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

C. Arpagaus, S.S. Bertsch

NTB Buchs

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

2nd Conference on High Temperature Heat Pumps (HTHP)
Copenhagen, Denmark
September 9, 2019

IES INSTITUTE FOR ENERGY SYSTEMS

Content

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

- 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), R1233zd(E) and R1224yd(Z)
- Conclusions

cordin.arpagaus@ntb.ch

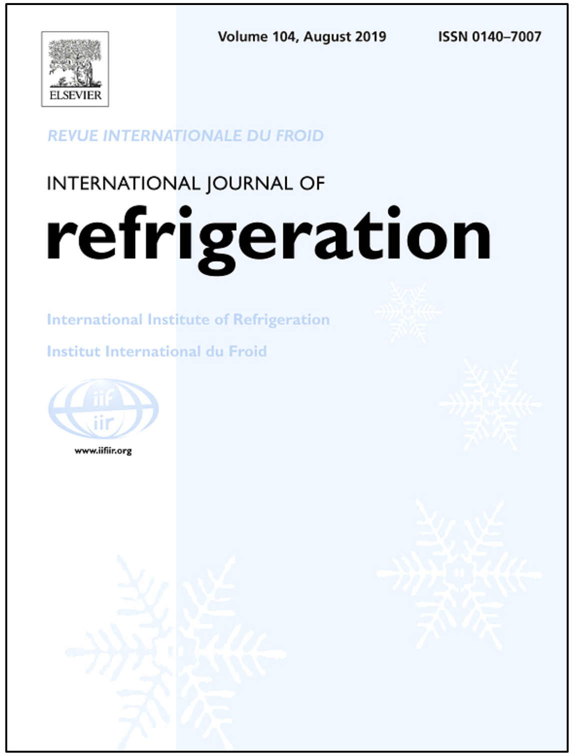
Introduction to high temperature heat pumps (HTHP)

cordin.arpagaus@ntb.ch

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



Volume 104, August 2019 ISSN 0140–7007

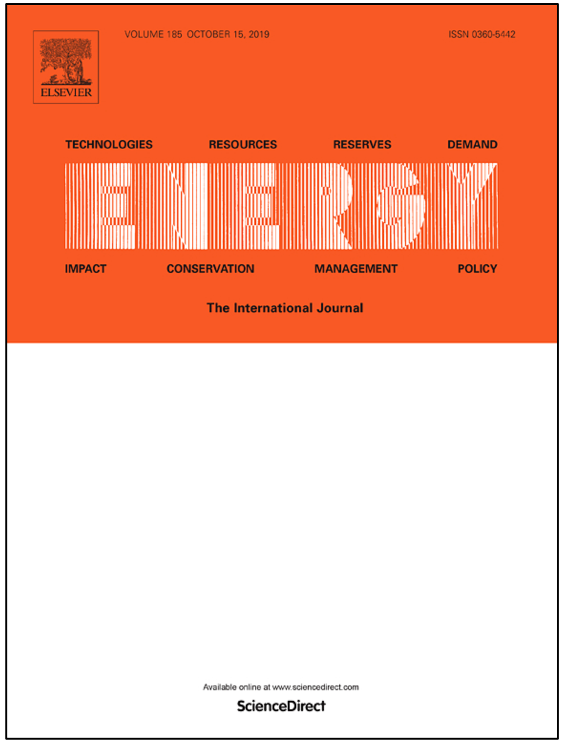
ELSEVIER

REVUE INTERNATIONALE DU FROID

INTERNATIONAL JOURNAL OF
refrigeration

International Institute of Refrigeration
Institut International du Froid

iif iir
www.iifiir.org



VOLUME 185 OCTOBER 15, 2019 ISSN 0360-5442

ELSEVIER

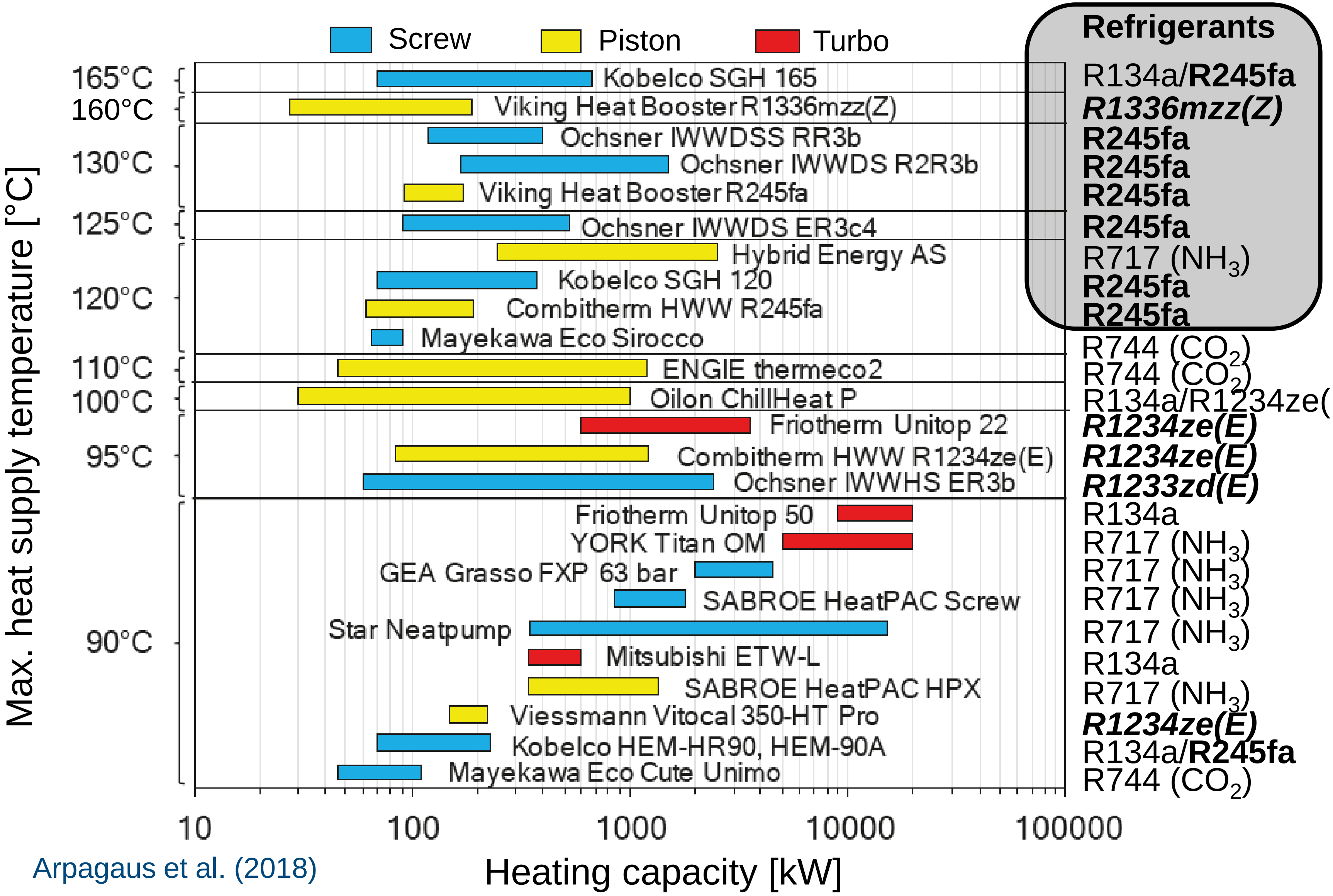
TECHNOLOGIES RESOURCES RESERVES DEMAND
ENERGY
IMPACT CONSERVATION MANAGEMENT POLICY

The International Journal

Available online at www.sciencedirect.com
ScienceDirect

> 26 industrial HTHP products with heat supply temperature ≥ 90 °C available

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)

cordin.arpagaus@ntb.ch

Research gaps in High Temperature Heat Pumps

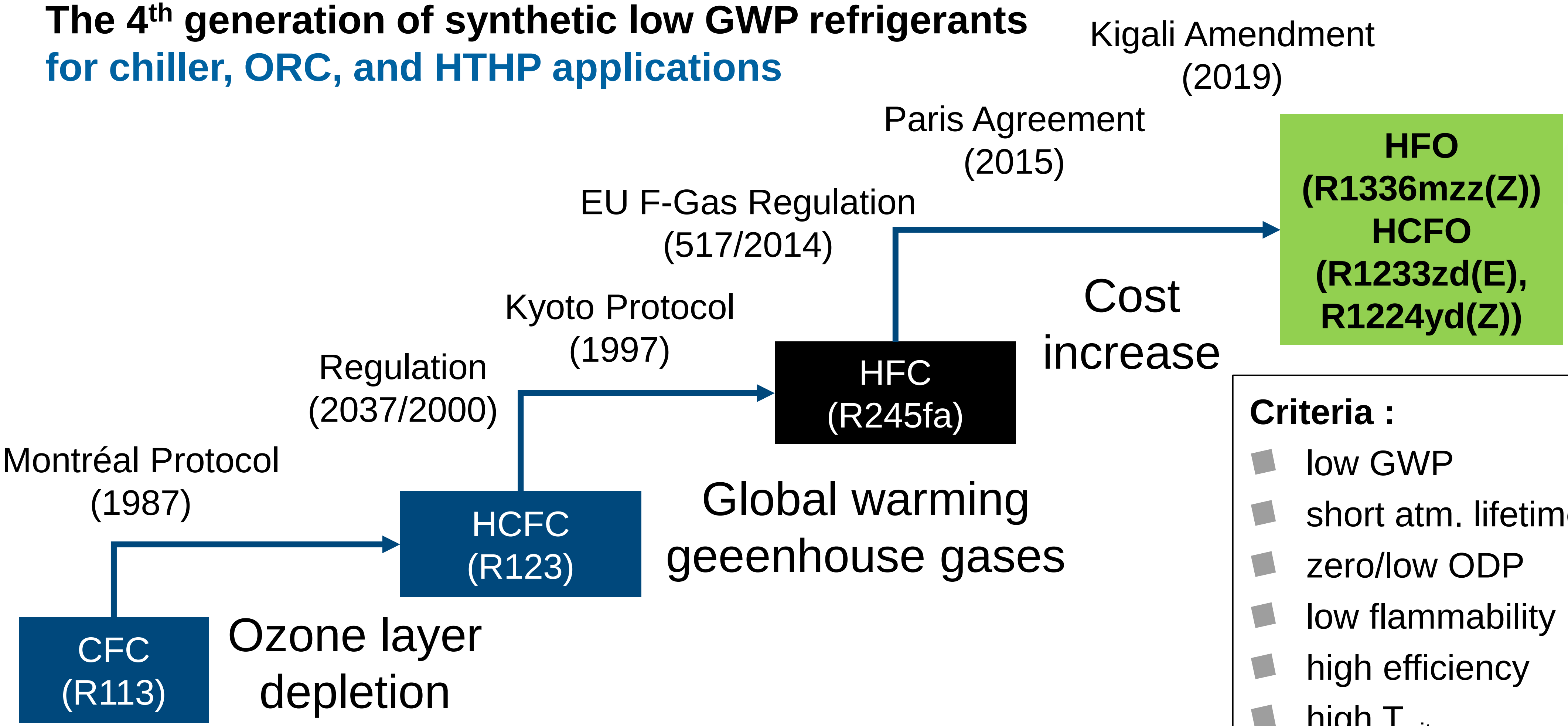
Focus

- 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

cordin.arpagaus@ntb.ch

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)

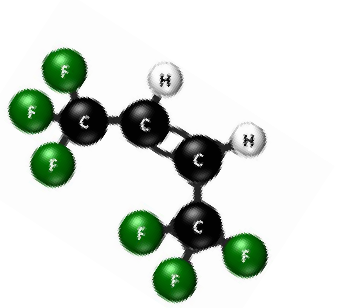
Cost increase

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

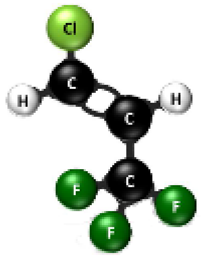
Criteria :

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

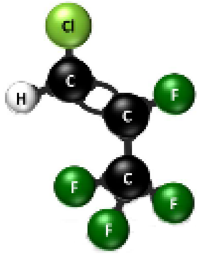
CFC:	fully halogenated chlorofluorocarbons
HCFC:	partially halogenated chlorofluorocarbons
HFC:	hydrofluorocarbons
HFO:	**hydrofluoroolefins**
HCFO:	**hydrochlorofluoroolefins**



R1336mzz(Z)



R1233zd(E)



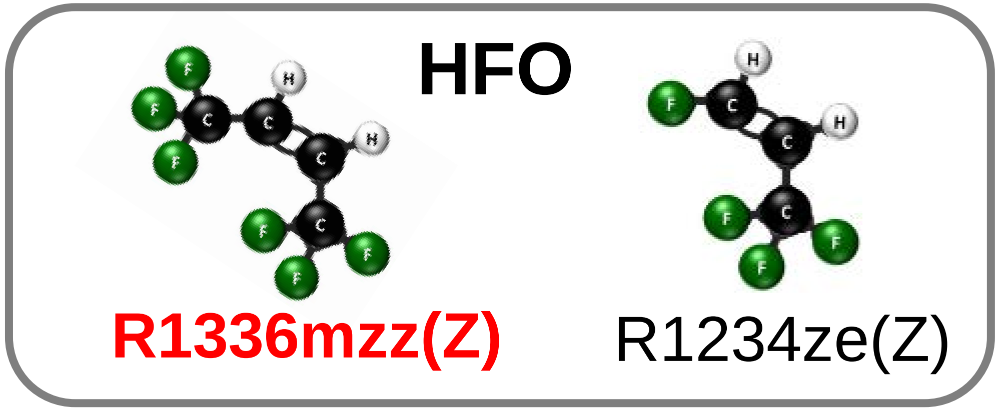
R1224yd(Z)

