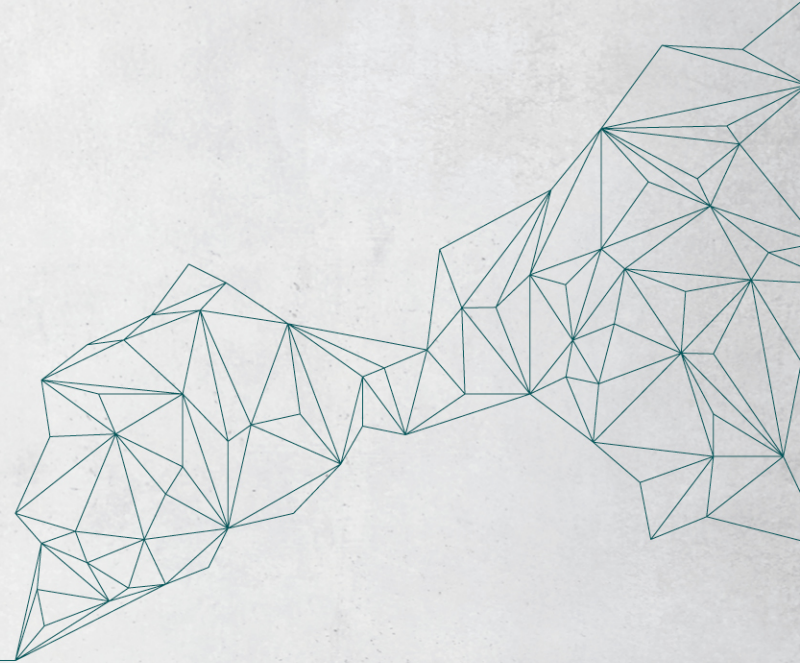


# Chillventa CONGRESS 2018

**CONNECTING  
EXPERTS.**





SCCER

EFFICIENCY OF  
INDUSTRIAL PROCESSES

# High Temperature Heat Pumps

- 1) **Market & Research Status, Refrigerants, Application Potentials**
- 2) **Results with a laboratory-scale heat pump using HCFO R1233zd**

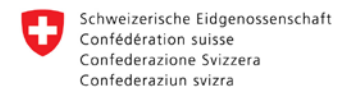
Cordin Arpagaus<sup>1</sup>, Frédéric Bless<sup>1</sup>, Michael Uhlmann<sup>1</sup>,  
Elias Büchel<sup>1</sup>, Stefan Frei<sup>1</sup>, Jürg Schiffmann<sup>2</sup>, Stefan S. Bertsch<sup>1</sup>

<sup>1</sup> NTB University of Applied Sciences of Technology Buchs, Switzerland

<sup>2</sup> Ecole Polytechnique Fédérale de Lausanne, Switzerland



In cooperation with the CTI



Swiss Confederation

Commission for Technology and Innovation CTI

# Outline

- 1) **Market overview** (application potentials, industrial processes, commercial products, operating ranges, efficiencies)
- 2) **Research status** (heat pump cycles, efficiency, temperature lifts)
- 3) **Refrigerants** (selection criteria, properties)
- 4) **Simulation results** of a one-stage heat pump cycle comparing different HFO and HFCO refrigerants
- 5) **Experimental test results** of a laboratory-scale high temperature heat pump using R1233zd(E) refrigerant
- 6) **Conclusions**



# SCCER Project (Swiss Competence Center of Energy Research)

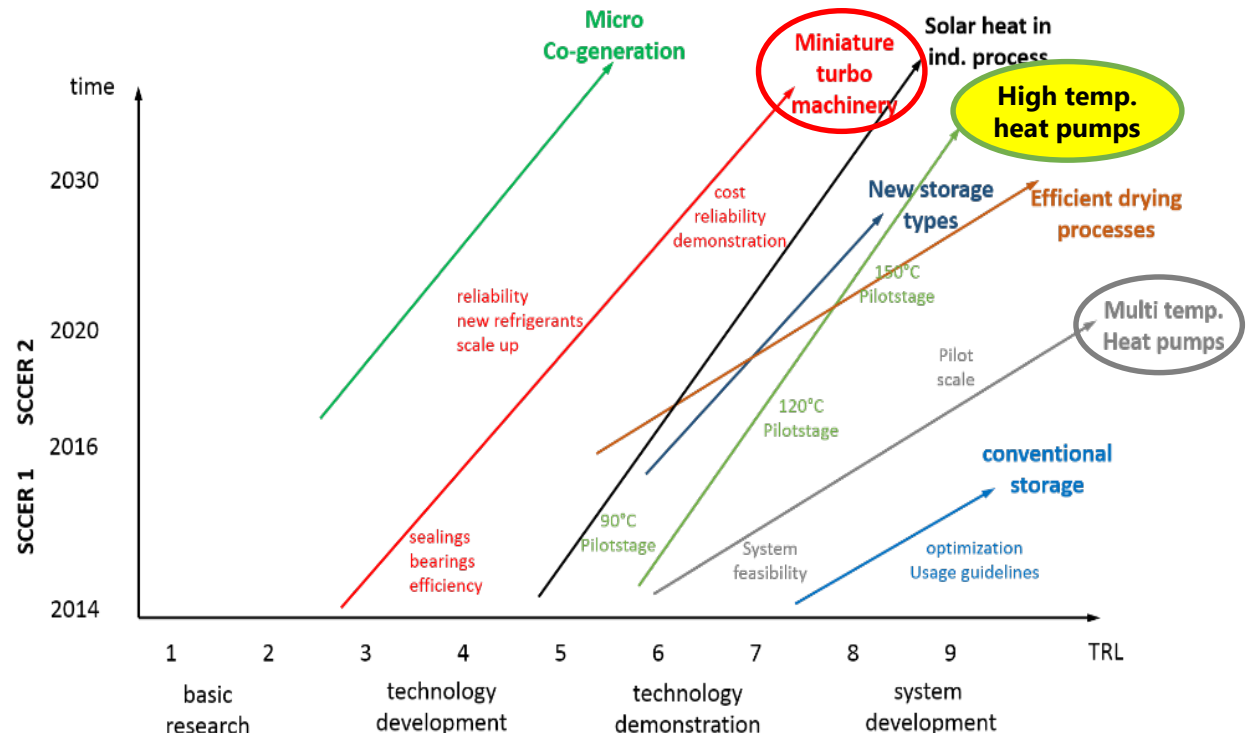
## SCCER EIP (Efficiency of Industrial Processes)



### Work Package 2:

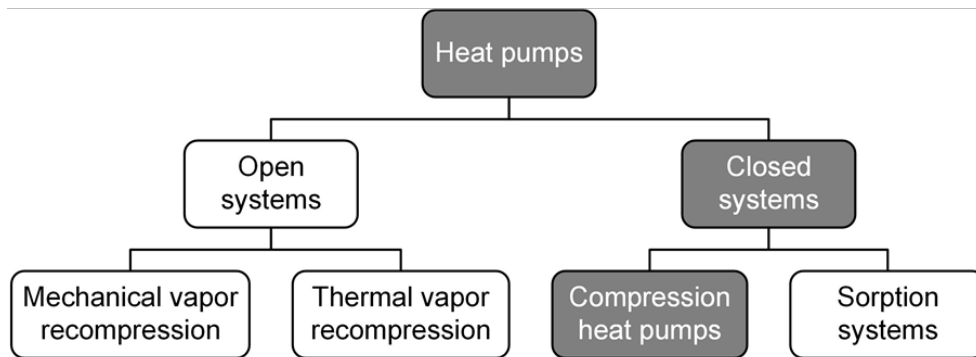
### Energy Efficiency (direkt)

- Goal: Development of highly efficient system solutions and technologies (e.g. cycle processes and heat pumps)



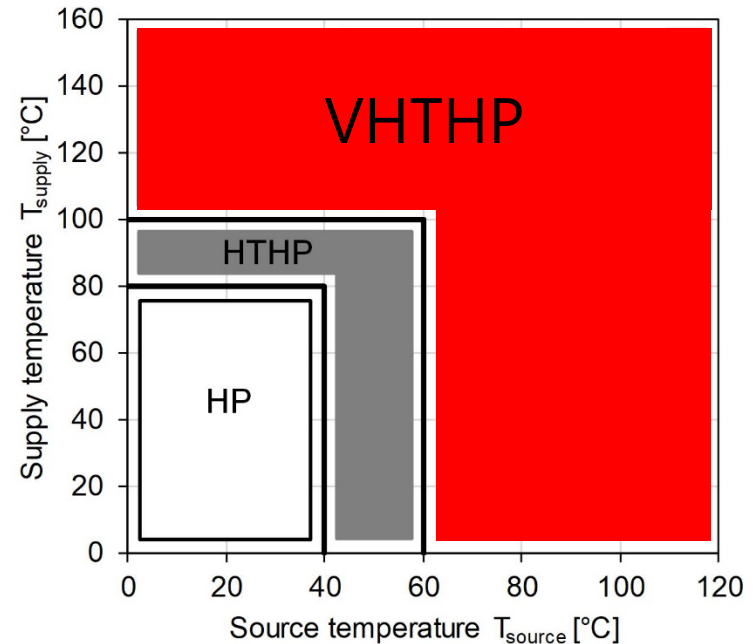
# Classification of High Temperature Heat Pumps (HTHPs)

## Focus on vapor compression heat pumps



adapted from Nellissen und Wolf (2015)

## Development of temperature levels



HP: conventional heat pump

HTHP: high temperature heat pump

**VHTHP: very high temperature heat pump**

adapted from Bobelin et al. (2012), IEA (2014), Jakobs und Laue (2015), Peureux et al. (2012, 2014)



# HTHPs with heat sink temperatures of 100 to 150°C are suitable systems for heat recovery in various industrial processes

