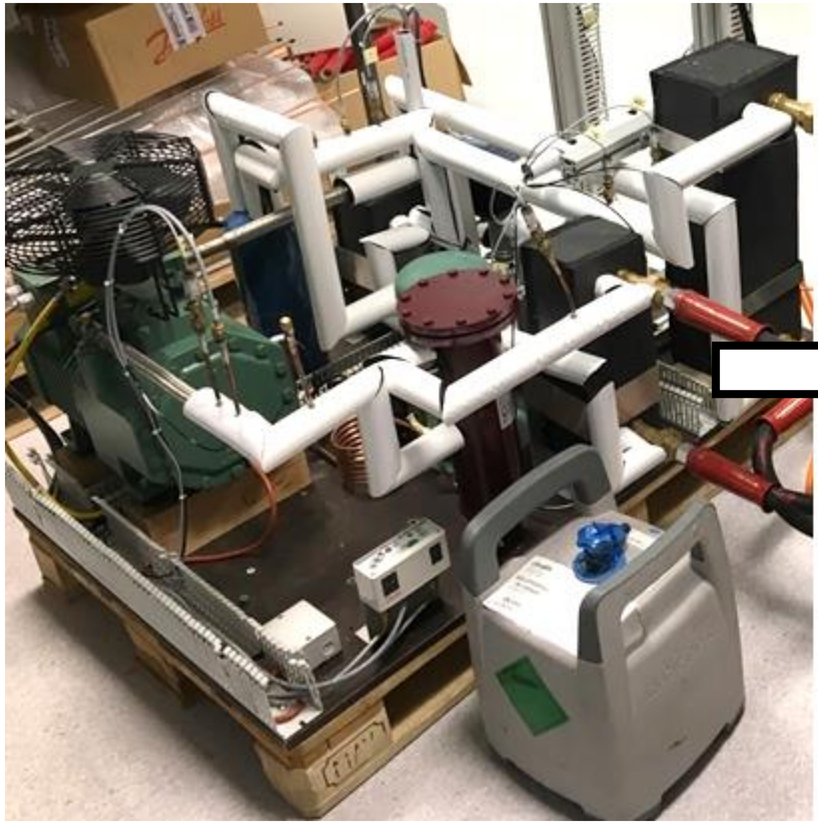
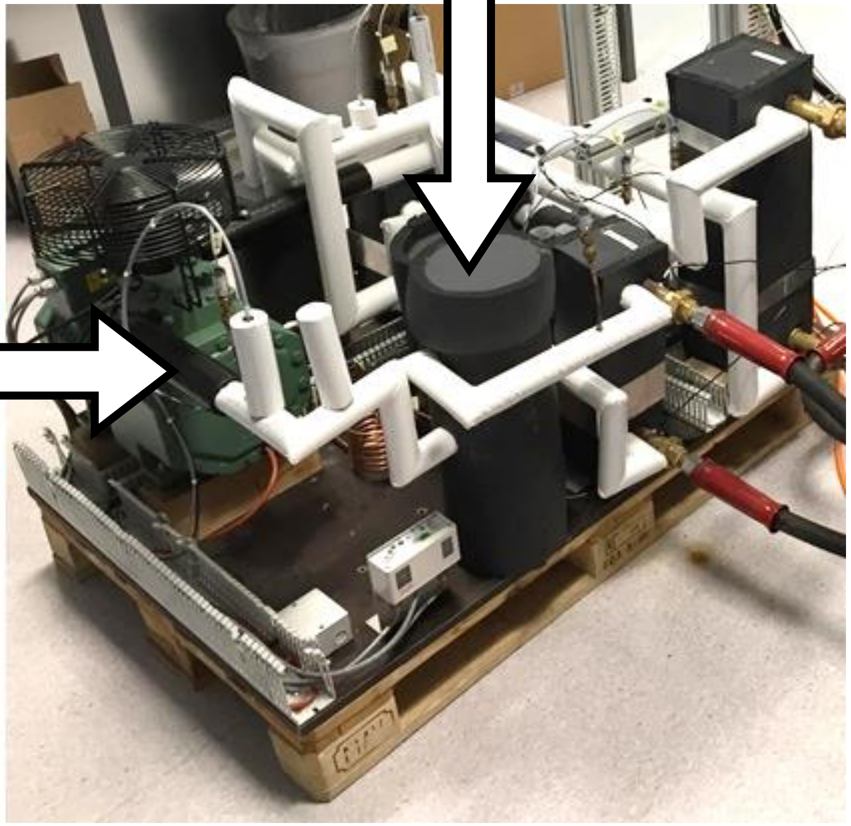
COP improvement with better insulation of oil separator, liquid receiver, and suction line accumulator with Armaflex®HT insulation

improved insulation





[1] Arpagaus et al. (2018), 17th Int. Refrig. Air Cond. Conf., Purdue, July 9-12, 2018.

