Thermodynamic assessment of ultra-low-global warming potential refrigerants for space and water heaters

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ABSTRACT

The current paper studies the most suitable ultra-low- global warming potential (GWP) (GWP< 30) candidates in the market, considering also its grade of flammability and toxicity, for heat pumps employed for different space heating and domestic hot water (DHW) applications. A pre-design thermodynamic model has been developed to evaluate the performance and size limits for any subcritical or transcritical heat pump under certain working conditions. This generic model is based on pinch point approach, so it does not depend on a certain type of heat exchangers, it only depends on the external working conditions. The results showed that the all subcritical ultra-low-GWP, nonflammable, and nontoxic refrigerants considered have either lower coefficient of performance (COP) or

volumetric heating capacity (VHC) compared with the reference high-GWP refrigerants R-410A and R-134a. Additionally, the only refrigerants with higher COP, such as R-717 (Ammonia) or R-290 (Propane), are either extremely flammable or toxic. For the applications need high water-side temperature lift, the transcritical refrigerants R-744 (CO_2) and R-170 (Ethane) showed the best performance, regarding both COP and VHC values, of all the refrigerants studied. R-161, R-1270 (Propylene), and R-1234yf presented a balanced performance in both space heating and DHW applications. This makes them potential candidates to be employed in subcritical multi-temperature levels heat pumps.

KEYWORDS

Heat pump, Water heaters, Ultra-low-GWP refrigerants, Pinch point, Thermal match.

NOMENCLATURE

COP	coefficient of performance (-)
c_p	specific heat ($J \cdot kg^{-1} \cdot K^{-1}$)
$\dot{E}_{elec}$	electrical power (W)
h	specific enthalpy ($J \cdot kg^{-1}$)
i	cell index for evaporator (-)
j	Cell index for condenser/gas cooler (-)
$\dot{m}$	mass flow rate ($kg \cdot s^{-1}$)
n	number of discretized cells
NBP	normal boiling point (°C)
P	pressure (Pa)
Pr	pressure ratio (-)
$\dot{Q}$	thermal power (W)
rps	compressor speed ($rev \cdot s^{-1}$)
s	specific entropy ($J \cdot kg^{-1} \cdot K^{-1}$)
SC	subcooling (K)
SH	superheat (K)

T	temperature (°C)
v	specific volume ($m^3 \cdot kg^{-1}$)
VHC	volumetric heating capacity ($J \cdot m^3$)
V_{swept}	swept volume ($m^3 \cdot rev^{-1}$)
η	thermal efficiency (-)
ρ	density ($kg \cdot m^3$)

SUBSCRIPTS

appr	approach
cell	discretized cell of the heat exchanger
comp	compressor
cond	Condenser/condensation
crit	critical
elec	electrical
evap	Evaporator/evaporation
gc	gas cooler
in	inlet
is	isentropic
max	maximum
mech	mechanical
out	outlet
pp	Pinch point
ref	refrigerant
sat	saturated
sf	secondary fluid
tot	total
vol	volumetric
w	water

1. INTRODUCTION

Based on Eurostat's 2018 figures, 75% of heating and cooling demand, in the European Union (EU), is still generated from fossil fuels while only 19% is generated from renewable energy (European Commission, 2020). This shows a great opportunity for CO_2 reduction by replacing the use of conventional fossil fuel-based equipment, such as water boilers, electrical heaters, etc., with more efficient heat pump systems, which also allow for better integration of renewable energy sources (RES).

Affected by the Montreal protocol, the heat pump sector has been experiencing a significant change influenced by the reduction in the use of high global warming potential refrigerants (United Nations, 1989). Notwithstanding the extended use of hydrofluorocarbons (HFCs) on the current commercial heat pump systems, with R-410A and R-404A as most employed refrigerants in heating and refrigeration applications respectively, a stepped phase-out of high-GWP refrigerant is currently been applied by F-Gas regulation, which limits the commercialization and use of fluorinated gases with high-GWP (European Union, 2014).

The choice of a substitutive refrigerant for a high-GWP one presents many limitations. This is not only related to the thermodynamic efficiency, but other factors, like commercial availability, production cost, and safety. In order to compare fairly between different refrigerants, firstly it is necessary to optimize the cycle performance to reach the highest possible COP regarding each refrigerant. Optimizing the heat exchangers, evaporator and condenser, is the most crucial process as it affects directly the condensation and evaporation temperatures which, in turn, affect the compressor pressure ratio and the system COP. Traditionally, it has always been assumed that the temperatures of source and sink are always constant (this means infinite heat reservoir).

But this hypothesis simplifies the analysis, since the optimal point of the cycle is achieved when the evaporation and condensation temperatures are equal to the source and sink temperatures, in the case of an infinite conductance (UA) heat exchanger. To consider a finite and typical conductance of the heat exchangers, what is normally done is imposing a temperature difference between source/sink and evaporation/condensation temperatures of approximately 15 K and a degree of subcooling (SC) and superheat (SH) between 5 K and 10 K.

An example of this kind of simplified analysis can be seen in the work published by Kujak and Schultz (2016). The authors listed and assessed both the past refrigerants and the current ones, considering the possible low-GWP alternatives, including the new hydrofluoroolefins (HFOs) mixtures. This study was done using a simple vapor compression cycle at different typical constant evaporation and condensation temperatures for air conditioning and refrigeration applications.

However, there are two limitations in this type of analysis. Firstly, the difficulty of analyzing non-azeotropic (zeotropic) mixtures, as a constant saturation temperature does not exist in this case. Secondly, the difficulty of analyzing transcritical refrigerants, such as carbon dioxide (CO_2), making the problem irresolvable.

On the other hand, in space heating and DHW applications, the consumer-side elements, such as the fan-coil terminal units, hot water storage tanks, etc., impose a certain temperature lift in the heat carrier fluid. With this temperature lift, the optimal condensation and evaporation temperatures are not evident, since they must be analyzed considering a degree of SC and SH. In this case, the assumption of having constant saturation temperatures near the source and sink temperatures is not a realistic one.

Pinch point methodology allows to study the previously mentioned situations which usually associated with local changes in fluids properties, temperature, and specific heat, in relation with the local heat transfer rate. The terminology “pinch point” is defined as the location where the temperature difference between the two fluid streams is a minimum. An excellent summary of this methodology can be found in Chapter 8, Nellis and Klein (2009). In this way it is possible to optimize the saturation temperatures with the required degrees of SC and SH to ensure minimum pinch points inside the evaporator and condenser, which, in turn, result to an optimum performance.

One of the first works that used the pinch point methodology for optimizing refrigeration cycles was the work done by Venkatarathnam et al. (1996) and (1999). The authors theoretically studied zeotropic mixtures and their composition to improve the cycle efficiency by matching the temperature lift in the secondary fluid with the temperature glide (difference between dew and bubble temperatures) of the mixture. The results were very interesting as they allow to identify criteria to match between the application needs and the required mixture characteristics. Later, Dai et al. (2015) evaluated, based also on pinch point approach, the heat pump performance using different CO_2 blends for DHW applications. The authors concluded that the maximum COP can be obtained when two pinch points occur simultaneously inside the condenser/gas cooler, one at the beginning of the two-phase zone and the other at the end of subcooling zone. Similar conclusions were reported by Pitarch et al. (2017) in their study to assess the optimal subcooling for subcritical heat pumps using different refrigerants.

The previously mentioned works employed the pinch point approach methodology for very particular cases; however, still there is no clear answer for the main question: What are the proper criteria to asses and select low-GWP alternatives for the current high-GWP refrigerants?

The most precise and rigorous study concerning this issue is the one published by McLinden et al. (2017) where 27 pure refrigerants in three different refrigeration cycle configurations of air conditioning applications are studied (evaporation and condensation temperatures of 10ºC and 40ºC, respectively). They focused on refrigerants composed of molecules ≤18 atoms by screening the PubChem database (Kim et al., 2019). The authors pointed out that the candidates for replacing the current high-GWP refrigerants are very limited. Moreover, it is a challenging process to compensate among COP, VHC, toxicity, and flammability.

The previous discussion and literature review motivated the current authors to pursue these ongoing efforts. This paper focuses on the theoretical assessment for refrigerants that have ultra-low-GWP (GWP< 30) (UNEP, 2010) and their applications for low- and high-temperature water heating and DHW. The current paper does not only revisit the refrigerant database proposed by McLinden et al. (2017), but it intends to extend this database further beyond by accounting for transcritical applications and some refrigerants recently added to the market.

To do so, a thermodynamic model for the proposed heat pump cycle was developed based on the pinch point approach and infinite heat transfer area for both evaporator and condenser. The novelty of the developed model that it considers more realistic parameters for the heat pump cycle such as temperature lift in the secondary fluid streams. It is worth mentioning that in the current model it is possible to have a condensation temperature below the secondary fluid outlet temperature. Consequently, the optimum condensation and evaporation temperatures and the degree of SC and SH for each refrigerant were calculated individually. This is the main difference compared to the classical approach where both condensation and evaporation temperatures are the same for all refrigerants.

2. HEAT PUMP CYCLE CONFIGURATION AND MODEL DEVELOPMENT

Fig. 1 shows the proposed heat pump configuration used in the current work. This configuration is mainly adopted for general space and water heaters. It comprises evaporator, compressor, condenser/gas cooler, and expansion valve. It can be seen (Fig. 1) that depending on the nature of refrigerant, the refrigeration cycle could be transcritical, in this case a gas cooler is used instead of condenser, or a conventional subcritical cycle.