Drying

Sterilization

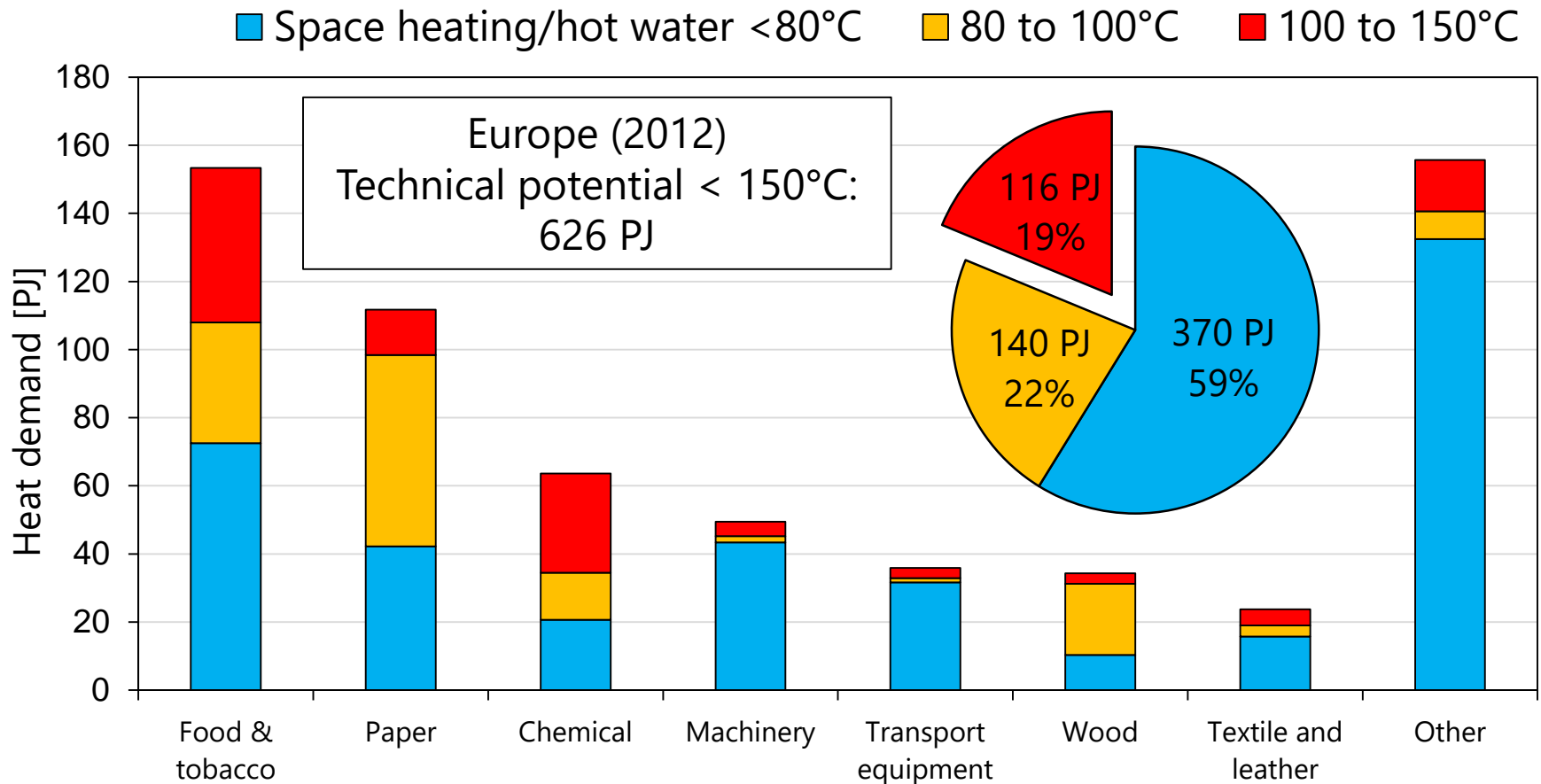
Steam generation

Papermaking

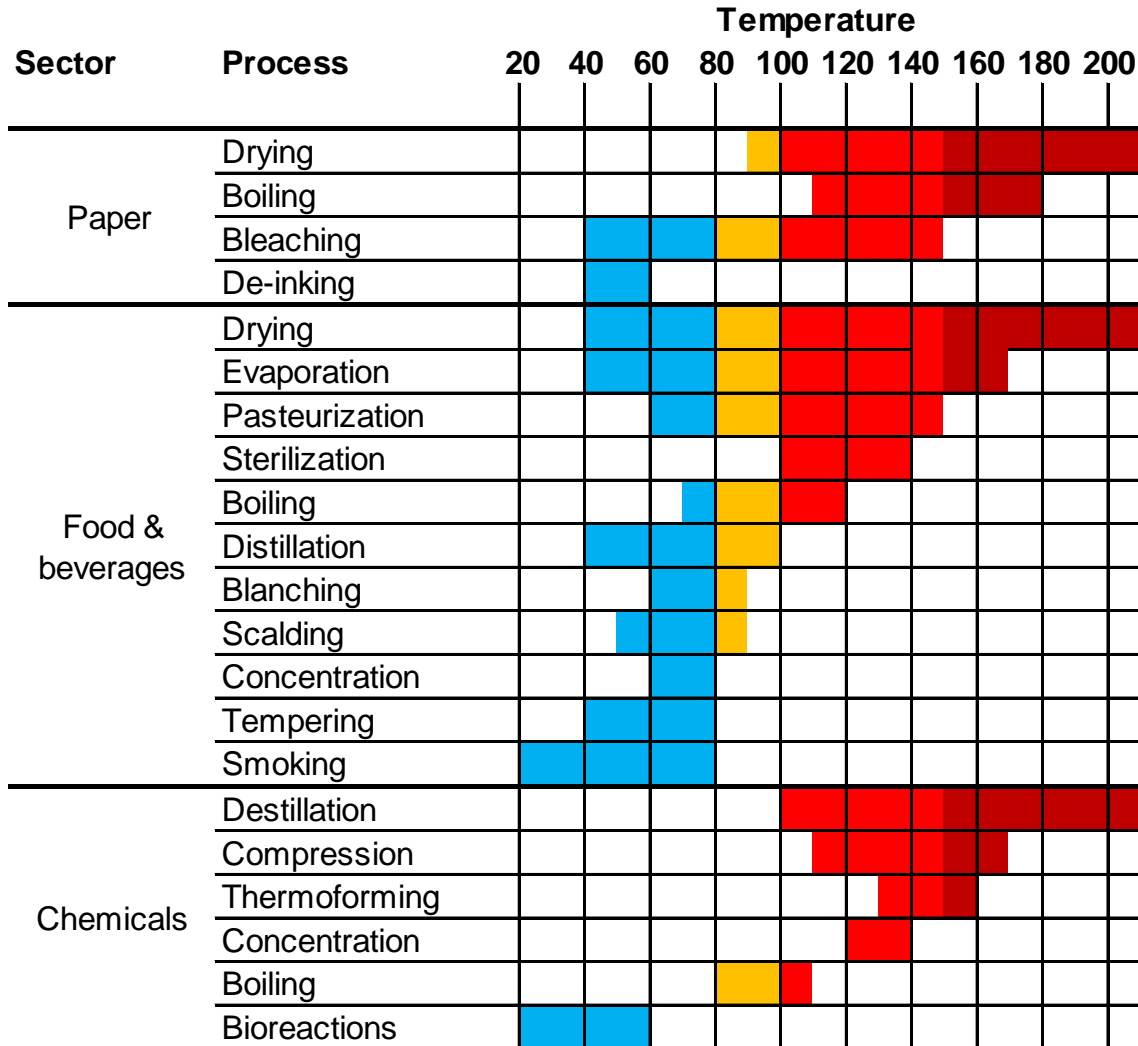
Food preparation



# Technical market potential of process heat in Europe – accessible with industrial heat pumps distributed by temperature and industrial sector



# Temperature levels of industrial processes & Heat Pump Technology Readiness







# Example of an industrial high temperature heat pump

**OCHSNER**  
ENERGIE TECHNIK

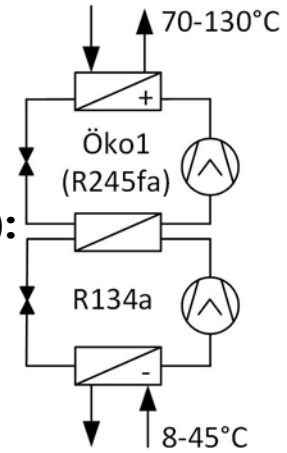


## IWWDS ER3b (1-stage):

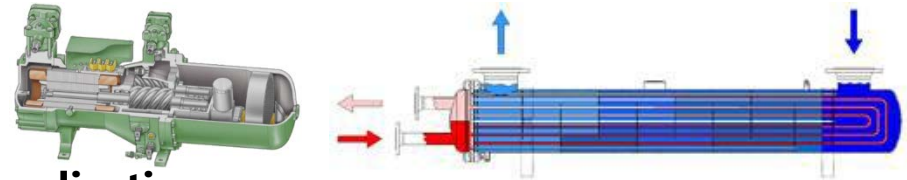
- 35 to 55 °C → 70 to 130 °C
- R245fa, 170 to 400 kW

## IWWDS R1R3b (2-stage cascade):

- 10 to 25 °C / 95 to 130 °C
- R134a/R245fa, 90 to 530 kW

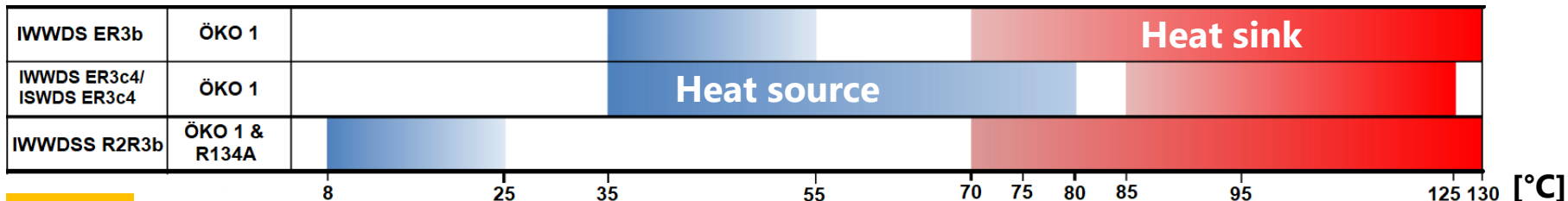


## Screw compressor & tube bundle HX



## Applications:

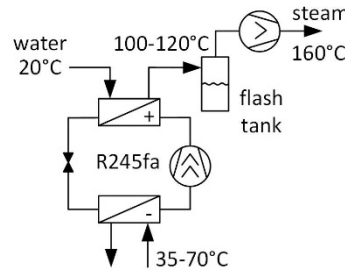
- district heating & heat recovery in industry



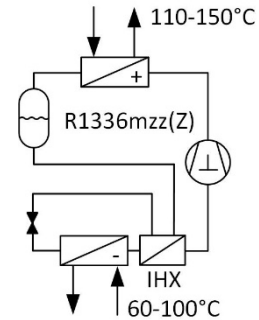
**New** IWWHS ER3b TWIN with R1233zd up to 2.4 MW

# Other examples of commercial high temperature heat pumps

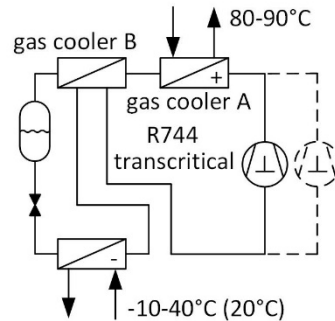
Kobelco SGH 120/165  
(Steam Grow HP)



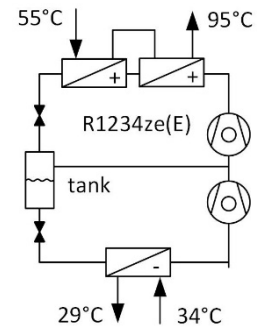
HeatBooster S4  
(Viking Heating Engines AS)