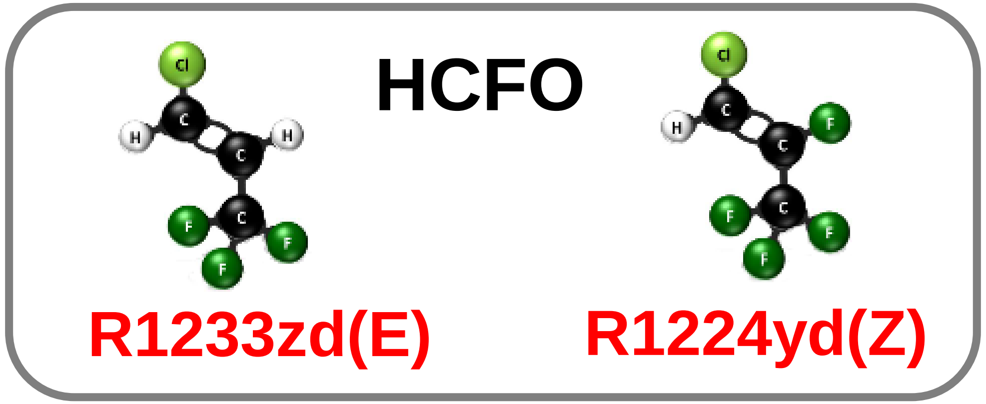
cordin.arpagaus@ntb.ch

Properties of suitable HFO and HCFO refrigerants for HTHPs

Tested in this study

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}**	**~14^{f},26^{a}, 36^{e}, 40.4^{d}**	**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

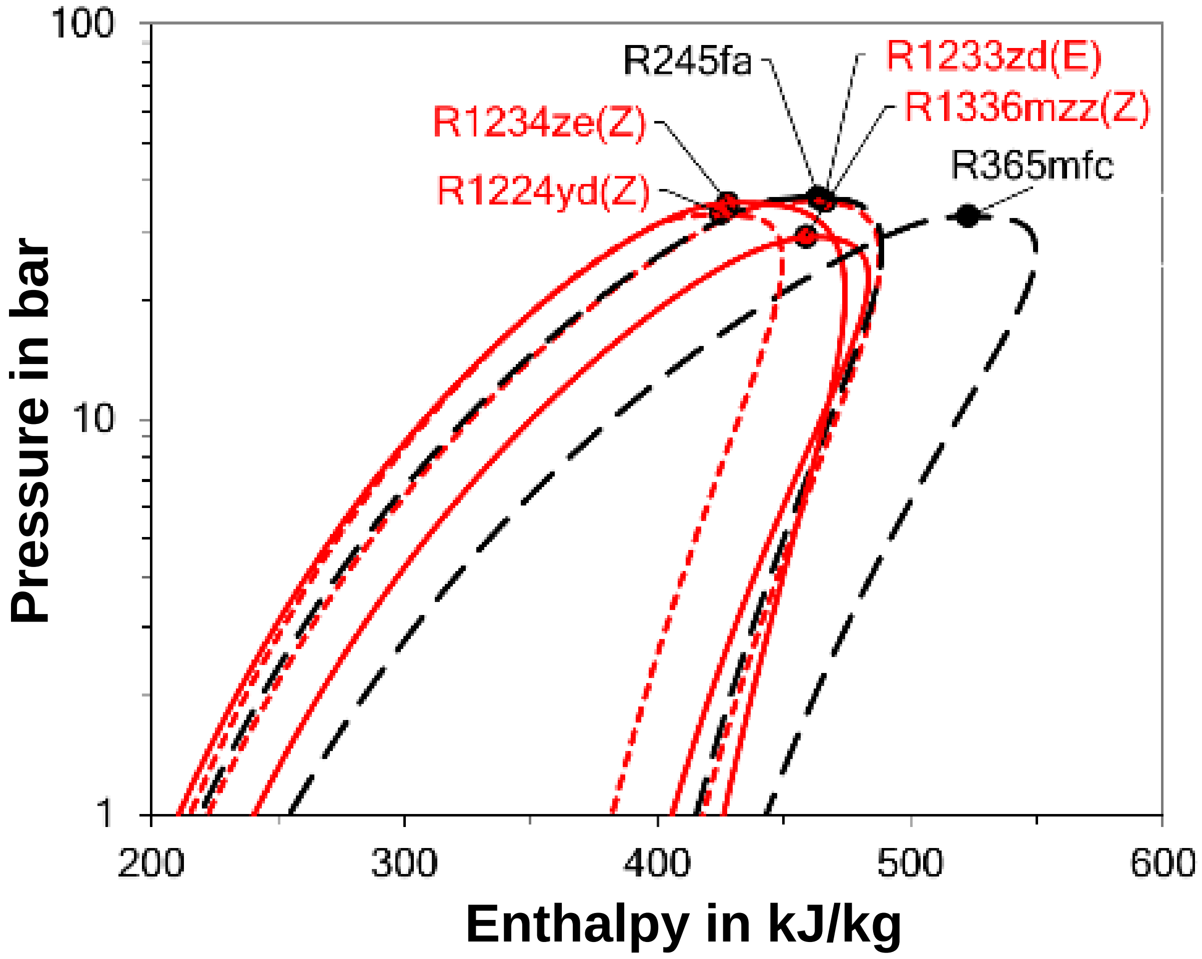


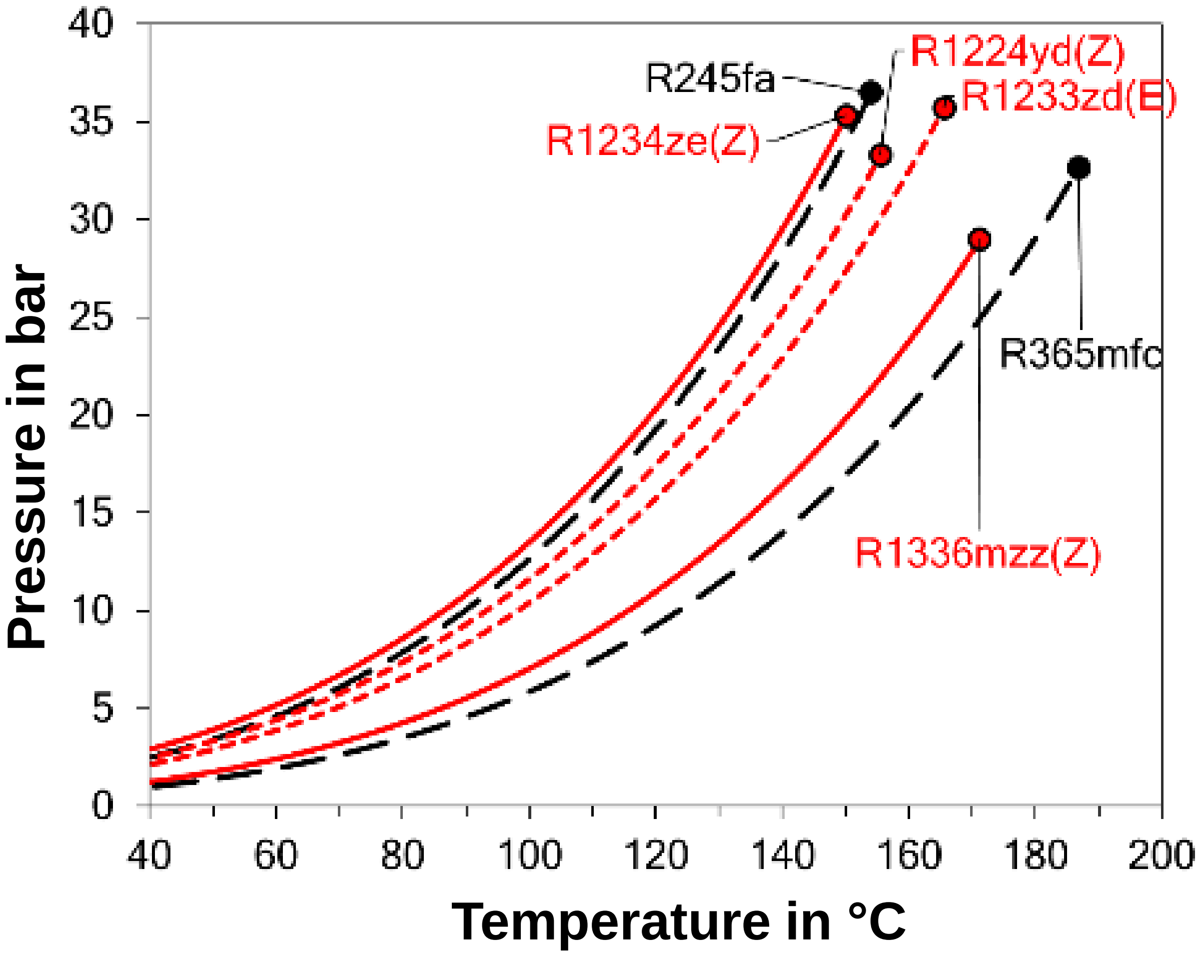


References:
T_{crit} and p_{crit} (EES F-Chart Software, V10.643, 2019), ODP basis R11=1.0 (UNEP, 2017), GWP_{100} (100-year time horizon, CO_2=1.0), SG: Safety group classification (ASHRAE 34, 2016), [a]Myhre et al. (2013, IPCC 5th assessment report), [b]Fukuda et al. (2014), [c]Tokuhashi et al. (2018), [d]Patten and Wuebbles (2010), [e]Sulbaek Andersen et al. (2018) (3D global model), [f]Andersen et al. (2015)

cordin.arpagaus@ntb.ch

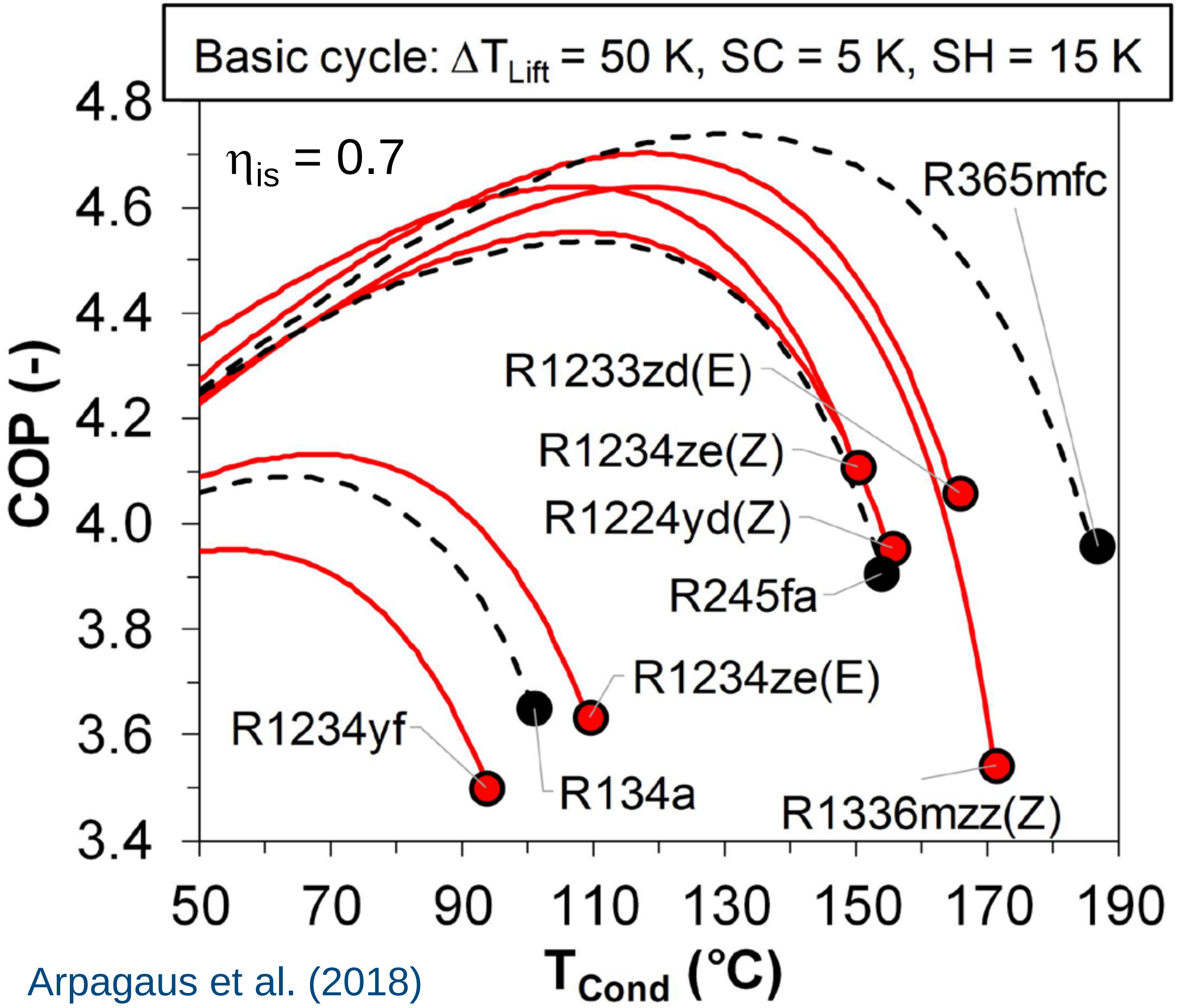
T-s, p-T diagrams of selected HFO and HCFO refrigerants





