Who Wants to Be a Millionfold Deployed Refrigerant?

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Heat pumps are a key technology to accelerate the defossilization of all sectors. Especially in residential applications, heat pumps serve as exchange technology for conventional heating technologies. The operation of heat pumps requires a refrigerant that significantly determines the system's efficiency. However, the refrigerant choice is complex due to interactions with all components and nonlinear thermodynamic behavior. Therefore, refrigerant selection is widely discussed in the literature. This work introduces the refrigerant selection problem and applies a simple screening method to identify proper refrigerants in residential heat pumps. The application reveals future work to improve the refrigerant selection aiming for the optimal refrigerant in heat pumps concerning their application.

The building sector in Germany currently comprises around 19 million buildings. In nine out of ten cases, the heat supply of these buildings is based on the combustion of oil and gas in conventional heating systems [1]. The combustion yields that 30% of total CO_2 emissions in Germany are attributable to the building sector, with almost 80% of these emissions being emitted in the provision of space heating and domestic hot water [2]. Reducing emissions of greenhouse gases (primarily CO_2) in the building sector is an essential pillar of the German government's comprehensive program to achieve Germany's climate targets.

The heat pump is an alternative, efficient and sustainable technology to supply a building with heat. Unlike conventional heating systems, the total emissions of a heat pump are differentiated into direct and indirect emissions. The direct emission results from the refrigerant used and the respective filling quantity. The lower the GWP and the refrigerant charge, the lower the direct emissions in the event of a leakage. On the other hand, indirect emissions result from electricity to drive the heat pump. Especially when the electricity used has a high share of renewable energy or is generated with highly efficient power plants, heat pumps lead to primary energy savings and thus to a reduction in emissions in general [3]. Furthermore, indirect emissions decrease if the heat pump's efficiency is increased. Basically, the higher the efficiency, the less electricity must be used to provide heat, whereby the efficiency strongly depends on the selected refrigerant.

Today, the most widely used refrigerants belong to the fluid group of fully or partially halogenated hydrocarbons (HCFC and HFC). Fully or partially halogenated hydrocarbons are non-flammable and also considered safety refrigerants. Furthermore, they have no ozone depletion potential (ODP value: "Ozone Depletion Potential") and are characterized by good thermodynamic properties. However, despite their advantages, HCFCs and HFCs are criticized for their very high GWP and will have to be replaced by more environmentally friendly refrigerants in the long term. In this regard, EU Regulation No. 517/2014 [4] provides a roadmap that regulates the gradual reduction of the sales volume of hydrofluorocarbons in the future. Thus, only refrigerants with a low GWP may be used in the future, leading to refrigerant selection problems.

Requirements for Refrigerant Selection

The choice of refrigerant is complex due to interactions in the process and thermodynamic nonlinearities. In addition, an enormous number of potential refrigerants and their mixtures exist, which must meet a variety of requirements see Figure 1. Essentially, these requirements can be divided into three areas: political (1), thermodynamic-technical (2), and economical-ecological (3).

1. Ever-increasing political requirements for refrigerants

Refrigerants with an ODP have been banned since the 1990s by resolutions based on the Montreal Protocol [5]. With the European F-Gas regulation, a gradual reduction of the sales volume of fluorinated by 79% until 2030 is currently being implemented [4]. Since 2020, the reduction amount has increased to 55% compared to 2015. In addition, bans on refrigerants with high GWP are being successively enacted for defined applications for specific filling quantities and refills. In order to offer sustainable and legally compliant heat pumps for the provision of heat for residential buildings in the long term, only refrigerants with a GWP of 150 or less should be used in the future.

2. Thermodynamic-technical requirements for refrigerants

Refrigerants have to fulfill many, partly conflicting thermodynamic-technical requirements despite the increasing political constraints. Refrigerants must generally be thermally and chemically stable [6]. Furthermore, the refrigerant must be sufficiently soluble in oil. Otherwise, sufficient lubrication of the compressor cannot be ensured. In addition, both the temperature and pressure levels must be suitable for the respective application. For example, a refrigerant should not be operated below atmospheric pressure. Low-pressure levels can lead to seal failure or unwanted diffusion of outside air into the circuit, which significantly reduces efficiency. Finally, a refrigerant should not be toxic to humans, especially in residential applications.