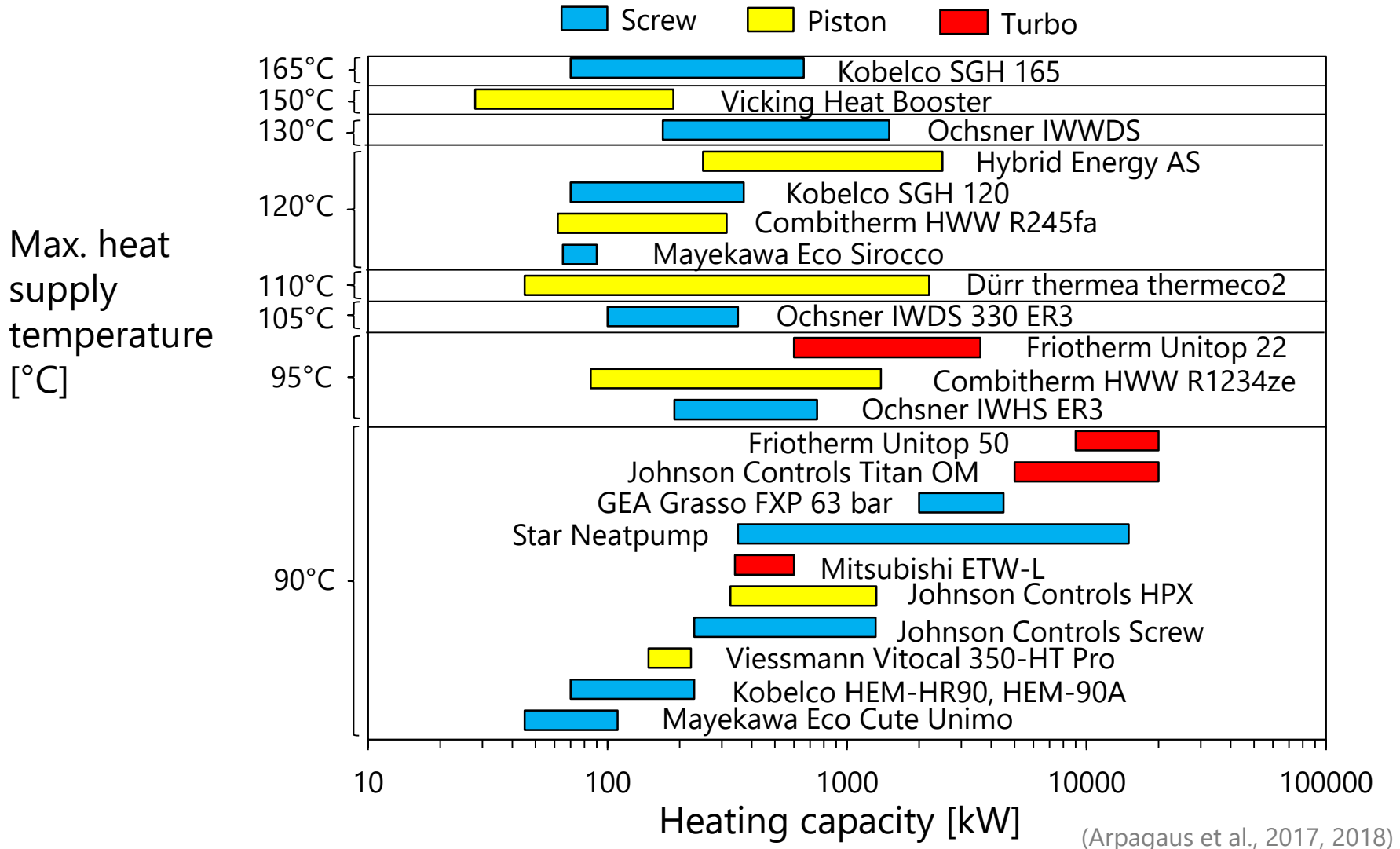
Thermeco<sub>2</sub> HHR 1000  
(Engie, ex-Hafner-Muschler,  
ex-Dürr thermea)



Unitop 22/22  
(Friotherm AG)

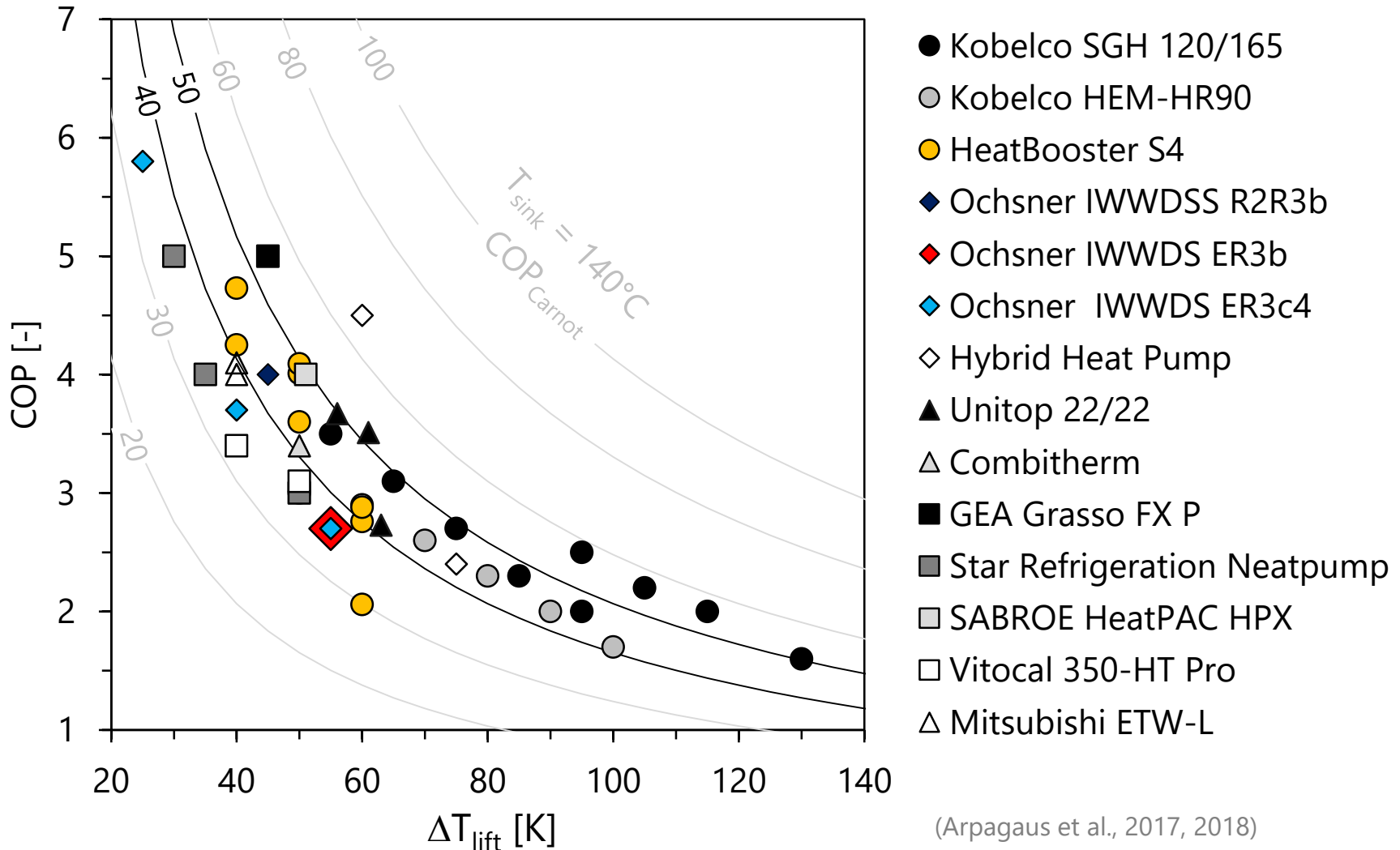


# > 20 industrial HTHPs with heat supply temperature above 90 °C exist



(Arpagaus et al., 2017, 2018)

# COP range between 1.6 to 5.8 at temperature lifts of 130 to 40 K



(Arpagaus et al., 2017, 2018)




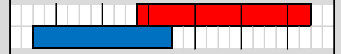





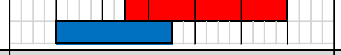

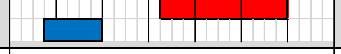



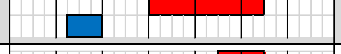

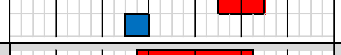



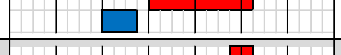

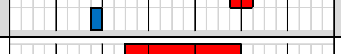

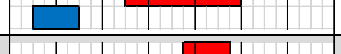



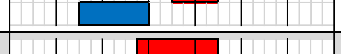






# What are the research gaps for HTHPs ?




















- 1) Pushing HTHPs from the laboratory scale **towards industry**
- 2) **Extending the limits** of heat supply temperatures to higher values
- 3) Improving heat pump **efficiency**
- 4) Testing new environmentally friendly **refrigerants**

# 17 research projects on HTHPs with heat supply temperatures > 100 °C

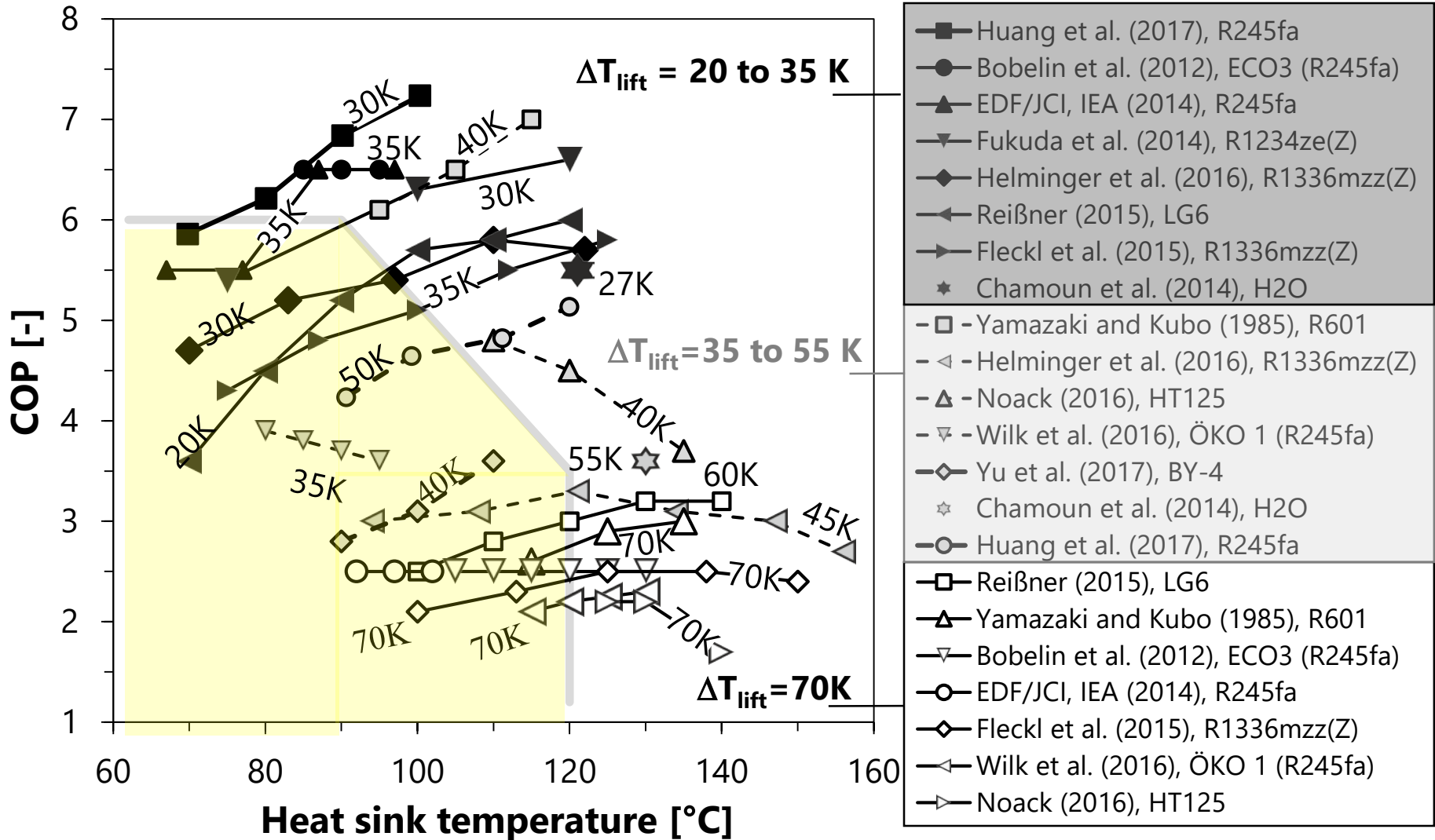
Organisation, Project partners	Country	Heat source (blue) and heat supply (red) temperatures [°C]	
		20	40 60 80 100 120 140 160
Austrian Institute of Technology, Vienna, Chemours, Bitzer, Austria			
Austrian Institute of Technology, Vienna, Chemours, Bitzer, Austria			
PACO, University Lyon, EDF Electricité de France			
Institute of Air Handling and Refrigeration, Dresden, Germany			
Friedrich-Alexander University Erlangen-Nürnberg, Siemens, Germany			
Alter ECO, EDF Electricité de France			
Tokyo Electric Power Company, Japan			
Austrian Institute of Technology, Edtmayer, Ochsner, Austria			
Tianjin University, China			
Kyushu University, Fukuoka, Japan			
ECN, SmurfitKappa, IBK, Bronswerk, The Netherlands			
Korea Institute of Energy Research, Daejeon, Korea			
GREE Electric Appliances, Zhuhai, China			
Norwegian University of Science and Technology, SINTEF, Norway			
Technical University Graz, Austria			
Tianjin University, China			
EDF Electricité de France, Johnson Controls			



