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Risk assessment and selection of low GWP refrigerants for heat pumps in residential applications

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This work deals with the risk related to the flammability and toxicity of low Global Warming Potential (GWP) refrigerants used in heat pumps for residential applications. Some new generation refrigerants were analyzed assuming to make a drop-in for a typical 50 kW heat pump, suited for small multi-family buildings (4 ÷ 6 dwellings). The theoretical maximum Coefficient of Performance (COP) was calculated for the selected fluids, identifying the best performing one from an energy point of view. Subsequently, an analysis of some of the potentially more dangerous accident scenarios was performed, considering the outdoor/indoor release of gases. More in detail, two accident scenarios were analyzed, assuming a refrigerant leak from a hole in the pipeline downstream of the heat pump compressor: in one case the gas is released in an open environment with an ignition near the release point (jet fire), in the other case the release happens within a confined environment. In both cases, the conditions in which it is possible to operate safely were determined.

1. Introduction

Heat pumps play a key role in reducing the energy and environmental impact in air conditioning of residential and tertiary buildings, since they allow heating, cooling and domestic hot water production with a unique machine. Historically, three generations of refrigerants have followed in HVAC&R (Heating, Ventilation, Air Conditioning, and Refrigeration) applications (Cavallini, 2007) each of them replaced by the subsequent one for environmental reasons. Currently, heat pumps use HFC (Hydrofluorocarbon) refrigerants, with a significant environmental impact in terms of Total Equivalent Warming Impact. Due to the increasing need to reduce greenhouse gases emissions and to contain the global warming, the recent EU F-Gas Regulation (EU REGULATION, 2014), fully compliant with the Kigali amendment requirements, imposes the use of low GWP refrigerants also in heat pumps. The 4th-generation refrigerants are candidates for replacing the fluids currently on the market; however, they show significant flammability and toxicity hazards. There are some studies on the safe use of refrigerants, precisely in terms of their flammability and toxicity (JSRAE, 2017; Lewandowski, 2011): both of them assess the possible accidental scenarios by means of typical tools of risk analysis, such as Fault Tree Analysis. One of them focuses on the cooling mode equipment only (JSRAE, 2017). In the present work a simplified quantitative analysis of a specific residential 50 kW HP machine is performed, which may give useful information about the safety measures to be adopted in a residential heating & cooling application.

2. Low GWP selected fluids

Some low GWP refrigerants have been proposed as substitutes for the fluids currently used in Heat Pumps (HP) assuming to make a drop-in of the machines currently on the market. In the following discussion R-410A (Table 1) is taken as reference fluid because it is the most widely used refrigerant for HP applications.

For the sake of completeness, two natural refrigerants, namely NH_3 and CO_2, could also be used as substitutes, however they would require a rather heavy re-design of the machine. The fluids selected are those suited for a drop-in of the machine without excessive costs and substantial modifications of the heat pump. The main features of these fluids are shown in Table 1 (Chemours, 2018; Honeywell, 2017; Lewandowski, 2011, JSRAE, 2017), in terms of environmental impact and safety.

Table 1 Selected fluids: composition and GWP

Fluid	R-410A	R-32	R-1234ze	R-1234yf	R-454B	R-452B
Composition	Mixture: R125/R32	Pure Substance	Pure Substance	Pure Substance	Mixture: R1234yf/R32	Mixture: R32/R125/R1234yf
GWP	2088	675	6	4	467	675
LFL (% volume in air)	n.f.	13.3	6.39	6.21	11.25	11.9
UFL (% volume in air)	n.f.	29.3	13.3	14.0	22.0	not determined
ASHRAE Safety Class	A1	A2L	A2L	A2L	A2L	A2L
LC50 (ppm)	763000	>760000	>207000	>406000	Not available	Not available