The values of superheat inside the evaporator (SH_{evap}) and subcooling inside the condenser/gas cooler (SC_{cond}) have a crucial impact on the global system performance as it was pointed out in the work of Pitarch et al. (2017). So, one of the main objectives of the current work is to optimize these values to obtain the highest COP for each refrigerant. The main performance parameters for the proposed heat pump are summarized in Table 1. To evaluate the performance of gas cooler similarly to condenser, the fictitious subcooling inside the gas cooler (SC_{gc}) is introduced to represent the difference between critical temperature ($T_{3,crit}$), evaluated as a function of the gas cooler outlet pressure (P_3) and critical specific volume (v_{crit}), and the outlet temperature from gas cooler (T_3).

The current heat pump configuration was mathematically modelled using engineering equation solver (EES) program (S.A. Klein, 2017). This tool has been chosen due to many advantages including modelling simplicity, fast calculation time, a database of thermophysical properties for vast number of refrigerants, many optimization procedures, detailed representation of refrigeration cycles on many property diagrams such as P-h and T-s diagrams.

The main modelling assumptions are listed as follows:

- The heat pump is assumed to be working in steady state conditions.
- The evaporator and condenser/gas cooler are assumed to be counter-flow heat exchangers with infinite heat transfer area, which allows fair and adequate comparison between different refrigerants.

- The compressor's volumetric efficiency is assumed to be 1.0.
- The heat losses from the compressor are neglected and the compressor's isentropic efficiency is fixed at 0.7. This common value is considered to evaluate the discharge temperature.
- The expansion process is assumed to be isenthalpic.
- When the water or brine is employed as secondary fluid on the evaporator, there is a temperature lift for water/brine that leads to a finite thermal capacitance; and in the case of air, an infinite thermal capacitance is assumed.
- The pressure drops and heat losses in heat exchangers and connection pipes are neglected.
- The pinch points inside heat exchangers are always assumed to be higher or equal to zero. This to avoid any violation of the second law of thermodynamics $\left(ds_{sys} \geq \frac{\delta Q}{T} + s_{gen}\right)$. Where ds_{sys} is the total entropy change for the system, and s_{gen} is the generated entropy due to irreversibility and It has to be positive.

2.1. Discretization Scheme and Governing Equations

Fig. 2 shows the discretization scheme of the condenser/gas cooler, the same scheme is used also for the evaporator. Discretization of heat exchanger permits making more approximate calculations, since the heat transfer coefficients and local thermal properties do not remain constant along the heat exchanger. It can be noticed that the condenser/gas cooler is divided into number of cells along the refrigerant- and water-side, for which the energy balance is applied. In the current study, each of evaporator and condenser/gas cooler are discretized into 100 cells. This number of cells was previously specified to give an acceptable error in the energy balance within the heat exchanger, considering also a reasonable calculation time.

The temperature difference between the inlet refrigerant and outlet water temperatures within the cell is defined in the current work as the approach point ΔT_{appr}. Finally, the pinch point ΔT_{pp} is selected as the minimum approach point within the whole heat exchanger. Table 2 lists, in details, the governing equations and energy balances within the evaporator and condenser/gas cooler.

2.2. Flowchart and Solution Procedure

Fig. 3 shows the flowchart of the proposed model. The final solution is obtained iteratively, where the condensation/gas cooling pressure, evaporation pressure, and evaporator superheat are assumed to be the iterative variables, while the maximum COP is the target of model through approaching the pinch points inside heat exchangers to zero. The maximum COP is obtained by using the GENETIC optimization method integrated in the EES program (Klein and Nellis, 2012). This algorithm is derived from the public domain PIKAIA optimization program (Charbonneau, 2002).

Another important consideration is the discharge temperature. If this temperature is too high it could damage the compressor, mainly due to the malfunction of the lubrication system. So, the proposed model gives a warning message if the discharge temperature is higher than 120 °C. This temperature limit is recommended by many polyolester (POE) oil and compressors manufacturers (Emerson, 2004).

3. CLASSIFICATION OF REFRIGERANTS AND WORKING CONDITIONS

In the current study, the refrigerants were categorized in four main groups based on the slope of saturated vapor curve on T-s diagram (dT/ds) and the working conditions. These groups are anterograde refrigerants (ANT) $dT/ds<0$, isentropic refrigerants (ISE) $dT/ds>>0$ (semi-vertical slope), retrograde refrigerants (RET) $dT/ds>0$, and, finally, transcritical refrigerants (TRA). An example for each group is demonstrated in Fig. 4.

It can be noticed from Fig. 4 that the retrograde refrigerants (such as R-1336mzz(Z)) require high values SH to prevent wet compression compared with other types of refrigerants. This high value of SH could result to a degradation in system performance, as it decreases the evaporation temperature. To prevent the crossing of saturated vapor line during the compression process, it was assured that the discharge temperature, for each working condition, is at least 5 K higher than the dew condensation temperature.

Table 3 lists, in alphabetical order, the 15 selected refrigerants that are considered in this work as an alternative of the current high-GWP refrigerants used in such applications. Some of these refrigerants have been already recommended by McLinden et al. (2017), especially those that have ultra-low-GWP. Some others were introduced recently in the market, so their thermal performance is still under investigation. Moreover, In the current study, transcritical refrigerants, ethane and carbon dioxide, were considered.

For each refrigerant, eight types of studies (or working conditions) were done. These studies reflect the common applications for the heat pump used for space and water heating. These applications include low- and high-temperature heating (LTH and HTH, respectively), and production of DHW. Table 4 summarizes the different working conditions, according to the standards used in order to know the efficiency of a heat pump (UNE-EN 14511-2, 2014; UNE-EN 16147, 2017), for aerothermal and geothermal heat pumps considered in the current study.

4. RESULTS AND DISCUSSION

Table 5 shows the relative COP and VHC values for the all refrigerants and working conditions proposed for the current study. As it can be noticed that for LTH and HTH applications the reference refrigerant selected is R-410A, while R-134a was considered as reference for DHW applications.

4.1. Analysis of Low- and High-temperature Heating (LTH and HTH) Applications

As mentioned before, for heating applications the reference refrigerant is the R-410A. It is worth mentioning that the reference point is not constant and it varies depending on the working condition. Fig. 5 shows the comparison of relative COP and VHC for LTH and HTH applications in aerothermal and geothermal conditions.

Fig. 5 shows that, generally, almost all the refrigerants that have higher relative COP, have lower relative VHC, compared with the reference case. Theoretically, Acetone, R-1234ze(Z), and R-1233zd(E) present the highest relative COP, that have average values of 1.13, 1.12, and 1.08, respectively. However, these refrigerants have extremely low relative VHC with average values of 0.03, 0.13, and 0.1, respectively. This means that, for example, to replace R-410A with Acetone it requires a compressor approximately 30 times bigger to provide the same heating capacity, which implies higher costs.

For all working conditions studied, the three mentioned refrigerants work under negative evaporation pressure, due to their high NBP, which represents a challenge for preventing the air infiltration to the cycle. Such refrigerants under these conditions can be used in compact (hermetic) systems. In fact, R-600a is currently used in most domestic and commercial refrigeration applications that usually work bellow its NBP (= -11.75 °C)

(Lee et al., 2002; Danfoss, 2000). Regarding the flammability, Acetone is an extremely flammable fluid (Kim et al., 2019), while R-1234ze(Z) is a mildly flammable fluid (A2L), so their charge is limited especially for indoor applications, if no additional safety measures are considered. On the other hand, R-1233zd(E) is a non-flammable and non-toxic refrigerant (A1). It is worth mentioning that around the world, regulations concerning flammable refrigerants are encouraging using mildly flammable fluids to substitute high-GWP refrigerants.

To the best of our knowledge, we have not found any study in the literature that employing Acetone as refrigerant for such applications, so it was excluded from the selection.

Replacing directly R-410A with either R-1234ze(Z) or R-1233zd(E) for an existing heat pump is not a practical solution. Their very low VHC and high NBP values require replacement of all heat pump components, including also the connection tubes. To avoid this, or at least to reduce the modifications in an existing heat pump, the candidate refrigerant should have values of relative VHC near 1, relative COP $\geq$ 1.0, and NBP < 0 °C.

The only refrigerants that meet these conditions are R-717, R-161, R-1270, and R-290. R-717 (Ammonia) shows the best performance among them, it has an average relative COP and VHC values of 1.08 and 0.76, respectively. The main drawback of these refrigerants that they are highly flammable fluids (A3), except R-717 which has a mild flammability. However, R-717 has other drawbacks that it is a high-toxic fluid (B2L), besides being incompatible with common materials used in refrigeration cycles.

From our point of view, the HFOs R-1225ye(Z) and R-1234yf represent a good compensation between safety issues, VHC, NBP, and COP. R-1225ye(Z) has an average COP and VHC values of 1.03 and 0.32, respectively, while R-1234yf has an average COP and VHC values of 1.0 and 0.41, respectively. Also, both refrigerants have very low NBP values, so this prevents the heat pump to work under negative evaporation pressure. R-1225ye(Z) has a low acute toxicity (McLinden et al., 2017), while R-1234yf is classified as mildly flammable (A2L).

