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Additional Information

## A review of refrigerant R1234ze(E) recent investigations

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### Abstract

Climate change is demonstrated through global surface temperatures increase in the last century. To stop this phenomenon, new regulations that ban or taxes greenhouse gas fluids (HFC among them) have being approved. In the medium term, only low-GWP refrigerants will be permitted in developed countries. HFO are synthetic fluids that show similar properties to used HFC. Among them, one of the most promising is R1234ze(E). This refrigerant presents good environmental properties and can be used in most of HVACR applications, pure or mixed with HFC or natural refrigerants (mainly CO<sub>2</sub>).

This paper collects the most relevant research about R1234ze(E) thermophysical and compatibility properties, heat transfer and pressure drop characteristics, and vapour compression system performance; separating those works that considers R1234ze(E) pure or blended. Once analyzed literature available, it can be concluded that pure R1234ze(E) is a good option only in new HVACR systems. Nevertheless, if it is combined with other refrigerants also reduces considerably the final GWP value, maintaining efficiency parameters at levels that allow them to replace R134a, R404A or R410A in existing systems with minor modifications.

**Keywords:** review, R1234ze(E), mixtures, HFO, GWP, HFC alternative.

### Nomenclature

$D_h$	Hydraulic diameter (mm)
$E_{\text{system}}$	System energy consumption (kW h)
$G$	Mass velocity ( $\text{kg m}^{-2} \text{s}^{-1}$ )
$H_{\text{rel}}$	Relative humidity (%)
$P_c$	Compressor consumption (kW)

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q''	Heat flux (kW m <sup>-2</sup> )
Q <sub>o</sub>	Cooling capacity (kW)
ShD	Superheat Degree (K)
T	Temperature (K)
x	Vapour quality (-)

#### *Subscripts*

amb	ambient
cond	condenser
evap	evaporator
in	inlet
L	Low Temperature
M	Medium Temperature
out	outlet

#### *Abbreviations*

AAD	Average Absolute Deviation
AHRI	Air-Conditioning, Heating, and Refrigeration Institute
COP	Coefficient of Performance
EOS	Equation of State
GWP	Global Warming Potential
HFC	HydroFluoroCarbon
HFO	HydroFluoroOlefine
HTC	Heat Transfer Coefficient
HVACR	Heating, Ventilation, Air Conditioning and Refrigeration
HX	Heat Exchanger
IHX	Internal Heat Exchanger
LCCP	Life Cycle Climate Performance
MAC	Mobile Air Conditioning
VLE	Vapor-Liquid Equilibrium

## **1. Introduction**

The application of Regulation EU No 517/2014 [1] is going to change drastically refrigeration and air conditioning systems, since most of the applications do not allow currently used refrigerants: R134a, R404A and R410A [2]. If the Global Warming Potential (GWP) limits does not avoid the HydroFluoroCarbons (HFC) usage, national GWP taxes (until twenty times greater than their acquisition price) can difficult their use.

Very different options have appeared to replace HFC. However, it is not yet clear which alternative will impose definitively in market because they have some disadvantages (tradeoffs are always necessary [3]). The options and some considerations are shown in Table 1.

Table 1. Considerations about candidates to replace HFC in HVACR systems.

HFOs are synthetic fluids that contain a carbon-carbon double bond. They are characterized by very low GWP values (under 10), low flammability and non-toxicity and similar properties to HFC (and materials and lubricants compatibility). R1234yf was the first HFC launched as low-GWP alternative. It is used as R134a drop-in replacement in Mobile Air Conditioning (MAC) systems [10]. R1234ze(E) is another alternative to R134a proposed in new systems of medium temperature applications [11]: air-cooled and water-cooled chillers, heat pumps, refrigerators, vending machines and CO<sub>2</sub> cascade systems. Other HFOs as R1243zf are still being studied prior to commercialize them [12].

Although HFOs have some disadvantages (low flammable fluid) they can reduce the final GWP value of new low-GWP mixtures (controlling both properties) [13]. These mixtures could replace R134a, R404A, R410A and R22 directly or with minor system modifications [14].

Due to the approved and expected environmental protection regulations, low-GWP refrigerant R1234ze(E) or its mixtures are going to impose in some HVACR applications. In a few years, lots of works have been conducted to characterize this refrigerant and help the correct design of R1234ze(E) systems. In this paper a revision of most relevant recent research conducted for R1234ze(E) is performed. As R1234ze(E) is commonly a component of new low-GWP mixtures, these works are also included. The aim of the paper is to introduce the reader to the current status of knowledge about this refrigerant.

First, papers that analyze thermophysical properties and system adaptation (compatibility and flammability) are included; then, two-phase heat transfer studies (evaporation and condensation) are collected and heat transfer coefficient and pressure drop are analyzed; and finally, system performance of vapour compression systems (mainly refrigeration and heat pump applications) are reviewed. As R134a alternative, special attention is given to compare both refrigerants in all the sections.

## **2. Refrigerant properties**

### *2.1 R1234ze(E) pure*

Although R1234ze(E) has been developed recently, many studies have been conducted to characterize the properties and therefore, thermal and energetic behavior of this fluid. Accurate

thermophysical properties are necessary to design and build efficient refrigeration and air conditioning components (and systems). These studies can report individual properties measured in specific test rigs or they can analyze the accuracy of different Equations of State (EOS) (or even modify them to improve their precision).

Qiu et al. [15] presented a density measurement system at pressures up to 100 MPa and temperature from 283 to 363 K, using a vibrating tube densimeter. The maximum expanded uncertainty for R1234ze(E) is 0.23%. Meng et al. [16] reported viscosity measurements at temperatures between 243 and 373 K and saturated pressures up to 30 MPa, using a vibrating-wire viscometer. The AAD (Average Absolute Deviation) of the experimental results for R1234ze(E) is 0.59%. Di Nicola et al. [17] measured R1234ze(E) triple point value and obtained results very close that present in open literature.

An EOS is a thermodynamic equation that relates state variables (temperature, pressure, volume, internal energy or specific heat) and allows calculating fluid properties. Brown et al. [18] first estimated the thermodynamic properties with the Peng-Robinson EOS for R1234ze(E) and other fluorinated olefins. Akasaka applied a new thermodynamic property model for R1234ze(E). Typical uncertainties of vapor pressure, liquid density and isobaric heat capacities (liquid and vapor) are 0.2%, 0.5% and 5%, respectively [19]. Then, he presented a new EOS valid for temperatures from 240 K to 420K and for pressures up to 15MPa in the case of R1234ze(E) [20] (and not recommendable for critical region). Average uncertainties are 0.1% in liquid density, 0.2% in vapor density, 3% in liquid heat capacities, 0.05% in the vapor-phase speed of sound, and 0.1% in vapor pressure. Developments in R1234ze(E) properties and properties calculations are included in fluid databases as REFPROP [21] that allow accurate property calculations.

Alavianmehr et al. [22] modified Tao-Mason EOS and the AAD of 34 R1234ze(E) points was 0.36 (it was the lowest deviation obtained). Lai et al. [23] used the molecular based BACKONE and PC-SAFT EOS to describe the thermodynamic properties of R1234ze(E). Relative differences are mostly within 1%, Table 2.

Table 2. Main results of Lai et al. [23].

As introduced in section 1, R1234ze(E) is a medium pressure refrigerant proposed as R134a alternative in new design systems. It is not recommended to drop-in or retrofit in R134a due to the difference in their thermophysical properties, as can be seen in Figure 1. The vapour pressure of R1234ze(E) is between -28% and -24% compared with R134a (Figure 1.a), so the compressors can work with R1234ze(E) at lower pressures. The liquid density of R1234ze(E) is between -4.7% and -1% compared with R134a (Figure 1.b), and the refrigerant charge needed for the alternative is also lower. In the case of vapour density, this is approximately 20% lower for R1234ze(E)). Finally, the R1234ze(E) liquid viscosity is slightly lower at low temperatures but

7.37% at 343K. This will imply lower pressure losses in pipes and components for the HFO. A summary of different properties is also shown in Table 3. Additionally to that discussed before, it highlights the great GWP reduction, 1300 versus 4 and low flammability of R1234ze(E).