3. Performance analysis of low GWP refrigerants in heat pumps

The HP performance depend on the working fluid temperature and the climatic conditions. These external parameters determine the COP, that is the HP performance index, defined as the ratio of the useful heat transfer for heating (or cooling) and the required drive energy. For a heat pump (Figure 1), once the operating thermodynamic features are known, the maximum theoretical COP is given by:

$$COP_{max} = \frac{Q_{cond}}{L} \tag{1}$$

where Q_{cond} is the heat exchanged at the condenser and L is the actual work of the compressor, calculated as shown below:

$$L = \frac{\left(h_{out,compr} - h_{in,compr}\right)}{0.89} \tag{2}$$

The coefficient 0.89 takes into account the electrical efficiency of the compressor and the heat losses of the motor (Dorin SpA, 2014; D'Annibale et al., 2019); $h_{in,compr}$ is the compressor inlet enthalpy, which depends on the superheat at the evaporator outlet and the evaporation pressure; $h_{out,compr}$ is the compressor outlet actual enthalpy, that is function of the isentropic efficiency, according to the following relationship:

$$h_{out,compr} = h_{in,compr} + \frac{\left(h_{out,compr_{theor.}} - h_{in,compr}\right)}{\eta_{is}} \tag{3}$$

$h_{out,compr_{theor.}}$ is the theoretical compressor outlet enthalpy, that is function of the condenser enthalpy and the compressor inlet entropy. The heat exchanged in the condenser, Q_{cond}, is calculated as the difference between the compressor outlet enthalpy and the condenser outlet enthalpy; for the selected compressor it is assumed equal to 0.75. For the sake of simplicity, the enthalpy at the compressor exit is set equal to the enthalpy entering the condenser, while the enthalpy leaving the condenser depends on the temperature at the condenser exit and the condensing pressure. All the thermodynamic quantities were calculated using REFPROP 9.1 (Lemmon et al., 2018).

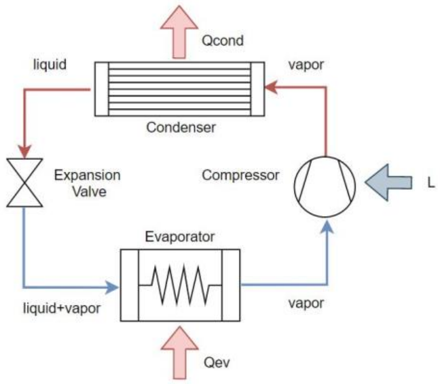
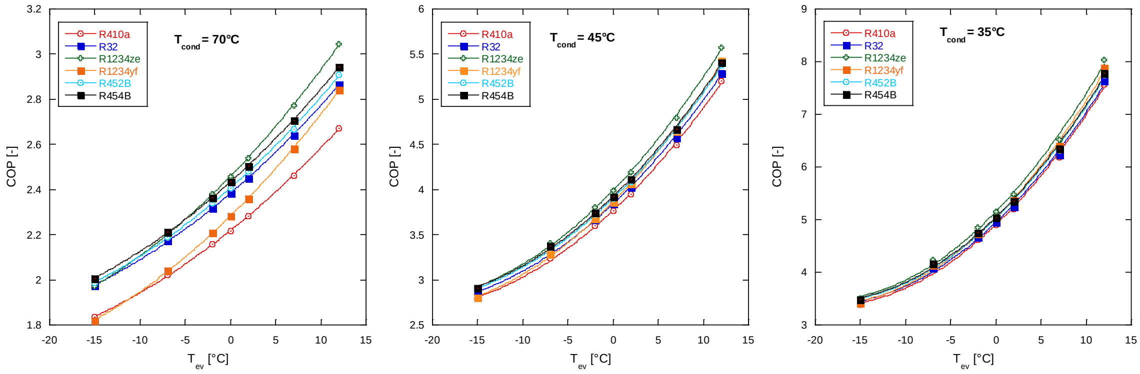