3. Economical-ecological requirements for the future

Last but not least, there are economical-ecological requirements. As already described, one of the most influential parameters of a heat pump is its efficiency in energy conversion. Despite the limitations mentioned above, the efficiency of a heat pump must not be negatively affected by a change of refrigerant, as this reduces the potential to be a sustainable technology. For example, although it is comparatively easy to reduce direct emissions, which occur in the event of refrigerant leakage. Changing the refrigerant to a low GWP refrigerant can also reduce the indirect emissions of a heat pump. At the same time, however, the indirect emissions of a heat pump can increase dramatically due to increased electricity consumption at a lower efficiency. A lower efficiency applies analogously to the costs and emissions, depending on the electricity. In addition, the cost of the refrigerant should be low not to inhibit the market penetration of heat pumps.

Automated Refrigerant Selection for a Residential Application

Due to the enormous number of requirements, which can often be simultaneous and partly nonlinear and opposing, a fully automated methodology has been developed at the Institute for Energy Efficient Buildings and Indoor Climate, which allows a rigorous investigation of the refrigerants under given boundary conditions. First, the refrigerants are automatically examined, filtered, and thus preselected according to the various requirements. Then, after the preselection, a detailed analysis of the heat pump circuit is performed to provide an evaluation of the refrigerants. For a simplified illustration of this methodology, the refrigerant selection is presented below using the example of an air-to-water heat pump to provide space heating and domestic hot water.

For refrigerant selection, the boundary conditions for the system to be designed must first be defined. The boundary conditions used in the presented study are shown in Table 1. Within the first preselection, the general properties of the refrigerant are checked. A maximum permitted GWP of 150 is used. Furthermore, the refrigerant must not have an ODP. Concerning flammability, all levels of the ASHRAE classification - from 1 (non-flammable) to 3 (highly flammable) - are permitted. However, the preselection process excludes toxic refrigerants, such as ammonia. The safety class summarizes these aspects (A: non-toxic, B: toxic).

Limit values of the operating range are checked. For this purpose, minimum and maximum operating temperatures and pressures are defined, which can occur during operation. For the provision of domestic hot water, condensation temperatures of up to 70 °C can occur to enable thermal disinfection. At the same time, due to maximum operating pressures above 50 bar, the durability of most materials will be shortened. The lower limit for the evaporation temperature in this study is -20 °C, which represents a cold winter day in Germany. At these cold temperatures, the system must continue to operate at positive pressure, as described initially. Therefore, a minimum operating pressure of 1.1 bar is assumed.

After preselection, a cycle calculation is performed, based on which various parameters such as efficiency (COP) and volumetric heating capacity (q_{vol}) are calculated [7]. The cycle calculation is based on a validated compressor model [8], and an additionally implemented optimization process so that the maximum efficiency at a defined operating point is calculated individually for each refrigerant. For this purpose, the optimal pressure levels in the condenser and evaporator and the optimal

Table 1. Boundary conditions used for the study

GWP_{max}	150
ODP_{max}	0
Safety classes	A1, A2L, A2, A3
Minimum evaporation temperature	-20 °C
Minimum operating pressure	1.1 bar
Maximum condensing temperature	70 °C
Maximum condensation pressure	50 bar