Figure 1. Comparison between R1234ze(E) and R134a at different temperatures [21]: a) Vapour pressure, b) Liquid density and c) Liquid viscosity.

Table 3. Main properties of R1234ze(E) and R134a [21].

As happens for R1234yf in MAC systems (German automotive companies are opposing to apply F-gas regulation and defends CO<sub>2</sub> as working fluid for this application), flammability difficult HFC substitution and is one of the most important barriers for the R1234ze(E) implementation.

R1234ze(E) is classified as low-flammable refrigerant (A2L) by ASHRAE 34 [24] even though is slightly less flammable than R1234yf. R1234ze(E) LFT becomes quite low when the humidity condition increases much [25] and it is non-flammable if the air humidity is equal to or less than 10% corrected for 296.15K [26]. For heat pump system, it is demonstrated that refrigerants will not pose an ignition risk during normal operation [27]. In the case of release in the outdoor unit, risks involving R1234ze(E) are equal to that calculate for R1234yf and four times lower than R32 (and well below the overall risk of house fires from any cause).

Besides, R1234ze(E) is compatible with that materials and oil lubricants used with HFC. Majurin et al. [28] studied the material compatibility of R1234ze(E) and blend of R1234yf, R1234ze(E), and R32, with nine different elastomers, three gaskets, five polymers, and ten motor materials and considering lubricant effect. Only higher risk was found with a few materials that will require more investigation. Sun et al. [29] proved that R1234ze(E) is highly soluble in two lubricants precursors of POE (PEC7 and PEC9) at temperatures from 283.15 to 353.15 K.

## 2.2 R1234ze(E) mixtures

In the case of mixtures, VLE (Vapor-Liquid Equilibrium) data is used to estimate the performance and the optimal concentration. In the case of R1234ze(E) mixtures with other synthetic refrigerants, Dong et al. [30] measured VLE values for R134/R1234ze(E) (azeotropic behaviour) at temperatures from 258.15 to 288.15K. The average absolute relative deviations (AARD) of pressure are between 0.09% and 0.28%. For R152a/R1234ze(E) mixture (zeotropic behavior) [31], it was correlated by the Peng-Robinson EOS and the maximum AARD of pressure is 0.17%. The viscosity AARD between the free-volume theory and experimental data was between 2.9 and 6.5% for R32/R1234ze(E) mixtures [32], applying the most precise mixing rule (for pure R1234ze(E) was 0.8%). Akasaka [33] also developed models to calculate VLE data for R1234ze(E)/R32 being the precision acceptable for most of HVACR systems.

Most of the studies presented for natural refrigerants mixed with R1234ze(E) are those performed considering CO<sub>2</sub>/R1234ze(E). Di Nicola et al. [34] correlated Carnahan-Starling-DeSantis EOS with experimental results at temperatures from 233 to 363 K and pressures from 104 to 1909 kPa. Two-phase pressure deviations within up to 5-6% and in the superheated vapor region were within  $\pm 1\%$ . Excluding the CO<sub>2</sub> concentrations above 80% [35], the Schröder equation does not describe the experimental result trend, showing very high discrepancies. Kiani et al. [36] obtained that for CO<sub>2</sub>/R1234ze(E), the Peng-Robinson EOS was the best performing (AAD=1.98%) and results with Tao-Mason EOS were considerably more deviated (AAD=7%). Dong et al. [37] also correlated VLE data for R290/R1234ze(E) (azeotropic behavior) by the Peng-Robinson EOS at temperatures from 258.15 to 283.15 K. The maximum AARD of pressure is 0.35%, while the maximum AAD of vapor phase mole fraction is 0.0033.

Although is low-flammable, R1234ze(E) can be used to reduce flammability potential of other fluids. For example, if it is mixed with ammonia can decrease the combustion power of the pure refrigerant [38]. Kondo et al. also supplied a formula to calculate the flammability limits in dry air of ammonia mixtures. R1234ze(E) cannot suppress completely the flammability of R161 (GWP=13, R22 replacement in stationary air conditioning systems) in the range 268 to 328K [39].

### **3. Two-phase heat transfer and pressure drop**

#### *3.1 R1234ze(E) pure*

In the following, R1234ze(E) two-phase heat transfer and pressure drop studies are reviewed. As well as in the heat exchanger design and building, where it is very important to know the fluid behavior; Heat Transfer Studies (HTC) and pressure drop also plays an important role in design and optimization of vapor compression systems (evaporator, condenser and intermediate heat exchanger).

According to the flow boiling studies analyzed, R1234ze(E) shows similar or lower HTC and higher pressure drop than R134a, Table 4. In a 6.00 mm circular smooth tube, Grauso et al. [40] found that local HTC of R1234ze(E) and R134a during flow boiling were very similar, especially at medium and high saturation temperatures. However, R1234ze(E) HTC falls more at low vapor qualities. Adiabatic pressure drop of R1234ze(E) is slightly higher than those obtained for R134a. Conclusions reached in a micro-fin tube connected by U-bend are similar [41], where the HTC difference between R134a and R1234ze(E) appears only at low vapour qualities (below 0.3). Diani et al. [42] tested R1234ze(E) inside a 3.4mm microfin tube, in this case R1234ze(E) flow boiling HTC was around 9% lower than those obtained with R134a.

R1234ze(E) heat transfer studies in other geometries are also common in open literature. Results were similar to that obtained with horizontal circular tubes (presented before). In an off-the-shelf roll-bond and adjusting the compressor displacement to deliver the proper refrigerant mass flow

rate [43], the average HTC was approximately the same between R134a, R1234yf, R600a and R1234ze(E). Mancin et al. [44] studied flow boiling heat transfer and pressure drop of R1234ze(E) and R134a inside an high porosity copper foam with 5 PPI and porosity of 0.93. They obtained similar HTC but, at the same operating test conditions, R1234ze(E) pressure drops are higher. Vakili-Farahani et al. [45] investigated experimentally the effects of heat flux, mass flux, vapor quality, and saturation temperature flow boiling heat transfer in a rectangular multiport aluminum extruded tube using R1234ze(E) and R245fa. Results predicted by correlations were deviated from experimental results.

Van Rooyen and Thome [46] investigated pool boiling data for enhanced boiling tubes and developed prediction method based on a boiling heat transfer mechanism in the near-wall region. R1234ze(E) HTC was 11% than R134a Wolverine Turbo-B5 and slightly lower in Wieland Gewa-B5 (R236fa HTC was much lower than others).

Despite that observed in evaporating studies, in condensation R1234ze(E) is about 10% lower than R134a and pressure drops are still higher. Del Col et al. [47] studied R1234ze(E) behavior in a 0.96 mm minichannel. R1234ze(E) HTC were lower than those of R32, similar with those of R134a (condenser heat transfer area needed for R1234ze(E) is 25% greater compared to that of R134a) and higher than those of R1234yf. In a brazed plate heat exchanger [48], R1234ze(E) exhibits lower (4%-6%) HTC and higher (10%) frictional pressure drops than those of R134a. Park et al. [49] compared R1234ze(E) with refrigerants R134a and R236fa for a vertically aligned, aluminum multi-port tube. R134a had higher HTC values (about 15-25%) than two other refrigerants, being R1234ze(E) the lowest.