Figure 1 Schematic of the Heat Pump system

For the fluids selected as potential substitutes of traditional HP refrigerants in residential applications, the theoretical COPs were calculated under the different operating conditions, in particular the condensing temperature (for heating applications it is a function of the hydronic loop temperature, thus of the terminals used) and the evaporation temperature. This latter is related to the thermal source temperature, which for air-water heat pumps is usually the outside air temperature. The terminals of a heating system and the consistent condensing temperatures assumed for the calculations are the following: radiators: Tcond = 70 °C; fan coil: Tcond = 45 °C; radiant floor panels: Tcond = 35 °C. The hydronic loop return temperatures are assumed as Tfluid = Tcond-5 °C. The evaporating temperatures here analyzed are: -15, -7, -2, 0, 2, 7 and 12 ° C. The COP trends of the different fluids are shown in Figure 2, for the different operating conditions, at fixed condensing temperature and varying the evaporation temperature. R1234ze showed the best theoretical energy efficiency in all operating conditions. With a condensing temperature of 70 °C the differences in the COP calculated for the various analyzed fluids become more relevant, especially with low evaporating temperatures. When the evaporating temperature increases, the theoretical COPs tend to differ more markedly, with R1234ze showing the best performance compared to R410A, with an increase up to about 15%.
It should be highlighted that the theoretical evaluation of the R452B and R454B performances (that are not azeotropic mixtures) is carried out considering the evaporation and condensation isobars at a mean temperature between the two limit curves that is equal to the saturation temperature of the reference fluids. A different calculation methodology could lead to different results. Moreover, the analysis was performed assuming the same isentropic efficiency for all the fluids. According to some literature results the performance would also significantly depend on the fluid considered (Bobbo et al., 2019).



(a) (b) (c)

Figure 2 COP trend vs evaporation temperature for 3 terminals: a) radiators, b) fan coil, c) radiant floor panels.

4. Accident scenarios analysis

The previous analysis shows that R12334ze is the refrigerant with the best energy performance. Two possible accidental scenarios were then analyzed, with a HP using R1234ze as working fluid. In particular, a reference 50 kW machine with R410A is considered in which to do the drop-in.
Usually, the evaporator is placed outside, but in several cases, such for houses located within historical centers or prestigious independent houses, the heat pump is more commonly located entirely within a closed room.
The two accident scenarios analyzed are:

- Refrigerant leak to the outside from a hole in the pipeline downstream of the heat pump compressor, and subsequent jet fire due to ignition;
- Sudden rupture of the piping leaving the compressor and consequent fluid release in a closed room with different surface areas.

Worst conditions are assumed (in terms of quantity of gas released and intensity of the release itself), considering that the leakage occurs downstream of the compressor, where the refrigerant pressure is at its maximum throughout the circuit.

4.1 Refrigerant leaks to the outside and consequent jet fire

It is assumed that the refrigerant is released from a 1 cm diameter hole along the piping downstream of the HP compressor.
In order to calculate the discharge rate of the fluid, three different case studies are considered based on the terminal used: radiators, fan coils or radiant panels. In Table 2 the upstream conditions, i.e. the working

conditions in the pipeline, at the time of release, are shown, varying the terminals used and therefore the condensation temperatures; an evaporation temperature was set equal to 0 °C.
REFPROP 9.1 allowed to calculate the ratios k = c_p/c_v for the various working conditions.
A sonic discharge is calculated for all the assumed operating conditions, so that the gas discharge flow rate was calculated as:

$$\dot{m} = C_D \cdot A \cdot P_1 \cdot \sqrt{\frac{k \cdot g \cdot M}{R_g \cdot T_1}\left(\frac{2}{k+1}\right)^{\frac{(k+1)}{(k-1)}}} \quad (4)$$

where: $\dot{m}$ is gas mass flow rate through the hole (kg/s); C_D is the discharge coefficient, equal to 0.85; A is the hole area (m^2); P_1 is the upstream pressure (Pa); g is the gravitational constant (N/(kg m/s^2)); M is the molecular weight of the gas (kg/kg-mole); k is the heat capacity ratio, c_p/c_v; R_g is the ideal gas constant (Pa m^3/kg-mole K)=8314; T_1 is the initial upstream temperature of the gas (K) (CCPS, 2000). The discharge flow rate calculated under the three operating conditions analyzed are reported in Table 2.