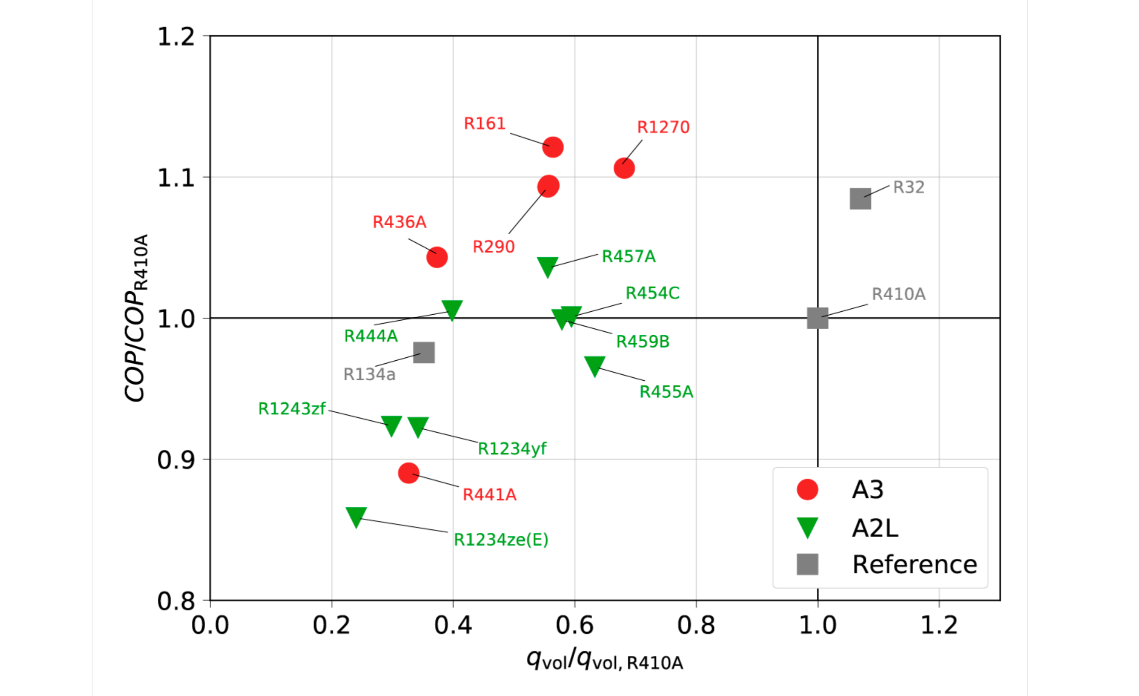

Figure 1. Efficiency versus volumetric heating energy for potential alternative refrigerants normalized to R410A for A2/W35 operating point.

superheat level at the compressor inlet and subcooling after the condenser are determined. Various constraints are used to ensure physically and technically feasible behavior. In addition to considering the secondary fluids (in this case, air and water), this also includes compliance with minimum superheating and subcooling and compliance with the second law of thermodynamics.

Furthermore, the calculation ensures that the optimum operating conditions for each refrigerant are guaranteed for an operating point. This setup allows a comparison of the refrigerants.

Refrigerant Selection and Conclusions

The presented method is applied in the following 268 fluids available on the market and belongs to the common RefProp database [9]. With the help of the various selection stages, the number is reduced to 31 fluids, which fulfill both the political and the operational specifications for air-water heat pumps [10]. Among them, only refrigerants of safety classes A2L to A3 are included. Non-flammable refrigerants of safety class A1 cannot meet either the political specifications or the technical requirements for an air-to-water heat pump in the future. However, it should be noted that CO_2 was not included in this study due to its supercritical operation.

Figure 2 shows the results for currently commonly used refrigerants. The heat pump's efficiency over the volumetric heating energy is shown, both normalized to a comparison process with R410A refrigerant for the other candidates. Further, R32 was used as a benchmark in the study since it is currently used in some systems. It is noticeable that none of the alternative refrigerants reaches the volumetric heating capacity of R410A or R32. This non-achievement is because both refrigerants are high-pressure fluids mainly used in refrigeration. Due to the high pressure, there is a higher density at the compressor inlet, which positively affects the delivered mass flow and thus the heat capacity in the condenser. Consequently, future heat pumps using alternative refrigerants will have to be equipped with larger components to provide the same heat capacity.

In addition, it can be shown that the A3 refrigerants tend to have higher efficiencies. Compared to HFOs (A2L), the natural refrigerants (A3) considered here achieve up to 20% higher efficiencies. It is also interesting to note that the development of blends - here using R454C as an example - can positively affect the potential of a refrigerant in a basic heat pump cycle. By blending a high-efficiency fluid (R32) and a low-GWP fluid, the overall properties can be adjusted to meet policy requirements and increase heat pump efficiency. However, even the blend shown still delivers efficiencies about 10% lower than propane, for example, at a moderately higher volumetric cooling capacity.