Agarwal and Hrnjak [50] developed a condenser model that considers five zones, eliminating discontinuities. The absolute mean deviation of R1234ze(E) was 15.7% (subcooled zone 26.6%). Then they studied condensation in two-phase and superheated-condensation zone respectively through experimental data (6.1 mm circular smooth copper tube) and correlations [51]. R134a presents approximately 10% higher HTC and much lower pressure drop compared to R1234ze(E).

Table 4. Summary of heat transfer and pressure drop studies for pure R1234ze(E).

### 3.2 R1234ze(E) mixtures

It is common found R32/R1234ze(E) heat transfer investigations that can be used in upcoming HFC/HFO blends to replace R410A or even R404A, Table 5. Koyama et al. [52] carried out drop-in experiments with R410A, R1234ze(E) and R1234ze(E)/R32 mixture. They proved that pressure drops are similar even though the mass flow rates are lower for R1234ze(E) and its mixture, the heating effect and performance of R1234ze can be improved noticeably by adding R32. In tests performed by Hossain et al. [53], it was found that the experimental of R1234ze(E)



HTC are below that of R1234ze(E)/R32 (55/45mass%) mixture, R410A and R32. At 0.48 vapor quality and  $300 \text{ kg m}^{-2} \text{ s}^{-1}$  mass velocity, R1234ze(E) HTC was 11%, 56% and 83% lower, respectively. Contrary to that, in horizontal microfin tube, Kondou et al. [54] concluded that the HTC of the R32/R1234ze(E) mixture is even lower than that of R1234ze(E). HTC is minimized at 0.2/0.8 by mass, where the mole fraction difference is maximized (and the temperature glide and the mass fraction distribution are maximized).

Table 5. Summary of heat transfer studies for R1234ze(E) mixtures.

## 4. System performance

### 4.1 R1234ze(E) pure

R1234ze(E) is a promising low-GWP alternative specially in new systems, if it is retrofitted or directly substituted (drop-in) performs under R134a, Table 6. Mota-Babiloni et al. [55] found at evaporation temperatures between 260 and 280K and condensation temperatures between 310 and 330K that the average cooling capacity and COP (Coefficient of Performance) reduction is 30% and 6%, respectively. Janković et al. [56] conclude that R1234ze(E) performs better than R134a and that it is necessary an overridden compressor to match the system cooling power. In new medium pressure air-cooled chillers, R1234ze(E) shows to 12% higher COP than R134a [57] and because of its lower pressure and higher efficiency, it achieves 7% lower Life Cycle Climate Performance (LCCP). In the light of this results, new medium pressure air-cooled chillers seems one of the most feasible applications for R1234ze(E),

In open literature more studies can be found that underline the necessity of modifications in R134a refrigeration systems to achieve high performances using R1234ze(E). In oil-free centrifugal compressors [58], R1234ze(E) efficiency increases due to lower viscous losses and greater compressors than R134a. A condenser redesign is also suggested to avoid excessive pressure drops.

In low refrigerant charge systems HFO compete with hydrocarbons to be the refrigerants that impose at low-term. In domestic refrigerators (Figure 2) [59], although R1234ze(E) presents lower energy consumption than R134a, it is not suitable for drop-in replacement due to lower capacity (greater compressor run time and shorter time between defrost cycles). Same conclusions was achieved by Leighton et al. [60], where R1234ze(E) presented 21.5% lower evaporator capacity, but 7.9% higher COP. In vending systems [61], R1234ze(E) efficiencies were lower than R134a (and R1234yf) due to pressure drop losses in the evaporator and compressor penalties (this effect can be diminished using a compressor properly sized for R1234ze(E)). These results are poorer that found with hydrocarbons, so, if the security normative allows a low-flammable refrigerant in low charge systems, hydrocarbons would be the fluids most used.

Figure 2. Two domestic refrigerator architectures studied by Karber et al. [59].

In other architectures, R1234ze(E) presents major benefits by the introduction of the basic cycle modifications (as a consequence, more expensive systems) than R134a. Molés et al. [62] studied different single stage vapour compression configurations and obtained great COP increments (11%-20%) for R1234ze(E) in an expander or ejector cycle with respect to the Basic Cycle working with R134a. Chen et al. [63] obtained higher COP for R1234ze(E) in an ejector refrigeration system (Figure 3) than R134a but lower than R600 and R245f. Lee et al. [64]. developed a theoretical model for different multi-stage cycles with two-phase refrigerant injection, showing that R1234yf and R1234ze can display better performance than other low-GWP refrigerants. Longo et al. [65] demonstrated that thermal effectiveness of R134a and R1234ze(E) is almost the same in a micro-fin tubes heat pipe heat exchanger (Figure 4) under the same conditions (exhaust air inlet between 280 and 313K at different humidity).

Figure 3. Ejector refrigeration system [63].

Figure 4. Micro-fin tubes heat pipe heat exchanger used by Longo et al. [65].

R1234ze(E) has an advantage for applications where energy consumption is a key parameter, like high-temperature heat pumps. Due to critical temperature, Fukuda et al. [66] concluded that R1234ze(E) can be a potential refrigerant in high-temperature heat pump systems for industrial purposes (Figure 5), rather than typical air conditioners or refrigeration systems. However, an isomer of R1234ze(E), R1234ze(Z) [67], looks more efficient in high temperature heat pumps. R1234ze(E) only performs better than R1234ze(Z) if condensation temperatures are above 348K [68].

Figure 5. Experimental high-temperature heat pump apparatus [66].

As refrigeration studies, Gao et al. [69] also notified the larger compressor and refrigerant mass charges necessity for R1234ze(E) in their direct expansion ground source heat pump study. R1234ze(E) maximum COP increment could reach to about 15% compared to a basic system in two-stage heat pump based on the combination of vapor expander and compressor [70]. Taking

an overall consideration, R152a is the most suitable working fluid for this system under the typical working condition.

Table 6. Summary of experimental performance studies for pure R1234ze(E).

Besides, R1234ze(E) performance has been calculated in studies different from vapour compression systems. It has shown a slightly higher performance than R134a in a based adsorption cooling cycle for different heating and cooling water inlet temperatures [71]. In supercritical ORC, the best working fluid (but not the most efficient) for net electrical power optimization of basic cycle is R1234ze(E) [72].

#### 4.2 R1234ze(E) mixtures

As it has been exposed in previous section, R1234ze(E) presents some advantages and disadvantages that does not allow it as low-GWP drop-in (or light retrofit) alternative for currently used refrigerants (R134a, R404A, R410A, R22). AHRI identified a group of mixtures, developed by different chemical companies as Honeywell, DuPont, Archema or Mexichem, that can be used as replacements [14]. They contain mostly HFC (R32, R125, R134a and R152a), HFO (R1234yf and R1234ze(E)) and R744. Some of this mixtures present great glide (around 7K) and that can be an additional problem if it is used as retrofit (drop-in) alternative (selective leakage is a relevant aspect). Considering specific heat exchanger technology in new systems it is possible to get benefit of the glide.

The consequence of choosing R1234ze(E) instead of R1234yf as former refrigerant is that the final mixture will be cheaper with a slightly lower capacity only in light retrofit or drop-in systems. At present, regarding mixtures that contains R1234ze(E) in their composition, there are registered by the ASHRAE three R134a alternatives (R444A, R445A and R450A; previously known as AC6, AC5 and N13), one R404A alternative (R448A, N40) and one R410A alternative (R446A, and R447A, previously known as L41), Table 7. In Figure 6 this mixtures are listed describing their GWP values, ASHRAE security classification and the mass% amount of this fluid.

Figure 6. Mixtures that contains R1234ze(E) in their composition.

