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# High temperature heat pumps – Theoretical study on low GWP HFO and HCFO refrigerants

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## ABSTRACT

High temperature heat pumps with heat sink temperatures of 100 to 160 °C have great application potential in the food, paper, and chemical industries for heat recovery and process heat generation in drying, sterilization, and evaporation processes. The present study compares the theoretical performance of the low GWP refrigerants R1336mzz(Z), R1224yd(Z), R1234ze(Z), and R1233zd(E) in common one- and two-stage heat pump cycles (internal heat exchanger, economizer, flash tank, cascade) at different temperature levels. The thermodynamic simulations reveal that, depending on the refrigerant and cycle, a trade-off between system complexity (e.g. control, number of components), efficiency, and volumetric heating capacity (VHC) has to be found. Optimal COPs are reached depending on the refrigerant and its heat outlet temperature. R1336mzz(Z) is suggested as the closest drop-in replacement for R365mfc, while R1224yd(Z), R1234ze(Z), and R1233zd(E) are closer to R245fa in terms of COP and VHC. A two-stage cascade with IHX and R1336mzz(Z) in both stages achieved the highest efficiency for high temperature lifts.
Keywords: COP, Cycle, Efficiency, HFO, HCFO, High temperature heat pump, Low GWP refrigerant

## 1. INTRODUCTION

Industrial high temperature heat pumps (HTHP) with heat sink temperatures in the range of 100 to 160 °C are expected to increasingly replace fuel-driven steam boilers for the generation of vapor, hot water and hot air (Arpagaus et al., 2018). The selection of the refrigerant is a key element in the design of HTHPs. The refrigerant must be safe to the environment, future-proof according to F-gas regulations, thermodynamically suitable, efficient, and commercially available. In addition, no or only low flammability (safety groups A1 or A2) are beneficial to reduce the complexity of the safety devices and thus the equipment costs of the heat pump. The critical temperature needs to be high enough to enable subcritical cycle operation, which is often required in industries.

Besides natural refrigerants, synthetic hydrofluoroolefins (HFOs) and hydrochlorofluoroolefins (HCFOs) are considered as part of the fourth generation of low GWP refrigerants to replace hydrofluorocarbons (HFCs) (Calm, 2008). Commercialized members of the HFO family are for instance R1234yf and R1234ze(E) and are possible substitutes for R134a in automotive air conditioners, refrigerators and freezers. The capacities and efficiencies are comparable. Recently, fluorinated butenes such as R1336mzz(Z) and chlorinated compounds like R1233zd(E) or R1224yd(Z) were introduced as attractive replacements for R245fa and R365mfc in HTHPs and Organic Rankine Cycle (ORC) applications. Although HCFOs are chlorinated, their ozone depleting potential (ODP) is negligibly small (~ 0.00034) due to their short lifetime in the atmosphere (AGC Chemicals, 2017; Patten and Wuebbles, 2010).

Table 1 compares the fundamental thermodynamic, environmental and technical characteristics of the mentioned refrigerants. Figure 1 illustrates their T-s and p-T diagrams, as well as the heating COP as a function of the condensation temperature for a basic heat pump cycle calculation at 50 K temperature lift between condensation and evaporation (5 K subcooling, 15 K superheat, 70% isentropic compressor efficiency). The simulated COPs rise to an optimum and decrease with the narrowing of the two-phase region (smaller condensation enthalpy) up to the critical temperature.

**Table 1. Properties of selected HFO and HCFO refrigerants for HTHP applications ([+]for comparison, *40 to 90 °C temperature lift, **fluid properties not yet available in the software EES)**

| Refrigerant | $T_{crit}$ (°C) | $p_{crit}$ (bar) | $p_{Sat,40°C}$ (bar) | $p_{Sat,90°C}$ (bar) | $p_{Ratio}$* (-) | ODP (-) | $GWP_{100}$ (-) | Lifetime (days) | SG | NBP (°C) | M (g/mol) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| R1336mzz(Z) | 171.3 | 29.0 | 1.3 | 5.6 | 4.3 | 0 | 2 | 22 | A1 | 33.4 | 164.1 |
| R1233zd(E) | 165.6 | 35.7 | 2.2 | 8.3 | 3.9 | 0.00034 | 1 | 40.4 | A1 | 18.0 | 130.5 |
| R1224yd(Z) | 155.5 | 33.4 | 2.5 | 9.3 | 3.8 | 0.00012 | <1 | 21 | A1 | 14.0 | 148.5 |
| R1234ze(Z) | 150.1 | 35.3 | 2.9 | 10.8 | 3.7 | 0 | <1 | 10 | A2L | 9.8 | 114.0 |
| R1336mzz(E)** | 137.7 | 31.5 | 3.2 | 12.2 | 3.8 | 0 | 18 | 90 | n.a. | 7.5 | 164.1 |
| R1234ze(E) | 109.4 | 36.3 | 7.7 | 24.8 | 3.2 | 0 | <1 | 16.4 | A2L | -19.0 | 114.0 |
| R1234yf | 94.7 | 33.8 | 10.2 | 30.8 | 3.0 | 0 | <1 | 11 | A2L | -29.5 | 114.0 |
| **R134a[+]** | **101.0** | **40.6** | **10.2** | **32.5** | **3.2** | **0** | **1300** | **13.4 years** | **A1** | **-26.3** | **102.0** |
| **R365mfc[+]** | **186.9** | **32.7** | **1.0** | **4.6** | **4.6** | **0** | **804** | **8.7 years** | **A2** | **40.2** | **148.1** |
| **R245fa[+]** | **154.0** | **36.5** | **2.5** | **10.1** | **4.0** | **0** | **858** | **7.7 years** | **B1** | **14.9** | **134.0** |