cordin.arpagaus@ntb.ch

Simulated COP of selected HFO and HCFO refrigerants in a basic HP cycle

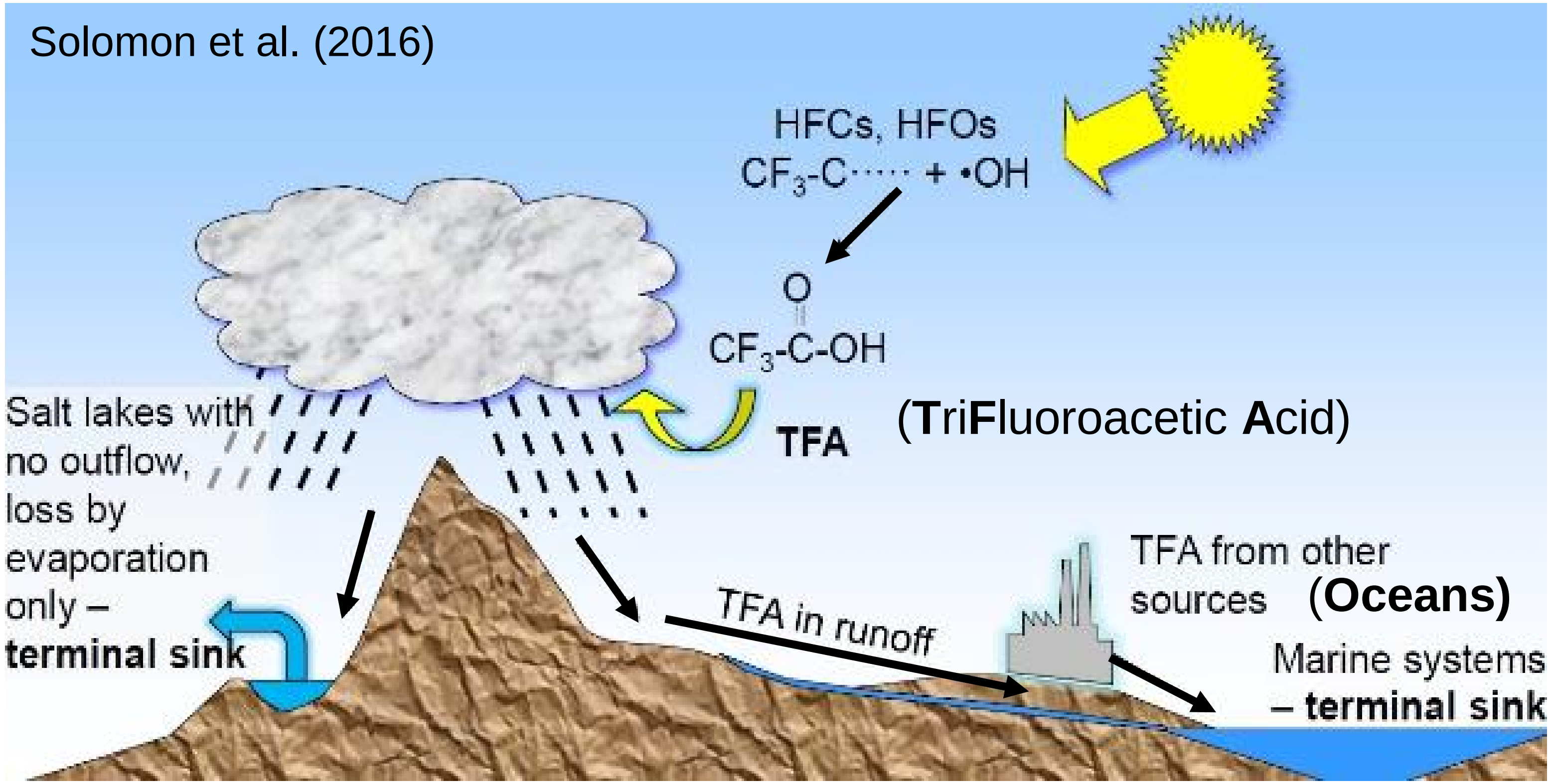


Arpagaus et al. (2018)

- Simulated COP rise to an optimum and decrease with the narrowing of the 2-phase region up to T_{crit}
- Optimal COP at about 30 K below the critical temperature
- R365mfc offers highest COP, followed by R1233zd(E) and R1336mzz(Z)
- R1234ze(Z) and R1224yd(Z) comparable to R245fa
- R1234yf and R1234ze(E) similar to R134a

cordin.arpagaus@ntb.ch

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 x 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

cordin.arpagaus@ntb.ch

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

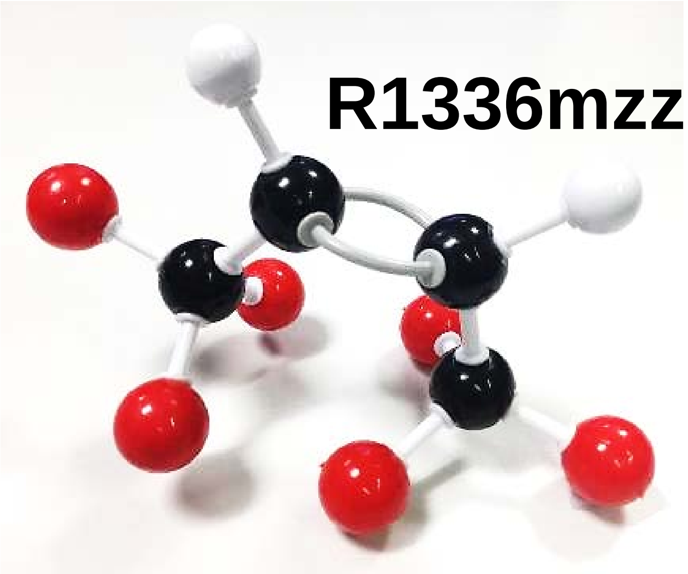
References:
Norwegian Environment Agency (2017), WMO (2018), Wallington et al. (2014), Juhasz & Kontomaris (2018), EFCTC (2019), [a]**Henne et. al. (2012)**, [b]**Sulbaek Andersen et al. (2008, 2012, 2018)**, Inoue et al. (2008), ECETOC (2004), Chen et al. (1997)

cordin.arpagaus@ntb.ch

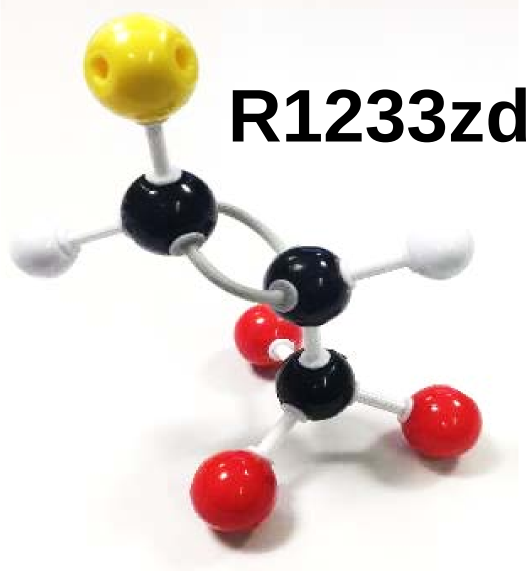
Goals of this study

Objectives:

- **Performance evaluation** of **R1336mzz(Z)** (Opteon^{TM}MZ, Chemours), **R1233zd(E)** (Solstice®zd, Honeywell), and **R1224yd(Z)** (AMOLEA®1224yd, AGC Chemicals) in a laboratory HTHP (**drop-in test**).



R1336mzz(Z)



R1233zd(E)

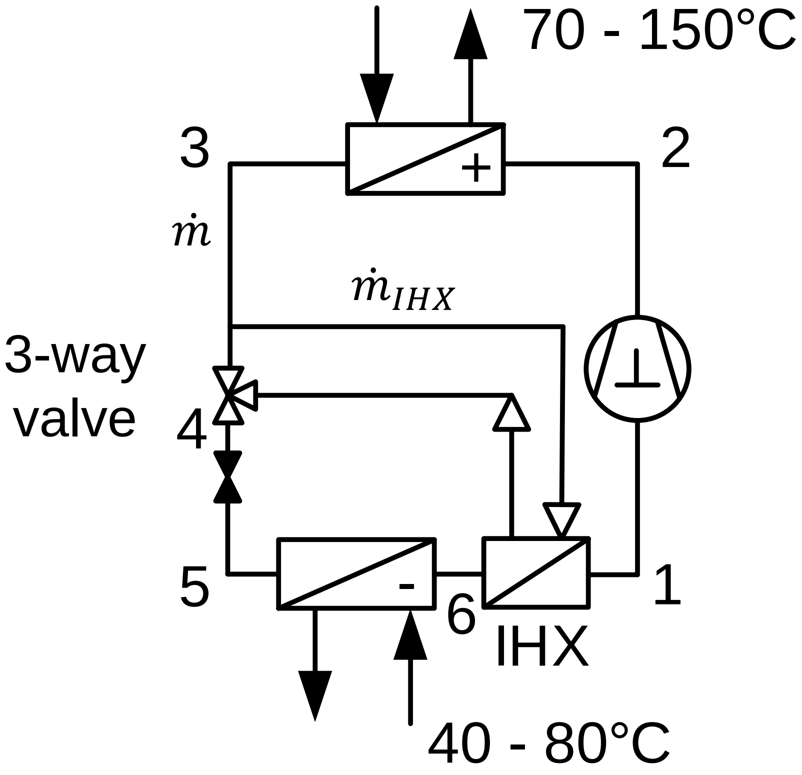
R1224yd(Z)

+ POE oil (SE 170)

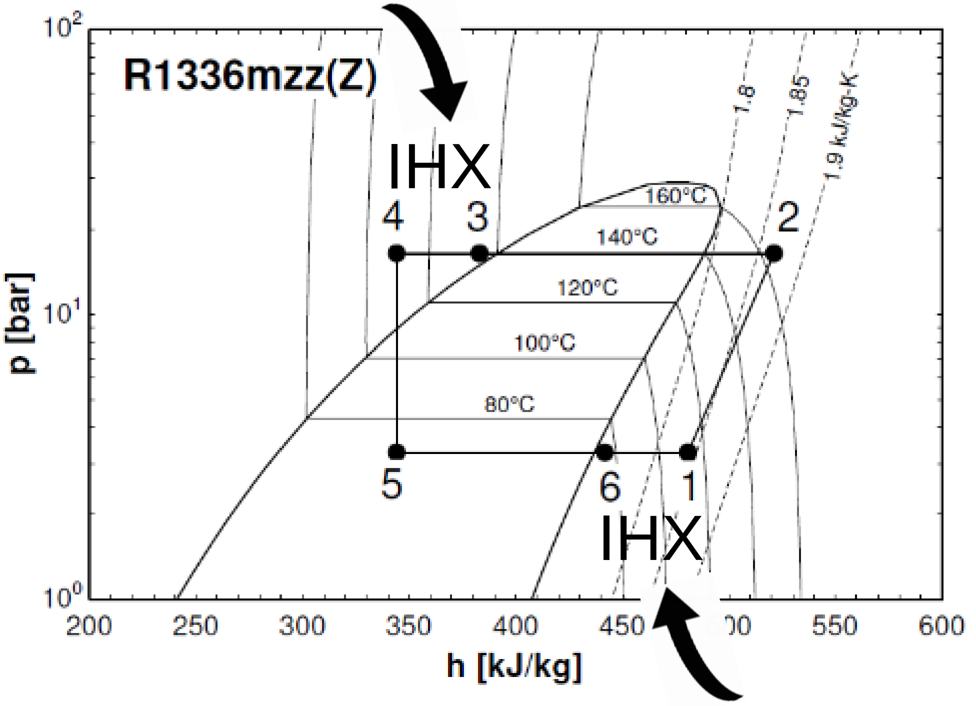
System design of the laboratory scale HTHP at NTB Buchs

cordin.arpagaus@ntb.ch

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



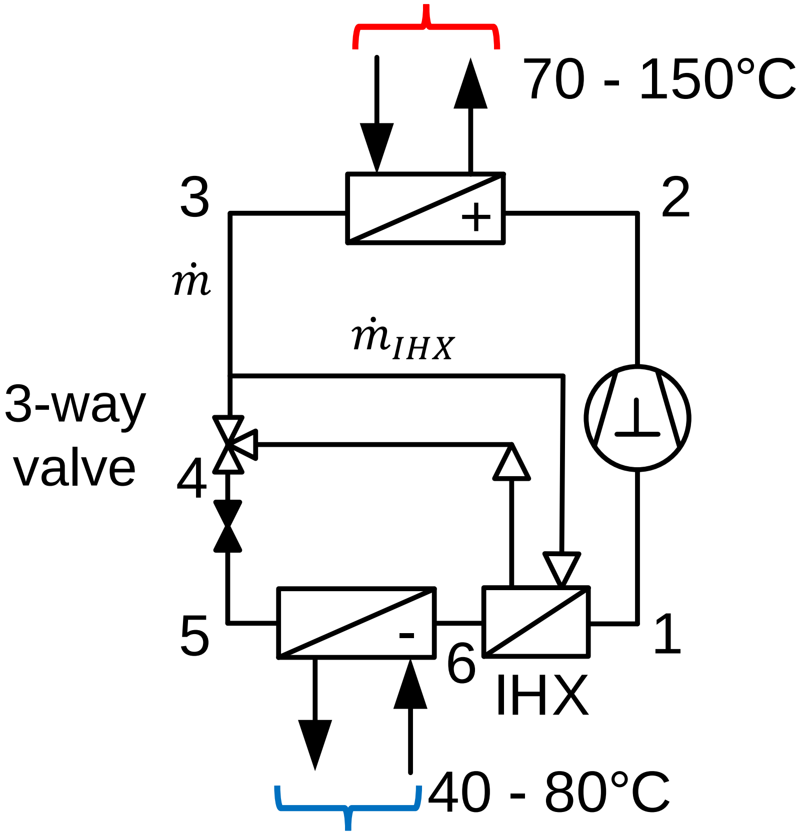
IHX: $\dot{m}_{IHX}/\dot{m} = 0\% \rightarrow 100\%$
(Opening degree 3-way-valve)



cordin.arpagaus@ntb.ch

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

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



ΔT_{Source} = 3 K (constant)

