High Temperature Heat Pump – Theoretical study on low GWP HFO and HCFO refrigerants

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Content

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Introduction

- High Temperature Heat Pumps (HTHPs): waste heat recovery in industry, products, research gaps
- Hydrofluoroolefins (HFOs) and hydrochlorofluoroolefins (HCFOs) as 4th generation of low GWP refrigerants for HTHPs
- Theoretical studies on different HTHP cycles with HFOs and HCFOs

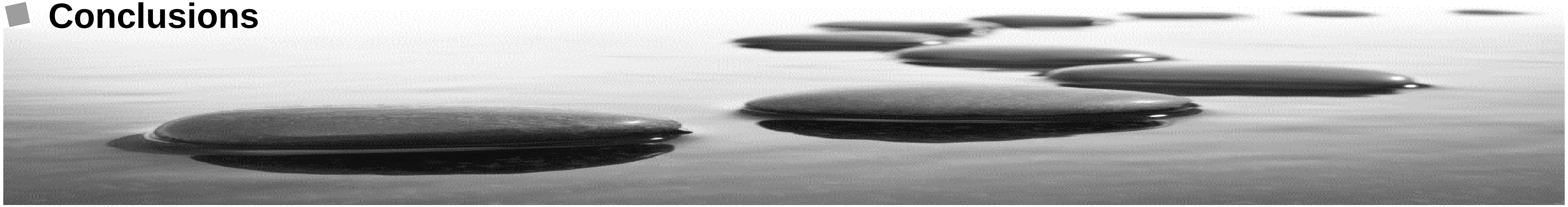
Simulation model

- Selected and investigated heat pump cycles
- Assumptions, parameters and variation range

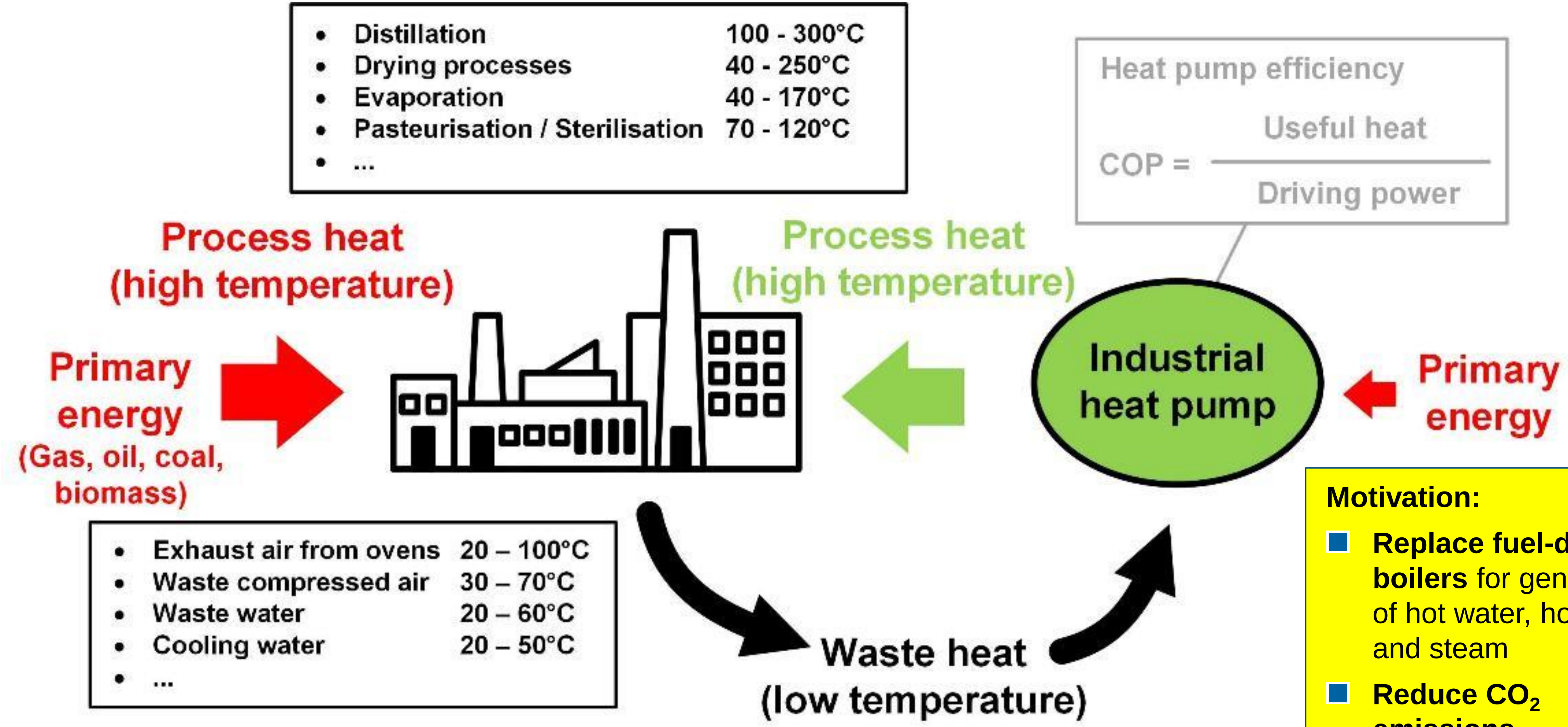
Simulation results and discussion

- Comparison of performance parameters (COP, VHC, p_{Ratio}, $T_{Discharge}$)
- Operating maps, optimal COP

Conclusions



Principle of waste heat recovery by industrial heat pumps



Motivation:

- **Replace fuel-driven boilers** for generation of hot water, hot air and steam
- **Reduce CO_2 emissions**
- **Energy savings**