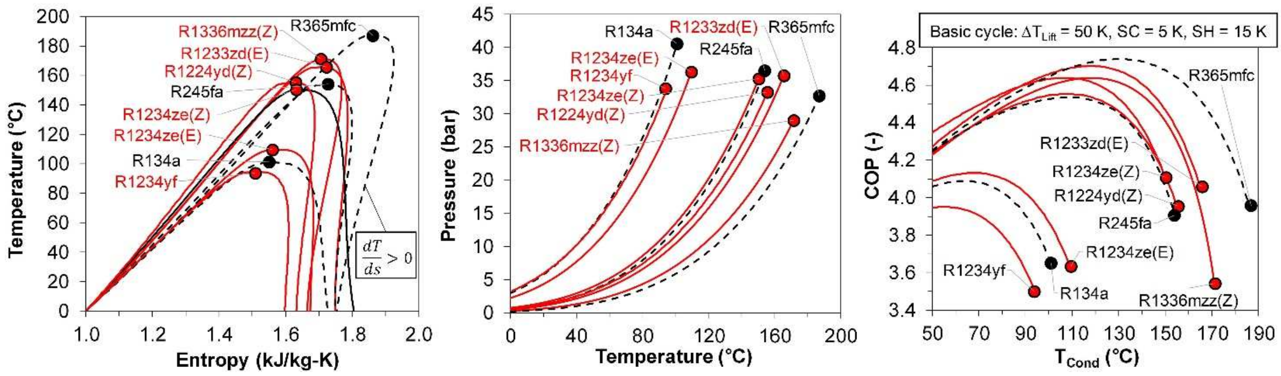


**Figure 1: T-s, p-T diagrams, and simulated COP of selected HFO and HCFO refrigerants**

R365mfc offers the highest COP over the entire temperature range, followed by R1233zd(E) and R1336mzz(Z). R1234ze(Z) and R1224yd(Z) are comparable to R245fa, while R1234yf and R1234ze(E) are similar to R134a. Among the HFO refrigerants, R1336mmz(Z) offers the highest critical temperature of 171.3 °C at a relatively low pressure of 29 bar. It is non-flammable (A1), has zero ODP, a GWP of about 2, and an atmospheric life of 22 days. According to Kontomaris (2014) it is stable up to 250 °C and therefore suitable for applications in waste heat recovery, ORC, and steam generation. Its isomer R1336mzz(E) has a GWP of about 18, a critical temperature of 137.7 °C and offers a higher volumetric heating capacity (VHC) (Juhasz, 2017). The VHC is an important performance parameter for the compressor design as it determines its size and cost. Little information is available on R1234ze(Z) (Fukuda et al., 2017, 2014; Kondou and Koyama, 2014), which is considered mildly flammable (A2L, burning velocity of ≤ 10 cm/s) but difficult to ignite.

A characteristic feature of some of the mentioned refrigerants is a positive slope (dT/ds > 0) of the saturated vapor curves (see Fig. 1, left). Sufficient superheating is thus required to ensure dry compression.

A cycle design with an internal heat exchanger (IHX) appears to be the most promising. Various studies demonstrated that a one-stage cycle with an IHX is an efficient configuration at temperature lifts up to about 40 K (Arpagaus et al., 2018; Bamigbetan et al., 2018; Frate et al., 2019; Helminger et al., 2016; Juhasz, 2017; Kontomaris, 2014; Mateu-Royo et al., 2018; Nilsson et al., 2017). As the temperature lift rises, a two-stage cycle becomes a more efficient system configuration. As shown in Table 2, several studies investigated the theoretical efficiency of HFO and HCFO refrigerants in different heat pump configurations. Efficiency optimizations are achieved in particular by the introduction of IHXs, two-stage cycles, and multi-stage extraction cycles.

