REFRIGERANTS

Technical Report of the IEA DHC TS3 “Hybrid Energy Networks”, subtask A “Technologies and synergy potential”, WP2 “Experiences with hybrid energy networks based on large-scale heat pumps”: *Refrigerants*.

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Content

1 Historical development of refrigerants

1.1 Overview

A simplified historical development of refrigerant categories is illustrated in Figure 1. Though the use of the refrigerant categories overlaps, the timeline illustrates the development towards the ambition of reducing the impact of their ozone depletion potential (ODP) and global warming potential (GWP). The natural refrigerants have been present along the way, but only to a smaller extent used.

The Montreal Protocol and the associated Kigali Amendment[1] has ensured a vital shift away from the most harmful substances in terms of their ODP and GWP. However, much work is still to be done with regards to the agreements' implementation, and natural refrigerants could be a suitable further step.

CFCs[2] have a high ODP caused by the gases rising to the atmosphere where they – as a result of ultraviolet radiation – react to release the chlorine atom, which reacts with ozone thereby reducing the ozone layer. Besides this, the GWP is high. HCFCs[3] have an ODP and GWP lower than CFCs but the values are still substantial. HFCs[4] have been implemented as replacements since they have no ODP due to the fact that – unlike CFCs and HCFCs – HFCs have no chlorine content. To reduce also the GWP, HFOs[5] have been implemented representing low GWP values.

Figure 1. Historical development within refrigerant use.

1.2 Concerning HFOs

Though the HFOs may by some be considered refrigerants for the future, they too involve drawbacks. HFOs are broken down in the atmosphere within two weeks to create trifluoroacetic acid (TFA) in the large category of per- and polyfluoroalkyl substances, PFAS

[1] See treaties.un.org/Pages/ViewDetails.aspx?src=IND&mtdsg_no=XXVII-2-f&chapter=27&clang=_en#1.
[2] Chlorofluorocarbons
[3] Hydrochlorofluorocarbons
[4] Hydrofluorocarbons
[5] Hydrofluoroolefins

(according to OECD's definition[6]) all containing carbon-fluorine bonds. As an example, R1234yf (with the chemical formula $C_3H_2F_4$) reacts and creates C_2F_4O which hydrolyses to TFA with the chemical formula $C_2HF_3O_2$. TFA accumulates in the environment since it is very stable.

Due to the concern related to the environmental and health effects of TFA, studies have been carried out to identify its presence. A study[7] funded by the German government investigated the presence of short chain and ultra-short-chain PFAS (with TFA being one of them). This study identified TFA in 47 samples, and in 2021 it was identified in 219 out of 247 (89%) of investigated groundwater boreholes in a Danish study[8].

A proposal regarding the restriction of PFAS substances including some HFC and HFO refrigerants have been submitted to the European Chemicals Agency (ECHA) by the five countries Germany, the Netherlands, Sweden, Norway, and Denmark[9].

The similarity to the effect seen for CFCs, where the chemical breakdown in the atmosphere results in undesired side-effects, are remarkable. Lack of awareness when the ambition to handle one problem ends up causing another cannot be an excuse not to act accordingly to mitigate the side-effect.

Since positive outcomes using natural refrigerants have been proven in many cases, their use can be applied as a prerequisite already in the tender documents as it is often done in Danish cases. From the knowledge available it can only be recommended to ensure the use of natural refrigerants in the expected deployment of large-scale heat pumps for district heating. This can be applied even without stating which type of heat pump (or type of natural refrigerant) to be used in a functional tender. More information on tendering process can be found in the document "Tendering process".

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[6] OECDs definition: *"PFAS's are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e. with a few noted exceptions, any chemical with at least a perfluorinated methyl group (–CF3) or a perfluorinated methylene group (–CF2–) is a PFAS."* Environment Directorate Chemicals and Biotechnology Committee, Series on Risk Management No.61, "Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance".

[7] "Ultra-Short-Chain PFASs in the Sources of German Drinking Water: Prevalent, Overlooked, Difficult to Remove, and Unregulated", May 4th 2022, Environmental Science & Technology, doi.org/10.1021/acs.est.1c07949.

[8] mst.dk/media/211541/fagligt-notat-om-resultater-af-massescreening-2020.pdf

[9] echa.europa.eu/da/-/echa-publishes-pfas-restriction-proposal

2 Natural refrigerants

2.1 Overview of commonly used natural refrigerants

The most typical natural refrigerants for large-scale DH heat pumps are:

- ammonia (NH_3) with the refrigerant number R717 (GWP: 0, ODP: 0)
- carbon dioxide[10] (CO_2) with the refrigerant number R744 (GWP: 1, ODP: 0)
- propane (C_3H_8) with the refrigerant number R290 (GWP: 3, ODP: 0)
- isobutane (C_4H_8) with the refrigerant number R600a (GWP: 3, ODP: 0)

Natural refrigerants are widely used in heat pumps for DH in Denmark. Most of the heat pump installations use ammonia as refrigerant though the market for CO_2 solutions is increasing. In the cases evaluated in "Market status, incentives and policies in Denmark", where data on refrigerants are gathered, more than two out of three systems use ammonia as refrigerant. Typically, CO_2 is found in smaller heat pumps (or in case more individual units are combined), whereas larger systems often use ammonia.

No single heat pump technology covers all applications and the best solution will depend on the given case. As an example, for CO_2 heat pumps, the COP is less sensitive to the required outlet temperature on the condenser side (i.e., the DH forward temperature) compared to ammonia heat pumps (but is in turn more sensitive to high inlet temperatures on the condenser side). Typically a transcritical CO_2 cycle is suited for systems where there is a small temperature difference of the heat source, while the heat sink (i.e., DH network) has a large difference between return and forward temperature. In general, high COP levels are key, but other factors such as flexibility, costs and control options are also important when it comes to evaluating the feasibility and choosing a solution.

2.2 Advantages and disadvantages

A list of key advantages and disadvantages of natural refrigerants is seen below.

- No ODP
- Low or no GWP.
- No TFA output to the environment
- CO_2 is operating under high pressure due to its properties
- Ammonia is toxic in case of leakages causing high concentrations
- The hydrocarbons propane and isobutane are flammable

The abovementioned disadvantages require precautionary measures but in turn, they will not leave a negative environmental impact behind as a result of the chosen refrigerant.

[10] Since the molecular formula CO_2 is often used instead of "carbon dioxide", this term is also used.