Fig. 6 explains why the performance of transcritical refrigerants, such as R-744 and R-170, is very low compared with other refrigerants for space heating applications. It should be noted that the x-axis corresponds to the duty of the heat exchanger, this means, in the current study, the ratio between the heat transfer rate till a certain position along the heat exchanger's length and the total heat transfer rate, where Duty(x)=$\dot{m}\Delta h(x)/\dot{m}\Delta h_{tot}$. As mentioned before, the required temperature lift, in such applications, for the secondary fluid-side inside the condenser/gas cooler is low (5-8 K). This small temperature lift results to a mismatch between the temperature profiles inside gas cooler, which, in turn, increases the temperature differences, irreversibilities, between refrigerant and secondary fluid.

The condensation temperatures for the working conditions considered are shown in Fig. 7a. It can be seen that all the subcritical refrigerants have a condensation temperature between 34 and 35.25 °C for LTH applications, and between 52.5 and 55.5 °C for HTH applications. Also, it can be noticed that regardless the refrigerant, the differences between the condensation temperatures are very small.

In LTH and HTH applications, the water-side temperature lift inside the condenser is low (5-8 K). This results that the pinch point occurs near the outlet of the water, as seen in Fig. 8. Additionally, the decrease of desuperheating zone affects the condensing temperature due to the shifting of pinch point toward the water outlet side, as in the case of R-1233zd(E).

Regarding the discharge temperatures (Fig. 7b), only R-717, under B0W35 and B0W55 working conditions, exceeded the maximum considered discharge temperature (120 °C) in this study. To use R-717 under these working conditions a two-stage compression or liquid injection techniques should be employed, which are out of the scope of the current work.

Fig. 7c, shows the different evaporation temperatures for the working conditions related to LTH and HTH applications. It can be clearly seen, for the A7W35 working condition, that the retrograde refrigerant R-1336mzz(Z) has the lowest evaporation temperature of 3.7 °C, compared with the isentropic refrigerants and the anterograde refrigerants that have the highest evaporation temperature ranges between 6.5 and 7 °C.

These differences in the evaporation temperature appears due to the need of superheating to avoid wet compression scenarios. The degree of superheat directly affects the evaporation temperature because in the current study there is no additional equipment, apart from the evaporator, to achieve superheat. Accordingly, to satisfy the second law of thermodynamics, the only possible way to increase the degree of superheat is by decreasing the evaporation temperature. The superheat range needed, in the current study, for the retrograde refrigerants is 3-5.2 K, for isentropic refrigerants and for anterograde refrigerants 0-3 K. As the evaporation temperature must decrease significantly in several cases, the COP is affected for this decrease, as the pressure ratio and, consequently, the compressor power increase. To clarify this issue, Fig. 9 shows the evaporation temperature and SH values for R-1234yf, R-1336mzz and Acetone for A7W55 working condition. As it can been seen, the retrograde refrigerant R-1336mzz needs at least a SH value of 5.2 K to prevent wet compression, compared with the isentropic refrigerant R-1234yf which requires only 0.2 K. A practical way to solve this problem is the introduction of an internal heat exchanger (IHX) in the heat pump cycle, which provides additional superheating and subcooling, moreover, in some cases, it can improve the system's COP.

4.2. Analysis of Domestic Hot Water (DHW) Applications

Fig. 10 shows a comparison between all the selected refrigerants for the production of DHW, and the possibility of reaching 75 °C as an outlet water temperature without using an electric resistance. For both DHW (1) and DHW (2) applications, the values of temperature lift in the water-side of condenser/gas cooler are 50 and 65 K, respectively. As these values are elevated, the location of pinch points inside the condenser/gas cooler in the DHW applications have a substantial impact on the heat pump performance compared with the previous LTH and HTH applications.

As it can be seen in Table 5 that the transcritical refrigerants R-744 and R-170 have, respectively, the highest relative COP and VHC values. As indicated by many authors in literature (Liu et al., 2019; Stene, 2007; Minetto, 2011), R-744 (CO_2) is considered to be one of the best candidates for transcritical domestic hot water applications due to perfect matching between the temperature profiles inside the gas cooler and high VHC values, besides being non-flammable and non-toxic fluid (A1). The results showed that R-744 has an average relative COP and VHC values of 1.07 and 7.49, respectively, compared with R-134a. Also, R-170 (Ethane) shows a good performance, with average relative COP and VHC values of 1.04 and 4.63, respectively; however, it is a highly flammable fluid (A3).

Regarding subcritical refrigerants, R-161, R-1270, and R-1234yf are the best refrigerant under the working conditions studied. The three refrigerants have similar average relative COP values of 1.0. Regarding the average relative VHC, R-1270 has the highest value of 1.61, then R-161 with 1.36, and finally R-1234yf with 1.0.

Finally, R-1336mzz(Z) shows the worst performance in this group with average relative COP and VHC values of 0.89 and 0.1, respectively. As discussed previously, the main reason for this low performance is that R-1336mzz(Z) is related to the retrograde fluids group which require high SH values to prevent the wet compression. In the current analysis, the SH value reached 8.6 K, in the case of R-1336mzz(Z), which results to an evaporation temperature lower than the one for R-134a by 8.6 K.

Fig. 11a illustrates different condensation temperatures for the working conditions under study. As the water-side temperature lift inside the condenser, for DHW applications, is considerably higher than the LTH and HTH applications (50-65 K instead of 5-8 K), the condensation temperature varies more from one refrigerant to another.

This is due to the fact that the superheated vapor portion of the condenser has a significant impact on the global system performance since it controls the location of the pinch point, and consequently, the condensation temperature.

To clarify this, Fig. 12 compares the temperature profiles inside the condenser for R-134a, R-161 and R744 in the working condition of A7W60. It can be seen that R-161 has a larger superheated vapor portion which, in turn, shifts down the pinch point and results to a lower condensation temperature (T_{cond}= 53.5 °C) compared with R-134a which has T_{cond}= 58.3 °C. Also, in Fig. 12, the one can compare easily the condensation profiles between the transcritical and subcritical refrigerants.

Fig. 11b shows the discharge temperature for different refrigerants. In some working conditions (e.g. B0W75), it can be observed the same problem explained before, where R-717 and Acetone have a discharge temperature greater than the maximum specified limit in the current study. This gives an indication that the single-stage heat pumps that use R-717 or Acetone as working fluid should employ an auxiliary heater (e.g. electrical resistance) to reach these high limits of hot water production. Compared to the LTH and HTH applications, similar results and conclusions regarding the evaporation temperatures can be derived from Fig. 11c, since the secondary fluid inlet conditions to the evaporator are the same for the two applications.

5. SUMMARY AND CONCLUSIONS

This paper investigates the ultra-low-GWP refrigerants that already exist in the market and the possibility of replacing the current high-GWP refrigerants for space and water heating applications. To do so, a thermodynamic model of a heat pump cycle was developed based on the pinch point approach for optimizing the heat exchangers. The current model is considered to be a pre-design tool to assess the performance and size limits for a heat pump using specific refrigerant and under certain working condition. This generic model does not depend in a certain type of heat exchangers, it only depends on the external working conditions. The main conclusions and recommendations are summarized next.

- Regarding the space heating applications (LTH and HTH), the results showed that almost all the ultra-low-GWP refrigerants had either lower values of COP or VHC relative to the reference refrigerant R-410A. If only theoretical COP is considered, R-1234ze(Z) and R-1233zd(E) are the most promising ultra-low GWP refrigerants in such applications. However, their main disadvantages are very low VHC values (< 0.13), and high NBP values (> 10 °C).

- To mitigate the resizing of R-410A heat pump's components, and as a general criterion, the candidate refrigerant should have a relative VHC value as near as possible to the reference case, relative COP ≥ 1.0, and very low NBP (< 0 °C).

The results showed that all the refrigerants that meet these criteria, such as R-717, R-161, R-1270, and R-290, are either extremely flammable or highly toxic.

- R-1234yf represents an intermediate solution for the above-mentioned challenges. It shows an average relative COP and VHC values of 1.0 and 0.41, respectively, besides, it has a low NBP of -29 °C. However, it is classified by ASHRAE as mildly flammable fluid (A2L).

- For DHW applications, generally, the transcritical refrigerants, such as CO_2 and R-170, show the best performance, as expected, due to the good matching between refrigerant temperature profile and high water-side temperature lift inside the gas cooler.

- Regarding subcritical refrigerants, R-161, R-1270 and R-1234yf present the best performance, with relative COP values near 1.0 and relative VHC values ≥ 1.0. These refrigerants show good performance in both space heating and DHW applications. This makes them potential candidates to be employed in multi-purpose heat pumps that are capable of providing multi-temperature levels of the hot water.

- Finally, it can be said that the door is still open for further investigation about feasible candidates to replace the current high-GWP refrigerants. Introducing new refrigerants mixtures can be promising to solve the dilemma of compensating between the COP and VHC values, besides, getting better matching between the temperature profiles inside the heat exchangers.

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REFRENCES

ASHRAE, Standard 34-Safety Standard for Refrigeration Systems and Designation and Classification of Refrigerants., 2016.

