The Future of Refrigerants for Heat Pump Applications

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Industry and other sectors are currently looking for solutions to decarbonize their processes, including heating, which is mainly based on fossil fuel boilers. Moving to the electrification of heat by implementing heat pump technologies to provide the demanded load can be complex. Choosing the right working fluid, synthetic or natural refrigerant, with less environmental harm (low GWP) and human (safety issues) is under debate globally and is urgently needed before 2030. Some measures have been taken to solve this problem by introducing short-term synthetic refrigerants such as R32 in Europe and R454B in the US with low GWP values. This article summarizes the debate of which refrigerants are suitable for usage in heating and cooling systems and their effects on the surroundings.

The thirst for energy around the world is growing exponentially, especially in China, the fastest-growing economy. The U.S. Energy Information Administration (EIA) estimates that the world energy usage will increase by 50% between 2018 and 2050 (IEO 2020), which will drive the levels of Greenhouse Gases (GHGs) such as carbon dioxide and different air pollution to higher values. With the current emission rates of GHGs, the earth's temperature will rise above (2°C) by 2036, and it is by UNIPCC standards harmful, devastating, and life-threatening. The 2030 climate and energy framework at Paris Agreement in 2015 has set a binding target between EU members to reduce the emissions of GHGs by 40% between 2021 and 2030, increase energy efficiency by 32.5%, and reach climate-neutral by 2050. In Early 2021, the European Commission proposed another increase to raise the target from 40% to at least 55% (2030 Climate Target Plan) for sectors covered under the existing EU Emissions Trading System. To achieve this reduction, the phase-out of HCFC and HFC with GWP_{100} values over 500 is necessary.

Refrigerants' Suitable Chemical Structure.

The progress towards the HFC phasedown targets by 2030 under the Kigali Amendment is an important step to save our planet. It is very important that policymakers and industry stakeholders understand on what basis we should approach the HFC phasedown and what measu-

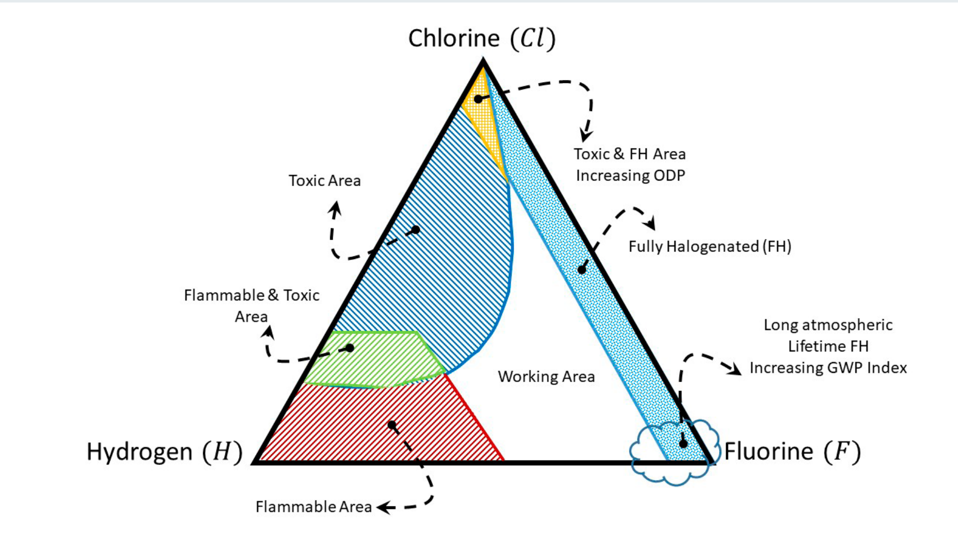

Figure 1. Triangel of Elements.