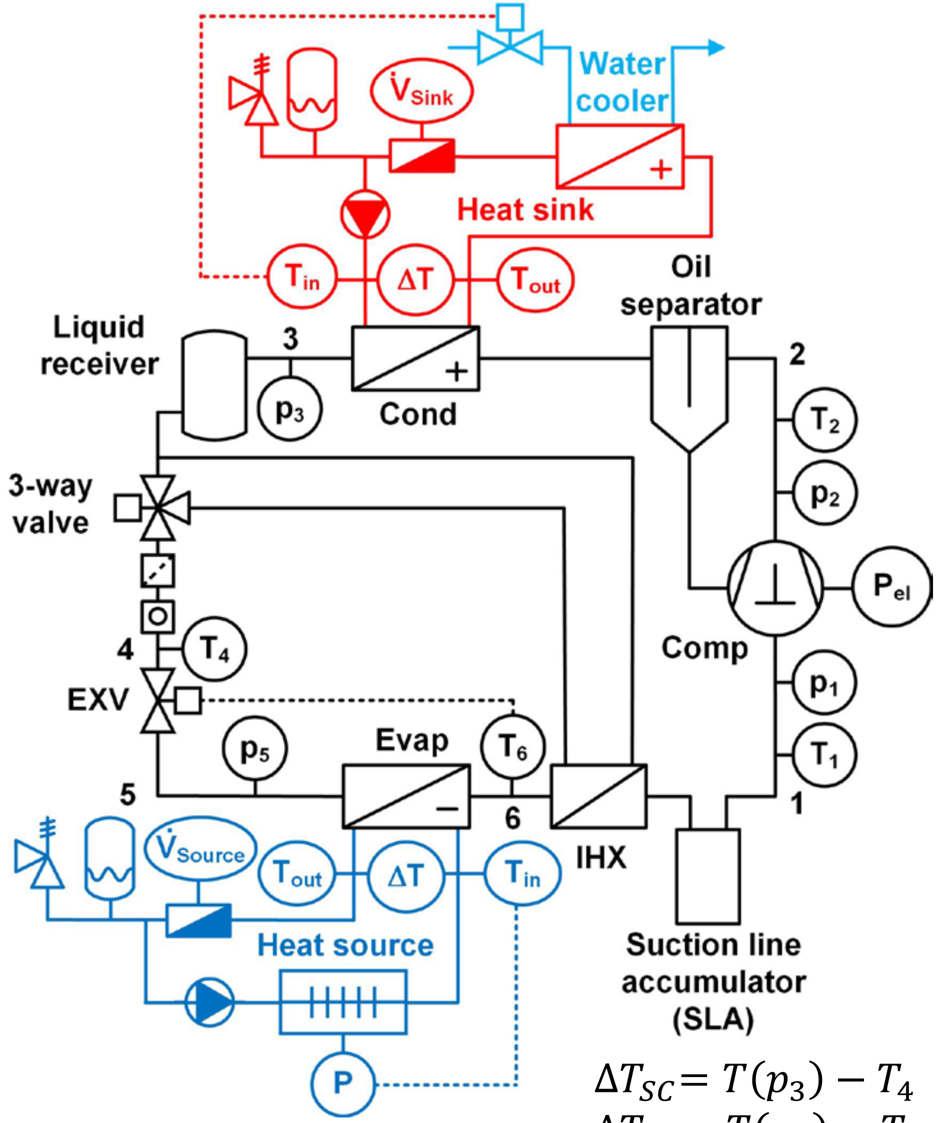
	Reference point (Ref)	Variation range
$T_{Sink,out}$	110 ± 1°C	70 to 150°C
$T_{Source,in}$	60 ± 1°C	40 to 80°C
ΔT_{Lift}	50 K	30 to 70 K
ΔT_{Sink}	5.0 ± 0.1 K	5 to 25 K
ΔT_{Source}	3.0 ± 0.1 K	constant
f_{Komp}	50 Hz	constant
IHX **(Opening angle of 3-way-valve)**	100%	0 to 100%

$$IHX\colon \dot{m}_{IHX}/\dot{m} = 0\% \rightarrow 100\%$$

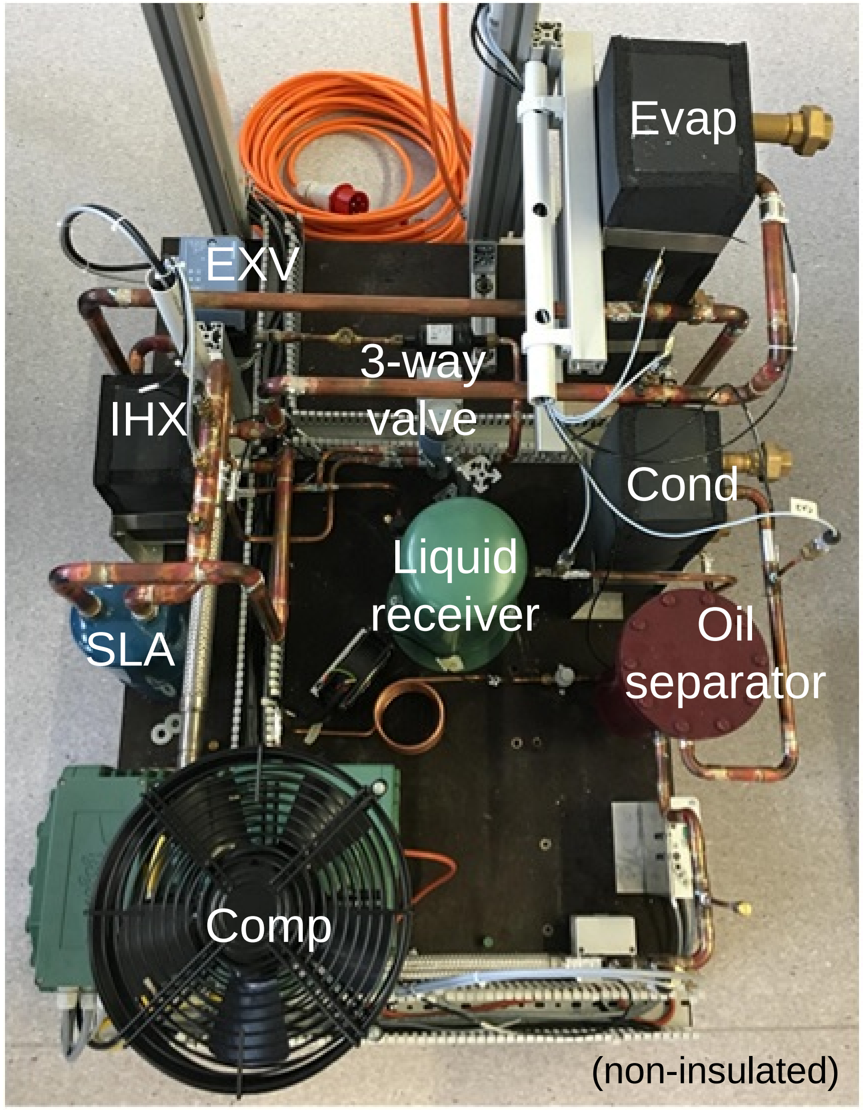
Superheating after evaporator:
$\Delta T_{SH} = T_6 - T(p_{Evap}) = 5$ K
IHX generates additional superheating

cordin.arpagaus@ntb.ch

Experimental set-up and schematics of the laboratory HTHP



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



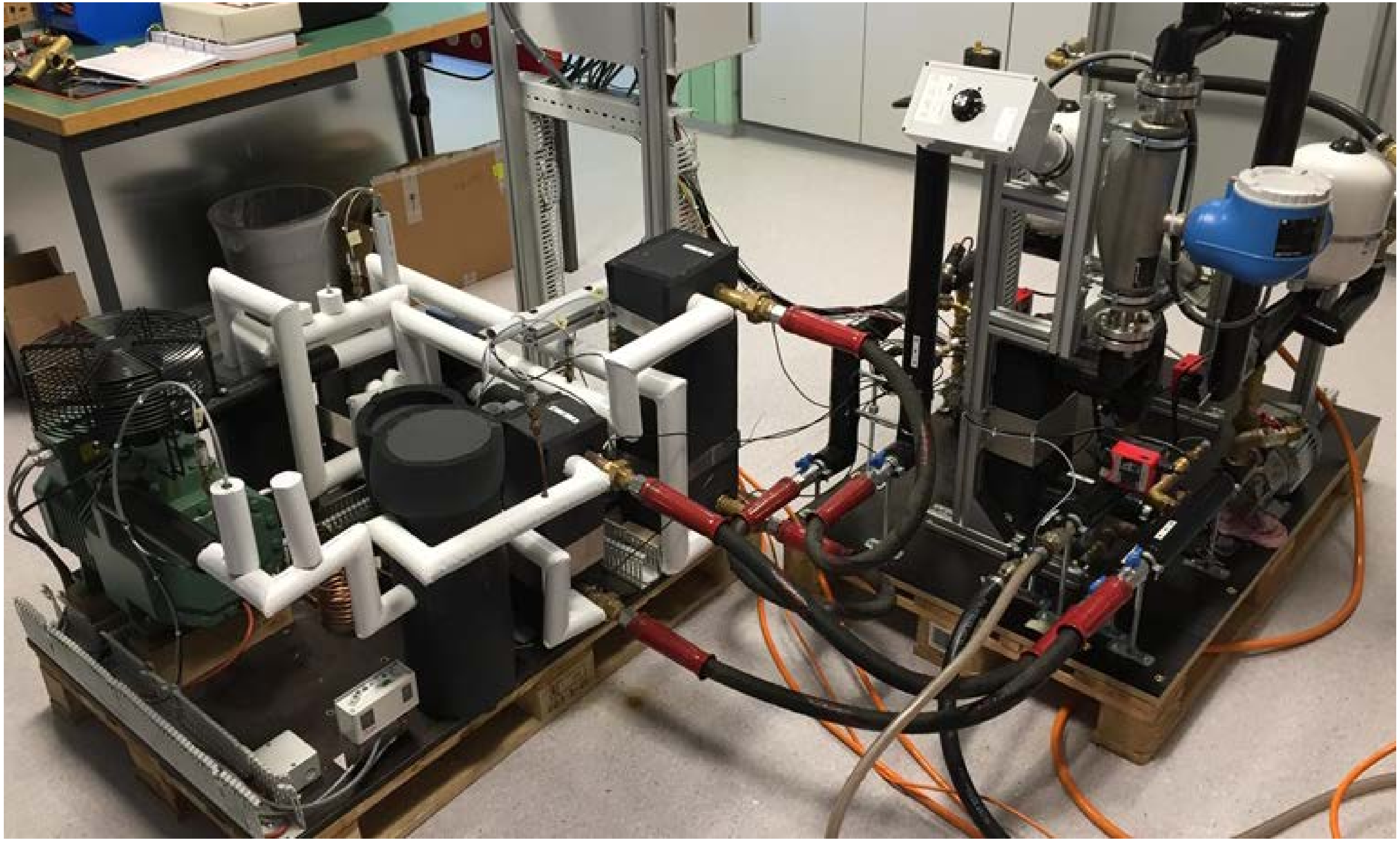
(non-insulated)

POE oil SE 170
kinematic viscosity
at 40 °C: 173 cSt
at 100 °C: 17,6 cSt

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

Motor switch-off
temperature
~110 °C

Laboratory HTHP with hydraulic loops for heat source and sink



System design – laboratory scale HTHP at NTB Buchs

Sensors and measurement uncertainties

Measured parameters	Sensor type		Uncertainities
Pressures	$p_{1 \ldots 6}$	Piezoelectric, 0 to 50 bar, max. 120°C	max. 1.5% of full scale reading
Temperatures	$T_{1 \ldots 6}$	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 %

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

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

2nd Law efficiency:

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

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

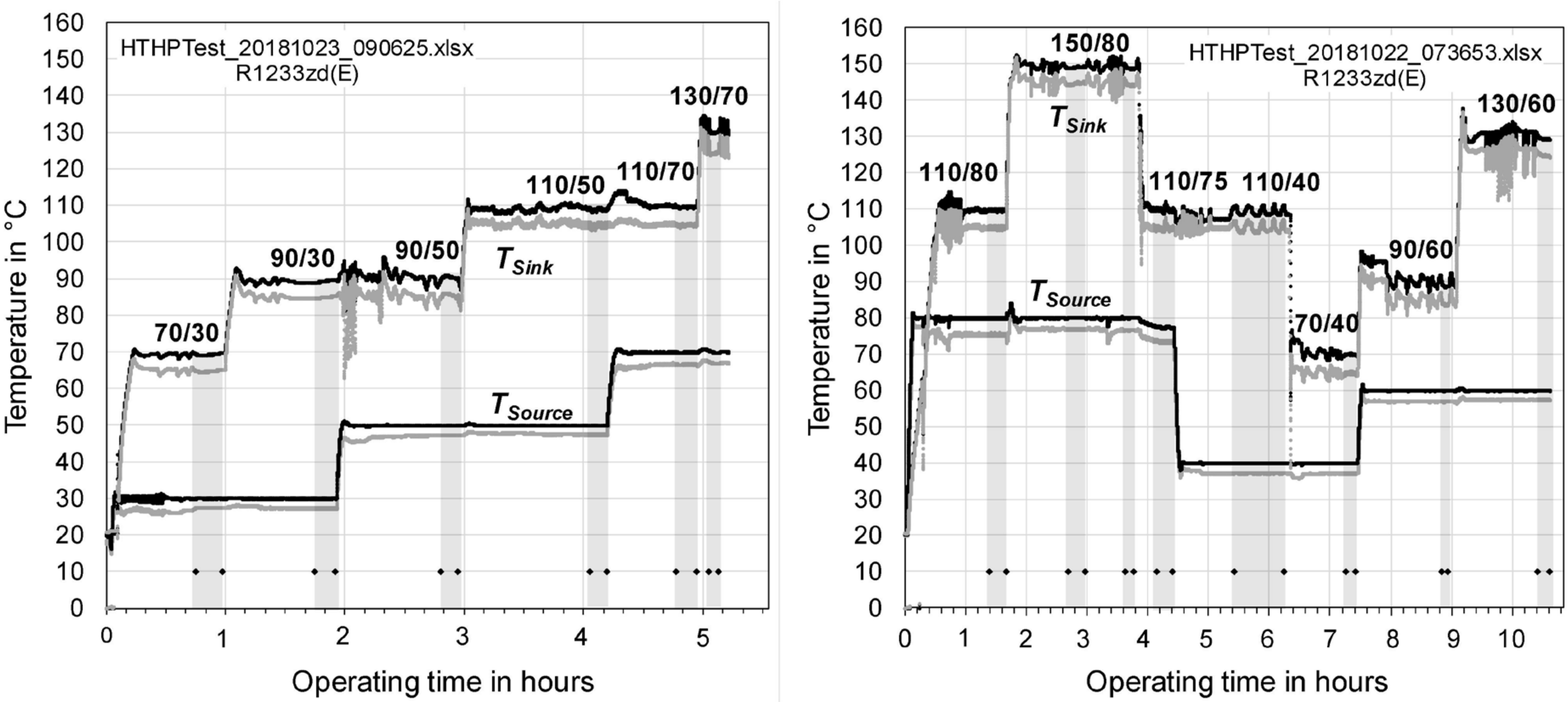
$$\Delta COP = \sqrt{\left(\frac{\partial COP}{\partial \dot{m}_{H_2O}} \cdot \Delta \dot{m}_{H_2O}\right)^2 + \left(\underbrace{\frac{\partial COP}{\partial c_{p,H_2O}(T)} \cdot \Delta c_{p,H_2O}(T)}_{\sim 0}\right)^2 + \left(\frac{\partial COP}{\partial \Delta T_{Sink}} \cdot \Delta(\Delta T_{Sink})\right)^2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

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

Test procedure

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

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

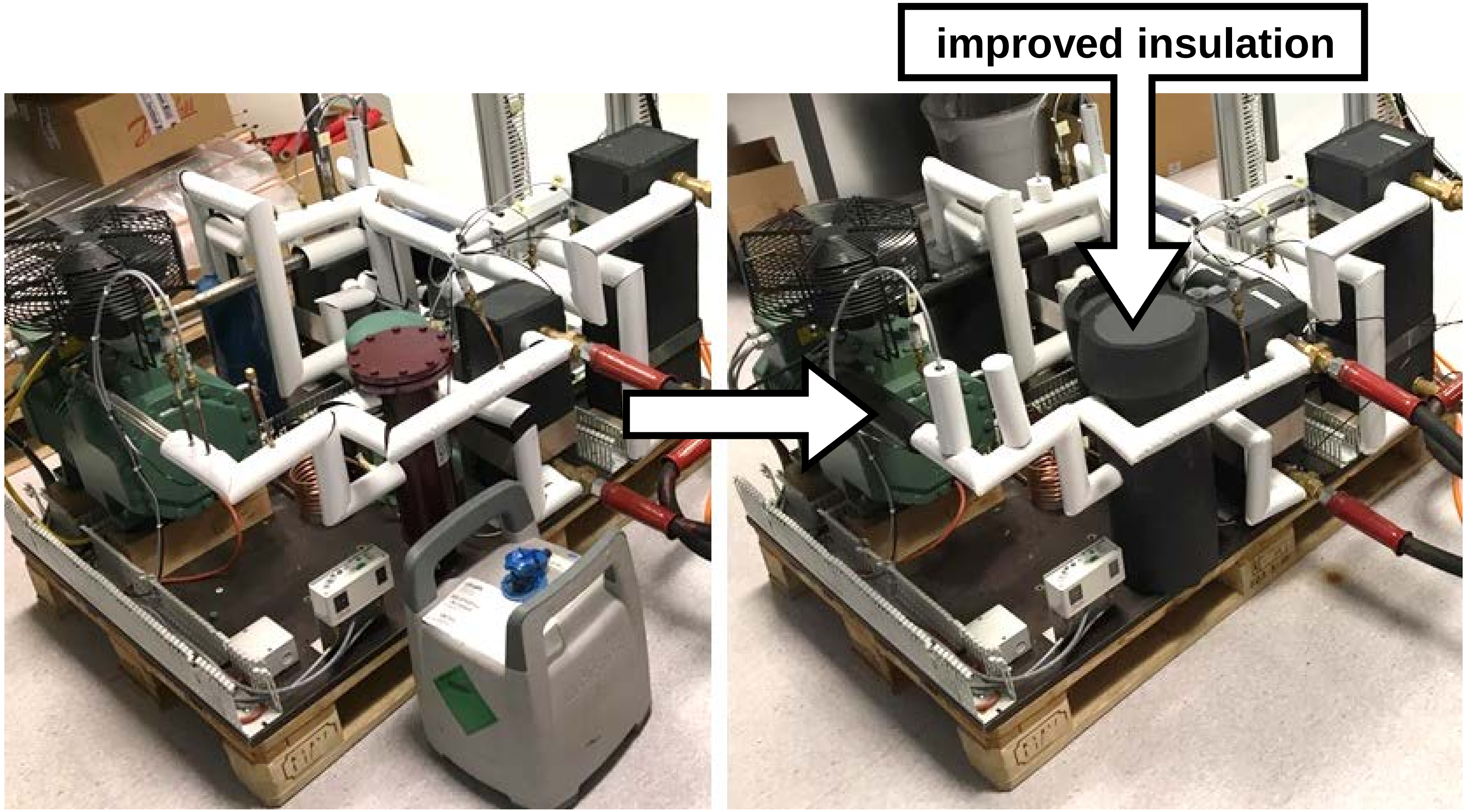


cordin.arpagaus@ntb.ch

Experimental results with R1336mzz(Z), R1233zd(E) and R1224yd(Z)

cordin.arpagaus@ntb.ch

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

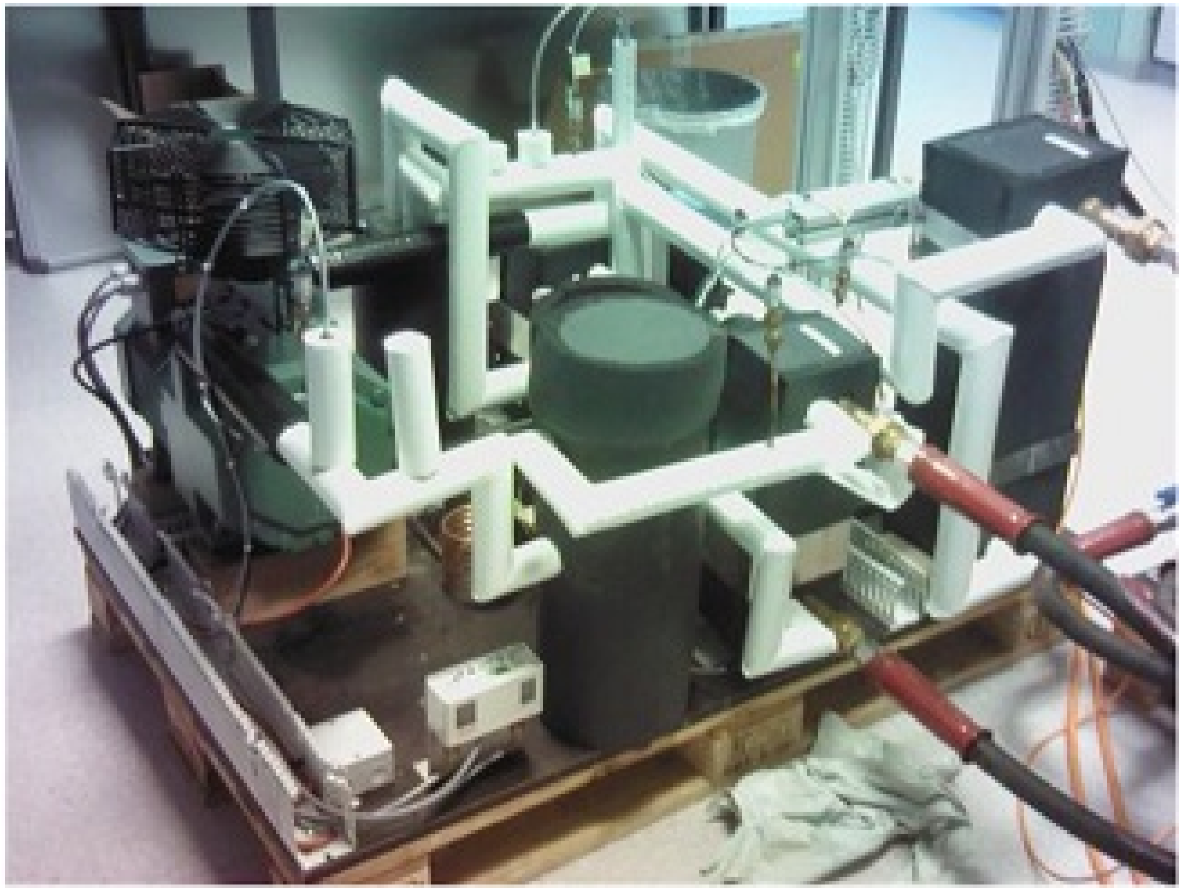
$T_{Source,in}$ / $T_{Sink,out}$ (ΔT_{Lift})	COP (before[1])	COP (after[2])	Δ
40/90 (50)	2.58	3.14	+22%
60/110 (50)	2.78	3.09	+11%
80/130 (50)	2.67	3.10	+16%

(1-stage cycle with 100% IHX)

cordin.arpagaus@ntb.ch

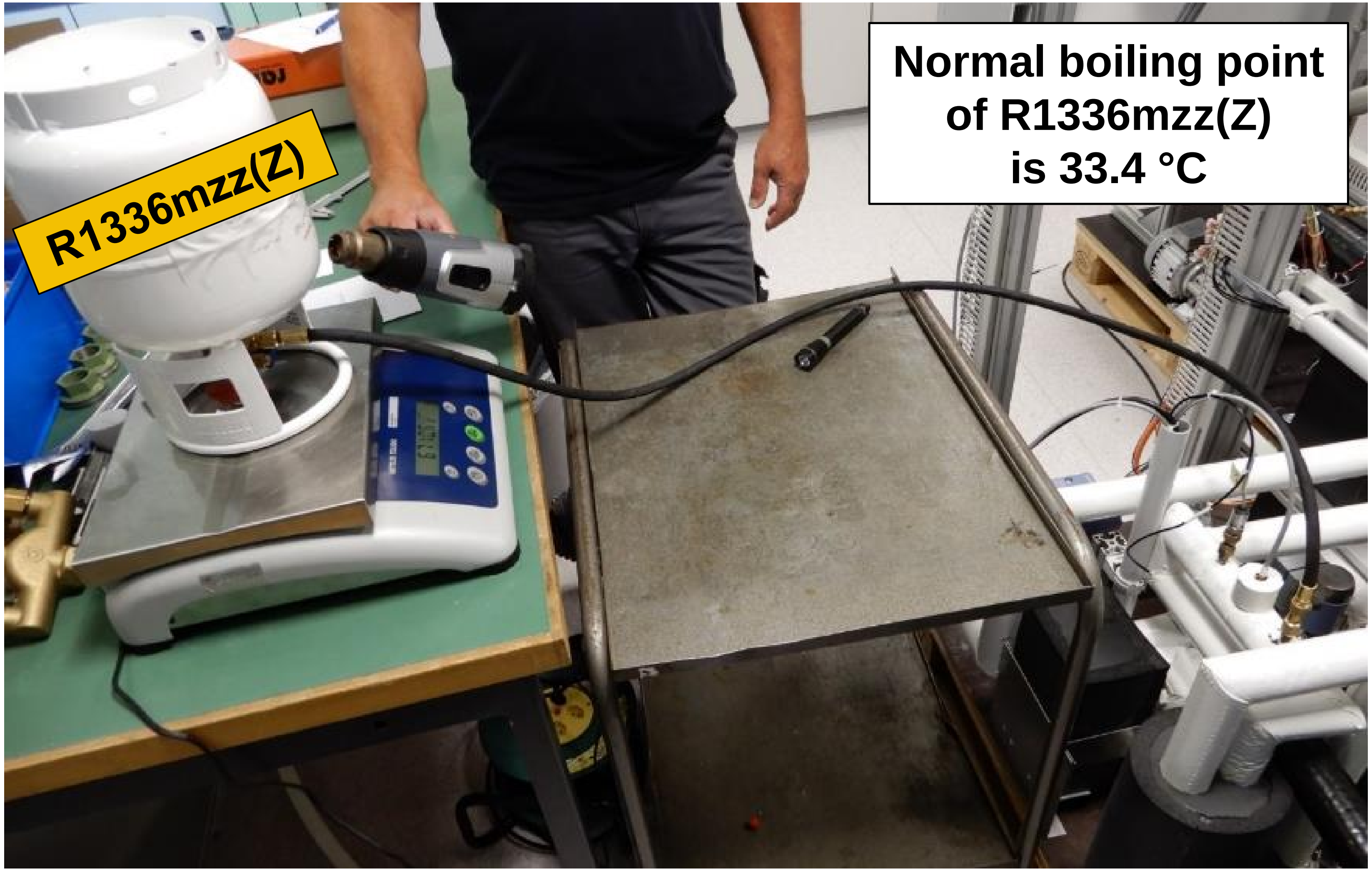
Experimental results – influence of insulation