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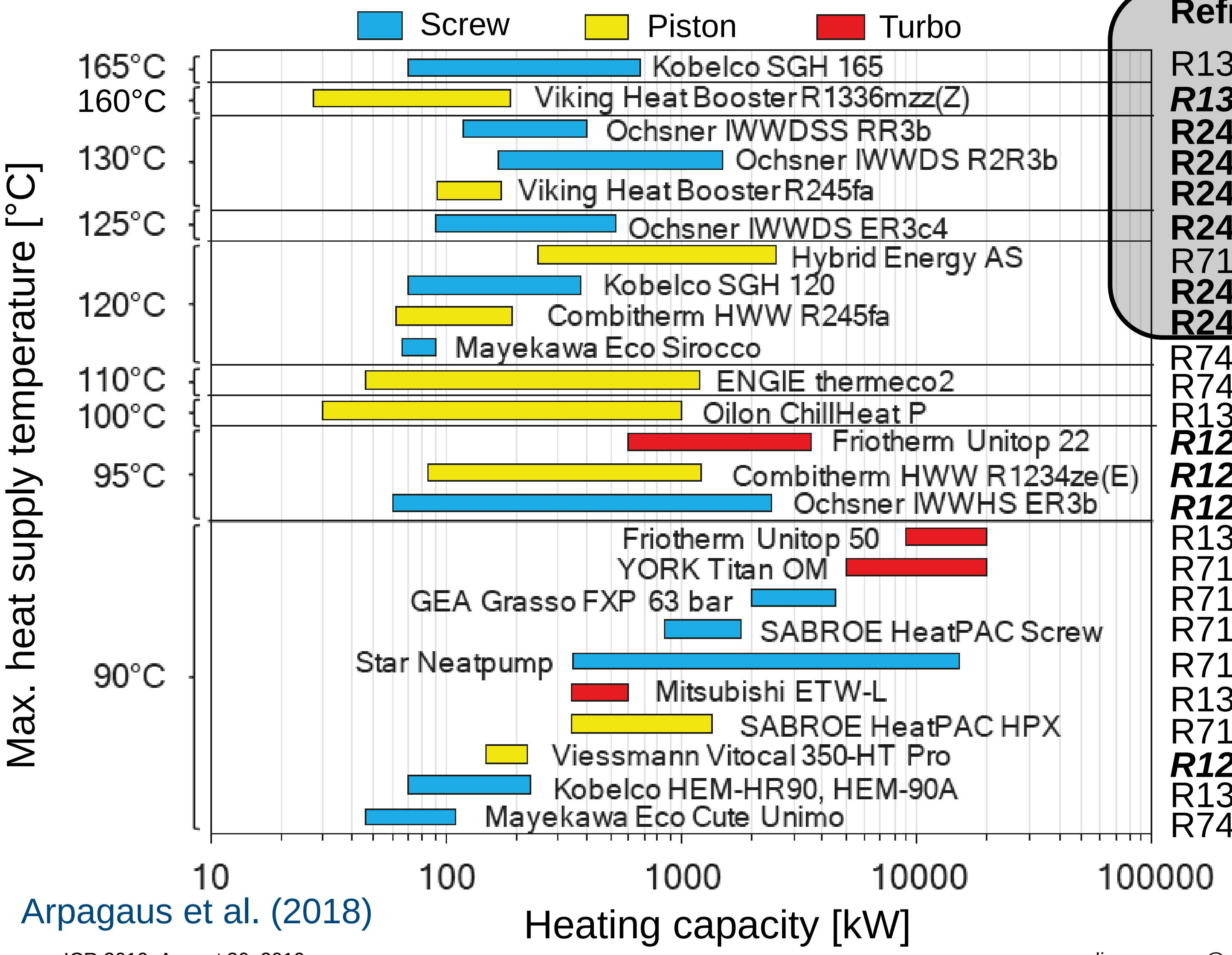
R245fa is predominantly used in today's industrial HTHP



Refrigerants

R134a/**R245fa**
R1336mzz(Z)
R245fa
R245fa
R245fa
R245fa
R717 (NH_3)
R245fa
R245fa
R744 (CO_2)
R744 (CO_2)
R134a/R1234ze(E)
R1234ze(E)
R1234ze(E)
R1233zd(E)
R134a
R717 (NH_3)
R717 (NH_3)
R717 (NH_3)
R717 (NH_3)
R134a
R717 (NH_3)
R1234ze(E)
R134a/**R245fa**
R744 (CO_2)

Arpagaus et al. (2018)

Kobelco SGH 120/165
(Steam Grow HP)

HeatBooster S4
(Viking Heating Engines AS)

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What are the research gaps in HTHPs?

- Development and testing of **new environmentally friendly synthetic refrigerants (e.g. HFOs and HCFOs with very low GWP)**
- Application of natural refrigerants, such as hydrocarbons (R600, R601), CO_2 or water
- **Extending the limits of heat source (T_{Source}) and heat supply temperatures (T_{Sink}) to higher values**
- **Improving heat pump efficiency (COP) (e.g. by multi-stage cycles**, oil-free compressors)
- Development of temperature-resistant components (e.g. valves, compressors)
- Optimization and development of heat pump systems with new control strategies for higher temperatures
- Scale-up of functional models to industrial scale (demonstration projects)

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

CFC (R113)

Montréal Protocol (1987)

Ozone layer depletion

HCFC (R123)

Regulation (2037/2000)

Kyoto Protocol (1997)

Global warming geeenhouse gases

HFC (R245fa)

EU F-Gas Regulation (517/2014)

Paris Agreement (2015)

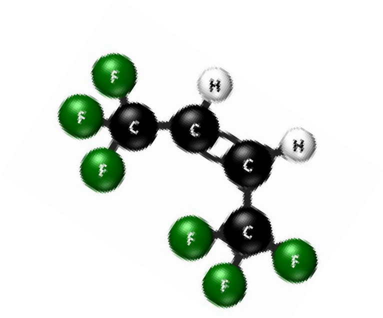
Cost increase

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

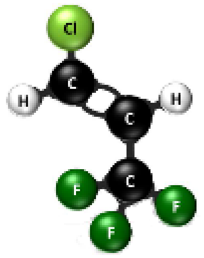
CFC: fully halogenated chlorofluorocarbons
HCFC: partially halogenated chlorofluorocarbons
HFC: hydrofluorocarbons
HFO: hydrofluoroolefins
HCFO: hydrochlorofluoroolefins

Criteria :

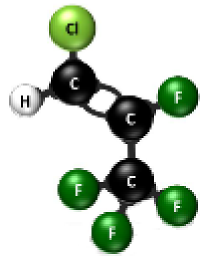
- low GWP
- short atm. lifetime
- zero/low ODP
- low flammability
- high efficiency
- high T_{crit}



R1336mzz(Z)



R1233zd(E)



R1224yd(Z)

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Properties of selected HFO and HCFO refrigerants for HTHP applications

Refrigerant	Structure	T_{crit} (°C)	p_{crit} (bar)	p_{Ratio}* (-)	ODP (-)	GWP_{100} (-)	Lifetime (days)	SG	NBP (°C)	M (g/mol)
R1336mzz(Z)	Z-CF_3-CH=$CHCF_3$	171.3	29	4.3	0	**2**	**22**	A1	33.4	164.1
R1233zd(E)	E-CF_3-CH=CHCl	165.6	35.7	3.9	0.00034	**1**	**26**	A1	18	130.5
R1224yd(Z)[a]	Z-CF_3-CF=CHCl	155.5	33.4	3.8	0.00023	**0.88**	**20**	A1	14	148.5
R1234ze(Z)	Z-CF_3-CH=CHF	150.1	35.3	3.7	0	**<1**	**10**	A2L	9.8	114
R1336mzz(E)**	E-CF_3-CH=$CHCF_3$	171.3	31.5	3.8	0	**18**	**90**	n.a.	7.5	164.1
R1234ze(E)+	E-CF_3-CH=CHF	109.4	36.3	3.2	0	**<1**	**16.4**	A2L	-19	114
R1234yf+	CF_3-CF=CH_2	94.7	33.8	3	0	**<1**	**11**	A2L	-29.5	114
R134a+	CF_3-CH_2F	101	40.6	3.2	0	**1300**	13.4 years	A1	-26.3	102
R365mfc+	CF_3-CH_2-CF_2-CH_3	186.9	32.7	4.6	0	**804**	8.7 years	A2	40.2	148.1
R245fa+	CHF_2-CH_2-CF_3	154	36.5	4	0	**858**	7.7 years	B1	14.9	134