The simulations of Mateu-Royo et al. (2018) in two-stage cycles and heat sink temperatures of up to 150 °C showed the highest COP using R601 (n-pentane), followed by R1336mzz(Z) and R1233zd(E). Mota-Babiloni et al., (2018) presented a theoretical study of a two-stage cascade using R1233zd(E), R1336mzz(Z), R1224yd(Z) and pentane in the high-stage (HS) and R1234yf, R1234ze(E), R600 (butane), R600a (isobutene) and R290 (propane) in the low-stage (LS). The highest efficiency was reached with the refrigerant pair pentane/butane (HS/LS). For HFO

refrigerants the combination R1336mzz(Z)/R1234ze(E) (HS/LS) achieved the highest COP, whereas R1224yd(Z)/R1234yf showed the lowest efficiency among the investigated refrigerants.
Cao et al. (2014) conducted thermodynamic and economic analyses of various two-stage cycles with refrigerant R152a and showed that a two-stage heat pump with flash tank provided highest COPs and lowest payback times. Hu et al. (2017) analysed two-stage and three-stage compression systems with R1234ze(Z) for waste heat recovery in industrial processes up to 120 °C. Compared to a one-stage cycle, the COP improvements were between about 9% and 15%. Kondou and Koyama (2014) explored different multi-stage and cascade cycles for upgrading waste heat from 80 to 160 °C and compared the efficiencies of R365mfc, R1234ze(E), and R1234ze(Z). A three-stage extraction cycle with R1234ze(Z) achieved the highest efficiency thanks to reduced exergy losses in the expansion valve and the condenser. A two-stage cascade cycle with R365mfc/R1234ze(Z) also provided high COPs and practical benefits (i.e. compressor control, lubricant selection).

**Table 2. Theoretical studies with HFO and HCFO refrigerants in different HTHP cycles**

| HFO and HCFO refrigerants | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| R1336mzz(Z) | R1233zd(E) | R1224yd(Z) | R1234ze(Z) | R1234ze(E) | R1336mzz(E) | R1234yf | R365mfc | R245fa | | Basic cycle | 1-stage with IHX | 2-stage with IHX | 2-stage with economizer and | 2-stage with flash tank and | 2-stage extraction | 2-stage cascade extraction | 2-stage cascade with IHX | Triple tandem with IHX | 3-stage with flash tanks | 3-stage extraction | Reference |
| | X | | X | X | | | X | X | | X | | | | | X | | | | | X | (Fukuda et al., 2017, 2014) |
| | X | | X | X | | | X | X | | | | | | | X | X | | X | | X | (Kondou and Koyama, 2015) |
| X | | | | X | X | X | | X | | X | | | | | | | | | | | (Juhasz, 2017; Kontomaris, 2014) |
| X | | | | | | | | | | | X | | | | | | | | | | (Helminger et al., 2016) |
| X | X | X | | X | | X | | | | | | | | | | | X | | | | (Mota-Babiloni et al., 2018) |
| | | | X | | | | | | | X | | | X | | | | | | X | | (Hu et al., 2017) |
| X | X | X | X | | | | X | | | X | | | | | | | | | | | (Frate et al., 2019) |
| X | X | | | | | | | X | | | X | X | | | | | | | | | (Mateu-Royo et al., 2018) |
| X | X | | X | X | | | X | X | | X | | | | | | | | | | | (Bamigbetan et al., 2018) |
| X | X | X | X | X | | | X | X | | | X | | | | | | | | | | (Arpagaus et al., 2018) |
| **X** | **X** | **X** | **X** | **X** | | **X** | **X** | **X** | | | **X** | | **X** | **X** | | | **X** | | | | **This study** |

As Table 2 shows, a comprehensive comparison of HFO and HCFO refrigerants with low GWP in different heat pump cycles is still a research gap. As a follow-up study to the review paper by Arpagaus et al. (2018), this study examines the suitability of the working fluids R1336mzz(Z), R1233zd(E), R1224yd(Z), R1234ze(Z), R1234ze(E) and R1234yf for HTHP application and presents simulations in the following heat pump cycles:

- One-stage cycle with IHX
- Two-stage cycle with economizer and IHX
- Two-stage cycle with flash tank and IHX
- Two-stage cascade with two IHX

The goal of this study is the evaluation of the thermodynamic efficiency (COP), volumetric heating capacity (VHC), pressure ratio, and discharge temperature of the selected HFO and HCFO refrigerants in the different heat pump cycles (see Table 2). In the two-stage cascade cycle, 24 refrigerant pairs are compared with each other. Finally, the results are compared with today's HFC refrigerants R365mfc, R245fa, and R245fa/R134a for potential drop-in replacements.