[2] Arpagaus et al. (2018), DKV-Tagung 2018, Aachen, November 21-23, 2018.

armacell
ArmaFlex

Temperature resistance: up to 150°C
Thermal conductivity (0°C): 0.038 W/m

COP improvement Δ with better insulation

$T_{Source,in}$ / $T_{Sink,out}$ (ΔT_{Lift})	COP (before[1])	COP (after[2])	Δ
40/90 (50)	2.58	3.14	+22%
60/110 (50)	2.78	3.09	+11%
80/130 (50)	2.67	3.10	+16%

(1-stage cycle with 100% IHX)

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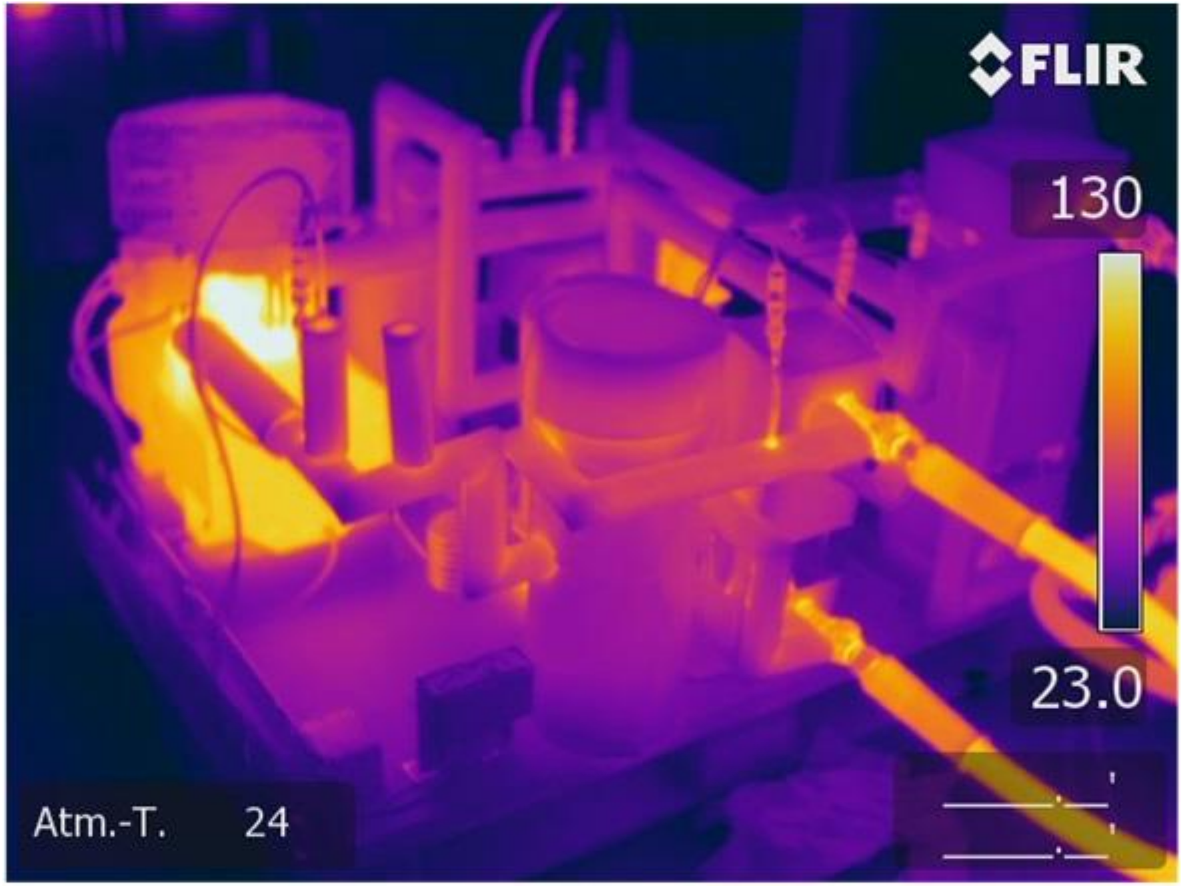
Infrared camera image for hot spot identification



- Heat losses of about 21 ± 7 % estimated from energy balance (major heat losses at the compressor)
- There is still potential for optimization in insulation and possibilities for increasing efficiency