Table 2 Operating conditions with T_{ev}=0°C, varying the condensation temperature.

Terminal	T1 (°C)	P1 (bar)	P2 (bar)	K (c_p/c_v)	Mass flow rate (kg/s)
Radiators	84.9	16.1	1	1.2629	0.44
Fan Coil	58.4	8.8	1	1.1834	0.24
Radiant panels	47.4	6.7	1	1.1643	0.19

The highest flow rate (highest risk) is obtained when radiators are used as terminals. The generated flame length can be calculated as:

$$\frac{L}{d_j} = \frac{5.3}{C_T}\sqrt{\frac{T_f/T_j}{\alpha_T}\left[C_T + (1 - C_T)\frac{M_a}{M_f}\right]} \quad (5)$$

where L is the length of the visible turbulent flame measured from the break point (m); d_j is the diameter of the jet, that is, the physical diameter of the release hole (m); C_T is the fuel mole fraction concentration in a stoichiometric fuel-air mixture; α_T is the ratio of moles of reactant per mole of product for a stoichiometric fuel-air mixture; M_a is the molecular weight of the air (g/mole); M_f is the molecular weight of the fuel (g/mole) (CCPS, 2000).
For the refrigerant R1234ze the C_T value is much lower than 1: furthermore, assuming that α_T is approximately 1 and the ratio T_f/T_j varies between 7 and 9, the length of the visible turbulent flame is equal to 62 cm.
The radiation received at a distance x from the center of the flame can be calculated by the following formula:

$$E_r = \tau_a \cdot Q_T \cdot F_P = \tau_a \cdot \eta \cdot \dot{m} \cdot \Delta H_C \cdot F_P \quad (6)$$

where: E_r is the radiant flux at the receiver (kW/m^2); τ_a is the atmospheric transmissivity (unitless); Q_T is the total energy radiated by the source (kJ/s); F_P is the point source view factor (m^{-2}) = $F_P = \frac{1}{4\pi x^2}$,; η is the fraction of total energy converted to radiation; $\dot{m}$ is the mass flow rate of the fuel (kg/s); ΔH_C is the energy of combustion of the fuel (kJ/kg), (CCPS, 2000).
An average value of 0.25 is assigned to η (usual range between 0.15 and 0.4). The heat of combustion for the fluid R1234ze is equal to 10.7 MJ/kg (Honeywell, 2019).
The transmissivity is calculated with the following formula (CCPS, 2000):

$$\tau_a = 2.02[P_w \cdot X_s]^{-0.09} \quad (7)$$

where: X_s is the path length distance from the flame surface to the target and P_w is the water partial pressure.

$$P_w = 101325 \cdot RH \cdot exp\left(14.4114 - \frac{5328}{T_a}\right) \quad (8)$$

where (RH) is the relative humidity (percent) and T_a is the ambient temperature (K).
The relative humidity is assumed equal to 50%, while the air temperature is 0 °C, as stated before for the case study. In case of a jet fire, the radiant flux should be kept lower than 3 kW/m^2 to avoid reversible injuries and lower than 12.5 kW/m^2 to avoid structural damages (D.M., 2001). As a consequence, the minimum safety

distances corresponding to the adopted scenarios, are as listed in Table 3. Radiant flux vs source distance is shown in Figure 3.