res we should adopt in this process. Up to date, HFCs are still in use in HVAC systems and heat pump applications. The choice for a suitable refrigerant depends on its chemical and thermal properties. Thermal factors affect the coefficient of performance (COP) and volumetric efficiency of the system, while chemical properties have important effects on the environment and on the selection of the refrigerant itself. Based on the triangle of element (Refrigerant Selections), shown in Figure 1, adding chlorine atoms to the chemical structure of the refrigerant would increase the Ozone Depletion Potential (ODP) values, increasing hydrogen atoms would elevate the flammability rates of the refrigerant, and more fluorine atoms would raise the Global Warming Potentials (GWPs) index. For example, the new refrigerant R-1336mzz(Z) with the chemical formula of ($C_4H_2F_6$), which is not flammable and of low GWP value, is based on Butene, also known as Butylene, with the chemical formula of (C_4H_8), which is highly flammable, and six hydrogen atoms have been replaced by flourine.

Refrigerants' Index Argument.
Table 1 shows some of the refrigerant's group, its GWP_{100} values based on IPCC Sixth Assessment Report (AR6), and its allocation in ASHRAE Safety classifications. A (low) or B (high) represent toxicity levels; and 1 (low), 2 (medium), 2L or 3 (high) represent levels of flammability . The notation A2L indicates a class 2 refrigerant with a burning velocity less than or equal to 10 cm/s. The table clearly demonstrates the tradeoff between GWP values and the flammability index. It shows that there are no non-flammable alternatives for $GWP_{100} \leq 150$. Danfoss gives a holistic flammability view based on refrigerants' densities and their GWP_{100} values and a short way of selecting a suitable refrigerant (Flammability Line).

The GWP_{100} values for synthetic refrigerants (CFC, HCFC, HFC, HFO) and natural refrigerants were adopted as a metric to implement the multi-gas approach embedded in the United Nations Framework Convention on Climate Change (UNFCCC), and made operational in the 1997 Kyoto Protocol. The choice of time horizon has a strong effect on the GWP values. Given that climate change signs have been observed and measured all over the world, policies based on GWP_{20} figures could accelerate the process of reaching the targets faster and would influence the order of how the control steps are executed. Figure 2 compares the values of two indexes. One of the

Table 1. Refrigerants with their corresponding GWP_{100} values (AR6 IPCC).

Group	Refrigerant	Safety Group	GWP_{100} (AR6)
Natural	R-218 (Water)	A1	0
	R-717 (Ammonia)	B2L	0
	R-744 (Carbon Dixiode)	A1	1
	R-1270 (Propylene)	A3	2
	R-290 (Propane)	A3	5
	R-600a (Isobutane)	A3	4
HFO	R-1243zf	A1	
	R-1336mzz(Z)	A1	2
	R-1234yf	A2L	0.5
	R-1234ze(E)	A2L	1
HCFO	R-1224yd	A1	1
	R-1233zd(E)	A1	4