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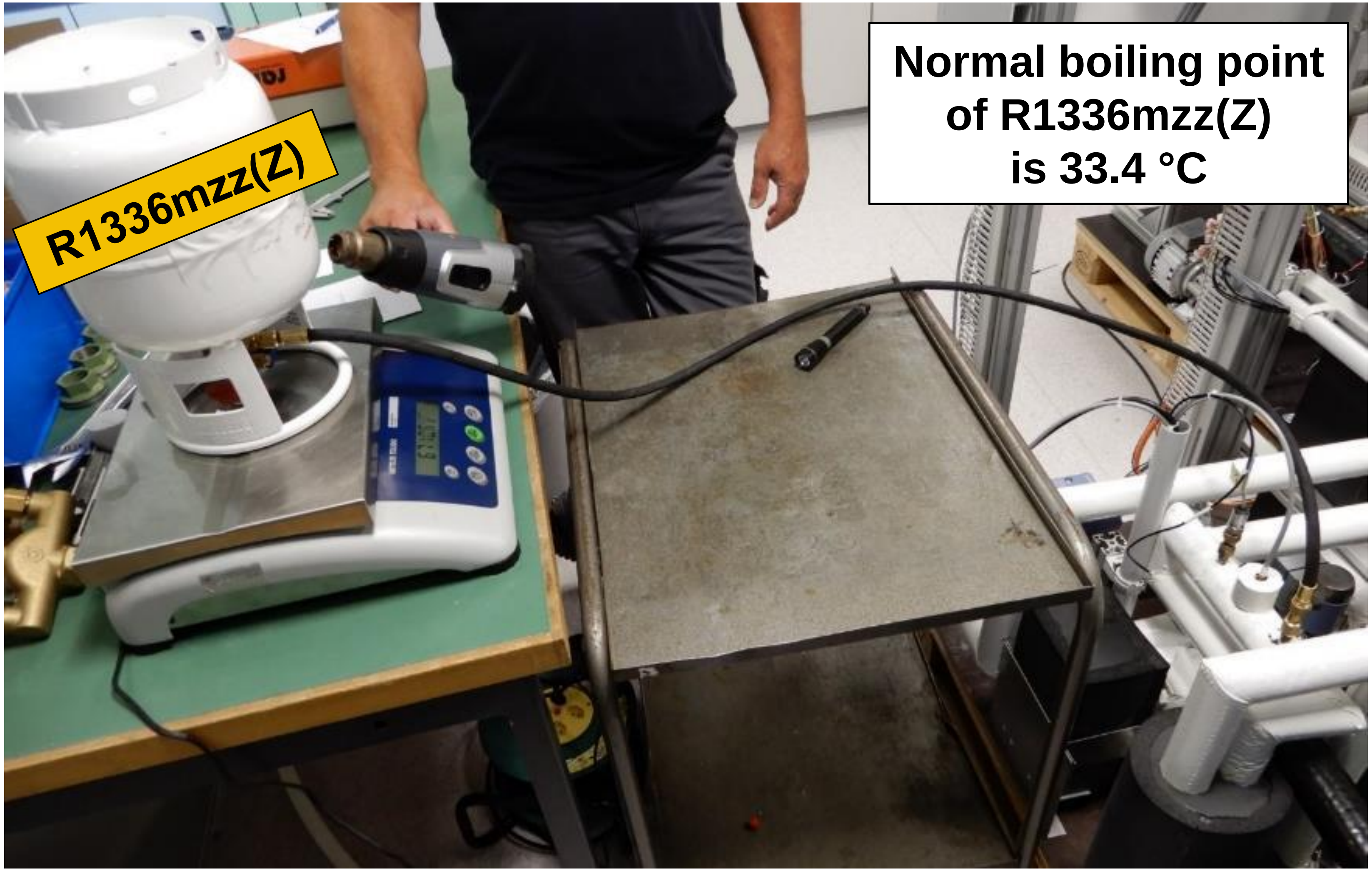
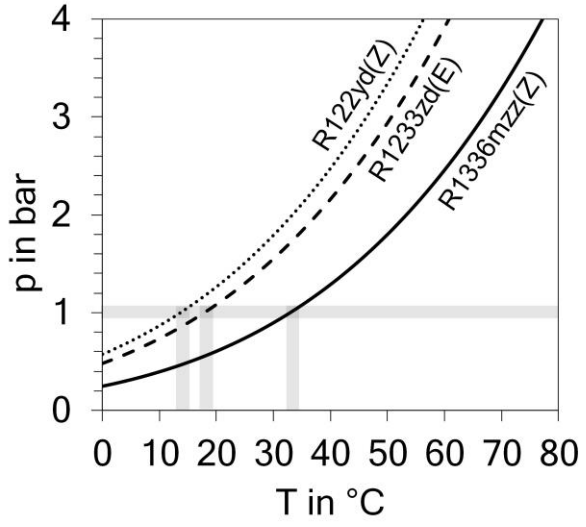