GWP_{100}, atmospheric lifetimes: Myhre et al. (2013), IPCC 5th assessment report, [a] Tokuhashi et al. (2018),
+ for a low stage (LS) cycle, ++ for comparison, * 40 to 90 °C temperature lift,
** fluid properties not yet available in the EES software (Engineering Equation Solver) V10.643 from F-Chart

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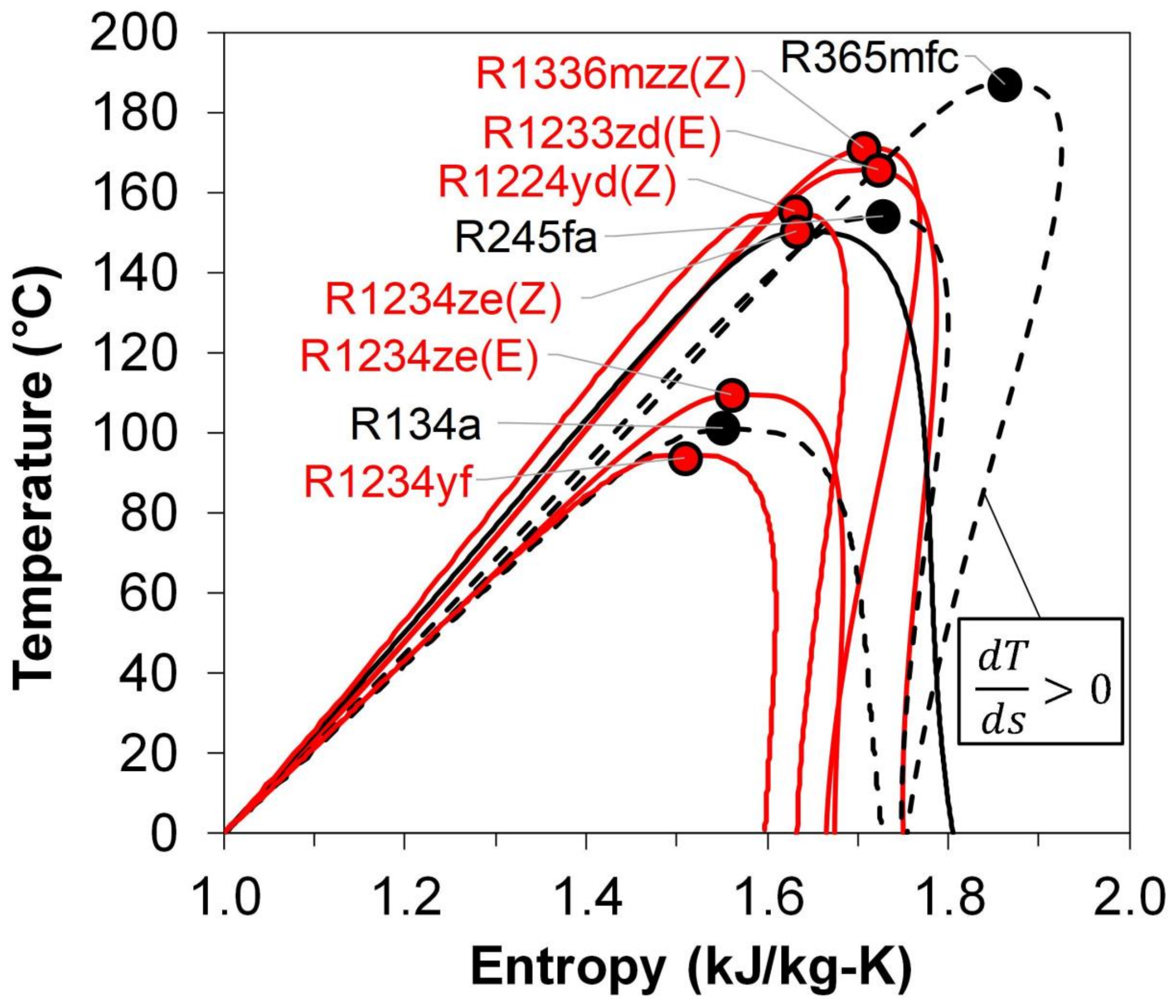
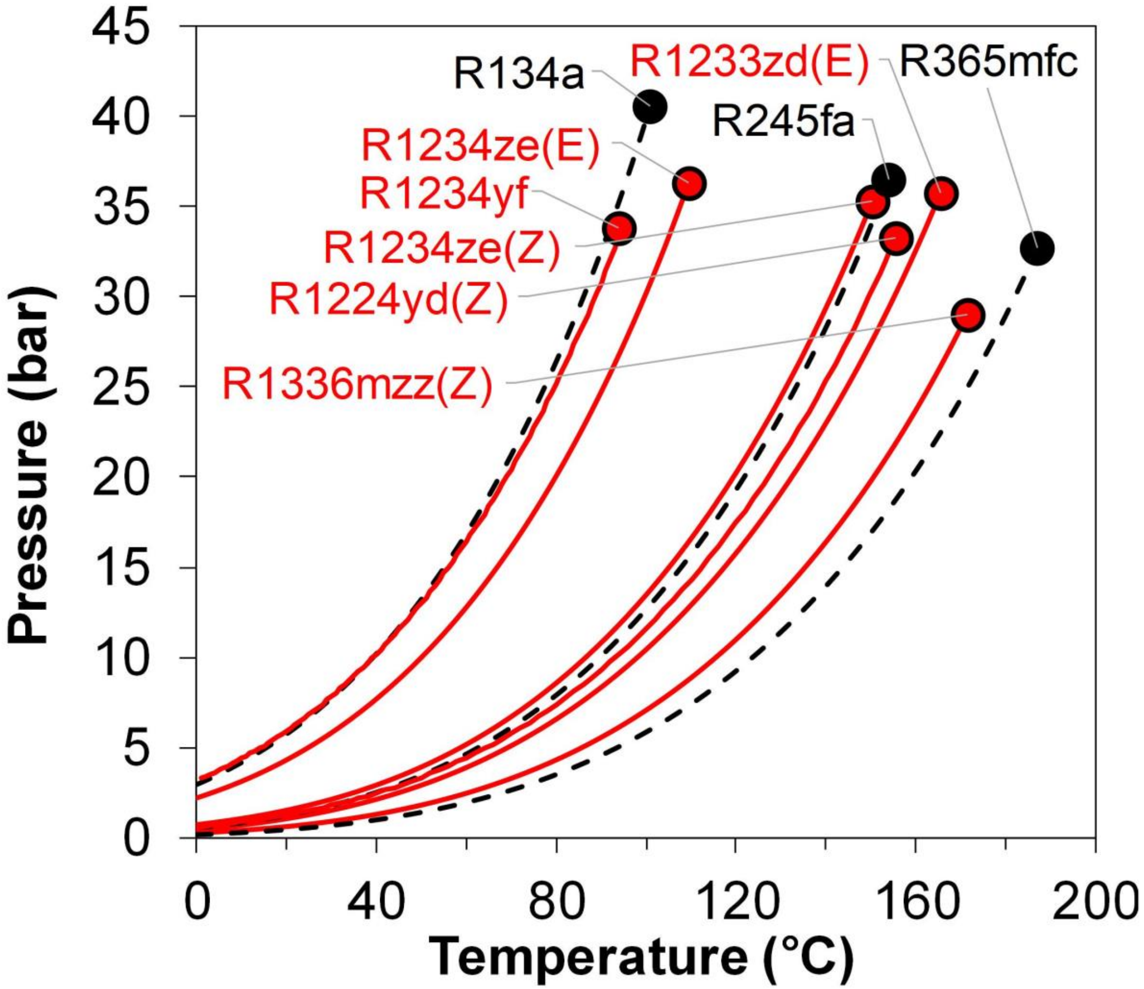
T-s, p-T diagrams of selected HFO and HCFO refrigerants