## 2. SIMULATION MODEL

Simplified thermodynamic cycle models have been developed in Engineering Equation Solver Software (EES, Version 10.268) (Klein, 2017). Figure 2 shows the schematics of the investigated cycles with the corresponding log(p)-h diagrams and the temperature profiles in the heat exchangers. The approach temperatures were considered constant for all operating conditions and are summarized in Table 3. The cycles were simulated in steady state conditions for several temperatures and refrigerant combinations using the following basic assumptions:

- No parasitic heat losses and pressure drops
- Isenthalpic expansion
- Constant compressor isentropic efficiency of $\eta_{is} = 0.7$
- Intermediate pressure in the two-stage economizer and flash tank cycle calculated as the geometric mean (square root) of the evaporation and condensation pressures

The operating point W60/W110 (50 K temperature lift) was considered as reference point (Ref) with constant temperature glides in the heat source and sink of 10 K. A parameter study was performed by varying the heat sink outlet temperature from 70 to 160 °C and the heat source inlet temperature from 40 to 90 °C (i.e. potential waste heat from an industrial process).
Finally, the COP was calculated as the ratio from the heating capacity and the total compressor work (i.e. in the IHX cycle: COP = $(h_2\text{-}h_3) / (h_2\text{-}h_1)$). The VHC was calculated in the IHX cycle as the product of the enthalpy difference supplied to the heat sink and the suction vapor density (VHC = $(h_2\text{-}h_3)\cdot\rho_1$)). It allows an estimation of the compressor size.

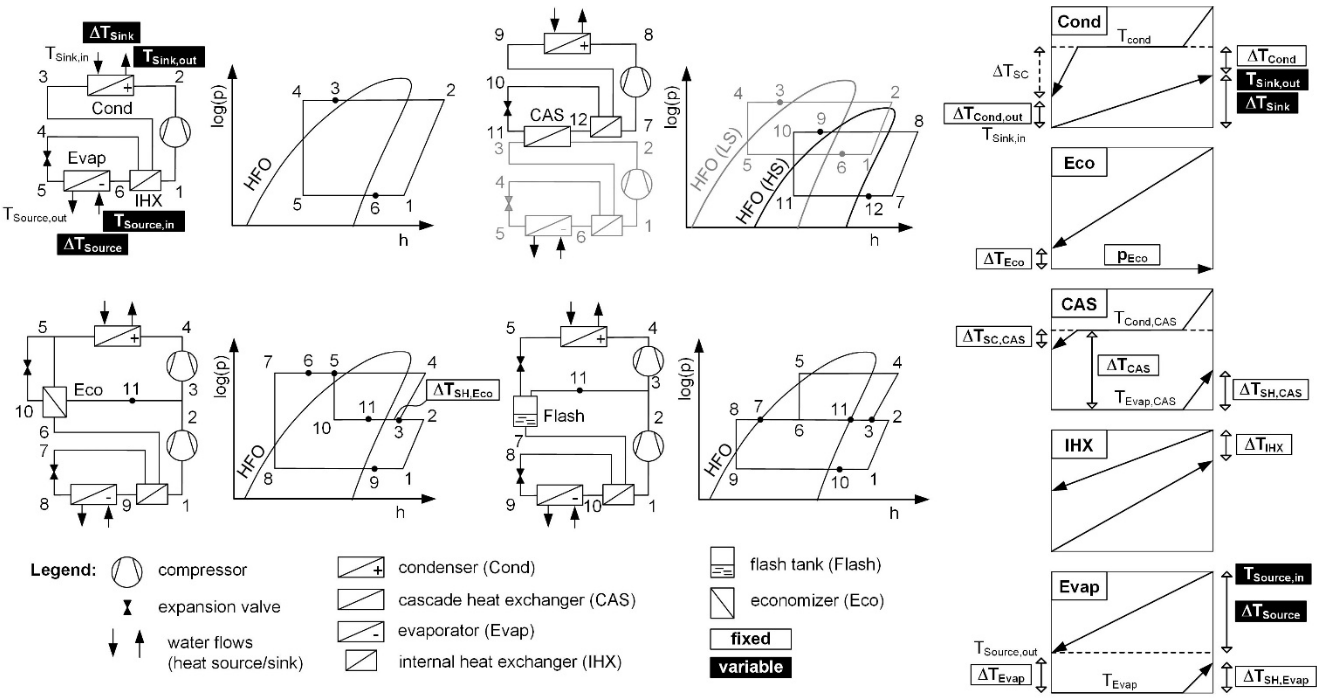


**Figure 2: Investigated heat pump cycles with log(p)-h diagrams and approach temperatures in the heat exchangers (Cond, Eco, CAS, IHX, Evap)**