CEN EN 378-1, Refrigerating Systems and Heat Pumps - Safety and Environmental Requirements - Part 1: Basic Requirements, Definitions, Classification and Selection Criteria, 2016.

Charbonneau, P., Release Notes for PIKAIA 1.2, NCAR Technical Note 451+STR, Boulder: National Center for Atmospheric Research, 2002.

Dai, B., Dang, C., Li, M., Tian, H. and Ma, Y., Thermodynamic Performance Assessment of Carbon Dioxide Blends with Low-Global Warming Potential (GWP) Working Fluids for a Heat Pump Water Heater, *International Journal of Refrigeration*, vol. **56**, pp. 1–14, from http://dx.doi.org/10.1016/j.ijrefrig.2014.11.009, 2015. DOI: 10.1016/j.ijrefrig.2014.11.009

Danfoss, Practical Application of Refrigerant R600a Isobutane in Domestic Refrigerator Systems, from http://www.folk.ntnu.no/skoge/book-cep/diagrams/additional_diagrams/more_on_refrigerants/isobutane(r600a)-danfos.pdf, 2000.

Emerson, Copeland Scroll Compressors for Dedicated Heat Pumps, ZH 56 K4E...ZH 11 M/E, 2004.

European Commission, Energy Efficiency: Heating and Cooling, from https://www.ec.europa.eu/energy/topics/energy-efficiency/heating-and-cooling_en, 2020.

European Union, Regulation (EU) No 517/2014 of the European Parliament and of the Council of 16 April 2014: On Fluorinated Greenhouse Gases and Repealing Regulation (EC) No 842/2006, *Official Journal of the European Union*, vol. **2014**, no. 517, p. L150/195-230, from http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=OJ:JOL_2014_150_R_0008, 2014.

Kim, S., Chen, J., Cheng, T., Gindulyte, A., He, J., He, S., Li, Q., et al., PubChem 2019 Update: Improved Access to Chemical Data, *Nucleic Acids Research*, vol. **47**, no. D1, pp. D1102–9, 2019. DOI: 10.1093/nar/gky1033

Klein, S. and Nellis, G., *Mastering EES*, Madison, WI: F-Chart Software, 2012.

Klein, S. A., Engineering Equation Solver (Version V10.451), 2017.

Kujak, S. and Schultz, K., Insights into the next Generation HVAC&R Refrigerant Future, *Science and Technology for the Built Environment*, vol. **22**, no. 8, pp. 1226–37, accessed May 24, 2019, from https://www.tandfonline.com/doi/full/10.1080/23744731.2016.1203239, November 16, 2016. DOI: 10.1080/23744731.2016.1203239

Lee, Y. S. and Su, C. C., Experimental Studies of Isobutane (R600a) as the Refrigerant in Domestic Refrigeration System, *Applied Thermal Engineering*, vol. **22**, no. 5, pp. 507–19, 2002. DOI: 10.1016/S1359-4311(01)00106-5

Lemmon, E. W., Bell, I. H., Huber, M. L., and McLinden, M. O., NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, 2018.

Liu, S., Li, Z., Dai, B., Zhong, Z., Li, H., Song, M. and Sun, Z., Energetic, Economic and Environmental Analysis of Air Source Transcritical CO2 Heat Pump System for Residential Heating in China, *Applied Thermal Engineering*, vol. **148**, no. August 2018, pp. 1425–39, from https://doi.org/10.1016/j.applthermaleng.2018.08.061, 2019. DOI: 10.1016/j.applthermaleng.2018.08.061

McLinden, M. O., Brown, J. S., Brignoli, R., Kazakov, A. F. and Domanski, P. A., Limited Options for Low-Global-Warming-Potential Refrigerants, *Nature Communications*, vol. **8**, pp. 1–9, from http://dx.doi.org/10.1038/ncomms14476, 2017. DOI: 10.1038/ncomms14476

Minetto, S., Theoretical and Experimental Analysis of a CO2 Heat Pump for Domestic Hot Water, *International Journal of Refrigeration*, vol. **34**, no. 3, pp. 742–51, May 2011. DOI: 10.1016/j.ijrefrig.2010.12.018

Nellis, G. F. and Klein, S., *Heat Transfer,* New York: Cambridge University Press, 2009.

Pitarch, M., Hervas-Blasco, E., Navarro-Peris, E., Gonzálvez-Maciá, J. and Corberán, J. M., Evaluation of Optimal Subcooling in Subcritical Heat Pump Systems, *International Journal of Refrigeration*, vol. **78**, pp. 18–31, accessed May 24, 2019, from https://www.sciencedirect.com/science/article/pii/S014070071730110X, June 1, 2017. DOI: 10.1016/J.IJREFRIG.2017.03.015

Stene, J., Integrated CO2 Heat Pump Systems for Space Heating and Hot Water Heating in Low-Energy Houses and Passive Houses, *International Energy Agency (IEA) Heat Pump Programme – Annex 32 – Workshop in Kyoto*, Kyoto, Japan, 2007.

UNE-EN 14511-2, Air Conditioners, Liquid Chilling Packages and Heat Pumps with Electrically Driven Compressors for Space Heating and Cooling - Part 2: Test Conditions, 2014.

UNE-EN 16147, Heat Pumps with Electrically Driven Compressors - Testing, Performance Rating and Requirements for Marking of Domestic Hot Water Units. (Consolidated Version), 2017.

UNEP, TEAP 2010 Progress Report: Assessment of HCFCs and Environmentally Sound Alternatives, from https://www.ozone.unep.org/, 2010.

United Nations, Montreal Protocol on Substances That Deplete the Ozone Layer (with Annex). Concluded at Montreal on 16 Sep Tember 1987, 1989.

Venkatarathnam, G., Mokashi, G. and Murthy, S. S., Occurrence of Pinch Points in Condensers and Evaporators for Zeotropic Refrigerant Mixtures, *International Journal of Refrigeration*, vol. **19**, no. 6, pp. 361–68, accessed May 24, 2019, from https://www.sciencedirect.com/science/article/pii/S0140700796000230, July 1, 1996. DOI: 10.1016/S0140-7007(96)00023-0

Venkatarathnam, G. and Srinivasa Murthy, S., Effect of Mixture Composition on the Formation of Pinch Points in Condensers and Evaporators for Zeotropic Refrigerant Mixtures, *International Journal of Refrigeration*, vol. **22**, no. 3, pp. 205–15, from https://linkinghub.elsevier.com/retrieve/pii/S0140700798000565, May 1999. DOI: 10.1016/S0140-7007(98)00056-5

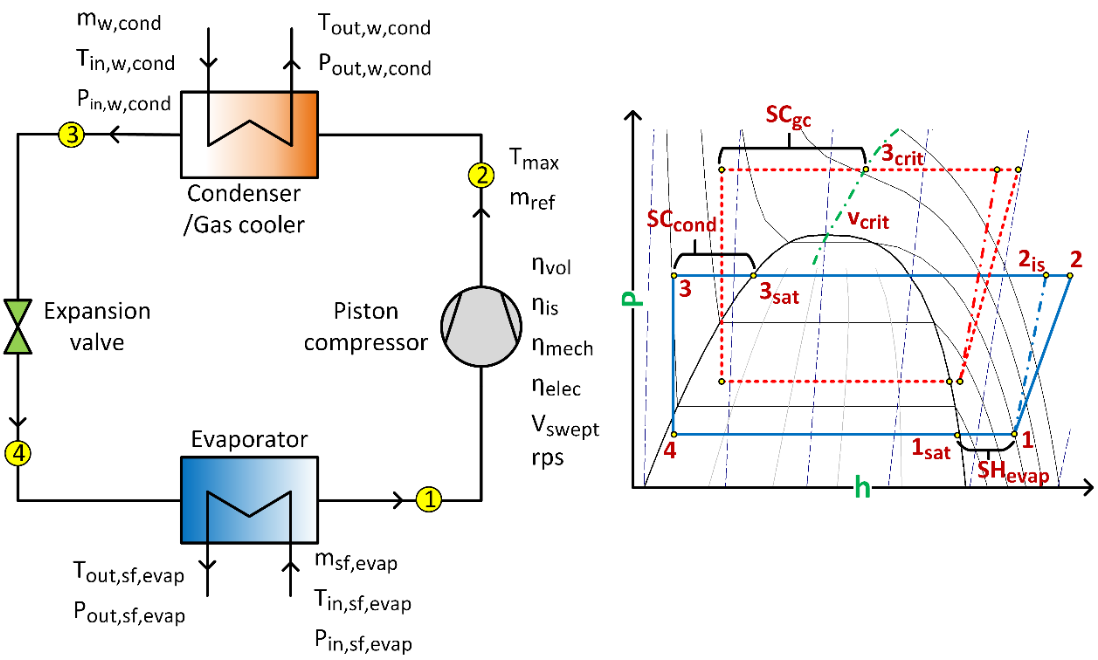

Fig. 1. (left) Schematic of the proposed heat pump cycle for the current work, and (right) representation of the subcritical (blue-continuous) and transcritical (red-dashed) refrigeration cycles on the P-h diagram.