R444A and R445A are R134a alternatives in MAC systems [73] (low refrigerant charge systems). Compared with R134a, while drop-in performance of R445A is similar at most a test conditions, that of R444A is only similar at high load (at part load performance can be incremented considering an well sized internal heat exchanger and separated receiver dryer). Schulze et al. [74] concluded that R445A COP is slightly lower (8%) and that there is a higher risk of ice formation at the evaporator. These mixtures are still low-flammable and they are another option to substitute

R134a as R1234yf. The final refrigerant imposed will depend on the GWP limitations and the system drop-in performance.

R450A (Solstice™ N13) is proposed to replace R134a (-58% GWP) alternative in chillers, heat pumps, cascade (taking advantage of European GWP limitation at 1500) and med-temperature refrigeration systems either in DX or flooded architectures [75]. As R450A has a lower vapor density than R134a (8% approximately) and a similar viscosity, it can behave quite well in piston compressors. R450A compressor operating map is significantly enlarged compared with R134a because present lower pressure and discharge temperature than R134a.

Good R450A performance has been obtained under different operating conditions and refrigeration applications. Mota-Babiloni et al. [76] obtained that R450A cooling capacity is slightly lower than R134a (6%) and similar COP between them (Figure 7). Schultz and Kujak [77] found poorer results in a water-cooled screw chiller installation, 12-15% reductions in capacity and 1-4% in energy efficiency. Tewis Smart Solutions [78] obtained energy savings of 3.10% using R450A in an R134a commercial refrigeration system under winter conditions (condensation temperature of 313K). When tested in an existing supermarket [79], the energy consumption of R450A/CO<sub>2</sub> cascade system is similar to that obtained with R134a/CO<sub>2</sub> (global saving of 90 tons CO<sub>2eq</sub> per year). Discharge and oil temperature was also reduced using R450A. It has been proved experimentally that Internal Heat Exchanger (IHX) can produce more benefits in R450A than R134a, even though they are lower than pure R1234ze(E) [80].

Figure 7. Performance comparison of R448A vs. R404A without IHX: a) Cooling capacity and b) COP [76].

HFO/HFC mixtures can be used as short- or mid-term replacements in commercial refrigeration systems [81]. Because R448A GWP is 1274 and it is classified as A1, can be used in large centralized systems (great refrigerant charge) with DX in public area (GWP above 150 and non-flammable) at low and medium evaporating conditions [82]. Mota-Babiloni et al. [83] studied theoretically six R404A alternatives in four vapour compression configurations, obtaining high efficiency simulating with R448A. In a 2.2 kW semi-hermetic condensing unit with evaporator for walk-in freezer/cooler [84] (Figure 8), R448A matches capacity of R404A with 6% higher efficiency, Figure 9. Rajendran [85] obtained lower energy consumption for R448A (3% to 8%) in a centralized DX system (scroll compressors) with cases and food simulators. In another test facility that uses reciprocating compressors and two separate temperature/humidity controlled rooms [86] (Figure 10), R448 average COP was 11.6% higher than that obtained with R404A.

Figure 8. Semi-hermetic condensing unit with evaporator for walk-in freezer/cooler [84].

Figure 9. Performance comparison of R448A vs. R404A at a) Low Temperature conditions and b) Medium Temperature conditions [84].

Figure 10. Commercial Refrigeration unit with two separate temperature/humidity controlled rooms [86]

Due to the European GWP limitation of 150 in self-contained units and hermetically sealed systems, Honeywell is testing HDR-110 [84]. It is a low-flammable R404A alternative and even though is less flammable than hydrocarbons, some system modification are necessary. In a reach-in freezer it showed higher 3% system efficiency and near match in capacity (4% lower). Energy efficiency of such systems could be enlarged using an intermediate heat exchanger.

In et al. [87] investigated the partial load performance of an RAC unit using R410A, R32 and R446A. The overall seasonal energy efficiency ratio and COP were higher by 1% for the R446A relative to R410A. Besides, the optimal refrigerant charge for R446A was 10% lower than R410A. Although R447A studies has not been found, Koyama et al. [52] demonstrated that the addition of R32 improve considerably the capacity of R1234ze(E) to replace R410A. For a cooling load of 2.8kW, COP of R1234ze(E)/R32 (50/50) is 7.5% lower than that of R410A whereas for R1234ze(E) is 20% lower (at 1.6kW).

Table 7. Summary of experimental performance studies for R1234ze(E) mixtures.

As happens for pure R1234ze(E), it also has been considered for transcritical Rankine cycle systems mixed with CO<sub>2</sub>. Dai et al. [88] recommends this blend for large scale applications due to their relatively low flammability to override the limitation in condensation temperature of pure CO<sub>2</sub>.

## 5. Conclusions

HVACR systems are moving towards the use of low-GWP fluids. So, in future years natural refrigerants or HFO will impose, depending on the tradeoffs (performance, costs, flammability, etc.). One of the most promising HFO option in refrigeration and air conditioning systems is R1234ze(E), with a GWP of 4 and lower flammability than R1234yf. In this paper recent studies of R1234ze(E) (pure or mixed with other refrigerants) are reviewed. Properties, heat transfer and

system performance studies are comprised in this work. The main conclusions of the paper are as follows.

Thermodynamic properties studies about this refrigerant are at an advanced stage and the accuracy provided by EOS for R1234ze(E) is at the same level that other commonly used refrigerants. Same conclusion can be reached for mixtures with R152a, R32 and CO<sub>2</sub> (especially this). Flammability of R1234ze(E) is not critical in heat pump systems under normal operation and at low humidity it becomes non-flammable.

R1234ze(E) evaporation HTC have been obtained in different geometries and seems to be similar to that performed by R134a. In contrast with this phenomenon, R1234ze(E) condensation HTC is 10% lower. Pressure drops of R1234ze(E) are always higher and it should be considered in heat exchanger optimization. To enlarge R1234ze(E) HTC R32 is added, even though this parameter is minimized at 20% in R1234ze(E) composition.

All the studies consulted agree that if R1234ze(E) is used in R134a systems, some modifications should be done to maintain energy performance. In chillers R1234ze(E) can reduce considerably CO<sub>2</sub> final emissions and although in heat pumps performs well, its isomer, R1234ze(Z), is recommended. R1234ze(E) responds positively (better energy efficiency increase than R134a) to basic cycle modifications.

HFO/HFC mixtures are the HFC replacements that require less systems changes of all the low-GWP alternatives. At present, different R1234ze(E) mixtures are registered to substitute R134a, R404A and R410A. These blends present good energy efficiency and adaptation to existing systems. Despite of that, either their GWP is still too high or they are low-flammable and cannot represent a definitive solution if the system architecture is not modified.

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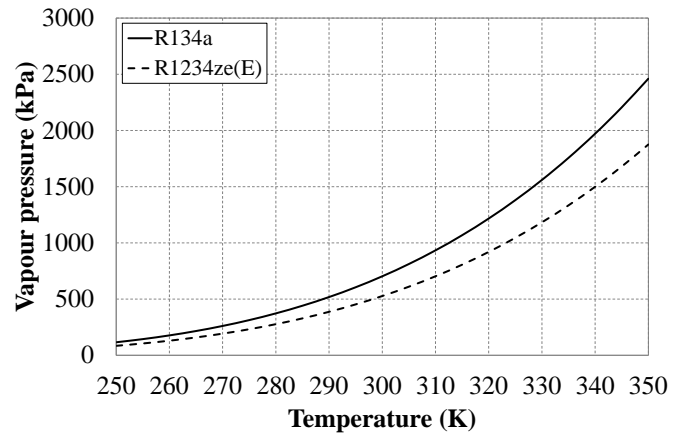