# 17 research projects on HTHPs with different heating capacities

Organisation, Project partners	Country	Heat source (blue) and heat supply (red) temperatures [°C]						Cycle type	Compressor	Refrigerant	Heating capacity [kW]	References
		20	40	60	80	100	120					
Austrian Institute of Technology, Vienna, Chemours, Bitzer, Austria											12	Helminger et al. (2016)
Austrian Institute of Technology, Vienna, Chemours, Bitzer, Austria											12	Fleckl et al. (2015)
PACO, University Lyon, EDF Electricité de France											300	Chamoun et al. (2014, 2013, 2012)
Institute of Air Handling and Refrigeration, Dresden, Germany											12	Noack (2016)
Friedrich-Alexander University Erlangen-Nürnberg, Siemens, Germany											10	Reißner (2015), Reißner et al. (2013)
Alter ECO, EDF Electricité de France											50-200	Bobelin et al. (2012), IEA (2014)
Tokyo Electric Power Company, Japan											150-400	Yamazaki and Kubo (1985)
Austrian Institute of Technology, Edtmayer, Ochsner, Austria											250-400	Wilk et al. (2016)
Tianjin University, China											16-19	Zhang et al. (2017)
Kyushu University, Fukuoka, Japan											1.8	Fukuda et al. (2014)
ECN, SmurfitKappa, IBK, Bronswerk, The Netherlands											160	Wemmers et al. (2017)
Korea Institute of Energy Research, Daejeon, Korea											20-40	Lee et al. (2017)
GREE Electric Appliances, Zhuhai, China											6-12	Huang et al. (2017)
Norwegian University of Science and Technology, SINTEF, Norway											20-30	Bamigbetan et al. (2017)
Technical University Graz, Austria											20-40	Moisi et al. (2017)
Tianjin University, China											44-141	Yu et al. (2014)
EDF Electricité de France, Johnson Controls											300-500 900-1'200	Assaf et al. (2010), IEA (2012, 2014), Peureux et al. (2014)

# R&D projects push COPs and heat supply temperatures to higher levels





# What would be the perfect refrigerant?

Criteria	Required properties
<b>Thermal suitability</b>	High critical temperature ( $> 150^{\circ}\text{C}$ ), low critical pressure ( $< 30$ bar)
<b>Environmental</b>	ODP = 0, low GWP, short atmospheric life
<b>Safety</b>	Non-toxic, no or only low flammability
<b>Efficiency</b>	High COP, low pressure ratio, minimal overheat to prevent fluid compression, high volumetric heating capacity
<b>Availability</b>	Available on the market, low price
<b>Other factors</b>	Good solubility in oil, thermal stability of the refrigerant-oil mixture, lubricating properties at high temperatures, material compatibility with steel and copper

Data sources: Bertinat (1986), Burtscher et al. (2009), Calm (2008), Eisa et al. (1986), Göktun (1995), Helminger et al. (2016), Klein (2009), Kujak (2016), Reißner et al. (2013), Rieberer et al. (2015)

# Refrigerants for HTHPs

★ Refrigerants selected  
 ☆ for investigation  
 in this study

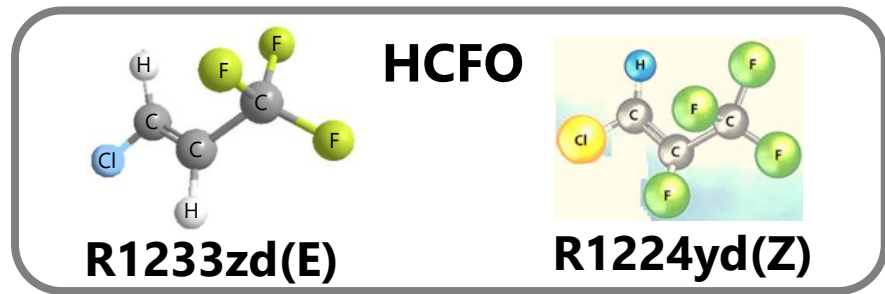
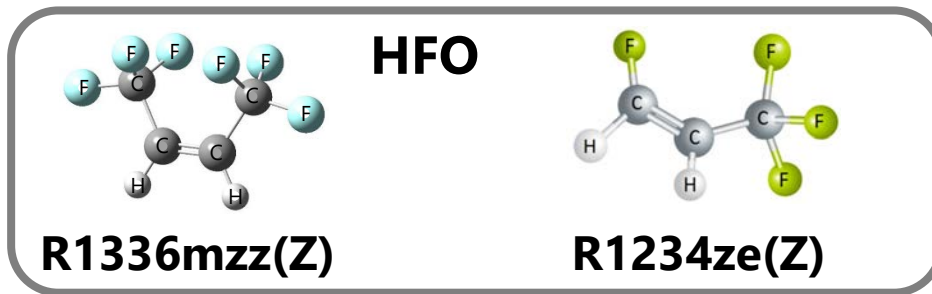


Type	Refrigerant	Description	Chemical Formula	T <sub>crit</sub> [°C]	p <sub>crit</sub> [bar]	ODP [-]	GWP [-]	SG	NBP [°C]	M [g/mol]	Relative price [-]	
CFC	R113	1,1,2-Trichloro-1,2,2-trifluoroethane	CCl <sub>2</sub> FCF <sub>2</sub>	214.0	33.9	0.85	5'820	A1	47.6	187.4	Prohibited according to Montréal Protocol	
	R114	1,2-Trichloro-1,1,2,2-tetrafluoroethane	CClF <sub>2</sub> CClF <sub>2</sub>	145.7	32.6	0.58	8'590	A1	3.8	170.9		
HCFC	R123	2,2-Dichloro-1,1,1-trifluoroethane	C <sub>2</sub> HCl <sub>2</sub> F <sub>3</sub>	183.7	36.6	0.03	79	B1	27.8	152.9		
	R21	Dichlorofluoromethane	CHCl <sub>2</sub> F	178.5	51.7	0.04	148	B1	8.9	102.9		
	R142b	1,1-Dichloro-1-fluoroethane	CH <sub>3</sub> CCl <sub>2</sub> F	137.1	40.6	0.065	782	A2	-10.0	100.5		
	R124	1-Chloro-1,2,2,2-tetrafluoroethane	C <sub>2</sub> HClF <sub>4</sub>	126.7	37.2	0.03	527	A1	-12.0	136.5		
HFC	★ R365mfc <sup>a</sup>	1,1,1,3,3-Pentafluorobutane	CF <sub>3</sub> CH <sub>2</sub> CF <sub>2</sub> CH <sub>3</sub>	186.9	32.7	0	804	A2	40.2	148.1		8.9
	★ SES36 <sup>b</sup>	R365mfc/perfluoro-polyether	R365mfc/PFPE (65/35)	177.6	28.5	0	3'126 <sup>c</sup>	A2	35.6	184.5		10.5
	R245ca	1,1,2,2,3-Pentafluoropropane	CHF <sub>2</sub> CF <sub>2</sub> CH <sub>2</sub> F	174.4	39.3	0	716	n.a	25.1	134.0		n.a.
	R245fa <sup>d</sup>	1,1,2,2,3-Pentafluoropropane	CHF <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>	154.0	36.5	0	858	B1	14.9	134.0		6.6
	R236fa	1,1,1,3,3,3-Hexafluoropropane	CF <sub>3</sub> CH <sub>2</sub> CF <sub>3</sub>	124.9	32.0	0	8'060	A1	-1.4	152.0	10.2	
	R152a	1,1-Difluoroethane	CH <sub>3</sub> CHF <sub>2</sub>	113.3	45.2	0	138	A2	-24.0	66.1	n.a.	
	R227ea	1,1,1,2,3,3,3-Heptafluoropropane	CF <sub>3</sub> CHFCF <sub>3</sub>	101.8	29.3	0	3'350	A1	-15.6	170.0	6.9	
	R134a	1,1,1,2-Tetrafluoroethane	CH <sub>2</sub> FCF <sub>3</sub>	101.1	40.6	0	1'300	A1	-26.1	102.0	1.2	
R410A	R32/R125 (50/50 mixture)	CH <sub>2</sub> F <sub>2</sub> /CHF <sub>2</sub> CF <sub>3</sub>	72.6	49.0	0	2'088	A1	-51.5	72.6	2.9		
HFO	★ R1336mzz(Z) <sup>e</sup>	1,1,1,4,4,4-Hexafluoro-2-butene	CF <sub>3</sub> CH=CHCF <sub>3</sub> (Z)	171.3	29.0	0	2	A1	33.4	164.1	n.a.	
	★ R1234ze(Z)	cis-1,3,3,3-Tetrafluoro-1-propene	CF <sub>3</sub> CH=CHF(Z)	150.1	35.3	0	<1	A2L <sup>f</sup>	9.8	114.0	n.a.	
	R1336mzz(E) <sup>g</sup>	trans-1,1,1,4,4,4-Hexafluoro-2-butene	CF <sub>3</sub> CH=CHCF <sub>3</sub> (E)	137.7	31.5	0	18	A1	7.5	164.1	n.a.	
	R1234ze(E)	trans-1,3,3,3-Tetrafluoro-1-propene	CF <sub>3</sub> CH=CHF(E)	109.4	36.4	0	<1	A2L	-19.0	114.0	5.6	
	R1234yf	2,3,3,3-Tetrafluoro-1-propene	CF <sub>3</sub> CF=CH <sub>2</sub>	94.7	33.8	0	<1	A2L	-29.5	114.0	13.8	
HCFO	★ R1233zd(E) <sup>h</sup>	1-chloro-3,3,3-Trifluoro-propene	CF <sub>3</sub> CH=CHCl(E)	166.5	36.2	0.00034	1	A1	18.0	130.5	6.3	
	★ R1224yd(Z) <sup>i</sup>	1-chloro-2,3,3,3-Tetrafluoro-propene	CF <sub>3</sub> CF=CHCl(Z)	155.5	33.3	0.00012	<1	A1	14.0	148.5	n.a.	
HC	R601	Pentane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	196.6	33.7	0	5	A3	36.1	72.2	4.9	
	R600	Butane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	152.0	38.0	0	4	A3	-0.5	58.1	1.8	
	R600a	Isobutane	CH(CH <sub>3</sub> ) <sub>2</sub> CH <sub>3</sub>	134.7	36.3	0	3	A3	-11.8	58.1	1.0	
	R290	Propane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	96.7	42.5	0	3	A3	-42.1	44.1	1.1	
	R1270	Propene	CH <sub>3</sub> CH=CH <sub>2</sub>	91.1	45.6	0	2	A3	-47.6	42.1	1.0	
CF6	Novec 649 <sup>j</sup>	Dodecafluoro-2-methyl-3-pentanone	CF <sub>3</sub> CF <sub>2</sub> C(O)CF(CF <sub>3</sub> ) <sub>2</sub>	168.7	18.8	0	<1	n.a.	49.0	316.0	6.8	
Ether	E170	Dimethyl ether	CH <sub>3</sub> OCH <sub>3</sub>	127.2	53.4	0	1	A3	-24.8	46.1	39.0	
Natural	R718	Water	H <sub>2</sub> O	373.9	220.6	0	0	A1	100.0	18.0	5.6 <sup>k</sup>	
	R717	Ammonia	NH <sub>3</sub>	132.3	113.3	0	0	B2L	-33.3	17.0	27	
	R744	Carbon dioxide	CO <sub>2</sub>	31.0	73.8	0	1	A1	-78.5	44.0	1.0	