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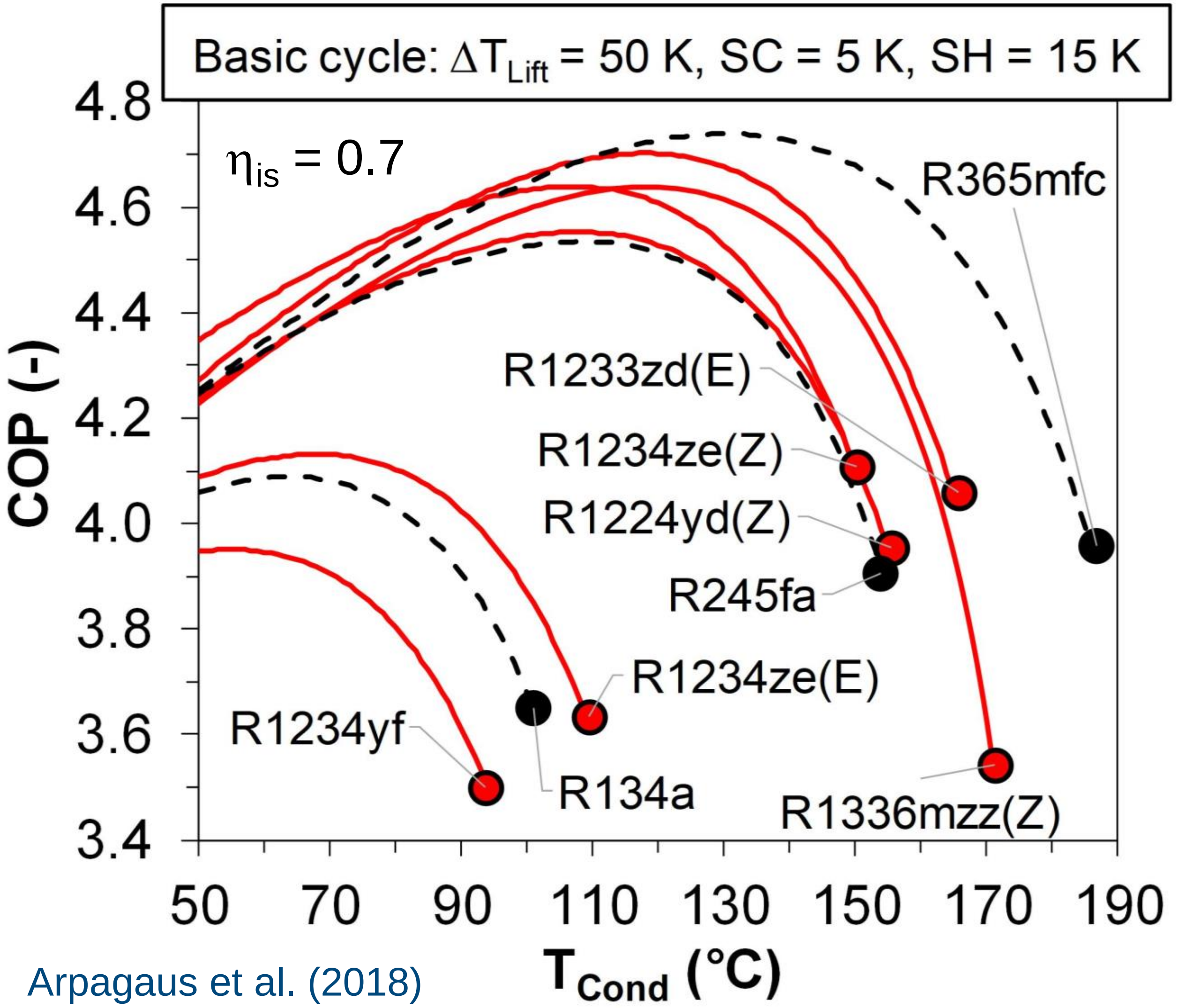
Simulated COP of selected HFO and HCFO refrigerants in a basic HP cycle



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

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Theoretical studies with HFO and HCFO refrigerants in different HTHP cycles

HFO and HCFO refrigerants

Reference	R1336mzz(Z)	R1233zd(E)	R1224yd(Z)	R1234ze(Z)	R1234ze(E)	R1336mzz(E)	R1234yf	R365mfc	R245fa
(Fukuda et al., 2017, 2014)		■		■	■			■	■
(Kondou and Koyama, 2015)		■		■	■			■	■
(Juhasz, 2017; Kontomaris, 2014)	■				■	■	■		■
(Helminger et al., 2016)	■								
(Mota-Babiloni et al., 2018)	■	■	■		■		■		
(Hu et al., 2017)				■					
(Frate et al., 2019)	■	■	■	■				■	
(Mateu-Royo et al., 2018)	■	■							■
(Bamigbetan et al., 2018)	■	■		■	■			■	■
(Arpagaus et al., 2018)	■	■	■	■	■			■	■
This study	X	X	X	X	X		X	X	X

Reference	Basic cycle	1-stage + IHX	2-stage + IHX	2-stage + economizer + IHX	2-stage + flash tank + IHX	2-stage extraction	2-stage cascade extraction	2-stage cascade + IHX	Triple tandem + IHX	3-stage + flash tanks	3-stage extraction
(Fukuda et al., 2017, 2014)	■					■					■
(Kondou and Koyama, 2015)						■	■		■		■
(Juhasz, 2017; Kontomaris, 2014)	■										
(Helminger et al., 2016)		■									
(Mota-Babiloni et al., 2018)								■			
(Hu et al., 2017)	■			■						■	
(Frate et al., 2019)	■										
(Mateu-Royo et al., 2018)		■	■								
(Bamigbetan et al., 2018)	■										
(Arpagaus et al., 2018)		■									
This study		X		X	X			X			

Goal of this study

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- This study examines the **suitability of R1336mzz(Z), R1233zd(E), R1224yd(Z), R1234ze(Z), R1234ze(E) and R1234yf for HTHP application** and presents simulations in the following heat pump cycles:
  - **1-stage cycle with IHX**
  - **2-stage cycle with economizer and IHX**
  - **2-stage cycle with flash tank and IHX**
  - **2-stage cascade with two IHX**

by evaluation of:

  - thermodynamic efficiency (**COP**),
  - volumetric heating capacity (**VHC**)
  - pressure ratio ($\mathbf{p_{Ratio}}$),
  - discharge temperature ($\mathbf{T_{Discharge}}$), and
  - **comparison with** today's HFC refrigerants **R365mfc, R245fa, and R245fa/R134a.**