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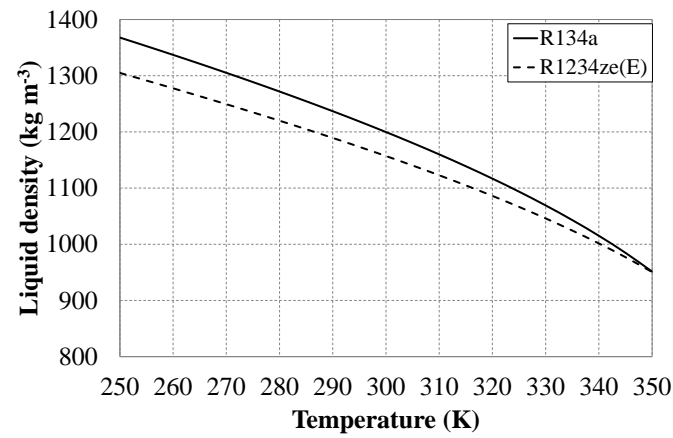
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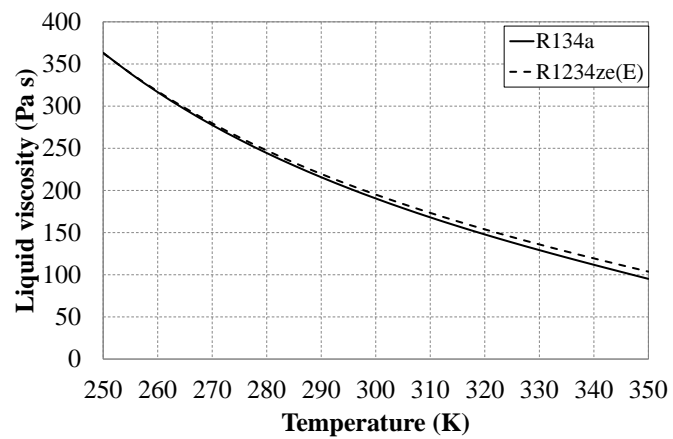
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a)



b)



c)

Figure 1. Comparison between R1234ze(E) and R134a at different temperatures [21]: a) Vapour pressure, b) Liquid density and c) Liquid viscosity.

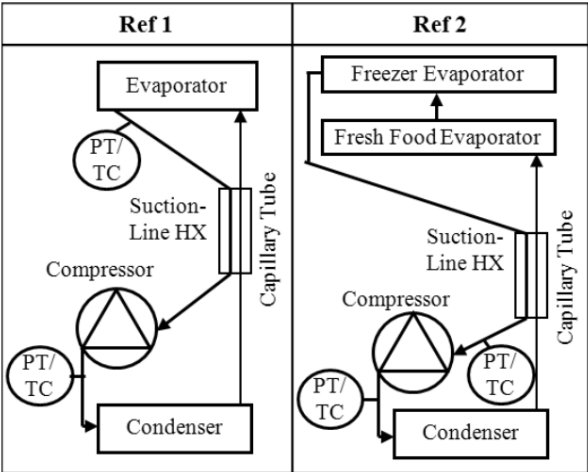


Figure 2. Two domestic refrigerator architectures studied by Karber et al. [59].

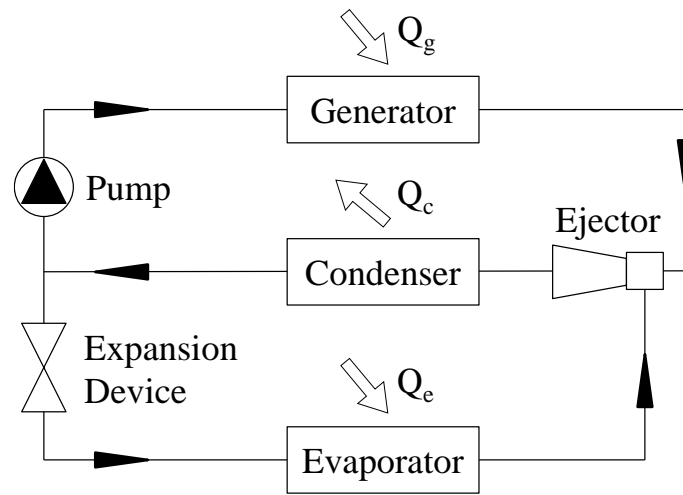


Figure 3. Ejector refrigeration system [63].

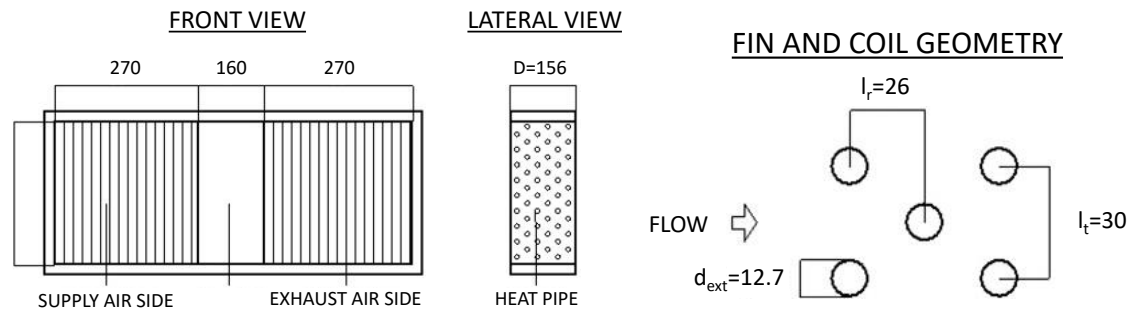


Figure 4. Micro-fin tubes heat pipe heat exchanger used by Longo et al. [65].



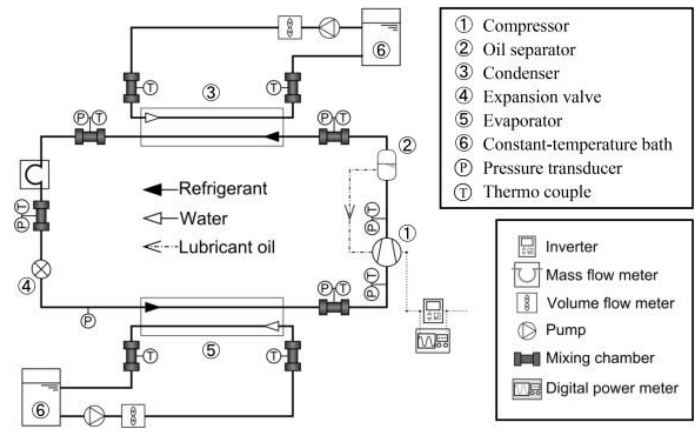


Figure 5. Experimental high-temperature heat pump apparatus [66].

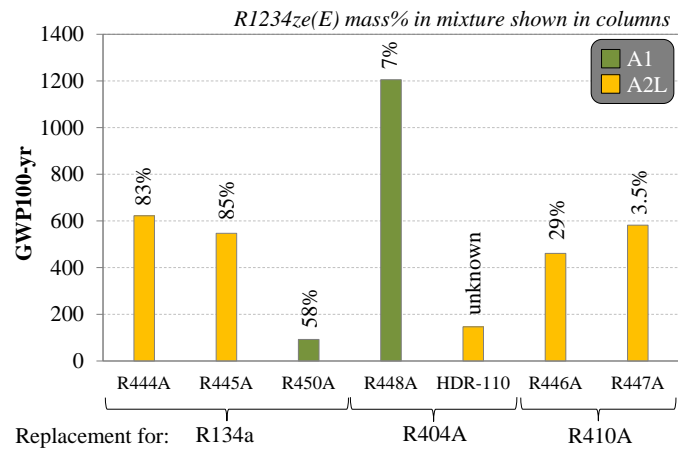


Figure 6. Mixtures identified by AHRI that contains R1234ze(E) in their composition.