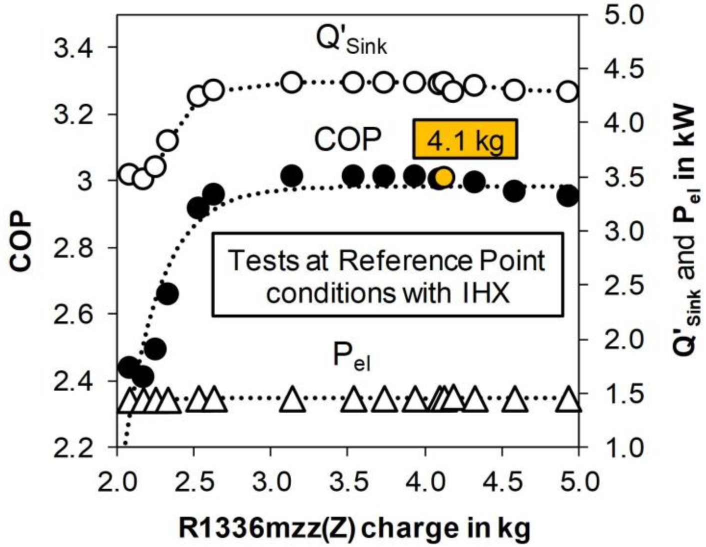
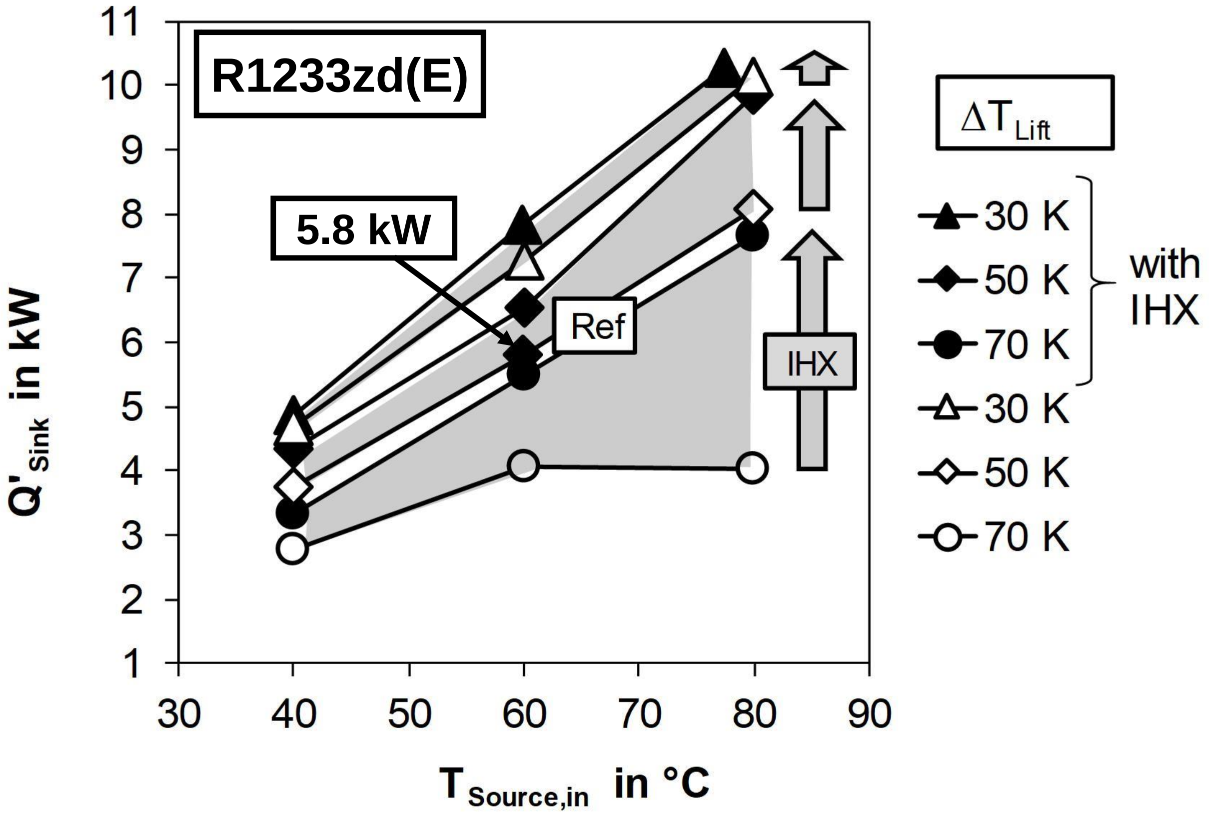
Refrigerant filling procedure with heating-up of the refrigerant cylinder