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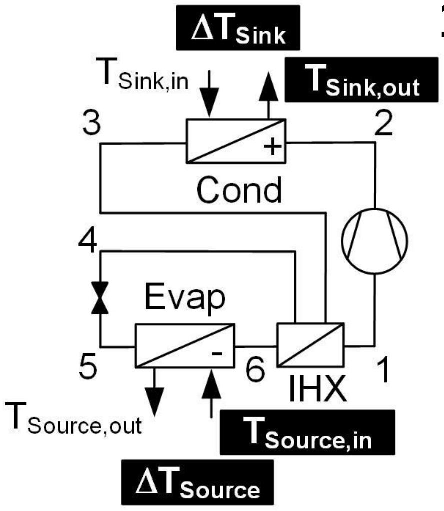
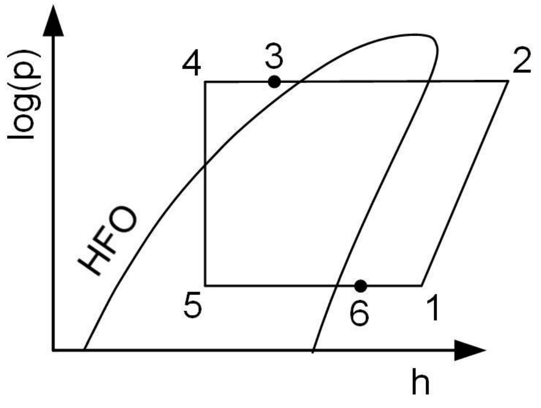
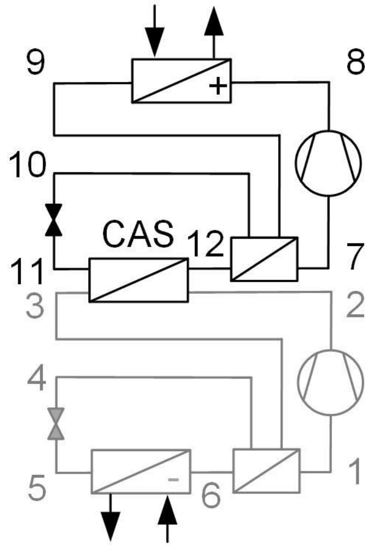
Investigated heat pump cycles with log(p)-h diagrams