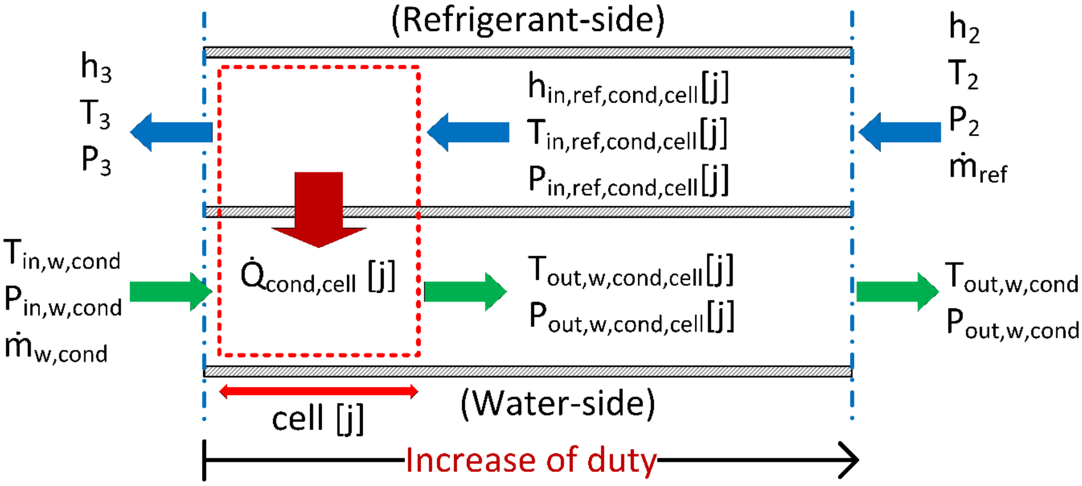

Fig. 2. Discretization scheme of the condenser/gas cooler and energy balance within the cell.

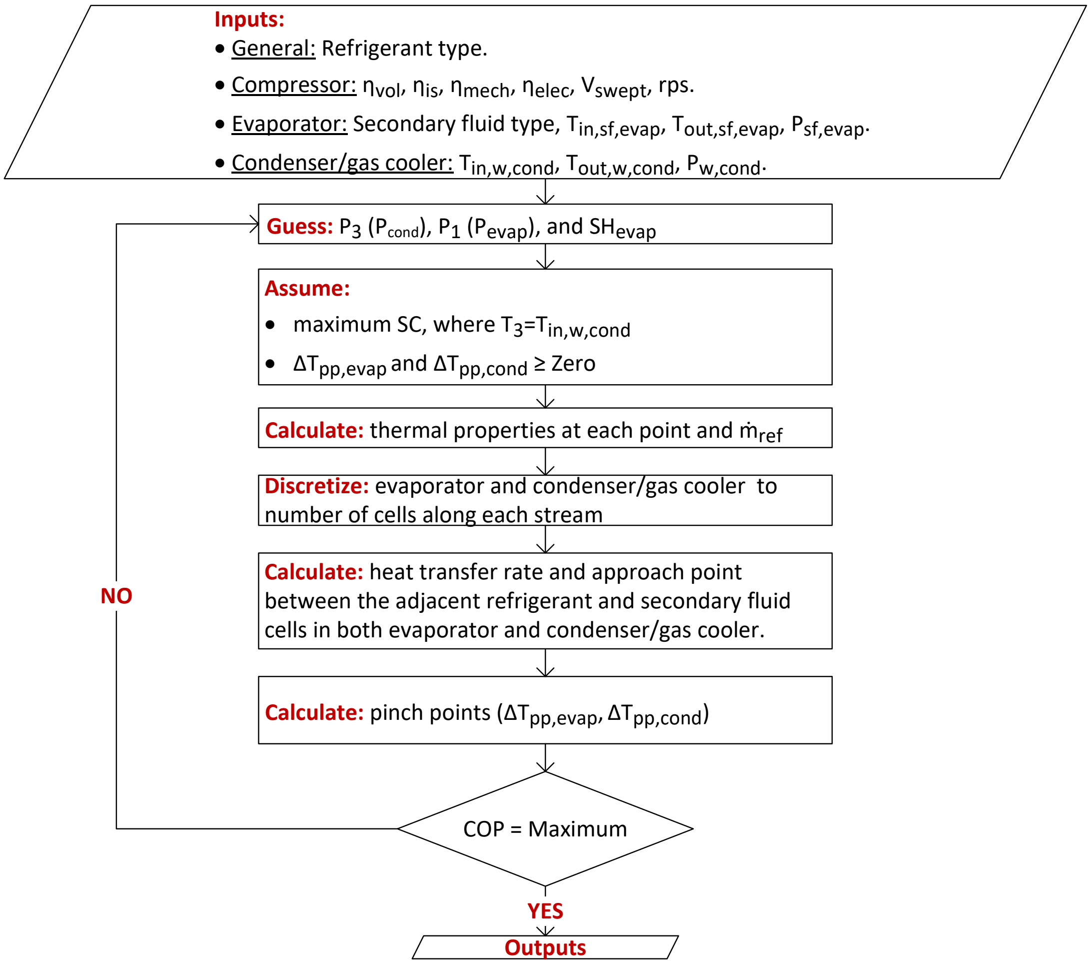

Fig. 3. Flowchart and solution procedure of the proposed numerical model.

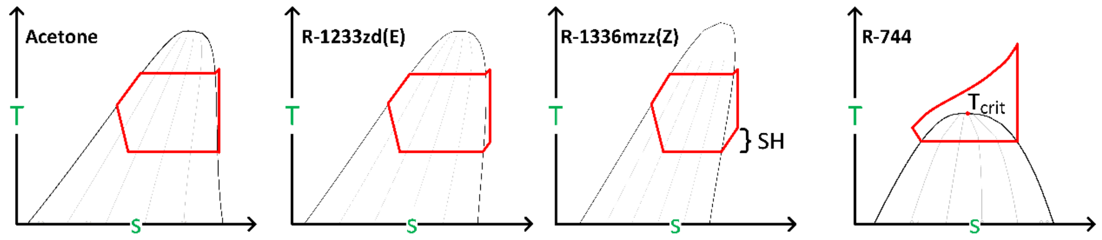

Fig. 4. From left to right: T-s diagrams for Acetone (ANT), R-1233zd(E) (ISE), R-1336mzz(Z) (RET), and R-744 (TRA).

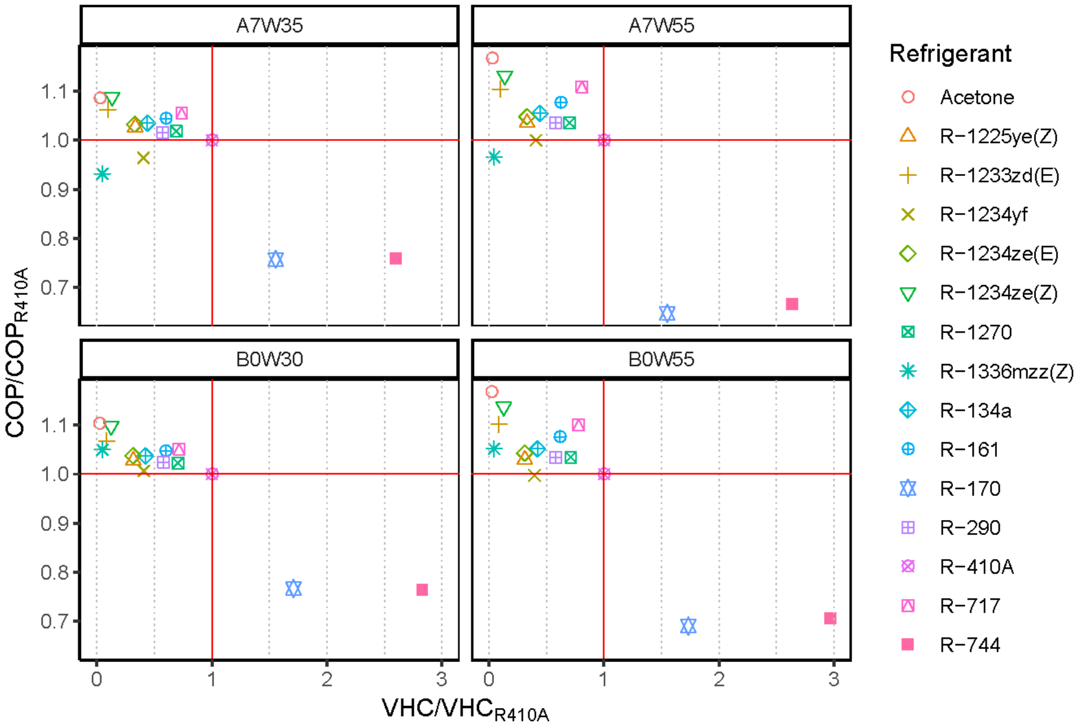

Fig. 5. Comparison of relative COP and VHC for the selected refrigerants, regarding the LTH and HTH applications (the reference refrigerant is R-410A).