CFC = Chlorofluorocarbons, HCFC = Hydrochlorofluorocarbons, HFC = Hydrofluorocarbons, HFO = Hydrofluoroolefins, HCFO = Hydrochlorofluoroolefins  
 HC = Hydrocarbons, T<sub>crit</sub> = critical temperature, p<sub>crit</sub> = critical pressure, ODP = Ozone Depletion Potential (R11=1.0, UNEP, 2017), GWP<sub>100</sub> = Global Warming Potential (CO<sub>2</sub>=1.0, 100 years, EU F-Gas Regulation 517/2014, Myhre et al., 2013), SG = Safety Group (DIN EN 378-1, 2008, ASHRAE 34), NBP = Boiling point at 1.013 bar, M = Molecular weight, Relative price per kg refrigerant compared to CO<sub>2</sub> of 9 Euro/kg (based on a 10 kg vessel, October 2017), n.a. = price not yet available but close to market, <sup>a</sup>Solkane® 365mfc from Solvay, <sup>b</sup>Solkatherm® SES36 from Solvay, <sup>c</sup>Lewandowski et al. (2010), <sup>d</sup>R245fa from Linde or Honeywell (Genetron® 245fa), <sup>e</sup>Opteon™ MZ from Chemours, <sup>f</sup>Fukuda et al. (2014), <sup>g</sup>Juhász (2017), <sup>h</sup>Solstice® zd from Honeywell, <sup>i</sup>AMOLEA® 1224yd from AGC Chemicals, <sup>j</sup>Novec™ 649 from 3M, <sup>k</sup>Molecular biological quality

# Suitable properties of HFO and HCFO refrigerants for HTHPs

Type	Refrigerant	Chemical formula	T <sub>crit</sub> [°C]	p <sub>crit</sub> [bar]	ODP [-]	GWP <sub>100</sub> [-]	SG	Price [EUR/kg]
<b>HFO</b>	R1336mzz(Z) <sup>a</sup>	CF <sub>3</sub> CH=CHCF <sub>3</sub> (Z)	171.3	29.0	0	2	A1	n.a.
	R1234ze(Z) <sup>b</sup>	CF <sub>3</sub> CH=CHF(Z)	150.1	35.3	0	<1	A2L	n.a.
<b>HCFO</b>	R1233zd(E) <sup>c</sup>	CF <sub>3</sub> CH=CHCl(E)	166.5	36.2	0.00034	1	A1	50
	R1224yd(Z) <sup>d</sup>	CF <sub>3</sub> CF=CHCl(Z)	155.5	33.3	0.00012	<1	A1	n.a.
<b>HFC (comparison)</b>	R365mfc <sup>e</sup>	CF <sub>3</sub> CH <sub>2</sub> CF <sub>2</sub> CH <sub>3</sub>	186.9	32.7	0	804	A2	80
	R245fa <sup>f</sup>	CHF <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>	154.0	36.5	0	858	B1	57



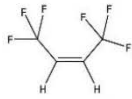
## Remarks

- ODP basis R11=1.0 (UNEP, 2017)
- GWP100 for 100-year time horizon: basis CO<sub>2</sub>=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)
- Approximate sales price per kg refrigerant (based on a 10 kg container, prices from PanGas, Climalife, and Solvay, October 2017), n.a. price not yet available but refrigerant is close to market
- <sup>a</sup>Opteon™ MZ from Chemours, <sup>b</sup>Fukuda et al. (2014), <sup>c</sup>Solstice® zd from Honeywell (2016), <sup>d</sup>AMOLEA® 1224yd from AGC Chemicals (2017), <sup>e</sup>Solkane® 365mfc from Solvay, <sup>f</sup>Genetron® 245fa from Honeywell

# Possible concept for a HTHP laboratory prototype

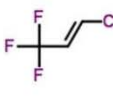
## HFO and HFCO refrigerants

R1336mzz(Z)



171.3°C  
29.0 bar  
A1

R1233zd(E)



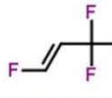
166.5°C  
36.2 bar  
A1

R1234ze(Z)



150.1°C  
35.3 bar  
A2L

R1234ze(E)

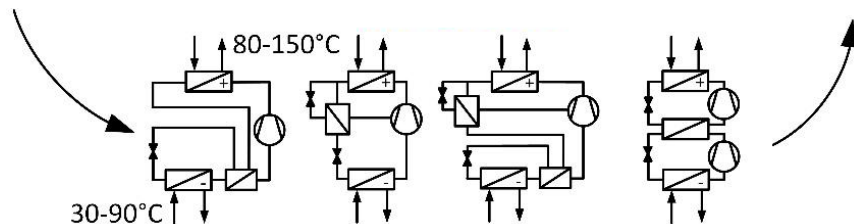
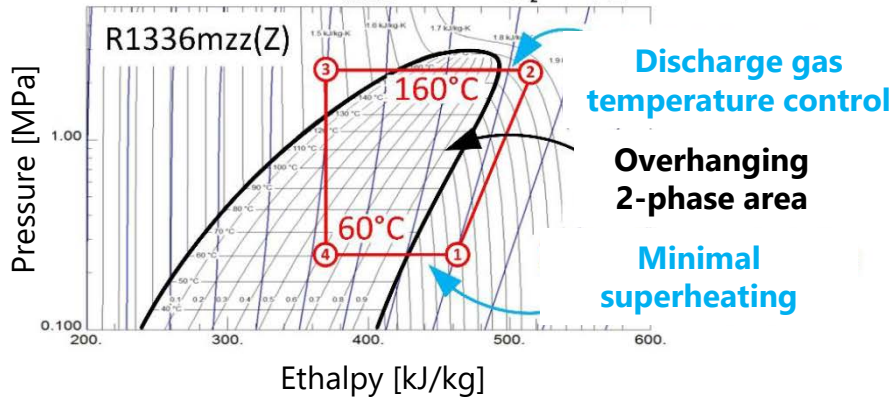


109.4°C  
36.4 bar  
A2L

R1234yf

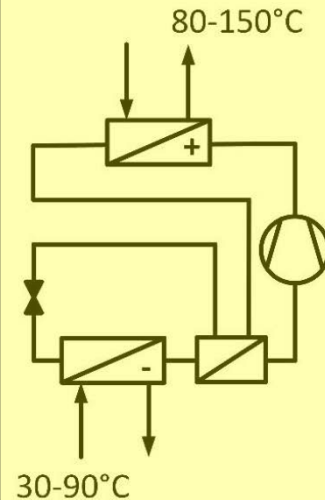


94.7°C  
33.8 bar  
A2



## Cycle

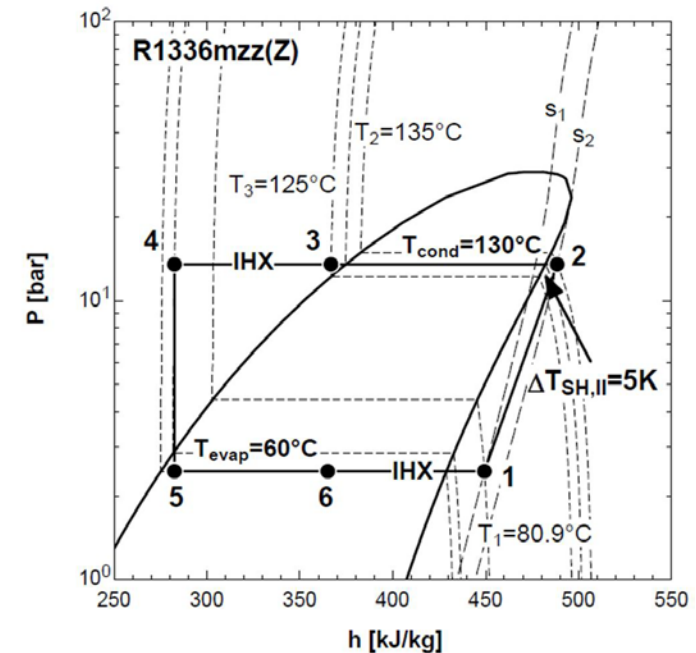
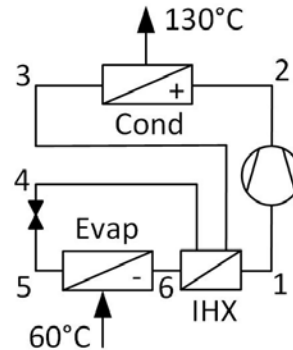
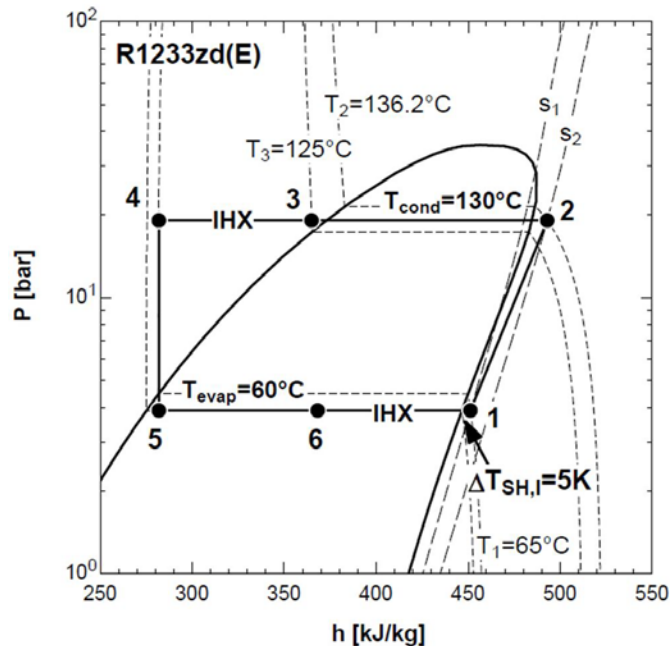
Single-stage  
with IHX