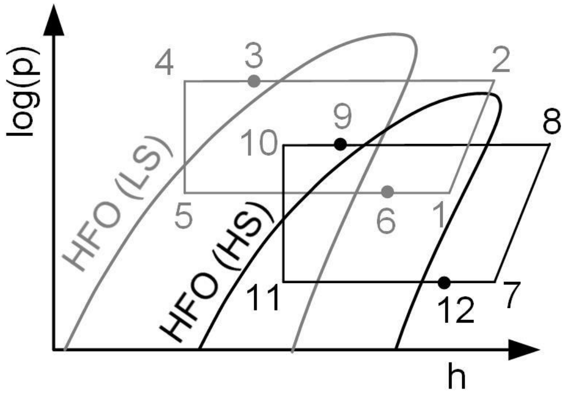
1-stage cycle with IHX



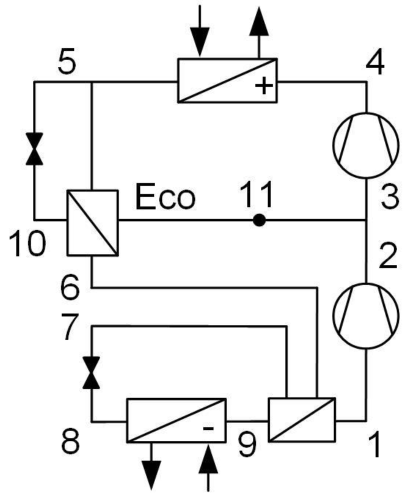


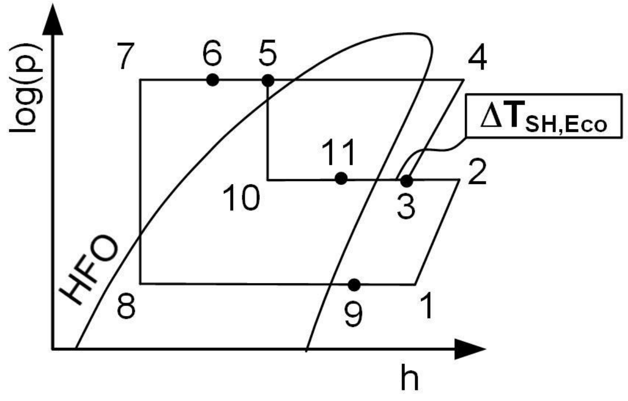
2-stage cascade with two IHX



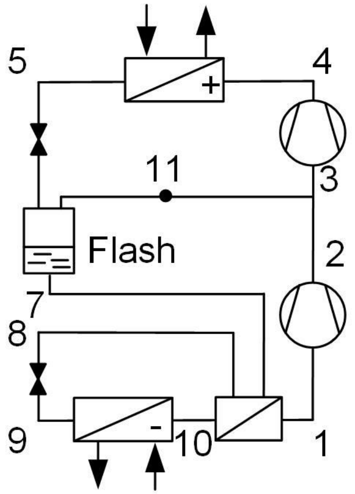


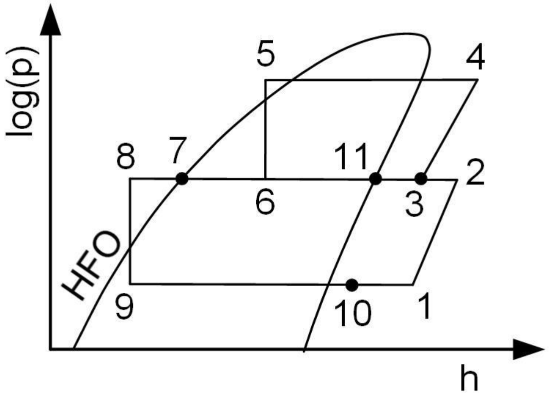
2-stage cycle with economizer and IHX





2-stage cycle with flash tank and IHX





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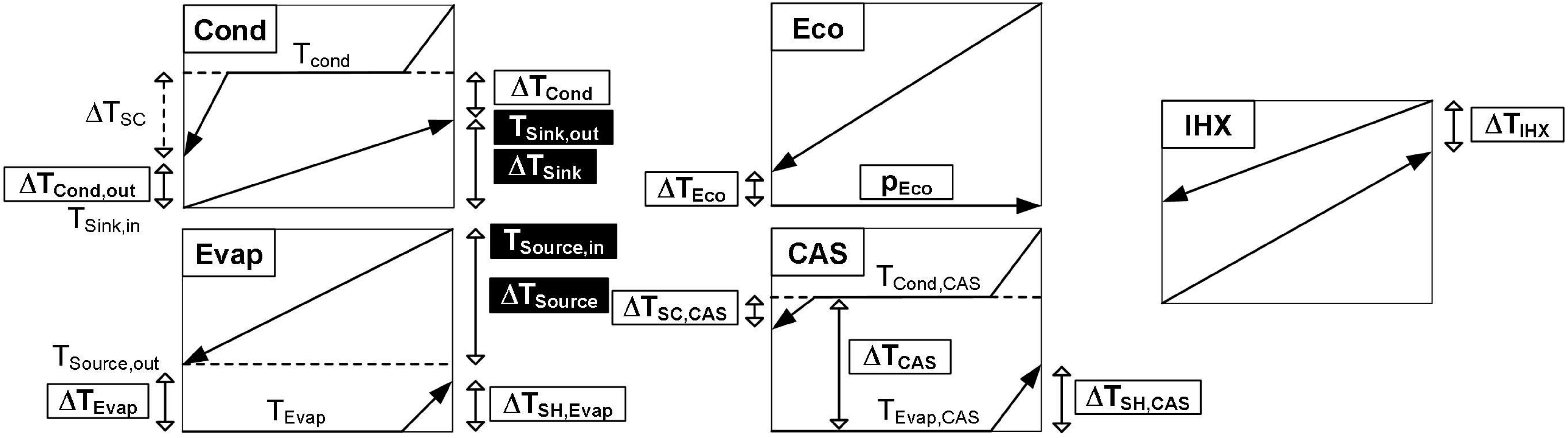
Parameters, reference conditions, and approach temperatures in the heat exchangers (Cond, Eco, CAS, IHX, Evap)



Fixed parameters				Variable parameters	Reference	Range
ΔT_{Cond}	2 K	ΔT_{Eco}	2 K	$T_{Sink,out}$	110 °C	70 to 160 °C
$\Delta T_{Cond,out}$	5 K	$\Delta T_{SH,Eco}$	5 (12*) K	$T_{Source,in}$	60 °C	40 to 90 °C
$\Delta T_{SC,CAS}$	1 K	ΔT_{IHX}	3 K	ΔT_{Lift} ($T_{Sink,out}$ - $T_{Source,in}$)	50 K	30 to 70 K
ΔT_{CAS}	3 K	ΔT_{Evap}	3 K	ΔT_{Sink}	10 K	5 to 30 K
$\Delta T_{SH,CAS}$	3 K	$\Delta T_{SH,Evap}$	5 K	ΔT_{Source}	10 K	5 to 30 K

(*12 K superheat for R1336mzz(Z) and R365mfc to assure dry compression)

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Basic assumptions

- **Simplified thermodynamic cycle models** developed in EES (Engineering Equation Solver), F-Chart Software, V10.643 (Klein, 2019)
  - **No parasitic heat losses and pressure drops**
  - **Isenthalpic expansion**
  - Constant compressor isentropic efficiency of η_{is} **= 0.7**
  - **Intermediate pressure** in the 2-stage economizer and flash tank cycle calculated as the **geometric mean (square root)** of the evaporation and condensation pressures
  - **Approach temperatures in heat exchangers** considered constant for all operating conditions
  - **Steady state** conditions

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Comparison of IHX cycle, 2-stage cycle with economizer and IHX, and 2-stage cycle with flash tank and IHX

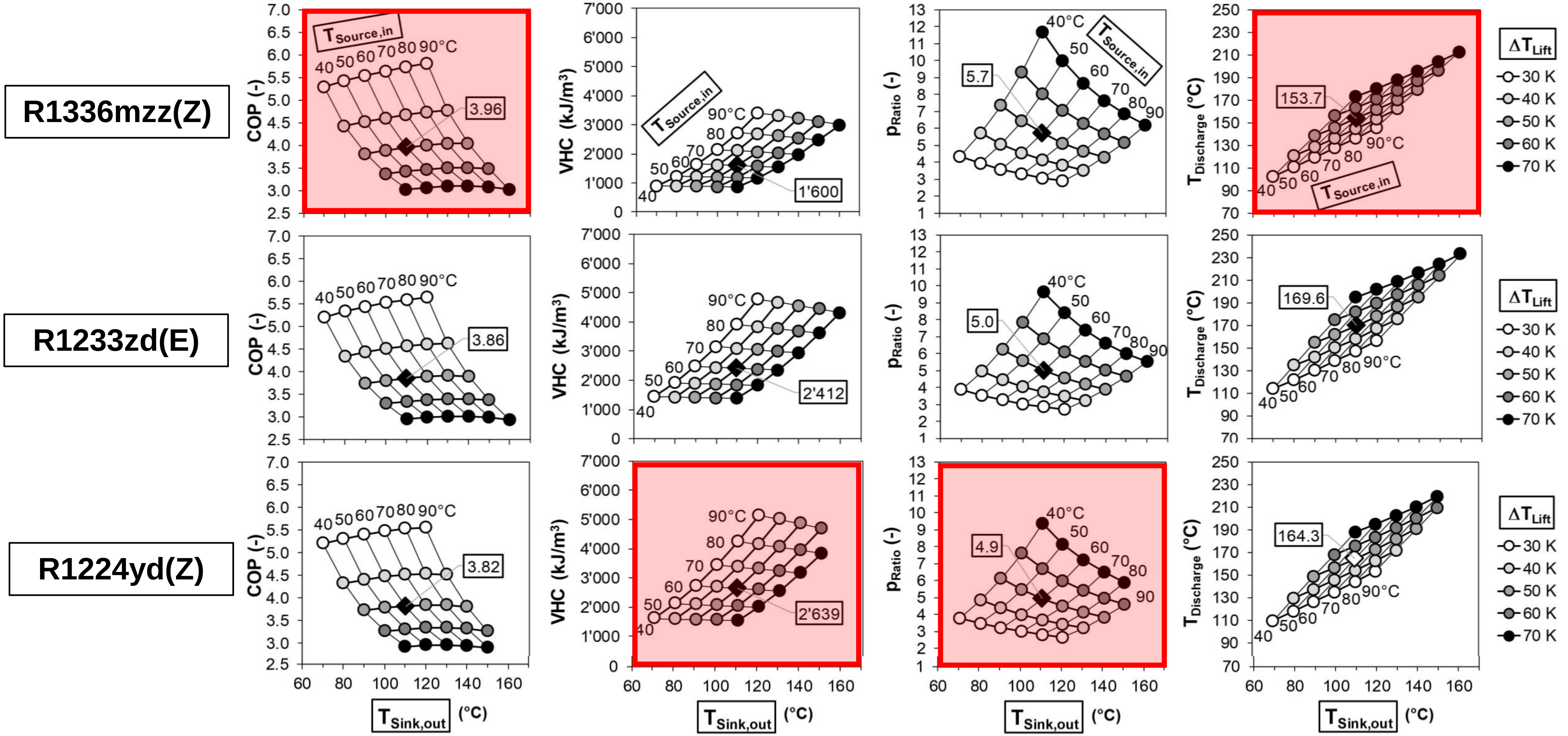
Parameter	R1336mzz(Z)	R1233zd(E)	R1224yd(Z)	R1234ze(Z)	R365mfc	R245fa
One-stage cycle with IHX (% relative to R245fa)						
COP_H (-)	3.96 (+4%)	3.86 (+1%)	3.82 (0%)	3.72 (-2%)	3.98 (+5%)	3.81
VHC (kJ/m³)	1'600 (-43%)	2'412 (-15%)	2'639 (-7%)	3'093 (+9%)	1'329 (-53%)	2'830
ρ_1 (kg/m³)	8.8 (-37%)	11.8 (-17%)	15.3 (+8%)	13.9 (-1%)	6.3 (-55%)	14.1
p_{Ratio} (-)	5.7 (+9%)	5.0 (-5%)	4.9 (-6%)	4.8 (-8%)	6.0 (+15%)	5.2
$T_{Discharge}$ (°C)	154 (-10 K)	170 (+6 K)	164 (0 K)	189 (+25 K)	154 (-10 K)	164
Two-stage cycle with economizer and IHX (*temperature difference compared to IHX cycle)						
COP_H (-)	3.95	3.90	3.84	3.85	3.99	3.82
$p_{Ratio,HS}$, $p_{Ratio,LS}$ (-)	2.4	2.2	2.2	2.2	2.5	2.3
$T_{Discharge,HS}$ (°C)	116 (-38 K)*	118 (-52 K)	116 (-49 K)	125 (-63 K)	116 (-38 K)	116 (-48 K)
$T_{Discharge,LS}$ (°C)	100	107	105	115	100	105
Two-stage cycle with flash tank and IHX (*temperature difference compared to IHX cycle)						
COP_H (-)	4.00	3.98	3.93	3.90	4.03	3.91
$p_{Ratio,HS}$, $p_{Ratio,LS}$ (-)	2.4	2.2	2.2	2.2	2.5	2.3
$T_{Discharge,HS}$ (°C)	120 (-34 K)*	134 (-36 K)	129 (-36 K)	148 (-41 K)	120 (-34 K)	103 (-35 K)
$T_{Discharge,LS}$ (°C)	98	105	103	113	98	103