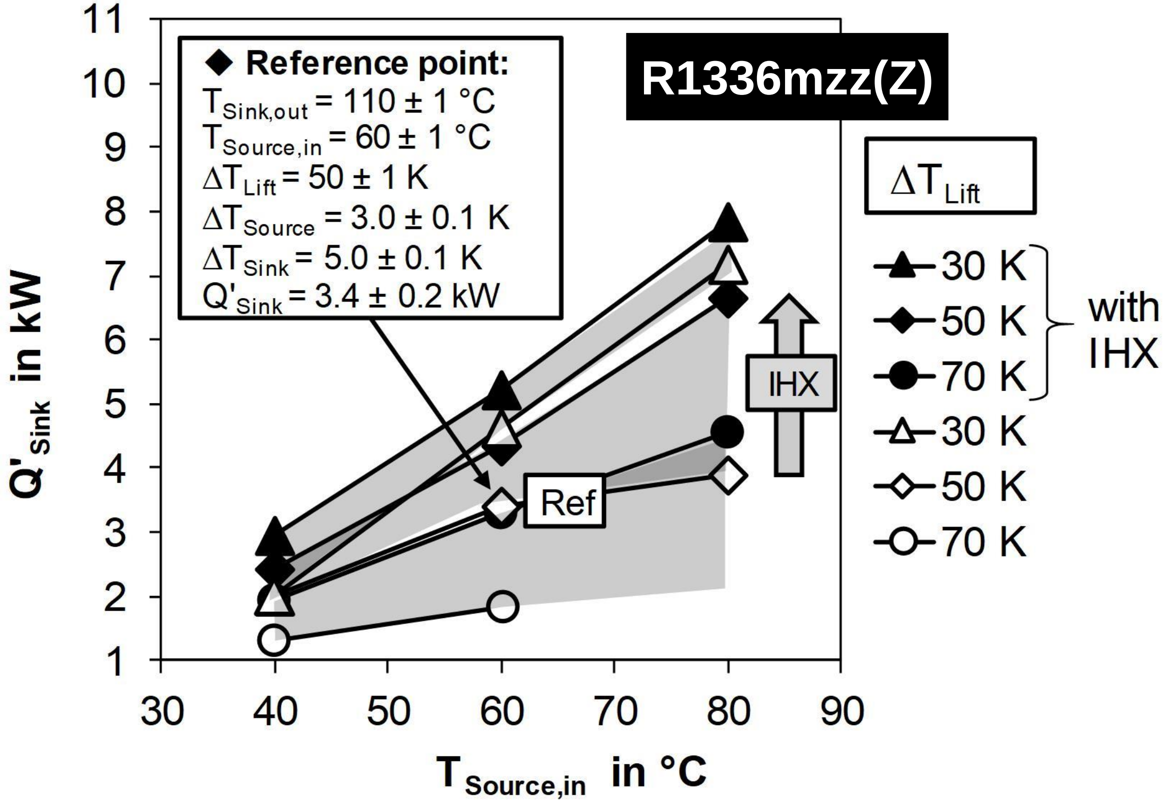






Comparison of heating capacity with the basic and IHX cycle

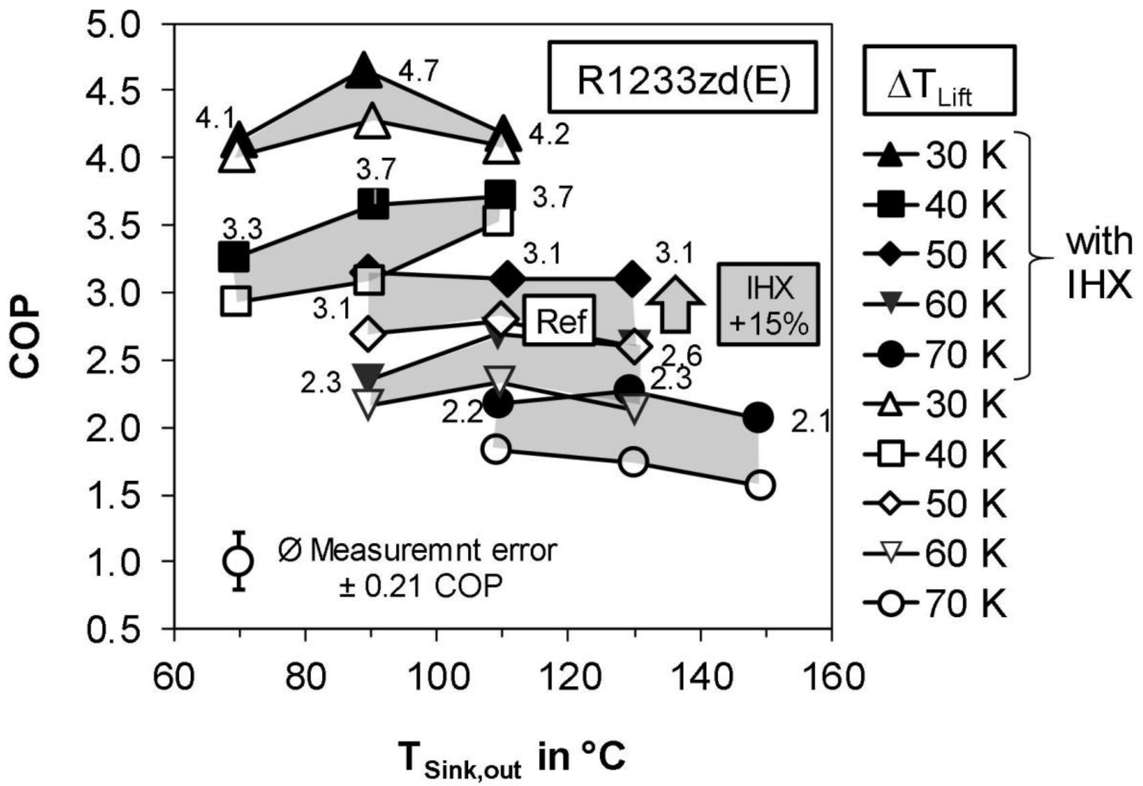


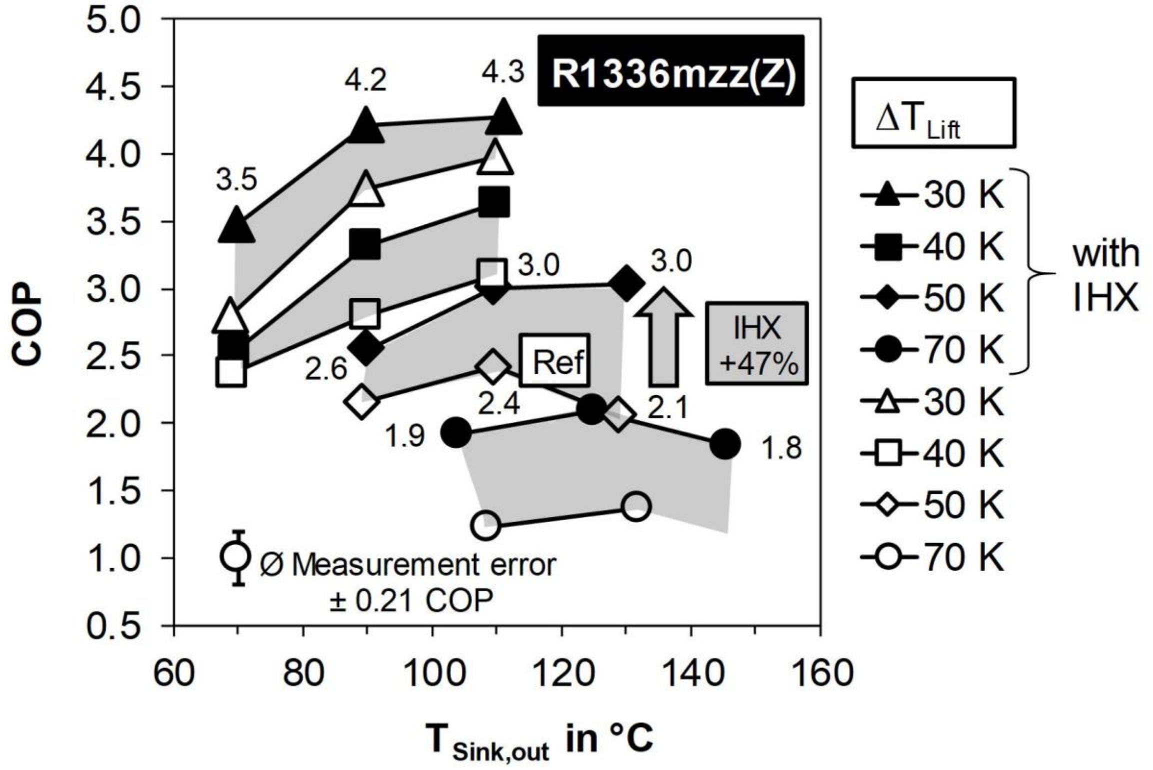


- R1233zd(E) provides 46 to 76% higher heating capacity than R1336mzz(Z) (e.g. 5.8 vs. 3.4 kW at W60/W110)
- R1336mzz(Z) would require a larger compressor to achieve similar heating capacities as R1233zd(E)