## Decision criteria:

- 1) Thermodynamic suitability** ( $T_{crit} > 150^\circ\text{C}$ , allows subcritical operation, good efficiency at high temperatures)
- 2) Environmental compatibility** (GWP < 10, ODP = 0, future-proof according to F-Gas regulation)
- 3) Safety** (no or only low flammability)
- 4) Natural refrigerants**, like R600, R600a and R601 **excluded** due to flammability (A3), other refrigerants due to lack of information and availability

# Single-stage cycle with IHX



## Assumptions:

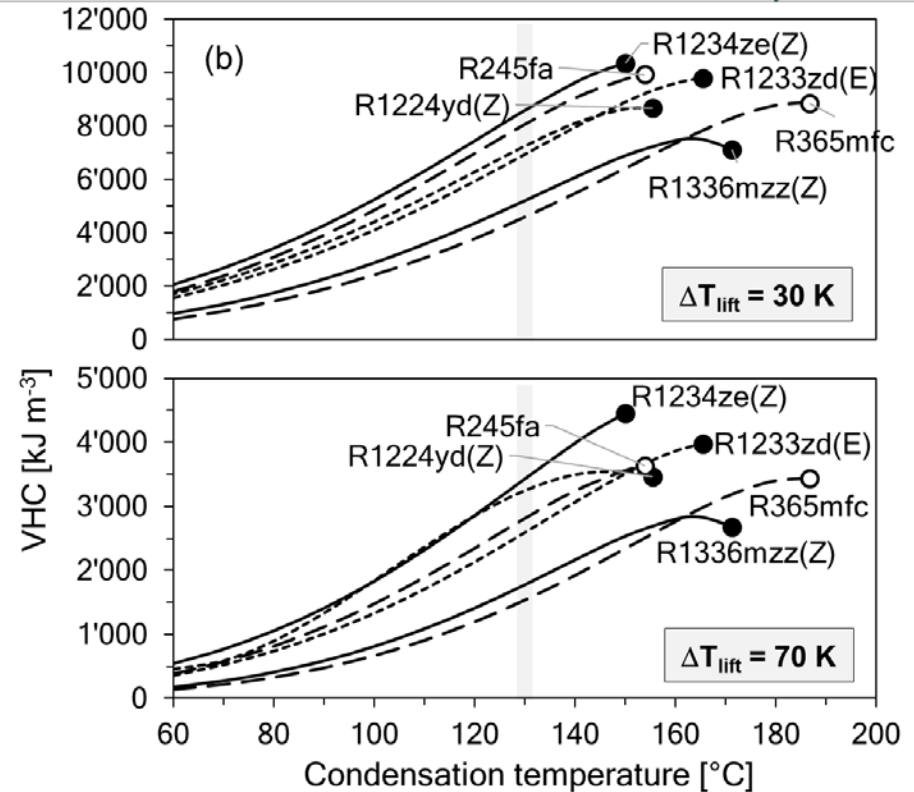
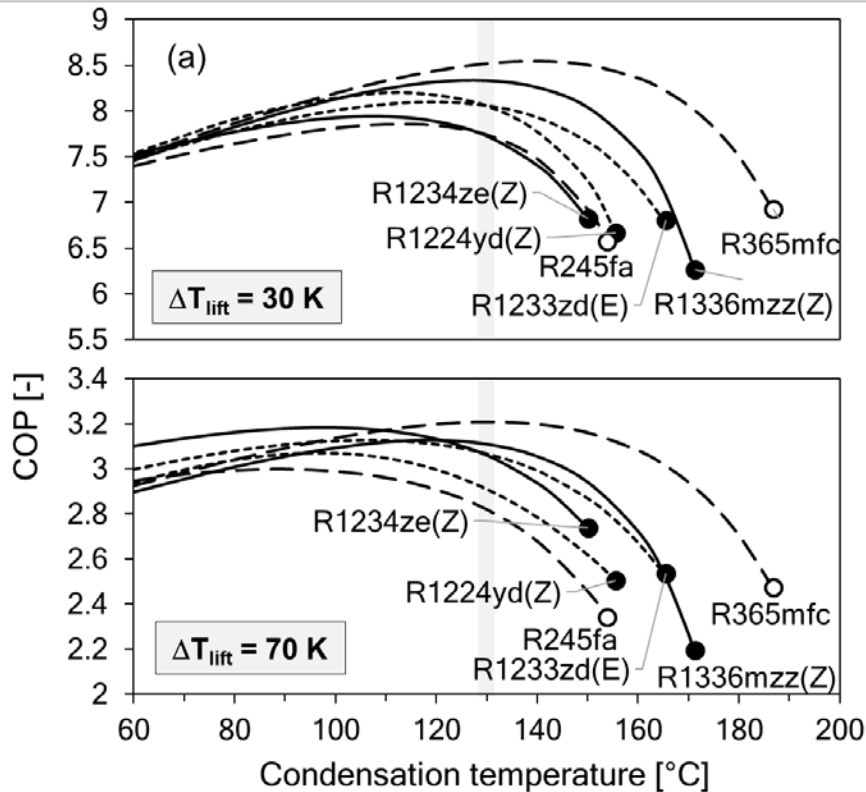
- Constant compressor isentropic efficiency of 0.7
- 5 K superheating ( $\Delta T_{SH,I}$ ) at compressor inlet for R1233zd(E), R1234ze(Z), R245fa
- 5 K superheating ( $\Delta T_{SH,II}$ ) at comp. outlet for R1336mzz(Z), R1224yd(Z), R365mfc
- 5 K subcooling ( $T_{SC} = 5 K$ ), i.e. low heat sink temperature glide
- 5 K minimum temperature difference within the IHX ( $\Delta T_{IHX} = T_6 - T_4 = 5 K$ )
- No parasitic pressure and heat losses ( $h_5 = h_4$ )

$$VHC = (h_2 - h_3)\rho_1$$

$$COP = (h_2 - h_3)/(h_2 - h_1)$$

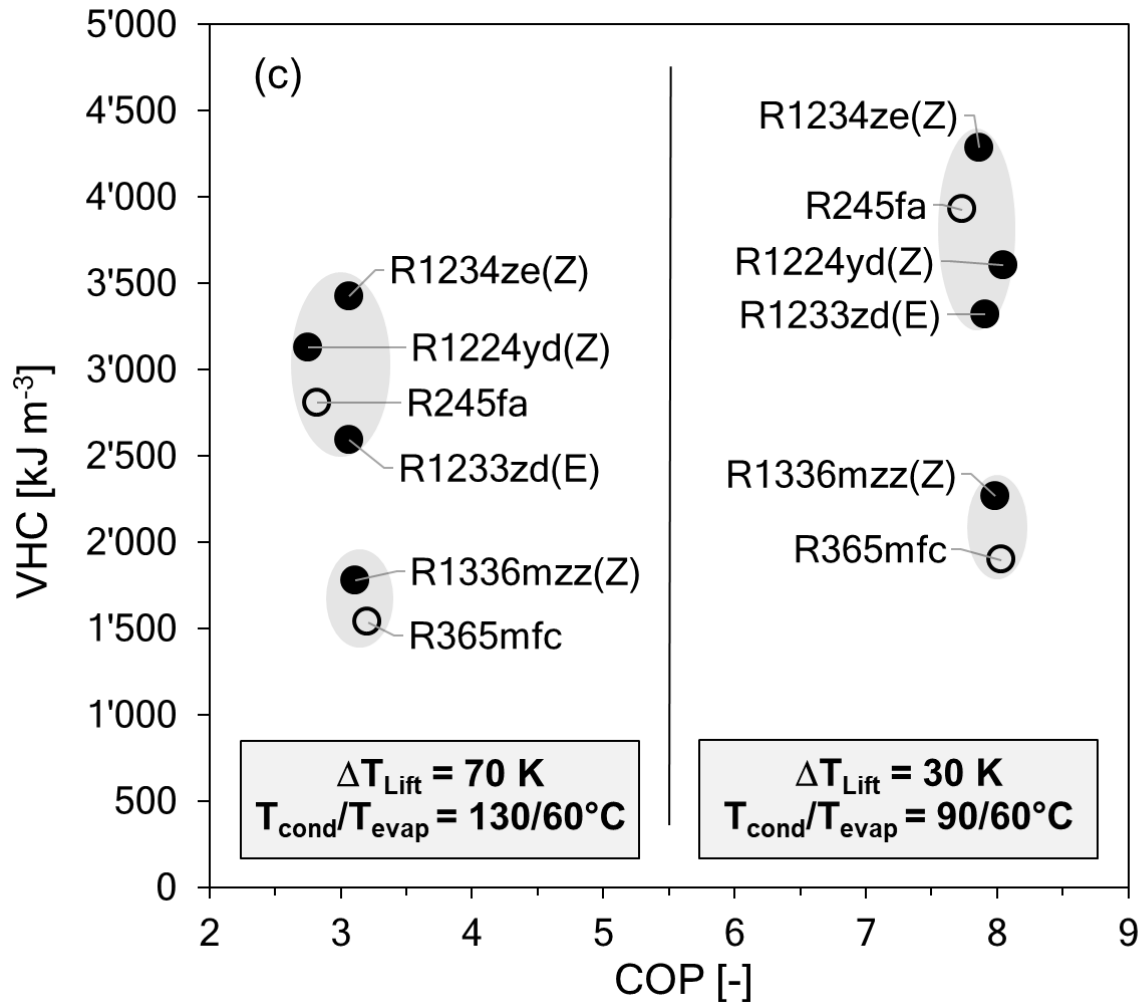


# Simulation results



- Optimum condensation temperatures depending on refrigerant type (about 40 to 60 K below critical temperature)
- R365mfc provides the highest COP, R245fa the lowest
- R1234ze(Z) offers the highest VHC