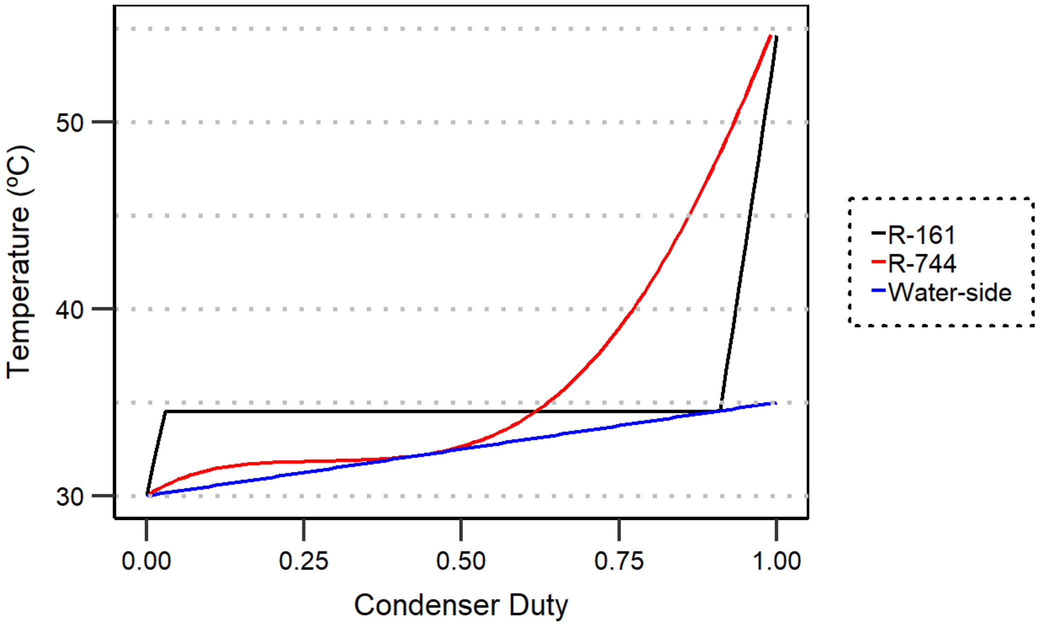

Fig. 6. Comparison of temperature profiles inside condenser/gas cooler, and pinch points, for transcritical refrigerant R-744 (CO_2) and subcritical refrigerant R-161, in A7W35 working condition.

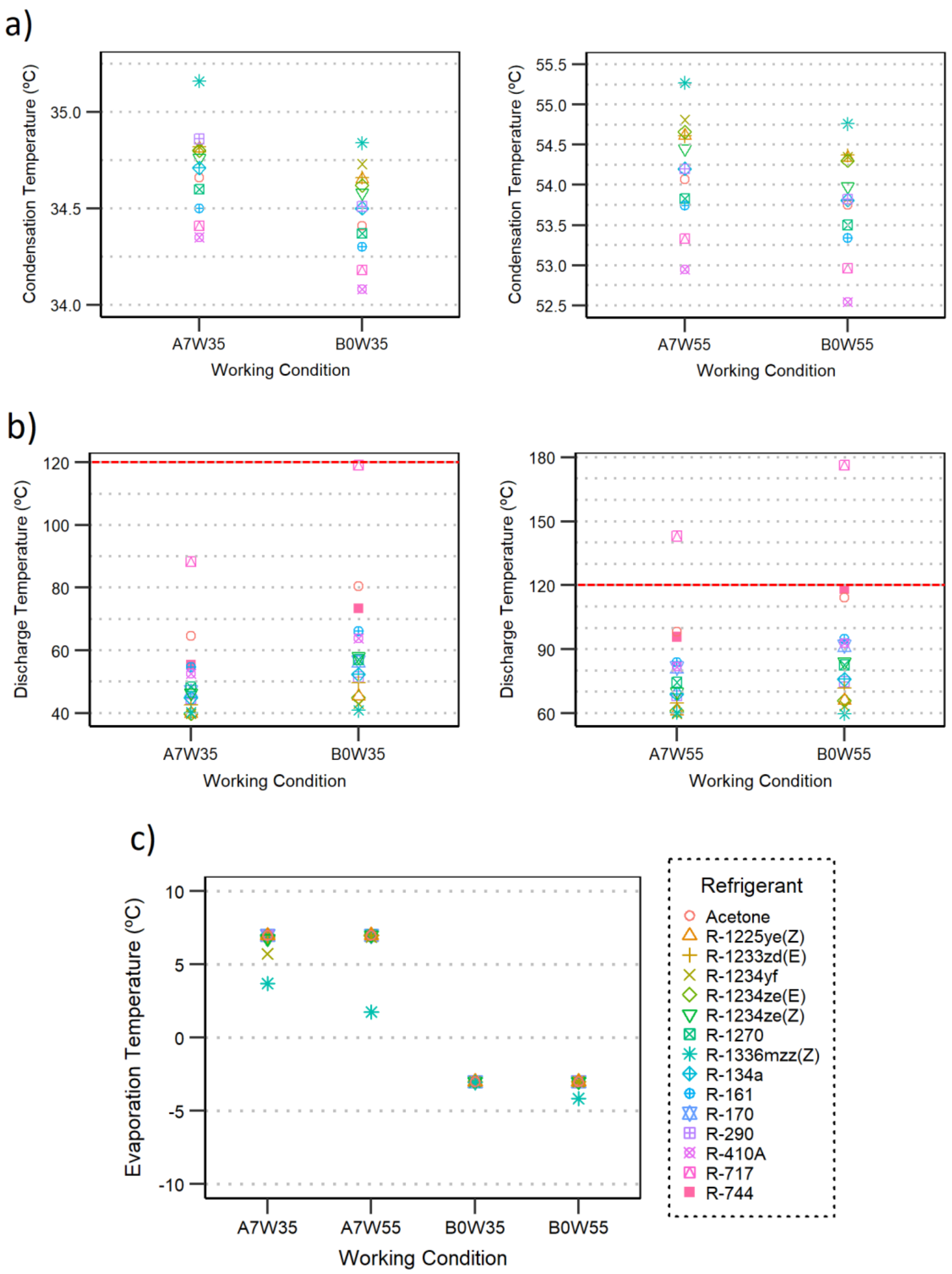

Fig. 7. (a) Condensation; (b) discharge; and (c) evaporation temperatures for the LTH and HTH applications (the red dashed line represents the limit for discharge temperature).

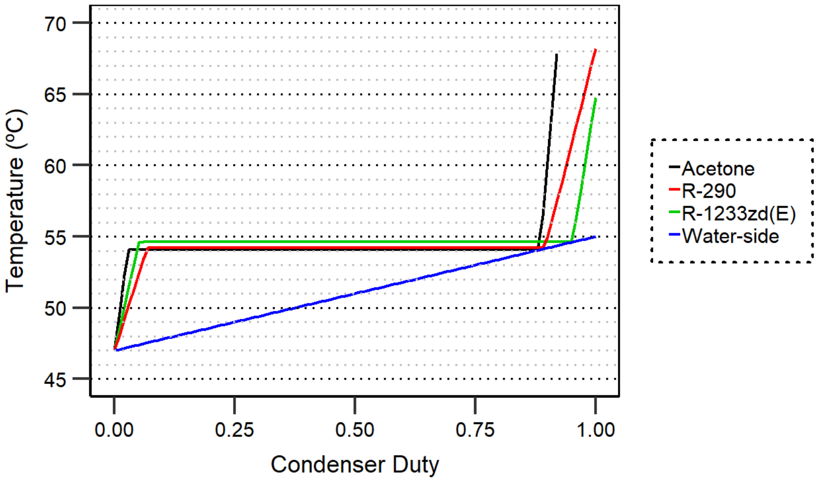

Fig. 8. Temperature profiles of refrigerant- and water-side, and pinch points inside the condenser for different refrigerants in A7W55 working condition.

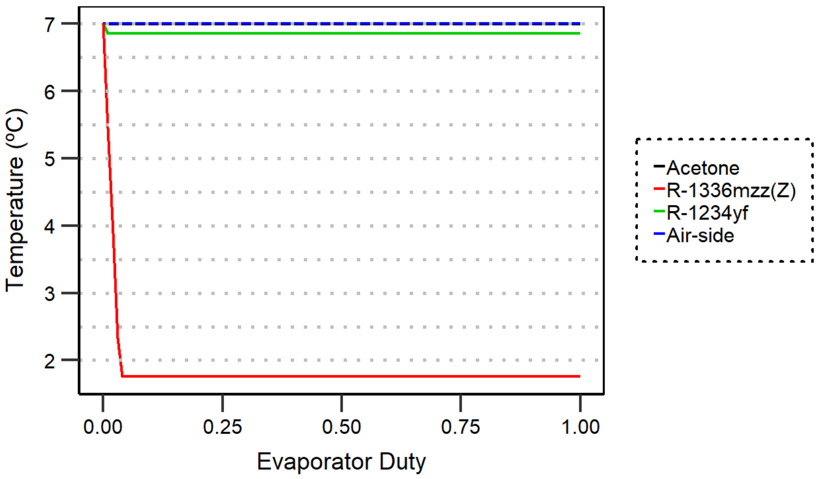

Fig. 9. Temperature profiles of the refrigerant and air inside the evaporator for different refrigerants in A7W55 working condition.