Simulation results – main performance parameters

Parameter study in the 1-stage IHX cycle

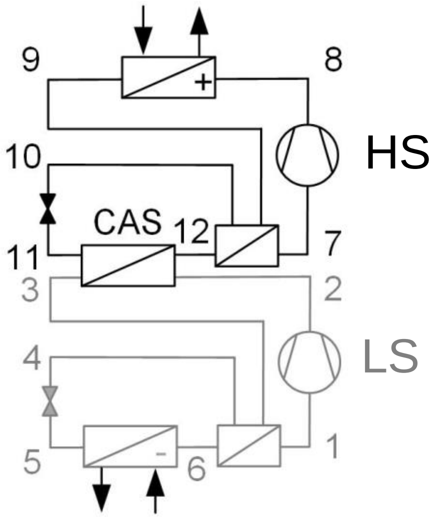
◆ Reference Point 60/110 (50)

$T_{Source,in}/T_{Sink,out}$ (ΔT_{Lift})

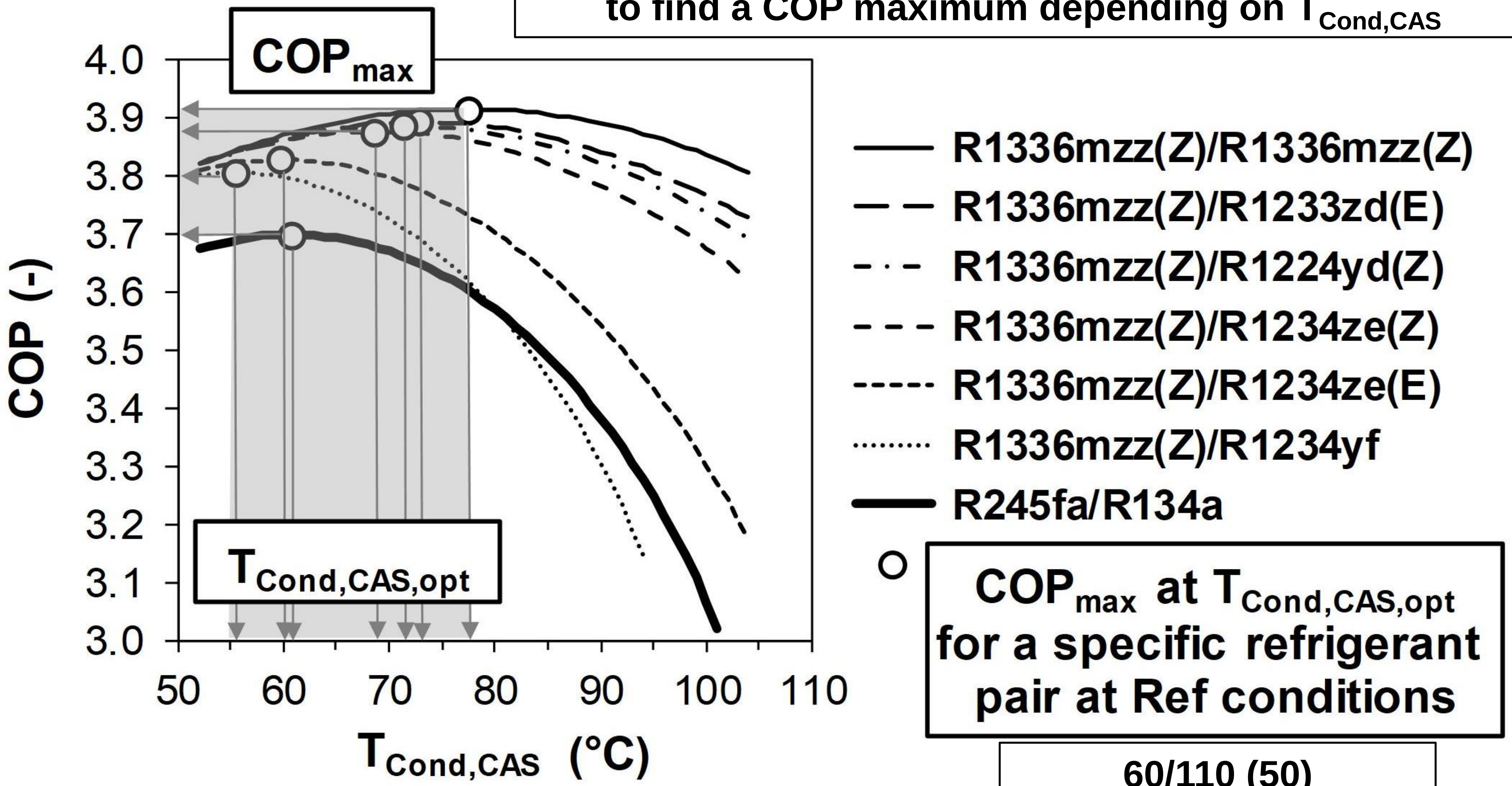


Maximum COP in the 2-stage cascade cycle wit IHX for different refrigerant pairs

Min/Max optimization method (Golden Section) of EES to find a COP maximum depending on $T_{Cond,CAS}$



HS: high stage
LS: low stage



60/110 (50)
$T_{Source,in}/T_{Sink,out}$ (ΔT_{Lift})