# Simulation results

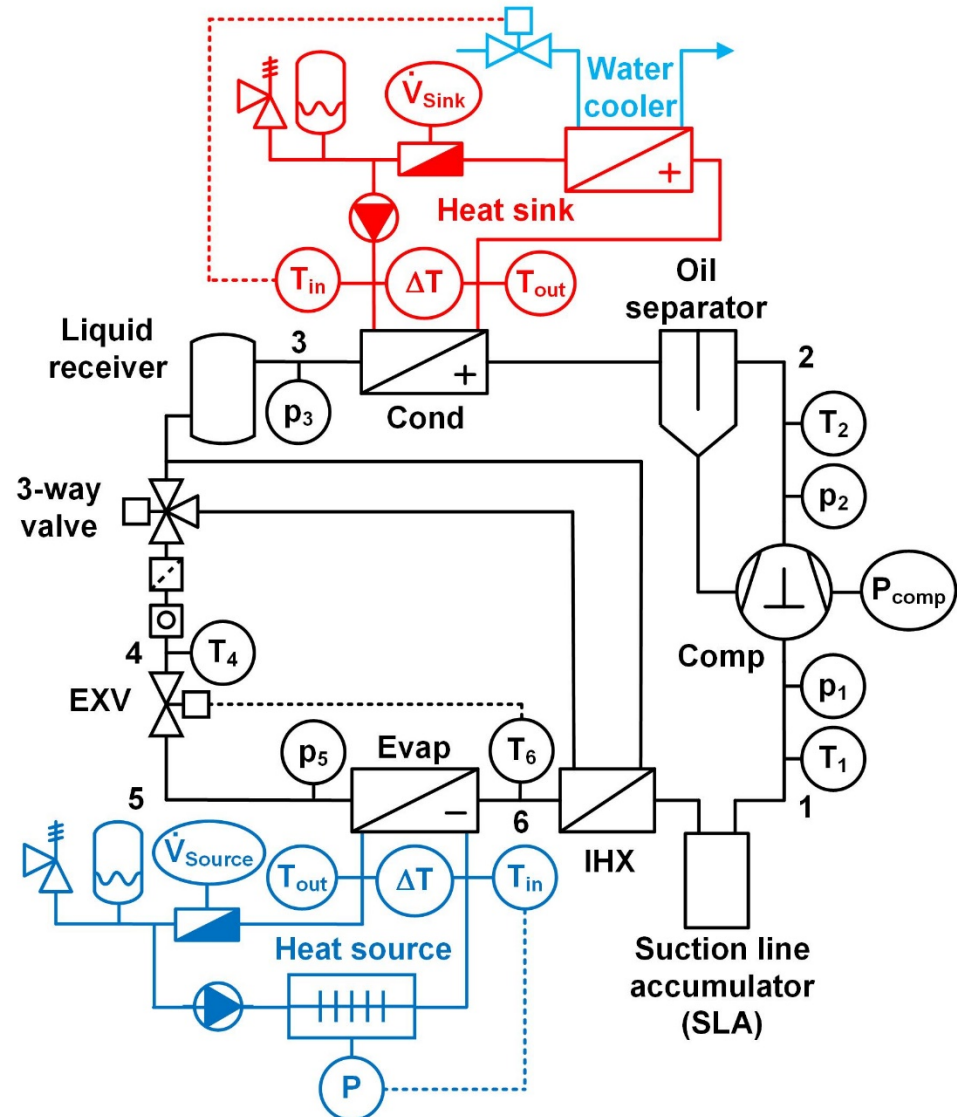
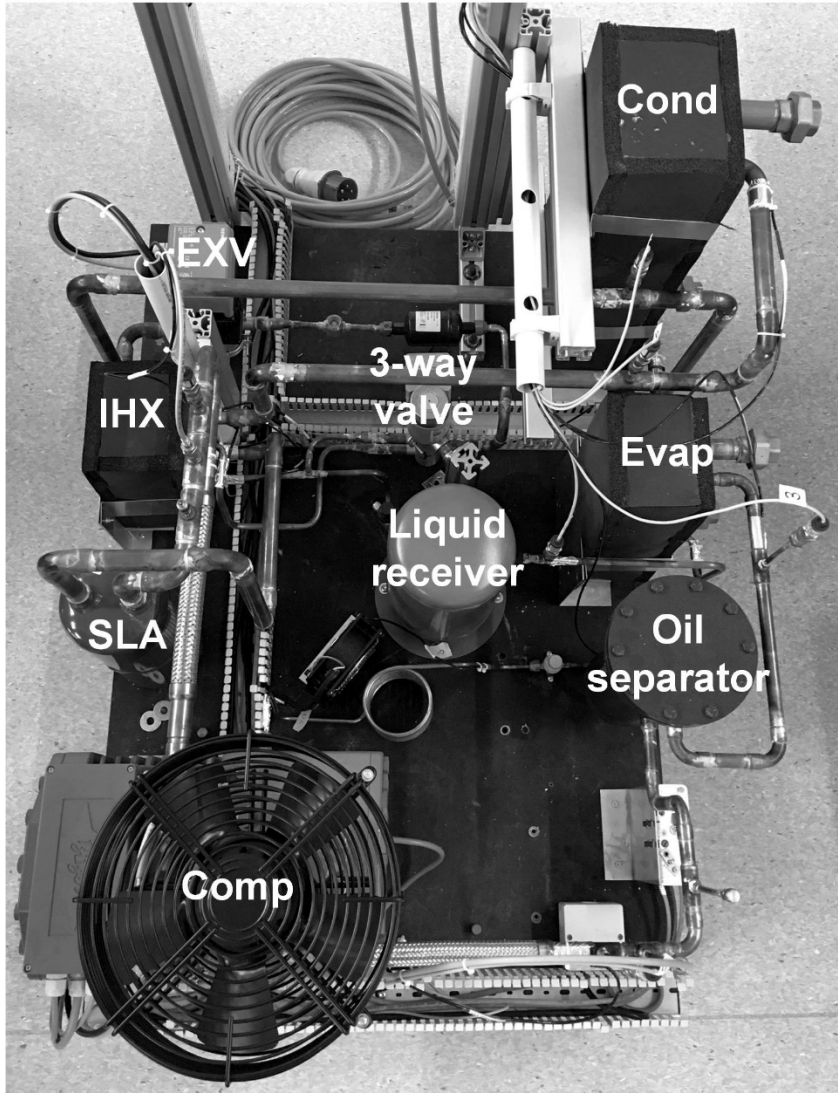


- R1336mzz(Z) is closest “drop-in” replacement for R365mfc
- R1224yd(Z), R1234ze(Z) and R1233zd(E) closer to R245fa

# Experimental setup

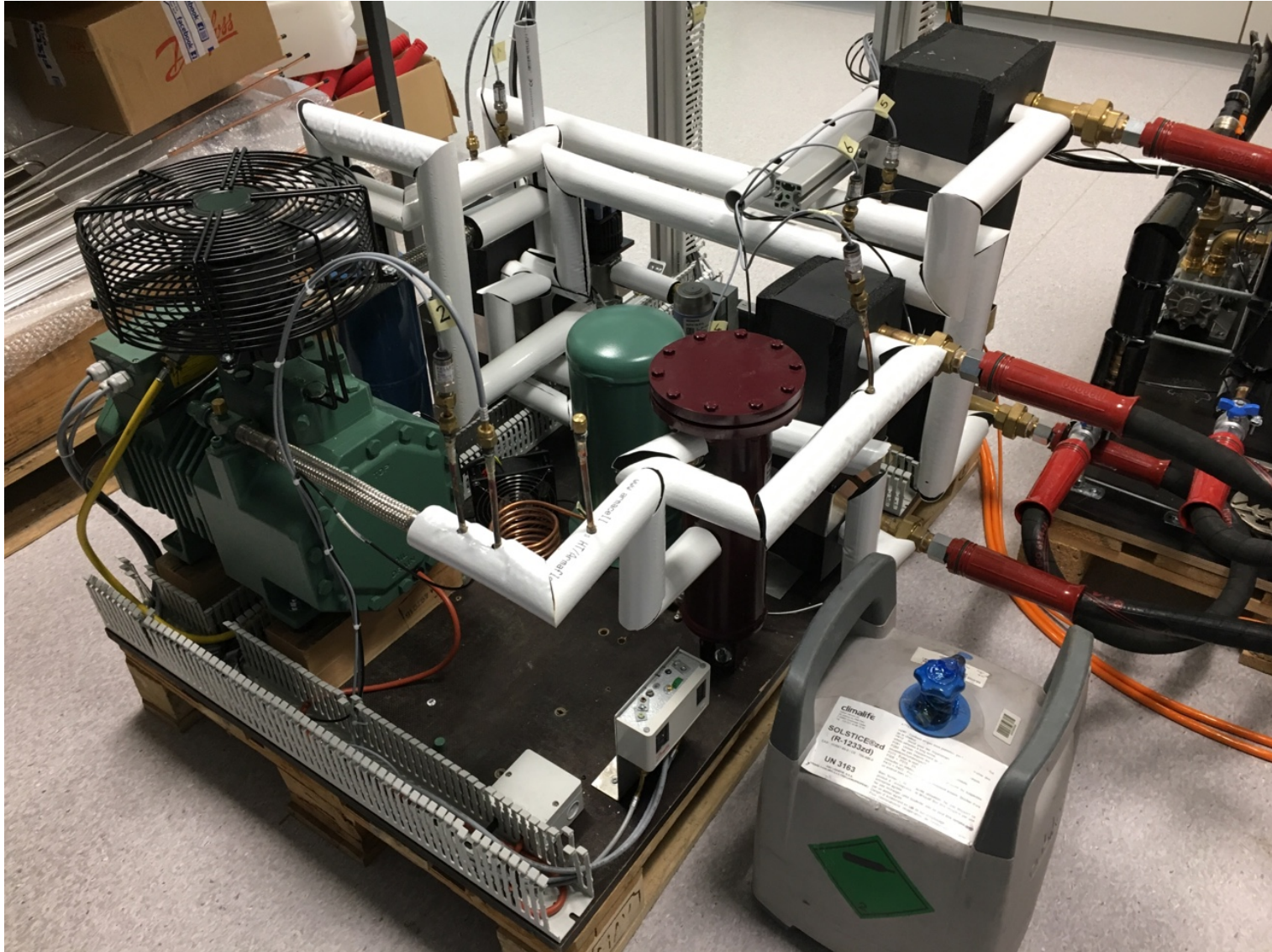
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# Laboratory scale HTHP