Infrared camera image for hot spot identification

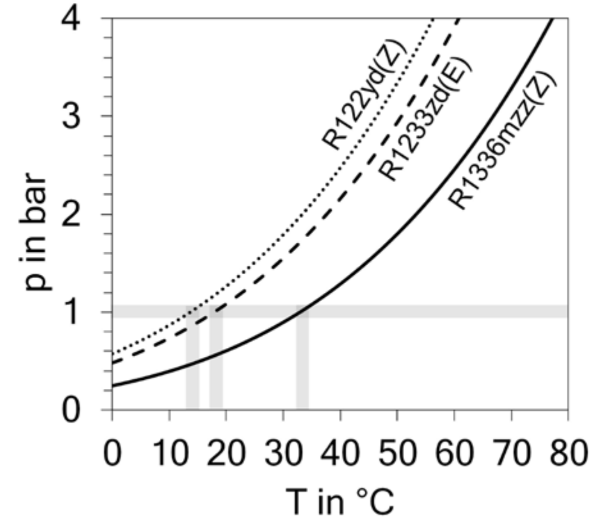


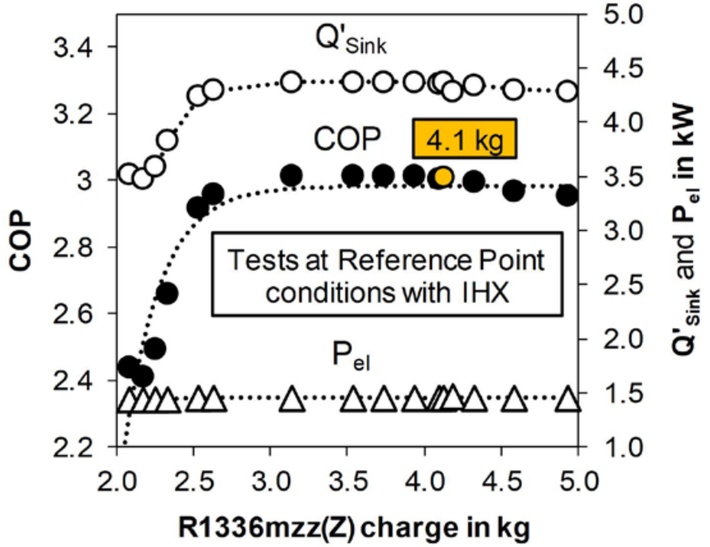
- Heat losses of about 21 ± 7 % estimated from energy balance (major heat losses at the compressor)
- There is still potential for optimization in insulation and possibilities for increasing efficiency

Refrigerant filling procedure with heating-up of the refrigerant cylinder



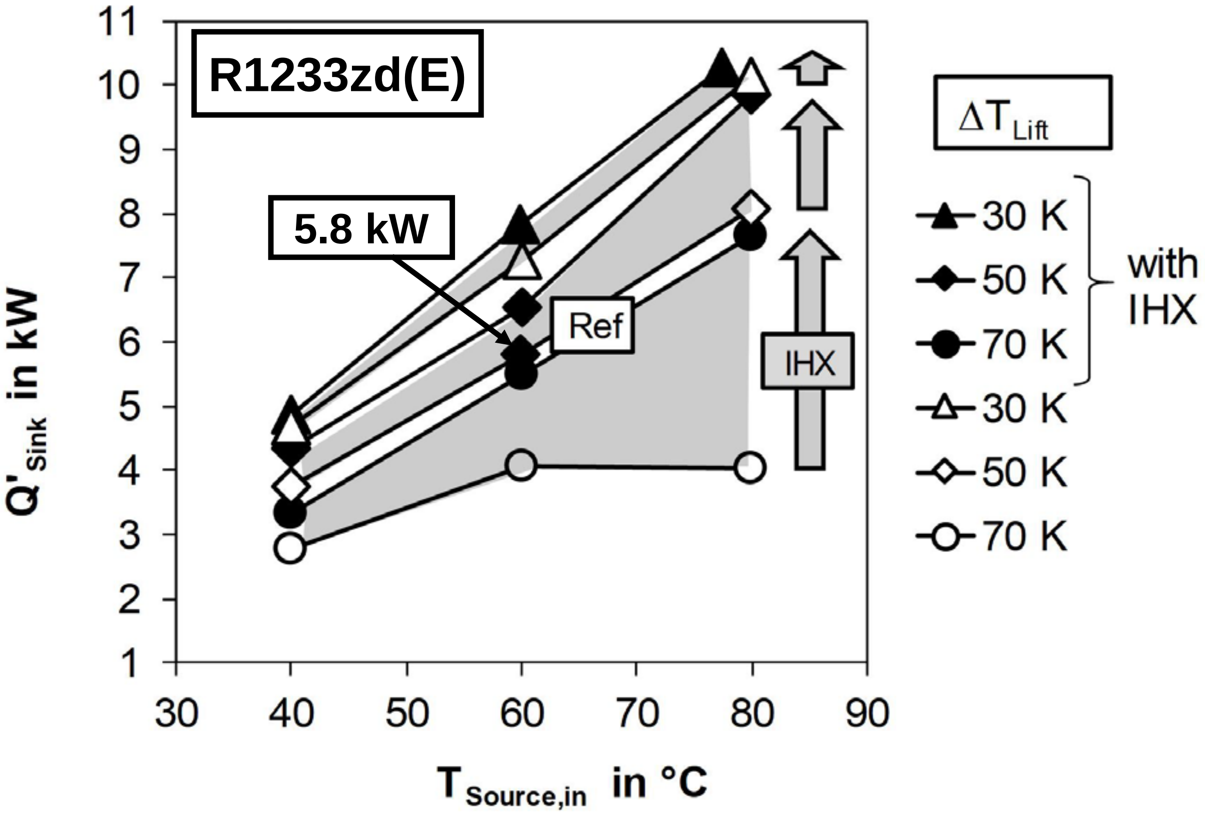
Normal boiling point of R1336mzz(Z) is 33.4 °C

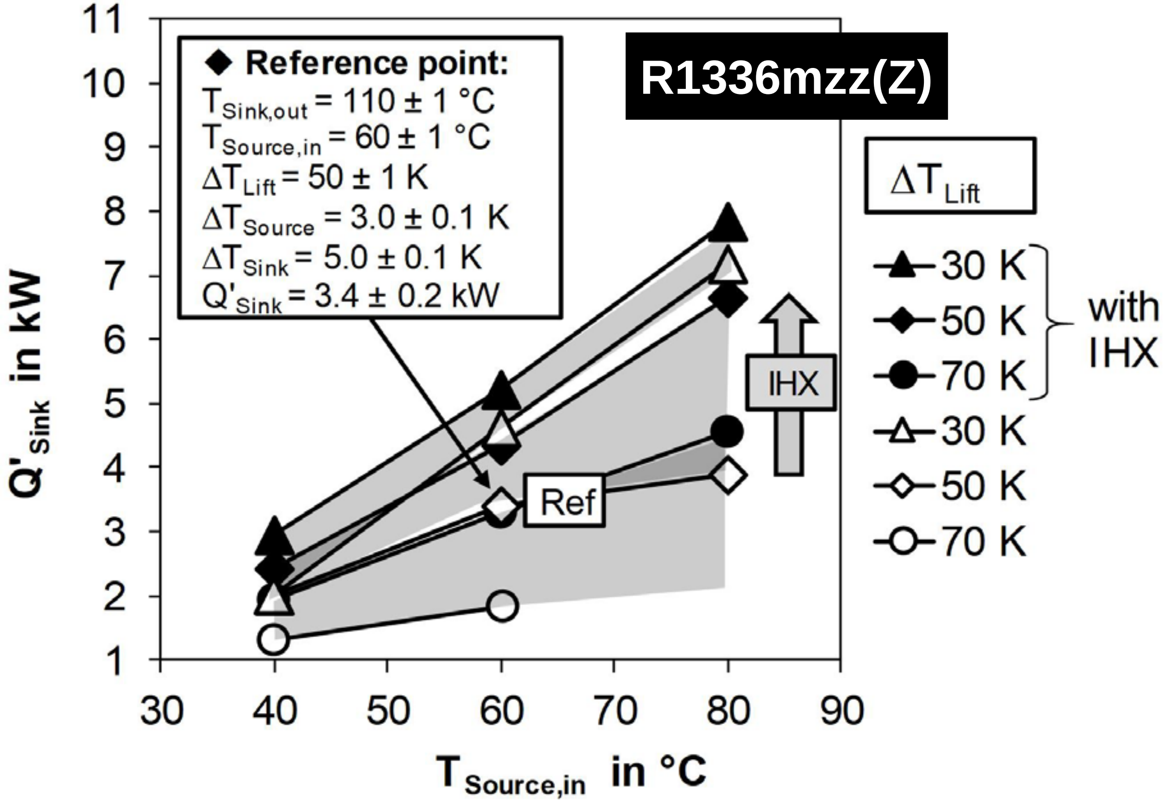




cordin.arpagaus@ntb.ch

Comparison of heating capacity with the basic and IHX cycle



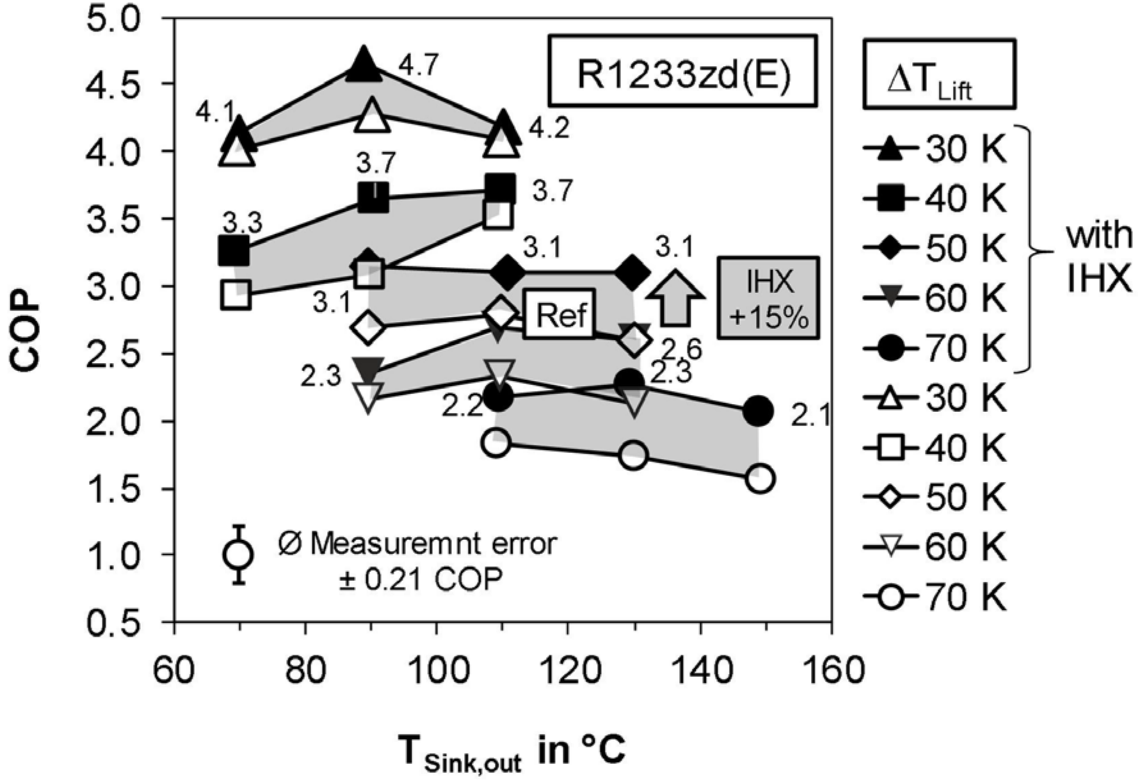


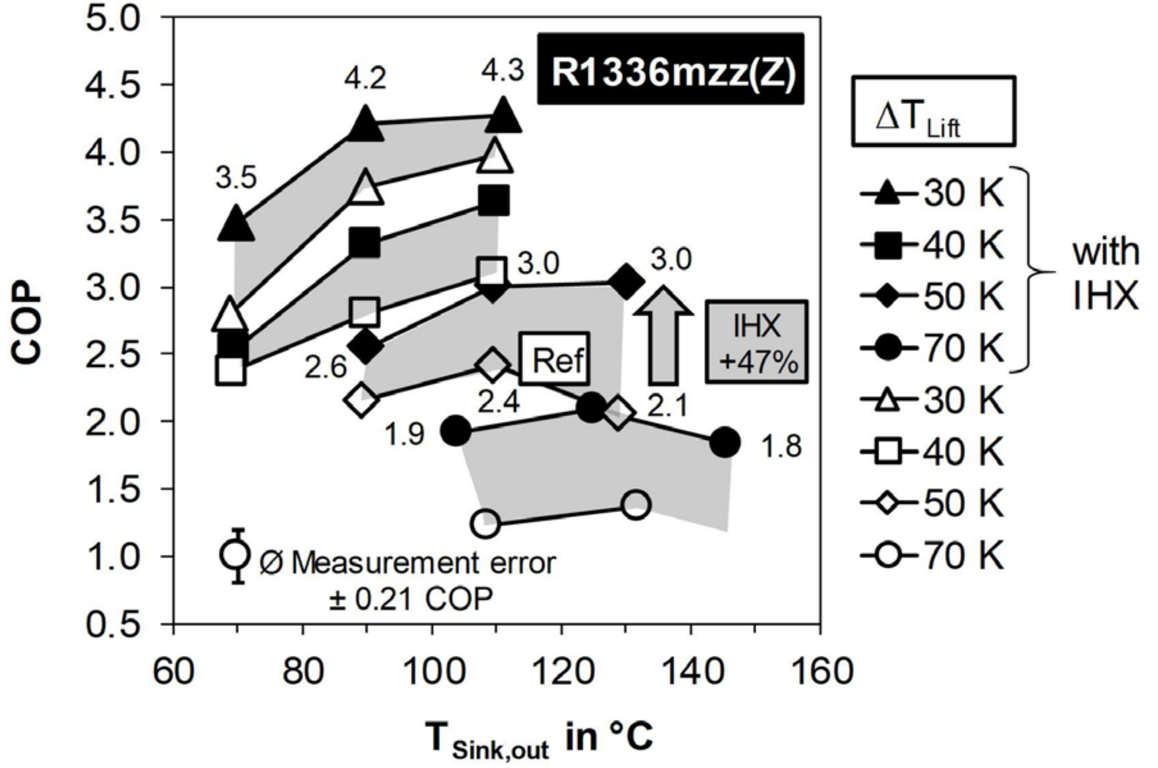
◆ **Reference point:**
$T_{Sink,out}$ = 110 ± 1 °C
$T_{Source,in}$ = 60 ± 1 °C
ΔT_{Lift} = 50 ± 1 K
ΔT_{Source} = 3.0 ± 0.1 K
ΔT_{Sink} = 5.0 ± 0.1 K
Q'_{Sink} = 3.4 ± 0.2 kW