Overall, the question remains which refrigerant should be a millionfold used refrigerant in the future. Natural refrigerants show proper behavior for air-to-water heat pumps - at least on a thermodynamic level. Compared

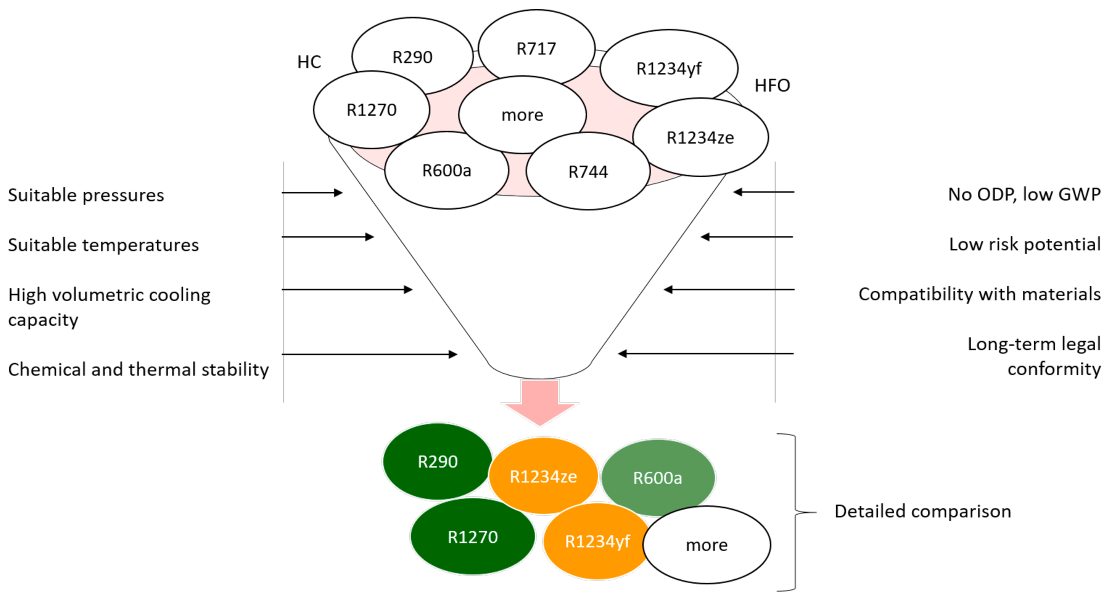

Figure 2. Requirements for refrigerants and reduction of potentially suitable candidates by external specifications.

to HFOs, higher efficiencies can be achieved using HCs. Higher efficiency reduces the overall power consumption and thus indirect emissions. In addition, higher volumetric heating capacities can, in principle, be achieved. A higher heating capacity has a positive effect on the size of the individual components and can thus be economically advantageous. Furthermore, natural refrigerants are also cheaper to procure than HFOs due to their high availability.

Ultimately, HFOs released into the atmosphere form trifluoroacetic acid (TFA for short) during their degradation process. TFA is highly soluble in water and is difficult to degrade. After TFA is formed in the atmosphere, it can enter groundwater via precipitation. It can no longer be removed from the water by conventional purification methods, thus contaminating the groundwater. Therefore, the Federal Environment Agency in Germany has already issued a recommendation in 2019 to minimize the use of TFAs [11]. However, it is questionable whether this recommendation will be formulated into political guidelines within the next few years, which is why the long-term use of HFOs is at least uncertain.

Within this study, we show that under current boundary conditions, the advantages of natural refrigerants outperform synthetic refrigerants, which is why it seems sensible to promote them. However, choosing a suitable natural refrigerant depends strongly on the application. For example, propane and propene's pure substances showed excellent results for air-to-water heat pumps in residential applications. Propane delivers about 10% higher volumetric heating capacities. Thus, to continue accelerating the sustainable use of heat pumps, the theoretically best refrigerants must be selected under given boundary conditions and transferred to practice. The presented methodology supports this process and will be further developed regarding mixtures, refrigerants cycles, and boundary conditions.

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