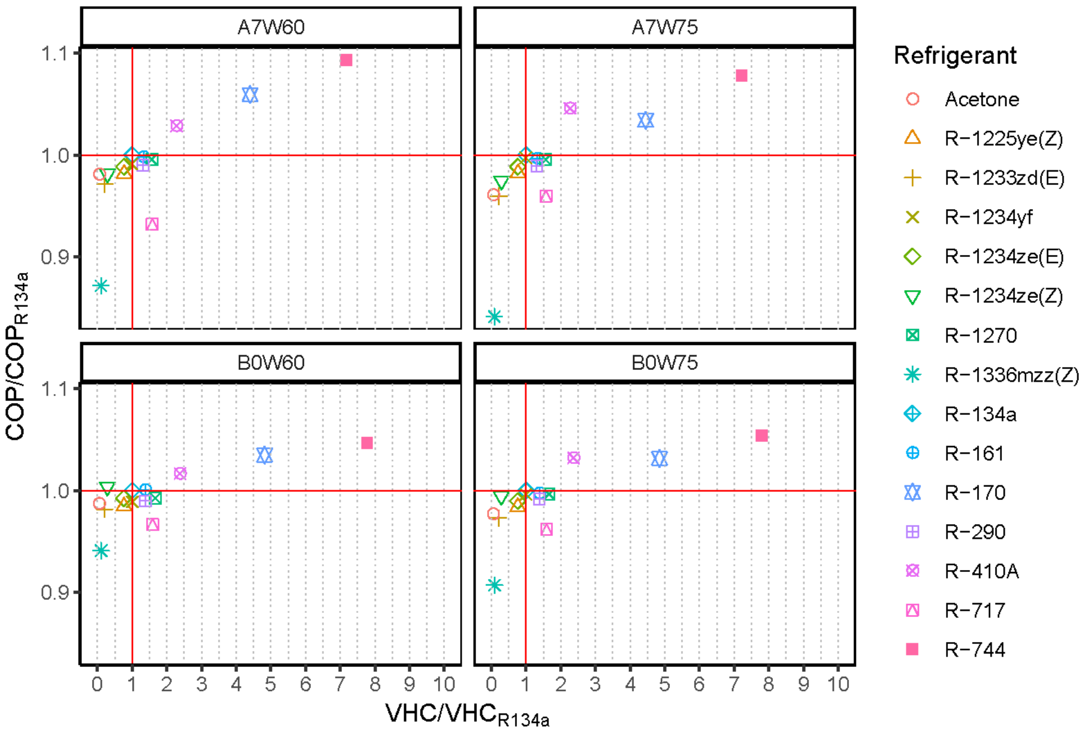

Fig. 10. Comparison of relative COP and VHC for the selected refrigerants, regarding the DHW applications (the reference refrigerant is R-134a).

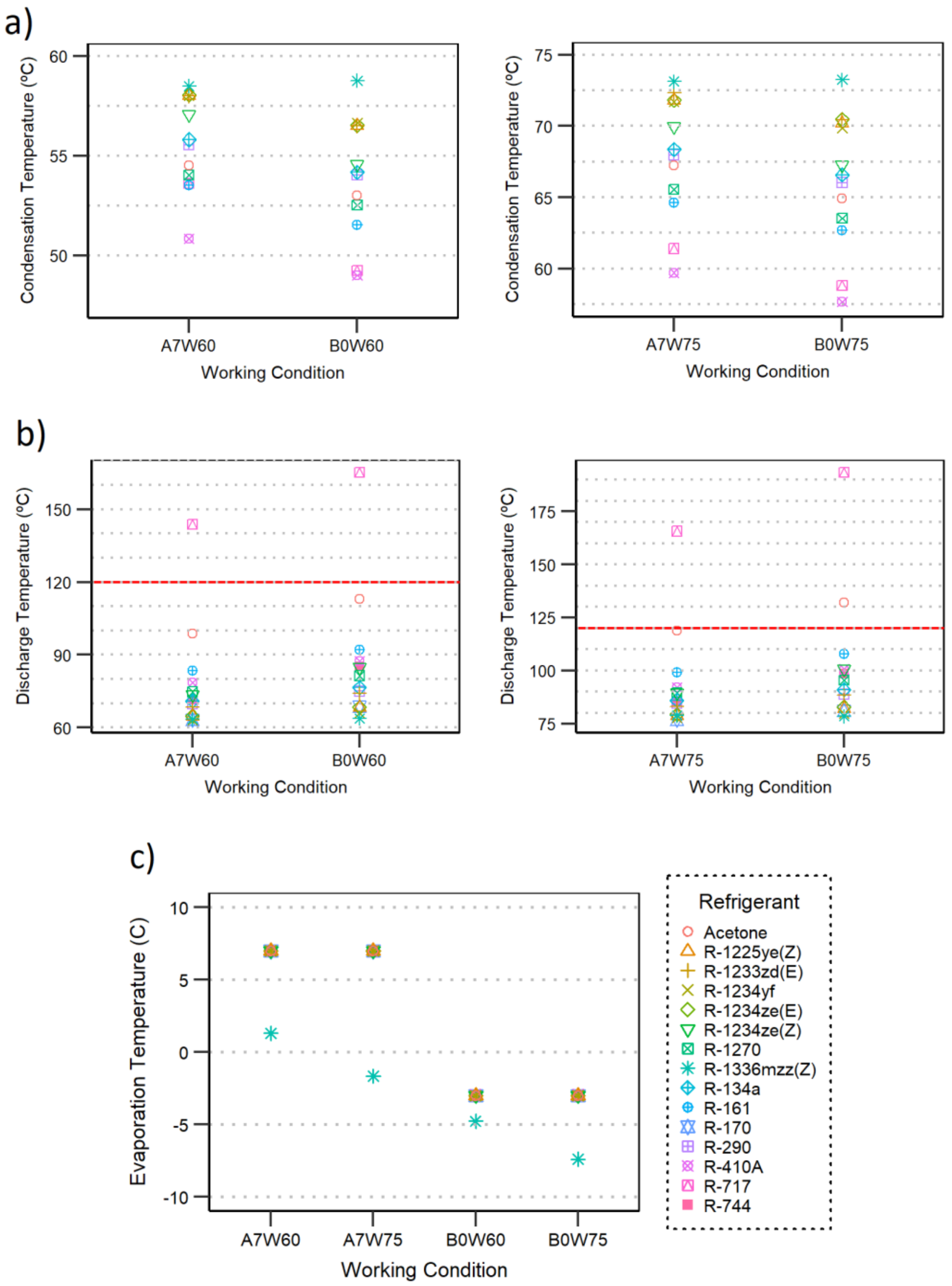

Fig. 11. (a) Condensation; (b) discharge; and (c) evaporation temperatures for the DHW applications (the red dashed line represents the limit for discharge temperature).

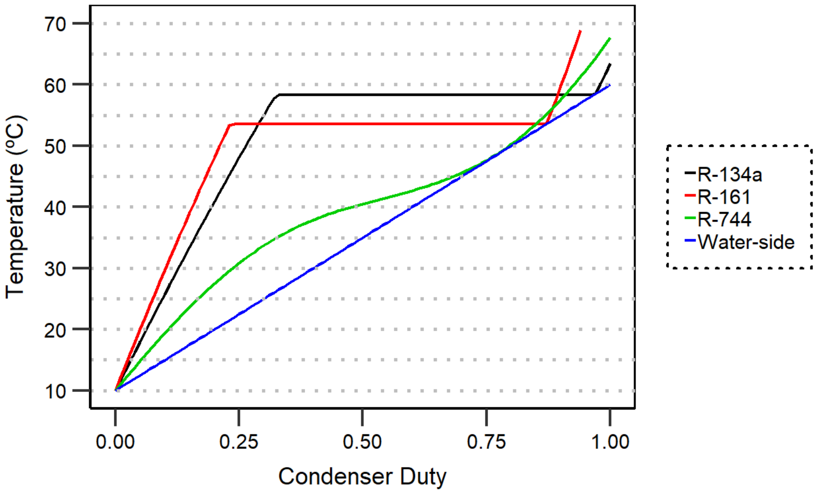

Fig. 12. Refrigerant and water temperature profiles inside the condenser for R-134a, R-161, and R744 under A7W60 working condition.

Table 1. Performance parameters for the proposed heat pump cycle.

Parameter	Equation
Subcooling (SC_{cond}) (K)	• For subcritical cycle: $SC_{cond}= T_{3,sat}-T_3$ • For transcritical cycle: $SC_{gc}= T_{3,crit}-T_3$, where $T_{3,crit}= f\ (P_3,v_{crit})$
Volumetric heating capacity (VHC) ($J{\cdot}m^{-3}$)	$VHC= \rho_1(h_2-h_3)$
Discharge temperature (T_{max}) (°C)	$T_{max}= T_2$
Pressure ratio (Pr) (-)	$Pr= P_2/P_1$
Compressor's inlet electrical power ($\dot{E}_{elec,comp}$) (W)	$\dot{E}_{elec,comp}= \dot{m}_{ref}(h_2-h_1)/\eta_{mech}\cdot\ \eta_{elec}$, where $h_2= ((h_{2,is}-h_1)/\eta_{is})+h_1$
Coefficient of performance (COP) (-)	$COP=\dot{Q}_{tot,cond}/\dot{E}_{elec,comp}$

Table 2. Governing equations used in modelling the evaporator and condenser/gas cooler.