- 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 swept volume to achieve similar heating capacities

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





- As expected, COP increase with smaller ΔT_{Lift} and higher $T_{Sink,out}$ according to Carnot relationship
- 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)

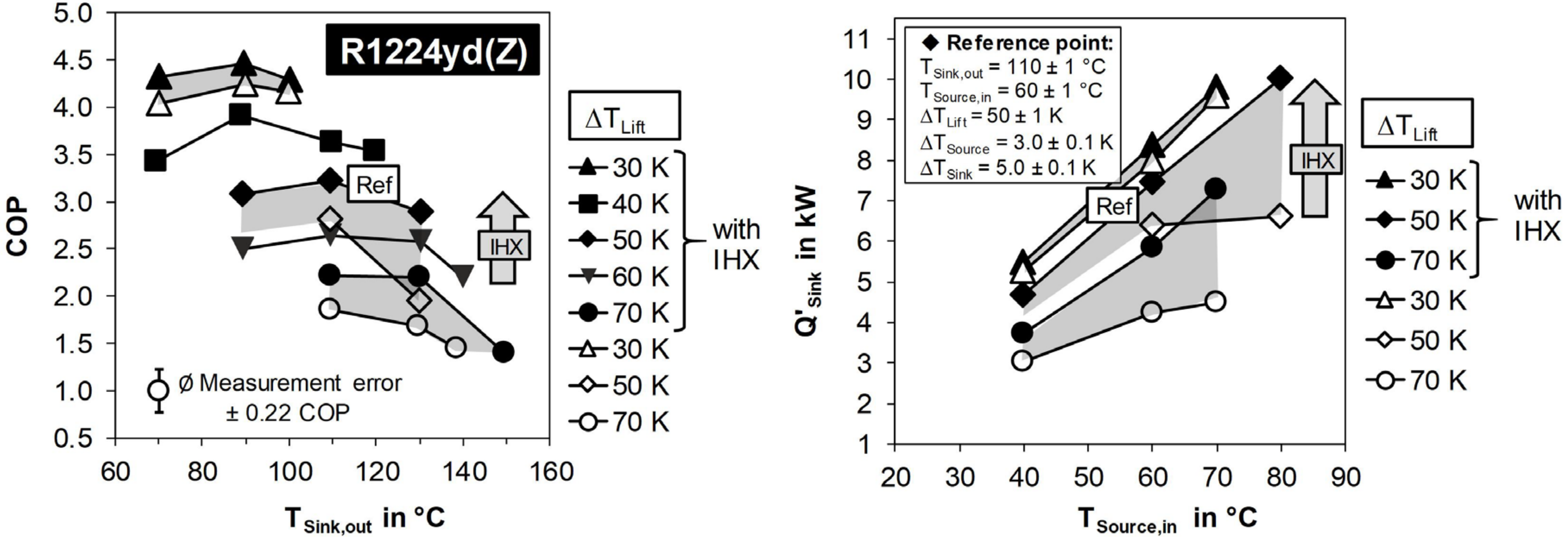
cordin.arpagaus@ntb.ch

Experimental results – R1224yd(Z)

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

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

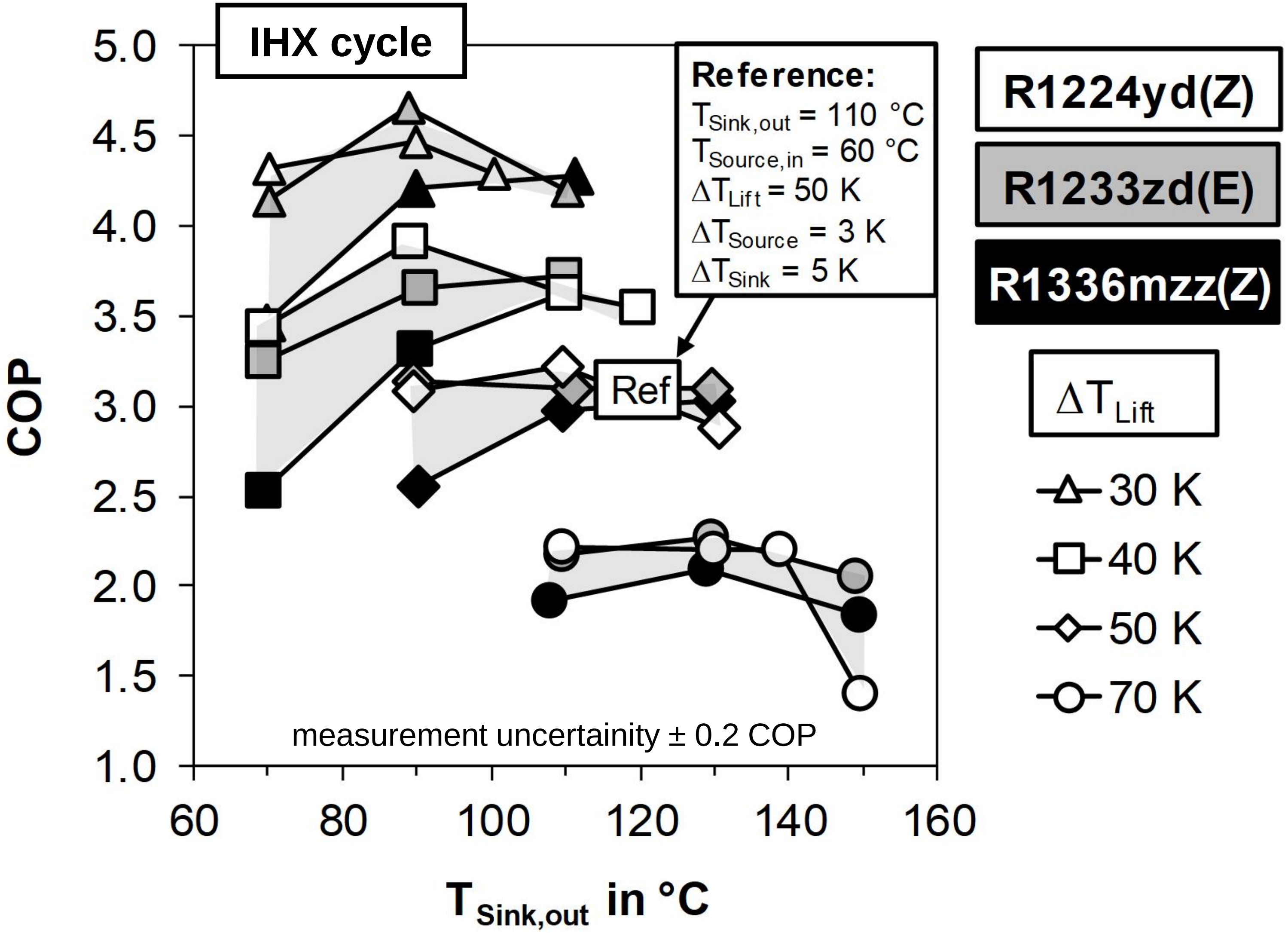


- IHX increases the COP about 14% compared to a basic cycle at Ref conditions
- COP of 3.2 reached at W60/W110 (50 K temperature lift, with IHX)
- 10 kW heating capacity reached at W80/W130 with IHX cycle

cordin.arpagaus@ntb.ch

Experimental results – R1336mzz(Z), R1233zd(E) and R1224yd(Z)

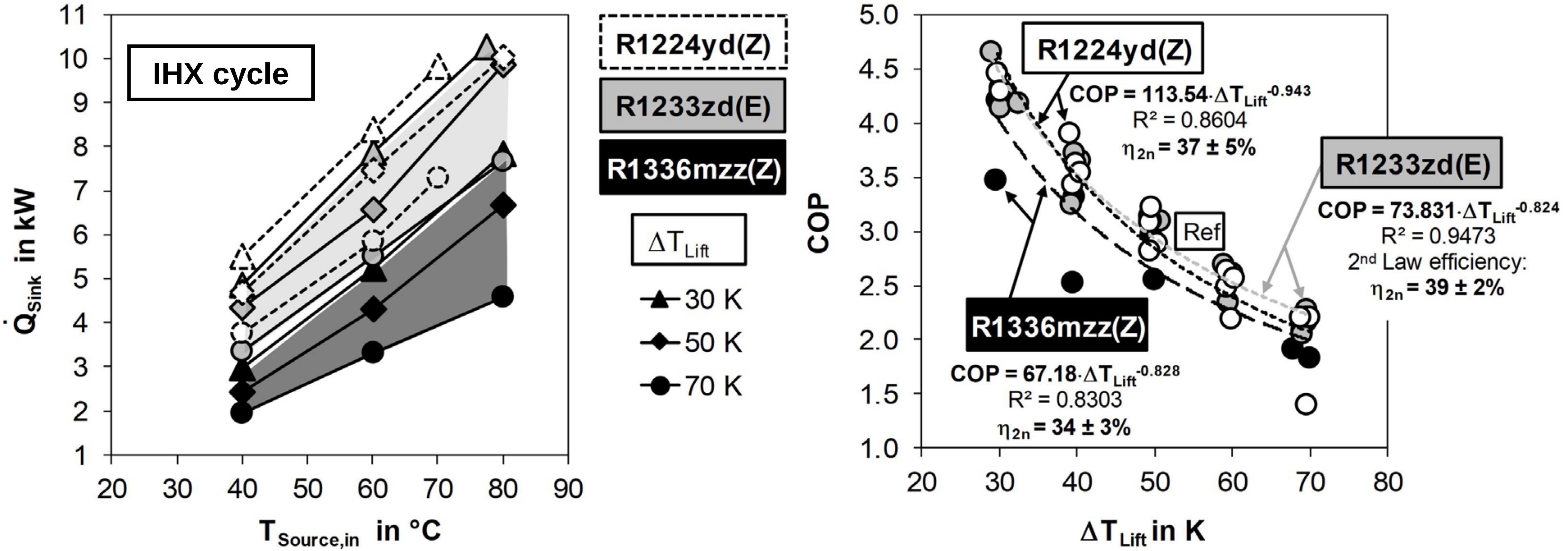
Comparison of efficiency maps



- R1233zd(E) and R1224yd(Z) provide 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)
- R1224yd(Z) efficiency drops at 150 °C (close to the critical temperature of 155.5°C)