Operating maps of efficiency with basic and IHX cycle

COP vs. $T_{Sink,out}$ at different temperature lifts ($\Delta T_{Lift} = T_{Sink,out} - T_{Source,in}$) from 30 to 70 K





- COP increase with smaller ΔT_{Lift} and higher $T_{Sink,out}$ according to Carnot relationship (as expected)
- IHX integration provides significant COP increase (superheat achieved in IHX, higher evaporation temperature)
- Max. heat sink temperature tested was 150 °C with a COP of 2.1 for R1233zd(E) and 1.8 for R1336mzz(Z)

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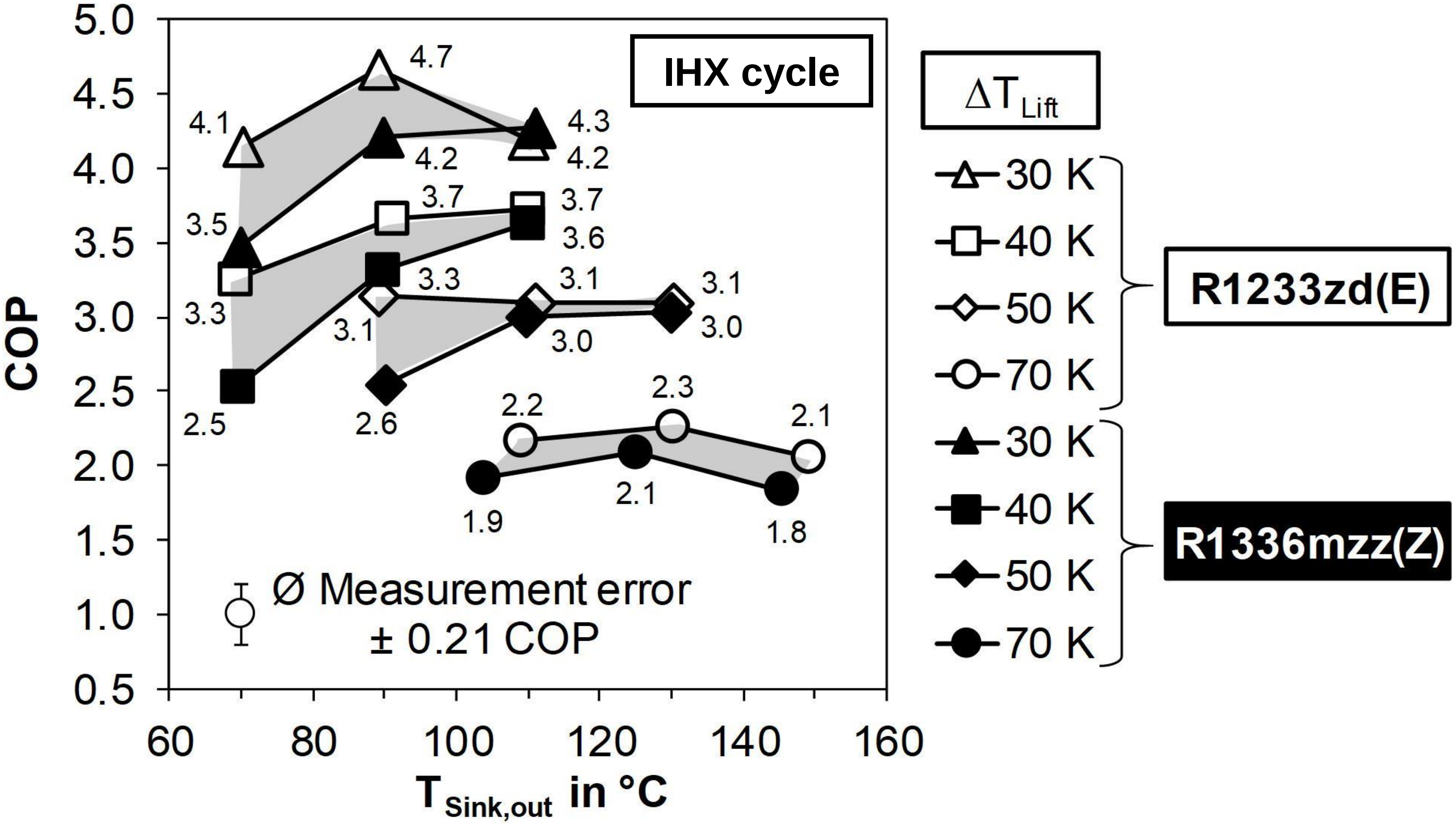
Overlap of operating maps



- R1233zd(E) provides higher COPs compared to R1336mzz(Z) up to about 110°C
- The smaller heating capacity of R1336mzz(Z) leads to more significant relative heat losses
- R1336mzz(Z) achieves potentially higher condensing temperatures (T_{crit} = 171.3°C)