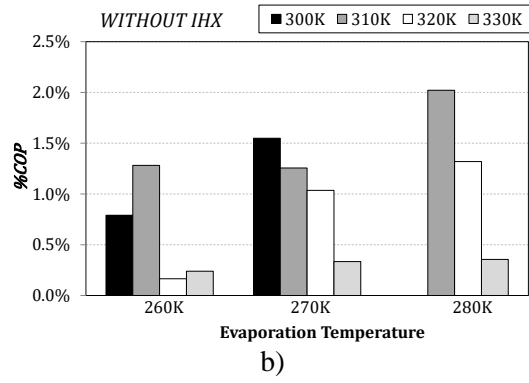
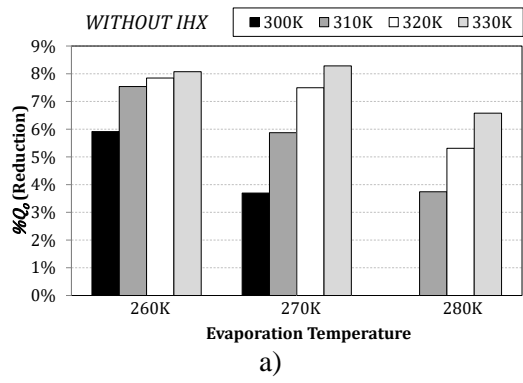


Figure 7. Performance comparison of R448A vs. R404A without IHX: a) Cooling capacity and b) COP [76].

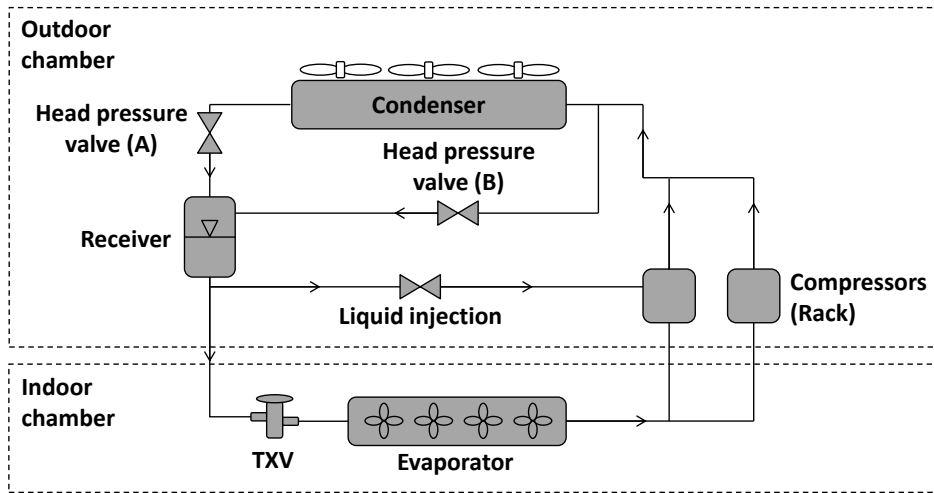


Figure 8. Semi-hermetic condensing unit with evaporator for walk-in freezer/cooler [84].

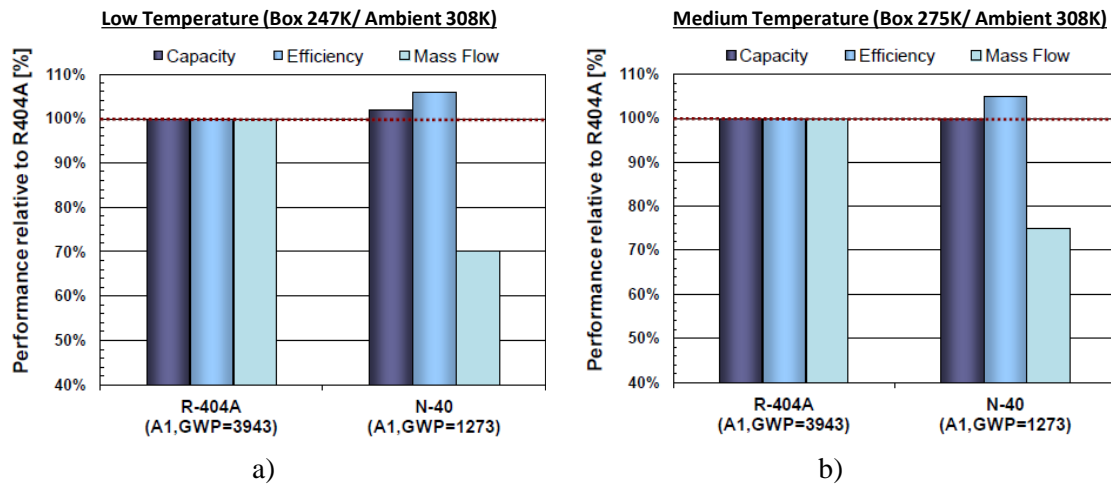


Figure 9. Performance comparison of R448A vs. R404A at a) Low Temperature conditions and b) Medium Temperature conditions [84].

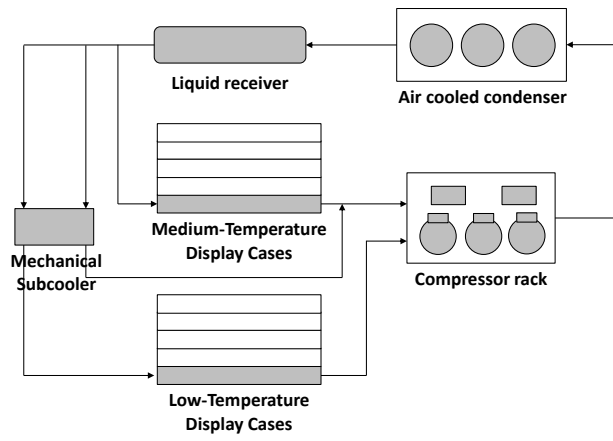


Figure 10. Commercial Refrigeration unit with two separate temperature/humidity controlled rooms [86].

## FIGURE CAPTIONS

Figure 1. Comparison between R1234ze(E) and R134a at different temperatures [21]: a) Vapour pressure, b) Liquid density and c) Liquid viscosity.

Figure 2. Two domestic refrigerator architectures studied by Karber et al. [59].

Figure 3. Ejector refrigeration system [63].

Figure 4. Micro-fin tubes heat pipe heat exchanger used by Longo et al. [65].

Figure 5. Experimental high-temperature heat pump apparatus [66].

Figure 6. Mixtures identified by AHRI that contains R1234ze(E) in their composition.

Figure 7. Performance comparison of R448A vs. R404A without IHX: a) Cooling capacity and b) COP [76].

Figure 8. Semi-hermetic condensing unit with evaporator for walk-in freezer/cooler [84].

Figure 9. Performance comparison of R448A vs. R404A at a) Low Temperature conditions and b) Medium Temperature conditions [84].

Figure 10. Commercial Refrigeration unit with two separate temperature/humidity controlled rooms [86].

Table 1. Considerations about candidates to replace high-GWP refrigerants used in supermarkets.

Candidate	Considerations
Natural Refrigerants	
Hydrocarbons [4]	<ul style="list-style-type: none"> <li>• Efficient, flammable and non-toxic.</li> <li>• Low charge systems.</li> <li>• Specially isobutene, R600A, or propane, R290</li> </ul>
Dioxide Carbone (R744) [5]	<ul style="list-style-type: none"> <li>• Not enough efficient, non-flammable and non-toxic.</li> <li>• In transcritical systems or at the low stage of cascade systems.</li> </ul>
Ammonia (R717) [6]	<ul style="list-style-type: none"> <li>• Very efficient, low flammable and toxic.</li> <li>• In large industrial refrigeration systems.</li> </ul>
Synthetic Refrigerants	
Low-GWP HFC [7]	<ul style="list-style-type: none"> <li>• Similar efficiency, low flammable and non-toxic</li> <li>• R32 (GWP=677) clear replacement to R410A in stationary air conditioning.</li> </ul>
HFO [8]	<ul style="list-style-type: none"> <li>• Less efficient, low flammable and non-toxic.</li> <li>• R1234yf, R1234ze(E), R1234ze(Z), R1233zd, ...</li> </ul>
HFO/HFC mixture [2,9]	<ul style="list-style-type: none"> <li>• Similar efficiency to HFC.</li> <li>• Can be used as drop-in or retrofit substitutes.</li> <li>• It can be low-GWP and low-flammable or medium-GWP and non-flammable, depending on the composition.</li> </ul>



Table 2. Main results of Lai et al. [23].