Table 3 Safety distances in case of Jet Fire for people and structures

Mass flow rate (kg/s)	Minimum safety distance for people (m)	Minimum safety distance for structures (m)
0.44	6	2.9
0.24	4.3	2.1
0.19	3.9	1.9

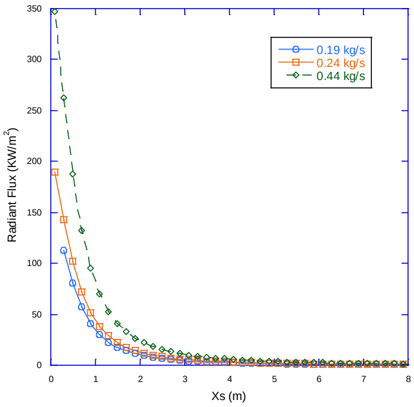
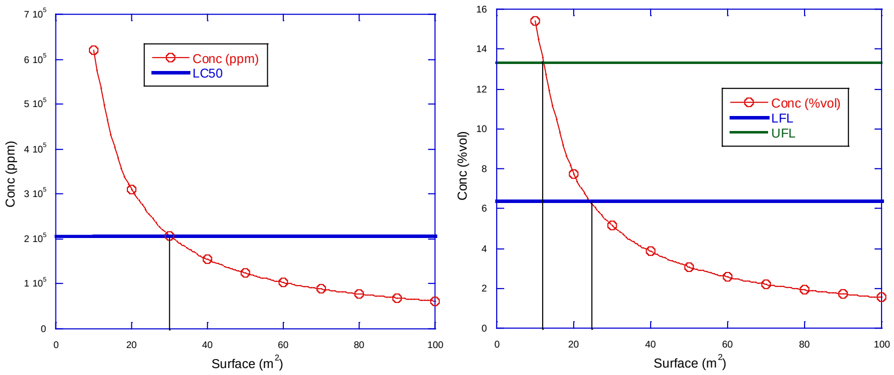


Figure 3 Radiant flux E_r vs source distance (0-8 m). Mass flow rates: 0.44 kg/s, 0.24 kg/s and 0.19 kg/s

4.2 Gas release within a confined environment

It is assumed that the entire machine body is placed indoors in a technical room of the house, having a height of 2.7 m and an air temperature of 7 °C. From the commercial datasheets of heat pumps (IT Wolf GmbH, 2013; INTEGRA) that use R410 A as refrigerant, it was possible to estimate the refrigerant mass of a 50 kW HP, equal to about 17 kg. It has been assumed that the refrigerant mass in the circuit is proportional to the density of the liquid at the condenser exit; referring to an evaporation temperature of 0 °C and to radiators as terminals (condensing temperature of 70 °C), the refrigerant mass obtained for R1234ze is about 21.6 kg. It is assumed that the entire mass of the fluid is released in a closed room.
It is assumed that the refrigerant is at the room temperature (7°C). The average concentration was estimated at varying surface areas of the room where the heat pump is located (and therefore at different room volumes). The results are reported for a surface area ranging from 10 to 100 m^2 (Figure 4): it is noted that toxic hazards may arise for surface areas lower than 30 m^2, while a fire hazard is present in the case of releases in rooms with a surface area between 12 and 25 m^2 approximately.



(a) (b)

Figure 4 R1234ze concentration vs surface in a closed environment: a) toxicity; b) flammability.

5. Conclusions

In this work, the risk related to the use of new low environmental impact refrigerants (low GWP) in heat pumps for residential applications was analyzed: these fluids are potentially toxic and flammable. In particular, it has been assumed to make a drop-in for a typical 50 kW heat pump, suited for small multi-family buildings. Among the analyzed fluids, the highest energetic efficiency was shown by R1234ze. For this fluid, two different accident scenarios were studied:

- a refrigerant leak from a hole in the pipeline downstream the heat pump compressor, and subsequent jet fire;
- a sudden rupture of the piping leaving the compressor, with fluid release in a closed room of varied surface area.

In the case of the jet fire for a gas mass flow rate of 0,44 kg/s (the maximum flow rate for the assumed operating conditions), the minimum safety distance to be maintained from the radiation source is 6 m.

For the second accidental scenario, it was concluded that, for safety reasons, the installation of 50 kW heat pumps inside small surface area technical rooms should be discouraged, due to the presence of both toxicity and fire hazards. In particular, for the fluid with the best energy performance (R1234ze), in the worst case (when exceeding toxicity limits) the minimum surface of the technical room should be equal to 30 m^2.

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