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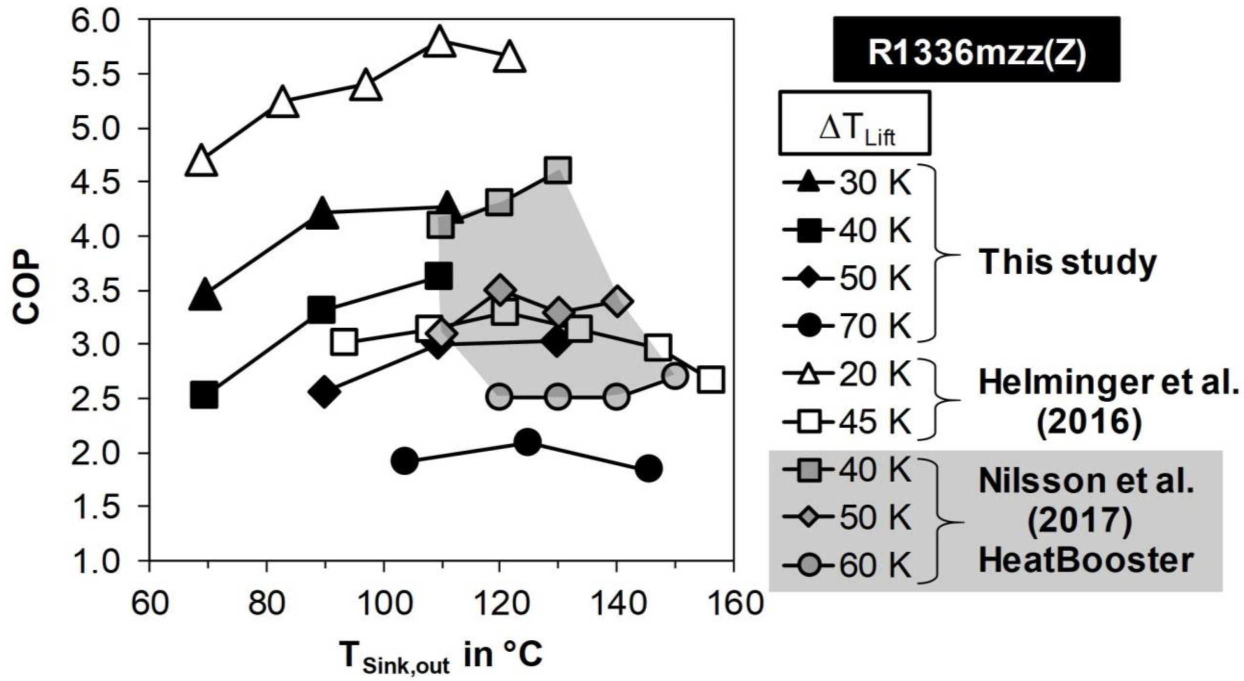
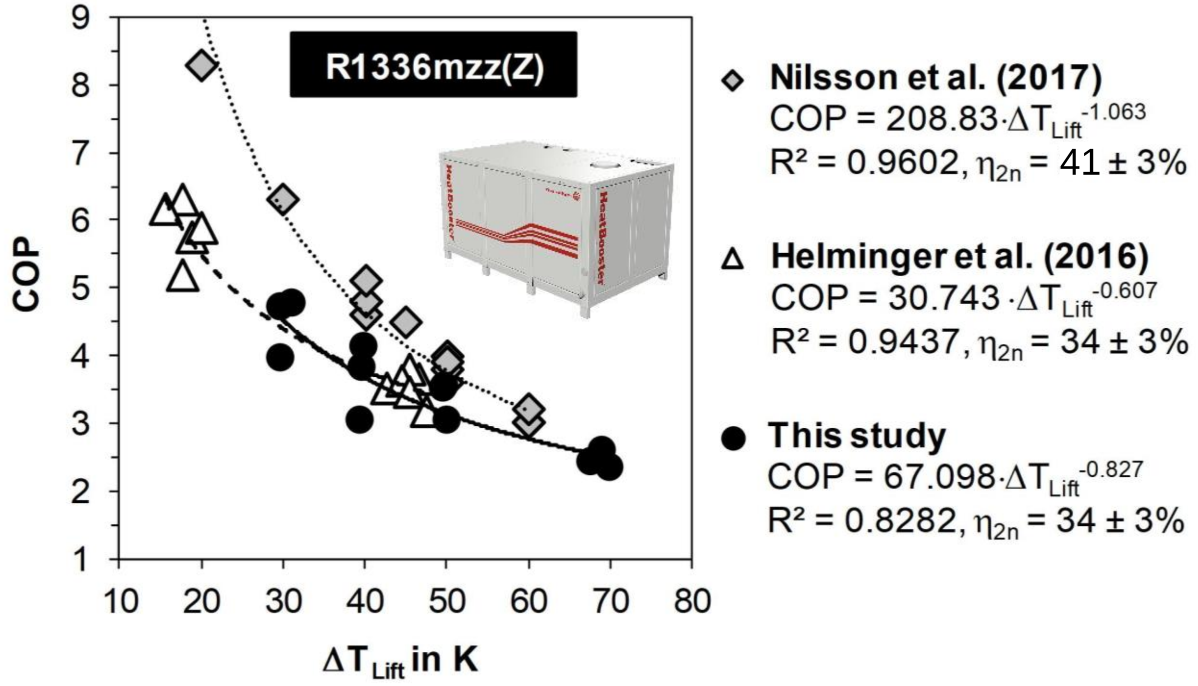
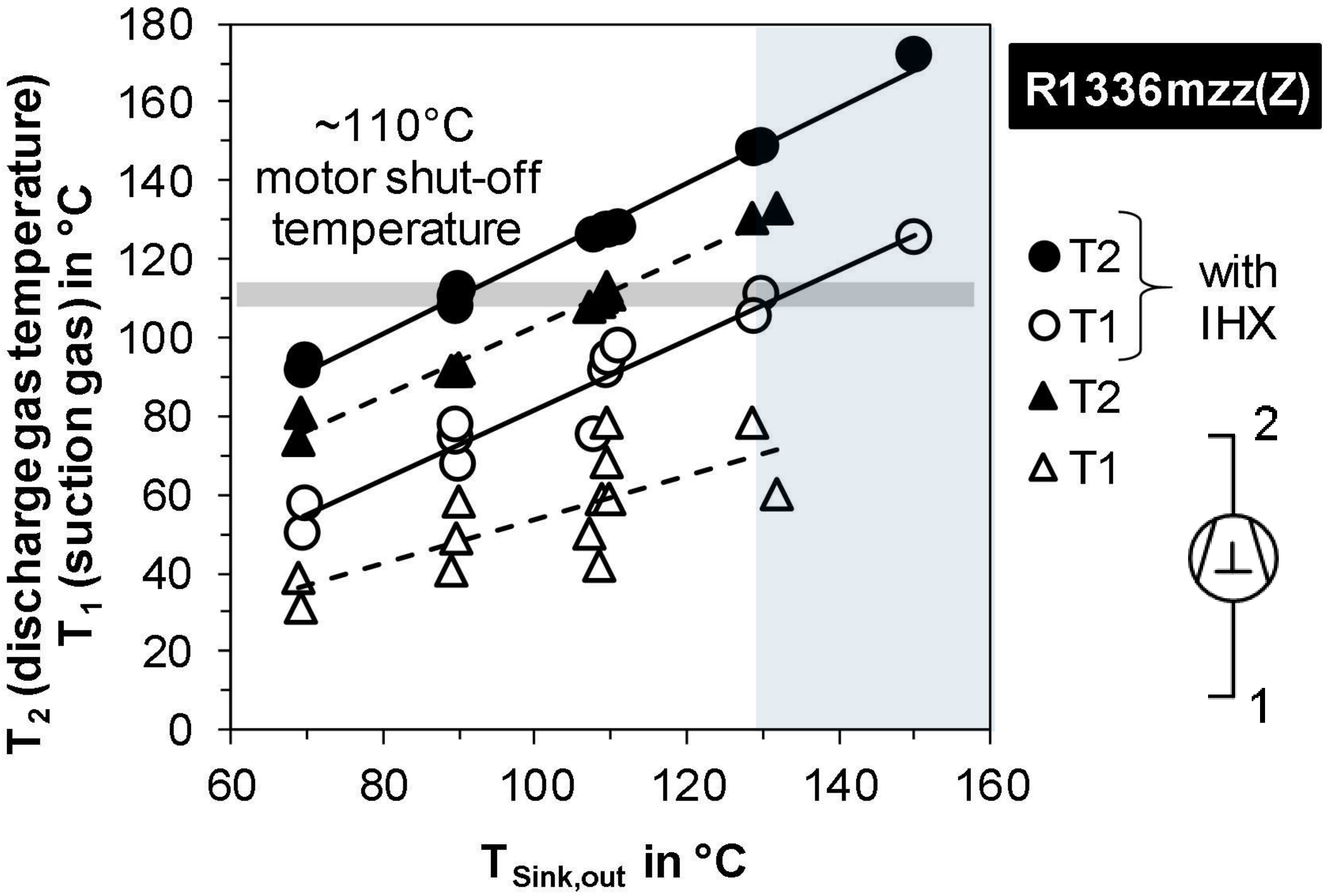
COP comparison with data from Helminger et al. (2016) and Nilsson et al. (2017)