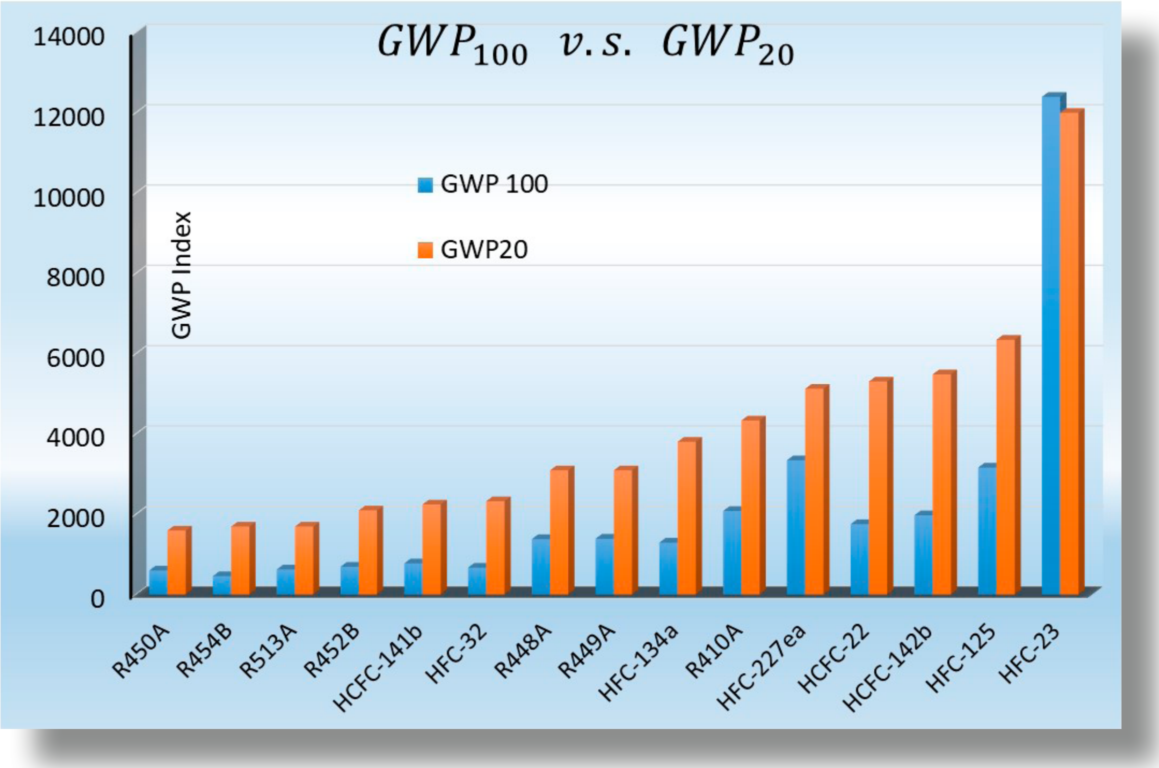

Figure 2. GWP_{20} versus GWP_{100} values.

reasons GWP_{20} values can be adopted is that the lifetime of HFCs ranges from 1.4 to 52 years and the average lifetime is 21.7 years (HFC Contribution). Not all agree with the move to the new index because the presented data over 20 years could be misleading to the public as well as policymakers in terms of which refrigerants are truly climate-friendly and sustainable. The GWP_{20} values would emphasize the removal of certain HFCs, such as R134a, and short-lived GHGs, such as methane, but would allow for a larger amount of carbon dioxide (century) and long-lived GHGs to not be reduced. This consequently will raise the earth's temperature for hundreds of years to come. It is also important to evaluate other indexes, as seen in Figure 3, the Total Equivalent Warming Impact (TEWI) and the Life Cycle Climate Performance (LCCP). TEWI is an index that assesses simultaneously the GHG emissions caused by the accidental refrigerant leakages (Direct Effects, DE) and those caused by electricity consumption during the system operation (Indirect Effects, IE). LCCP takes into account other CO_2-equivalent emissions not included in the TEWI analysis, should also be considered in selecting the right refrigerant (Warming Impact Metrics).

Refrigerants' Environmental Effects.

Another issue that affects the selection of a suitable synthetic refrigerant is Per- and PolyFluoroAlkyl Substances (PFAS) and its sub-groups. PFAS dissolve in drinking water, dangerous to humans if they are consumed in large quantities, and breakdown slowly in time. The Organisation for Economic Co-operation and Development (OECD) (OECD 39) identified over 4700 substances as PFAS in their risk management report published in 2018. In the same report, they define new groups that fulfill the common definition of PFASs, which include hydrofluorocarbons (HFCs) and hydrofluoroolefins (HFOs) refrigerants. In the atmosphere, some of these refrigerants breakdown because their chemical formula contains double bonds, which makes their molecules less stable. The result of the decomposition is a TriFluoroacetic Acid (TFA) which is yet another sub-group of PFAS. Table 2 shows some synthetic refrigerants with their TFA yield. The European FluoroCarbons Technical Committee (EFCTC), which provide an up to date information about applications, safety, health and environmental effects for HFCs, HCFOs, and HFOs, does not classify these gases to meet the criteria of Persistent, Bioaccumulative, and Toxic substances (PBT), and it claims that these gases pose no harm to the environment. We should not be alarmed by PFAS or TFA now because they already exist in small amounts in food packaged; commercial household products such as water-repellent fabrics, nonstick products (e.g., Teflon), and so forth (PFAS Explained), but the breakdown of fluorocarbons mentioned before would increase their dosages in the environment. EU REACH Regulation from the European Chemical Agency (ECHA) said, "Without taking action, [PFAS'] concentrations will continue to increase, and their toxic and polluting effects will be difficult to reverse."