cordin.arpagaus@ntb.ch

Comparison of heating capacity and COP fit curves with 2nd Law efficiencies

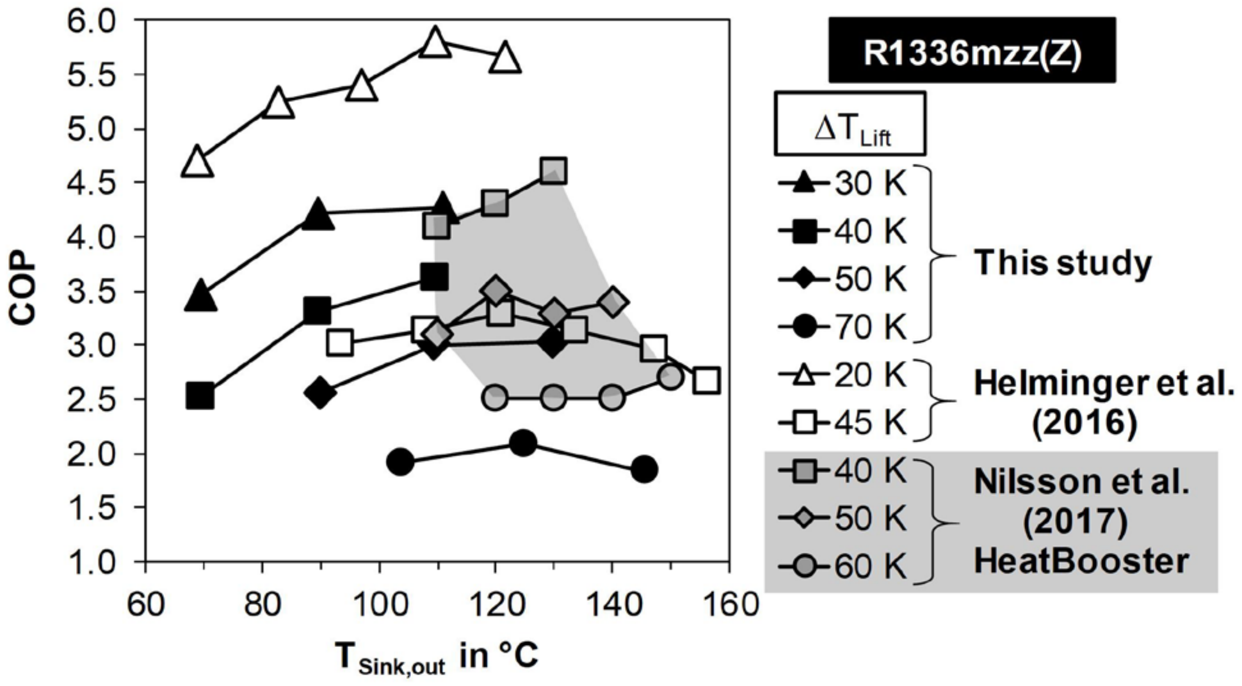


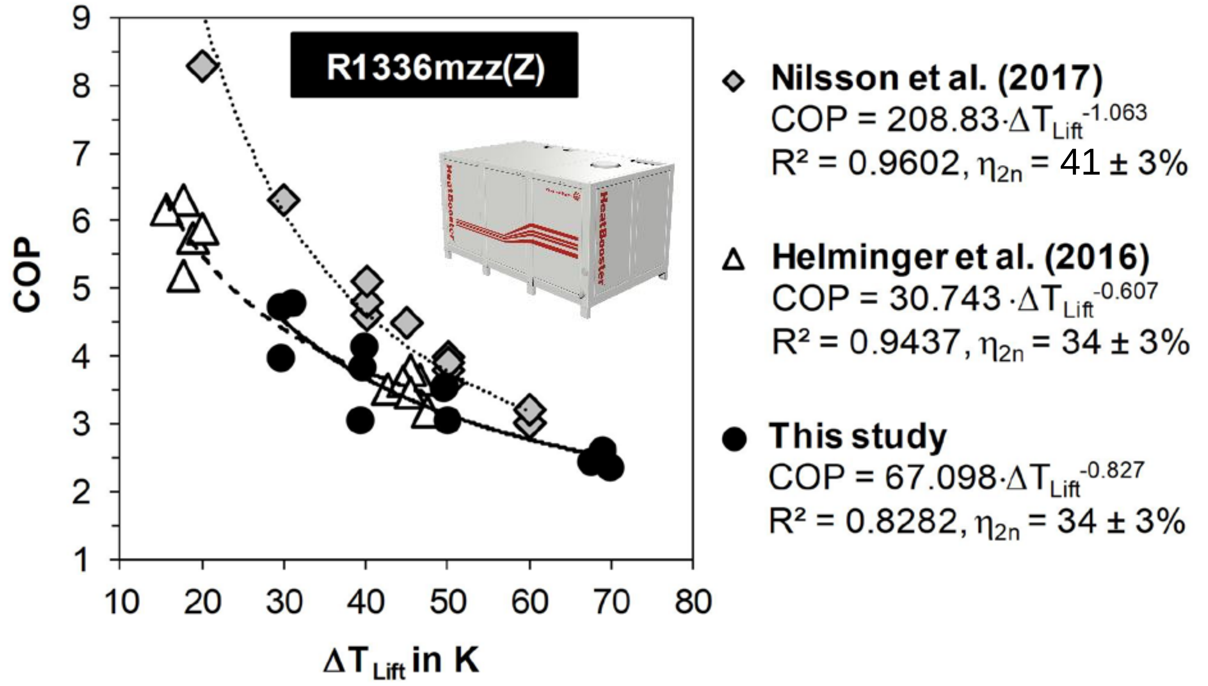
- R1233zd(E): heating capacity of 5.8 kW at Ref and approx. 10 kW at W80/W110
- R1336mzz(Z): maximum heating capacity of 7.8 kW at W80/W111
- R1224yd(Z): heating capacity on average 9% higher than R1233zd(E)

cordin.arpagaus@ntb.ch

Experimental results – R1336mzz(Z)

Comparison of COP data from Helminger et al. (2016) and Nilsson et al. (2017)

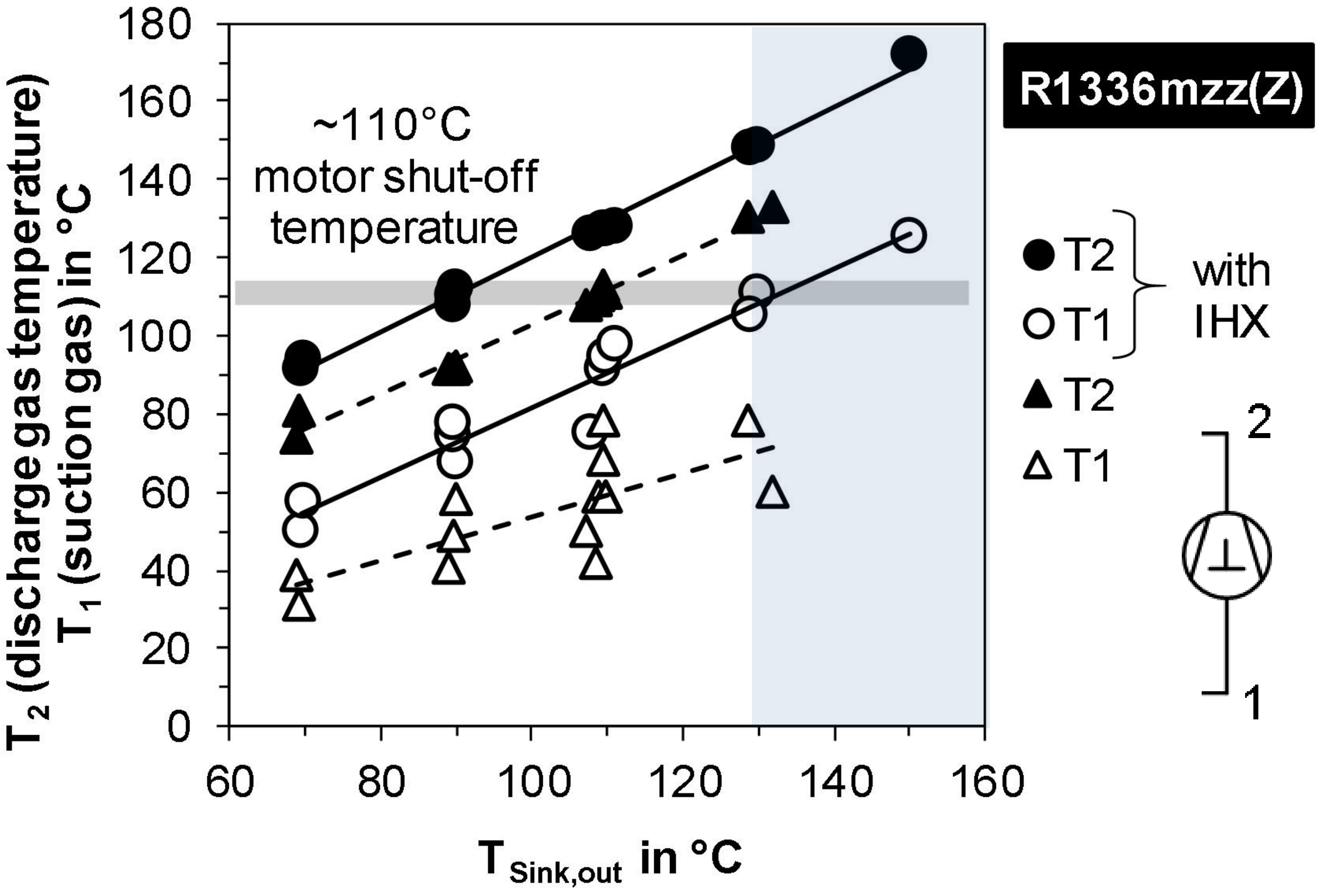




- Helminger et al. (2016):
  - 156.3°C and COP of almost 2.7 at 45 K ΔT_{Lift}
  - 2nd Law efficiency of 34 ± 3% similar to this study
- Nilsson et al. (2017):
  - Commercial HeatBooster technology achieves higher COP and 2nd Law efficiency of 41 ± 3 %
  - COP of 2.5 at 60 K ΔT_{lift}
  - With larger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

cordin.arpagaus@ntb.ch

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



Basic cycle:

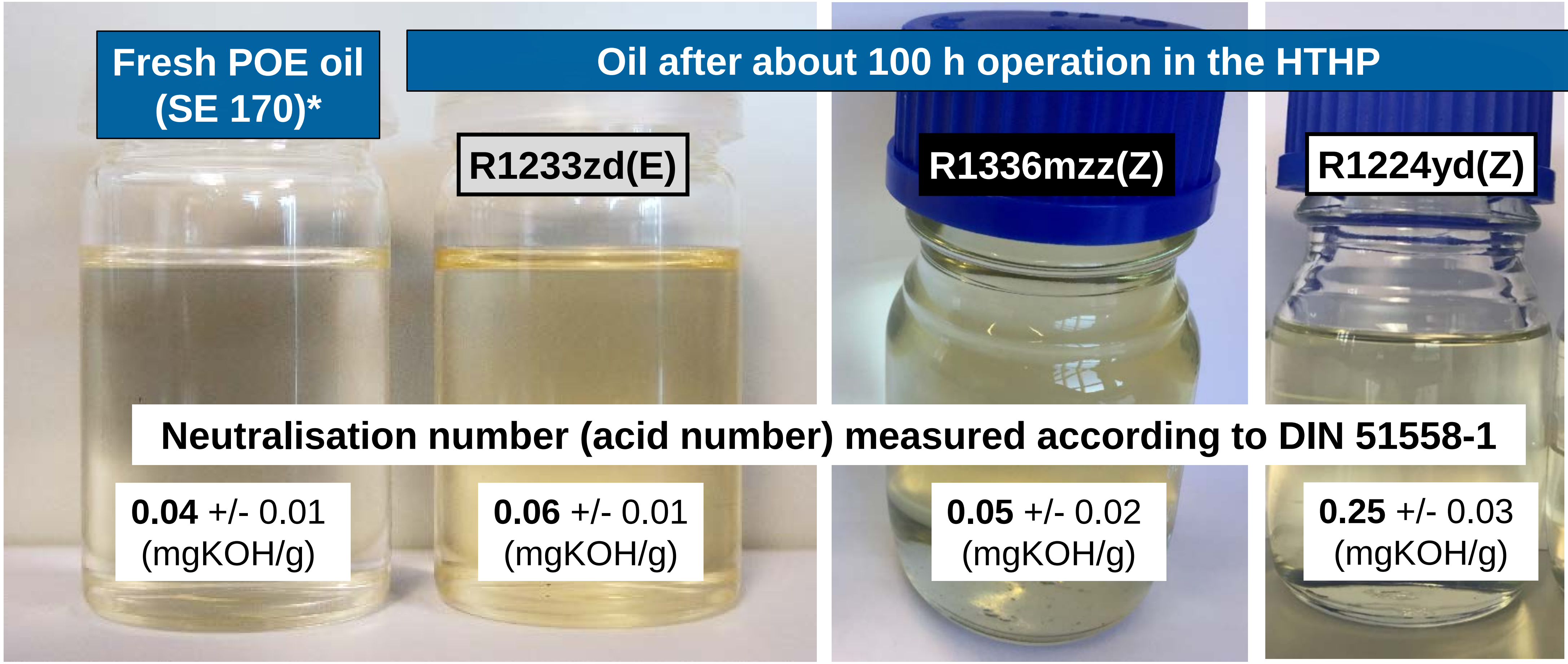
- Suction temperature (Δ T1) well below the motor shut-off temperature of approx. 110 °C (grey line)

Cycle with IHX:

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

Oil degradation measurement - neutralization number (acid number)

Negligible oil degradation after about 100 h operation in the HTHP



Fresh POE oil (SE 170)*	Oil after about 100 h operation in the HTHP		
	R1233zd(E)	**R1336mzz(Z)**	**R1224yd(Z)**
0.04 +/- 0.01 (mgKOH/g)	**0.06** +/- 0.01 (mgKOH/g)	**0.05** +/- 0.02 (mgKOH/g)	**0.25** +/- 0.03 (mgKOH/g)

Neutralisation number (acid number) measured according to DIN 51558-1

< 0.5 warning value

* 0.03 mgKOH/g according to product information from FUCHS

RENISO TRITON SE 170 – synthetic oil based on polyolester (POE) suitable for HFO refrigerants (complete miscibility with R1233zd(E) and R1336mzz(Z) between +100°C and -40°C)

Conclusions

- **R1336mzz(Z), R1233zd(E) and R1224yd(Z) successfully tested in single -stage lab-scale HTHP with IHX cycle and up to 10 kW**
- **Operation of demonstrated** at **30 to 80°C heat source** and **70 to 150°C heat sink temperatures** (30 to 70 K temperature lifts) for possible application of **waste heat recovery, steam generation or drying**
- At **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) slightly higher COP than R1336mzz(Z)** due to higher heating capacities and lower relative heat losses at the same temperature conditions
- **At 150 °C R1233zd(E) and R1336mzz(Z) more efficient** than R1224yd(Z) due to higher critical tempeatures
- **Integration of an IHX increased COP** (+15 to 47%) and heating capacity **significantly**
- **Negligible oil degradation after about 100 h operation in HTHP** (acid numbers < 0.5 mgKOH/g level)
- **Very low GWP, non-flammability, and negligible environmental impact** (low TFA formation during atmospheric degradation) indicate a **high potential for future use as refrigerant in HTHP** applications and retrofit systems

cordin.arpagaus@ntb.ch

Thanks

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.

Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Swiss Confederation

Innosuisse – Swiss Innovation Agency

SCCER eip
EFFICIENCY OF
INDUSTRIAL PROCESSES

cordin.arpagaus@ntb.ch

Thank you for your attention

Dr. Cordin Arpagaus

NTB University of Applied Sciences
of Technology Buchs
Institute for Energy Systems IES

cordin.arpagaus@ntb.ch
Tel. +41 81 377 94 34
www.ntb.ch/en/team/cordin-arpagaus

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

2nd Conference on High Temperature Heat Pumps (HTHP)
Copenhagen, Denmark
September 9, 2019

IES INSTITUTE FOR
ENERGY SYSTEMS