	Evaporator	Condenser/ Gas cooler
Total capacity	$\dot{Q}_{tot,evap} = \dot{m}_{ref}(h_1 - h_4) = \dot{m}_{sf,evap} \cdot \bar{c}_{p,sf,evap}\left(T_{in,sf,evap} - T_{out,sf,evap}\right)$	$\dot{Q}_{tot,cond} = \dot{m}_{ref}(h_2 - h_3) = \dot{m}_{w,cond} \cdot \bar{c}_{p,w,cond}\left(T_{out,w,cond} - T_{in,sf,cond}\right)$
Fractional capacity	$\Delta\dot{Q}_{evap} = \frac{\dot{Q}_{tot,evap}}{n_{evap}}$	$\Delta\dot{Q}_{cond} = \frac{\dot{Q}_{tot,cond}}{n_{cond}}$
	where n_{evap} and n_{cond} are the total number of evaporator and condenser/gas cooler cells, respectively.	
Energy balance (cell)	$\dot{Q}_{evap,cell}[i] = \Delta\dot{Q}_{evap} \cdot i = \dot{m}_{ref}\left(h_1 - h_{in,ref,evap,cell}[i]\right) = \dot{m}_{sf,evap} \cdot \bar{c}_{p,sf,evap}\left(T_{in,sf,evap} - T_{out,sf,evap,cell}[i]\right)$, where i= 1→$n_{evap}$	$\dot{Q}_{cond,cell}[j] = \Delta\dot{Q}_{cond} \cdot j = \dot{m}_{ref}\left(h_{in,ref,cond,cell}[j] - h_3\right) = \dot{m}_{w,cond} \cdot \bar{c}_{p,w,cond}\left(T_{out,w,cond,cell}[j] - T_{in,w,cond}\right)$, where j= 1→$n_{cond}$
Approach temperature (cell)	$\Delta T_{appr,evap,cell}[i] = T_{out,sf,evap,cell}[i] - T_{in,ref,evap,cell}[i]$, where $T_{in,ref,evap,cell}[i] = f\left(h_{in,ref,evap,cell}[i], P_1 = P_{evap}\right)$	$\Delta T_{appr,cond,cell}[j] = T_{in,ref,cond,cell}[j] - T_{out,w,cond,cell}[j]$, where $T_{in,ref,cond,cell}[j] = f\left(h_{in,ref,cond,cell}[j], P_3 = P_{cond}\right)$
Pinch point	$\Delta T_{pp,evap} = min\left(\Delta T_{appr,evap,cell}[i]\right)_{i=1\rightarrow n_{evap}}$	$\Delta T_{pp,cond} = min\left(\Delta T_{appr,cond,cell}[j]\right)_{j=1\rightarrow n_{cond}}$

Table 3. Properties of the refrigerants selected in the current study.

Refrigerant	Group	GWP[a]	Safety Group[b]	T_{crit}[c] (ºC)	Pcrit[c] $\times 10^6$ (Pa)	NBP[c] (ºC)
Acetone	ANT	5	n.a.	234.95	4.7	56.07
R-170 (Ethane)	TRA	6	A3	32.17	4.87	-88.58
R-1225ye(Z)	ISE	<1	n.a.	105.85	3.34	-20.00
R-1233zd(E)	ISE	4.5	A1	165.60	3.57	18.32
R-1234yf	ISE	4	A2L	94.70	3.38	-29.45
R-1234ze(E)	ISE	7	A2L	109.36	3.64	-18.97
R-1234ze(Z)	ISE	7	A2L	150.12	3.53	10.25
R-1270 (Propylene)	ANT	2	A3	91.06	4.56	-47.62
R-1336mzz(Z)	RET	9	A1	171.30	2.9	33.40
R-134a[d]	**ANT**	**1430**	**A1**	**101.06**	**4.06**	**-26.07**
R-161	ANT	12	A3	102.10	5.01	-37.55
R-290 (Propane)	ANT	3	A3	96.74	4.25	-42.11
R-410A[e]	**ANT**	**2088**	**A1**	**71.34**	**4.9**	**-51.44**
R-717 (Ammonia)	ANT	0	B2L	132.25	11.33	-33.33
R-744 (CO_2)	TRA	1	A1	30.98	7.38	-78.46

[a] values of GWP are based on European Union (European Union, 2014); [b] values of safety group are based on CEN EN 378-1:2016 (CEN EN 378-1, 2016) and ASHRAE (ASHRAE, 2016); [c] thermal properties of refrigerants are based on Klein (2017) and Lemmon et al. (2018); [d] R-134a is the reference refrigerant for domestic hot water applications; [e] R-410A is the reference refrigerant for low- and high-temperature heating applications.

Table 4. Working conditions considered for the proposed heat pump (UNE-EN 14511-2, 2014; UNE-EN 16147, 2017).

Application	Working Condition	Secondary fluid in evaporator	Secondary fluid in condenser	$T_{in,sf,evap}$ (°C)	$T_{out,sf,evap}$ (°C)	$T_{in,w,cond}$ (°C)	$T_{out,w,cond}$ (°C)
LTH	A7W35	Air	Water	7	7	30	35
	B0W35	Brine	Water	0	-3	30	35
HTH	A7W55	Air	Water	7	7	47	55
	B0W55	Brine	Water	0	-3	47	55
DHW (1)	A7W60	Air	Water	7	7	10	60
	B0W60	Brine	Water	0	-3	10	60
DHW (2)	A7W75	Air	Water	7	7	10	75
	B0W75	Brine	Water	0	-3	10	75

Table 5. Relative COP and VHC values for the all selected refrigerants regarding the working conditions of the current study.

		$COP/COP_{R\text{-}410A}$				$VHC/VHC_{R\text{-}410A}$				$COP/COP_{R\text{-}134a}$				$VHC/VHC_{R\text{-}134a}$			
Application		LTH		HTH		LTH		HTH		DHW (1)		DHW (2)		DHW (1)		DHW (2)	
Refrigerant	Group	Aero.	Geo.	Aero.	Geo.	Aero.	Geo.	Aero.	Geo.	Aero.	Geo.	Aero.	Geo.	Aero.	Geo.	Aero.	Geo.
Absolute reference values		7.11 (-)	4.14 (-)	5.15 (-)	3.39 (-)	$7.78\cdot10^{6}$ ($J\cdot m^{-3}$)	$5.91\cdot10^{6}$ ($J\cdot m^{-3}$)	$7.27\cdot10^{6}$ ($J\cdot m^{-3}$)	$5.59\cdot10^{6}$ ($J\cdot m^{-3}$)	5.55 (-)	4.57 (-)	4.78 (-)	4.06 (-)	$4.22\cdot10^{6}$ ($J\cdot m^{-3}$)	$3.04\cdot10^{6}$ ($J\cdot m^{-3}$)	$4.38\cdot10^{6}$ ($J\cdot m^{-3}$)	$3.15\cdot10^{6}$ ($J\cdot m^{-3}$)
Acetone	ANT	1.09	1.10	1.17	1.17	0.03	0.02	0.03	0.02	0.98	0.99	0.96	0.98	0.05	0.05	0.05	0.05
R-1225ye(Z)	ISE	1.03	1.03	1.04	1.03	0.33	0.32	0.33	0.31	0.98	0.98	0.98	0.98	0.77	0.76	0.77	0.76
R-1233zd(E)	ISE	1.06	1.07	1.10	1.10	0.10	0.09	0.10	0.09	0.97	0.98	0.96	0.97	0.21	0.20	0.22	0.20
R-1234yf	ISE	0.96	1.01	1.00	1.00	0.41	0.41	0.41	0.40	0.99	0.99	1.00	1.00	0.99	1.00	0.99	1.00
R-1234ze(E)	ISE	1.03	1.04	1.05	1.04	0.33	0.31	0.33	0.31	0.99	0.99	0.99	0.99	0.76	0.76	0.76	0.76
R-1234ze(Z)	ISE	1.09	1.10	1.13	1.14	0.13	0.12	0.14	0.13	0.98	1.00	0.97	0.99	0.29	0.28	0.29	0.28
R-1270	ANT	1.02	1.02	1.04	1.03	0.69	0.70	0.70	0.71	1.00	0.99	1.00	1.00	1.56	1.66	1.56	1.66
R-1336mzz(Z)	RET	0.93	1.05	0.97	1.05	0.05	0.05	0.05	0.04	0.87	0.94	0.84	0.91	0.10	0.10	0.09	0.09
R-134a	ANT	1.04	1.04	1.06	1.05	0.44	0.42	0.44	0.42	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**
R-161	ANT	1.04	1.05	1.08	1.08	0.60	0.60	0.62	0.62	1.00	1.00	1.00	1.00	1.33	1.38	1.33	1.38
R-170	TRA	0.76	0.77	0.65	0.69	1.55	1.71	1.55	1.73	1.06	1.03	1.03	1.03	4.40	4.82	4.45	4.85
R-290	ANT	1.02	1.02	1.04	1.03	0.57	0.58	0.58	0.58	0.99	0.99	0.99	0.99	1.31	1.38	1.31	1.38
R-410A	ANT	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	1.03	1.02	1.05	1.03	2.28	2.38	2.27	2.37
R-717	ANT	1.06	1.05	1.11	1.10	0.74	0.71	0.81	0.78	0.93	0.97	0.96	0.96	1.58	1.59	1.57	1.59
R-744	TRA	0.76	0.76	0.67	0.71	2.60	2.83	2.64	2.97	1.09	1.05	1.08	1.05	7.17	7.77	7.22	7.79