**Table 3. Fixed parameters, reference conditions and variation range of the variable parameters (*12 K superheat for R1336mzz(Z) and R365mfc to assure dry compression)**

| Fixed parameters | | | | Variable parameters | Reference | Range |
|---|---|---|---|---|---|---|
| $\Delta T_{Cond}$ | 2 K | $\Delta T_{Eco}$ | 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 | $\Delta T_{IHX}$ | 3 K | $\Delta T_{Lift}$ ($T_{Sink,out}$ - $T_{Source,in}$) | 50 K | 30 to 70 K |
| $\Delta T_{CAS}$ | 3 K | $\Delta T_{Evap}$ | 3 K | $\Delta T_{Sink}$ | 10 K | 5 to 30 K |
| $\Delta T_{SH,CAS}$ | 3 K | $\Delta T_{SH,Evap}$ | 5 K | $\Delta T_{Source}$ | 10 K | 5 to 30 K |

## 3. SIMULATION RESULTS AND DISCUSSION

Table 4 compares the cycle performances of the investigated HFO and HCFO refrigerants at reference conditions in the IHX, economizer, and flash tank cycles. The values in brackets indicate the relative comparison to R245fa. The data show that the COP and the pressure ratio of R1336mzz(Z) are the highest among the investigated HFO and HCFO refrigerants, and the lowest for R1234ze(Z). However, the variation of the COPs from 3.72 to 3.96 stays within a few percent. Compared to R245fa, the COPs are also very similar. The calculated pressure ratios of 4.8 to 5.7 are considered manageable for common compressors. The VHC of R1336mzz(Z) and R365mfc are significantly lower than for the other substances due to the lower suction vapor densities ($\rho_1$), which in practice, will result in larger compressors to achieve comparable heating capacity. Compared to a basic cycle, the IHX provides additional superheating of the suction gas, which in turn increases the discharge gas temperature of the compressor and the potential heating capacity of the heat pump application. On the other side, too high temperatures can lead to overheating of the compressor motor and thermal decomposition of the lubricant oil. As a conservative hypothesis the compressor oil temperature should not exceed 180 °C (Frate et al., 2019).

**Table 4. Comparison of the main performance parameters for the selected refrigerants in the IHX cycle, two-stage economizer cycle and two-stage flash tank cycle at reference conditions.**

| 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 |
| $\rho_1$ (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 (-6%) | 170 (+4%) | 164 (0%) | 189 (+15%) | 154 (-6%) | 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 |

Figure 3 illustrates the results of the parameter study in the one-stage IHX cycle for the HFO and HCFO refrigerants over the entire operating range. The graphs provide a more qualitative comparison of the examined refrigerants. In general, the COP increases with heat sink temperature, heat source temperature, and smaller temperature lift. The VHC increases with increasing heat sink temperature and smaller temperature lift. A higher VHC is advantageous for positive displacement compressors, as it requires a smaller swept volume at a given capacity, and thus smaller size and investment costs. Common values are between 3’000 and 6’000 kJ/m³ (Arpagaus et al., 2018). Overall, the analyses indicate that R1336mzz(Z) is the most suitable replacement fluid for R365mfc, whose COP and VHC are comparable (similar COP and 20% higher VHC). R1233zd(E), R1223yd(Z), and R1234ze(Z) are closest to R245fa in terms of COP and VHC. When selecting a refrigerant for a HTHP application, it is necessary to make a compromise between efficiency and capacity. As soon as the VHC becomes a decision parameter, R1233zd(E) becomes favorable. An efficiency loss of about 3% compared to R1336mzz(Z) is compensated with approximately 50% higher VHC. This is consistent with the calculations of Frate et al. (2019) in a basic cycle.

High compressor discharge temperatures ($T_{Discharge}$) can be observed especially for R1234ze(Z). To mitigate the relatively high discharge temperatures in the one-stage cycle with IHX, a two-stage cycle design with economizer functions is a valuable option. As shown in the Table 4, the two-stage cycles significantly reduce the discharge temperatures in the upper compressor stage (i.e. 34 to 41 K and 38 to 63 K reduction for the flash tank and closed economizer cycle). In the economizer, a certain amount of two-phase refrigerant is fed into the suction line of the high-stage compressor, where it is mixed with the discharge gas of the low-pressure compressor. This enables precise control of a specified superheat value at the inlet of the high-stage compressor (e.g. 5 K superheat, or 12 K for R1336mzz(Z) and R365mfc, which exhibit a saturation curve dT/ds > 0). The flash tank system achieves slightly higher efficiency (1 to 3%) and about 2 K additional reduction in discharge temperature (see Table 4). Here, saturated vapor is pulled from the top of the flash tank and is fed to the suction line of the high-stage compressor. The superheat is controlled by mixing the saturated vapor with the discharge gas of the first-stage compressor.