AAD between	BACKONE EOS	PC-SAFT EOS	Multi-parameter EOS
Vapour pressures	0.34%	0.16%	0.55%
Saturated liquid densities	0.42%	1.51%	0.17%
Compressed liquid densities	0.60%	1.35%	0.07%
Isobaric heat capacities	2.29%	2.91%	2.21%
Pressures in gaseous phase	0.99%	1.84%	0.11%

Table 3. Main refrigerant properties of R1234ze(E) and R134a [21].

	R134a	R1234ze(E)	Sign / Influence on vapour compression system
ASHRAE safety classification	A1	A2L	
ODP	0	0	
100-year GWP	1300	4	
Critical Temperature (K)	374.21	382.51	2% higher / Lower volumetric capacity and higher COP
Critical Pressure (kPa)	4059.28	3634.90	10% lower
NBP (K)	247.08	253.88	3% higher / Lower evaporation range
Liquid density <sup>a</sup> (kg m <sup>-3</sup> )	1295.27	1240.56	4% lower / Lower pressure drop
Vapor density <sup>a</sup> (kg m <sup>-3</sup> )	14.35	11.65	19% lower / Lower mass flow rate per unit volume of compression
Liquid $c_p$ <sup>a</sup> (kJ kg <sup>-1</sup> K <sup>-1</sup> )	1.34	1.32	2% lower / Higher liquid subcooling at the exit of condenser
Vapor $c_p$ <sup>a</sup> (kJ kg <sup>-1</sup> K <sup>-1</sup> )	0.90	0.88	similar <sup>b</sup>
Latent heat of vaporization (kJ kg <sup>-1</sup> )	198.72	184.28	7% lower / Lower refrigerating effect
Liquid therm. cond. <sup>a</sup> (W m <sup>-1</sup> K <sup>-1</sup> )	92.08·10 <sup>-3</sup>	83.11·10 <sup>-3</sup>	10% lower / Lower heat transfer
Vapor therm. cond. <sup>a</sup> (W m <sup>-1</sup> K <sup>-1</sup> )	11.50·10 <sup>-3</sup>	11.57·10 <sup>-3</sup>	similar <sup>b</sup>
Liquid viscosity <sup>a</sup> (Pa s <sup>-1</sup> )	267.04·10 <sup>-6</sup>	269,44·10 <sup>-6</sup>	similar <sup>b</sup>
Vapor viscosity <sup>a</sup> (Pa s <sup>-1</sup> )	10.72·10 <sup>-6</sup>	11,19·10 <sup>-6</sup>	4% higher / Higher pressure drop

<sup>a</sup> at 273K.

<sup>b</sup> relative difference less than 1.5%.

Table 4. Summary of heat transfer and pressure drop studies for pure R1234ze(E).

Reference	Test section	Conditions	Results for R1234ze(E) compared to R134a
<b>Flow Boiling</b>			
Grauso et al. [40]	6mm circular smooth tube	T=[270, 285] K G=[146, 520] kg m <sup>-2</sup> s <sup>-1</sup> q"=[5, 20.4] kW m <sup>-2</sup>	- HTC similar to R134a except at low quality. - Frictional pressure gradients are slightly higher (12% if G≈350 kg m <sup>-2</sup> s <sup>-1</sup> ).
Kedzierski and Park [41]	5.45 mm (D <sub>h</sub> ) microfin tube connected by U-bend.	T=[293, 323] K G=[100,418] kg m <sup>-2</sup> s <sup>-1</sup> q"=[2.6, 42.2] kW m <sup>-2</sup> x=[0.003, 0.82]	- 700 kW K <sup>-1</sup> m <sup>-2</sup> less below x=0.3.
Diani et al. [42]	3.4mm microfin tube.	T=303K G=[190, 940] kg m <sup>-2</sup> s <sup>-1</sup> q"=10, 25, 50 kW m <sup>-2</sup> x=[0.2, 0.99]	- HTC 8-10% lower. - The maximum frictional pressure gradient (at x <sub>mean</sub> =0.85 and G=940 kg m <sup>-2</sup> s <sup>-1</sup> ) is 18% higher.
Righetti et al. [43]	Off-the-shelf roll-bond evaporator.	T <sub>cond</sub> =313 K T <sub>sub</sub> =[21, 25] K G=[10,56] kg m <sup>-2</sup> s <sup>-1</sup> x <sub>evap,in</sub> =[0.27, 0.3]	- HTC very similar (also with R1234yf and R600a).
Mancin et al. [44]	High porosity copper foam with 5 PPI and porosity of 0.93.	T=303.15 K G=[30, 225] kg m <sup>-2</sup> s <sup>-1</sup> q"=[50, 100] kW m <sup>-2</sup> x=[0.2,0.95]	- Lower HTC, especially at high G. - If G=200 kg m <sup>-2</sup> s <sup>-1</sup> and x <sub>mean</sub> =0.5, HTC is 14% lower. - Pressure drop is 30% higher.
<b>Pool boiling</b>			
Van Rooyen and Thome [46]	Wolverine Turbo-B5 and Wieland Gewa-B5.	T=278 and 288 K G=[4, 35] kg m <sup>-2</sup> s <sup>-1</sup> q"=[15, 70] kW m <sup>-2</sup>	- Turbo-B5 HTC 11% greater. - Gewa-B5 HTC 2% lower.
<b>Condensation</b>			
Del Col et al. [47]	0.96 mm diameter minichannel.	T=[311.8, 314] K G=[200, 800] kg m <sup>-2</sup> s <sup>-1</sup>	- If low x and G= 200 kg m <sup>-2</sup> s <sup>-1</sup> , HTC is 16% higher. - If G= 800 kg m <sup>-2</sup> s <sup>-1</sup> , HTC is between 20 and 28% higher. - If G= 200 kg m <sup>-2</sup> and G= 200 kg m <sup>-2</sup> the pressure drop is 18 and 24% higher.
Longo et al. [48]	BPHE of 10 plates: - Inclination of 65° - Corrugation of 2 mm.	T <sub>cond</sub> =[298, 313.4] K G=[10.7, 39.9] kg m <sup>-2</sup> s <sup>-1</sup> q"=[5.3, 26] kW m <sup>-2</sup>	- Lower (4%–6%) HTC and higher (10%) frictional pressure drops.
Park et al. [49]	1.45 mm (D <sub>h</sub> ) aluminum multi-port tube with rectangular channels.	T=[298, 343] K G=[50, 260] kg m <sup>-2</sup> s <sup>-1</sup> q"=[1, 62] kW m <sup>-2</sup> x= [0, 1]	- If G=150 kg m <sup>-2</sup> s <sup>-1</sup> and T=313 K HTC is between 15 and 25% lower than for R134a (but slightly lower than R236fa).
Agarwai and Hrnjak [51]	6.1 mm circular smooth copper tube	T=[303, 323] K G=[100, 300] kg m <sup>-2</sup> s <sup>-1</sup> x>0.05	- Much higher pressure drop.

		ShD up to 50K	
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Table 5. Summary of heat transfer and pressure drop studies for R1234ze(E) mixtures.