- Helminger et al. (2016):
  - 156.3°C and COP of almost 2.7 at 45 K ΔT_{Lift}
  - 2nd Law efficiency of 34 ± 3% similar to this study
- Nilsson et al. (2017):
  - Commercial HeatBooster technology achieves higher COP and 2nd Law efficiency of 41 ± 3 %
  - COP of 2.5 at 60 K ΔT_{lift}
  - With larger heating power the relative heat losses are getting smaller

Discharge and suction gas temperatures for tests with R1336mzz(Z)



Basic cycle:

- Suction temperature (Δ T1) well below the motor shut-off temperature of approx. 110 °C (grey line)

Cycle with IHX:

- Suction temperature (O T1) exceeded the motor limit temperature at a heat sink outlet temperature of about 130 °C and higher.

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Conclusions

- **R1336mzz(Z) and R1233zd(E) are suitable refrigerants for HTHP (negligible environmental impacts)**
- **Operating maps of lab-scale HTHP with HCFO R1233zd(E) and HFO R1336mzz(Z) established** at 40 to 80°C heat source and 70 to 150°C heat sink temperatures (drop-in tests)
- R1233zd(E) provided 46 to 76% higher heating capacity than R1336mzz(Z) (e.g. 5.8 vs. 3.4 kW at W60/W110)
- **COP fit-curves** (IHX cycle):
  - **R1233zd(E):** $COP = 73.832 \cdot \Delta T_{Lift}^{-0.824}$, $R^2 = 0.9473$, $\eta_{2n} = 39 \pm 2\%$
  - **R1336mzz(Z):** $COP = 67.098 \cdot \Delta T_{Lift}^{-0.827}$, $R^2 = 0.8282$, $\eta_{2n} = 34 \pm 3\%$
- **Integration of an IHX significantly increased COP** (+15 to 47%) and heating capacity
- **R1233zd(E)** delivered **slightly higher COP than R1336mzz(Z) up to about 110°C** due to **higher heating capacity** and **smaller relative heat losses** at the same temperature conditions
- At higher temperatures the COPs of R1233zd(E) and R1336mzz(Z) were comparable (differences within measurement uncertainity, R1336mzz(Z) achieves potentially higher condensing temperatures)
- **R1336mzz(Z) results are comparable to Helminger et al. (2016)** (lab setup), but **lower than commerical HeatBooster technology (Nilsson et al., 2017)** (η_{2n} = approx. 41%)

NTB
Interstate University of Applied Sciences of Technology Buchs
University of Applied Sciences of Eastern Switzerland

Acknowledgements

This research project is part of the

Swiss Competence Center for Energy Research SCCER EIP

of the Swiss Innovation Agency Innosuisse.

We would like to thank Innosuisse for their support.

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