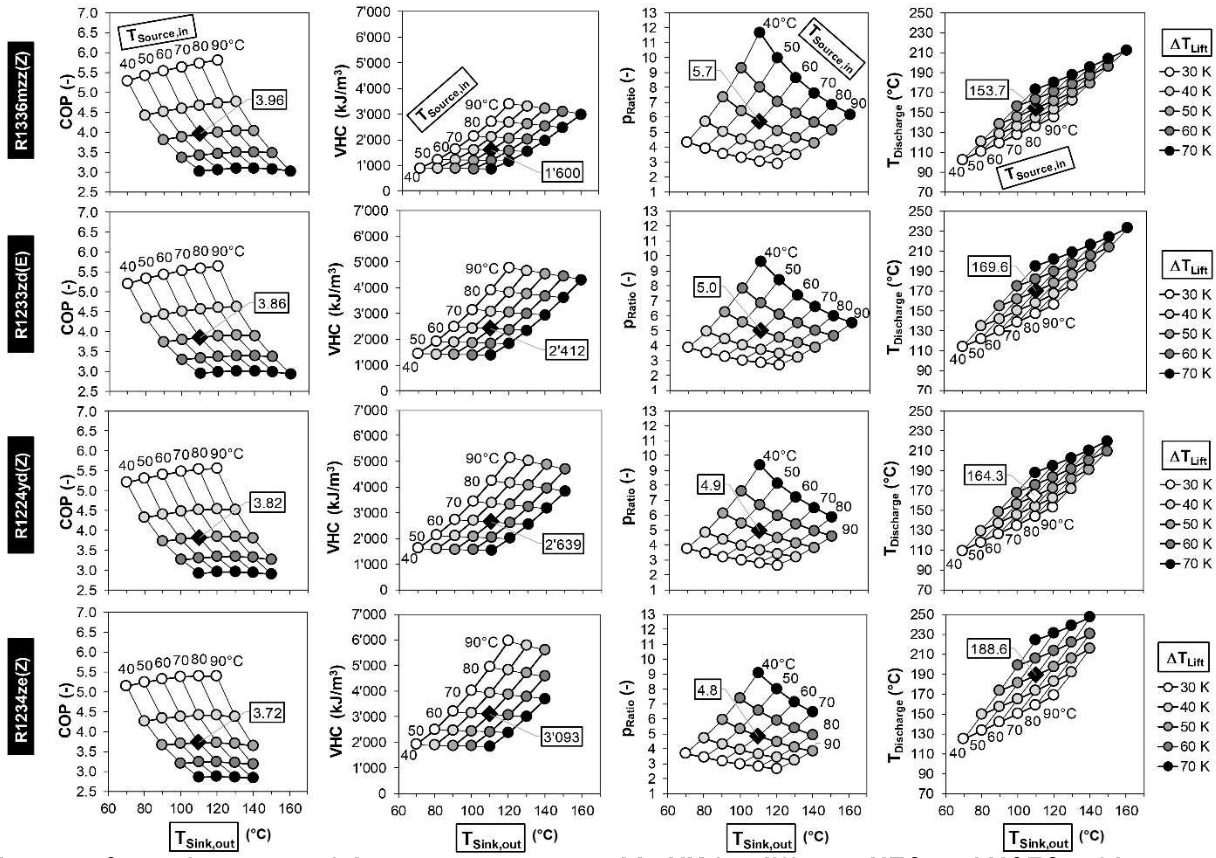


**Figure 3: Operating maps of the one-stage cycle with IHX for different HFO and HCFO refrigerants. (A) COP, (B) VHC, (C) pressure ratio, (D) discharge temperature.**