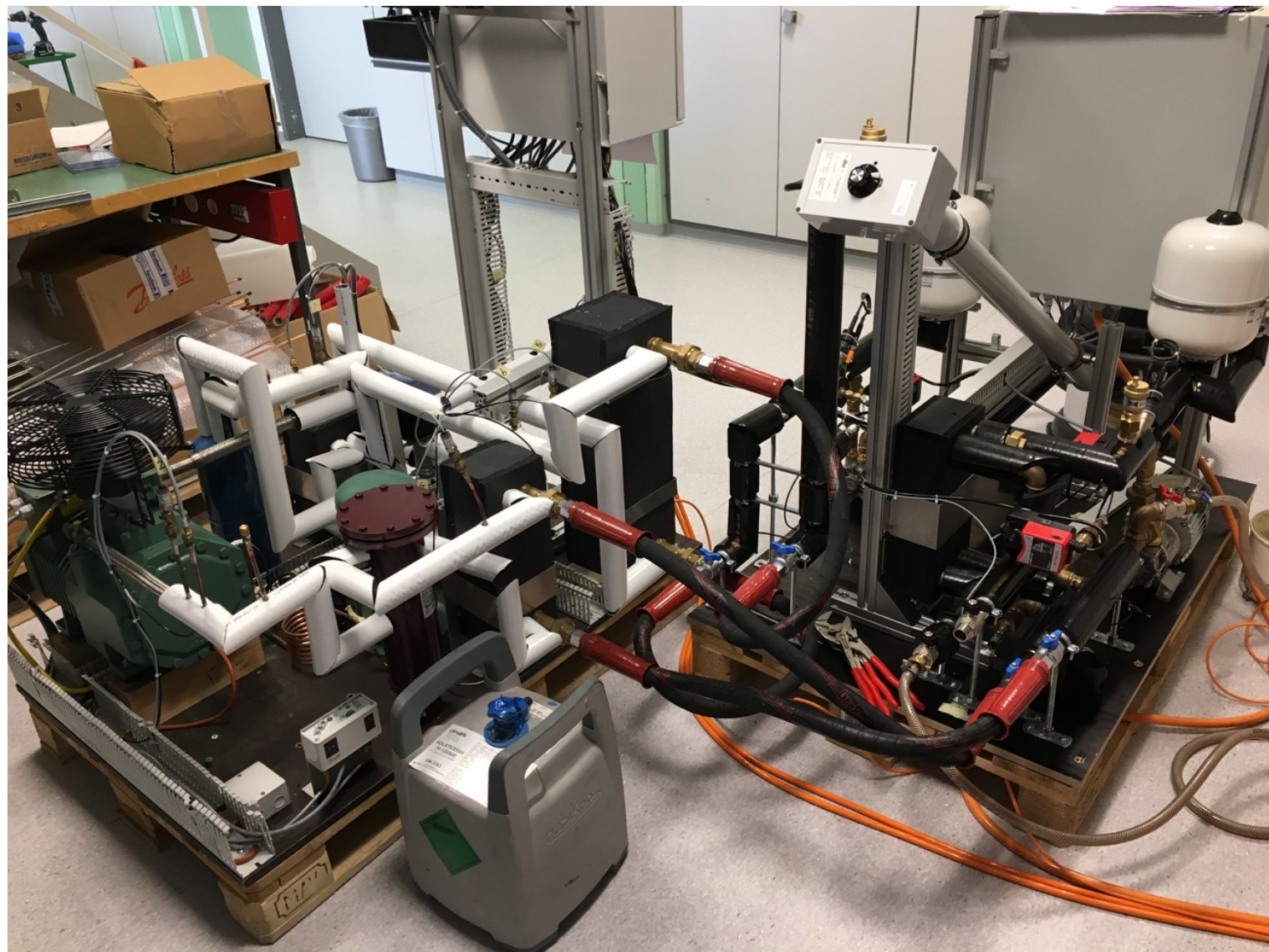




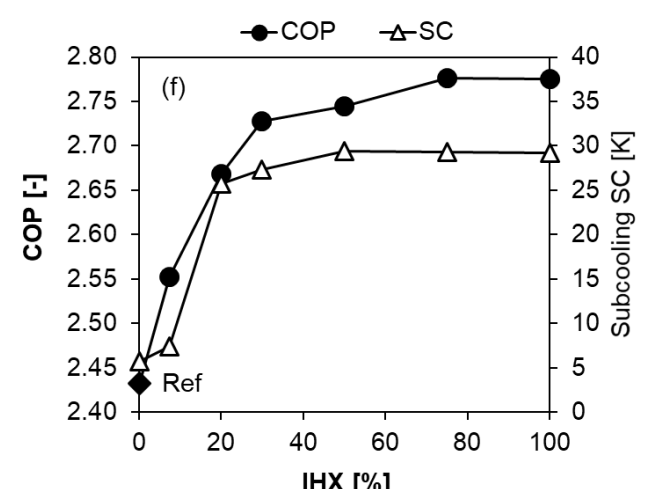
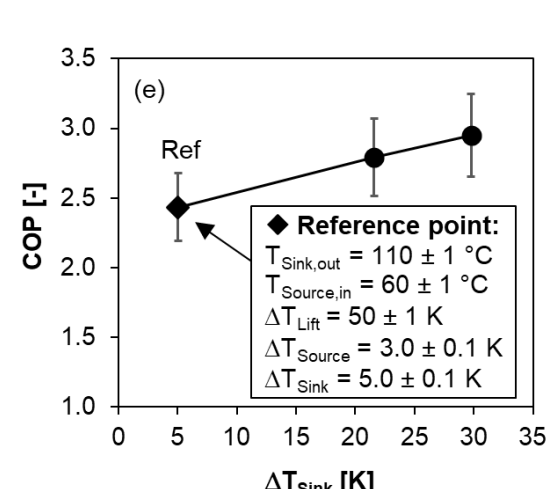
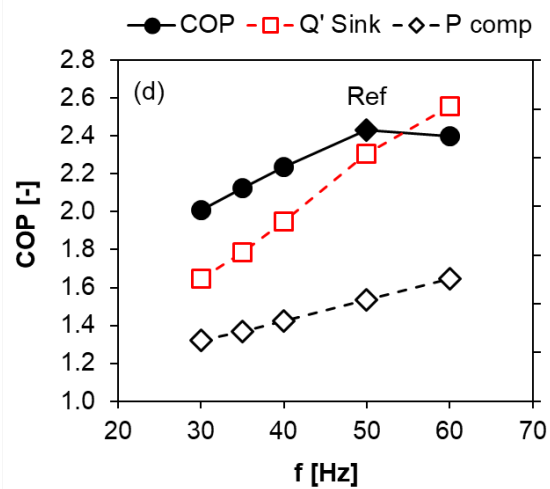
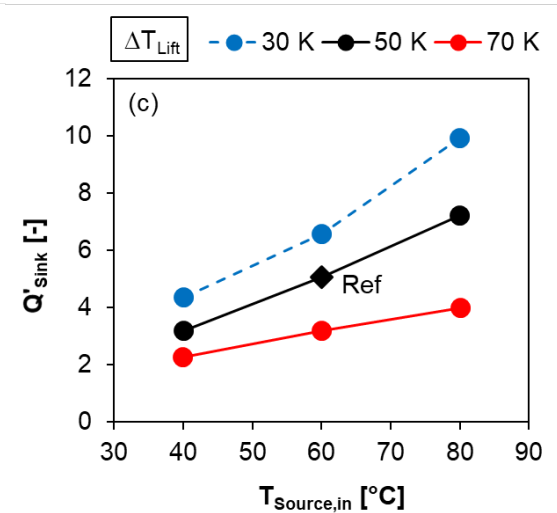
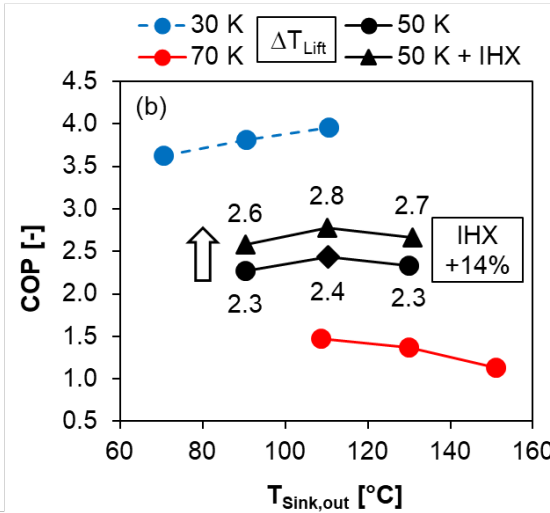
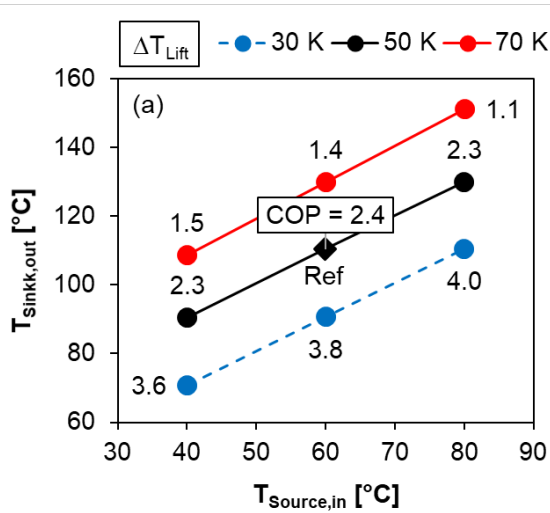
# HTHP with hydraulic loops for heat source and heat sink



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# Experimental parameter study – Preliminary test results with R1233zd





# Conclusions

- **More than 20 industrial HTHPs identified on the market** with heat supply temperatures  $> 90^{\circ}\text{C}$ . A few HTHPs exceed  $120^{\circ}\text{C}$  (using R245fa or R365mfc)
- **COPs range between 1.6 and 5.8** with a temperature lift of 130 to 25 K (40 to 60% 2<sup>nd</sup> Law efficiency)
- **Application potentials in industrial waste heat recovery** (e.g. drying & sterilization processes, papermaking, food preparation)
- **Several R&D projects on an international level** (COPs in the range of 5.7 to 6.5 at 30 K temperature lift, 2.2 to 2.8 at 70 K, max.  $160^{\circ}\text{C}$ )
- **Research trend** towards testing
  - natural refrigerants (e.g. R718, R744),
  - hydrocarbons (e.g. R600, R601)
  - and synthetic HFOs (e.g. R1336mzz(Z), R1234ze(Z), R1233zd(E), and R1224yd(Z)) with low GWP ( $< 10$ )

# Conclusions

## ■ Theoretical simulations

- **Tradeoff** between COP and VHC
- **R1336mzz(Z)** is next drop-in replacement for R365mfc
- **R1224yd(Z), R1234ze(Z) and R1233zd(E)** are closer to R245fa

## ■ Experimental HTHP set-up

- **Standard components** (single-stage with adjustable IHX for superheating and efficiency increase of +14%)
- **Tested with** commercially available HCFO **R1233zd(E)**
- **Operation demonstrated** at 40 to 80°C heat source and 70 to 150°C heat supply temperatures (e.g. drying processes or steam generation)
- **COP of 2.43** at W60 / W110 (50 K temperature lift)
- **+21% COP** by increasing heat sink temp. difference from 5 to 30 K

## ■ Future work

- **Testing R1336mzz(Z) and R1224yd(Z)**
- **Reduction of thermal losses** (better insulation)

# Acknowledgement



This research project is part of the Swiss Competence Center for Energy Research SCCER EIP of the Swiss Innovation Agency Innosuisse.

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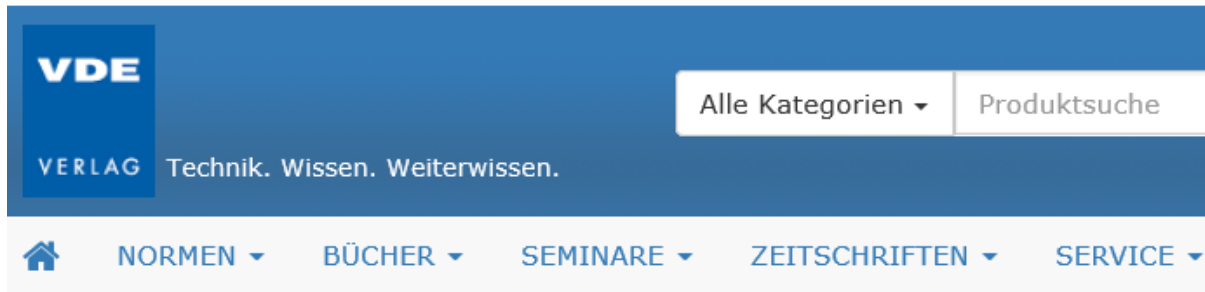
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# Thank you for your attention!



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