Reference	Test section	Conditions	Results
Koyama et al. [52]	Heat pump system: - Double-tube type condenser.	$Q_o=[1, 2.8]$ kW $ShD_{evap}=3K$ $T_{sink,in}=293K$ $T_{sink,out}=318K$ $T_{source,in}=288K$ $T_{source,out}=282K$	- R1234ze(E) and R1234ze(E)/R32 has similar $\Delta P$ than R410A. - COP of mixture is affected by ScD.
Hossain et al. [53]	4.35 mm water heated double tube HX.	$T=278,283$ K $G=[150, 445]$ kg m <sup>-2</sup> s <sup>-1</sup> $x=[0, 1]$	- R1234ze(E)/R32 HTC is higher than R1234ze(E) at low x only. - If $x=0.48$ and $G=300$ kg m <sup>-2</sup> s <sup>-1</sup> : R1234ze(E) HTC 11%, 56% and 83% lower than R1234ze(E)/R32, R410A and R32.
Kondou et al. [54]	5.21 mm horizontal microfin tube.	$T=283.15K$ $G=[150, 400]$ kg m <sup>-2</sup> s <sup>-1</sup> $q=10$ and $15$ kW m <sup>-2</sup>	- R32/R1234ze(E) HTC is lower than R1234ze(E). - HTC is minimized at 0.2/0.8 by mass.

Table 6. Summary of experimental performance studies for pure R1234ze(E).

Reference	System	Conditions	Results for R1234ze(E) compared to R134a
Mota-Babiloni et al. [55]	Vapour compression system: - Piston compressor. - Shell-and-tube condenser and evaporator.	$T_{\text{evap}}=260, 270, 280$ K $T_{\text{cond}}=310, 320, 330$ K	- 30% lower $Q_o$ and 6% lower COP. - IHX greater influence on R1234ze(E) COP.
Jankovic et al. [56]	Small power refrigeration system: - reciprocating compressor.	$T_{\text{evap}}=[263,283]$ K $T_{\text{cond}}=[308, 328]$ K $ShD_{\text{evap}}= 5$ K	- $Q_o$ 27% lower. - Similar COP.
Spatz [57]	Adapted medium pressure air-cooled chillers	$T_{\text{amb}}=[15,42]$ K	- COP and LCCP 12% higher 7% lower.
Brasz [58]	Oil-free centrifugal compressors TT300 and DTC TT300D compressors.	Flow factor = [0.00025, 0.00085] $m^2$	- COP is 4% higher.
Karber et al. [59]	Two domestic refrigerators: - Ref1: traditional 0.49 $m^3$ top freezer model. - Ref2: advanced 0.74 $m^3$ bottom freezer French door model.	$T_{\text{amb}}=305.4$ K $H_{\text{rel}}=50\%$ $T_{\text{case,L}}=255.4$ K $T_{\text{case,M}}=269.3$ K	- $E_{\text{system}}$ : 15.5 and 5.4% lower in Ref1 and Ref2. - Run time: 50.8% and 40% in Ref1 and Ref2.
Leighton et al. [60]	0.782 $m^3$ domestic French door refrigerator-freezer.	DOE 2005 $T_{\text{amb}}= 305.4$ K	- 21.5% lower $Q_o$ , 27.3% $P_c$ and 7.9% higher COP.
Yana Motta et al. [61]	Vending system: - Tube-and-fin HX. - 75% larger displacement reciprocating compressor for R1234ze(E). - Needle valve.	$T_{\text{amb}}=305.3$ K $H_{\text{rel}}=65\%$ $T_{\text{interior}}=375$ K	- 12% larger $Q_o$ , 8% lower COP, 5% higher $T_{\text{disch}}$
Longo et al. [65]	Micro-fin tubes heat pipe HX.	$T_{\text{air}}=[280, 313]$ K $H_{\text{rel}}=[26, 90]$ % $V_{\text{air}}=[400, 1000]$ $m^3$ $h^{-1}$	- Similar thermal effectiveness.
Fukuda [66] <sup>a</sup>	Heat pump system: - Double-tube-type HX. - Heat sink water loop. - Heat source water loop.	$T_{\text{sink,in}}=275$ K $T_{\text{sink,out}}=348$ K $T_{\text{source,in}}=318$ K $T_{\text{source,out}}=312$ K $ShD_{\text{evap}}=3$ K $ScD_{\text{cond}}=[20,25]$ K $Q_{\text{cond}}=[1.2, 2.4]$ kW	- $P_{\text{comp}}$ is lower than R1234ze(Z) below 348K.

<sup>a</sup> Compared to R1234ze(Z)

Table 7. Summary of experimental performance studies for R1234ze(E) mixtures.

Reference	System	Conditions	Results
Mota-Babiloni et al. [76]	Vapour compression system: - Piston compressor. - Shell-and-tube HX.	$T_{\text{evap}}=260, 270, 280$ K $T_{\text{cond}}=300, 310, 320, 330$ K	- R450A $Q_o$ is from 8% to 4% lower than R134a. - R450A COP up to 2% greater than R134a.
Schultz and Kujak [77]	230 tons RTWD dual-circuit screw compressor water cooled chiller.	AHRI Standard 550/590-2011	- R450A $Q_o$ , COP and is 15%, 1.4% and 6K lower than R134a.
Tewis Smart Solutions [78]	Commercial refrigeration system central : - Piston compressors rack.	$T_{\text{suction}}=263$ K $T_{\text{discharge}}=313$ K $T_{\text{case}}=274$ K	- R450A $E_{\text{system}}$ is 3.10% lower than that of R134a.
Honeywell International Inc [79]	CO <sub>2</sub> refrigerated distribution circuit freeze containers, cold rooms and display cabinets. Liquefaction unit uses screw compressors of 800kW capacity.	$T_{\text{evap}}=262$ K $T_{\text{cond}}=318$ K $Q_o=800$ kW	- R450A/CO <sub>2</sub> annual savings are 90 tons CO <sub>2eq</sub> compared with a secondary glycol/R134a/CO <sub>2</sub> and 960 tons CO <sub>2eq</sub> compared with a R404A DX. - R450A/CO <sub>2</sub> $T_{\text{disch}}$ is 383K.
	Condensing unit and an evaporator for a walk-in freezer/cooler: - Semi-hermetic reciprocating compressor. - Fin HX. - Same TXV for both refrigerants.	$T_{\text{evap,L}}=[247, 255]$ K $T_{\text{evap,M}}=[275, 308]$ K $T_{\text{amb}}=286, 297$ and 308 K	- If $T_{\text{amb}}=308$ K, $T_{\text{evap,L}}=247$ K and $T_{\text{evap,L}}=275$ K; R448A have similar $Q_o$ , 6% higher COP and 4% lower $T_{\text{disch}}$ than R404A.
	560 W single-door reach-in freezer: - Hermetic compressor - Air-to-refrigerant tube-in-fin HX - TXV - SLHX	ASHRAE 72-2005	- HDR-110 $Q_o$ and COP is 4% lower and 3% higher than R404A.
Rajendran [84]	Centralized DX system: - Scroll compressors. - Air-cooled condensers. - Food cases simulators.	$T_{\text{evap,L}}=243$ K $T_{\text{evap,M}}=262$ K $T_{\text{cond}}=305, 314$ and 322 K	- R448 $E_{\text{system}}$ is 3% and between 3 and 8% lower than that of R404A in LT and MT systems. - R448A LCCP improved by 41%.
Abdelaziz and Fricke [85]	Supermarket refrigeration system: - Reciprocating compressors. - Two controlled rooms.	$T_{\text{amb}}=[289, 314]$ K	- R448 $Q_o$ and COP is 7.5% and 11.6% higher than R404A.