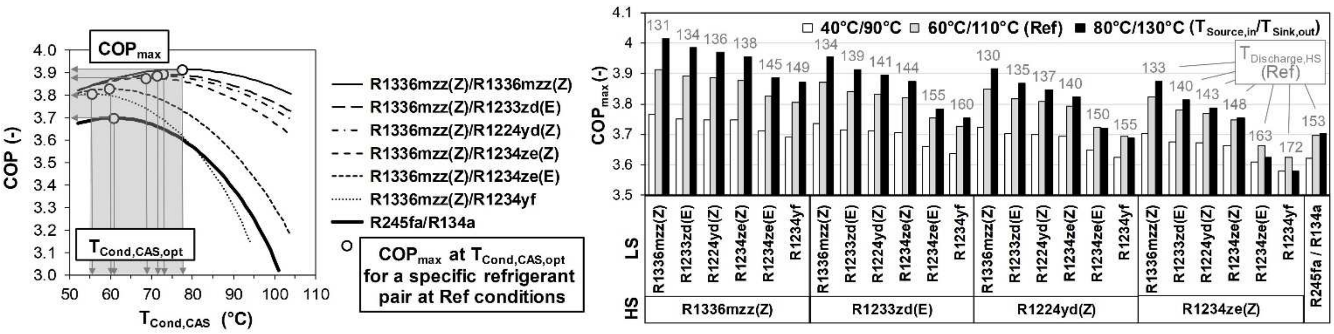


**Figure 4: Maximum COP in the two-stage cascade cycle with IHX for different refrigerant pairs**

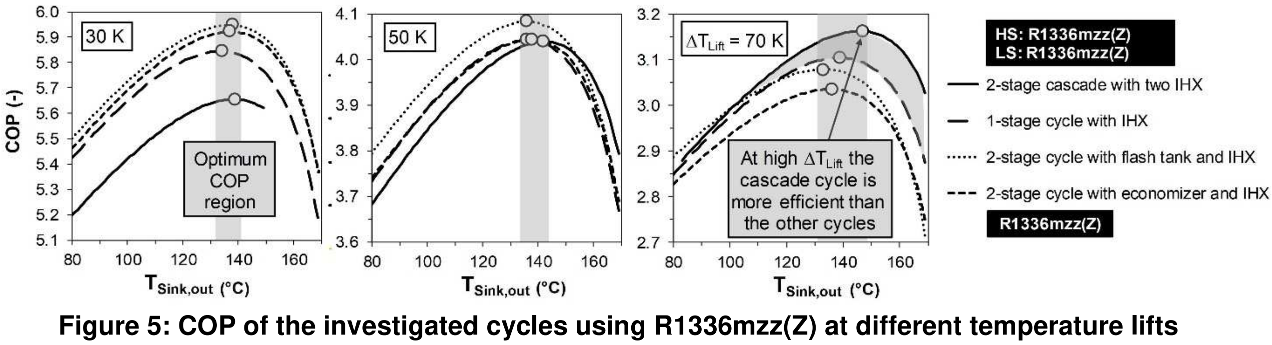


**Figure 5: COP of the investigated cycles using R1336mzz(Z) at different temperature lifts**

The two-stage cascade cycle enables testing different refrigerant combinations in the LS and HS cycles. Compared to a one-stage system, the pressure ratio per stage is lower and the efficiency higher, so that a higher COP can be achieved (Figure 5). In addition, there are no oil management issues between the two stages, which may compensate for higher installation and maintenance costs. A disadvantage is the temperature gap in the intermediate CAS heat exchanger ($\Delta T_{CAS}$ = 3 K) reducing efficiency. Depending on the operating conditions and refrigerant combination, an optimum intermediate temperature needs to be found to achieve maximum COP. The approach used in this study utilizes the Min/Max optimization method (Golden Section) of EES to find a COP maximum depending on the condensation temperature of the LS cycle ($T_{Cond,CAS}$).

Figure 4 (left) shows some COP curves for different refrigerant pairs as a function of $T_{Cond,CAS}$ at reference point condition. The optimal values are in the range of about 55 to 78 °C. Figure 4 (right) compares the optimal COPs of 24 pairs of HFO and HCFO refrigerants. R1336mzz(Z), R1233zd(E), R1224yd(Z), and R1234ze(Z) were selected for the HS, R1336mzz(Z), R1233zd(E), R1224yd(Z), R1234ze(Z), R1234yf, and R1234ze(E) for the LS. The presented results are calculated at a constant temperature lift of 50 K. The highest COP was achieved using R1336mzz(Z) in both stages (COP of 3.91 at Ref conditions 60 °C/110 °C, grey bars), followed by R1336mzz(Z)/R1233zd(E), R1336mzz(Z)/R1224yd(Z), and R1336mzz(Z)/R1234ze(Z) with a similar COP of 3.9. R1336mzz(Z)/R1234ze(E) presented a slightly higher performance than R1336mzz(Z)/R1234yf which is in agreement with simulations by Mota-Babiloni et al. (2018). Compared to a HTHP cascade with HFC refrigerants R245fa/R134a, the combination of R1336mzz(Z)/R1336mzz(Z) resulted in a 6% higher COP. The discharge temperatures were between 130 and 172 °C and thus lower than in the one-stage cycle with IHX, but higher than in the two-stage economizer and flash tank cycle.

Figure 5 shows the COP for the different cycles with refrigerant R1336mzz(Z) as a function of the heat sink outlet temperature for 30, 50, and 70 K temperature lift. As can be seen, the two-stage flash tank and economizer cycles are more efficient for small and medium lifts. With a higher lift, the two-stage cascade compensates for the losses of the cascade heat exchanger and clearly achieves the highest efficiency at 70 K lift.