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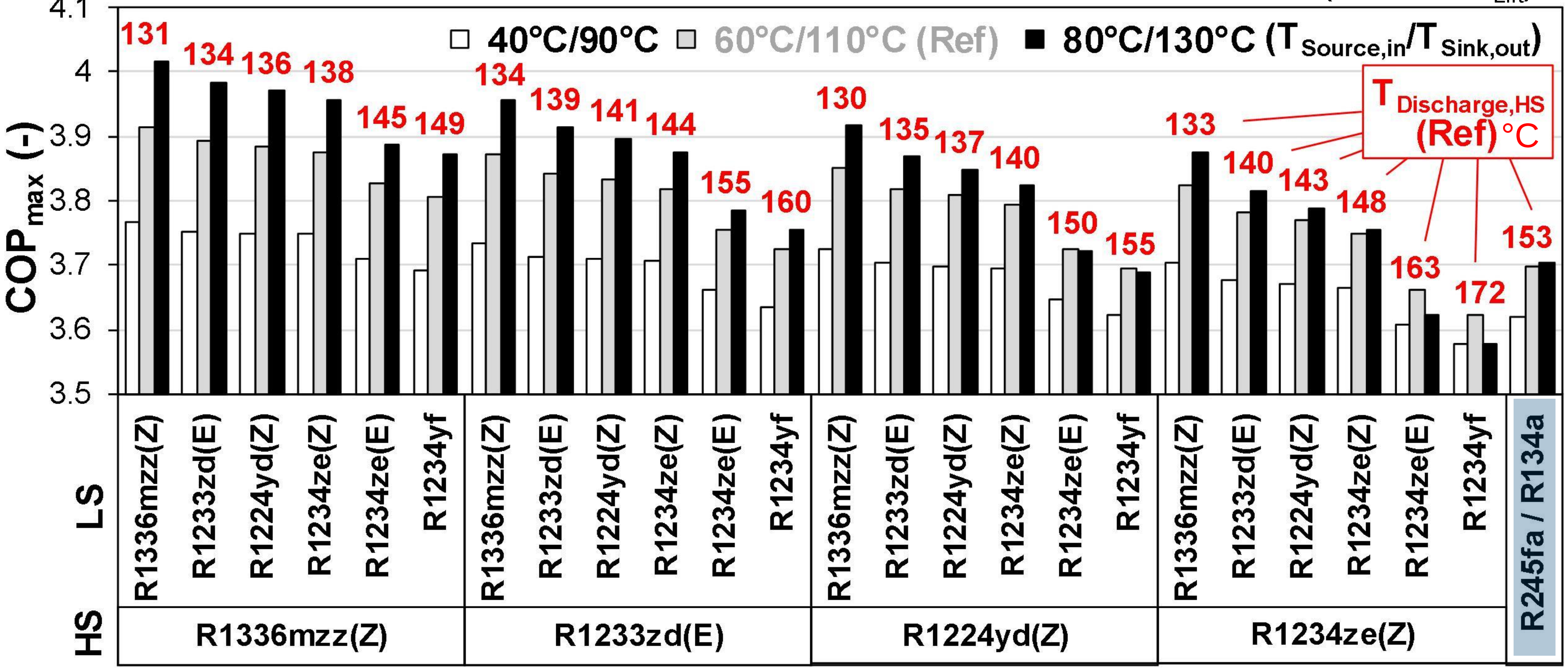
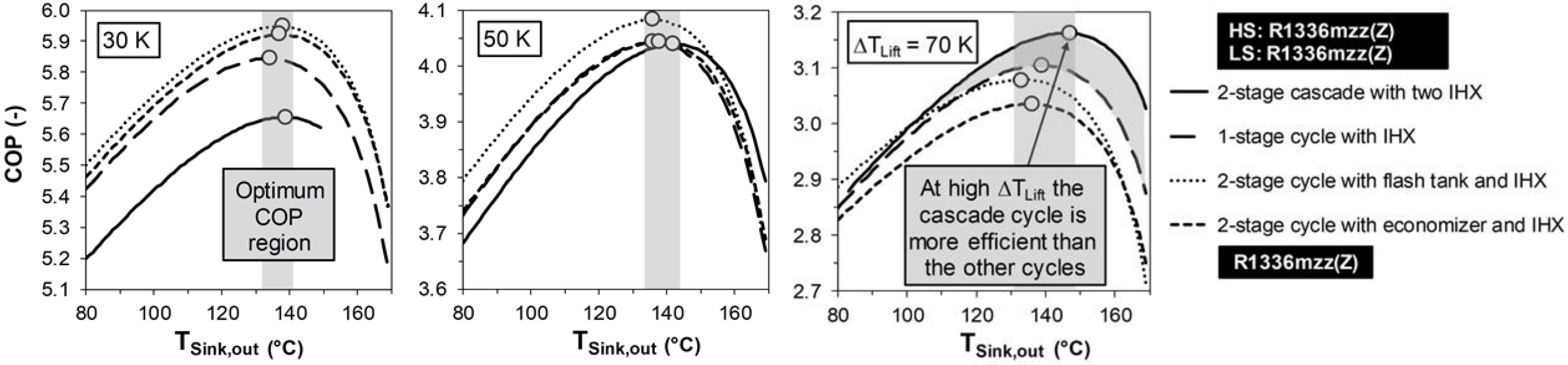
Max. COP in the 2-stage CAS cycle with IHX for 24 pairs of HFO/HCFO refrigerants

(at 50 K ΔT_{Lift})



- Highest COP with R1336mzz(Z) in both stages (COP of 3.91 at 60°C/110°C (Ref) conditions, 6% higher compared to R245fa/R134a)
- $T_{Discharge,HS}$ between 130 and 172 °C (lower than in 1-stage cycle with IHX, but higher than in 2-stage economizer and flash tank cycle

COP comparison of the investigated cycles using R1336mzz(Z) at different temperature lifts (30, 50, and 70 K)



- The 2-stage flash tank (···) and economizer (---) cycles are more efficient for small and medium ΔT_{lift}
- With higher ΔT_{Lift}, the 2-stage cascade cycle (—) compensates for the losses of the CAS heat exchanger and achieves highest efficiency at 70 K lift

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Conclusions

- Simulation results show that **R1336mzz(Z) achieves the highest COP of all investigated HFO and HCFO refrigerants** in the temperature range from 120 to 160 °C, **no matter which heat pump cycle** is used.
- R1336mzz(Z) achieves an **optimal COP** at a heat sink temperature of **about 30 K below the critical temperature**.
- A **compromise** must be found **between COP and VHC** when selecting refrigerants.
- **R1336mzz** is proposed as the next replacement **for R365mfc**, while **R1233zd(E), R1224yd(Z), R1234ze(Z), R1234yf, and R1234ze(E)** are **closer to R245fa**.
- The use of an IHX in the cycle is recommended **to ensure dry compression**.
- A **two-stage cascade cycle** is highly recommended **for high temperature lifts** of 70 K and higher.
- In **further studies**, the theoretical calculations can be extended to **multi-stage extraction cycles** and **cycles with subcooler**, **ejectors**, or **multi-temperature cycles** to further increase efficiency.

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