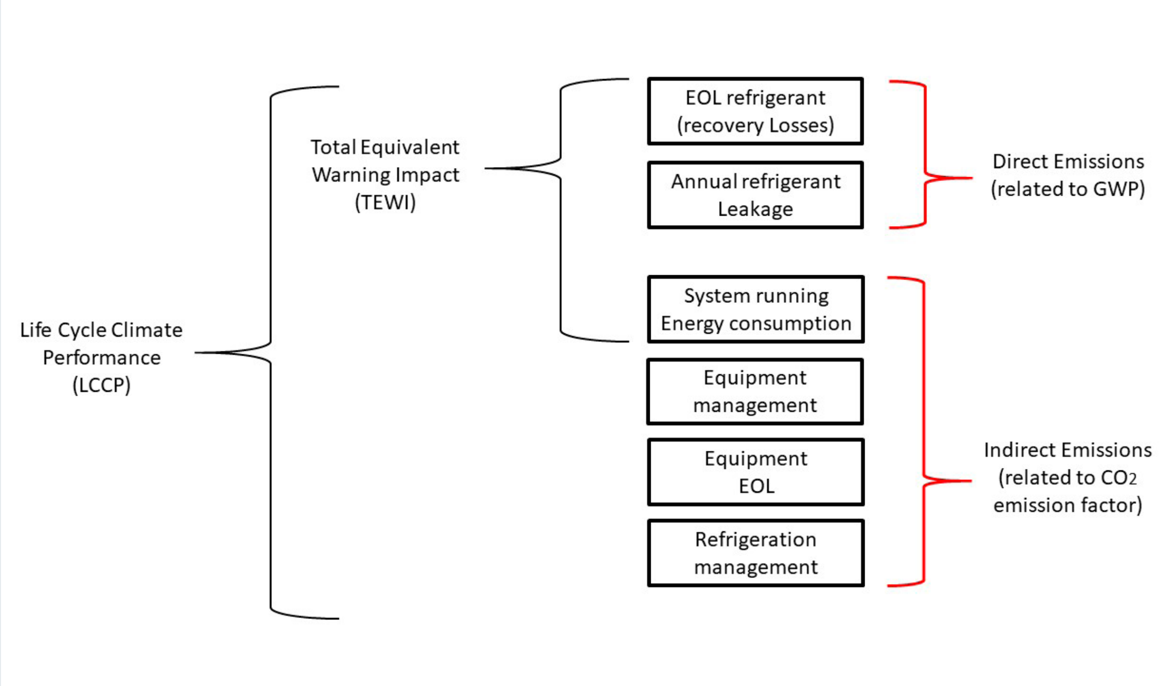

Figure 3. TWEI and LCCP indexes.

Table 2. TFA Yield of Fluorocarbon Synthetic Refrigerant (F-gas Breakdown).

Refrigerant	TFA Yield
HFC-134a	21%
HFC-245fa	Less than10%
HFO-1234ze(Z)	0%
HFO-1234yf	100%
HFO-1336mzz(Z)	4%
HCFO-1233zd(E)	0%

Conclusions

We are still debating how to address the problem of limiting the rise in global temperatures, and time is passing by as we fail to take drastic actions to halt this trend. Natural refrigerants may be viable answers for the current challenges, but they are flammable and/or toxic, although extra design measures and safety requirements could help us avoid these issues.

The industry is technically ready to replace high-GWP refrigerants with new synthetic refrigerants with low GWP values, but compatibility issues such as compressor oil, thermal performance characteristics, and their impact on the environment and humans must be addressed. The time to save our planet is running out, and we need to find a solution to this vague picture as soon as possible.

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