## 4. CONCLUSIONS

The simulation results show that R1336mzz(Z) achieves the highest COP of all HFO and HCFO refrigerants in the temperature range from 120 to 160 °C, no matter which heat pump cycle is used. Each refrigerant 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 for high temperature lifts of 70 K and higher. In further studies, the 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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## NOMENCLATURE

| | | | |
|---|---|---|---|
| *CAS* | cascade heat exchanger | *in, out* | inlet, outlet |
| *Cond* | condenser | *Lift* | temperature lift from heat source to sink |
| *COP* | coefficient of performance (-) | *ODP* | ozone depletion potential |
| *$\Delta T$* | temperature difference (K) | *opt, max* | optimal, maximum |
| *Eco* | economizer | *p* | pressure (bar) |
| *Evap* | evaporator | *SC, SH* | subcooling, superheating |
| *HFO* | hydrofluorolefin | *SG* | safety group classification |
| *HCFO* | hydrochlorofluoroolefin | *Sink, Source* | heat sink, heat source |
| *HS, LS* | high-stage, low-stage | *T* | temperature (°C) |
| *IHX* | internal heat exchanger | *VHC* | volumetric heating capacity (kJ/m$^3$) |

## REFERENCES


AGC Chemicals, 2017. AMOLEA® 1224yd, Technical Information, ASAHI Glass Co., Ltd.

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

Bamigbetan, O., Eikevik, T.M., Nekså, P., Bantle, M., Schlemminger, C., 2018. Theoretical analysis of suitable fluids for high temperature heat pumps up to 125 °C heat delivery. Int. J. Refrig. 92, 185–195.

Calm, J.M., 2008. The next generation of refrigerants - Historical review, considerations, and outlook. Int. J. Refrig. 31, 1123–1133.

Cao, X.-Q., Yang, W.-W., Zhou, F., He, Y.-L., 2014. Performance analysis of different high-temperature heat pump systems for low-grade waste heat recovery. Appl. Therm. Eng. 71, 291–300.

Frate, G.F., Ferrari, L., Desideri, U., 2019. Analysis of suitability ranges of high temperature heat pump working fluids. Appl. Therm. Eng. 150, 628–640.

Fukuda, S., Kondou, C., Takata, N., Koyama, S., 2014. Low GWP refrigerants R1234ze(E) and R1234ze(Z) for high temperature heat pumps. Int. J. Refrig. 40, 161–173.

Fukuda, S., Kondou, C., Takata, N., Koyama, S., 2017. Thermodynamic Analysis on High Temperature Heat Pump cycles using Low-GWP refrigerants for Heat recovery. In: 12th IEA Heat Pump Conference 2017, Rotterdam. pp. 1–7.

Helminger, F., Kontomaris, K., Pfaffl, J., Hartl, M., Fleckl, T., 2016. Measured Performance of a High Temperature Heat Pump with HFO-1336mzz-Z as the W orking F luid. In: ASHRAE 2016 Annual Conference, St. Louis, Missourii, 25-29 June 2016. pp. 1–8.

Hu, B., Wu, D., Wang, L.W., Wang, R.Z., 2017. Exergy analysis of R1234ze(Z) as high temperature heat pump working fluid with multi-stage compression. Front. Energy 1–10.

Juhasz, J.R., 2017. Novel Working Fluid HFO-1336mzz(E) for Use in Waste Heat Recovery Application. In: 12th IEA Heat Pump Conference, Rotterdam, May 14-17, 2017. pp. 1–10.

Klein, S.A., 2017. Engineering Equation Solver (Version V10.268): F-Chart Software.

Kondou, C., Koyama, S., 2014. Thermodynamic Assessment of High-Temperature Heat Pumps for Heat Recovery. In: 15th International Refrigeration and Air Conditioning Conference at Purdue, July 14-17, 2014. pp. 1–10.

Kondou, C., Koyama, S., 2015. Thermodynamic assessment of high-temperature heat pumps using low-GWP HFO refrigerants for heat recovery. Int. J. Refrig. 53, 126–141.

Kontomaris, K., 2014. Zero-ODP, Low-GWP, Nonflammable Working Fluids for High Temperature Heat Pumps. In: ASHRAE Annual Conference, Seattle, Washington, July 1, 2014. pp. 1–40.

Mateu-Royo, C., Navarro-Esbrí, J., Mota-Babiloni, A., Amat-Albuixech, M., Molés, F., 2018. Theoretical evaluation of different high-temperature heat pump configurations for low-grade waste heat recovery. Int. J. Refrig. 90, 229–237.

Mota-Babiloni, A., Mateu-Royo, C., Navarro-Esbrí, J., Molés, F., Amat-Albuixech, M., Barragán-Cervera, Á., 2018. Optimisation of high-temperature heat pump cascades with internal heat exchangers using refrigerants with low global warming potential. Energy 165, 1248–1258.

Nilsson, M., Risla, H.N., Kontomaris, K., 2017. Measured performance of a novel high temperature heat pump with HFO-1336mzz-Z as the working fluid. In: 12th IEA Heat Pump Conference 2017, Rotterdam. pp. 1–10.

Patten, K.O., Wuebbles, D.J., 2010. 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, 10867–10874.